STRUCTURAL STUDIES OF YLIDES AND RELATED DERIVATIVES, AND OF SEVERAL NATURAL PRODUCTS.

A thesis submitted to the University of Glasgow for the degree of Doctor of Philosophy in the Faculty of Science

by

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To My Wife

Lillian

And My Children

Tamir And Liana

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Summary

This thesis is essentially divided into two parts, one theoretical (Chapters 1 and 2) and the other experimental (Chapters 3 - 5). A supplement to this thesis includes a listing of all structure factors.

The first part (of the thesis) deals with the theory of X-ray diffraction and with various methods for the determination of structures and their refinement. Of these methods, direct methods have been extensively applied in the study of twelve organic molecules and therefore its theoretical basis is described in more detail (Chapter 2).

Chapter 3 reports the crystal and molecular structures of two sulphur-nitrogen ylides and of five of their reaction products with electrophilic acetylenes, the reaction products themselves (betaines) having been described as possessing ylide-like skeletons.

These investigations were undertaken because the compounds were of chemical interest and because there seemed to be a complete lack of X-ray structural information on N-arylsulphilimines ($R^1R^2S^+ - \bar{N}Ar$) and their corresponding sulphur betaines (N-arylsulphilimines + electrophilic acetylene $\longrightarrow$ betaine) while their phosphorus analogues have been long known and investigated. It was also felt that in view of the structural information (from X-ray studies) on N-acylsulphilimines ($R^1R^2S^+ - \bar{N}\,COR^3$) and N-sulphonylsulphilimines ($R^1R^2S^+ - \bar{N}SO_2R^3$) the structural studies on N-arylsulphilimines could be of comparative value.

The X-ray analyses revealed unhindered geometries for the sulphilimines whereby the N-S bonding systems are almost coplanar with the aromatic

rings. The nitrogen atoms are probably sp^2 hybridized and the N-S bonds were found to be 1.622 (2) Å and 1.640 (4) Å (for the two ylides), thus being similar (within experimental error) to the lengths found for N-sulphonylsulphilimines [1.628 (2) Å] and significantly below the length of 1.670 (2) Å given for N-acylsulphilimines.

For the sulphur betaines, steric strain which causes conformational distortions has been observed in all five structures. The bond angles were found to be influenced by this effect while only one $C(sp^2)$ - $C(sp^2)$ bond length appeared to be influenced appreciably by this effect (1.520 Å - 1.549 Å).

A 'through conjugation' effect was also observed.

The structures of a related arsenic betaine and of a C-nitroso-imine-N-oxide are reported in Chapter 4. Interesting conformational distortion originating from the As ... O interactions, and a shortened As - $C(sp^2)$ bond length [e.g. 1.835 (5) Å] are observed for the arsenic ylide.

The C-nitroso-imine-N-oxide reveals a planar geometry of the central framework of the molecule which is almost perpendicular to the two aromatic systems. A transoid arrangement of the -N = C - N = O group of atoms is also observed.

The structural analyses of two new diterpenoids and a tetranortriterpenoid spiro-lactone are reported in Chapter 5. The novel feature of a fully substituted cresol ring system was shown to exist in one of the diterpenoids while in the other the unique feature of a seven-membered hemiacetal

ring B has been established.

The tetranortriterpenoid was shown to possess a δ -lactone ring system and a cyclic ether in which the oxygen is attached to two secondary carbon atoms.

CONTENTS

CHAPTER I

BASIC CONCEPTS IN CRYSTALLOGRAPHY

1.1 The Symmetry of Direct Space Lattices

Three dimensional patterns

Crystals are three-dimensional patterns and must obey the laws of symmetry which govern three-dimensional patterns of any kind.

If we have a repeated pattern in space such as the distribution of atoms in a crystal, we can relate to it a three-dimensional lattice of points (the so called 'unit structures') which defines the repetition characteristics without reference to the details of the repeated motif/ unit structure.

Point groups

A general rotation of vector $\bar{r}$ around a unit vector $\bar{k}$ ($\bar{k} \parallel$ Z axis in a cartesian system) by an angle of α in the positive direction (conventionally counter clockwise) will result in a new vector $\bar{r}'$ which will be given by the expression:

$$\bar{r}' = \bar{k}(\bar{k}\cdot\bar{r})(1 - \cos\alpha) + \bar{r}\cos\alpha + (\bar{k} \times \bar{r}) \sin\alpha$$

where $\bar{r}' = C(\alpha)\bar{r}$

and $C(\alpha)$ = the transformation matrix given by[1]

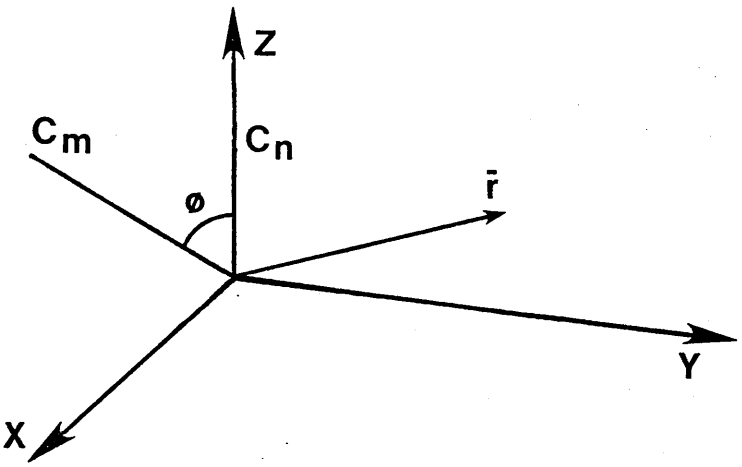
$$C(\alpha) = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Restricting $\bar{r}$ and $\bar{r}'$ to be lattice vectors and $C(\alpha)$ to be a symmetry operation matrix, will result in the trace of the matrix being an integer[2], hence Trace $C(\alpha) = 1 + 2\cos\alpha = \pm$ integer and the five permissible rotations constitute five monaxial point groups, 1,2,3,4,6 (C_1, C_2, C_3,

C_4, C_6 - in the Schoenflies symbolism).

Introducing the symmetry operation $\bar{1}$, will result in five new centrosymmetric point groups $\bar{1}$, $\frac{2}{m}$, $\bar{3}$, $\frac{4}{m}$ and $\frac{6}{m}$ (C_i, C_{2h}, C_{3i}, C_{4h}, C_{6h}).

Looking for a third axis when two rotational symmetry operations are assumed to be permissible will result in the generation of additional six point groups as follows:



C_m and C_n are the two permissible operations.

If $\bar{r}$ is a lattice vector then

$$\bar{r}_n = C_n \bar{r}$$

$$\bar{r}_{nm} = C_m C_n \bar{r} = C_k \bar{r}$$

and $\bar{r}_{nm}$ is a lattice vector too.

The trace of $C_k = 1 + 2\cos(\frac{2\pi}{k}) =$ integer, l, and in terms of the variable ϕ, it can be shown to have the expression of:

$$\text{Trace } C_k = A\cos^2\phi + B\cos\phi + C = \text{integer, } l, \text{ where:}$$

$$A = \cos(\tfrac{2\pi}{n}).\cos(\tfrac{2\pi}{m}) - \cos(\tfrac{2\pi}{n}) - \cos(\tfrac{2\pi}{m}) + 1$$

$$B = -2\sin(\tfrac{2\pi}{n}) \cdot \sin(\tfrac{2\pi}{m})$$

$$C = \cos(\tfrac{2\pi}{n})\cos(\tfrac{2\pi}{m}) + \cos(\tfrac{2\pi}{n}) + \cos(\tfrac{2\pi}{m})$$

As an example, assuming n = m = 2 will cause A, B and C to be equal to 4, 0 and -1 respectively and hence Trace $C_k = 4\cos^2\phi - 1 = 1$, this last result could be summarized as follows:

1	-1	0	1	2	3
$\cos^2\phi$	0	1/4	1/2	3/4	1
ϕ	90	60	45	30	0
$\cos(\frac{2\pi}{k})$	-1	-1/2	0	1/2	1
k	2	3	4	6	1

It can be seen that if the angle ϕ between the two permissible axes is $\phi = 90^\circ$, this will produce a third permissible rotation axis C_k, where k = 2 (C_2) which can be shown to be perpendicular to the other two. This will constitute the 222 point group (D_2). In a similar way one can get the point groups 32, 42, 62 (D_3, D_4, D_6), and the point groups 23, 43 (T, O) when instead of n = m = 2, one chooses n = 2 and m = 3. Adding $\bar{1}$ to each of the last 6 point groups will introduce another new 6 centrosymmetric point groups, mmm, $\bar{6}$ m, 4/mmm, 6/mmm, m3, m3m (D_{2h}, D_{3h}, D_{4h}, D_{6h}, T_h, O_h). The rest of the 10 point groups can be evaluated as subgroups of the groups shown up till now (i.e. m = C_s from C_{2h} and mm = C_{2v} from D_{2h} etc.), and all together 32 point groups will be produced.

Restrictions imposed on the lattice structure by the symmetry [3]

If a crystal has an n-fold axis, then a prominent row of lattice points will be associated with this direction and a prominent lattice plane will be found perpendicular to the axis of rotation. Similarly, if the lattice possesses a symmetry plane, m, a lattice plane parallel to m and a lattice row perpendicular to it will be found. These correlations between symmetry and structure are the 'guide lines' for choosing a unit cell, since it will be chosen in such a way as to coincide with the symmetry restrictions of the lattice.

A number of point groups which define a unit cell, constitutes a Crystallographic System. It can be shown that few types of unit cells are possible for each crystallographic system, and there are 14 possibilities altogether - the so called 14 Bravais lattices.

Space symmetry and space groups

Space symmetry can be defined as a geometrical connection between equivalent points, expressed by a pure symmetry operation and a translation. Hence a space symmetry operation can be written as $(P/\bar{t}) = (P/\bar{U}_{\parallel} + \bar{U}_{\perp})$, where P is the 'pure' symmetry operation, $\bar{t}$ the translation vector, $\bar{U}_{\parallel}$ and $U_{\perp}$ the vector components of $\bar{t}$, parallel to P and perpendicular to P.

Looking at a permissible space symmetry operation as for example $(C_2^{y}/\alpha\bar{a} + \beta\bar{b} + \gamma\bar{c})$, where $0 < \alpha.\beta.\gamma < 1$, the perpendicular components to C_2, chosen as $\alpha\bar{a} + \gamma\bar{c}$, can be ignored [since it is possible to translate the pure symmetry operation by $\frac{1}{2}(\alpha\bar{a} + \gamma\bar{c})$].

As $(C_2^y/\beta\,\bar{b})\,(C_2^y/\beta\,\bar{b}) = (E/2\,\beta\,\bar{b})$ (E = identity operation), $2\beta\,\bar{b}$ is a lattice vector and hence $\beta = 0, 1/2$. This constitutes the possible screw axis $C_2/\frac{\bar{b}}{2}$ $(= 2_1)$. In the general case of an n-fold axis symmetry operation with translation, the possible screw axes will be defined as n_k, where $k = 1, 2, \ldots, n-1$.

The possible existence of glide planes can be shown in the same way $\left\{ (\sigma^y/\frac{\bar{a}}{2} = a),\ (\sigma^y/\frac{\bar{c}}{2} = c) \text{ and } \left[\sigma^y/(\frac{\bar{a}}{2} + \frac{\bar{c}}{2}) = n\right]\right\}$

A space group constitutes a number of symmetry elements that are consistent with an infinitely extended, regularly repeating pattern. All the possible combinations of the 32 point groups with the different space translations will contain all the possible space groups.

1.2 Intensity from Diffraction of a Finite/Infinite Three Dimensional Lattice. Scattering from a unit structure and Laue equations

The wave scattered by a unit structure (in a crystal) relative to the wave scattered by a single electron (located at the origin) is given by

$$\bar{F}'(\bar{S} - \bar{S}_0) = \int_{\text{all } \bar{r}} \rho(\bar{r}) \exp\left[2\pi i\, \bar{r}(\bar{S} - \bar{S}_0)\right] d\bar{r}$$

where $\rho(\bar{r})$ describes the electron density function in the unit structure that takes zero values outside it and $\bar{S}$ and $\bar{S}_0$ are both wave vectors representing the direction and magnitude of the scattered and incident wave correspondingly $(|\bar{S}| = |\bar{S}_0| = 1/\lambda)$.

Since $\rho(\bar{r})$ is a periodic function and can be represented by a Fourier integral, $F(\bar{S} - \bar{S}_0)$ is the Fourier transform of the electron density function. The intensity of the wave scattered from the entire lattice is given by the following expression:

$$\left|F(\bar{S}-S_0)\right|^2 = \left|F'(\bar{S}-S_0)\right|^2 \frac{\sin^2\pi N_1\bar{a}(\bar{S}-\bar{S}_0)}{\sin^2\pi\bar{a}(\bar{S}-\bar{S}_0)} \cdot \frac{\sin^2\pi N_2\bar{b}(\bar{S}-\bar{S}_0)}{\sin^2\pi\bar{b}(\bar{S}-\bar{S}_0)} \cdot \frac{\sin^2\pi N_3\bar{c}(\bar{S}-\bar{S}_0)}{\sin^2\pi\bar{c}(\bar{S}-\bar{S}_0)}$$

N_1, N_2 and N_3 are integers relating to the number of the repeating units in the lattice. The conditions for a diffraction maxima can be seen to be when the following equations are simultaneously satisfied:

$$\bar{a}.(\bar{S}-\bar{S}_0) = m \text{ (integer)}$$

$$\bar{b}.(\bar{S}-\bar{S}_0) = n \text{ (integer)}$$

$$\bar{c}.(\bar{S}-\bar{S}_0) = p \text{ (integer)}$$

These equations are the so called Laue equations and their solution is known to be the reciprocal lattice vector

$$\bar{H} = \bar{S}-\bar{S}_0 = h\bar{a}^* + k\bar{b}^* + l\bar{c}^*$$

where the set of integers m, n, p can be identified with the set of indices h, k, l. The width of the diffraction maximas and the subsidiary peaks depends on the number of unit structures in the lattice, and since the crystal has a finite size, the reciprocal space points will not correspond to mathematical points but to smeared out points. This finite size effect is bound to have an influence on what is called the Lorentz factor.

Bragg's law in direct and reciprocal space

From the expression for $\left|F(\bar{S}-\bar{S}_0)\right|^2$ it is possible to see that the intensity of the scattering from the entire lattice can be looked on as proportional to the scattering from one unit structure lying on one of the parallel lattice planes to whom the direction of $\bar{S}$ and $\bar{S}_0$ corresponds.

In fact the justification for the concept of each diffraction as a 'reflection' of the rays from lattice planes can be found in the proof of Bragg's law itself [3]. Bragg's equation states that

$$2d_{(hkl)} \sin\theta = n\lambda$$

where 2θ is the angle between the incident and scattered ray, d is the interplanar spacing of a set of parallel lattice planes (hkl) and the integer n is the order of the reflection. By considering an n^{th} order reflection as a reflection from a set of planes with indices nh, nk, nl, Bragg's equation could be written as $2d_{hkl} \sin\theta = \lambda$, where hkl are the indices of the reflection (in contrast to Miller indices of the lattice planes). The condition for reflection to occur can be reformulated in terms of the geometrical device known as the reciprocal lattice [4], as is shown in the two dimensional diagram of Figure 1.1. The reciprocal lattice has its origin at 0 and any reciprocal point P which lies within the boundaries of the limiting sphere can be brought into a position such that $OP = (1/d) = |H| = \frac{2\sin\theta}{\lambda}$ which is in fact Bragg's law.

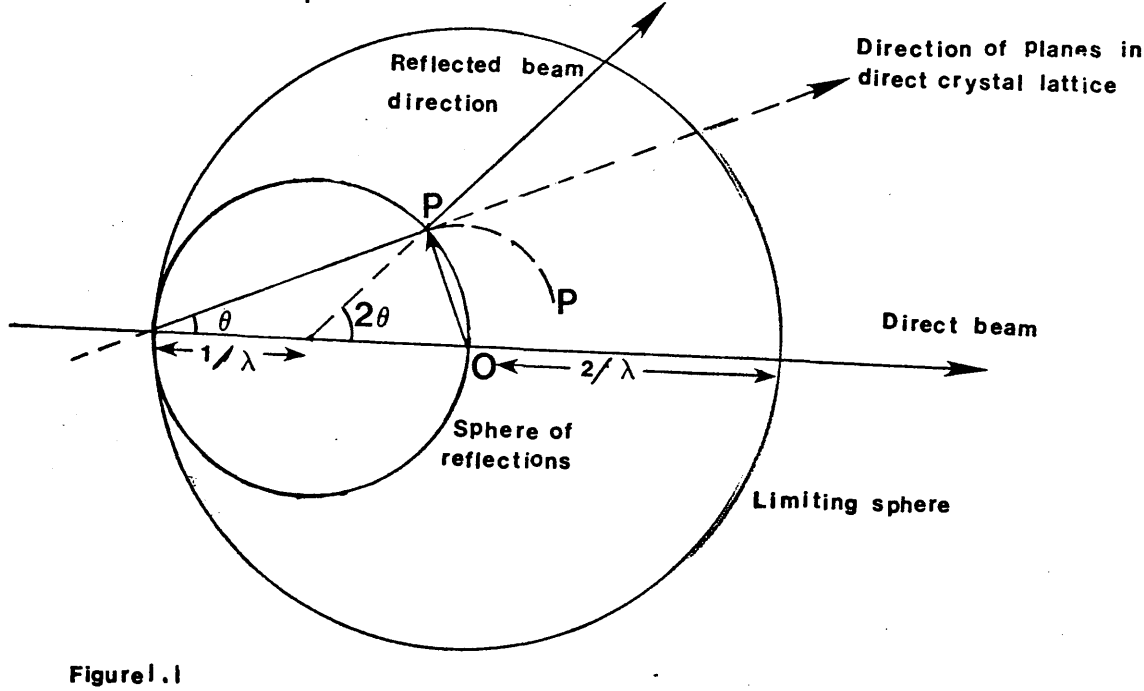


Figure 1.1

1.3 Structure Factors and Scattering Factors

The structure factor

An expression for the structure factor can be given in the vector form as: $F(H) = \int_{\text{unit cell}} \rho(\bar{r}).\exp(2\pi i\ \bar{r}.\bar{H})d\bar{r}$

This quantity is a function of h,k,l and its modulus is called the structure amplitude and is defined as the ratio of the amplitude of the radiation scattered in the order h, k, l by the contents of one unit cell, to that scattered by a single electron under the same conditions. The non-vector form of the structure factor can be written as

$$F(hkl) = V\int_0^1\int_0^1\int_0^1 \rho(x,y,z)\exp\left[2\pi i(hx + ky + lz)\right] dxdydz$$

where V is the volume of the unit cell, and $\rho(x,y,z)$ describes the overall electron density in the unit cell.

Looking at the distribution of atoms in the unit cell, the superposition of several atomic electron density functions will give the overall electron density function, and F(hkl) will take the form of

$$F(hkl) = \sum_j f_j \exp\left[2\pi i(hx_j + ky_j + lz_j)\right]$$

where f_j is the quantity described as the atomic scattering factor and x_j, y_j, z_j designate the atomic positions in the unit cell.

Atomic scattering factor

If we consider scattering by an atom where the electronic charge is distributed around the nucleus then the wave scattered by the atom relative to a point electron situated at the atomic centre is given by:

$$f_j(\bar{H}) = \int_{\text{atom}} \rho_j(\bar{R}_j)\exp\left[2\pi i\ \bar{R}_j.\bar{H}\right] d\bar{R}_j$$

where $\rho_i(\bar{R}_i)$ describes the electron density function of the particular atom, and R_i specifies the location of the electron with respect to its associated nucleus.

If we make the assumption that the electron distribution is spherically symmetric, then f_i becomes a real number and is given by the expression:

$$f_i(\bar{H}) = 4\pi \int_0^\infty \rho_i(R) R^2 \frac{\mathrm{Sin}SR}{SR} \, dR$$

$$(S = 4\pi \, \mathrm{Sin}\,\theta/\lambda \,).$$

This quantity can be found tabulated for the various atoms [5].

In this thesis the scattering factors for non-hydrogen atoms have been calculated from numerical Hartree-Fock wave functions. These scattering factors have been fitted to the analytic function,

$$f(S) = \sum_{i=1}^{4} a_i \exp(-b_i S^2) + c$$

whereby $S = \mathrm{Sin}\,\theta/\lambda$, and the values for the different coefficients were those supplied by Cromer and Mann (1968) [6a] . For hydrogens the scattering factors used, were those given by Stewart [6b] (1965). Essentially, the atomic scattering factor depends upon the model chosen for $\rho(R)$, upon $\mathrm{Sin}\,\theta$, as it falls off slowly with increasing θ, and upon λ as it falls off as the wavelength of the radiation decreases.

1.4 Corrections to the Measured Intensities

The Lorentz factor

As was already mentioned, because of the crystal finite size effect, the time taken for a point to pass through its reflecting condition varies

with the position of the point and its motion (angular velocity w). The time taken for a reciprocal lattice point to cut the sphere of reflection is expressed in proportional terms as

$$t \propto 1/\left[(w/\lambda) \sin 2\theta \right] \qquad \text{hence,}$$

$$\text{Intensity} \propto 1/\text{Sin } 2\theta \ (= \text{Lorentz factor}).$$

Whence $\bar{H}$ is large (high θ) the vector will pass through the reflection sphere faster and the intensity of the reflected radiation will be smaller. Lorentz factor depends on the geometry of the diffraction [7]. For zero level Weissenberg photographs, rotations and oscillation photographs and for diffractometer data obtained by the usual θ/w scans the last expression is valid.

The polarization factor

As the X-ray electromagnetic radiation is reflected by a crystal plane, one of the electric field components suffers reduction while the other component does not. This results in the reflected radiation being partially polarized and the intensity hence being reduced. The correction for this effect, the polarization factor p, takes the form:

$$P = (1 + \cos^2 2\theta)/2.$$

If a crystal monochromator is used to obtain monochromatic radiation, then the expression above might take a form which will include the Bragg angle for the monochromator.

The temperature factor [8]

It can be shown that the overall effect of the temperature is to reduce the scattering factor of the atom by an amount which increases

with the angle. Assuming the thermal vibration to be isotropic

$$\left[f_i\right]_T = f_i \exp(-2\pi^2 \overline{U_\perp^2} \, |H|^2) = f_i \exp(-B_i \sin^2\theta/\lambda^2)$$

where $B_i = 8\pi^2 \overline{U_\perp^2}$ is the temperature factor of the i^{th} atom, $\overline{U_\perp^2}$ is the mean square displacement of the atom perpendicular to the reflecting planes (in the $\bar{H}$ direction) and f_i is the scattering factor without the thermal motion ($0^\circ K$).

If the values of B are the same for each atom then $\exp(-2B \sin^2\theta/\lambda^2)$ is the factor by which the observed intensity is reduced by the thermal vibration and is called the Debye Waller factor. In the case of vibrational anisotropy, the temperature factor takes the form of:

$$\exp\left[-2\pi^2(a^{*2} U_{11} h^2 + b^{*2} U_{22} k^2 + c^{*2} U_{33} l^2 + 2a^*b^* U_{12} hk + 2b^*c^* U_{23} kl + 2c^*a^* U_{31} lh)\right]$$

Absorption of X-rays

When X-rays pass through a crystal the intensity is attenuated by absorption. A beam of original intensity I_0 will suffer a reduction which will be expressed by the formula:

$$I = I_0 \exp(-\mu l)$$

where l is the length the beam is travelling through and μ is the linear absorption coefficient.

To none of the data given in this thesis was absorption correction applied.

Primary and secondary extinction

This is a phenomenon of weakening of a primary X-ray beam by means of multiple reflections which bring about destructive interferences as the beam penetrates further into the crystal.

Primary extinction is significant when the mosaic elements are so large that they behave as fragments of perfect crystals and so give a smaller integrated intensity. In general, this effect is negligible because of the ideally imperfect structure of crystals.

Secondary extinction is the effect of reduction of the intensity with depth of penetration of the primary beam due to diversion of some of the energy into the reflected beam. It can be thought of as a shielding effect which exists at a point in a crystal due to diffraction by the layers of crystals above it which are closer to the incident X-ray beam. This effect can be reduced to some extent by increasing the imperfection of the crystal.

1.5 The Symmetries of the Reciprocal of a Crystal

The actual symmetry

The symmetry of the reciprocal structure conforms to the point group symmetry of the crystal. Therefore a symmetry element $(P/\bar{t})$ in the direct space where $\rho(\bar{r}) = \rho(P\bar{r} + \bar{t})$ will show up as the symmetry element without the translation in the reciprocal space, hence, $P\bar{H}_1 = \bar{H}_2$ where $\bar{H}_1$ and $\bar{H}_2$ are both reciprocal lattice vectors.

Relationships among structure factors

Assuming $(P/\bar{t})$ to be a symmetry operation in direct space it can be shown that

$$F(P\bar{H}) = \exp(2\pi i\, \bar{t}.\bar{H}).F(\bar{H})$$

If the space group does not possess any translation element, then the relationships among the structure factors will be $F(P\bar{H}) = F(\bar{H})$. Finding a reciprocal lattice vector such that $P\bar{H} = \bar{H}$, will impose the exponential term to be equal to unity (in order to observe a reflection). It is from this latter condition that the systematic absences of the space group could be derived.

Relationships among the phases of the structure factors [9]

Assuming the operation $(P/\bar{t})$ to exist,

$$F(P\bar{H}) = F(H)\exp(2\pi i\, \bar{t}.\bar{H})$$

$$\left|F(P\bar{H})\right| = \left|F(H)\right|$$

$$F(P\bar{H}) = \left|F(P\bar{H})\right| \exp[\, i\, \phi(P\bar{H})]$$

$$= \left|F(H)\right| \exp[\, i\, \phi(P\bar{H})]$$

$$F(\bar{H})\exp(2\pi i\, \bar{t}.\bar{H}) = \left|F(\bar{H})\right| \exp[\, i\, \phi(P\bar{H})\,]$$

$$F(\bar{H}) = \left|F(\bar{H})\right| \exp\left\{ i\left[\phi(P\bar{H}) - 2\pi \bar{t}.\bar{H} \right] \right\}$$

$$\phi(\bar{H}) = \phi(P\bar{H}) - 2\pi\, \bar{t}.\bar{H}$$

Hence, once the phases of one vector $\bar{H}$ are known, the phases of all the symmetrical vectors are known too.

An application of the formula derived, to the case of space group $P2_12_12_1$ will produce the following phase relationships:

$$\phi(hkl) = -\phi(\bar{h}kl) + \pi(h+k) = -\phi(h\bar{k}l) + \pi(k+l) = -\phi(hk\bar{l}) + \pi(h+l)$$

CHAPTER 2

STRUCTURE DETERMINATION

2.1 The Phase Problem

The Fourier transform of $F(\bar{H})$ produces the electron density function

$$\rho(\bar{r}) = \int_{\substack{\text{reciprocal} \\ \text{space}}} F(\bar{H}) \exp(-2\pi i\, \bar{r}.\bar{H})\, d\bar{H}$$

and hence it can be shown that

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F(hkl) \exp\left[-2\pi i(hx + ky + lz)\right]$$

Assuming that Friedel's law holds, the electron density function takes the following form without the complex quantity,

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l \left|F(hkl)\right| \cos\left[2\pi i(hx + ky + lz) - \phi(hkl)\right]$$

where h,k,l include the two fragments of indices hkl and $\bar{h}\bar{k}\bar{l}$.

The fact that the Fourier series cannot be calculated directly from the experimental data, but, only the magnitudes $F(\bar{H})$ are directly derivable [not the phases $\phi(hkl)$] gives rise to the so called phase problem. That this problem is in principle solvable is realized from the expression for the structure factor:

$$\left| F(\bar{H}) \right| \exp\left[i\, \phi(\bar{H}) \right] = \sum_{j=1}^{N} f_j \exp(2\pi i\, \bar{r}.\bar{H}).$$

Since a large number n of vectors $\bar{H}$ is considered and if the real and the imaginary parts are equated, this results in a system of 2n equations. The unknowns constitute the 3N components of the vectors $\bar{r}_j$ and n phases $\phi(hkl)$.

In general it can be said that the number of equations 2n exceeds by far the number of unknowns n + 3N, so the phase problem is greatly overdetermined and theoretically solvable.

2.2 The Different Phasing Techniques

The Patterson function

Patterson (1934) introduced the Fourier series known as the Patterson function.

$$P(u,v,w) = \frac{1}{V} \sum_{h,k,l} \left| F(hkl) \right|^2 \exp \left[-2\pi i(hu + kv + lw) \right]$$

the maxima of which represent the interatomic vectors in the structure.

Assuming the summation of the series to be over all h,k,l and Friedel's law to hold will result in a centrosymmetric expression for the Patterson function

$$P(u,v,w) = \frac{1}{V} \sum_{h,k,l} \left| F(hkl) \right|^2 \cos 2\pi (hu + kv + lw).$$

It is by means of the convolution theory that the Patterson function relates to the structure of the unit cell and it can be shown that the Patterson function is the convolution of the electron density function $\rho(x,y,z)$ and its centrosymmetric image $\rho(-x, -y, -z)$ scaled by V the unit cell volume. Hence

$$P(\bar{u}) = V \left[\rho(\bar{r}) * \rho(-\bar{r}) \right] = V \int_{\text{all } \bar{r}} \rho(\bar{r})\, \rho(\bar{u} + \bar{r})\, d\bar{r}$$

The analysis of the function is generally difficult due to the lack of resolution of the $N^2 - N$ interatomic vectors. However in the case that the structure possesses only few heavy atoms, the interatomic vectors associated with the heavy atoms are readily identified and it is then that the atomic coordinates can be obtained directly from the analysis of the Patterson function.

The heavy atom method

The positions of the heavy atom, having been located by a three-dimensional Patterson function (or from a Harker section) can be used to calculate initial sets of phases (based on the heavy atom alone) which in most cases are sufficiently accurate for subsequent determination of the structure. The phase angles thus deduced, will be approximations to the true phases and the resultant Fourier map is hence an approximation for the electron density distribution.

The efficiency of this process for the noncentrosymmetric case has been thoroughly investigated by Sim [10] (1961).

Methods based on isomorphous crystals [11-13]

This technique is an important tool in crystal structure analysis and in particular in protein crystallography where it has been the only way of solving structures. Essentially, two different types of isomorphism can be described between a pair of crystals - the 'addition' type and the 'replacement' type. In the addition type of isomorphism one should have a series of derivatives of a parent molecule (i.e. protein), and in the replacement type isomorphism of structure determination one should have in hand two or more crystalline derivatives which have the same crystal structure but which contain different heavy atoms.

In the case where all heavy atoms occupy the same sites, the anomalous scattering information is of primary value. It is by means of the imaginary part in the expression for the contribution of the anomalous scatterer to the overall structure factor that the phase

ambiguity can be solved. It is also evident that in the case of a single isomorphous derivative when the heavy atom is an anomalous scatterer it is possible to solve the phase problem unambiguously by a comparison[7] of F_{hkl} and $F_{\bar{h}\bar{k}\bar{l}}$.

Direct methods

Direct methods attempt to derive the phases of the structure factors directly from the measured intensities by mathematical means.

Two closely related concepts, the 'normalized structure factor' and the concept of structure invariants are commonly used in direct methods. The 'normalized structure factor' is defined as,

$$E_{\bar{h}}^2 = F_{\bar{h}}^2 \Big/ \overline{F_{\bar{h}}^2} = F_{\bar{h}}^2 \Big/ \epsilon \sum_{j=1}^{N} f_j^2$$

where N is the total number of atoms in the unit cell and ϵ is a space group dependent integer. A structure invariant (with the same value for every choice of origin[14]) is defined as a linear combination of phases $\sum_{\bar{h}} A_{\bar{h}} \phi_{\bar{h}}$ where $A_{\bar{h}}$ are integers satisfying $\sum_{\bar{h}} A_{\bar{h}} \bar{h} = 0$.

The first step in direct methods was made by Harker and Kasper[15-17] (1948) who showed that inequality relations capable of giving phase information do exist.

Following this development by Harker and Kasper and later by Karle and Hauptman[18] (1950), an exact equation relating the structure factors for equal-atom structures, based on the correspondence of the

electron density and the square of the electron density was introduced by Sayre[19] (1952)

$$F_{\bar{h}} = \frac{f_{\bar{h}}}{V.f^{s}_{\bar{h}}} \sum_{\bar{k}} F_{\bar{k}} \; F_{\bar{h}-\bar{k}} \qquad (2.1)$$

where $f^{s}_{\bar{h}}$ is the scattering factor of the squared atom. The relation applies to any equal-atom structure whether centrosymmetric or not. However, in the mathematical sense, Sayre's equation is only valid if one includes all possible terms in the summation. Multiplying both sides of (2.1) by $F_{-\bar{h}}$

$$\left| F_{\bar{h}} \right|^2 = \frac{1}{V} \; \frac{f_{\bar{h}}}{f^{s}_{\bar{h}}} \sum_{\bar{k}} F_{\bar{k}} \; F_{\bar{h}-\bar{k}} \; F_{-\bar{h}} \qquad (2.2)$$

For large $\left| F_{\bar{h}} \right|$ the left hand side of equation (2.2) will be large, real and positive. We may therefore expect a large product on the right hand side of equation (2.2) to be real and positive too. Hence the approximate relationship:

$$\phi_{-\bar{h}} + \phi_{\bar{h}-\bar{k}} + \phi_{\bar{k}} \approx 0 \quad (\text{module } 2\pi) \qquad (2.3)$$

which constitutes the so called $\sum_2$ relationship results. The initial steps of phase determination are based upon the assumption that the invariant $(\phi_{-\bar{h}} + \phi_{\bar{h}-\bar{k}} + \phi_{\bar{k}})$ is equal to zero. Probability theory (and experience) has shown that invariants associated with large normalized structure magnitudes obey the rule quite well.

For centrosymmetric crystals where all phases are either 0 or π, or equivalently, the signs of the structure factors are either + or −, the $\sum_2$ relationships applies,

$$s(E_{\bar{h}}) \sim s(E_{\bar{k}} . E_{\bar{h}-\bar{k}}) \tag{2.4}$$

or for several contributors

$$s(E_{\bar{h}}) \sim s \sum E_{\bar{k}} \cdot E_{\bar{h}-\bar{k}} \tag{2.5}$$

where the symbol $\sim$ means 'probably equal'. The implication of relations (2.4) and (2.5) is that probability relationships do exist. The actual approximate probability relationship which was derived by Woolfson[20] (1954) and Cochran and Woolfson[21] (1955) is of the form,

$$P_+(E_{\bar{h}}) = \tfrac{1}{2} + \tfrac{1}{2} \tanh\left[\sigma_2^{-3/2} \sigma_3 \left|E_h\right| \sum_{\bar{k}} E_{\bar{k}} E_{\bar{h}-\bar{k}}\right] \tag{2.6}$$

which shows the probability that $E_{\bar{h}}$ is positive

where $\sigma_m = \sum_{j=1}^{N} Z_j^m$, and Z_j is the atomic number of the j^{th} atom. The quantity $\dfrac{\sigma_3}{\sigma_2^{3/2}}$ is equal to $N^{-\frac{1}{2}}$ for an equal-atom structure, where N is the total number of atoms in the unit cell. The larger the magnitudes of $E_{\bar{h}}$, $E_{\bar{k}}$ and $E_{\bar{h}-\bar{k}}$ are, the higher will be the probability of a correct sign assignment (the opposite holds for large number of atoms). Therefore any phase determination process should be initiated with reflections of the largest E magnitudes.

For <u>non-centrosymmetric</u> crystals, although zero is the most probable value of the invariant, the value of $\phi_{-\bar{h}} + \phi_{\bar{h}-\bar{k}} + \phi_{\bar{k}}$ can range over $-\pi$ to $+\pi$.

Cochran[22] (1955) found that the probability distribution for $\phi_{\bar{h}}$, given a fixed $\phi_{\bar{h}-\bar{k}} + \phi_{\bar{k}}$ and the accompanying $|E|$ values is given by:

$$P(\phi_{\bar{h}} / \left|E_{-\bar{h}}\right|, \left|E_{\bar{k}}\right|, \left|E_{\bar{h}-\bar{k}}\right|) = P(\phi / \left|E_{-\bar{h}}\right|, \left|E_{\bar{k}}\right|, \left|E_{\bar{h}-\bar{k}}\right|)$$

$$= \frac{1}{2\pi I_0(A)} \exp(A \cos \phi) \tag{2.7}$$

where

$$A = K_{\bar{h},\bar{k}} = A(\bar{h},\bar{k}) = 2\sigma_3\,\sigma_2^{-3/2} \left| E_{-\bar{h}}\; E_{\bar{k}}\; E_{\bar{h}-\bar{k}} \right| \text{ and}$$

is related to the variance of the probability distribution, $\phi = \phi_{-\bar{h}} + \phi_{\bar{k}} + \phi_{\bar{h}-\bar{k}}$ and I_0 is a modified Bessel function of the second kind. For an equal-atom structure $A = 2N^{-1/2} \left| E_{-\bar{h}}\; E_{\bar{k}}\; E_{\bar{h}-\bar{k}} \right|$. Clearly (2.7) has a maximum when $\phi_{-\bar{h}} + \phi_{\bar{k}} + \phi_{\bar{h}-\bar{k}} = 0$, and the larger the value of A (i.e. the larger the $|E|$ values) the steeper will this maximum be (the smaller the variance will be).

Given several fixed 'addition pairs', $\phi_{\bar{k}} + \phi_{\bar{h}-\bar{k}}$, and probability distribution for each value of $\bar{k}$, Karle and Karle[23] showed that formula (2.7) can be used to derive the phase determining formula known as the tangent formula:

$$\tan \phi_{\bar{h}} \approx \frac{\sum_{\bar{k}} \left| E_{\bar{k}}\; E_{\bar{h}-\bar{k}} \right| \sin(\phi_{\bar{k}} + \phi_{\bar{h}-\bar{k}})}{\sum_{\bar{k}} \left| E_{\bar{k}}\; E_{\bar{h}-\bar{k}} \right| \cos(\phi_{\bar{k}} + \phi_{\bar{h}-\bar{k}})} \qquad (2.8)$$

whereas now the probability distribution of $P(\phi_{\bar{h}})$ takes the form of:

$$P(\phi_{\bar{h}}) = C \exp \alpha_{\bar{h}} \cos(\phi_{\bar{h}} - \beta_{\bar{h}}) \qquad (2.9)$$

and $\tan\beta$ is equal to the expression on the right hand side of equation (2.8).

It is important to note that the same relationship which exists between the variance of the distribution (2.9) to $\alpha_{\bar{h}}$ does exist between the variance of the distribution (2.7) to A.

It has been found advantageous to use a modified tangent formula[24] which incorporates a weighting scheme. When a phase $\phi_{\bar{h}}$ is derived an associated weight ($w_{\bar{h}}$) is also derived. Simply stated, the tangent formula enables one to calculate unknown phases once a sufficient number of initial phases has been determined.

Among the methods for phase determination which have proved very effective and are still in common use, are the symbolic addition techniques and the multiple solution techniques. In a typical multiple solution technique for noncentrosymmetric structures, the set of starting phases consists of phases with special values to fix the origin and enantiomorph, some phases with values determined by auxiliary formula (i.e. $\sum_1$), and n additional phases with trial values which are required to initiate the phase determination. Restricting the trial values of the n additional phases to $\pm \frac{\pi}{4}$ and $\pm \frac{3\pi}{4}$, 4^n extended and refined phase sets are obtained, each of which is a possible solution. Figures of merit to associate with each set of phases are established in order to judge their relative plausibilities, and the corresponding E - map/s are produced.

However the present common techniques of direct methods do not always lead to a successful structure determination and different techniques should be used (i.e. invariants estimates based on the neighbourhoods[25] concept, least squares analysis of cosine invariants triplets and quartets[26] etc.).

The two packages of crystallographic computer programs which have been used to solve the structures appearing in this thesis by direct methods are i) 'MULTAN'[27] versions 1974, 1976 and 1978 and ii) 'X-RAY 72'[28].

2.3 Least-Squares Refinement

Crystallographic refinement is usually carried out by assuming the validity of the non-linear least squares procedure and minimizing the function:

$$D = \sum_{hkl} w_{hkl}(|F_0| - |F_c|)^2$$

where w_{hkl} is the weight of the observation and the summation is over all the observed reflections. The set of normal equations one gets in the least-squares procedure[29] is of the form,

$$\sum_{k=1}^{n} N_{ik} \Delta P_k = d_i$$

$$\vdots \qquad\qquad \vdots$$

where $$N_{jk} = \sum_{r=1}^{m} w_r \frac{\partial |F_c^r|}{\partial P_j} \cdot \frac{\partial |F_c^r|}{\partial P_k}$$

and $$N_{ii} = \sum_{r=1}^{m} w_r \left(\frac{\partial |F_c^r|}{\partial P_i}\right)^2$$

n is the number of parameters, ΔP_k the difference between the approximate and true values of the parameters and m, the number of observations. In matrix notation, N_{jk} and N_{ii} are matrix elements of the matrix

N(nxm) and so are ΔP and d (l x n). Since, if this set of normal equations has a solution, the inverse matrix N^{-1} must exist:

$$N^{-1}N \Delta P = N^{-1} d \quad \text{and} \quad \Delta P = N^{-1}d.$$

In practice the process might repeat itself with corrected parameters until the average and maximum shifts over errors are smaller than unity. The standard deviation derived, is given by,

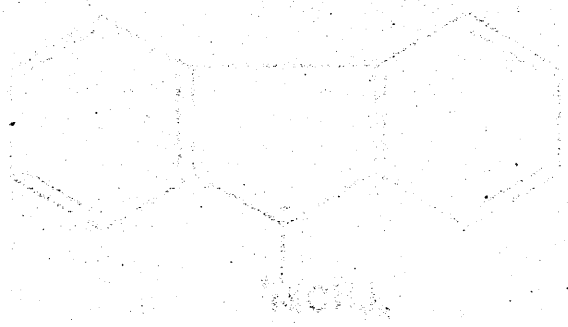
$$\sigma_i^2 = (N_{ii}^{-1}) \sum_{r=1}^{m} w_r (\Delta F^r)^2 / (m - n)$$

where w_r is the weight of the r^{th} ΔF, m the number of observations, n the number of parameters, and N_{ii}^{-1} the i^{th} diagonal element of the inverse matrix.

The most commonly used least-squares techniques are the so called 'block diagonal least-squares' and the 'full matrix least-squares' whereby the former is assumed to be an approximation to the 'full matrix' technique[29].

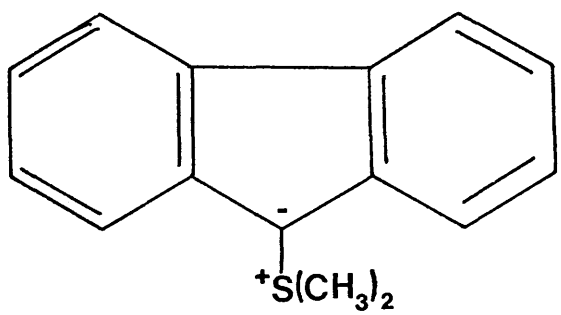
CHAPTER 3

STRUCTURAL STUDIES OF YLIDES AND RELATED YLIDES



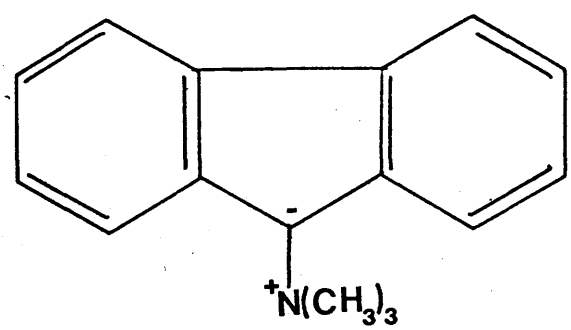
INTRODUCTION

Ylides, formally zwitterions in which a negatively charged carbon atom achieves stabilization by an interaction with an adjacent positively charged hetero atom, have been known for over forty years since the report by Ingold and Jessop[1] (1930) on the isolation of dimethylsulphonium fluorenylid (I).



1

The history of ylides thus predates their name, the term 'ylide' (or ylid) having been introduced by Wittig[2,3] (1944) while working with the compound trimethylammonium fluorenylid (2), and its use was then immediately extended by him to include the sulphonium analogues of (I).



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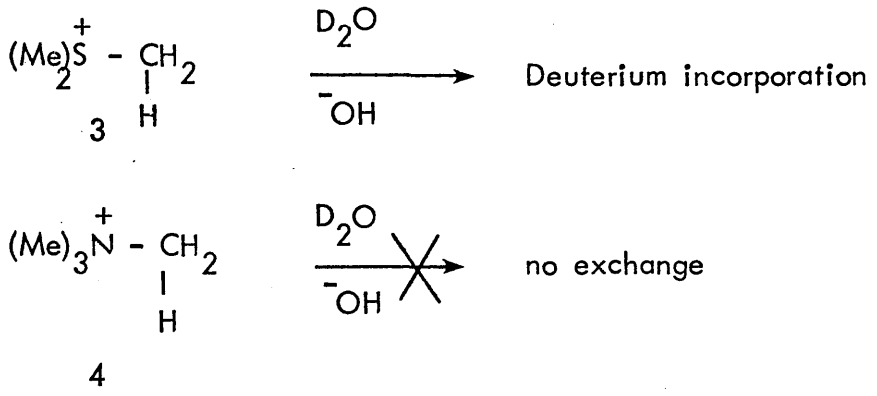
The current definition of ylides is extended to all compounds for which a vicinal zwitterionic electronic structure may reasonably be written e.g. $\rangle \overset{+}{X} - \overset{-}{Y} \langle$ where $\overset{+}{X}$ = (P,N,As,Sb,S,Se), and Y^- = (C,N,O). Compounds which fall into this category include carbon-sulphur ylides ($\rangle \overset{+}{S} - \overset{-}{C} \langle$), carbon-phosphorus ylides ($\rightarrow \overset{+}{P} - \overset{-}{C} \langle$), and 'onium imine' ylides ($\rangle \overset{+}{X} - \overset{-}{N} -$).

It was the introduction of Wittig's olefin synthesis[4] (1953) which led to the extensive investigation of the properties and reactions of phosphorus ylides and thereafter to the explorations of the properties of ylides of nitrogen, arsenic and sulphur.

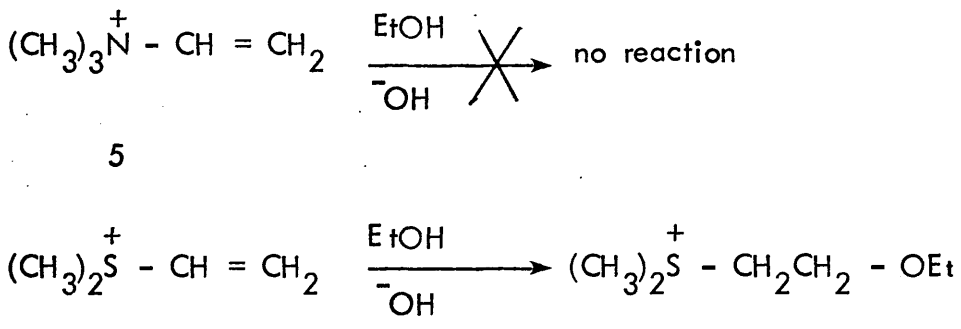
Since the main work in this thesis is devoted to sulphur-containing ylides ($\rangle \overset{+}{S} - \overset{-}{C} \langle$ and $\rangle \overset{+}{S} - \overset{-}{N} -$) the forthcoming discussion of the chemistry and bonding characteristics will tend to refer to this class of compounds.

Amongst the many examples which indicate that 'unusual' stabilization is inherent where a sulphonium centre is bonded to an adjacent negatively charged atom, the most noteworthy are the following two observations made by Doering and Hoffman[5] (1955) and Doering and Schreiber[6] (1955),

(i) Trimethylsulphonium iodide (3) undergoes 98% deuterium incorporation at 62°C after 3 hours, whereas tetramethylammonium iodide (4) shows no observable exchange after 504 hours under the same conditions.



(ii) It has been impossible to add bases to the vinyltrimethylammonium ion (5) while the vinyldimethylsulphonium ion (6) reacts very rapidly (10^5 times faster) with a variety of bases by addition, to give the 2-substituted ethyldimethylsulphonium ions (7).



However, the chemistry of sulphur ylides and its practical application in organic synthesis came to light only after the demonstration by Corey and Chaykovsky[7] (1962, 1965) of the selective methylene transfer capability of dimethylsulphonium and dimethylsulphoxonium methylides.

The enhanced stability of sulphur ylides in contrast to their first row analogues[8-11] has been attributed to the possibility of valence-shell expansion by π bonding in which overlap occurs between a vacant 3d orbital on the sulphur atom and a filled 2P orbital on the adjacent

anionic first row atom (Fig. 1). However, the possibility that the 2P orbital may rotate (by 90°) and overlap with an equivalent d-orbital may explain why no unusual barrier to rotation about the S-C bond should necessarily develop (Fig. 1).

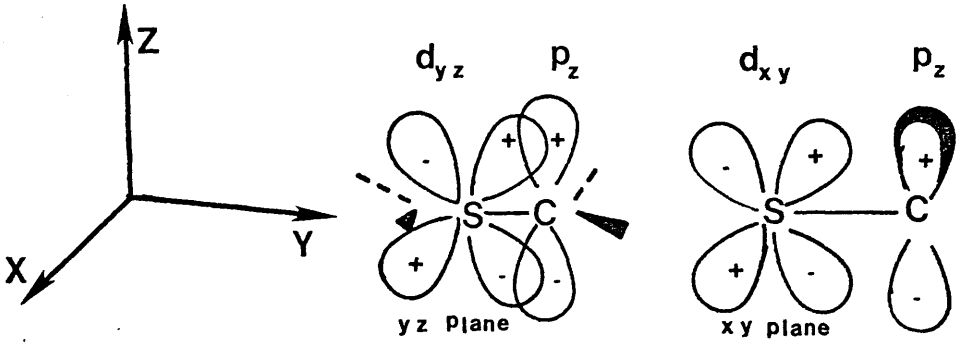


Figure 1. d_π - P_π orbital overlap[24].

A critical review of the evidence for such interactions has been given by Mitchell[12] (1969) and relevant discussions concerning the ability of d orbitals to participate in the chemical bond have been given by Clark[13] (1970), Coulson[14] (1969) and by Kwart and King[15] (1977).

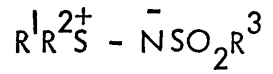
In contrast to the 'second row' ylides, no formal bonding of $(d\text{-}P)_\pi$ type between the 'onium' group and the vicinal atom can occur in ylides of first row elements since the energy gap to the next highest vacant orbital is too great for effective bonding[16].

Although recent reports[17] of theoretical examination of the essence of the chemical bonds in ylides have claimed to demonstrate the importance of ionic interactions as opposed to $(d\text{-}P)_\pi$ interactions, the nature of the stabilization remains complex and debatable, and might be attributed to several, not necessarily, independent factors.

Thus, by attaching different groups to the anionic centre (in sulphonium ylides) additional stabilizing/destabilizing effects can be envisaged and the relative stabilities of such ylides may be qualitatively reflected in the ease of their formation from the corresponding sulphonium cations $R_2\overset{+}{S} - CH\,Z^1Z^2$, which varies markedly with the nature of Z^1 and Z^2. If Z^1 and Z^2 are electron withdrawing groups (e.g. carbonyl, cyano carbonyl etc.), the ylides are in general sufficiently stable to permit isolation by simple procedures. In contrast, if Z^1 and Z^2 are hydrogens (e.g. dimethylsulphonium methylide), the resulting ylide is generally unstable and the process requires a strong base such as t-butoxide ion and working temperatures of below 0°C. Sulphonium n-alkylides (Z^1 = H, Z^2 = n-alkyl) are even less stable than sulphonium methylides and can only be generated efficiently by careful selection of base, temperature and solvent (e.g. diphenylsulphonium methylide is generated at -78°C in T.H.F. with t-butyllithium as a base). Ylides where both substituents Z^1 and Z^2 are alkyl groups are thus expected to be the least stable of all sulphonium alkylides and the most difficult to prepare. Indeed this latter fact was well illustrated by Corey's preparation of diphenylsulphonium isopropylide[18] ($Ph_2\overset{+}{S} - \overset{-}{C}(CH_3)_2$).

The same qualitative picture can be applied to sulphur-nitrogen ylides[19] ($\rangle\overset{+}{S} - \overset{-}{N}-$). Therefore N-sulphonyliminosulphuranes (8) and N-acyliminosulphuranes (9) are non hygroscopic and stable solids at room temperature, while the N-aryliminosulphuranes (10), with electron

withdrawing groups (CN or NO_2) on the ring, are only moderately stable (1-12 months at room temperature) and N-aryliminosulphuranes with electron donating substituents on the ring are hygroscopic and decompose within a few days or weeks at room temperature.



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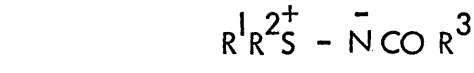

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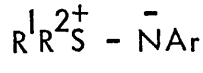

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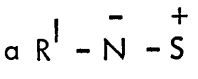
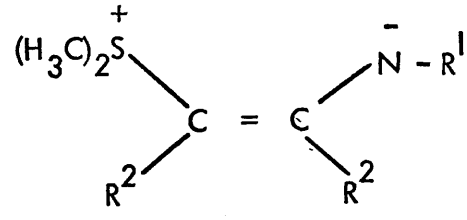
Brief reviews of the chemistry of sulphur ylides have been given by Johnson[9] (1966), Lawe[20] (1970), Block[21] (1971), Hudson[10] (1971), Field[22] (1972), Stirling[23] (1975), Trost and Melvin[24] (1975), Gilchrist and Moody[25] (1977), Oae[26,27] (1977), Block[28] (1978) and Field[29] (1978).

It can be seen that the bonding and conformational characteristics of ylides have in recent years become the subject of considerable systematic structural studies. Continuing previous work carried out in Glasgow, the crystal structures of 2 sulphur-nitrogen ylides of the general formula  and of five related ylides (Betaines) of the general formula (II) have been determined as part of the work for the present thesis.



II

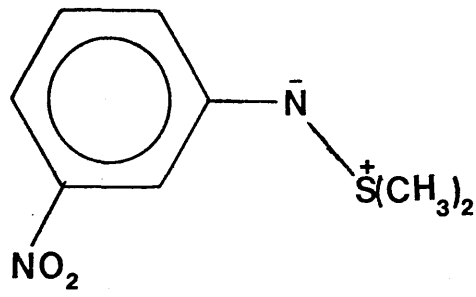
The latter compounds are structural variants of the former in which the group $(\rangle_{R^2} C = C\langle_{R^2})$ has been interposed between the sulphonium and the imine species. Both groups are chemically related and provide novel routes to the synthesis of heterocycles[13] (i.e. pyrroles). The results of these structure determinations are presented in the following 7 sections. Section 8 is an overall discussion of the implications of these analyses.

THE CRYSTAL AND MOLECULAR STRUCTURES OF TWO YLIDES OF THE FORM $(CH_3)_2S^{+}\overline{N}Ar$

I. R = m - $O_2NC_6H_4$

II. R = p - $O_2NC_6H_4$

3.1 Experimental and Results for I.



I

S,S - Dimethyl-N-m-nitrophenylsulphimide

Preparation of Crystals

The title compound (I) was prepared by the published procedure described by Claus and Vilsmaier[30] (1975) and which can be summarized in the following chemical equation:

$$\text{m-Nitroaniline} + (CH_3)_2S + X - Cl \longrightarrow \quad (I)$$

$$X = N\begin{cases} COCH_2 \\ \\ COCH_2 \end{cases} \quad \text{(N-succinimidyl)}$$

Crystallization from 'ether-hexane-dichloromethane' yielded red coloured needle shaped crystals with a melting point of 97 - 99°C (Lit.[25,31] m.p. 100 - 101). The structure was confirmed by its own characteristic I.R. band positions[32] (960, 965, CH_2Cl_2 as solvent) and the typical fragments in the mass spectrum[25]:

m/e, 198(M^+), 183($M^+ - CH_3$), 168($M^+ - 2CH_3$), 151($M^+ - CH_3S$),
136($M^+ - S(CH_3)_2$), 122($M^+ - (CH_3)_2SN$).

Crystal Data

Molecular Formula	$C_8H_{10}N_2O_2S$
Molecular Weight	198.24 a.m.u.
Crystal System	Orthorhombic
Unit Cell Dimensions	$a = 13.663(3)$ Å
	$b = 13.850(3)$ Å
	$c = 5.008(1)$ Å
Unit Cell Volume	$V = 947.74$ Å^3
Number of Molecules per Unit Cell	$Z = 4$
Calculated Density	$D_c = 1.39$ g.cm^{-3}
Number of Molecules per Asymmetric Unit	$N = 1$
Spare Group	$P2_12_12_1$ (D_2^4 , No.19)
Equivalent Positions	x,y,z
	$\frac{1}{2}-x, -y, \frac{1}{2}+z$
	$\frac{1}{2}+x, \frac{1}{2}-y, -z$
	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
Linear Absorption Coefficient	$\mu = 2.96$ cm^{-1}
Number of Electrons per Unit Cell	$F(000) = 416$

Data Collection

Diffractometer Used	Hilger and Watts Y290
Radiation Used	Mo - K_α , $\overline{\lambda} = 0.71069$ Å
Filter	Graphite Monochromator
	$\cos^2 2\theta_m = 0.970$
Upper Limit for Data Collection	2θ max = 60°

Number of Observed Independent Reflections	$m = 1348$
Unobserved Cut-Off	$2.5\sigma_I$
Number of Parameters Refined	$n = 158$
Number of Reflections per Parameter	$m/n = 8.5$

Structure Determination and Refinement

The diffraction pattern exhibited orthorhombic symmetry conforming to the space group $P2_12_12_1$ (D_2^4, no.19), based on the systematic absences hoo for $h = 2n + 1$, oko for $k = 2n + 1$ and ool for $l = 2n + 1$.

The crystal structure was solved by direct methods using the set of programs incorporated in the 1976 version of 'MULTAN'. 1500 $\sum_2$ relationships among the 150 reflections with $|E| > 1.45$ were included in the phase determination by the weighted-tangent formula (10 relationships per reflection and 11.5 reflections per nonhydrogen atom). The weighted figure of merit of the set of phases from which the structure was eventually obtained was the highest of the 64 sets calculated. The various parameters used with 'MULTAN' are summarized in Table 3.1.1. The positions of 11 atoms (out of 13 nonhydrogen atoms in the asymmetric unit) were revealed from the initial E-map, while the positions of the remaining 2 nonhydrogen atoms were derived from a difference-electron-density synthesis phased on the 11 atoms. The calculated R and R_w at this stage were equal to 0.226 and 0.289 respectively.

The crystal structure was fully refined to convergence by 14 cycles of full matrix least-squares minimizing the function $\sum w(|F_o| - |F_c|)^2$.

The refinement of the atomic positional and anisotropic thermal parameters for C, N, O and S atoms and positional and isotropic thermal parameters for hydrogen atoms led to a conventional R factor of 0.030 and a weighted R-factor of 0.036. Towards the later stages of the refinement the observations were weighted according to their estimated errors and a weighting scheme of the form $w = 1/\sigma^2(F_o)$ was used instead of unit weights which were applied initially. The agreement analysis of averaged $w\Delta^2$ with groups of increasing $|F_o|$ at the end of the refinement showed little variation of $\overline{w\Delta^2}$ with $|F_o|$ and the weighting scheme was therefore considered adequate.

The different stages in the refinement are outlined in Table 3.1.2. A difference synthesis calculated after cycle 14 was featureless and revealed no errors in the model, the maximum electron density being 0.19 $e\text{A}^{o\,-3}$. The refinement was assumed complete with average shift/error of 0.013, maximum shift of 0.129 σ and standard deviation of an observation of unit weight equal to 0.2463. No absorption correction was applied. In all structure factor calculations the atomic scattering factors for C, O, N and S were computed from numerical Hartree-Fock wave functions whilst those for hydrogen were given by Stewart et al (1965).

Final values of the observed and calculated structure factors, including phases, are given in the supplement to this thesis.

The crystal and molecular structure together with a numbering scheme are given in Figures 3.1.1(a) and 3.1.1(b). The atomic coordinates

and thermal parameters with e.s.d.'s, bond lengths, valency angles and torsion angles with e.s.d.'s and other relevant data are given in Tables 3.1.3 to 3.1.6.

Table 3.1.1.

SUMMARY OF THE CONDITIONS (INCLUDING VARIOUS FIGURES OF INTEREST) ASSOCIATED WITH SOLVING THE STRUCTURE OF I.

In this table:

1. NE - is the number of the largest $|E|$'s chosen to define the structure.
2. NSRT - is the number of $\sum_2$ relationships to be retained.
3. NSRTT - is the total number of $\sum_2$ relationships.
4. PROB - is the probability acceptance limit chosen for $\sum_1$.
5. NSPEC - is the number of special phases (permutations restricted to ϕ_{spec}, $\phi_{spec} + 180^\circ$).

   NGEN - is the number of general phases (phase permutation 45°, 135°, 225°, 315°).

   NANY - is the number of phases of either sort.
6. NSET - is the total number of phase sets that have been developed.
7. PUB - is the published phase.
8. NAT - is the number of nonhydrogen atoms in the asymmetric unit.
9. ABS FOM, PSI ZERO, RESID and CFOM are all figures of merit.

$C_8H_{10}N_2O_2S$, $P2_12_12_1$, NAT = 13

PARAMETERS		STARTING SET TYPE	hkl	PHI (o)	PUB (o)	RESULTS PHASE SET CONSIDERED	FIGURES OF MERIT ABS FOM	PSI ZERO	RESID	TOTAL NUMBER OF CORRECT PEAKS FOUND IN E-MAP
SIGMA-2		SIGMA-1	0,10,0	180	180	Max.	1.4102	236.7	39.49	11
NE(|E|>1.45)	150					Min.	0.5613	113.7	17.83	
NSRT	1500	Origin defining phases	8,3,0	360	360	CFOM56 = 2.0045	1.4100	236.1	17.83	
NSRTT	1658		0,14,1	360	360					
CONVERGE			5,4,2*	45	94					
PROB	0.95	Permuted Phases	8,13,0	360 180	180					
NSPEC,NGEN, NANY	2,2,0		1,0,3	±90	270					
FASTAN			2,6,4	±45 ±135	273					
NSET	64		2,8,3	±45 ±135	269					

*The enantiomorph is fixed by the 5,4,2 reflection.

Table 3.1.2.

PROGRESS OF LEAST-SQUARES REFINEMENT

CYCLES	PARAMETERS REFINED	R	Rw
0	None	0.226	0.289
4	x,y,z U(iso) for C,N,O,S; scale factor; full matrix; unit weights.	0.096	0.118
2	x,y,z, U_{ij} for C,N,O,S; scale factor; full matrix; unit weights.	0.067	0.102
3	x,y,z, U_{ij} for C,N,O,S; x,y,z, U(iso) for H atom; scale factor; full matrix; unit weights.	0.051	0.075
3	As above but after applying counting loss correction.	0.038	0.051
2	As after cycle 9 but applying a weighting scheme instead of unit weights.	0.030	0.036

Table 3.1.3(a,b,c,d)

(a) Fractional atomic coordinates ($\times 10^4$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM X/A Y/B Z/C

(b) Anisotropic thermal parameters ($\mathring{A}^2$, $\times 10^3$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}.

(c) Fractional atomic coordinates ($\times 10^3$) of hydrogen atoms with e.s.d.'s in parentheses. The hydrogens are numbered according to the atoms to which they are attached.

(d) Isotropic thermal parameters ($\mathring{A}^2$, $\times 10^2$) of hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM $U_{(iso)}$.

C(1)	3054(1)	7970(1)	8192(4)
C(2)	3690(1)	7613(1)	10145(4)
C(3)	3469(1)	6757(1)	11449(4)
C(4)	2645(2)	6207(1)	10904(5)
C(5)	2031(2)	6555(2)	8948(5)
C(6)	2219(1)	7408(1)	7608(5)
C(7)	5043(2)	9344(2)	5674(6)
C(8)	3610(2)	10665(2)	6594(6)
N(1)	3156(1)	8827(1)	6769(4)
N(2)	4152(1)	6416(1)	13507(4)
O(1)	3960(2)	5672(1)	14705(4)
O(2)	4888(1)	6890(1)	13964(5)
S	4019(0)	9532(0)	7831(1)

3.1.3 (a)

C(1)	37(1)	37(1)	38(1)	0(1)	0(1)	-3(1)
C(2)	35(1)	37(1)	44(1)	-3(1)	-2(1)	-2(1)
C(3)	39(1)	36(1)	41(1)	3(1)	1(1)	-3(1)
C(4)	51(1)	41(1)	57(1)	-8(1)	-1(1)	2(1)
C(5)	47(1)	47(1)	68(1)	-12(1)	-10(1)	0(1)
C(6)	42(1)	47(1)	52(1)	-4(1)	-11(1)	-2(1)
C(7)	50(1)	66(1)	57(1)	-9(1)	4(1)	-9(1)
C(8)	65(1)	40(1)	64(2)	-3(1)	-7(1)	5(1)
N(1)	45(1)	43(1)	46(1)	-8(1)	-10(1)	3(1)
N(2)	48(1)	43(1)	48(1)	7(1)	-2(1)	2(1)
O(1)	85(1)	51(1)	75(1)	-2(1)	-16(1)	21(1)
O(2)	52(1)	79(1)	86(1)	-11(1)	-25(1)	25(1)
S	45(0)	39(0)	35(0)	-6(0)	-5(0)	2(0)

3.1.3 (b)

H(2)	425(2)	792(2)	1058(5)
H(4)	257(2)	560(2)	1186(6)
H(5)	147(2)	614(2)	847(7)
H(6)	177(2)	759(2)	617(5)
H(71)	554(2)	986(2)	598(7)
H(72)	485(2)	936(2)	388(7)
H(73)	528(2)	863(2)	592(6)
H(81)	416(2)	1115(2)	665(7)
H(82)	348(2)	1056(2)	472(7)
H(83)	304(2)	1087(2)	755(7)

3.1.3 (d)

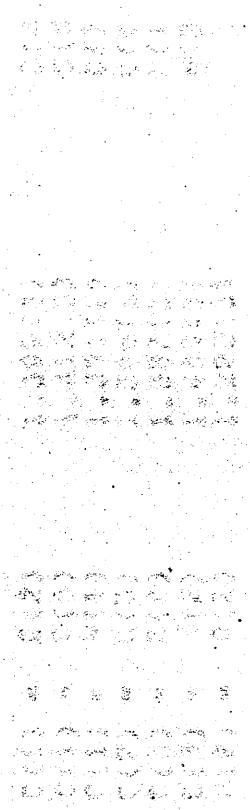
H(2)	5(1)
H(4)	6(1)
H(5)	8(1)
H(6)	5(1)
H(71)	9(1)
H(72)	8(1)
H(73)	6(1)
H(81)	8(1)
H(82)	7(1)
H(83)	7(1)

Table 3.1.4(a,b,c)

(a) Interatomic distances (Å) with e.s.d.'s in parentheses. The hydrogen atoms are numbered according to the atoms to which they are attached.

(b) Interbond angles (in degrees) with e.s.d.'s (degrees) in parentheses.

(c) Torsion angles (degrees) with e.s.d.'s (degrees) in parentheses.



C(1) - C(2)	1.399(3)		C(4) - C(5)	1.376(3)	
C(1) - C(6)	1.412(3)		C(5) - C(6)	1.382(3)	
C(1) - N(1)	1.391(2)		C(7) - S	1.787(3)	
C(2) - C(3)	1.386(3)		C(8) - S	1.777(2)	
C(3) - C(4)	1.387(3)		N(1) - S	1.622(2)	
C(3) - N(2)	1.468(3)		N(2) - O(1)	1.221(2)	
N(2) - O(2)	1.222(3)				

3.1.4 (a)

C(2)	H(2)	0.899(23)	C(7)	H(72)	0.939(36)
C(4)	H(4)	0.970(25)	C(7)	H(73)	1.041(28)
C(5)	H(5)	0.988(29)	C(8)	H(81)	1.001(30)
C(6)	H(6)	0.983(24)	C(8)	H(82)	0.967(35)
C(7)	H(71)	0.995(31)	C(8)	H(83)	0.959(31)

3.1.4 (a) continued.

C(6)	C(1)	C(2)	116.83(17)	N(1)	C(1)	C(2)	126.74(17)
C(3)	C(2)	C(1)	119.79(17)	N(1)	C(1)	C(6)	116.43(17)
C(5)	C(6)	C(1)	121.41(20)	S	N(1)	C(1)	114.73(14)
C(4)	C(3)	C(2)	123.57(19)	N(2)	C(3)	C(2)	117.86(16)
N(2)	C(3)	C(4)	118.57(18)	C(5)	C(4)	C(3)	116.29(20)
O(1)	N(2)	C(3)	118.68(18)	O(2)	N(2)	C(3)	118.80(18)
C(6)	C(5)	C(4)	122.08(21)	C(8)	S	C(7)	99.46(13)
N(1)	S	C(7)	106.45(11)	N(1)	S	C(8)	100.89(11)
O(2)	N(2)	O(1)	122.52(21)				

3.1.4 (b)

C(6)	C(1)	C(2)	C(3)	-1.7(3)		N(1)	C(1)	C(2)	C(3)	177.9(2)
C(2)	C(1)	C(6)	C(5)	1.4(3)		N(1)	C(1)	C(6)	C(5)	-178.3(2)
C(2)	C(1)	N(1)	S	-9.3(3)		C(6)	C(1)	N(1)	S	170.4(1)
C(1)	C(2)	C(3)	C(4)	1.1(3)		C(1)	C(2)	C(3)	N(2)	-179.2(2)
C(2)	C(3)	C(4)	C(5)	0.0(3)		N(2)	C(3)	C(4)	C(5)	-179.7(2)
C(2)	C(3)	N(2)	O(1)	178.8(2)		C(2)	C(3)	N(2)	O(2)	-0.9(3)
C(4)	C(3)	N(2)	O(1)	-1.5(3)		C(4)	C(3)	N(2)	O(2)	178.8(2)
C(3)	C(4)	C(5)	C(6)	-0.4(3)		C(4)	C(5)	C(6)	C(1)	-0.3(3)
C(1)	N(1)	S	C(7)	99.6(2)		C(1)	N(1)	S	C(8)	-157.1(2)

3.1.4 (c)

Table 3.1.5.

A. Selected intramolecular non-bonded distances (< 4.0 Å)

S	... C(2)	2.93	N(2)	... C(2)	2.44
S	... H(2)	2.65	N(2)	... C(4)	2.45
N(1)	... C(2)	2.49	O(1)	... C(4)	2.72
N(1)	... C(6)	2.38	O(1)	... H(4)	2.38
N(1)	... H(2)	2.73	O(2)	... C(2)	2.71
N(1)	... H(6)	2.58	O(2)	... H(2)	2.38
N(1)	... C(8)	2.62	C(7)	... H(2)	3.33

B. Selected intermolecular distances (< 4.5 Å).

S	... $N(1)^{i}$	4.23	C(8)	... $O(2)^{ii}$	3.47
S	... $O(1)^{ii}$	3.41	C(8)	... $N(1)^{i}$	3.61
S	... $O(2)^{ii}$	3.93	C(8)	... $N(1)^{iii}$	3.49
C(7)	... $O(1)^{ii}$	3.26			

Roman numeral superscripts refer to the following equivalent positions relative to the molecule at (x,y,z):

(i) 1/2 - x, 2 - y, 1/2 + z

(ii) 1 - x, 1/2 + y, 5/2 - z

(iii) 1/2 - x, 2 - y, -1/2 + z.

Table 3.1.6

LEAST–SQUARES PLANES

Planes are in the form of $Ax + By + Cz - D = 0$ where x,y and z refer to an orthogonalized set of axes, D is the perpendicular distance from the plane to the origin and A, B and C refer to the components of unit vector normal to the best plane. An asterisk denotes atoms used to define the plane.

A.

(I) Equation of the plane

$0.5121x - 0.5052y - 0.6947z + 6.2820 = 0$

$\chi^2 = 43.35$ with 3 degrees of freedom.

The deviations (Å) of the atoms from the plane are:

C(1)*	-0.008(2)	S	-0.3003(5)
C(2)*	0.008(2)	C(7)	1.298 (3)
C(3)*	-0.002(2)	C(8)	-0.949 (3)
C(4)*	-0.005(2)	N(2)	-0.002 (2)
C(5)*	0.003(2)	O(2)	-0.033 (2)
C(6)*	0.005(2)	O(1)	0.022 (2)
N(1)	-0.041(2)		

(2) Equation of the plane

$0.6480x - 0.4463y - 0.6172z + 4.7550 = 0$

The deviations (Å) of the atoms from the plane are:

C(1)*	0.0	C(6)	-0.211(2)
N(1)*	0.0	C(7)	1.690 (3)
S*	0.0	C(8)	-0.680 (3)
C(2)	0.180(2)		

(3) Equation of the plane

$$0.2128x - 0.0183y + 0.9769z - 4.005 = 0$$

The deviations (Å) of the atoms from the plane are:

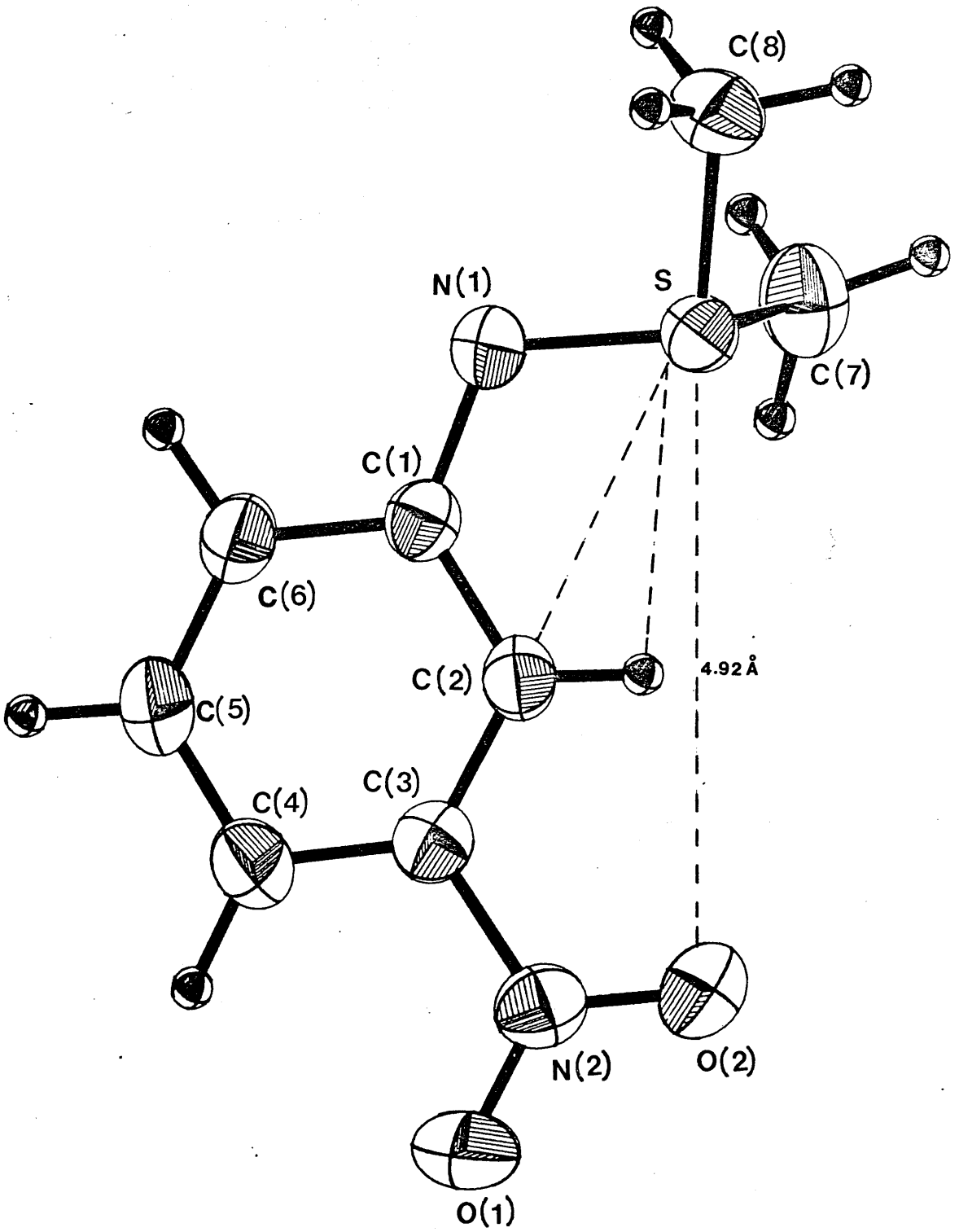
C(7)*	0.0
C(8)*	0.0
N(1)*	0.0
S	0.7529(5)

B. Dihedral angle between planes (1) and (2) is 9.6°, between (1) and (3) is 124.1° and between (2) and (3) is 117.2°.

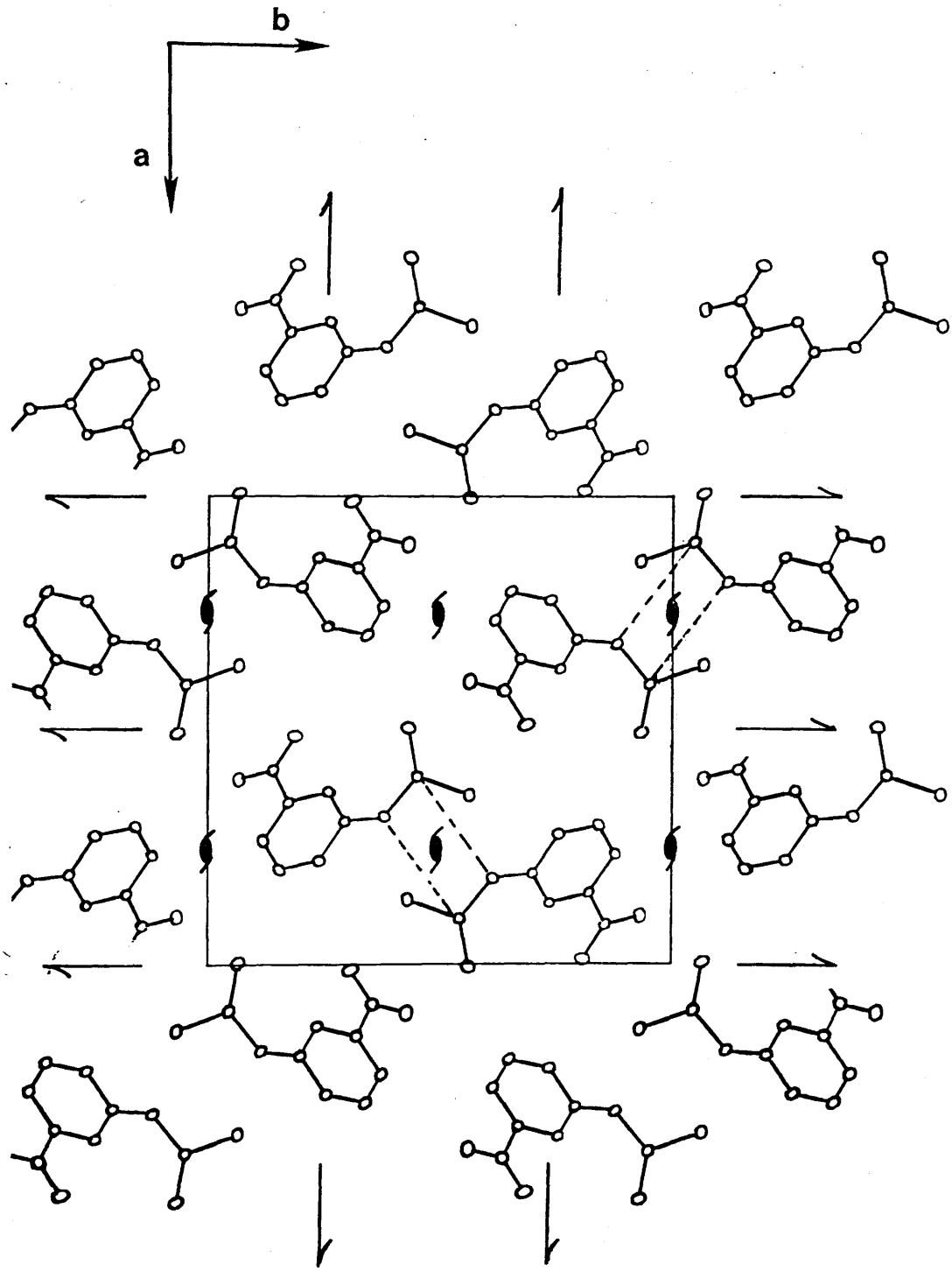
Figure 3.1.1 (a and b)

a. A general view of I giving the atomic numbering scheme. Hydrogen atoms are numbered according to the atoms to which they are bonded.

b. The molecular packing of I viewed along the short axis 'c'.



(a)



(b)

Discussion of I

The major conformational features as revealed by the crystal structure analysis of I are illustrated by the three Newman projections given in Figure 3.1.2, along the N(2) - C(3), C(1) - N(1) and N(1) - S bonds respectively. The structure with the bond lengths and bond angles included in it, is shown in Figure 3.1.3(a) and 3.1.3(b) respectively.

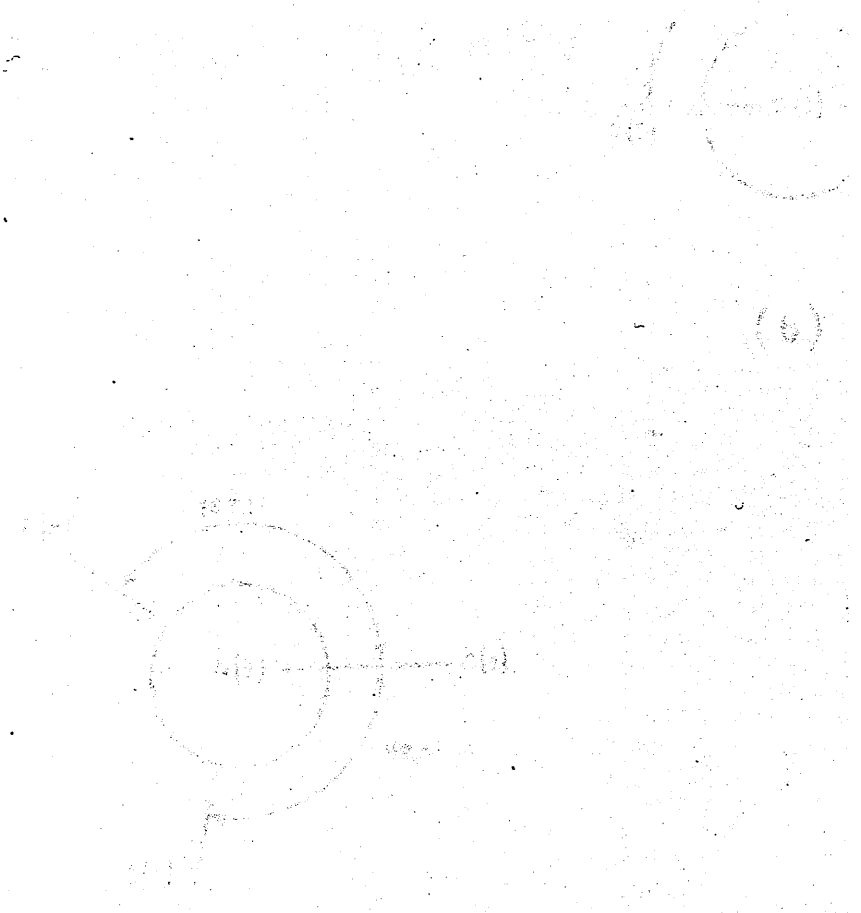
The cisoid conformation of the $-S(CH_3)_2$ group with respect to the m - NO_2 group in (I), is of some interest. The consequence of this conformation, which allows the closest approach of the S^+ and $O^{\delta-}$ entities, is that H(2) is placed in a potentially overcrowded environment. It is to be noted that hydrogen atoms may accommodate[35a] non-bonded separations which are shorter than those which would be expected on the basis of Pauling's van der Waals' radii, and this is probably a factor in permitting the observed conformation. Whereas, in the case of m-Dinitrobenzene[35b-37], the two nitro groups gain release of non-bonded interactions by twisting (13°) along the C-N bonds, the fact that N(1) is only dicoordinated (in I) enables the nitrogen atom to perform a pronounced in-plane bending.

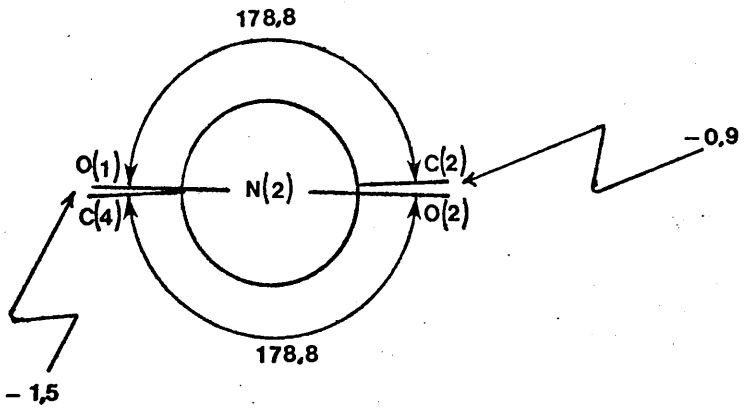
As a whole, it seems that the molecule gains the required conformational relief in the following two ways: a.) in-plane bending of N(1) [the exocyclic N(1) - C(1) - C(2) and N(1) - C(1) - C(6) angles equal to $126.7(2)^\circ$ and $116.4(2)^\circ$ respectively] and a slight out of plane bending [N(1) - C(1) - C(2) - C(3) and N(1) - C(1) - C(6) - C(5) dihedral angles equal to $177.9(2)^\circ$ and $-178.3(2)^\circ$ respectively], b.) a rotation of about 9° along the C(1) - N(1) bond (Figure 3.1.2.b)

Figure 3.1.2

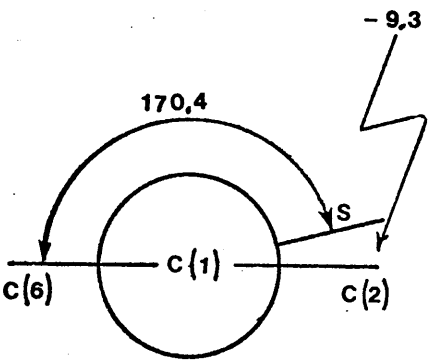
Newmann projections (with torsion angles) along (a) N(2) - C(3) (b) C(1) - N(1) and (c) N(1) - S bonds.

A torsion angle A-B-C-D is considered to be positive if when viewed down the B-C bond the A-B bond will eclipse the C-D bond when rotated less than 180° in a clockwise direction.

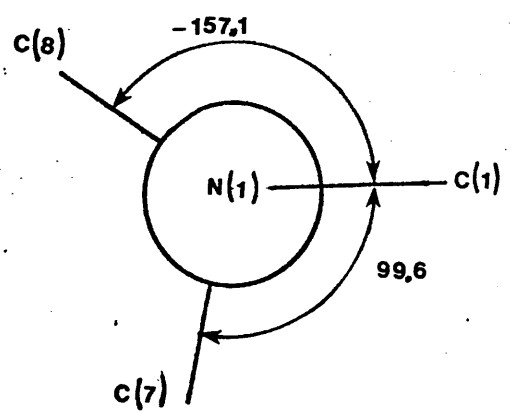



178,8
O(1)
C(2)
N(2)
C(4)
O(2)
-0,9
178,8
- 1,5

(a)


- 9,3
170,4
S
C(6)
C(1)
C(2)

(b)


C(8)
-157,1
N(1)
C(1)
99,6
C(7)

(c)

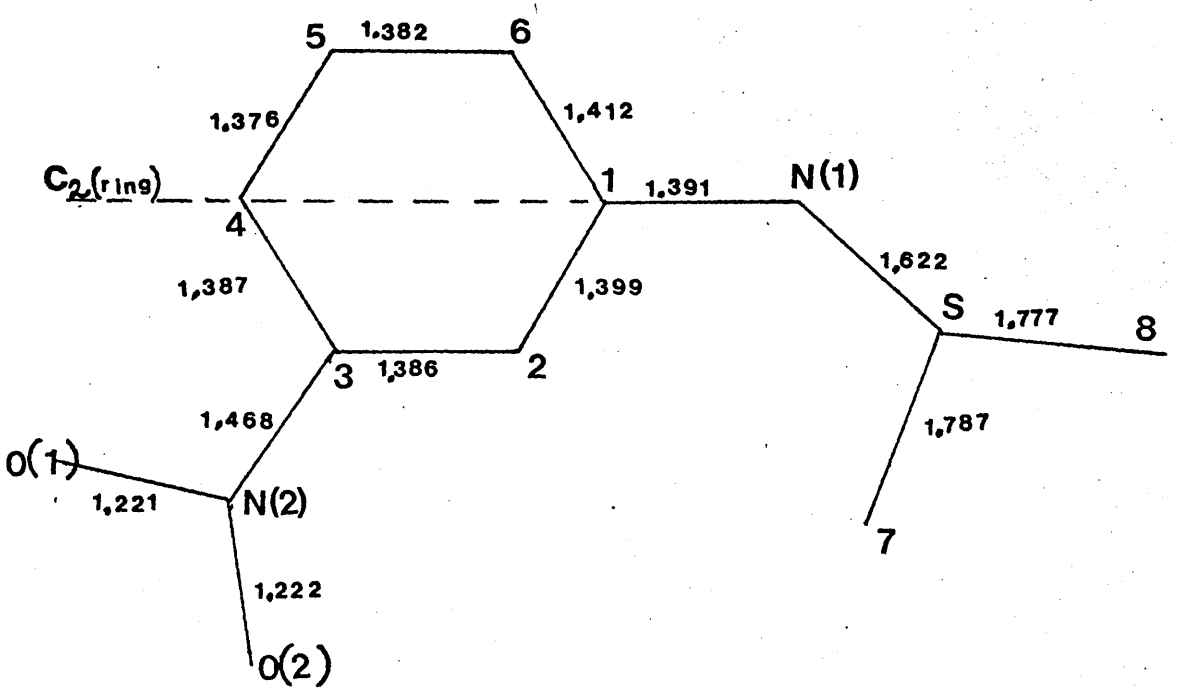

5
1.382
6
1.376
1.412
C2 (ring)
1
1.391
N(1)
4
1.387
1.399
1.622
S
1.777
8
3
1.386
2
1.468
1.787
O(1)
1.221
N(2)
7
1.222
O(2)

Figure 3.1.3 (a)

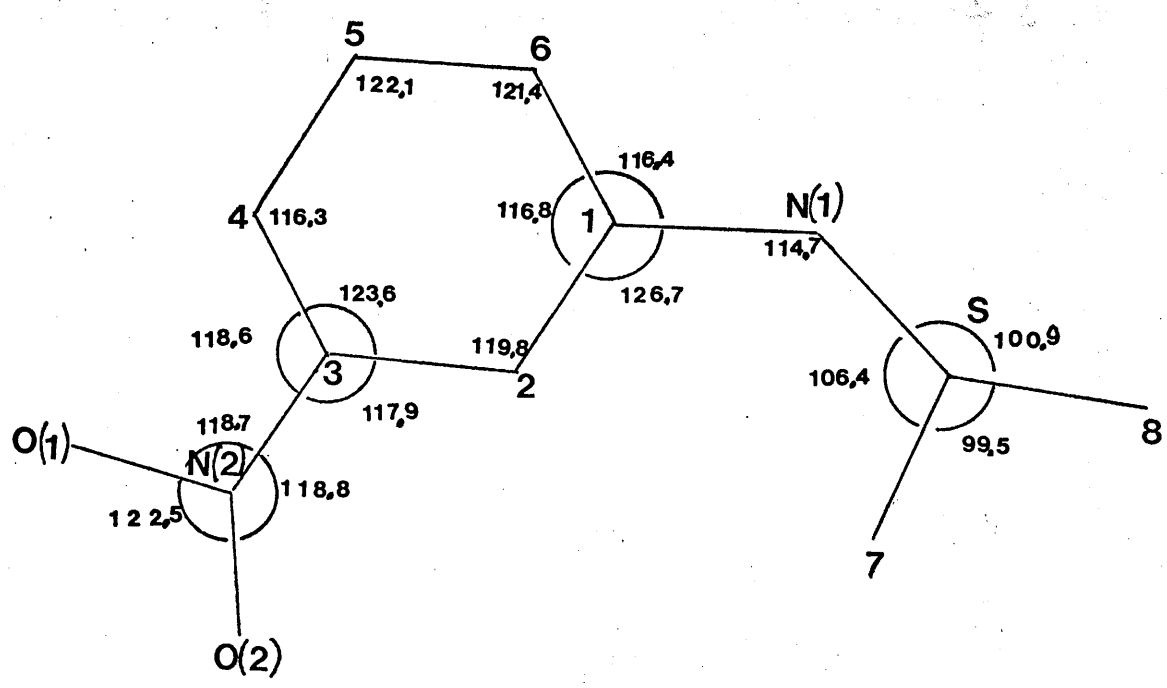

5
6
122,1
121,4
116,4
4
116,3
116,8
1
N(1)
114,7
123,6
126,7
S
100,9
118,6
119,8
106,4
3
2
8
118,7
117,9
O(1)
N(2)
118,8
99,5
122,5
7
O(2)

Figure 3,1,3 (b)

followed by a rotation along the N(I) - S bond. The latter rotation reduces interactions between the methyl groups on the sulphur atom and the ortho hydrogen on the ring. This steric effect seems to 'provide' the approximately staggered arrangement of the sulphonium methyl groups relative to the C-N bond (Figure 3.1.2.c), an arrangement, that otherwise would not have been predicted and favoured by the so called 'Gauche effect'.[38]

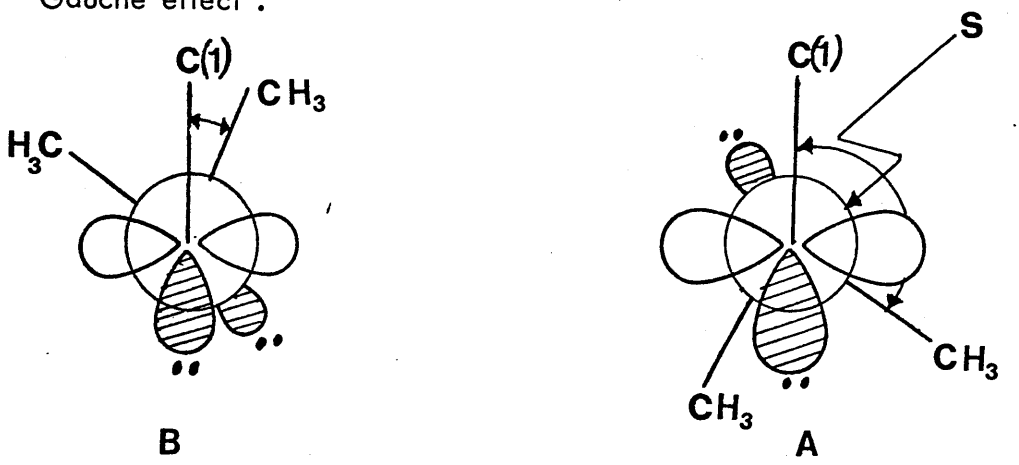


Figure 3.1.4: Possible projections along the N(I) - S bond.

The 'Gauche effect' is the tendency to adapt that structure which has the maximum number of gauche interactions between the adjacent electron pairs and/or polar bonds. Thinking of the electron pairs (in a qualitative way) as directed ligands which are capable of displaying stereochemical properties and visualizing the two conformations A and B one can see that the favourable conformation, by the 'Gauche effect' will be the + syn-periplanar conformation (B) in which the two lone pairs of electrons are cis to each other.

The + anti-clinal conformation (A) that the molecule adopts (Figure 3.1.4.), and in which the two lone pairs are 'trans' to each other seems to be supported by the steric effects already mentioned.

A noteworthy fact is the approximate coplanarity of the nitro group with the C-hexagon, as is indicated in Figure 3.1.2a and which has been pointed out in a few previous structures as well (Trotter 1959, for nitrobenzene; Cameron et al 1976).[39,40]

Essentially, the m-O_2N-C_6H_4NS moiety is close to planarity, as can be seen from the appropriate dihedral angles (Figure 3.1.2 a-c) and approximately from the value of 9.6° for the angle between the least-squares plane representing the aromatic ring atoms (χ^2 = 43.3 with 3 degrees of freedom) and the plane passing through the atoms C(1), N(1) and S, (Table 3.1.6). This small deviation suggests that there is no geometrical barrier to delocalisation from the nitrogen into the aromatic ring system.

The configuration at the sulphur atom is basically pyramidal, the angles C(7) - S - C(8), C(7) - S - N(1) and C(8) - S - N(1) being 99.5°, 106.4° and 100.9° respectively with a mean valency angle of 102.3° which is similar for geometries previously observed for sulphur atoms in comparable environments[41-46] (mean pyramidal angle: 100.8° - 104.0°). The sulphur atom in molecule I deviates by 0.75 Å from the plane passing through the atoms C(7), C(8) and N(1) (Table 3.1.6).

The C(1) - N(1) - S valency angle is 114.7(1)° which is consistent with sp^2 hybridization at N(1) whereby two of the hybrid orbitals are

used to form σ bonds and the third is mainly a lone-pair orbital. Any marked tendency for electrons in this orbital to take part in the S-N bonding would lead to an increased C-N-S angle. It seems as if this lone-pair of electrons displays a repulsion effect upon the S-N(I) and C(I) - N(I) bonds causing the angle to decrease from 120°. This distortion from 120° has been dealt with by Gillespie[47] (1963, 1967, Valence-Shell Electron Pair Repulsion, VSEPR).

The sulphonium-imine bond length $\overset{+}{S}$ (IV) - $\overset{-}{N}$ is 1.622(2)Å, considerably shorter than the value which might possibly be expected for a sulphur-nitrogen single bond [1.772(1)Å from sulphamic acid[48,49] and 1.74 Å from Pauling's covalent radii[50] corrected for electronegativity with Schomaker-Stevenson coefficient of 0.08Å] and which would seem to indicate considerable $(d - P)_{\pi}$ bonding if one follows the usual assumption, which has recently been questioned[51,52] (Trost 1975, Whangbo, Wolfe and Bernardi, 1975), that a decrease in bond lengths is associated with increased double bond character.

This bond length is within the experimental error, similar to the $\overset{+}{S}$(IV) - $\overset{-}{N}$ bond lengths in the N-sulphonyl sulphilimines, $R^1R^2S^+ - \bar{N}SO_2R^3$, (called also N-sulphonyl iminosulphuranes), which have a weighted mean* bond length value of 1.628(2)Å, and is below the $\overset{+}{S}$(IV) - $\overset{-}{N}$ weighted-mean bond length value of 1.670(2)Å found for N-Acylsulphilimines, $R^1R^2S^+ - \bar{N}COR^3$, (N-Acyliminosulphuranes),

* $x_i \text{ mean} = \dfrac{\sum x_i/\sigma_i^2}{\sum 1/\sigma_i^2}$; $\sigma_i = \sqrt{\dfrac{\sum (x_i - \bar{x})^2/\sigma_i^2}{(N-1)\sum 1/\sigma_i^2}}$

(Cameron et al, 1976)[53]. This would appear to indicate equal capabilities for negative charge delocalization by the sulphonyl and aryl groups in the above systems.

The two S-C(methy) bonds of 1.787(3)Å and 1.777(2)Å to C(7) and C(8) respectively and a weighted-mean bond length of 1.780(3)Å differ by only 2.8σ (σ of the population of the difference values) and therefore this difference cannot be considered significant. The S-C single bond in dimethylsulphide was found to be 1.809(5)Å (Maier, 1961)[54] and from the sum of covalent radii given by Pauling[50] it is postulated to be 1.81Å. This difference between 1.809(5)Å and the mean value of 1.780(3)Å which is significantly different ($\sim 5\sigma$) had been accounted for previously to be of a 'hyperconjugative like' nature (Kalman, 1967)[41] or as indicative to the dipolar characteristic of $\overset{+}{S}$ (IV) - $\overset{-}{N}$ (Trost, 1975)[51].

The imino-nitrogen bond to the C-ring [N(1) - C(1) bond] which is 1.391(2)Å would support the suggestion that there is minimal delocalization of the negative charge into the aromatic system [C(2) - C(1) - N(1) - S dihedral angle = -9.3°] since this bond is significantly longer than the N-C bond in free pyridine [1.340(5)Å] (Bak, Hansen and Rastrup-Andersen, 1954)[55] and appears to represent within the experimental error a typical Nsp^2 - Csp^2 single bond.[56]

The C-N (nitro) bond of 1.468(3)Å is comparable in length to a Csp^3 - Nsp^3 bond of 1.465(2)Å (in methylamine)[57]. It is possible that steric interactions (geminal and non-geminal non-bonded repulsions)

are factors in determining this bond length. The mean N-O (nitro) bond length is 1.221(2)Å which is within the range of the expected value.

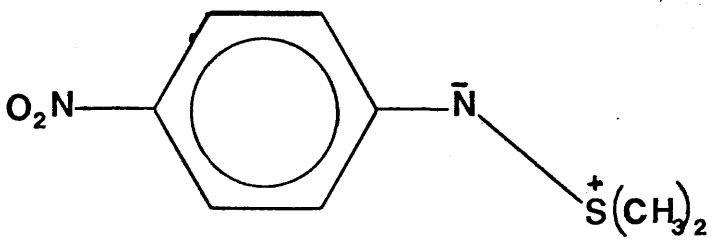
It is worth noting that within experimental error there is no difference between the dimensions of these nitro groups and those which are twisted[58] or almost perpendicular with respect to the benzene ring[59].

The ring deformations seem to depend markedly upon the electronic properties of the two substituents. The known D_{6h} is essentially (within experimental error) reduced to C_{2V} symmetry where the C_2 axis is along the C(1) ... C(4) line (Figure 3.1.3a). The most significant deviations from D_{6h} symmetry are the increase by 3.6° from 120° of the endocyclic bond angle C(2) - C(3) - C(4) opposite to the nitro group, the slight decreases in the endocyclic angle C(3) - C(4) - C(5) and the two bonds C(2) - C(3) and C(3) - C(4) by the approximate amounts of 3.7° and 0.01 Å respectively (C-C in benzene, 1.397 Å)[58], the decrease by 3.2° of the endocyclic bond angle C(6) - C(1) - C(2) opposite the - $NS(CH_3)_2$ substituent and the minor increases in the endocyclic bond angle C(5) - C(6) - C(1) and the bond C(6) - C(1) by the corresponding amounts of 1.4° and 0.015 Å. All the effects are consistent with the strong σ -electron withdrawing character of the nitro group and the small conjugative interference with the ring of the -$NS(CH_3)_2$ substituent, and it appears as if the angular deformations are basically not affected by the meta-substitution apart from where they do overlap and produce a superimposition of separate effects (Domenicano, Vaciago and Coulson 1975)[60]. The latter is well

demonstrated by the endocyclic bond angle C(1) - C(2) - C(3) $\left[119.8(2)^{\circ}\right]$ which is a result of opposite effects from both substituents.

Intra-and intermolecular contacts of interest are given in Table 3.1.5 and few of them are indicated in Figures 3.1.1(a) and 3.1.1b. The molecular packing is in accord with minimizing these contacts leaving van der Waals interaction to be the dominant characteristic force in the solid state, though, it is interesting to note that the molecules in the crystals are arranged in pairs (related by a screw axis parallel to Z) whereby each pair has two parallel N-S bonds and it seems as if some charge-dipole and/or dipole-dipole interactions might exist in the solid state $\left[S^{+} \ldots N(1) \text{ is equal to } 4.23\,\mathring{A} \right]$.

3.2 Experimental and Results for II.



II

S,S - Dimethyl-N-P-nitrophenylsulphimide.

Preparation of Crystals

The title compound (II) was prepared by the published procedure described by Claus and Vilsmaier[30] (1975). Crystallization from 'dichloromethane-ether' yielded yellow crystals with m.p. = 165 - 168°C (Lit.[25] m.p. 148 - 151°C; 163 - 165°C; 167 - 168°C).

The structure was verified by its characteristic I.R. bands[25,32] in the region 970 - 890 cm^{-1} (905, 945, 980, CH_2Cl_2 as solvent) and by the expected fragments in the mass spectrum[25].

m/e: 198(M^+), 183($M^+ - CH_3$), 168($M^+ - 2CH_3$), 153($M^+ - NO - CH_3$), 151($M^+ - CH_3S$), 137($M^+ - CH_3 - SCH_2$), 136($M^+ - (CH_3)_2S$), 122($M^+ - (CH_3)_2SN$), 61($CH_3SCH_2^+$) and 62($CH_3\overset{+}{S}CH_3$).

Crystal Data

Molecular Formula	$C_8H_{10}N_2O_2S$
Molecular Weight	198.24 a.m.u.
Crystal System	Monoclinic

Unit Cell Dimensions	$a = 4.811(1)\ \text{Å}$
	$b = 9.874(2)\ \text{Å}$
	$c = 19.947(4)\ \text{Å}$
	$\beta = 97.45(3)^\circ$
Unit Cell Volume	$V = 939.6\ \text{Å}^3$
Number of Molecules per Unit Cell	$Z = 4$
Calculated Density	$D_c = 1.40\ \text{g.cm}^{-3}$
Number of Molecules per Asymmetric Unit	$N = 1$
Space Group	$P2_1/c(C_{2h}^5$, No.14)
Equivalent Positions	$x, y, z;$
	$-x, 1/2 + y, 1/2 - z$
Linear Absorption Coefficient	$\mu = 2.98\ \text{cm}^{-1}$
Number of Electrons per Unit Cell	$F(000) = 416$

Data Collection

Diffractometer Used	Hilger and Watts Y290
Radiation Used	$M_o - K_\alpha$, $\overline{\lambda} - 0.71069\ \text{Å}$
Filter	Zirconium (Zr)
Upper Limit for Data Collection	$2\theta_{max} = 60^\circ$
Number of Observed Independent Reflections	$m = 868$
Unobserved Cut-Off	$2.5\sigma_I$
Number of Parameters Refined	$n = 158$
Number of Reflections per Parameter	$m/n = 5.5$

Structure Determination and Refinement

The space group $P2_1/c$ (C_{2h}^5, No.14) was determined uniquely from the systematic absences in the diffraction data (ok0 absent when k is odd, hol absent when l is odd).

The crystal structure was resolved by application of the multisolution direct methods program 'MULTAN' (version 1976), and by conventional structure factor and electron density calculation. The largest 100 E values ($|E| \rangle$ 1.36) were chosen to define the structure (7.7 E's per nonhydrogen atom) and the number of $\sum_2$ relationships was found to be 538 (5.38 phase relationships per one E value). A total of 16 sets were produced from 4 permuted special phases and the set with the largest 'combined figure of merit' (CFOM) resulted in the correct solution. The various parameters used with 'MULTAN' are summarized in Table 3.2.1. Nine atoms found from the initial E-map were assigned isotropic thermal parameters of $U = 0.051\ \text{Å}^2$ and by computing a difference Fourier synthesis the sites of the other four nonhydrogen atoms were revealed. The calculated R at this stage was found to be 0.263.

The full matrix least-squares refinement of the positional, thermal and scale parameters minimizing the function $\sum w(|F_o| - |F_c|)^2$, converged after 13 cycles when R was 0.052 and R_w ($=\sum w\Delta^2/\sum wF_o^2$) was equal to 0.047. Details on the progress of the least-squares refinement are given in Table 3.2.2.

Initially, unit weights were applied to all the reflections. In later stages a Cruickshank-type weighting scheme of the form $w^{-1} =$

$7.8190 - 0.9188|F_o| + 0.0280|F_o|^2$ was employed. The coefficients in this latter quadratic expression were obtained by plotting the graph of $\overline{w\Delta^2}$ against $|\overline{F_o}|$ in groups of increasing $|F_o|$ values and fitting a 2nd order polynomial $y = q_o + q_1x + q_2x^2$ to the observed curve. This weighting scheme gave an approximately 'flat' distribution of $\overline{w\Delta^2}$ by $|F_o|$. For reflections with $|F_o|$.'s less than $|\overline{F_o}|_{min}$ weights of $w = 1/2.3488$ were adapted ($w = 1/\overline{\Delta^2}$, $\overline{\Delta^2}$ belonging to the $|\overline{F_o}|$ min group).

The refinement was assumed complete when the parameter shifts, calculated by a cycle of least-squares were insignificant compared to the corresponding estimated standard deviations. The average and maximum shift/error were 0.032 and 0.163 respectively and the standard deviation of an observation of unit weight was equal to 1.5008. A calculation of a difference Fourier synthesis revealed no errors in the structure. No absorption correction was applied. In all structure factor calculations the atomic scattering factors for C, O, N and S were computed from numerical Hartree-Fock wave functions whilst the scattering factors for H were those given by Stewart et al (1965).

Final values of observed and calculated structure amplitudes, including phases, are given in the Supplement to this thesis. A perspective view of the molecule with its thermal ellipsoids (50% probability for nonhydrogen atoms) and their principal sections is illustrated, together with the numbering scheme used, in Figure 3.2.1(a). The molecular arrangement viewed along the shortest 'a' axis is shown

in Figure 3.2.1.(b).

The final fractional coordinates for nonhydrogen atoms, their anisotropic thermal parameters and fractional coordinates for hydrogen atoms with their isotropic temperature factors are listed in Table 3.2.3 (a,b,c and d). Their e.s.d.'s were derived from the inverse of the least-square matrix. Tables 3.2.4 to 3.2.6 list molecular dimensions with e.s.d.'s and non-bonded distances with other relevant intra/ intermolecular data.

Table 3.2.I

SUMMARY OF THE CONDITIONS (INCLUDING VARIOUS FIGURES OF INTEREST) ASSOCIATED WITH SOLVING THE STRUCTURE OF II.

In this table:

1. NE - is the number of the largest $|E|$'s chosen to define the structure.
2. NSRT - is the number of $\sum_2$ relationships to be retained.
3. NSRTT - is the total number of $\sum_2$ relationships.
4. PROB - is the probability acceptance limit chosen for $\sum_1$.
5. NSPEC - is the number of special phases (permutations restricted to ϕ_{spec}, $\phi_{spec} + 180^\circ$).

   NGEN - is the number of general phases (phase permutation 45°, 135°, 225°, 315°)

   NANY - is the number of phases of either sort.
6. NSET - is the total number of phase sets that have been developed.
7. PUB - is the published phase.
8. NAT - is the number of nonhydrogen atoms in the asymmetric unit.
9. ABS FOM, PSI ZERO, RESID and CFOM are all figures of merit.

$C_8H_{10}N_2O_2S$, $P2_1/c$, NAT = 13.

PARAMETERS		STARTING SET TYPE	hkl	PHI (o)	PUB (o)	RESULTS PHASE SET CONSIDERED	FIGURES OF MERIT ABS FOM	PSI ZERO	RESID	TOTAL NUMBER OF CORRECT PEAKS FOUND IN E-MAP
SIGMA-2		SIGMA-1	0,2,0	180	180	Max	1.4512	70.6	31.81	9
NE(|E| > 1.36)	100		2,4,4	360	360	Min	1.0722	42.9	17.69	
NSRT	538	Origin defining phases	1,2,2	360	360	CFOM1= 2.0000	1.4512	70.6	17.69	
NSRTT	538		1,1,2	360	360					
CONVERGE			2,7,1	360	360					
PROB	0.95	Permuted phases	1,1,-8	360° 180°	360					
NSPEC,NGEN, NANY	4,0,0		2,3,4	360° 180°	360					
FASTAN			1,3,3	360° 180°	360					
NSET	16		3,1,-12	360° 180°	360					

Table 3.2.2.

PROGRESS OF LEAST-SQUARES REFINEMENT

CYCLES	PARAMETERS REFINED	R	Rw
0	none	0.263	0.309
4	x,y,z U(iso) for C,N,O,S; scale factor; full matrix; unit weights.	0.115	0.124
3	x,y,z,U_{ij} for C, N, O, S; scale factor; full matrix; unit weights.	0.091	0.106
4	x,y,z,U_{ij} for C,N,O,S; x,y,z,U(iso) for H atom; scale factor; full matrix; weighting scheme.	0.064	0.082
2	As above but excluding 7 extinction reflections from the least-squares calculations.	0.052	0.047

Table 3.2.3(a,b,c,d)

(a) Fractional atomic coordinates ($\times 10^4$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM X/A Y/B Z/C

(b) Anisotropic thermal parameters (Å^2, $\times 10^3$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}

(c) Fractional atomic coordinates ($\times 10^3$) of hydrogen atoms with e.s.d.'s in parentheses. The hydrogens are numbered according to the atoms to which they are attached.

(d) Isotropic thermal parameters (Å^2, $\times 10^2$) of hydrogen-atoms with e.s.d.'s in parentheses. The table shows:

ATOM $U_{(iso)}$.

C(1)	-1420(9)	8492(5)	1949(2)
C(2)	-0499(10)	7407(5)	2390(2)
C(3)	-1386(10)	7296(6)	3013(3)
C(4)	-3266(10)	8233(5)	3216(2)
C(5)	-4251(11)	9279(6)	2793(3)
C(6)	-3381(10)	9419(5)	2171(3)
C(7)	2681(16)	8684(8)	0396(3)
C(8)	0080(17)	6324(7)	0662(4)
N(1)	-0711(8)	8711(4)	1316(2)
N(2)	-4183(9)	8089(5)	3864(2)
O(1)	-3440(10)	7083(4)	4207(2)
O(2)	-5646(10)	8974(4)	4070(2)
S	1782(3)	7738(1)	1096(1)

3.2.3 (a)

C(1)	39(2)	39(3)	49(3)	-9(2)	5(2)	-2(2)
C(2)	49(3)	38(3)	53(3)	3(2)	7(2)	-1(2)
C(3)	53(3)	41(3)	53(3)	2(3)	5(2)	5(3)
C(4)	47(3)	42(3)	45(3)	-4(2)	7(2)	-2(2)
C(5)	47(3)	41(3)	57(3)	3(2)	13(3)	-12(3)
C(6)	46(3)	37(3)	52(3)	4(2)	7(2)	-4(3)
C(7)	79(5)	71(5)	58(4)	2(4)	27(4)	9(3)
C(8)	84(5)	55(4)	81(5)	-1(4)	9(4)	-24(4)
N(1)	57(3)	48(3)	43(2)	10(2)	9(2)	3(2)
N(2)	61(3)	63(3)	53(3)	-3(2)	14(2)	-3(2)
O(1)	117(4)	85(3)	63(3)	20(3)	41(2)	20(2)
O(2)	98(3)	86(3)	77(3)	20(2)	45(2)	-8(2)
S	47(1)	49(1)	48(1)	3(1)	9(1)	-3(1)

3.2.3 (b)

H(2)	074(10)	671(6)	227(3)
H(3)	-075(9)	660(5)	329(2)
H(5)	-545(10)	987(5)	289(3)
H(6)	-407(10)	1014(5)	188(2)
H(71)	335(14)	951(8)	058(3)
H(72)	100(12)	882(6)	008(3)
H(73)	393(14)	809(9)	020(4)
H(81)	143(11)	581(6)	045(3)
H(82)	-128(13)	667(7)	033(3)
H(83)	-077(16)	574(8)	100(4)

3.2.3 (c)

H(2)	7(2)
H(3)	4(1)
H(5)	6(2)
H(6)	6(1)
H(71)	11(3)
H(72)	8(2)
H(73)	12(3)
H(81)	7(2)
H(82)	9(2)
H(83)	14(3)

3.2.3 (d)

Table 3.2.4(a,b,c)

(a) Interatomic distances (Å) with e.s.d.'s in parentheses. The hydrogen atoms are numbered according to the atoms to which they are attached.

(b) Interbond angles (degrees) with e.s.d.'s (degrees) in parentheses.

(c) Torsion angles (degrees) with e.s.d.'s (degrees) in parentheses.

C(1)	-	C(2)	1.420(7)	C(4)	-	N(2)	1.426(7)
C(1)	-	C(6)	1.426(7)	C(5)	-	C(6)	1.368(8)
C(1)	-	N(1)	1.366(6)	C(7)	-	S	1.780(8)
C(2)	-	C(3)	1.370(7)	C(8)	-	S	1.785(8)
C(3)	-	C(4)	1.390(7)	N(1)	-	S	1.640(4)
C(4)	-	C(5)	1.378(7)	N(2)	-	O(1)	1.233(6)
N(2)	-	O(2)	1.226(7)				

3.2.4 (a)

C(2)	H(2)	0.965(57)	C(7)	H(72)	0.971(55)
C(3)	H(3)	0.908(46)	C(7)	H(73)	0.959(79)
C(5)	H(5)	0.860(52)	C(8)	H(81)	0.950(58)
C(6)	H(6)	0.947(49)	C(8)	H(82)	0.931(62)
C(7)	H(71)	0.934(72)	C(8)	H(83)	1.014(83)

3.2.4 (a) (continued)

C(6)	C(1)	C(2)	117.22(43)	N(1)	C(1)	C(2)	126.63(42)
C(3)	C(2)	C(1)	120.91(45)	N(1)	C(1)	C(6)	116.09(41)
C(5)	C(6)	C(1)	120.64(47)	S	N(1)	C(1)	115.66(31)
C(4)	C(3)	C(2)	124.15(48)	C(5)	C(4)	C(3)	120.36(45)
N(2)	C(4)	C(3)	119.19(44)	N(2)	C(4)	C(5)	120.45(44)
C(6)	C(5)	C(4)	120.68(48)	O(1)	N(2)	C(4)	118.77(44)
O(2)	N(2)	C(4)	119.49(45)	C(8)	S	C(7)	99.96(36)
N(1)	S	C(7)	99.38(29)	N(1)	S	C(8)	106.42(30)
O(2)	N(2)	O(1)	121.73(46)				

3.2.4 (b)

C(6)	-	C(1)	-	C(2)	-	C(3)	-2.5(7)	N(1)	-	C(1)	-	C(2)	-	C(3)	-179.5(5)
C(2)	-	C(1)	-	C(6)	-	C(5)	1.9(7)	N(1)	-	C(1)	-	C(6)	-	C(5)	179.3(5)
C(2)	-	C(1)	-	N(1)	-	S	-9.0(6)	C(6)	-	C(1)	-	N(1)	-	S	173.9(3)
C(1)	-	C(2)	-	C(3)	-	C(4)	1.6(8)	C(2)	-	C(3)	-	C(4)	-	C(5)	-0.0(8)
C(2)	-	C(3)	-	C(4)	-	N(2)	179.3(5)	C(3)	-	C(4)	-	C(5)	-	C(6)	-0.5(8)
N(2)	-	C(4)	-	C(5)	-	C(6)	-179.9(5)	C(3)	-	C(4)	-	N(2)	-	O(1)	-5.2(7)
C(3)	-	C(4)	-	N(2)	-	O(2)	173.7(5)	C(5)	-	C(4)	-	N(2)	-	O(1)	174.2(5)
C(5)	-	C(4)	-	N(2)	-	O(2)	-6.9(7)	C(4)	-	C(5)	-	C(6)	-	C(1)	-0.5(8)
C(1)	-	N(1)	-	S	-	C(7)	-163.6(4)	C(1)	-	N(1)	-	S	-	C(8)	93.2(4)

3.2.4 (c)

Table 3.2.5

A. Selected intramolecular non-bonded distances (< 4.0 Å)

C(8) ...	H(2)	3.20			
N(1) ...	C(2)	2.49	O(2) ...	C(5)	2.73
N(1) ...	C(6)	2.37	O(2) ...	H(5)	2.53
N(1) ...	H(2)	2.77	S ...	C(2)	2.95
N(1) ...	H(6)	2.52	S ...	H(2)	2.65
O(1) ...	C(3)	2.70			
O(1) ...	H(3)	2.42			

B. Selected intermolecular distances (< 4.0 Å)

N(1) ...	S^{i}	3.71
S ...	$N(1)^{ii}$	3.71
O(1) ...	$C(7)^{iii}$	3.46
O(1) ...	$C(7)^{iv}$	3.61
O(1) ...	$C(7)^{v}$	3.29
O(2) ...	$C(8)^{vi}$	3.53
O(2) ...	$C(8)^{vii}$	3.24

Roman numeral superscripts refer to the following equivalent positions relative to the molecule at (x,y,z):

(i)	-1 + x, y, z	(v)	-1 + x, 5/2 - y, 3/2 + z
(ii)	1 + x, y, z	(vi)	-x, 1/2 + y, 1/2 - z
(iii)	-x, -1/2 + y, 1/2 - z	(vii)	-1 - x, 1/2 + y, 1/2 - z
(iv)	x, 5/2 - y, 3/2 + z		

Table 3.2.6

LEAST-SQUARES PLANES

Planes are in the form of $Ax + By + Cz - D = 0$ where x,y,z refer to an orthogonal set of axes, D is the perpendicular distance from the plane to the origin and A, B and C refer to the components of unit vector normal to the best plane. An asterisk denotes atoms used to define the plane.

A. (1) Equation of the plane.

$-0.7162x - 0.5697y - 0.4031z + 5.4684 = 0$

$\chi^2 = 16.02$ with 3 degrees of freedom. The deviations (Å) of the atoms from the plane are:

C(1)*	-0.012(4)	S	-0.169(1)
C(2)*	0.011(5)	C(7)	-0.583(8)
C(3)*	-0.002(5)	C(8)	1.478(8)
C(4)*	-0.005(5)	N(2)	-0.005(5)
C(5)*	0.004(5)	O(2)	-0.125(4)
C(6)*	0.006(5)	O(1)	0.095(4)
N(1)	0.008(4)		

(2) Equation of the plane

$-0.6417x - 0.6692y - 0.3747z + 6.2936 = 0$

$\chi^2 = 0$ with zero degrees of freedom. The deviations (Å) of the atoms from the plane are:

C(1)*	0.0	C(6)	-0.135(5)
N(1)*	0.0	C(7)	-0.500(8)
S*	0.0	C(8)	1.709(8)
C(2)	0.179(5)		

Table 3.2.6 (continued)

(3) Equation of the plane

$-0.6779x + 0.2258y - 0.6996z - 0.5841 = 0$

$\chi^2 = 0$ with zero degrees of freedom. The deviations (Å) of the atoms from the plane are:

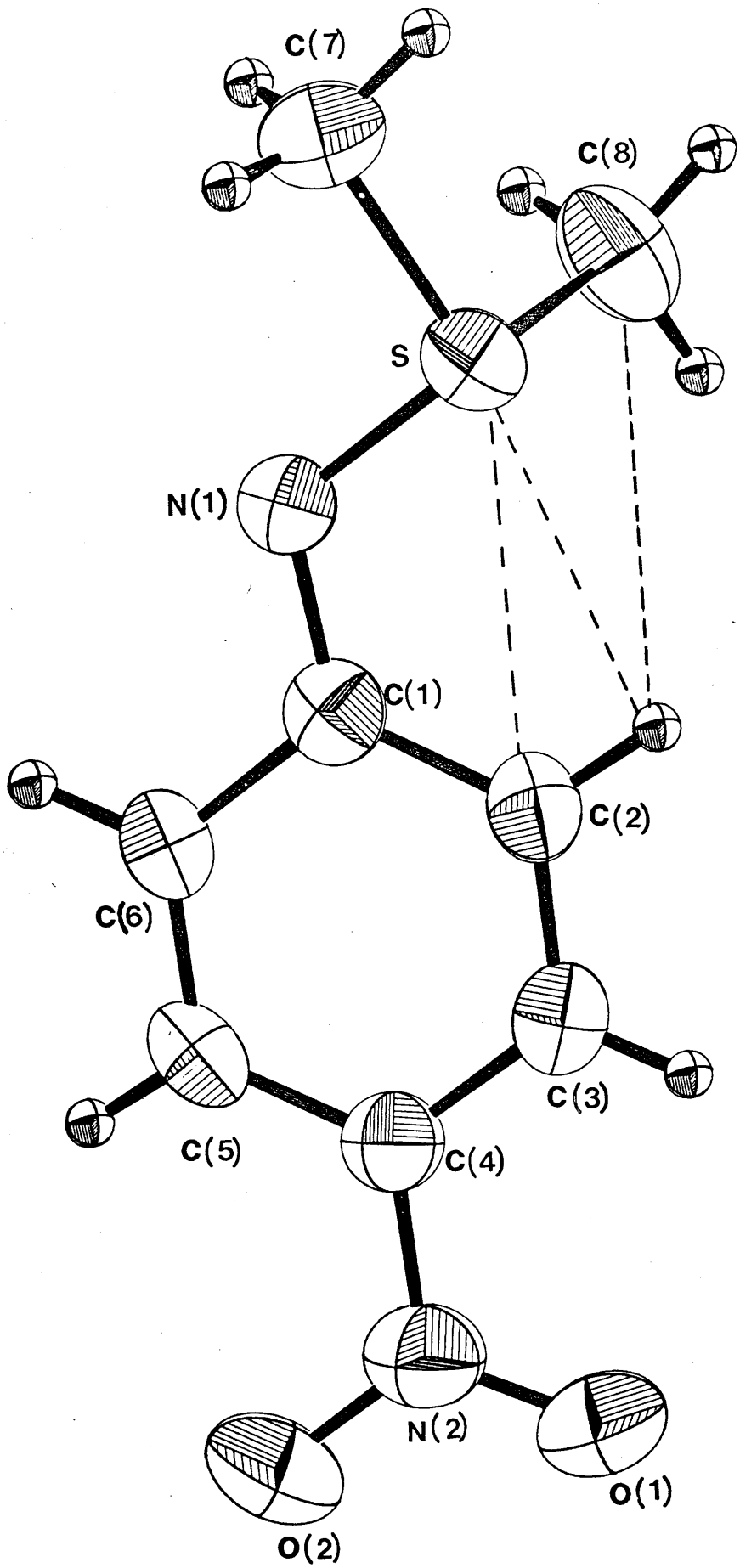
C(7)*	0.0
C(8)*	0.0
N(1)*	0.0
S	-0.764(1)

B. Dihedral angle between planes (1) and (2) is 7.3°, between (1) and (3) is 50.3 and between (2) and (3) is 56.9°.

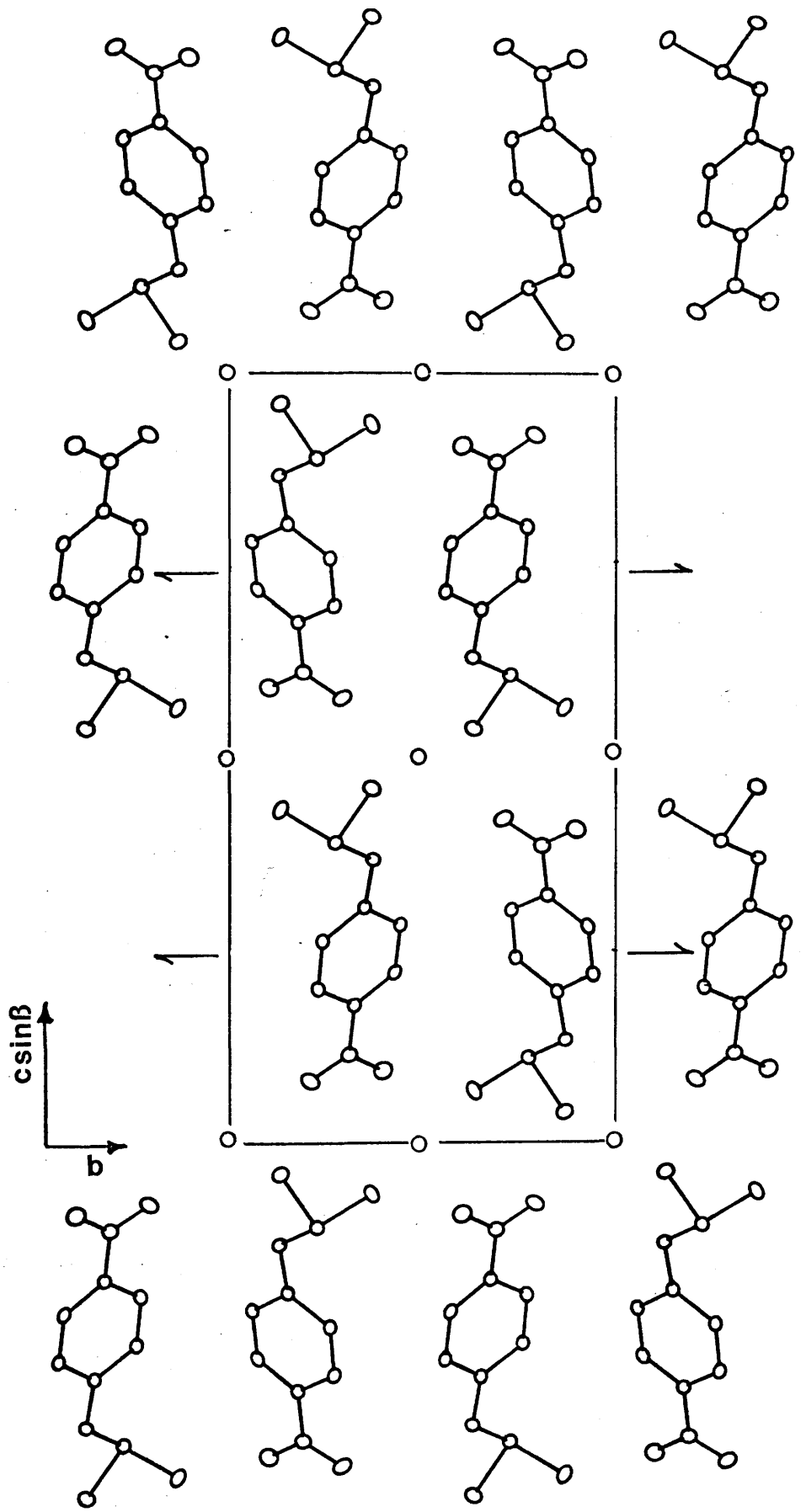
Figure 3.2.1 (a and b)

(a) A general view of II giving the atomic numbering scheme. Hydrogen atoms are numbered according to the atoms to which they are bonded.

(b) The molecular packing of II viewed along the short axis 'a'.



(a)



(b)

Discussion of II

As an introduction to the forthcoming discussion, it should be mentioned that after we had completed the analysis of this compound, a paper describing the X-ray structure determination of the same compound (within the framework of extended dipole-moment calculations and measurements in similar systems) was published elsewhere[62] (Eliel, Koskimies, McPhail & Swern, 1976). A careful examination of the cell dimensions and systematic absences appropriate to the crystals prepared and studied by ourselves has confirmed a unit cell of dimensions $a = 4.811$, $b = 9.874$, $c = 19.947$ Å, $\beta = 97.45^\circ$, and space group $P2_1/c$. Re-indexing this cell would lead to a cell of dimensions $a = 4.811$, $b = 9.874$, $c = 21.117$ Å, $\beta = 110.51^\circ$, in which the space group is $P2_1/n$.

In the paper describing the other analysis, the cell dimensions are quoted as $a = 4.845$, $b = 9.886$, $c = 21.018$ Å, $\beta = 109.49^\circ$, and the space group is given as $P\,2_1/c$. The similarity between this cell (quoted space group $P\,2_1/c$) and the $P\,2_1/n$ setting of our own cell is remarkable, and leads us to suspect that there are <u>not</u> two crystalline forms, but that a possible error (perhaps typographical) has been made in describing the space group of the compound in the above paper. We are consulting with the authors of this paper to draw this to their attention.

The solid state conformation of II is best described in terms of

the Newman projections (Figure 3.2.2) along the N(2) - C(4), C(1) - N(1) and N(1) - S bonds respectively. Figures 3.2.3(a) and 3.2.3(b) indicate bond lengths and bond angles in the structure.

The remarkable similarity between the conformations of I (3.1 - discussion) and II, in particular, the 'trans' position [Figures 3.1.1(a) and 3.2.1(a)] of the two lone-pairs of electrons on the sulphur and nitrogen atoms, the approximately staggered arrangement of the two methyl groups relative to the C(1) - N(1) bonds [Figures 3.1.2(c) and 3.2.2(c)] and the identical (within the experimental error) in-plane deformation of the $-NS(CH_3)_2$ groups in both structures [the exocyclic angle C(2) - C(1) - N(1) is equal to 126.7(2) for I and 126.6(4) for II] seem to indicate, despite the different crystal environments, an adopted characteristic conformation determined mainly by the intramolecular non-bonded repulsive interactions between the $-S(CH_3)_2$ group and the ring carbon and hydrogen atoms in orthoposition (Table 3.2.7).

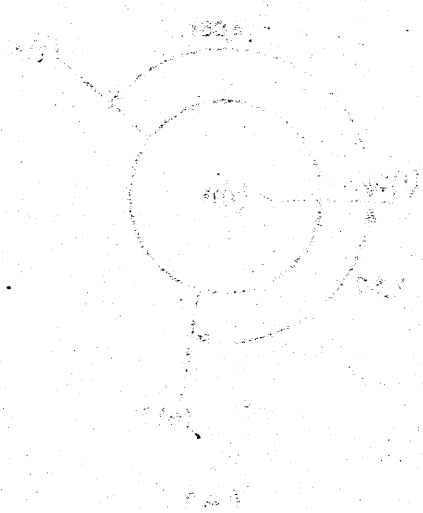
Table 3.2.7.

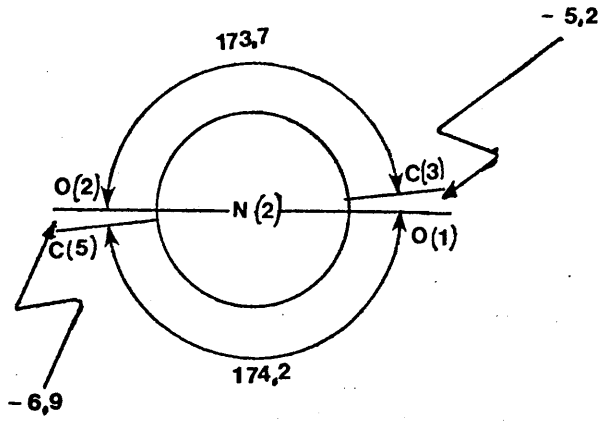
	Structure I	Structure II
S ... C(2)(Å)	2.93	2.95
S ... H(2)	2.65	2.65
Cmethyl .. C(2)	3.77	3.66
Cmethyl .. H(2)	3.33	3.20
C(1) - N(1) - S (°)	114.7	115.7
C(1) - N(1) - S - C methyl	99.6	93.2

Figure 3.2.2.

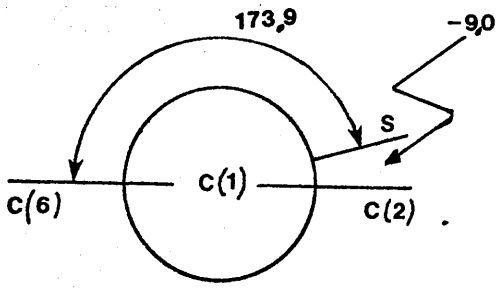
Newman projections (with torsion angles) along (a) N(2) - C(3) (b) C(1) - N(1) and (c) N(1) - S bonds.

A torsion angle A-B-C-D is considered to be positive if when viewed down the B-C bond the A-B bond will eclipse the C-D bond when rotated less than 180° in a clockwise direction.

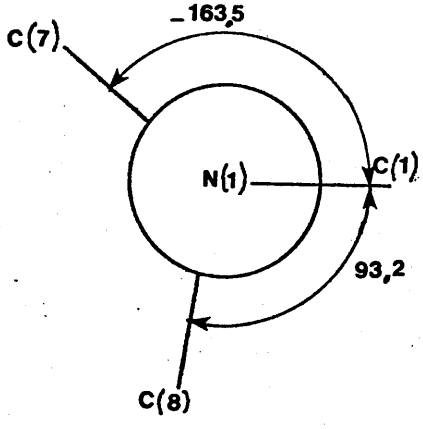



- 5,2
173,7
O(2)
C(3)
N (2)
O(1)
C(5)
174,2
- 6,9

(a)


173,9
-9,0
S
C(1)
C(6)
C(2)

(b)


-163,5
C(7)
N(1)
C(1)
93,2
C(8)

(c)

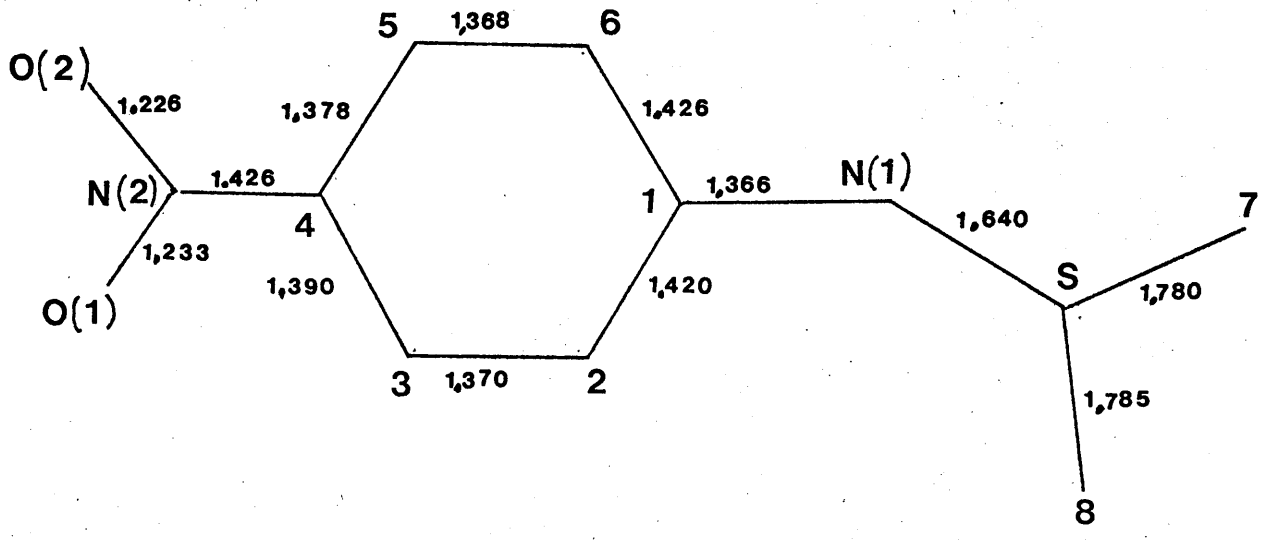

O(2)
1,226
N(2)
1,233
O(1)
1,426
1,378
1,390
5
1,368
6
1,426
4
1
1,420
3
1,370
2
1,366
N(1)
1,640
S
1,780
7
1,785
8

Figure 3.2.3(a)

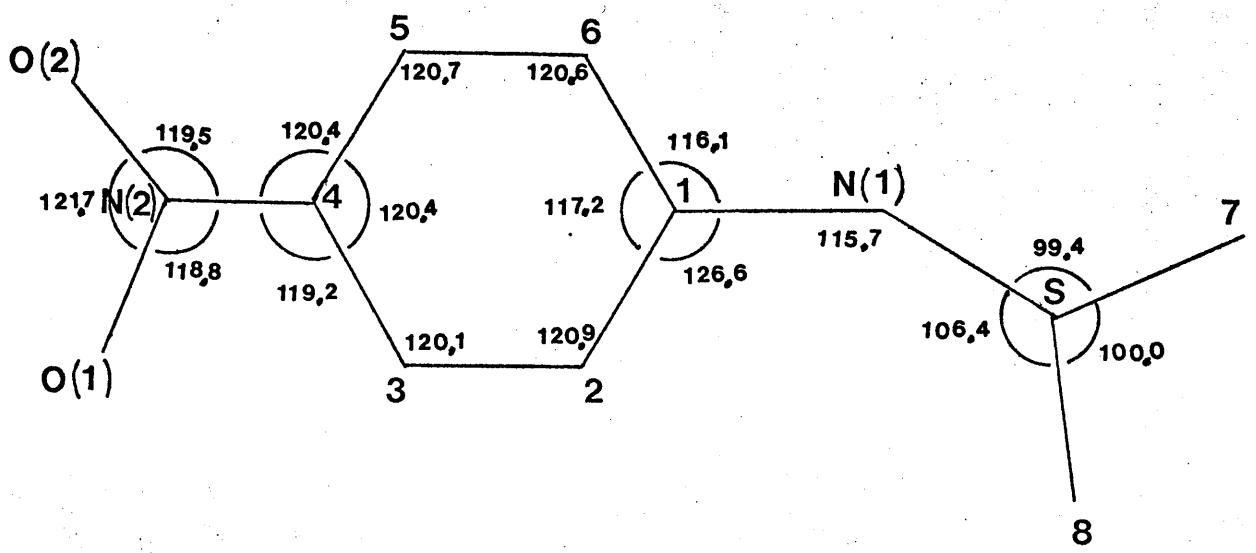

O(2)
O(1)
N(2)
121,7
119,5
118,8
4
120,4
119,2
5
120,7
6
120,6
116,1
117,2
1
126,6
N(1)
115,7
S
99,4
106,4
100,0
7
8
120,1
3
120,9
2

Figure 3.2.3(b)

The P - $O_2NC_6H_4NS$ (=) moeity is close to planarity (Figure 3.2.2 and Table 3.2.6) as is the case in molecule I, though the apparent shortening of the C(4) - N(2) bond (from 1.468 Å in I to 1.426 Å in II) induces a slight torsional movement along this bond as a result of the non-geminal non-bonded O(1) ... H(3) and O(2) ... H(5) interactions [O(2) - N(2) - O(3) - C(2) in I is equal to -0.90 while in II O(1) - N(2) - C(4) - C(3) is equal to -5.2°].

The benzene-ring skeleton is only nearly planar, yet the deviation from planarity[63] (expressed in terms of χ^2 = 16, Table 3.2.6) is less than the corresponding one in molecule I (χ^2 = 43). The latter observation, conjointly with the bonding pattern in II is in keeping with the effect of through-conjugation on the bond lengths which is well known. [The expected lengthening of the C(1) - C(2) bond which is accompanied by a 'quinonoidal' shortening of C(2) - C(3) followed by a shortening of the N(2) - C(4) bond]

Although basically the right pattern of change in the bond and angular deformations (as has been already previously described[60]) is observed, due to the relatively high standard deviations (~0.007 Å and ~0.4° in bond lengths and bond angles respectively) some ambiguity remains [e.g. C(3) - C(4) is equal to 1.390(7) Å and the endocyclic bond angle C(3) - C(4) - C(5) is equal to 120.4(4)°].

The S(IV) - N1 bonds, 1.640(4) Å in II and 1.622(2) Å in I differ by 4 σ when using Cruickshank's significant t-test[64] (Cruickshank, 1965), however, although just at the level of significance this small difference

might be considered to be consistent with the small, but apparent perturbation of electron density between the formally negatively charged nitrogen atom and the ring system, as for example, is the case when an acyl group is introduced instead of the aryl one (ref. 53 pp.2001 Table 4).

Another feature of the geometry of II is the approximately pyramidal stereochemistry of sulphur (mean pyramidal angle 101.9°) which has been discussed in Chapter 3.1 for I and other comparable systems.[41-46]

Apart from the intramolecular short contacts mentioned in Table 3.2.7 and indicated in Figure 3.2.1(a), some other selected contacts are given in Table 3.2.5.

There are no abnormally short intermolecular distances though the contacts $\overset{+}{S}(iv) \ldots \overset{-}{N}(1)$ appear to be shorter (by c.a. 0.5 Å) than the same contacts in structure I (3.71 Å in II and 4.23 Å in I). From Table 3.2.5 it could be seen that the dipolar attractions, originating from the polar bond N(1) - S, if at all significant, are arranged in a way as to connect the molecules related by the simple translations along $\bar{a}$ in stacks (Figure 3.2.4).

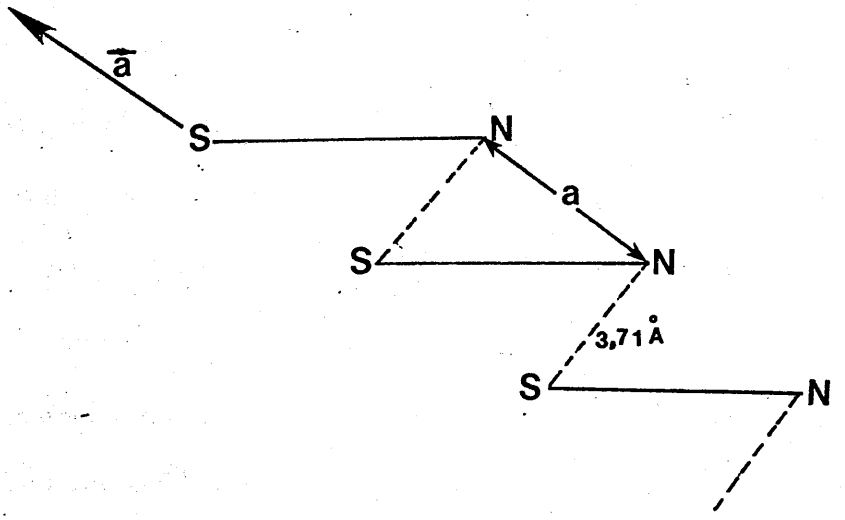


Figure 3.2.4.

This latter description of the molecular packing in II might provide an indication as to the slightly higher melting point of II when compared with I (97 - 99°C for I and 165 - 168°C for II).

A list of selected intermolecular contacts is given in Table 3.2.5 and is indicated as well in Figure 3.2.1(b).

3.I Discussion of I and II

From the X-ray analysis of m-nitrophenylsulphimide and p-nitrophenylsulphimide a 'conformational-picture' emerges whereby the N-S bonding system is almost coplanar with the aromatic ring. That near-planarity can be achieved is explained in terms of (i) the high degree of free rotation along the N(1) - S bond (calculated barrier to rotation in the model compound $H_2\overset{+}{S} - \overset{-}{N}H$ is 9.6 Kcal mol^{-1} and is considered to be small)[65] and (ii) the pyramidal stereochemistry around the sulphur atom. When (i) and (ii) cannot be attained, a twisted conformation must be assumed as is the case of 4-isopropylidene-aminophenol[66] (Figure 3.I.1) where atom C(7) is sp^2 hybridized (planar) and C(7) = N is a normal 'p-p' double bond (Holmes & Powell, 1953). Using the coordinates given for this molecule an angle of 65° is evaluated between the least-squares planes defining the aromatic ring and the N, C(7), C(8), C(9) group of atoms (This angle could be estimated simply by using Dreiding stereomodels with van der Waals' H-radii). Planarity in the sulphimide molecule is yet further favoured

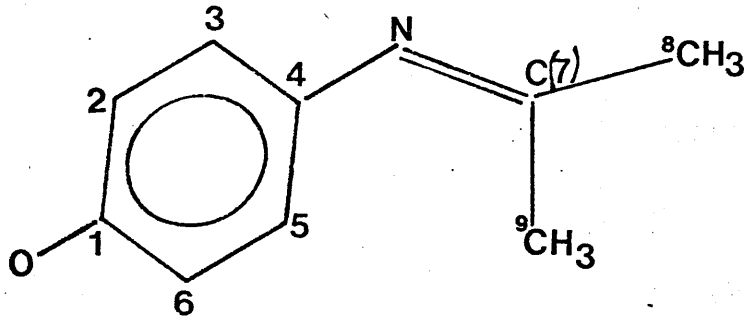


Figure 3.I.1

by the possibility of interactions between the N-S bonding system and the aromatic one (compound I to a small extent and II to a greater one).

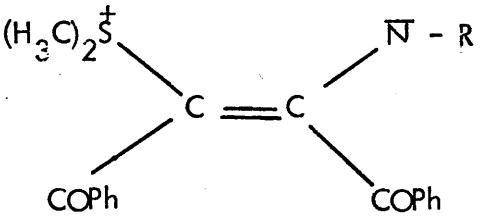
Although short distances are found to exist in the two N-arylsulphimides that have been investigated, (1.622 Å and 1.640 Å), the problem of the nature of the sulphur-nitrogen linkage remains still open. As was already pointed out by Trost & Melvin[24] (1975) and also mentioned in the introduction to Chapter 3 (this thesis), a quantitative separation of the factors affecting the stability of such compounds $\left[(d\text{-}p)_{\pi}\text{bonding, dipolar interactions}\right]$ is needed and has not been generally achieved. However, it should be stressed that in 'non-simple' systems, where the nature of the stabilization becomes complex (e.g. existence of different degrees of conjugations and perturbations of electron densities by inductive effects) a conventional picture of separate $(d\text{-}p)_{\pi}$ and ionic contributions to the bonding is an oversimplification and an individual evaluation on the basis of available information is needed. Such an approach is in fact applied in the recent results[62] published on the dipole moment calculations and measurements whereby a 40% - 60% ionic character has been attributed to the N-S bond in different N-arylsulphimides(e.g. 58% ionic character has been assigned to the p-nitrophenylsulphimide which is compound II in this thesis).

We can thus say that sulphimides in general could probably be described as dipole stabilized, but the actual extent of that contribution for each compound remains to be determined.

From the structure analysis of I and II it seems that a possible direct correlation between basicity and nucleophilicity could exist in these compounds, while the slight non-coplanarity already mentioned [9.6° and 7.3° in I and II respectively, between the least-squares planes representing the aromatic ring and the C(1), N(1), S group of atoms] is not prominent enough to impose any steric constraints.

THE CRYSTAL AND MOLECULAR STRUCTURES OF THREE YLIDES

OF THE FORM

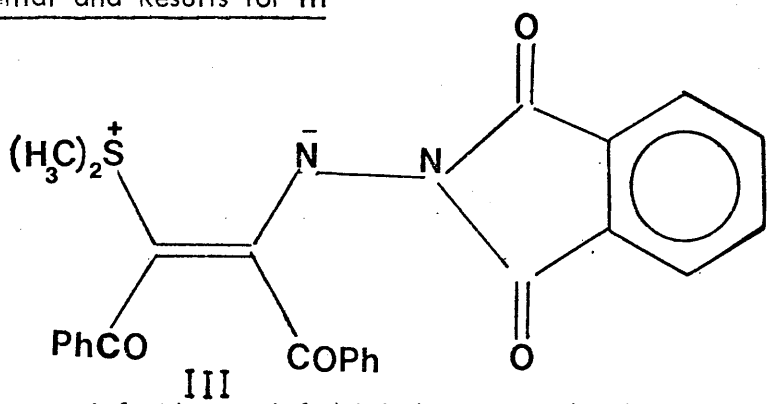


III R = $C_8H_4NO_2$ (Phthalimido)

IV R = C_6H_4Cl

V R = C_5H_4N (Pyridyl)

3.3 Experimental and Results for III



III

Dimethylsulphonium 1,2-dibenzoyl-2-(phthalimidoimino) ethylide.

Preparation of Crystals

The title compound (III) was prepared by the published procedure described by Gilchrist[33] (1976). Pure crystals were made by crystallization from a mixture of the solvents tetrachloromethane, acetone and toluene. The structure was substantiated by I.R (1720, 1785 and 1685 cm^{-1}, in CH_2Cl_2) and by mass spectrum analysis: m/e, 456(M^+), 441($M^+ - 15$), and 394 ($M^+ - (CH_3)_2S$).

Crystal Data

Molecular Formula	$C_{26}H_{20}N_2O_4S$
Molecular Weight	456.52 a.m.u.
Crystal System	Orthorhombic
Unit Cell Dimensions	a = 13.548 (3) Å
	b = 29.591 (5) Å
	c = 12.418 (2) Å
Unit Cell Volume	V = 4978.36 $Å^3$
Number of Molecules per Unit Cell	Z = 8
Calculated Density	D_c = 1.30 $g.cm^{-3}$

Number of Molecules per Asymmetric Unit	$N = 2$
Space Group	$P2_12_12_1$ (D_2^4, No 19)
Equivalent Positions	x,y,z
	$\frac{1}{2} - x, -y, \frac{1}{2} + z$
	$\frac{1}{2} + x, \frac{1}{2} - y, -z$
	$-x, \frac{1}{2} + y, \frac{1}{2} - z$
Linear Absorption Coefficient	$\mu = 1.61\ cm^{-1}$
Number of Electrons per Unit Cell	$F(000) = 2032$

Data Collection

Diffractometer Used	Hilger and Watts Y290
Radiation Used	$M_0 - K_\alpha$ $\overline{\lambda} = 0.71069\text{Å}$
Filter	Graphite Monochromator
	$\cos^2 2\theta_m = 0.970$
Upper Limit for Data Collection	$2\theta_{max} = 60^\circ$
Number of Observed Independent Reflections	$m = 3209$
Unobserved Cut-Off	$2.5\sigma_I$
Number of Parameters Refined	$n = 612$
Number of Reflections per Parameter	$m/n = 5.24$

Structure Determination and Refinement

The crystal structure was solved in space group $P2_12_12_1$ (from systematic absences in the diffraction data) with two molecules in the asymmetric unit. 400 $|E|$ values > 1.43 with 6000 Σ_2 phase relationships were used in the MULTAN program (version 1976) to

produce 32 sets of solution of which that with the highest 'combined figure of merit' proved to be correct (5.7 $|E|$ values per atom and 15 Σ_2 relations per $|E|$ value). The positions of 42 nonhydrogen atoms were located in the E-map and the remaining 24 were revealed in difference syntheses evaluated after successive cycles of isotropic least-squares, which converged to R and R_w factors of 0.144 and 0.186 respectively. The different parameters used with 'MULTAN' are summarized in Table 3.3.1. Since the hemisphere of reflections chosen by 'MULTAN' differs from the data set collected (h, -k, l) the proper phase relationship is given in Table 3.3.1 also. A difference synthesis evaluated after the 17th cycle of refinement [minimizing the function $\Sigma w(|F_o| - |F_c|)^2$] revealed four diffuse maxima of 1.05 - 1.22 e $\AA^{-3}$ which stereochemically corresponded to the molecular structure of acetone used to prepare the crystals (crystallization solvent). The absence of the solvent molecules from the structure factor calculations could be indicated by systematic discrepancies between the observed and calculated structure amplitudes ($|F_o| > |F_c|$) which became more obvious at low angles ($\sin\theta / \lambda$ = 0.08 - 0.2). Additional 9 cycles of block diagonal least-squares (allowing the positional and thermal parameters of the atoms of the acetone molecule to vary isotropically) were sufficient to bring the refinement to convergence. R and R_w were 0.055 and 0.071 respectively and the standard deviation of an observation of unit weight was 2.39. All parameter shifts (not including the overall

temperature factor and scale factor shifts which were $\simeq 0.77\sigma$) did not exceed 0.25σ , the average shift/error being equal to 0.05. The weighting scheme applied (after the 17th cycle of refinement) was of the Cruickshank type $w^{-1} = 15.020 - 0.9823|F_o| + 0.040|F_o|^2$ for $|F_o| > 9.19$ and $w = 1/11.2359$ for $|F_o| < 9.19$. A final analysis showed no systematic deviations from an approximately flat distribution of $\overline{w\Delta^2}$ with $|F_o|$. A detailed description of the course of refinement is given in Table 3.3.2. Hydrogen atoms were introduced as fixed contributors $\left[U_{(iso)} = 0.051\ \text{Å}^2\right]$ at calculated positions. No attempt was made to apply absorption corrections. The final three dimensional difference Fourier synthesis revealed no errors in the model. Scattering factors for the C, N, O, and S atoms were taken from Cromer and Mann (1968) and those for H from Stewart et al (1965). Final values for the calculated and observed structure amplitudes with the appropriate phases are given in the supplement to this thesis. Figure 3.3.1(a) is an 'ORTEP' drawing of the molecules and defines the atomic numbering scheme.

Figure 3.3.1(b) shows the molecular packing viewed along $\bar{c}$. Final atomic coordinates, thermal parameters and esd's, bond lengths, valence angles and other relevant data is listed in Tables 3.3.3(a,b and c) and 3.3.4(a,b,c) to 3.3.6 respectively.

Table 3.3.I

SUMMARY OF THE CONDITIONS (INCLUDING VARIOUS FIGURES OF INTEREST) ASSOCIATED WITH SOLVING THE STRUCTURE OF III.

In this table:

1. NE - is the number of the largest $|E|$'s chosen to define the structure.
2. NSRT - is the number of Σ_2 relationships to be retained.
3. NSRTT - is the total number of Σ_2 relationships.
4. PROB - is the probability acceptance limit chosen for Σ_1.
5. NSPEC - is the number of special phases (permutations restricted to ϕspec, ϕspec + 180°).

   NGEN - is the number of general phases (phase permutation 45°, 135°, 225°, 315°).

   NANY - is the number of phases of either sort.
6. NSET - is the total number of phase sets that have been developed.
7. PUB - is the published phase.
8. NAT - is the number of nonhydrogen atoms in the asymmetric unit.
9. ABS FOM, PSI ZERO, RESID and CFOM are all figures of merit.

$C_{26}H_{20}N_2O_4S$, $P2_12_12_1$, NAT = 70

PARAMETERS		STARTING SET TYPE	hk l	PHI	PUB	RESULTS PHASE SET CONSIDERED	FIGURES OF MERIT ABS FOM	PSI ZERO	RESID	TOTAL NUMBER OF CORRECT PEAKS FOUND IN E-MAP
SIGMA - 2		SIGMA - 1	-	-	-	MAX	1.5919	387.3	45.81	42
NE(|E| >1.43)	400					MIN	0.7295	191.1	34.07	
NSRT	6000	Origin defining phases	4,0,1	90	90	CFOM 23 = 2.1628	1.5913	355.2	34.07	
NSRTT	11171		5,4,0*	90	90					
CONVERGE			8,1,0	360	360					
PROB	0.95	Permuted phases	12,1,1**	±45 ±135	94					
NSPEC, NGEN, NANY	0,0,3		3,11,2	±45 ± 135	252					
FASTAN			8,7,2	±45 ±135	171					
NSET	32									

* $\phi(5,4,0) = -\phi(5,-4,0)$ and in general for the space group $P2_12_12_1$

$\phi(h,k,l) = -\phi(h,-k,l) + \pi(k + l)$;** The enanhomorph is fixed by the 12,1,1 reflection.

Table 3.3.2.

PROGRESS OF LEAST-SQUARES REFINEMENT

CYCLES	PARAMETERS REFINED	R	R_w
A series of successive least-squares and Fourier synthesis calculations with increasing numbers of atoms	$x,y,z,U_{(iso)}$ for C, N, O, S; scale factor; unit weights; block diagonal (last cycle of refinement with 66 atoms).	0.144	0.186
2	As above, but after counting loss corrections to 17 reflections.	0.139	0.182
6	x,y,z,U_{ij} for C, N, O, S; scale factor; unit weights; block diagonal; damping factor of 0.9.	0.118	0.168
1 (not converged)	x,y,z,U_{ij} for C, N, O, S, with fixed contribution of 40 H-atoms (in their calculated positions); scale factor; unit weights; block diagonal; damping factor of 0.5.	0.108	0.159
8	As after the 9th cycle, but 13 reflections not included in the least squares refinement (affected by extinction).	0.088	0.125

CYCLES	PARAMETERS REFINED	R	R_w
9	x,y,z,U_{ij} for C, N, O, S; x,y,z $U_{(iso)}$ for C and O of the solvent molecule acetone; scale factor; weighting scheme; block diagonal; damping factor = 0.6).	0.055	0.071

Table 3.3.2 (contd.) PROGRESS OF LEAST SQUARES REFINEMENT.

Table 3.3.3 (a,b,c,d)

(a) Fractional atomic coordinates ($\times 10^4$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM X/A Y/B Z/C

(b) Anisotropic thermal parameters (Å^2, $\times 10^3$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}

(c) Fractional atomic coordinates ($\times 10^4$) of the hydrogen and solvent atoms. The hydrogens are numbered according to the atoms to which they are attached.

(d) Isotropic thermal parameters ($\text{Å}^2 \times 10^3$) of the hydrogen and solvent atoms. The table shows:

ATOM $U_{(iso)}$.

C(1)	9575(6)	1059(2)	5085(9)
C(2)	9322(5)	1376(3)	4324(7)
C(3)	9067(5)	1809(2)	4636(5)
C(4)	9044(4)	1923(2)	5740(5)
C(5)	9330(6)	1596(2)	6488(6)
C(6)	9576(7)	1160(3)	6190(8)
C(7)	11265(7)	3819(3)	5709(8)
C(8)	11173(6)	3774(3)	6787(8)
C(9)	10271(6)	3613(3)	7171(6)
C(10)	9527(5)	3498(2)	6477(6)
C(11)	9642(6)	3559(2)	5379(6)
C(12)	10529(6)	3725(3)	5017(7)
C(13)	6634(7)	4974(3)	6203(10)
C(14)	6155(10)	5239(3)	6985(11)
C(15)	5774(8)	5041(3)	7848(12)
C(16)	5798(7)	4577(3)	8016(7)
C(17)	6236(6)	4311(2)	7255(6)
C(18)	6399(5)	3816(2)	7170(5)
C(19)	7103(6)	4157(2)	5684(6)
C(20)	6660(6)	4504(2)	6364(7)
C(21)	8853(4)	2383(2)	6157(5)
C(22)	8020(4)	2637(2)	5810(5)
C(23)	7861(4)	3094(2)	6150(5)
C(24)	8594(5)	3309(2)	6932(5)
C(25)	5995(4)	2420(2)	5880(6)
C(26)	6817(5)	2655(3)	3867(5)
N(1)	6995(4)	3755(2)	6276(4)
N(2)	7097(4)	3322(2)	5802(5)
O(1)	9436(3)	2543(1)	6839(4)
O(2)	8382(3)	3342(2)	7872(3)
O(3)	7494(5)	4176(2)	4793(5)
O(4)	6089(4)	3519(2)	7738(4)
S(1)	7898(1)	2353(1)	5096(1)
C(27)	8471(6)	0959(2)	0085(7)
C(28)	8749(6)	1274(3)	-0656(6)

C(29)	8930(5)	1720(2)	-0319(5)
C(30)	8809(4)	1844(2)	0725(5)
C(31)	8504(7)	1531(3)	1436(6)
C(32)	8342(7)	1085(3)	1128(7)
C(33)	11381(7)	4885(2)	0862(7)
C(34)	11908(7)	5145(3)	1527(10)
C(35)	12403(7)	4969(3)	2413(11)
C(36)	12287(6)	4526(3)	2677(7)
C(37)	11701(5)	4264(2)	2033(6)
C(38)	11501(5)	3763(2)	2056(6)
C(39)	10753(5)	4069(2)	0531(6)
C(40)	11264(5)	4442(2)	1127(6)
C(41)	6706(5)	3911(3)	0897(8)
C(42)	7365(6)	3759(3)	0170(7)
C(43)	8223(5)	3541(2)	0482(5)
C(44)	8403(4)	3473(2)	1566(5)
C(45)	7739(5)	3641(2)	2329(6)
C(46)	6897(6)	3853(3)	1983(7)
C(47)	9004(4)	2318(2)	1129(5)
C(48)	9868(4)	2564(2)	0818(5)
C(49)	9998(5)	3024(2)	1131(5)
C(50)	9304(5)	3240(2)	1974(5)
C(51)	11918(5)	2381(2)	0897(6)
C(52)	11067(6)	2562(3)	-1073(5)
N(3)	10854(4)	3688(2)	1192(4)
N(4)	10742(4)	3253(2)	0747(5)
O(5)	8394(3)	2479(1)	1744(4)
O(6)	9519(4)	3224(2)	2904(3)
O(7)	11826(4)	3482(2)	2662(4)
O(8)	10359(5)	4071(2)	-0319(4)
S(2)	10804(1)	2279(1)	0159(1)

3.3.3 (a) (continued)

C(1)	56(4)	48(4)	135(8)	7(4)	9(6)	-10(6)
C(2)	50(4)	82(6)	79(5)	8(4)	11(4)	-27(5)
C(3)	43(4)	63(4)	51(4)	0(3)	-6(3)	1(3)
C(4)	37(3)	47(4)	57(4)	5(3)	-5(3)	0(3)
C(5)	66(5)	56(4)	58(4)	5(4)	2(4)	5(4)
C(6)	84(6)	60(5)	96(7)	15(5)	-2(6)	2(5)
C(7)	77(6)	123(8)	134(8)	-36(6)	26(7)	-23(7)
C(8)	58(5)	129(8)	119(8)	-24(5)	-28(6)	-28(7)
C(9)	62(5)	89(6)	68(5)	-15(4)	-15(4)	-6(4)
C(10)	46(4)	45(4)	60(4)	-2(3)	-5(4)	-10(3)
C(11)	70(5)	69(5)	54(4)	-9(4)	9(4)	-17(4)
C(12)	84(6)	104(6)	74(5)	-36(5)	30(5)	-25(5)
C(13)	86(6)	48(5)	172(10)	2(5)	-4(7)	13(6)
C(14)	153(11)	45(5)	144(10)	29(6)	-16(9)	4(7)
C(15)	117(9)	59(6)	197(14)	31(6)	-34(10)	-73(8)
C(16)	95(6)	97(7)	87(6)	28(6)	-5(6)	-11(5)
C(17)	66(5)	51(4)	75(5)	2(4)	-16(4)	-13(4)
C(18)	64(4)	48(4)	66(5)	10(4)	-19(4)	3(4)
C(19)	72(5)	49(4)	81(5)	-2(4)	-17(5)	-2(4)
C(20)	61(5)	48(4)	101(6)	-4(4)	-17(5)	3(5)
C(21)	42(3)	49(4)	47(4)	-9(3)	0(3)	-1(3)
C(22)	40(3)	42(3)	44(3)	-2(3)	-12(3)	-7(3)
C(23)	39(3)	47(3)	46(4)	-7(3)	-2(3)	2(3)
C(24)	54(4)	47(4)	45(4)	2(3)	-3(3)	-8(3)
C(25)	38(4)	66(4)	71(5)	-2(3)	2(4)	6(4)
C(26)	61(4)	93(5)	44(4)	-2(4)	3(4)	0(4)
N(1)	62(4)	42(3)	58(3)	4(3)	-2(3)	-4(3)
N(2)	55(3)	48(3)	68(4)	5(3)	-12(3)	-16(3)
O(1)	62(3)	63(3)	72(3)	9(3)	-33(3)	-19(3)
O(2)	62(3)	87(3)	43(3)	-7(3)	4(2)	-13(2)
O(3)	113(4)	80(3)	85(4)	-14(4)	10(4)	8(3)
O(4)	72(3)	70(3)	79(3)	3(3)	2(3)	12(3)
S(1)	38(1)	50(1)	52(1)	-3(1)	-8(1)	-9(1)
C(27)	69(5)	60(4)	91(6)	-14(4)	2(5)	-16(4)
C(28)	86(6)	70(5)	60(5)	-21(5)	-7(5)	-15(4)

C(29)	62(4)	67(5)	46(4)	-11(4)	-7(4)	5(4)
C(30)	30(3)	49(4)	55(4)	-4(3)	-6(3)	6(3)
C(31)	100(6)	62(5)	63(5)	-6(5)	15(5)	7(4)
C(32)	118(7)	57(5)	90(6)	-32(5)	9(6)	19(5)
C(33)	92(6)	39(4)	107(7)	9(4)	3(6)	1(4)
C(34)	85(7)	46(5)	164(10)	-8(5)	-4(7)	-3(6)
C(35)	60(5)	73(6)	172(11)	-17(5)	-6(7)	-55(7)
C(36)	70(5)	62(5)	102(6)	4(4)	-13(5)	-29(5)
C(37)	44(4)	49(4)	76(5)	2(3)	13(4)	-10(4)
C(38)	43(4)	56(4)	65(5)	-1(3)	14(4)	-11(4)
C(39)	65(4)	51(4)	64(5)	8(4)	2(4)	-3(4)
C(40)	59(4)	38(4)	66(5)	8(3)	14(4)	2(4)
C(41)	44(4)	89(6)	121(7)	35(4)	-1(5)	-4(6)
C(42)	69(5)	70(5)	79(6)	16(4)	-33(5)	-7(5)
C(43)	48(4)	54(4)	48(4)	2(3)	-3(3)	-10(3)
C(44)	37(3)	45(4)	53(4)	4(3)	-1(3)	-5(3)
C(45)	59(4)	73(5)	57(5)	18(4)	16(4)	-2(4)
C(46)	64(5)	89(5)	93(6)	30(5)	14(5)	-2(5)
C(47)	42(4)	57(4)	46(4)	0(3)	9(3)	-5(3)
C(48)	36(3)	49(4)	42(3)	2(3)	2(3)	0(3)
C(49)	41(4)	48(4)	47(4)	5(3)	-7(3)	0(3)
C(50)	38(3)	53(4)	51(4)	-2(3)	-3(3)	-4(3)
C(51)	45(4)	61(4)	68(5)	12(4)	-11(4)	-6(4)
C(52)	68(5)	107(6)	42(4)	-8(5)	14(4)	-1(4)
N(3)	49(3)	40(3)	66(4)	-5(3)	10(3)	-7(3)
N(4)	53(3)	41(3)	67(4)	-2(3)	17(3)	-7(3)
O(5)	54(3)	61(3)	86(3)	-2(2)	21(3)	-7(3)
O(6)	77(3)	100(4)	35(3)	18(3)	-5(3)	-5(3)
O(7)	74(3)	65(3)	69(3)	4(3)	3(3)	1(3)
O(8)	135(5)	66(3)	75(4)	2(4)	-28(4)	-2(3)
S(2)	40(1)	50(1)	51(1)	-1(1)	5(1)	-9(1)

3.3.3 (b) - (continued)

C(53)	9587(11)	4946(5)	7489(13)
C(54)	9572(11)	4866(5)	6355(13)
C(55)	8870(11)	4730(5)	8144(11)
O(9)	10229(11)	5135(4)	8016(10)
H(1)	9762	0750	4849
H(2)	9331	1292	3538
H(3)	8903	2045	4085
H(5)	9369	1685	7261
H(6)	9731	0924	6744
H(7)	11926	3926	5447
H(8)	11710	3855	7305
H(9)	10168	3583	7967
H(11)	9895	3483	4884
H(12)	10637	3774	4233
H(13)	6964	5127	5616
H(14)	6643	5562	6890
H(15)	5471	5236	8426
H(16)	5488	4450	8696
H(251)	6088	2284	6627
H(252)	5824	2747	5971
H(253)	5470	2255	5490
H(261)	6574	2968	4037
H(262)	7418	2678	3401
H(263)	6284	2492	3450
H(27)	8352	0637	-0119
H(28)	8821	1193	-1441
H(29)	9154	1953	-0855
H(31)	8398	1619	2211
H(32)	8119	0865	1694
H(33)	11076	5021	0223
H(34)	11966	5477	1401
H(35)	12865	5164	2871
H(36)	12608	4399	3342
H(41)	6695	4066	0685
H(42)	7213	3801	-0602

H(43)	8703	3435	-0074
H(45)	7884	3603	3122
H(46)	6412	3964	2550
H(511)	12068	2707	0927
H(512)	11850	2257	1652
H(513)	12456	2211	0515
H(521)	10449	2567	-1529
H(522)	11273	2879	-0920
H(523)	11595	2397	-1460
H(541)	9752	5163	5989
H(542)	10178	4655	6217
H(543)	9065	4732	5863
H(551)	9148	4485	8597
H(552)	8542	4961	8670
H(553)	8291	4600	7712

C(53)	145(5)
C(54)	161(5)
C(55)	159(5)
O(9)	227(5)
H(1)	51
H(2)	51
H(3)	51
H(5)	51
H(6)	51
H(7)	51
H(8)	51
H(9)	51
H(11)	51
H(12)	51
H(13)	51
H(14)	51
H(15)	51
H(16)	51
H(251)	51
H(252)	51
H(253)	51
H(261)	51
H(262)	51
H(263)	51
H(27)	51
H(28)	51
H(29)	51
H(31)	51
H(32)	51
H(33)	51
H(34)	51
H(35)	51
H(36)	51
H(41)	51
H(42)	51

Table 3.3.4(a,b,c)

(a) Interatomic distances ($\mathring{A}$) with e.s.d.'s in parentheses.

(b) Interbond angles (in degrees) with e.s.d.'s (degrees) in parentheses.

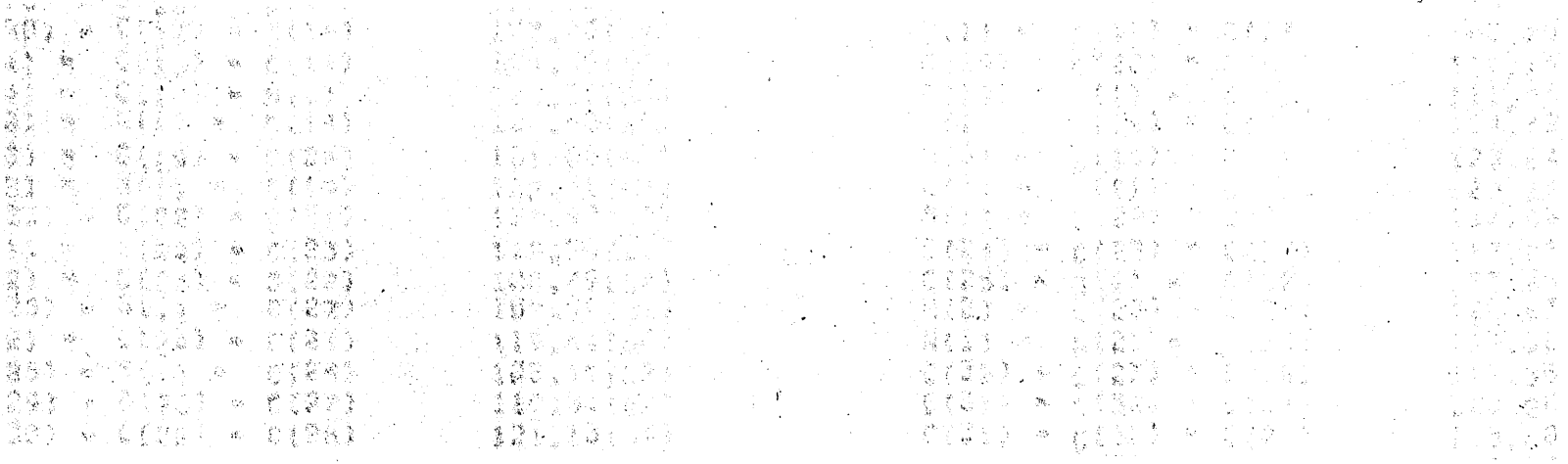
(c) Selected torsion angles (degrees) with e.s.d.'s (degrees) in parentheses.

A torsion angle A - B - C - D is considered to be positive if when viewed down the B-C bond the A-B bond will eclipse the C-D bond when rotated less than 180° in a clockwise direction.

C(1) - C(2)	1.375(13)	C(27) - C(32)	1.360(12)
C(1) - C(6)	1.404(15)	C(28) - C(29)	1.407(10)
C(2) - C(3)	1.382(11)	C(29) - C(30)	1.357(10)
C(3) - C(4)	1.412(10)	C(30) - C(31)	1.344(10)
C(4) - C(5)	1.397(9)	C(30) - C(47)	1.514(9)
C(4) - C(21)	1.478(9)	C(31) - C(32)	1.392(11)
C(5) - C(6)	1.381(11)	C(33) - C(34)	1.334(14)
C(7) - C(8)	1.360(14)	C(33) - C(40)	1.362(9)
C(7) - C(12)	1.346(13)	C(34) - C(35)	1.391(17)
C(8) - C(9)	1.396(12)	C(35) - C(36)	1.360(13)
C(9) - C(10)	1.370(10)	C(36) - C(37)	1.368(11)
C(10) - C(11)	1.384(10)	C(37) - C(38)	1.508(9)
C(10) - C(24)	1.492(9)	C(37) - C(40)	1.376(10)
C(11) - C(12)	1.374(11)	C(38) - N(3)	1.404(9)
C(13) - C(14)	1.408(16)	C(38) - O(7)	1.204(8)
C(13) - C(20)	1.405(10)	C(39) - C(40)	1.498(9)
C(14) - C(15)	1.326(19)	C(39) - N(3)	1.402(8)
C(15) - C(16)	1.387(13)	C(39) - O(8)	1.184(9)
C(16) - C(17)	1.367(12)	C(41) - C(42)	1.348(12)
C(17) - C(18)	1.484(9)	C(41) - C(46)	1.384(13)
C(17) - C(20)	1.372(11)	C(42) - C(43)	1.386(10)
C(18) - N(1)	1.384(9)	C(43) - C(44)	1.383(9)
C(18) - O(4)	1.203(8)	C(44) - C(45)	1.398(9)
C(19) - C(20)	1.459(11)	C(44) - C(50)	1.492(9)
C(19) - N(1)	1.406(9)	C(45) - C(46)	1.370(11)
C(19) - O(3)	1.229(10)	C(47) - C(48)	1.432(8)
C(21) - C(22)	1.424(8)	C(47) - O(5)	1.222(8)
C(21) - O(1)	1.250(8)	C(48) - C(49)	1.427(9)
C(22) - C(23)	1.434(8)	C(48) - S(2)	1.730(6)
C(22) - S(1)	1.747(6)	C(49) - C(50)	1.545(9)
C(23) - C(24)	1.527(9)	C(49) - N(4)	1.305(8)
C(23) - N(2)	1.309(8)	C(50) - O(6)	1.191(8)

C(24) - O(2)	1.206(7)	C(51) - S(2)	1.791(7)
C(25) - S(1)	1.794(7)	C(52) - S(2)	1.779(7)
C(26) - S(1)	1.809(7)	N(3) - N(4)	1.407(7)
N(1) - N(2)	1.417(7)	C(53) - C(54)	1.427(23)
C(27) - C(28)	1.362(10)	C(53) - C(55)	1.420(21)
C(53) - O(9)	1.222(21)		

3.3.4 (a) - (continued)



C(6) - C(1) - C(2)	121.75(74)	C(3) - C(2) - C(1)	120.17(77)
C(5) - C(6) - C(1)	117.39(75)	C(4) - C(3) - C(2)	119.91(64)
C(5) - C(4) - C(3)	118.26(59)	C(21) - C(4) - C(3)	124.35(58)
C(21) - C(4) - C(5)	116.97(59)	C(6) - C(5) - C(4)	122.41(69)
C(22) - C(21) - C(4)	121.25(53)	O(1) - C(21) - C(4)	118.44(54)
C(12) - C(7) - C(8)	122.99(86)	C(9) - C(8) - C(7)	117.00(81)
C(11) - C(12) - C(7)	120.81(79)	C(10) - C(9) - C(8)	120.89(73)
C(11) - C(10) - C(9)	120.32(65)	C(24) - C(10) - C(9)	118.53(62)
C(24) - C(10) - C(11)	121.14(60)	C(12) - C(11) - C(10)	117.90(68)
C(23) - C(24) - C(10)	117.76(53)	O(2) - C(24) - C(10)	122.52(59)
C(20) - C(13) - C(14)	117.69(94)	C(15) - C(14) - C(13)	119.35(88)
C(17) - C(20) - C(13)	121.20(80)	C(19) - C(20) - C(13)	128.65(82)
C(16) - C(15) - C(14)	123.38(112)	C(17) - C(16) - C(15)	118.49(93)
C(18) - C(17) - C(16)	133.10(73)	C(20) - C(17) - C(16)	119.85(70)
C(20) - C(17) - C(18)	107.03(64)	N(1) - C(18) - C(17)	105.75(55)
O(4) - C(18) - C(17)	128.89(66)	C(19) - C(20) - C(17)	110.16(62)
O(4) - C(18) - N(1)	125.36(59)	C(19) - N(1) - C(18)	111.75(52)
N(2) - N(1) - C(18)	120.52(49)	N(1) - C(19) - C(20)	104.49(62)
O(3) - C(19) - C(20)	131.88(67)	O(3) - C(19) - N(1)	123.64(62)
N(2) - N(1) - C(19)	122.51(53)	O(1) - C(21) - C(22)	120.30(54)
C(23) - C(22) - C(21)	121.90(53)	S(1) - C(22) - C(21)	117.83(43)
S(1) - C(22) - C(23)	119.74(43)	C(24) - C(23) - C(22)	118.87(51)
N(2) - C(23) - C(22)	120.49(54)	C(25) - S(1) - C(22)	105.45(30)
C(26) - S(1) - C(22)	109.96(31)	N(2) - C(23) - C(24)	120.63(52)
O(2) - C(24) - C(23)	119.61(58)	N(1) - N(2) - C(23)	113.96(51)
C(26) - S(1) - C(25)	103.15(32)	C(32) - C(27) - C(28)	119.36(66)
C(29) - C(28) - C(27)	119.31(67)	C(31) - C(32) - C(27)	120.20(73)
C(30) - C(29) - C(28)	121.13(64)	C(31) - C(30) - C(29)	118.60(63)
C(47) - C(30) - C(29)	123.16(58)	C(47) - C(30) - C(31)	118.24(61)
C(32) - C(31) - C(30)	121.35(71)	C(48) - C(47) - C(30)	121.60(53)
O(5) - C(47) - C(30)	116.82(64)	C(40) - C(33) - C(34)	117.90(83)
C(35) - C(34) - C(33)	122.07(81)	C(37) - C(40) - C(33)	121.08(68)

C(39) - C(40) - C(33)	130.14(70)	C(36) - C(35) - C(34)	119.83(94)
C(37) - C(36) - C(35)	118.11(84)	C(38) - C(37) - C(36)	130.51(66)
C(40) - C(32) - C(36)	120.74(63)	C(40) - C(37) - C(38)	108.39(58)
N(3) - C(38) - C(37)	104.66(63)	O(7) - C(38) - C(37)	128.67(62)
C(39) - C(40) - C(37)	108.66(55)	O(7) - C(38) - N(3)	126.66(58)
C(39) - N(3) - C(38)	112.36(61)	N(4) - N(3) - C(38)	120.78(49)
N(3) - C(39) - C(40)	105.05(56)	O(8) - C(39) - C(40)	130.17(63)
O(8) - C(39) - N(3)	124.75(62)	N(4) - N(3) - C(39)	119.72(53)
C(46) - C(41) - C(42)	119.16(73)	C(43) - C(42) - C(41)	121.65(75)
C(45) - C(46) - C(41)	121.20(73)	C(44) - C(43) - C(42)	119.16(62)
C(45) - C(44) - C(43)	119.67(58)	C(50) - C(44) - C(43)	122.82(56)
C(50) - C(44) - C(45)	117.48(58)	C(46) - C(45) - C(44)	119.10(67)
C(49) - C(50) - C(44)	117.32(53)	O(6) - C(50) - C(44)	123.15(58)
O(5) - C(42) - C(48)	121.58(58)	C(49) - C(48) - C(47)	120.83(55)
S(2) - C(48) - C(47)	118.68(46)	S(2) - C(48) - C(49)	120.23(45)
C(50) - C(49) - C(48)	120.19(53)	N(4) - C(49) - C(48)	119.42(56)
C(51) - S(2) - C(48)	107.09(31)	C(52) - S(2) - C(48)	108.95(33)
N(4) - C(49) - C(50)	120.27(53)	O(6) - C(50) - C(49)	119.49(56)
N(3) - N(4) - C(49)	114.45(52)	C(52) - S(2) - C(51)	101.12(34)
C(55) - C(53) - C(54)	118.70(132)	O(9) - C(53) - C(54)	127.87(149)
O(9) - C(53) - C(55)	112.67(146)		

3.3.4 (b) - (continued)

Table 3.3.4(c)

C(3)	-C(4)	-C(21)	-C(22)	51.1 (9)
C(5)	-C(4)	-C(21)	-C(22)	-136.5 (6)
C(11)	-C(10)	-C(24)	-C(23)	12.6 (9)
C(16)	-C(17)	-C(18)	-O(4)	7.5 (14)
O(3)	-C(19)	-C(20)	-C(13)	-5.7 (15)
C(4)	-C(21)	-C(22)	-C(23)	-175.6 (6)
C(4)	-C(21)	-C(22)	-S(1)	12.8 (8)
O(1)	-C(21)	-C(22)	-C(23)	5.4 (9)
C(21)	-C(22)	-C(23)	-C(24)	-1.7 (9)
C(21)	-C(22)	-C(23)	-N(2)	178.8(6)
S(1)	-C(22)	-C(23)	-C(24)	169.7 (4)
S(1)	-C(22)	-C(23)	-N(2)	-9.8 (8)
C(23)	-C(22)	-S(1)	-C(26)	59.1 (6)°
C(22)	-C(23)	-C(24)	-C(10)	81.8 (7)
C(29)	-C(30)	-C(47)	-C(48)	-44.8 (9)
C(31)	-C(30)	-C(47)	-C(48)	135.0 (7)
C(36)	-C(37)	-C(38)	-O(7)	-0.2 (13)
O(8)	-C(39)	-C(40)	-C(33)	2.5 (13)
C(30)	-C(47)	-C(48)	-C(49)	174.6 (6)°
C(47)	-C(48)	-C(49)	-C(50)	10.8 (9)
C(49)	-C(48)	-S(2)	-C(52)	-60.5 (6)°
C(47)	-C(48)	-C(49)	-N(4)	-173.2 (6)
S(2)	-C(48)	-C(49)	-C(50)	-163.3 (5)

S(2)	-C(48)	-C(49)	-N(4)	12.8 (8)
C(48)	-C(49)	N(4)	-N(3)	-174.0 (5)
C(48)	-C(49)	-C(50)	-O(6)	90.9 (8)
C(49)	-C(50)	-C(44)	-C(43)	-6.4 (9)
C(44)	-C(50)	-C(49)	-C(48)	-91.3 (7)
C(18)	-N(1)	-N(2)	-C(23)	-94.2 (7)
C(19)	-N(1)	-N(2)	-C(23)	113.5 (7)
N(1)	-N(2)	-C(23)	-C(22)	175.0 (5)
C(38)	-N(3)	-N(4)	-C(49)	95.4 (7)°

3.3.4 (c) - (continued)

Table 3.3.5

A. Selected intramolecular non-bonded distances (< 4.0 Å)

C(3) ... C(22)	3.18	C(30) ... S(2)	3.08
C(3) ... O(1)	3.53	C(38) ... C(49)	3.20
C(3) ... S(1)	3.17	C(38) ... C(50)	3.36
C(4) ... S(1)	3.03	C(39) ... C(44)	3.86
C(5) ... O(1)	2.84	C(39) ... C(49)	3.34
C(11) ... O(3)	3.51	C(39) ... C(50)	3.62
C(13) .. O(3)	3.16	C(43) ... O(5)	3.52
C(18) .. C(23)	3.18	C(43) ... C(48)	3.67
C(18) ... C(24)	3.34	C(43) ... C(49)	2.96
C(18) ... O(2)	3.15	C(44) ... C(48)	3.47
C(19) ... C(23)	3.36	C(44) ... O(5)	2.95
C(19) ... C(24)	3.57	C(47) ... C(50)	2.95
C(21) ... C(24)	2.93	C(50) ... O(5)	2.58
C(23) ... O(1)	2.82	C(50) ... O(7)	3.59
C(23) ... O(4)	3.35	C(50) ... N(3)	2.67
C(24) ... N(1)	2.66	O(3) ... N(2)	2.87
C(24) ... O(4)	3.59	S(1) ... N(2)	3.0
C(24) ... O(1)	2.54	S(2) ... N(4)	2.97
C(29) ... S(2)	3.09		

B. Selected intermolecular distances (< 4.0 Å)

C(3) ... $C(25)^{i}$	3.53	C(55) ... $C(20)^{ii}$	3.78
O(3) ... $C(45)^{ii}$	3.46	C(55) ... $O(8)^{iii}$	3.39
C(54) ... $C(7)^{ii}$	3.94	O(9) ... $C(6)^{iv}$	3.20
C(54) ... $C(8)^{ii}$	3.93	O(9) ... $C(35)^{v}$	3.31

Roman numeral superscripts refer to the following equivalent positions relative to the molecule at (x,y,z):

(i) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$

(ii) x,y,z

(iii) x,y, 1 + z

(iv) $2 - x, \frac{1}{2} + y, 3/2 - z$

(v) $5/2 - x, 1 - y, \frac{1}{2} + z$

Table 3.3.5 - (continued)

Table 3.3.6

LEAST-SQUARES PLANES

Planes are in the form of $AX + BY + CZ - D = 0$ where X, Y and Z refer to an orthogonalized set of axes. D is the perpendicular distance from the plane to the origin and A, B and C refer to the components of unit vector normal to the best plane. An asterisk denotes atoms used to define the plane.

A.

(I) Equation of the plane

$-0.4387X + 0.8844Y - 0.1595Z - 2.2012 = 0$

$\chi^2 = 16.66$ with one degree of freedom.

The deviations (Å) of the atoms from the plane are:

C(10)*	0.007 (6)	C(11)	0.3158 (7)
C(23)*	0.006 (6)	C(9)	-0.2716 (8)
C(24)*	-0.022 (6)		
O(2)*	0.005 (5)		

(2) Equation of the plane

$-0.5487X - 0.3915Y + 0.7387Z + 3.6880 = 0$

$\chi^2 = 0.94$

The deviations (Å) of the atoms from the plane are:

C(4)*	0.002 (6)	S(1)	0.360 (2)
C(21)*	-0.005 (6)	C(23)	-0.099 (6)
C(22)*	0.001 (6)	N(2)	-0.114 (5)
O(1)*	0.001 (5)	C(24)	-0.176 (6)
C(3)	-0.895 (7)		

(3) Equation of the plane

$-0.5404X - 0.3344Y + 0.7721Z + 2.9198 = 0$

The deviations ($\mathring{A}$) of the atoms from the plane are:

C(23)*	0.0	S(1)	0.281 (2)
C(24)*	0.0	C(22)	0.011 (6)
N(2)*	0.0	C(21)	-0.015 (6)
N(1)	0.101(5)		

(4) Equation of the plane

$0.5820X - 0.3483Y + 0.7348Z - 5.7992 = 0$

The deviations ($\mathring{A}$) of the atoms from the plane are:

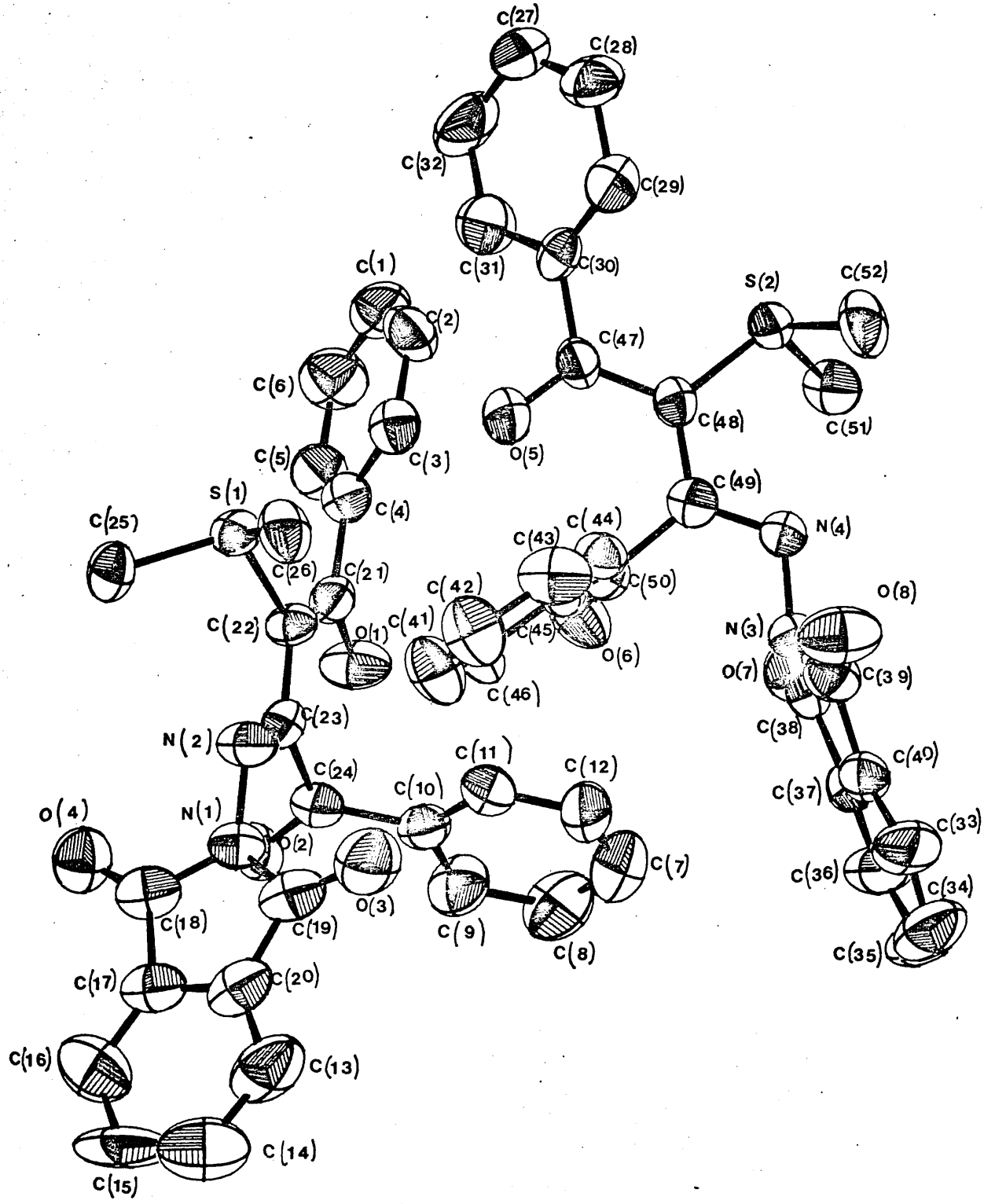
C(49)*	0.0	C(48)	0.085(6)
C(50)*	0.0	S(2)	0.516(2)
N(4)*	0.0		
C(47)	-0.058(6)		

B. Dihedral angle between planes (1) and (2) is 102.9°, between (2) and (3) is 3.8° and between (1) and (3) is 100.5°.

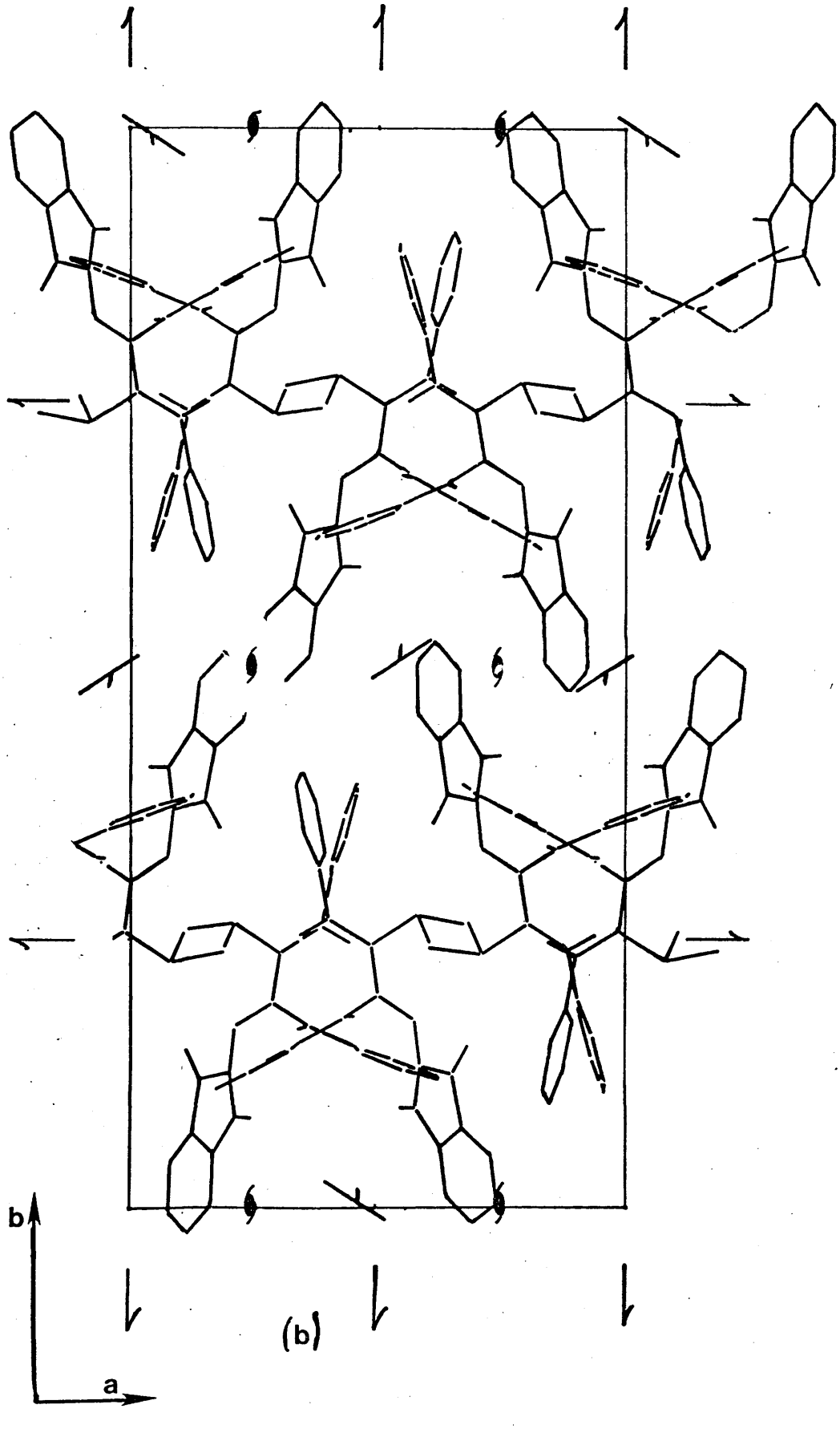
Figure 3.3.1 (a and b)

(a) A general view of III (without hydrogens) giving the atomic numbering scheme for both molecules in the asymmetric unit (molecules A and B).

(b) The molecular packing of III viewed along the short axis $\bar{c}$.


C(27)
C(28)
C(32)
C(29)
C(31)
C(30)
C(1)
S(2)
C(52)
C(2)
C(47)
C(6)
C(48)
C(51)
C(5)
C(3)
O(5)
S(1)
C(49)
C(25)
C(4)
C(44)
N(4)
C(43)
C(26)
C(21)
C(42)
C(50)
O(8)
C(22)
O(1)
C(41)
C(45)
N(3)
O(6)
O(7)
C(39)
C(46)
C(23)
C(38)
N(2)
C(11)
C(12)
C(40)
C(24)
C(10)
C(37)
O(4)
N(1)
C(33)
O(2)
C(7)
C(36)
C(34)
O(3)
C(18)
C(19)
C(9)
C(8)
C(35)
C(17)
C(20)
C(16)
C(13)
C(14)
C(15)

(a)



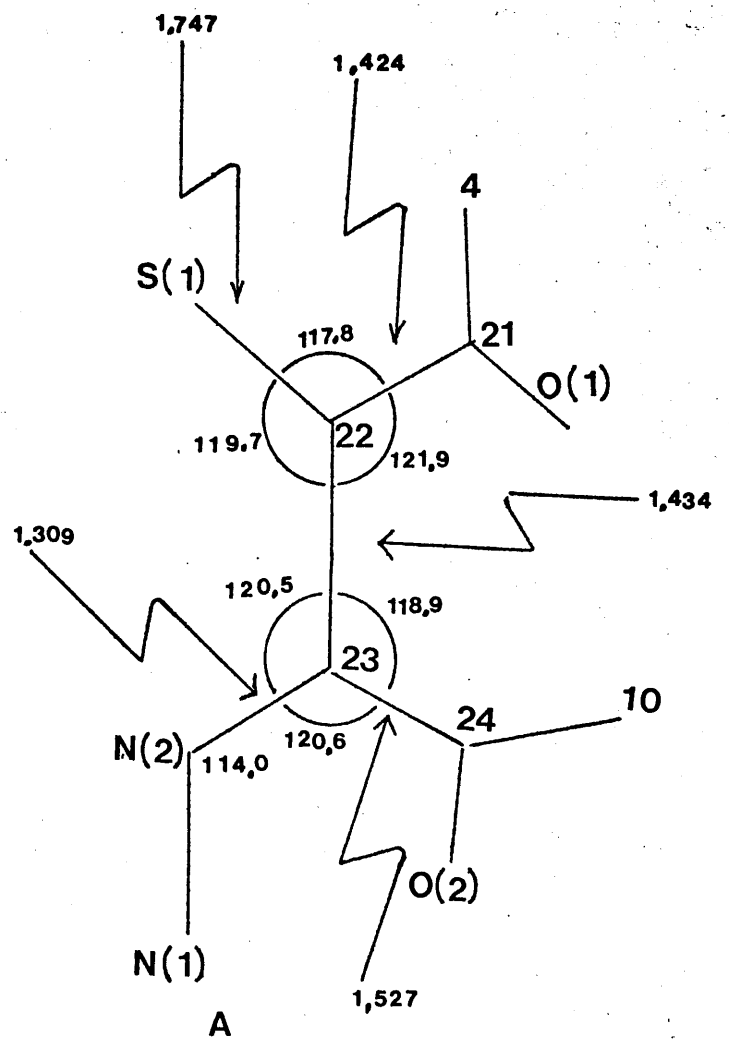
(b)

Discussion of III

The main features of the conformations and geometries of the two molecules (A and B) of betaine III are illustrated in Figures 3.3.1 and 3.3.2.

The spatial arrangement about the tricoordinated sulphur atom is pyramidal (or tetrahedral if the unshared electron pair is considered), the mean values of the pyramidal valency angle being 106.2° for A and 105.7° for B. The central frameworks of both molecules [i.e. atoms N(2), C(24), C(23), C(22), C(21) and S(1) in molecule A, and atoms N(4), C(50), C(49), C(48), C(47) and S(2) in molecule B] deviate slightly from planarity, as indicated by the torsion angles in Table 3.3.4(c). However, whereas in molecule A, the deviation from planarity results mainly from the sulphur atom which is significantly distant from the plane of atoms C(21), C(22), C(23), C(24) and N(2), in molecule B the deviations from planarity are less localized.

This latter observation is possibly indicative of different environments capable of imposing slightly different steric constraints. There is pronounced torsional movement of the benzoyl rings, [C(1), C(2), C(3), C(4), C(5), C(6) in A and C(27), C(28), C(29), C(30), C(31), C(32) in B] resulting in torsion angles of C(3) - C(4) - C(21) - C(22) [51.1(9)°] and C(29) - C(30) - C(47) - C(48) [-44.8(9)°] in A and B respectively. This twisting along the C(carbonyl) - C(ring) bonds seems likely to be mainly dictated by the non-bonded intramolecular repulsive interactions


1,747
1,424
4
S(1)
21
O(1)
117,8
119,7
22
121,9
1,434
1,309
120,5
118,9
23
10
24
N(2)
114,0
120,6
O(2)
N(1)
1,527
A

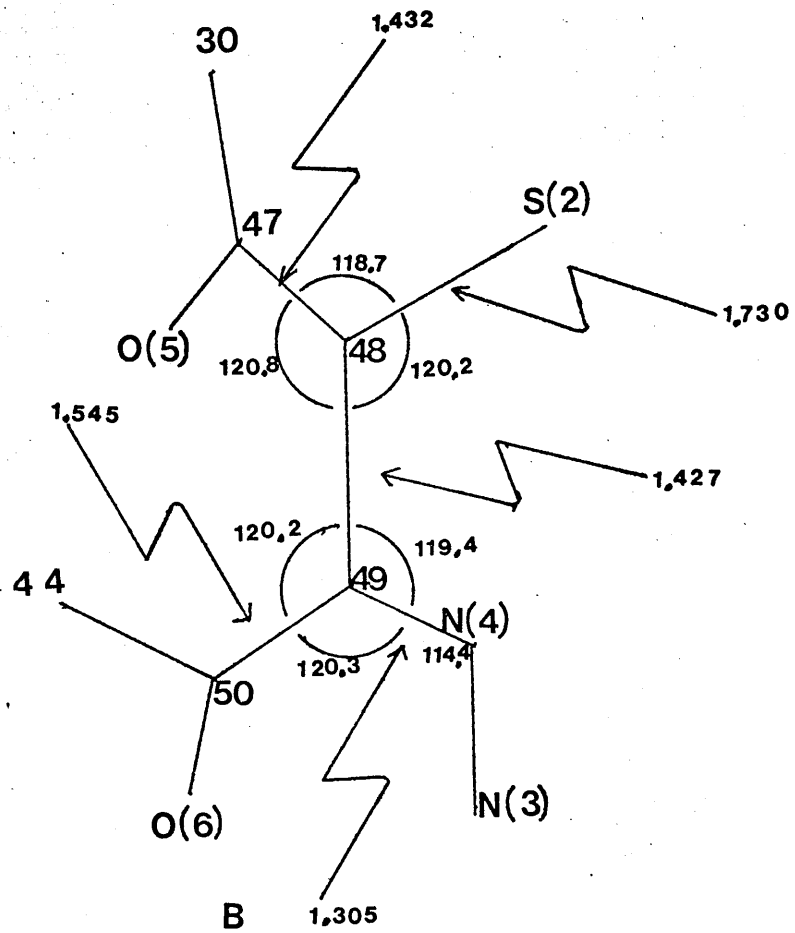

30
1,432
47
S(2)
118,7
1,730
O(5)
120,8
48
120,2
1,545
1,427
120,2
119,4
4 4
49
N(4)
114,4
120,3
50
O(6)
N(3)
B
1,305

Figure 3.3.2

which would otherwise exist between the dimethyl-sulphur groups and - the nearest atoms of the benzoyl rings. The staggered position of the two methyl groups (with respect to central C-C bond) pointing away from the ring is also a manifestation of these repulsions.

The out-of-plane deformations exhibited by the sulphur atoms could also be explained in terms of the same stereochemical arguments though these deformations would be expected to be small in view of the relative rigidity of the central framework of both molecules.

Since chemically, it is unlikely for the second benzoyl group [C(7), C(8), C(9), C(10), C(11), C(12), C(24 and O(2) in A and C(41), C(42), C(43), C(44), C(45), C(46), C(50) and O(6) in B] to be involved in any resonance interactions which might stabilize the betaine, the stereochemical arrangement would be expected to correspond to one which could remove any appreciable molecular strain. Therefore in both molecules these benzoyl groups are very close to being perpendicular to the central framework of the molecule. A slight but apparent twisting of the carbonyls with respect to the ring is also observed in these benzoyl groups (Table 3.3.4c).

The adopted conformation of the phthalimido groups, reflected by the C(19) - N(1) - N(2) - C(23) [113.5(7)°] and C(39) - N(3) - N(4) - C(49) [-116.4(6)°] torsion angles in A and B respectively seems to be determined by the relative positions of the carbon atoms [C(18) and C(19), C(38) and C(39)] with respect to the atoms in the 'neighbouring' benzoyl group [e.g. atoms C(10), C(11), C(23), C(24), O(2) and H(11)

in molecule A] as is evident from the non-bonded intramolecular contacts (Table 3.3.5).

Figure 3.3.2 seems to indicate a similar bonding pattern in both molecules. Moreover, a systematic comparison between the chemically equivalent bonds, using Cruickshank's t-test[64] did not reveal any significant difference between them.

The near trigonal geometry at the central C-C bond (Figure 3.3.2) and the corresponding bond lengths of 1.434(8)Å and 1.427(9)Å in A and B respectively [weighted mean 1.431(3)Å] which are shorter than the expected[67] $C(sp^2)$ - $C(sp^2)$ single bond length (1.48 Å in butadiene, biphenyl etc.) and appreciably longer than the accepted[68] $C(sp^2)$ - $C(sp^2)$ double bond [1.337(5)Å in ethylene] seems to suggest double bond character at the C-C central bond. Similarily a high degree of π-bond character can be attributed to the N(2) - C(23) [1.309(8)Å] and N(4) - C(49) [1.305(8)Å] bonds which compare with the carbon-nitrogen bond length found in formamide[56] [1.322(3) Å] and comparable systems[69-70] [e.g. 1.303(5), ref. 70]. The $C(sp^2)$ - $N(sp^2)$ double bond in formaldoxine $H_2C = N - OH$ is given as 1.276 Å[71].

The C(21) - C(22) [1.424(8) Å] and the C(47) - C(48) bonds [1.432(8) Å] are both comparable (within experimental error) with the C-C central bonds 1.434(8) and 1.427(9) respectively, while the C(21) - O(1) [1.250(8) Å] and C(47) - O(5) [1.222(8) Å] bonds reveal a slight lengthening when compared to the bonds C(24) - O(2) [1.206(7)Å] and C(50) - O(6) [1.191(8) Å].

These observations are in keeping with an extended π -bond system in which a formal negative charge on a nitrogen atom is being delocalized into a benzoyl group. The S(IV) - C(22) [1.747(6) Å] and S(IV) - C(48) [1.730(6) Å] bonds [mean value, 1.738(9) Å)] compare well with an analogous system[70] [1.721(4) Å] and with bonds of length 1.730(8) Å (Christensen and Witmore, 1969)[72] and 1.707(5) Å (Christensen and Thom, 1971)[73]. These bonds are shorter than the lengths [1.772(2) Å, 1.769(8) Å and 1.799(8) Å - mean weighted value 1.77(1) Å] postulated for the C(sp^2) - S(sp^3) single bond (Cameron, Duncanson & Morris, 1976[40]; Kalman, Duffin & Kucsman, 1971[74]), but are significantly longer than the bond length of 1.645(6) Å suggested for a nearly 'localized' C(sp^2) - Sulphur double bond[75]. [The sum of Pauling's covalent radii is 1.81 Å[50] and the C(sp^3) - S(sp^3) bond length in dimethylsulphide is 1.809(5) Å[54]].

However, as mentioned in the overall discussion of the previous analyses (for sulphur-nitrogen bonding) the existence of appreciable double bond character between the ylide carbon and sulphur can not be supported from the combined structural studies mentioned so far though, in the valence-bond notation the best approximation of the molecular structure might contain in it both polar (ylide) and covalent (ylene) contributions (Figure 3.3.3).

The lengthening of the C(23) - C(24) [1.527(9) Å] and C(49) - C(50) [1.545(9) Å] bonds in molecules A and B respectively is

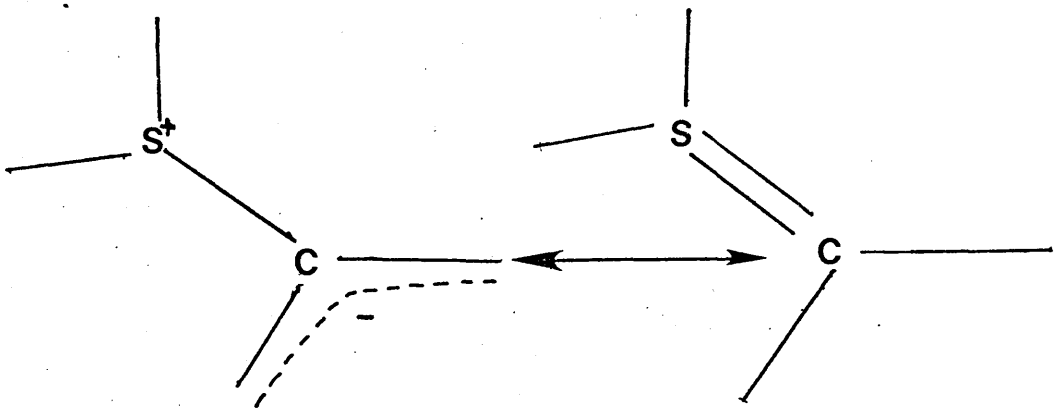


Figure 3.3.3

interesting (the bond length expected might rather have been similar to a typical $C(sp^2)$ - $C(sp^2)$ single bond of c.a. 1.48 Å). However, a calculated average $C(sp^2$ - $C(sp^2)$ single bond of 1.485(7) [from the C(10) - C(24) and C(4) - C(21) single bonds] would differ from the C(23) - C(24) bond by 3.7 σ . Applying a similar test to molecule B would produce a difference of 3.3 σ . Though systematic in trend but not high enough as to indicate a significant difference (taken as $> 4\sigma$) this bond discrepancy does become significant in other betaine molecules when the same test is applied. It should be noted that steric influences do exist whereby atoms C(24) and C(50) exhibit a considerable number of short intramolecular contacts (Table 3.3.5).

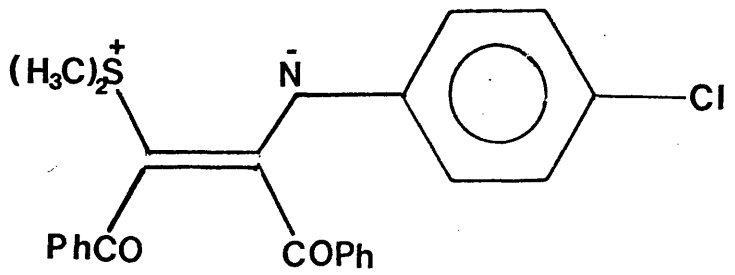
The spatial geometry and bond lengths of the phthalimide group reveal no unusual features and are comparable to other models which have been described elsewhere[76,77] (Andreetti, Bocelli, Coghi and Sgarabotto, 1974, 1975; Apreda et al, 1978).

Other dimensions within the molecules are as expected although the peripheral ring atoms in both molecules appear to show large thermal

motion which results in a corresponding bond shortening.

Apart from the short contacts already pointed out some other contacts are given in Table 3.3.5. There are no abnormally short intermolecular distances and as can be seen from the packing diagram (projection along the short $\bar{c}$ axis) presented in Figure 3.3.1b the solvent molecules (acetone) which have crystallized with the betaine molecules seem to be held by the van der Waals' interactions in cavities formed by stacks of pairs of betaine molecules arranged along the $\bar{c}$ axis.

3.4 Experimental and Results for IV



IV

Dimethylsulphonium 1,2-dibenzoyl-2-(4-chlorophenylimino) ethylide.

Preparation of Crystals

The title compound (IV) was prepared by the published procedures described by Claus and Vilsmaier[30] (1975) for N-aryl-sulphimides and by Gilchrist[33] (1976) for betaines. Pure crystals were prepared by successive crystallizations from 'hexane-dichloromethane'.

$$\text{Sulphimide} + \text{PhCO} - \text{C} \equiv \text{C} - \text{COPh} \longrightarrow \text{IV}$$

Crystal Data

Molecular Formula	$C_{24}H_{20}Cl\,NO_2S$
Molecular Weight	421.95 a.m.u.
Crystal System	Monoclinic
Unit Cell Dimensions	$a = 8.157(2)$ Å
	$b = 16.741(3)$ Å
	$c = 15.859(3)$ Å
	$\beta = 103.15(3)^\circ$
Unit Cell Volume	$V = 2108.86$ Å^3
Number of Molecules per Unit Cell	$Z = 4$
Calculated Density	$D_c = 1.33$ g.cm^{-3}
Number of Molecules per Asymmetric Unit	$N = 1$
Space Group	$P2_1/c(C_{2h}^5$, No 14)
Equivalent Positions	x,y,z
	$-x, \frac{1}{2} + y, \frac{1}{2} - z$
Linear Absorption Coefficient	$\mu = 2.94$ cm^{-1}
Number of Electrons per Unit Cell	$F(000) = 880$

Data Collection

Diffractometer Used	Hilger and Watts Y290
Radiation Used	$M_o - K_\alpha$, $\overline{\lambda} = 0.71069$ Å
Filter	Graphite Monochromator
	$\cos^2 2\theta_m = 0.970$
Upper Limit for Data Collection	$2\theta_{max} = 60^\circ$

Number of Observed Independent Reflections	$m = 2324$
Unobserved Cut-Off	$2.5\,\sigma_I$
Number of Parameters Refined	$n = 343$
Number of Reflections per Parameter	$m/n = 6.8$

Structure Determination and Refinement

The crystal structure was solved in space group $P2_1/c$ by direct methods using the multisolution program 'MULTAN' (version 1974). The trial phasing model was derived using 250 reflections with $|E|$ values greater than 1.55 and 2000 Σ_2 phase relationships (8.6 reflections per atom and 8 phase relationships per reflection). The positions of 27 atoms were clearly established from the E-map produced, and the missing 2 atoms were located by a conventional structure factor and difference electron density calculations. R and R_w at this stage were 0.232 and 0.235 respectively. The various parameters used with 'MULTAN' are summarized in Table 3.4.1. The refinement was carried out by the block diagonal least-squares method. The function minimized was $\Sigma w (|F_o| - |F_c|)^2$ with final weights of $w^{-1} = 1.6630 - 0.0837 |F_o| + 0.0020 |F_o|^2$ and $w = 1/1.5220$ for $|F_o| > 6.91$ and $|F_o| < 6.91$ respectively. Parameter shifts in the last cycle of refinement were only a small fraction of their standard deviations, the maximum one being equal to 0.19 of its σ. The final conventional and weighted R factors were 0.040 and 0.050 and the standard deviation of an observation of unit weight was equal to 1.19.

Alternate least-squares refinements with variable anisotropic thermal parameters and difference Fourier syntheses yielded the coordinates for all the 20 hydrogen atoms and consequently their positional and isotropic thermal parameters were allowed to vary during the last 6 cycles of the refinement. There were no significant residual peaks in the final difference Fourier, the highest peak having an electron density of 0.3 $e\mathring{A}^{-3}$. No absorption correction was applied.

A detailed description outlining the different stages in the refinement process is given in Table 3.4.2. The atomic scattering factors for C, N, O, Cl and S atoms were those given by Cromer and Mann (1968), and the one for H were those given by Stewart et al (1965).

Values for the observations, the calculated structure amplitudes and phases are given in the supplement to this thesis. Final atomic coordinates, thermal parameters, bond lengths, valency angles and torsion angles with e.s.d.'s are all given in Tables 3.4.3 to 3.4.5. The molecular and crystal structures are shown in Figures 3.4.1(a) and 3.4.1(b) which include the atomic numbering scheme.

Table 3.4.I

SUMMARY OF THE CONDITIONS (INCLUDING VARIOUS FIGURES OF INTEREST) ASSOCIATED WITH SOLVING THE STRUCTURE OF IV.

In this table:

1. NE - is the number of the largest $|E|$'s chosen to define the structure.
2. NSRT - is the number of Σ_2 relationships to be retained.
3. NSRTT - is the total number of Σ_2 relationships.
4. PROB - is the probability acceptance limit chosen for Σ_1.
5. NSPEC - is the number of special phases (permutations restricted to ϕ_{spec}, $\phi_{spec} + 180^\circ$).

   NGEN - is the number of general phases (phase permutation 45°, 135°, 225°, 315°)

   NANY - is the number of phases of either sort.
6. NSET - is the total number of phase sets that have been developed.
7. PUB - is the published phase.
8. NAT - is the number of nonhydrogen atoms in the asymmetric unit.
9. ABS FOM, PSI ZERO, RESID and CFOM are all figures of merit.

$C_{24}H_{20}ClNO_2S$, $P2_1/c$, NAT = 29

PARAMETERS		STARTING SET TYPE	hk l	PHI	PUB	RESULTS PHASE SET CONSIDERED	FIGURES OF MERIT ABS FOM	PSI ZERO	RESID	TOTAL NUMBER OF CORRECT PEAKS FOUND IN E-MAP
SIGMA - 2		SIGMA - 1				Max	1.5229	262.0	42.02	27
NE(|E| > 1.55)	250		-	-	-	Min	0.7111	152.7	20.85	
NSRT	2000	Origin defining phases	0,6,11	360	360	CFOM2= 2.0	1.5229	262.0	20.85	
NSRTT	not known		5,8,-1	360	360					
CONVERGE			4,13,12	360	180					
PROB	0.95	Permuted phases	2,4,0	180 360	180					
NSPEC,NGEN,NANY	4,0,0		7,6,-3	180 360	360					
FASTAN			4,4,-6	180 360	360					
NSET	16		2,10,2	180 360	180					

Table 3.4.2

PROGRESS OF LEAST-SQUARES REFINEMENT

CYCLES	PARAMETERS REFINED	R	R_w
0	none	0.232	0.235
4	x,y,z $U_{(iso)}$ for C, N, O, Cl, S; scale factor; full matrix; unit weights.	0.118	0.124
4	x,y,z,U_{ij}, for C, N, O, Cl, S; block diagonal; unit weights; scale factor.	0.072	0.090
6	x,y,z,U_{ij} for C, N, O, Cl, S; H atom contributions to structure factor calculations, but their positional and thermal parameters not allowed to vary; block diagonal; weighting scheme (calculated after cycle 8) applied; scale factor.	0.047	0.082
6	x,y,z,U_{ij} for C, N, O, Cl, S; x,y,z,$U_{(iso)}$ for H atoms; block diagonal; newly calculated Cruickshank type weighting scheme applied; scale factor.	0.040	0.050

Table 3.4.3(a,b,c,d)

(a) Fractional atomic coordinates ($\times 10^4$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM X/A Y/B Z/C

(b) Anisotropic thermal parameters ($\text{Å}^2 \times 10^3$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}

(c) Fractional atomic coordinates ($\times 10^3$) of hydrogen atoms with e.s.d.'s in parentheses. The hydrogens are numbered according to the atoms to which they are attached.

(d) Isotropic thermal parameters ($\text{Å}^2 \times 10^2$) of hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM $U_{(iso)}$.

C(1)	2803(4)	9243(2)	-0576(2)
C(2)	3848(4)	8604(2)	-0331(2)
C(3)	3285(4)	7942(2)	0043(2)
C(4)	1655(4)	7925(2)	0184(2)
C(5)	0638(4)	8590(2)	-0046(2)
C(6)	1192(5)	9243(2)	-0432(2)
C(7)	-0202(4)	6906(2)	0494(2)
C(8)	-1720(4)	7218(2)	-0187(2)
C(9)	-1762(4)	7062(2)	-1108(2)
C(10)	-2857(5)	7507(2)	-1740(2)
C(11)	-2900(6)	7376(2)	-2608(2)
C(12)	-1888(6)	6813(2)	-2848(2)
C(13)	-0814(6)	6368(2)	-2235(3)
C(14)	-0752(5)	6493(2)	-1368(2)
C(15)	-0494(4)	6256(2)	1021(2)
C(16)	-2051(4)	5823(2)	0850(2)
C(17)	-2527(4)	5255(2)	1488(2)
C(18)	-2265(5)	5419(2)	2364(2)
C(19)	-2817(5)	4885(3)	2910(2)
C(20)	-3616(5)	4188(3)	2589(3)
C(21)	-3908(5)	4034(2)	1720(3)
C(22)	-3392(5)	4560(2)	1166(2)
C(23)	2867(5)	5653(3)	1418(3)
C(24)	1918(5)	6791(3)	2502(2)
CL(1)	3479(1)	10058(1)	-1090(1)
N(1)	1265(3)	7241(2)	0616(2)
O(1)	-2729(3)	7650(2)	0045(2)
O(2)	-3064(4)	5919(2)	0143(2)
S(1)	1109(1)	5930(1)	1868(1)

Table 3.4.3 (a)

C(1)	50(2)	39(2)	38(2)	-8(2)	4(2)	1(2)
C(2)	37(2)	51(2)	48(2)	0(2)	10(2)	5(2)
C(3)	35(2)	45(2)	44(2)	4(2)	4(1)	7(2)
C(4)	36(2)	51(2)	34(2)	1(2)	4(1)	3(2)
C(5)	37(2)	56(2)	62(2)	8(2)	18(2)	3(2)
C(6)	52(2)	42(2)	55(2)	10(2)	8(2)	4(2)
C(7)	34(2)	50(2)	29(2)	3(2)	5(1)	3(1)
C(8)	32(2)	50(2)	39(2)	-2(2)	5(1)	6(2)
C(9)	37(2)	39(2)	37(2)	-6(1)	6(1)	3(1)
C(10)	56(2)	49(2)	41(2)	5(2)	1(2)	4(2)
C(11)	77(3)	60(3)	39(2)	-7(2)	-5(2)	18(2)
C(12)	96(3)	56(2)	39(2)	-17(2)	14(2)	-7(2)
C(13)	78(3)	60(3)	56(2)	-2(2)	21(2)	-7(2)
C(14)	58(2)	53(2)	41(2)	9(2)	8(2)	2(2)
C(15)	30(2)	54(2)	38(2)	2(2)	0(1)	8(2)
C(16)	43(2)	63(2)	38(2)	-5(2)	3(2)	2(2)
C(17)	31(2)	53(2)	44(2)	1(2)	9(1)	6(2)
C(18)	44(2)	57(2)	45(2)	1(2)	10(2)	4(2)
C(19)	46(2)	88(3)	49(2)	2(2)	13(2)	13(2)
C(20)	53(2)	72(3)	78(3)	-2(2)	19(2)	25(2)
C(21)	50(2)	58(3)	83(3)	-14(2)	10(2)	4(2)
C(22)	43(2)	65(3)	54(2)	-6(2)	6(2)	-2(2)
C(23)	50(2)	70(3)	86(3)	20(2)	17(2)	11(2)
C(24)	70(3)	75(3)	46(2)	-14(2)	-11(2)	10(2)
CL(1)	75(1)	54(1)	69(1)	-14(1)	9(1)	17(1)
N(1)	34(1)	55(2)	40(2)	-4(1)	3(1)	10(1)
O(1)	44(1)	91(2)	48(1)	25(1)	8(1)	-1(1)
O(2)	56(2)	116(3)	52(2)	-33(2)	-13(1)	26(2)
S(1)	36(0)	53(1)	46(0)	1(0)	1(0)	15(0)

H(21)	490(4)	862(2)	-047(2)
H(31)	411(5)	748(2)	021(2)
H(51)	-041(4)	862(2)	006(2)
H(61)	049(4)	970(2)	-064(2)
H(101)	-360(4)	790(2)	-155(2)
H(111)	-365(5)	770(2)	-302(2)
H(121)	-191(5)	672(2)	-346(2)
H(131)	-010(5)	597(2)	-240(2)
H(141)	002(4)	620(2)	-093(2)
H(181)	-173(4)	589(2)	262(2)
H(191)	-266(5)	499(2)	349(2)
H(201)	-401(6)	383(3)	300(3)
H(211)	-448(5)	357(2)	145(2)
H(221)	-355(4)	446(2)	060(2)
H(231)	312(6)	611(3)	109(3)
H(232)	248(7)	518(3)	106(3)
H(233)	375(6)	544(3)	188(3)
H(241)	218(6)	717(3)	219(3)
H(242)	114(7)	696(3)	285(3)
H(243)	284(6)	659(3)	291(3)

3.4.3 (c)

H(21)	4(1)
H(31)	7(1)
H(51)	5(1)
H(61)	5(1)
H(101)	5(1)
H(111)	7(1)
H(121)	7(1)
H(131)	7(1)
H(141)	5(1)
H(181)	4(1)
H(191)	7(1)
H(201)	11(2)
H(211)	7(1)
H(221)	5(1)
H(231)	10(2)
H(232)	12(2)
H(233)	9(1)
H(241)	10(1)
H(242)	14(2)
H(243)	9(1)

3.4.3 (d)

Table 3.4.4(a,b,c)

(a) Interatomic distances (Å) with e.s.d.'s in parentheses. The hydrogen atoms are numbered according to the atoms to which they are attached.

(b) Interbond angle (degrees) with e.s.d.'s (degrees) in parentheses.

(c) Torsion angles (degrees) with e.s.d.'s (degrees) in parentheses. A torsion angle A-B-C-D is considered to be positive if when viewed down the B-C bond the A-B bond will eclipse the C-D bond when rotated less than 180° in a clockwise direction.

C(1) - C(2)	1.368(5)	C(10) - C(11)	1.387(5)
C(1) - C(6)	1.383(6)	C(11) - C(12)	1.363(6)
C(1) - CL(1)	1.742(4)	C(12) - C(13)	1.372(6)
C(2) - C(3)	1.383(5)	C(13) - C(14)	1.380(6)
C(3) - C(4)	1.398(5)	C(15) - C(16)	1.434(5)
C(4) - C(5)	1.387(5)	C(15) - S(1)	1.736(3)
C(4) - N(1)	1.407(5)	C(16) - C(17)	1.502(5)
C(5) - C(6)	1.378(6)	C(16) - O(2)	1.243(4)
C(7) - C(8)	1.537(4)	C(17) - C(18)	1.384(5)
C(7) - C(15)	1.425(5)	C(17) - C(22)	1.395(5)
C(7) - N(1)	1.295(4)	C(18) - C(19)	1.388(6)
C(8) - C(9)	1.476(5)	C(19) - C(20)	1.376(6)
C(8) - O(1)	1.214(5)	C(20) - C(21)	1.369(7)
C(9) - C(10)	1.397(4)	C(21) - C(22)	1.376(6)
C(9) - C(14)	1.382(5)	C(23) - S(1)	1.802(5)
C(24) - S(1)	1.794(4)		

3.4.4 (a)

C(2) - H(21)	0.938(33)	C(19) - H(191)	0.920(38)
C(3) - H(31)	1.014(38)	C(20) - H(201)	0.996(51)
C(5) - H(51)	0.915(36)	C(21) - H(211)	0.954(36)
C(6) - H(61)	0.968(32)	C(22) - H(221)	0.896(32)
C(10) - H(101)	0.988(34)	C(23) - H(231)	0.977(49)
C(11) - H(111)	0.960(35)	C(23) - H(232)	0.985(48)
C(12) - H(121)	0.977(38)	C(23) - H(233)	0.965(40)
C(13) - H(131)	0.964(40)	C(24) - H(241)	0.858(47)
C(14) - H(141)	0.965(31)	C(24) - H(242)	0.970(64)
C(18) - H(181)	0.950(29)	C(24) - H(243)	0.928(40)

3.4.4 (a) - (continued)

C(6) - C(1) - C(2)	120.50(33)	CL(1) - C(1) - C(2)	120.11(29)
C(3) - C(2) - C(1)	120.09(34)	CL(1) - C(1) - C(6)	119.38(27)
C(5) - C(6) - C(1)	119.54(34)	C(4) - C(3) - C(2)	120.40(33)
C(5) - C(4) - C(3)	118.33(32)	N(1) - C(4) - C(3)	115.05(30)
N(1) - C(4) - C(5)	126.40(32)	C(6) - C(5) - C(4)	121.09(35)
C(7) - N(1) - C(4)	125.65(29)	C(15) - C(7) - C(8)	117.12(29)
N(1) - C(7) - C(8)	121.80(29)	C(9) - C(8) - C(7)	117.93(28)
O(1) - C(8) - C(7)	118.90(29)	N(1) - C(7) - C(15)	121.00(29)
C(16) - C(15) - C(7)	122.31(30)	S(1) - C(15) - C(7)	119.78(25)
O(1) - C(8) - C(9)	122.67(30)	C(10) - C(9) - C(8)	118.87(30)
C(14) - C(9) - C(8)	122.44(30)	C(14) - C(9) - C(10)	118.69(30)
C(11) - C(10) - C(9)	119.77(35)	C(13) - C(14) - C(9)	120.89(35)
C(12) - C(11) - C(10)	120.39(36)	C(13) - C(12) - C(11)	120.50(36)
C(14) - C(13) - C(12)	119.76(40)	S(1) - C(15) - C(16)	117.80(26)
C(17) - C(16) - C(15)	123.11(30)	O(2) - C(16) - C(15)	118.92(33)
C(23) - S(1) - C(15)	107.58(19)	C(24) - S(1) - C(15)	107.31(19)
O(2) - C(16) - C(17)	117.97(33)	C(18) - C(17) - C(16)	123.08(32)
C(22) - C(17) - C(16)	117.89(31)	C(22) - C(17) - C(18)	118.82(33)
C(19) - C(18) - C(17)	120.02(35)	C(21) - C(22) - C(17)	120.21(35)
C(20) - C(19) - C(18)	120.59(37)	C(21) - C(20) - C(19)	119.39(41)
C(22) - C(21) - C(20)	120.90(40)	C(24) - S(1) - C(23)	101.84(21)

C(6)	C(1)	C(2)	C(3)	1.7(5)	CL(1)	C(1)	C(2)	C(3)	-177.2(3)
C(2)	C(1)	C(6)	C(5)	-0.5(6)	CL(1)	C(1)	C(6)	C(5)	178.4(3)
C(1)	C(2)	C(3)	C(4)	-0.8(5)	C(2)	C(3)	C(4)	C(5)	-1.2(5)
C(2)	C(3)	C(4)	N(1)	-176.3(3)	C(3)	C(4)	C(5)	C(6)	2.4(5)
N(1)	C(4)	C(5)	C(6)	176.9(3)	C(3)	C(4)	N(1)	C(7)	-147.2(3)
C(5)	C(4)	N(1)	C(7)	38.2(5)	C(4)	C(5)	C(6)	C(1)	-1.6(6)
C(15)	C(7)	C(8)	C(9)	-109.5(4)	C(15)	C(7)	C(8)	O(1)	78.3(4)
N(1)	C(7)	C(8)	C(9)	73.8(4)	N(1)	C(7)	C(8)	O(1)	-98.4(4)
C(8)	C(7)	C(15)	C(16)	9.6(5)	C(8)	C(7)	C(15)	S(1)	-174.2(2)
N(1)	C(7)	C(15)	C(16)	-173.7(3)	N(1)	C(7)	C(15)	S(1)	2.5(5)
C(8)	C(7)	N(1)	C(4)	2.2(5)	C(15)	C(7)	N(1)	C(4)	-174.3(3)
C(7)	C(8)	C(9)	C(10)	-163.2(3)	C(7)	C(8)	C(9)	C(14)	16.6(5)
O(1)	C(8)	C(9)	C(10)	8.7(5)	O(1)	C(8)	C(9)	C(14)	-171.6(3)
C(8)	C(9)	C(10)	C(11)	179.2(3)	C(14)	C(9)	C(10)	C(11)	-0.6(5)
C(8)	C(9)	C(14)	C(13)	-179.4(4)	C(10)	C(9)	C(14)	C(13)	0.3(5)
C(9)	C(10)	C(11)	C(12)	0.4(6)	C(10)	C(11)	C(12)	C(13)	0.0(6)
C(11)	C(12)	C(13)	C(14)	-0.3(7)	C(12)	C(13)	C(14)	C(9)	0.1(6)
C(7)	C(15)	C(16)	C(17)	-167.0(3)	C(7)	C(15)	C(16)	O(2)	12.7(5)
S(1)	C(15)	C(16)	C(17)	16.7(5)	S(1)	C(15)	C(16)	O(2)	-163.6(3)
C(7)	C(15)	S(1)	C(23)	-57.8(3)	C(7)	C(15)	S(1)	C(24)	51.1(3)
C(16)	C(15)	S(1)	C(23)	118.6(3)	C(16)	C(15)	S(1)	C(24)	-132.5(3)
C(15)	C(16)	C(17)	C(18)	42.6(5)	C(15)	C(16)	C(17)	C(22)	-142.6(4)
O(2)	C(16)	C(17)	C(18)	-137.2(4)	O(2)	C(16)	C(17)	C(22)	37.6(5)
C(16)	C(17)	C(18)	C(19)	176.6(4)	C(22)	C(17)	C(18)	C(19)	1.8(5)
C(16)	C(17)	C(22)	C(21)	-177.8(4)	C(18)	C(17)	C(22)	C(21)	-2.7(6)
C(17)	C(18)	C(19)	C(20)	0.5(6)	C(18)	C(19)	C(20)	C(21)	-1.9(7)
C(19)	C(20)	C(21)	C(22)	0.9(7)	C(20)	C(21)	C(22)	C(17)	1.4(6)

Table 3.4.5

A. Selected intramolecular non-bonded distances (< 4.0 Å).

C(4) ... C(8)	2.93	C(9) ... C(15)	3.56
C(4) ... C(9)	3.38	C(9) ... O(2)	3.11
C(5) ... C(8)	2.97	S(1) ... C(17)	3.10
C(5) ... C(9)	3.42	S(1) ... C(18)	3.14
C(8) ... C(16)	2.90	S(1) ... N(1)	2.98
C(8) ... O(2)	2.54	S(1) ... H(181)	2.83
C(8) ... H(51)	2.58	C(14) ... C(7)	2.97

B. Selected intermolecular distances (< 4.0 Å)

C(1) ... $C(24)^{i}$	3.44
C(2) ... $C(24)^{i}$	3.50
C(2) ... $Cl(1)^{ii}$	3.55
C(2) ... $O(1)^{iii}$	3.15
C(3) ... $O(1)^{iii}$	3.29
C(12) .. $Cl(1)^{iv}$	3.49

Roman numeral superscripts refer to the following equivalent positions relative to the molecule at (x,y,z):

(i) x, 3/2 - y, - 1/2 + z

(ii) 1 - x, 2 - y, -z

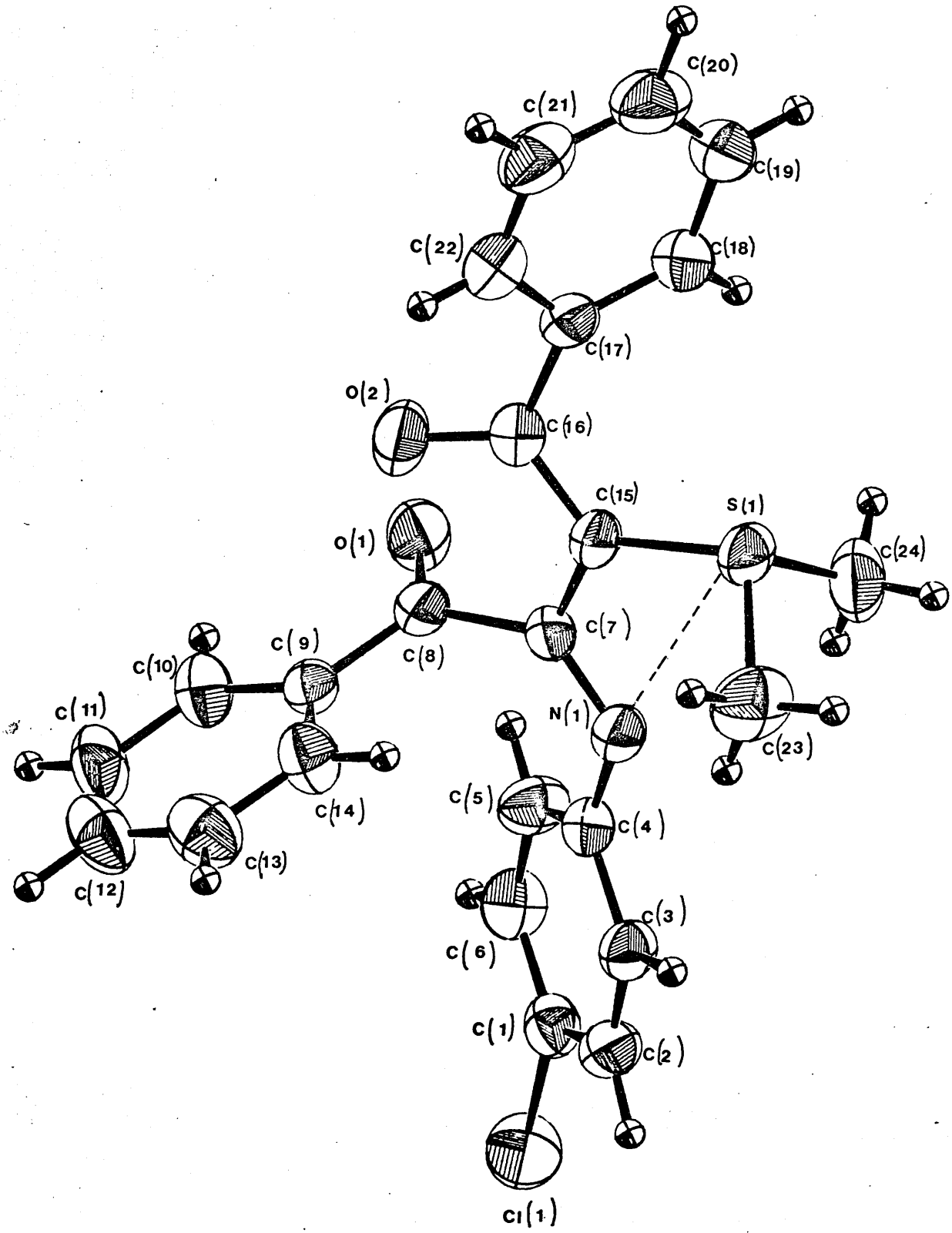
(iii) 1 + x, y, z

(iv) -x, -1/2 + y, - 1/2 - z

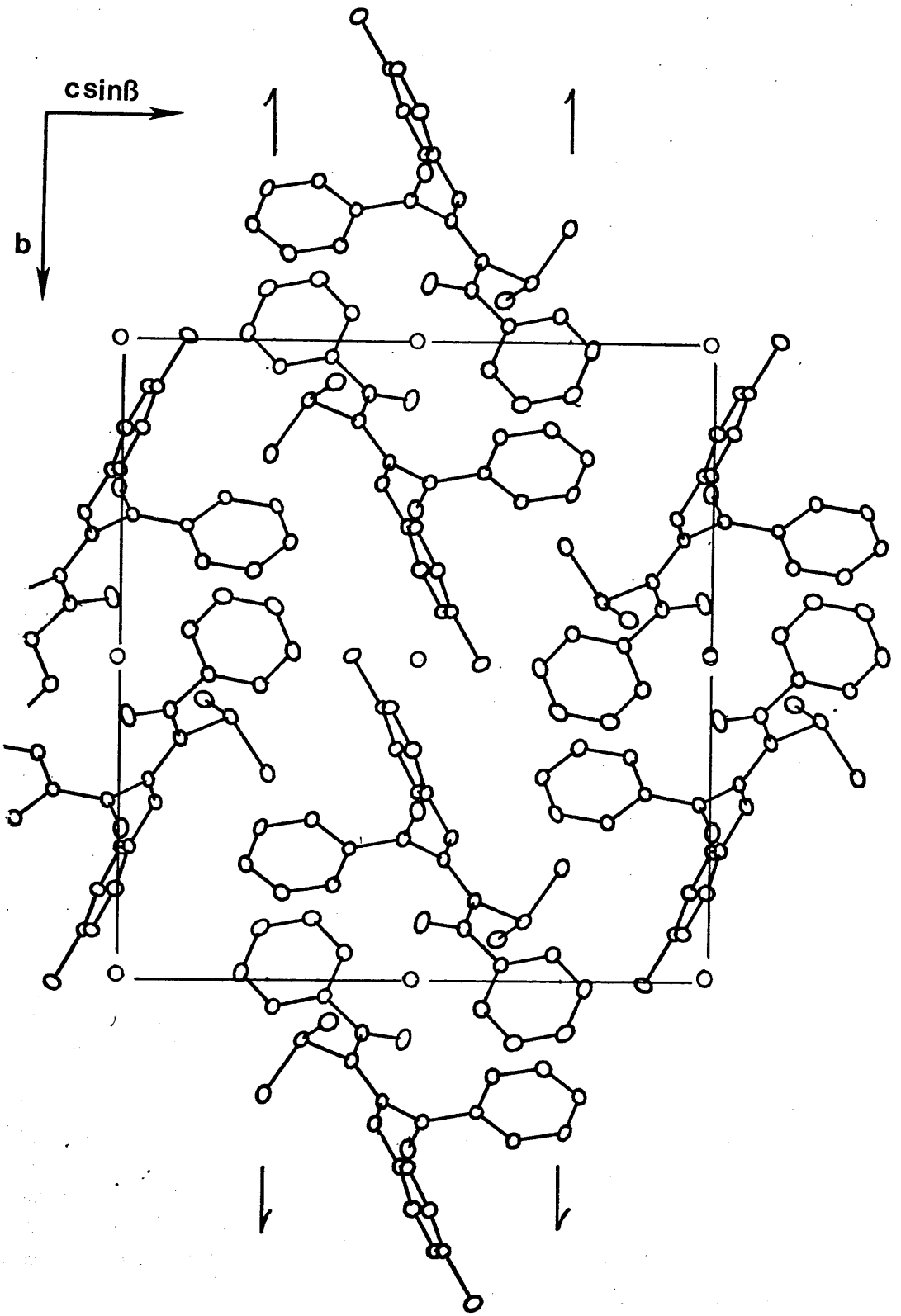
Figure 3.4.1(a and b)

(a) A general view of IV giving the atomic numbering scheme. Hydrogen atoms are numbered according to the atoms to which they are bonded.

(b) The molecular packing of IV viewed along the short axis $\bar{a}$.


C(20)
C(21)
C(19)
C(22)
C(18)
C(17)
O(2)
C(16)
C(15)
S(1)
O(1)
C(24)
C(7)
C(8)
C(9)
C(10)
C(11)
N(1)
C(23)
C(5)
C(4)
C(14)
C(13)
C(12)
C(3)
C(6)
C(1)
C(2)
Cl(1)

(a)



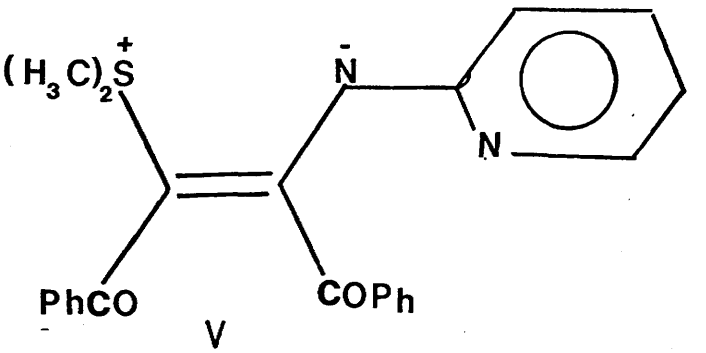
(b)

The general features of the molecular conformation of IV as shown in Figure 3.4.1 indicate a close similarity with molecule III (A or B) which is expressed in terms of i) the nearly planar arrangement along the central C-C bond [the torsion angles N(1) - C(7) - C(15) - S(1), N(1) - C(7) - C(15) - C(16), C(8) - C(7) - C(15) - S(1) and C(8) - C(7) - C(15) - C(16) being equal to 2.5(5)°, -173.7(3)°, -174.2(2)° and 9.6(5)° respectively] , ii) the staggered position of the methyl groups with relation to the C(7) - C(15) bond and iii) the pronounced twisting of the benzoyl ring (corresponding benzoyl group - geminal to the sulphur atom) along the C(carbonyl) - C(ring) bond [C(15) - C(16) - C(17) - C(18) being equal to 46.6(5)°] . However the dihedral angles C(15) - C(7) - C(8) - C(9) [-109.5(3)°] and C(7) - N(1) - C(4) - C(5) [38.2(5)°] and the valency angle C(7) - N(1) - C(4) [125.6(3)°] do differ significantly from the same parameters given for molecule III [e.g. for molecule III B the values given for the torsion angles C(48) - C(49) - C(50) - C(44) and C(38) - N(3) - N(4) - C(49) and the valency angle C(49) - N(4) - N(3) are equal to -91.3(7)°, 95.4(7)° and 114.4(5)° respectively] . This phenomenon which presumably can be ascribed to the fact that the groups attached to the dicoordinated nitrogen atom in both molecules are different (C_6H_4Cl group in contrast to a phthalimido group) signifies a slightly different way in which the betaine molecule can adopt a conformation of minimal strain.

The bond lengths and angles [Table 3.4.4(a) and Table 3.4.4(b)] do (within experimental error) compare well with the chemically equivalent ones given for molecule III (Figure 3.3.2). As already mentioned in the previous section (3.3), there seems to be an appreciable lengthening in the $C(sp^2) - C(sp^2)$ C(7) - C(8) bond length [1.537(4) Å]. Comparing the average C(carbonyl) - C(ring) bond of length 1.49(1)Å with the given value [1.537(4) Å] indicates a difference of 4.4 σ (Cruickshank t-test) which could be considered significant.

Selected intramolecular and intermolecular distances are given in Table 3.4.5 though there are no unusually short contacts. The molecular packing of IV conforms to one with normal van der Waals' separations and does not seem to possess any marked characteristic.

3.5 Experimental and Results for V



V

Dimethylsulphonium 1,2-dibenzoyl-2-(2-pyridylimino)ethylide

Preparation of Crystals

N-2-pyridyl-S,S-dimethylsulphimide was first prepared by the published procedure described by Claus and Vilsmaier[30](1975). The pale yellow oily product (which contained the sulphimide) then reacted with dibenzoylacetylene[33] to give a mixture of products from which the title compound (V) was isolated by layer chromatography. (eluent: acetone-

chloroform 1:3). Pure crystals of the betaine were prepared by crystallization from 'acetone-p.ether' as well as from ethanol.

$$\text{Sulphimide} + \text{PhCO} - \text{C} \equiv \text{C} - \text{COPh} \longrightarrow \text{V}$$

Crystal Data

Molecular Formula	$C_{23}H_{20}N_2O_2S$
Molecular Weight	388.49 a.m.u.
Crystal System	Monoclinic
Unit Cell Dimensions	$a = 8.092(2)$ Å
	$b = 16.365\ (3)$ Å
	$c = 15.068\ (3)$ Å
	$\beta = 92.50\ (3)^\circ$
Unit Cell Volume	$V = 1993.49$ Å^3
Number of Molecules per Unit Cell	$Z = 4$
Calculated Density	$D_c = 1.29$ g.cm^{-3}
Number of Molecules per Asymmetric Unit	$N = 1$
Space Group	$P2_1/n$
Equivalent Positions	x,y,z
	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
Linear Absorption Coefficient	$\mu = 1.73$ cm^{-1}
Number of Electrons Per Unit Cell	$F(000) = 816$

Data Collection

Diffractometer Used	Hilger and Watts Y290
Radiation Used	$M_o - K_\alpha$, $\overline{\lambda} = 0.71069$

Filter	Graphite Monochromator
	$\cos^2 2\theta_m = 0.970$
Upper Limit for Data Collection	$2\theta_{max} = 58^\circ$
Number of Observed Independent Reflections	m = 1223
Unobserved Cut-Off	$2.5\,\sigma_I$
Number of Parameters Refined	n = 254
Number of Reflections per Parameter	m/n = 4.8

Structure Determination and Refinement

The space group $P2_1/n$ was uniquely identified from the systematic absences in the diffraction data. The crystal structure was solved by the routine application of direct methods ('MULTAN' - version 1974). An E-map derived from the best solution revealed the locations of 27 nonhydrogen atoms (out of 28), the missing atom being located by a difference Fourier map phased on those 27 atoms.

The various parameters used with 'MULTAN' are listed in Table 3.5.1. The reflections used with 'MULTAN' do not correspond to the reflections in the data set collected ($h \longrightarrow -h$, $0 \longrightarrow -k$, $0 \longrightarrow -l$), a fact which evolves from 'MULTAN' choosing a hemisphere in which every first non zero index in all the reflections is positive. The phase relation in this case is:

$$\phi(hkl) = \phi(h\bar{k}l) + \pi(h + k + l)$$

Refinement of the structure by the block diagonal least-squares method minimizing the function $\sum w(|F_o| - |F_c|)^2$ was carried out while varying the positional and thermal parameters of the nonhydrogen atoms

only. Hydrogen atoms were introduced at calculated positions using a distance of 1.0 Å for the C–H bonds and $U_{(iso)}$ of 0.051. The anisotropic refinement converged at a conventional R of 0.048 and a weighted $R(R_w)$ of 0.065. The largest shift of any parameter during the final cycle of refinement was less than 0.28 of its estimated standard deviation. A final difference Fourier map showed no feature greater than 0.19 $eÅ^{-3}$.

Unit weights used in the initial stages of the refinement, were changed by a weighting scheme of the form $w^{-1} = 1.7270 + 0.1639|F_o| + 0.0022|F_o|^2$ for $|F_o| > 8.1$ and $w = 1/3.6431$ for $|F_o| < 8.1$. The standard deviation of an observation of unit weight was 0.763 but no systematic variation of $\overline{w(\Delta F)^2}$ versus $|F_o|$ was observed in the final analysis though the weighting scheme was derived prior to the stage where hydrogen-atom contribution to the structure factor calculations was considered. No absorption correction was applied.

A detailed description of the course of refinement is given in Table 3.5.2. Scattering factors for C, N, O and S atoms were taken from Cromer and Mann (1968) and those for H from Stewart et al (1965).

The observed and calculated structure amplitudes with the appropriate phases are listed in the supplement to this thesis. Final values of positional and thermal parameters with their e.s.d.'s bonded and non-bonded distances with valency angles and e.s.d.'s, and other relevant data are given in Tables 3.5.3 to 3.5.5. Crystal structure illustrations obtained with the program 'ORTEP' (Johnson, 1965) and the labelling scheme that was used are given in Figures 3.5.1(a) and 3.5.1(b).

Table 3.5.1

SUMMARY OF THE CONDITIONS (INCLUDING VARIOUS FIGURES OF INTEREST) ASSOCIATED WITH SOLVING THE STRUCTURE OF V.

In this table:

1. NE - is the number of the largest $|E|$'s chosen to define the structure.
2. NSRT - is the number of Σ_2 relationships to be retained.
3. NSRTT - is the total number of Σ_2 relationships.
4. PROB - is the probability acceptance limit chosen for Σ_1.
5. NSPEC - is the number of special phases (permutations restricted to ϕ_{spec}, $\phi_{spec} + 180^\circ$).

   NGEN - is the number of general phases (phase permutation 45°, 135°, 225°, 315°).

   NANY - is the number of phases of either sort.
6. NSET - is the total number of phase sets that have been developed.
7. PUB - is the published phase.
8. NAT - is the number of nonhydrogen atoms in the asymmetric unit.
9. ABS FOM, PSI ZERO, RESID and CFOM are all figures of merit.

$C_{23}H_{20}O_2S$, $P2_1/n$, NAT = 28.

PARAMETERS		STARTING SET TYPE	hkl	PHI	PUB	RESULTS PHASE SET CONSIDERED	FIGURES OF MERIT ABS FOM	PSI ZERO	RESID	TOTAL NUMBER OF CORRECT PEAKS FOUND IN E-MAP
SIGMA - 2		SIGMA-1	-	-	-	Max	2.0731	194.0	47.85	27
NE(|E| > 1.28)	250					Min	0.8843	95.8	28.13	
NSRT	2000	Origin defining phases	1,3,-2	360	360*	CFOM7 =2.0159	2.0731	192.4	28.14	
NSRTT	not known		2,1,-1	360	360					
CONVERGE			2,4,3	360	180					
PROB	0.95	Permuted phases	5,4,-1	180 360	180					
NSPEC, NGEN, NANY	4,0,0		1,5,-4	180 360	180					
FASTAN			5,5,-4	180 360	180					
NSET	16		2,3,2	180 360	360					

*$\phi(1,3,-2) = \phi(1,-3,-2)$ and in general, in space group $P2_1/n$ $\phi(h,k,l) = \phi(h,-k,l) + \pi(h+k+l)$.

Table 3.5.2.

PROGRESS OF LEAST-SQUARES REFINEMENT

CYCLES	PARAMETERS REFINED	R	R_w
0	none	0.216	0.224
4	x,y,z,U_{iso}, for C, N, O, S; scale factor; full matrix; unit weights.	0.100	0.116
3	x,y,z,U_{ij} for C, N, O, S; scale factor; block diagonal; unit weights.	0.081	0.095
6	x,y,z,U_{ij} for C, N, O, S; scale factor; weighting scheme; 20 geometrically calculated H atoms added, but their positional and thermal parameters not varied; block diagonal.	0.049	0.066
2	As above, but without 2 reflections considered to be affected by extinction.	0.048	0.065

Table 3.5.3(a,b,c)

(a) Fractional atomic coordinates (x 10^4) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM X/A Y/B Z/C.

(b) Anisotropic thermal parameters ($\mathring{A}^2$ x 10^3) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}.

(c) Fractional atomic coordinates (x 10^4) of hydrogen atoms, with e.s.d.'s in parentheses. The hydrogens are numbered according to the atoms to which they are attached.

C(1)	5538(8)	2970(4)	4383(5)
C(2)	4701(9)	3656(5)	4638(6)
C(3)	4582(11)	4319(5)	4054(9)
C(4)	5333(12)	4234(6)	3258(8)
C(5)	6115(10)	3539(6)	3060(6)
C(6)	4740(7)	1904(4)	5373(4)
C(7)	2885(8)	2116(4)	5212(5)
C(8)	2120(7)	1889(4)	4338(4)
C(9)	0616(8)	2233(4)	4063(5)
C(10)	-0125(8)	2011(5)	3253(6)
C(11)	0596(9)	1442(5)	2724(5)
C(12)	2073(8)	1085(4)	2999(5)
C(13)	2821(8)	1310(4)	3794(5)
C(14)	5165(7)	1311(4)	6027(4)
C(15)	3948(8)	0771(4)	6375(4)
C(16)	4268(8)	0273(4)	7189(4)
C(17)	5029(8)	0583(4)	7956(5)
C(18)	5165(9)	0096(6)	8712(5)
C(19)	4585(10)	-0692(6)	8697(5)
C(20)	3838(9)	-1000(5)	7939(6)
C(21)	3657(8)	-0518(5)	7196(5)
C(22)	8324(9)	0848(5)	5402(5)
C(23)	8146(9)	2115(5)	6620(6)
N(1)	6227(7)	2909(4)	3606(4)
N(2)	5855(6)	2305(3)	4964(4)
O(1)	2215(6)	2525(3)	5758(3)
O(2)	2543(5)	0735(3)	5989(3)
S(1)	7228(2)	1139(1)	6358(1)

C(1)	43(4)	54(5)	60(5)	-5(3)	-9(3)	8(4)
C(2)	70(5)	55(5)	95(6)	1(4)	4(4)	-6(5)
C(3)	70(6)	53(6)	160(11)	8(4)	-15(6)	3(7)
C(4)	81(6)	71(7)	117(8)	-19(5)	-26(6)	37(7)
C(5)	69(6)	90(7)	83(6)	-19(5)	1(5)	26(5)
C(6)	47(4)	51(4)	43(4)	8(3)	-1(3)	-5(3)
C(7)	50(4)	47(4)	62(5)	-1(3)	1(3)	4(4)
C(8)	38(3)	44(4)	55(4)	-3(3)	6(3)	1(3)
C(9)	37(4)	59(5)	78(5)	13(3)	10(4)	0(4)
C(10)	41(4)	72(5)	90(6)	14(4)	-11(4)	9(5)
C(11)	50(4)	72(5)	73(5)	-3(4)	-12(4)	-2(4)
C(12)	56(4)	56(4)	62(5)	6(3)	2(4)	-5(4)
C(13)	50(4)	53(4)	58(5)	5(3)	-6(3)	-2(4)
C(14)	37(3)	53(4)	48(4)	-3(3)	2(3)	7(3)
C(15)	46(4)	55(4)	54(4)	0(3)	2(3)	-8(4)
C(16)	46(4)	45(4)	49(4)	-2(3)	9(3)	8(3)
C(17)	58(4)	53(5)	61(5)	-4(4)	4(4)	1(4)
C(18)	73(5)	80(6)	49(5)	-1(4)	5(4)	-3(5)
C(19)	79(5)	85(7)	52(5)	1(5)	1(4)	21(5)
C(20)	58(4)	65(5)	74(5)	-10(4)	5(4)	6(5)
C(21)	46(4)	66(5)	55(5)	-1(3)	1(3)	5(4)
C(22)	54(4)	67(5)	73(5)	7(3)	8(4)	-7(4)
C(23)	62(5)	66(5)	90(6)	-4(4)	-8(4)	-12(5)
N(1)	60(4)	76(4)	71(4)	-8(3)	1(3)	28(4)
N(2)	44(3)	59(4)	65(4)	-4(3)	1(3)	9(3)
O(1)	63(3)	81(4)	69(3)	19(3)	3(2)	-25(3)
O(2)	48(3)	79(3)	63(3)	-10(2)	-6(2)	13(3)
S(1)	42(1)	55(1)	59(1)	-1(1)	-1(1)	5(1)

H(21)	4190	3679	5231
H(31)	3975	4831	4206
H(41)	5299	4696	2821
H(51)	6638	3497	2470
H(91)	0065	2641	4449
H(101)	-1196	2269	3050
H(111)	0048	1288	2138
H(121)	2593	0661	2619
H(131)	3901	1053	3986
H(171)	5483	1153	7965
H(181)	5691	0322	9273
H(191)	4702	-1040	9244
H(201)	3429	-1577	7924
H(211)	3070	-0741	6649
H(221)	7830	0337	5140
H(222)	8252	1295	4950
H(223)	9505	0749	5591
H(231)	8079	2476	6086
H(232)	7551	2378	7114
H(233)	9327	2016	6811

Table 3.5.4(a,b,c)

(a) Interatomic distances (Å) with e.s.d.'s in parentheses.

(b) Interbond angles (degrees) with e.s.d.'s (degrees) in parentheses.

(c) Torsion angles (degrees) with e.s.d.'s (degrees) in parentheses.

A torsion angle A-B-C-D is considered to be positive if when viewed down the B-C bond the A-B bond will eclipse the C-D bond when rotated less than 180° in a clockwise direction.

C(1)	C(2)	1.374(10)	C(10)	C(11)	1.372(11)
C(1)	N(1)	1.322(9)	C(11)	C(12)	1.378(10)
C(1)	N(2)	1.412(9)	C(12)	C(13)	1.369(10)
C(2)	C(3)	1.397(14)	C(14)	C(15)	1.438(9)
C(3)	C(4)	1.375(17)	C(14)	S(1)	1.744(6)
C(4)	C(5)	1.341(14)	C(15)	C(16)	1.487(9)
C(5)	N(1)	1.319(11)	C(15)	O(2)	1.255(7)
C(6)	C(7)	1.549(9)	C(16)	C(17)	1.382(10)
C(6)	C(14)	1.415(9)	C(16)	C(21)	1.385(10)
C(6)	N(2)	1.294(8)	C(17)	C(18)	1.391(11)
C(7)	C(8)	1.478(9)	C(18)	C(19)	1.372(13)
C(7)	O(1)	1.207(8)	C(19)	C(20)	1.365(11)
C(8)	C(9)	1.387(9)	C(20)	C(21)	1.373(11)
C(8)	C(13)	1.391(9)	C(22)	S(1)	1.788(8)
C(9)	C(10)	1.385(11)	C(23)	S(1)	1.799(8)

3.5.4 (a)

N(1) - C(1) - C(2)	122.67(68)	N(2) - C(1) - C(2)	122.34(65)
C(3) - C(2) - C(1)	118.69(81)	N(2) - C(1) - N(1)	114.75(58)
C(5) - N(1) - C(1)	118.32(66)	C(6) - N(2) - C(1)	125.04(53)
C(4) - C(3) - C(2)	116.70(85)	C(5) - C(4) - C(3)	120.75(98)
N(1) - C(5) - C(4)	122.86(87)	C(14) - C(6) - C(7)	117.83(53)
N(2) - C(6) - C(7)	120.21(57)	C(8) - C(7) - C(6)	116.69(54)
O(1) - C(7) - C(6)	118.56(59)	N(2) - C(6) - C(14)	121.77(55)
C(15) - C(14) - C(6)	121.68(52)	S(1) - C(14) - C(6)	120.67(45)
O(1) - C(7) - C(8)	124.26(59)	C(9) - C(8) - C(7)	119.51(58)
C(13) - C(8) - C(7)	122.04(55)	C(13) - C(8) - C(9)	118.38(60)
C(10) - C(9) - C(8)	119.82(64)	C(12) - C(13) - C(8)	121.54(59)
C(11) - C(10) - C(9)	120.76(66)	C(12) - C(11) - C(10)	119.90(70)
C(13) - C(12) - C(11)	119.58(66)	S(1) - C(14) - C(15)	117.34(47)
C(16) - C(15) - C(14)	122.67(54)	O(2) - C(15) - C(14)	118.78(57)
C(22) - S(1) - C(14)	108.35(32)	C(23) - S(1) - C(14)	107.46(33)
O(2) - C(15) - C(16)	118.52(56)	C(17) - C(16) - C(15)	122.92(60)
C(21) - C(16) - C(15)	117.97(59)	C(21) - C(16) - C(17)	118.92(63)
C(18) - C(17) - C(16)	119.38(66)	C(20) - C(21) - C(16)	121.15(66)
C(19) - C(18) - C(17)	120.68(69)	C(20) - C(19) - C(18)	119.98(75)
C(21) - C(20) - C(19)	119.86(73)	C(23) - S(1) - C(22)	101.47(36)

3.5.4 (b)

N(1)	C(1)	C(2)	C(3)	-0.4(12)	N(2)	C(1)	C(2)	C(3)	173.7(7)
C(2)	C(1)	N(1)	C(5)	0.7(11)	N(2)	C(1)	N(1)	C(5)	-173.9(7)
C(2)	C(1)	N(2)	C(6)	55.9(10)	N(1)	C(1)	N(2)	C(6)	-129.5(7)
C(1)	C(2)	C(3)	C(4)	-0.4(13)	C(2)	C(3)	C(4)	C(5)	1.0(15)
C(3)	C(4)	C(5)	N(1)	-0.7(16)	C(4)	C(5)	N(1)	C(1)	-0.1(13)
C(14)	C(6)	C(7)	C(8)	-113.7(7)	C(14)	C(6)	C(7)	O(1)	74.0(8)
N(2)	C(6)	C(7)	C(8)	71.2(8)	N(2)	C(6)	C(7)	O(1)	-101.1(8)
C(7)	C(6)	C(14)	C(15)	15.5(9)	C(7)	C(6)	C(14)	S(1)	-171.1(5)
N(2)	C(6)	C(14)	C(15)	-169.5(6)	N(2)	C(6)	C(14)	S(1)	3.9(9)
C(7)	C(6)	N(2)	C(1)	2.7(10)	C(14)	C(6)	N(2)	C(1)	-172.2(6)
C(6)	C(7)	C(8)	C(9)	-164.0(6)	C(6)	C(7)	C(8)	C(13)	19.0(9)
O(1)	C(7)	C(8)	C(9)	7.8(10)	O(1)	C(7)	C(8)	C(13)	-169.1(6)
C(7)	C(8)	C(9)	C(10)	-178.7(6)	C(13)	C(8)	C(9)	C(10)	-1.6(10)
C(7)	C(8)	C(13)	C(12)	177.8(6)	C(9)	C(8)	C(13)	C(12)	0.8(10)
C(8)	C(9)	C(10)	C(11)	1.2(11)	C(9)	C(10)	C(11)	C(12)	0.1(12)
C(10)	C(11)	C(12)	C(13)	-0.9(11)	C(11)	C(12)	C(13)	C(8)	0.5(10)
C(6)	C(14)	C(15)	C(16)	-166.3(6)	C(6)	C(14)	C(15)	O(2)	11.8(9)
S(1)	C(14)	C(15)	C(16)	20.1(8)	S(1)	C(14)	C(15)	O(2)	-161.8(5)
C(6)	C(14)	S(1)	C(22)	-58.6(6)	C(6)	C(14)	S(1)	C(23)	50.3(6)
C(15)	C(14)	S(1)	C(22)	115.1(5)	C(15)	C(14)	S(1)	C(23)	-136.0(5)
C(14)	C(15)	C(16)	C(17)	44.7(10)	C(14)	C(15)	C(16)	C(21)	-140.4(7)
O(2)	C(15)	C(16)	C(17)	-133.4(7)	O(2)	C(15)	C(16)	C(21)	41.5(9)
C(15)	C(16)	C(17)	C(18)	174.9(7)	C(21)	C(16)	C(17)	C(18)	0.1(10)
C(15)	C(16)	C(21)	C(20)	-176.9(6)	C(17)	C(16)	C(21)	C(20)	-1.8(10)
C(16)	C(17)	C(18)	C(19)	1.5(11)	C(17)	C(18)	C(19)	C(20)	-1.3(12)
C(18)	C(19)	C(20)	C(21)	-0.5(12)	C(19)	C(20)	C(21)	C(16)	2.1(11)

Table 3.5.5

A. Selected intramolecular non-bonded distances (< 4.0 Å)

C(1) ... C(13)	3.58	C(9) ... O(1)	2.85
C(2) ... C(6)	3.07	C(10) ... N(1)	3.36
C(2) ... O(1)	3.26	C(14) ... C(17)	3.15
C(6) ... C(13)	2.95	C(14) ... O(1)	3.12
C(6) ... C(23)	3.28	C(15) ... O(1)	3.31
C(6) ... O(2)	2.80	C(21) ... O(2)	2.86
C(7) ... C(1)	2.89	C(22) ... N(2)	3.16
C(7) ... C(2)	3.06	C(23) ... N(2)	3.06
C(7) ... C(15)	2.92	N(2) ... O(1)	3.25
C(7) ... O(2)	2.57	S(1) ... C(16)	3.09
C(7) ... H(21)	2.77	S(1) ... C(17)	3.19
C(8) ... C(1)	3.28	S(1) ... N(2)	3.01
C(8) ... C(2)	3.58	S(1) ... H(171)	2.86
C(8) ... C(14)	3.59		
C(8) ... N(2)	3.20		
C(8) ... O(2)	3.13		

B. Selected intermolecular distances (< 4.0 Å)

C(4) ... $C(17)^{i}$	3.86
C(5) ... $C(16)^{i}$	3.51
C(5) ... $C(17)^{i}$	3.49
C(5) ... $C(23)^{ii}$	3.34
C(12) .. $C(21)^{iii}$	3.60

Roman numeral superscripts refer to the following equivalent positions relative to the molecule at (x,y,z):

(i) 1/2 + x, 1/2 - y, -1/2 + z (iii) 1 - x, - y, 1 - z

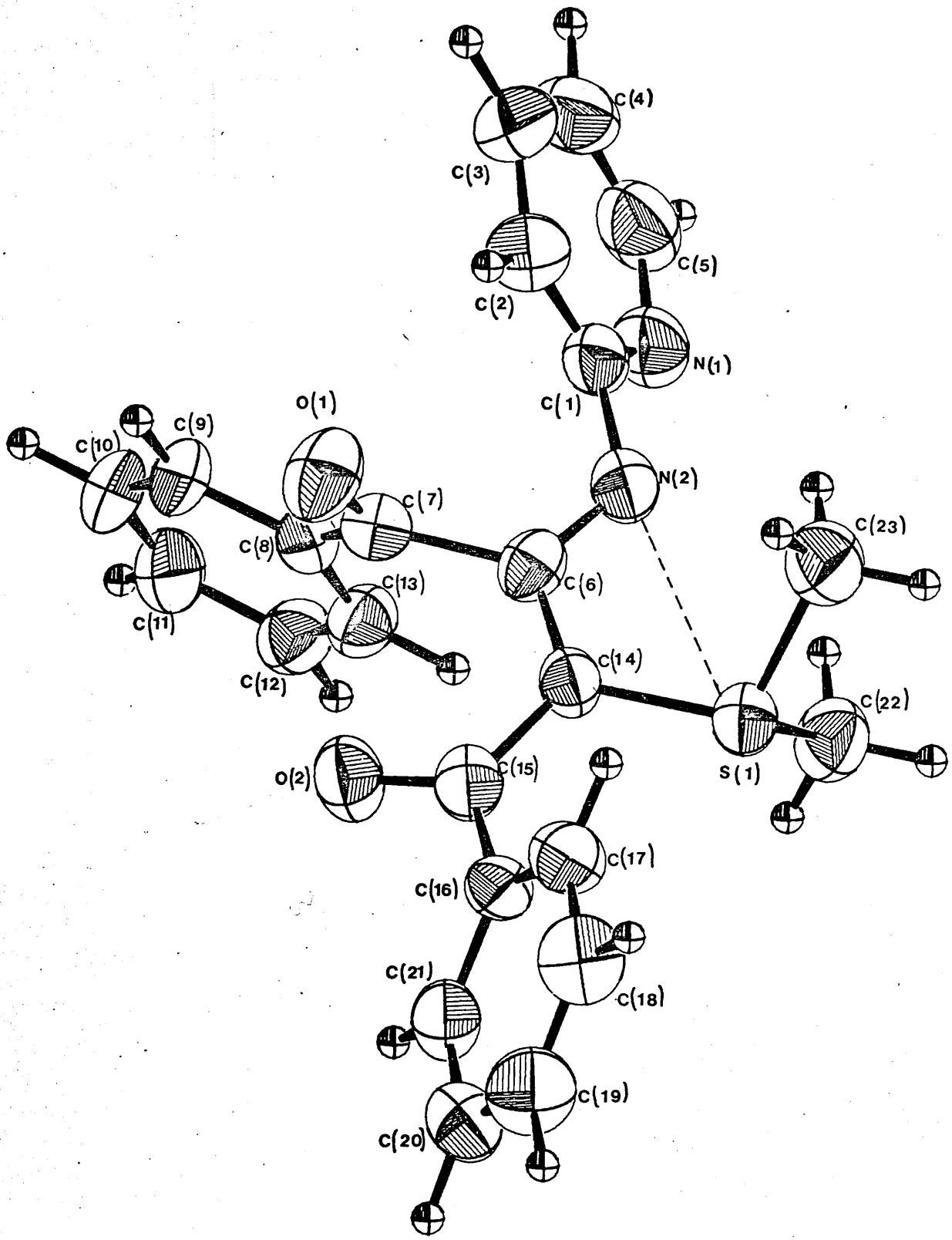
(ii) -1/2 + x, 1/2 - y, -1/2 + z

Table 3.5.5 (continued)

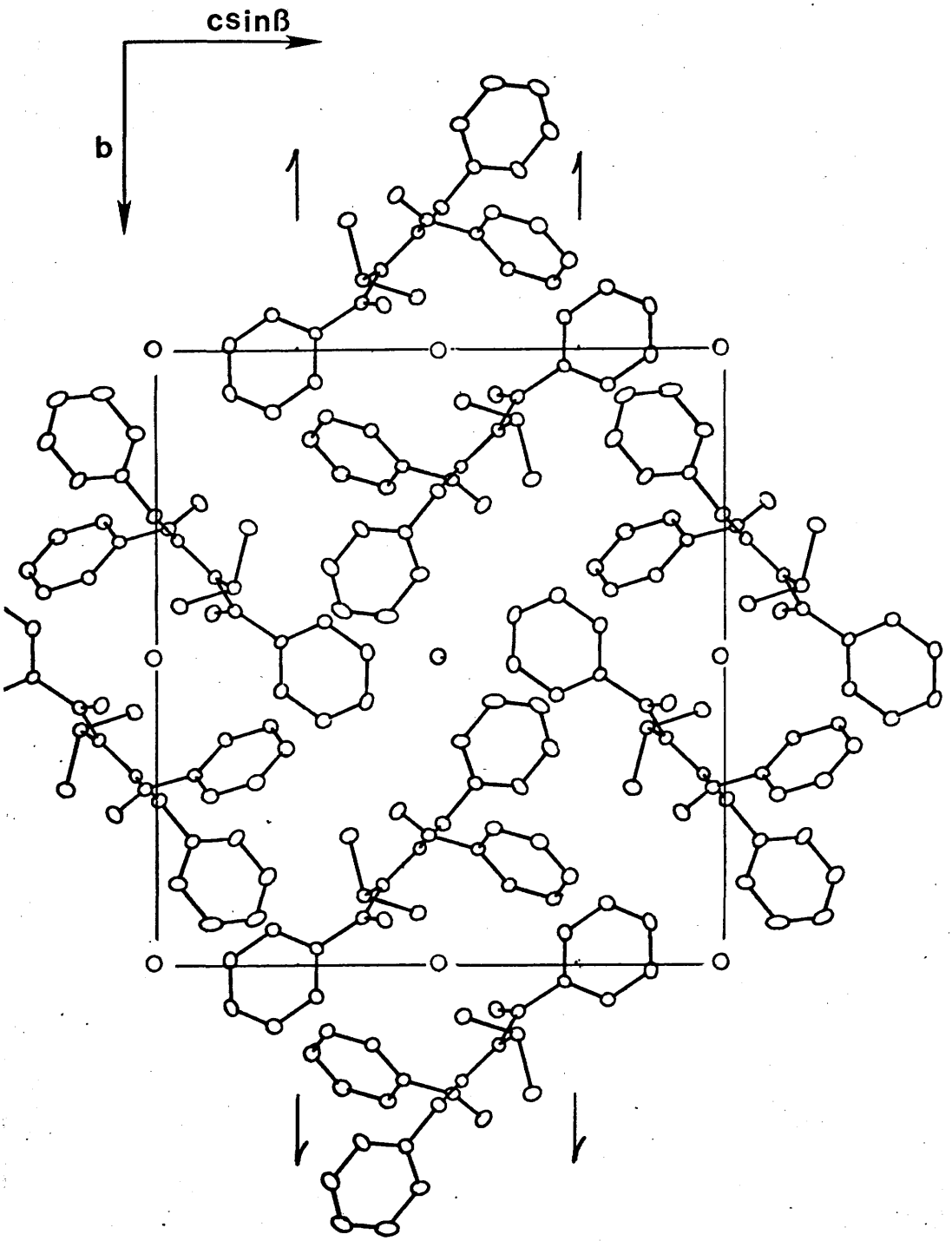
Figure 3.5.1(a and b)

(a) A general view of V giving the atomic numbering scheme. Hydrogen atoms are numbered according to the atoms to which they are bonded.

(b) The molecular packing of V viewed along the short axis $\bar{a}$.


C(4)
C(3)
C(5)
C(2)
N(1)
C(1)
O(1)
C(9)
C(10)
N(2)
C(7)
C(23)
C(8)
C(6)
C(13)
C(11)
C(14)
C(12)
C(22)
O(2)
C(15)
S(1)
C(17)
C(16)
C(21)
C(18)
C(19)
C(20)

(a)



(b)

Discussion of V

With the exception of the dihedral angles, C(2) - C(1) - N(2) -C(6), [5 6(1)°] in V and C(5) - C(4) - N(1) - C(7) [38.2(5)°] in IV the other features of the molecular geometries of structures IV and V are markedly similar. Thus the other torsion angles, defining the conformations of the molecules, are virtually identical and the bonding pattern and nearly planar arrangement around the central C-C bond are in keeping with the suggestion of 'extended delocalization' made previously. The C(6) - C(7) bond [of length 1.549(9) Å] is here too elongated with respect to the average C(ring) - C(carbonyl) bond [of length 1.482(5) Å] by c.a. 6.5 σ , a difference which could be considered significant.

The angle C(carbonyl) - C(central bond) - S which is equal to 117.3(5)° for structure V seems to be consistently smaller (for all betaines) than the trigonal value of 120°, and it might be possible that a pattern of values for the valency angles in the central framework of the molecule could have emerged had the estimated standard deviations been smaller. The pattern would have probably provided further evidence for crowding in such molecules. Selected intramolecular non-bonded distances are given in Table 3.5.5. and the molecular packing is illustrated in Figure 3.5.1(b). Several intermolecular contacts are given in Table 3.5.5 too, but no unusually short ones could be found.

3.II Discussion of III, IV and V

Table 3.II.1 summarizes the main structural features of molecules III, IV and V. Two noticeable observations could be made with regard to this Table i) structures IV and V adopt almost the same conformation, the only important difference being the amount of torsional movement along the N(imine) - C(ring), which seems to have originated from the different groups attached to the nitrogen atom ($\diagup\bar{N}\diagdown$) in both molecules, ii) molecules IIIA and IIIB relate to each other as two mirror images, though slightly distorted.

While the betaine molecules would be capable of exhibiting different conformations due to rotations about the single bonds that they possess, an examination of their molecular models would indicate two distinct conformations a) one with a dihedral angle C(central) - C(central)--C(carbonyl) - C(benzoyl ring) smaller than zero (negative) and b) one with a positive dihedral angle. The benzoyl group concerned, is the one geminal to the imino group. Assuming the central frameworks of these molecules remain rigid, an assumption that can be ascribed to the 'extended delocalization' and dipolar interactions ($\overset{+}{S}$ ... $\bar{N}$) in these systems, any equilibrium between these two conformations will have to involve the overcoming of a repulsive dominant potential barrier which will consist of very short C ... C and C ... O non-bonded contacts (c.a. < 2.5 Å).

Thus it would seem almost impossible for such rotations to take place and the existence of such conformers in the crystals analysed (space groups,

Table 3.II.1

	STRUCTURE III		STRUCTURE IV	STRUCTURE V
	A	B		
1	C(22) -C(23) -C(24) -C(10) 81.8(7)°	C(48) -C(49) -C(50) -C(44) -91.3(7)°	C(15) -C(7) -C(8) -C(9) -109.5(3)°	C(14) -C(6) -C(7) -C(8) -113.7(7)°
2	C(11) -C(10) -C(24) -C(23) 12.6(9)°	C(43) -C(44) -C(50) -C(49) -6.4(9)°	C(7) -C(8) -C(9) -C(14) 16.6(5)°	C(6) -C(7) -C(8) -C(13) 19.0(9)°
3	C(3) -C(4) -C(21) -C(22) 51.1(9)°	C(29) -C(30) -C(47) -C(48) -44.8(9)°	C(15) -C(16) -C(17) -C(18) 42.6(5)°	C(14) -C(15) -C(16) -C(17) 44.7(1)°
4	C(4) -C(21) -C(22) -C(23) -175.6(6)°	C(30) -C(47) -C(48) -C(49) 174.6(6)°	C(7) -C(15) -C(16) -C(17) -167.0(3)°	C(6) -C(14) -C(15) -C(16) -166.3(6)°
5	C(18) -N(1) -N(2) -C(23) -94.2(7)	C(38) -N(3) -N(4) -C(49) 95.4(7)°	C(5) -C(4) -N(1) - C(7) 38.2(5)°	C(2) -C(1) -N(2) -C(6) 56.0(1)°
6	C(22) -C(23) -N(2) -N(1) 175.0(5)°	C(48) -C(49) -N(4) -N(3) -174.0(5)°	C(15) -C(7) -N(1) -C(4) -174.3(3)°	C(14) -C(6) -N(2) -C(1) -172.2(6)°
7	C(23) -C(22) -S(1) -C(26) 59.1(6)°	C(49) -C(48) -S(2) -C(52) -60.5(6)°	C(7) -C(15) -S(1) -C(23) -57.8(3)°	C(6) -C(14) -S(1) -C(22) -58.6(6)°
8	C(23) -N(2) -N(1) 114.0(5)	C(49) -N(4) -N(3) 114.4(5)°	C(4) -N(1) -C(7) 125.6(3)°	C(1) -N(2) -C(6) 125.0(5)°
9	C(21) -C(22) -S(1) 117.8(4)°	C(47) -C(48) -S(2) 118.7(5)°	C(16) -C(15) -S(1) 117.8(3)°	C(15) -C(14) -S(1) 117.3(5)°
10	C(23) - C(24)o 1.527(9) A	C(49) - C(50)o 1.545(9) A	C(7) - C(8)o 1.537(4) A	C(6) - C(7)o 1.549.(9) A

$P2_12_12_1$; $P2_1/c$; $P2_1(n)$, do point to the fact that the two distinct conformations might have already been produced in the formation reaction:-

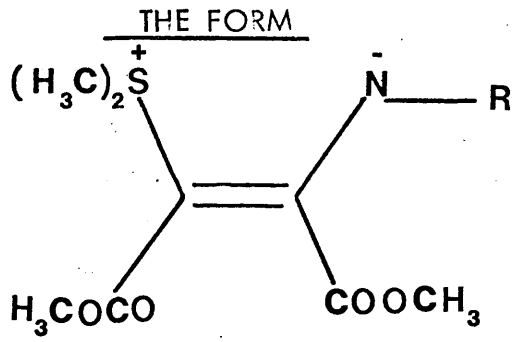
sulphimide + Ph–CO - C ≡ C - CO-Ph ⟶ betaine.

The compensation for internal strain in such molecules and as a result, the gaining of a conformational relief has taken place in the following way: i) by the pronounced twisting of both planes containing the carbonyl groups and benzoyl rings from the planes containing the central frameworks of the molecules [Table 3.II.1 (1,2) and (3,4)] ii) by the twisting of the imino group along the C(central) - N bond followed by rotations of the phthalimido, P-Cl C_6H_4 and pyridyl groups with respect to the plane defined by the grouping C(central), N, C(ring) [Table 3.II.1 (5,6)] , iii) by the apparent lengthening of the C(23) - C(24), C(49) - C(50), C(7) - C(8) and C(6) - C(7) bonds in molecules IIIA, IIIB, IV and V respectively [Table 3.II.1 (10)] iv) by the opening of the $\diagup\bar{N}\diagdown$ valency angle [Table 3.II.1(8)] , v) by the small but significant decrease in the C(carbonyl) - C(central) - S(1) valency angle in all betaines [Table 3.II.1 (9)] , and vi) by the staggered position of the methyl groups with respect to the C(central) - C(central) bond while pointing towards the imino group. It is interesting to note that a similar pattern of steric relief has been previously observed with the crowded 'triphenyl phosphorus ylides' (Speziale and Ratts, 1965; Stephens, 1965)[78,79].

The reduced reactivity of the betaine compared to the sulphimides (3.1 and 3.2) can be explained in terms of the decrease in formal charge

on the imino nitrogen ('through conjugation effect') and an overall steric hindrance affecting the nucleophilicity of the negatively charged atom. Therefore reactions of sulphimides with electrophilic acetylenes are usually carried out at room temperature while the reactions of betaines with electrophilic acetylenes (to produce pyrroles) are carried out in reflux conditions[33].

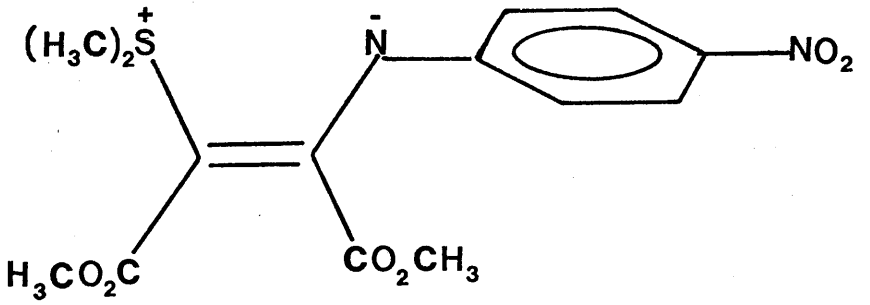
THE CRYSTAL AND MOLECULAR STRUCTURES OF TWO YLIDES OF THE FORM



VI. R = p - $O_2NC_6H_4$

VII. R = m - $O_2NC_6H_4$

3.6 Experimental and Results for VI



VI

Dimethylsulphonium-2-(4-nitrophenylimino)-1,2-bismethoxycarbonylethylide.

Preparation of Crystals

The title compound (VI) was prepared by the published procedures described by Claus and Vilsmaier[30] (1975) for N-aryl-sulphimides and by Hayashi and Swern[34] for betaines. Pure crystals were obtained by crystallization from ethanol (m.p 199-206°C) and the structure was substantiated by I.R.[34] (Nujol, 1730 and 1648 cm^{-1}) and mass spectra:

m/e, 340(M^+), 325($M^+ - CH_3$), 293($M^+ - SCH_3$), 281($M^+ - CO_2CH_3$) and 278($M^+ - (CH_3)_2S$).

$$\text{N - aryl - sulphimide} + H_3CO_2C - C \equiv C - CO_2CH_3 \longrightarrow VI$$

Crystal Data

Molecular Formula	$C_{14}H_{16}N_2O_6S$
Molecular Weight	340.2 a.m.u.
Crystal System	Monoclinic
Unit Cell Dimensions	a = 9.698(1) Å
	b = 22.545(2) Å
	c = 7.744(1) Å
	β = 108.49(1)°

Unit Cell Volume	$V = 1605.76\ \text{Å}^3$
Number of Molecules per Unit Cell	$Z = 4$
Calculated Density	$D_c = 1.41\ \text{g.cm}^{-3}$
Number of Molecules per Asymmetric Unit	$N = 1$
Space Group	$P2_1/c$ (C_{2h}^5, No.14)
Equivalent Positions	x,y,z
	-x, 1/2 + y, 1/2 - z
Linear Absorption Coefficient	$\mu = 2.23\ \text{cm}^{-1}$
Number of Electrons per Unit Cell	$F(000) = 712$

Data Collection

Diffractometer Used	Enraf-Nonius CAD-4
Radiation Used	$M_o - K_\alpha$, $\overline{\lambda} = 0.7114\ \text{Å}$
Filter	Graphite Monochromator
	$\cos^2 2\theta_m = 0.960$
Upper Limit for Data Collection	$2\theta_{max} = 60^\circ$
Number of Observed Independent Reflections	$m = 2972$
Unobserved Cut-Off	$2.0\ \sigma_I$
Number of Parameters Refined	$n = 273$
Number of Reflections per Parameter	$m/n = 10.9$

Structure Determination and Refinement

The space group $P2_1/c$ was uniquely identified from the systematic absences in the diffraction data. (oko absent when k is odd, hol absent when l is odd).

The crystal structure was solved by the routine application of direct methods ('MULTAN' - Version 1978). An E-map derived from the best solution revealed the location of 22 nonhydrogen atoms (out of 23), the missing atom being located after 6 cycles of isotropic full-matrix least-squares refinement minimizing the function $\sum w(|F_o| - |F_c|)^2$. The various parameters used with 'MULTAN' are outlined in Table 3.6.1 together with the 'phase transformation' from the 'MULTAN hemisphere of reflection' to the parallel reflections in the data set collected.

The positions of the hydrogen atoms were located in a difference map after cycle 13 and their positional and isotropic thermal parameters were allowed to vary during the last 12 cycles of the least-squares refinement. The weighting scheme based on counting statistics $w = 1/\sigma^2(F_o)$ was found to be satisfactory and the refinement converged when R was equal to 0.039 and R_w to 0.058. All calculated shifts were $< 0.78\,\sigma$, the average shift/error being equal to 0.06 and the final value for the standard deviation of an observation of unit weight was equal to 1.5020. No absorption correction was applied and no significant peaks were found in the final difference Fourier synthesis. The course of the refinement is summarized in Table 3.6.2. Scattering factors for the C, N, O and S atoms were those given by Cromer and Mann (1968) and those for H were given by Stewart et al. (1965).

A listing of the observed and calculated structure factors with the appropriate phases is given in the supplement to this thesis. The crystal and molecular structure together with a numbering scheme are given in Figures 3.6.1(a) and 3.6.1(b). The atomic coordinates and thermal parameters, bond lengths, valency angles and torsion angles with e.s.d.'s and other relevant data are given in Tables 3.6.3 to 3.6.6.

Table 3.6.I

SUMMARY OF THE CONDITIONS (INCLUDING VARIOUS FIGURES OF INTEREST) ASSOCIATED WITH SOLVING THE STRUCTURE OF VI.

In this table:

1. NE - is the number of the largest $|E|$'s chosen to define the structure.
2. NSRT - is the number of Σ_2 relationships to be retained.
3. NSRTT - is the total number of Σ_2 relationships.
4. PROB - is the probability acceptance limit chosen for Σ_1.
5. NSPEC - is the number of special phases (permutations restricted to ϕ_{spec}, $\phi_{spec} + 180^{\circ}$).

   NGEN - is the number of general phases (phase permutation 45°, 135°, 225°, 315°).

   NANY - is the number of phases of either sort.
6. NSET - is the total number of phase sets that have been developed.
7. PUB - is the published phase.
8. NAT - is the number of nonhydrogen atoms in the asymmetric unit.
9. ABS FOM, PSI ZERO, RESID and CFOM are all figures of merit.

$C_{14}H_{16}N_2O_6S$, $P2_1/c$, NAT = 23

PARAMETERS		STARTING SET				RESULTS				TOTAL NUMBER OF CORRECT PEAKS FOUND IN E-MAP
		TYPE	hkl	PHI	PUB	PHASE SET CONSIDERED	FIGURES OF MERIT			
							ABS FOM	PSI ZERO	RESID	
SIGMA -2		SIGMA - 1	2,0,0*	180	180	Max.	1.3390	2.8	36.78	22
NE($\|E\| > 1.62$	240		0,10,0	360	360	Min	1.0255	2.1	22.39	
NSRT	1500	Origin defining phases	3,4,-6	360	360	CFOM4 = 2.3433	1.3389	2.5	22.39	
NSRTT	2724		0,12,3	360	360					
CONVERGE			1,7,-2	360	360					
PROB	0.95	Permuted phases	0,8,2	180 360	180					
NSPEC, NGEN, NANY	4,0,0		0,11,1	180 360	180					
FASTAN			4,11,-8	180 360	360					
NSET	16		1,7,0	180 360	180					

* For space group $P2_1/c$ in general: $\phi(h,k,l) = \phi(-h,k,-l) + \pi(k+l)$.

Table 3.6.2.

PROGRESS OF LEAST-SQUARES REFINEMENT

CYCLES	PARAMETERS REFINED	R	R_w
0	None; 22 atoms present (out of 23).	0.396	0.391
6	$x,y,z,U_{(iso)}$ for 22 C, N, O and S atoms; scale factor; unit weights; full matrix.	0.208	0.207
3	$x,y,z,U_{(iso)}$ for all 23 C, N, O and S atoms; scale factor; unit weights; full matrix.	0.162	0.161
4	x,y,z,U_{ij} for C, N, O, S; full matrix; scale factor; weights from counting statistics.	0.063	0.106
12	x,y,z, U_{ij} for C, N, O, S; $x,y,z,$ $U_{(iso)}$ for H atoms; weighting scheme; scale factor; block diagonal.	0.039	0.058

Table 3.6.3 (a,b,c,d)

(a) Fractional atomic coordinates ($\times 10^4$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM X/A Y/B Z/C

(b) Anisotropic thermal parameters (Å^2, $\times 10^3$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}

(c) Fractional atomic coordinates ($\times 10^3$) of hydrogen atoms with e.s.d.'s in parentheses. The hydrogens are numbered according to the atoms to which they are attached.

(d) Isotropic thermal parameters (Å^2, $\times 10^2$) of hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM $U_{(iso)}$.

C(1)	7575(3)	6951(1)	8860(3)
C(2)	8682(3)	6650(1)	8502(3)
C(3)	8664(2)	6040(1)	8477(3)
C(4)	7535(2)	5730(1)	8815(2)
C(5)	6412(2)	6043(1)	9152(3)
C(6)	6446(2)	6658(1)	9177(3)
C(7)	7366(2)	4763(1)	9916(2)
C(8)	7235(2)	4137(1)	9686(2)
C(9)	8662(2)	3984(1)	7055(3)
C(10)	5701(2)	4207(1)	5885(3)
C(11)	7440(2)	3750(1)	11205(2)
C(12)	7561(4)	2759(1)	12227(4)
C(13)	7245(2)	5016(1)	11689(2)
C(14)	8481(2)	5553(1)	14329(3)
N(1)	7547(2)	5109(1)	8681(2)
N(2)	7601(3)	7600(1)	8873(3)
O(1)	6574(3)	7862(1)	9095(4)
O(2)	8638(3)	7854(1)	8662(4)
O(3)	7745(2)	3908(1)	12783(2)
O(4)	7303(2)	3171(1)	10759(2)
O(5)	6138(1)	5036(1)	12055(2)
O(6)	8506(1)	5249(1)	12693(2)
S	7060(1)	3810(0)	7615(1)

C(1)	81(2)	33(1)	47(1)	-7(1)	8(1)	2(1)
C(2)	72(1)	46(1)	47(1)	-18(1)	16(1)	5(1)
C(3)	62(1)	41(1)	37(1)	-9(1)	17(1)	1(1)
C(4)	55(1)	31(1)	28(1)	-4(1)	11(1)	1(1)
C(5)	57(1)	37(1)	53(1)	-2(1)	18(1)	0(1)
C(6)	71(1)	39(1)	62(1)	6(1)	17(1)	-3(1)
C(7)	43(1)	33(1)	27(1)	-2(1)	12(1)	-3(1)
C(8)	55(1)	31(1)	26(1)	-2(1)	17(1)	-1(1)
C(9)	61(1)	77(1)	35(1)	8(1)	21(1)	-4(1)
C(10)	60(1)	67(1)	33(1)	9(1)	7(1)	-6(1)
C(11)	59(1)	36(1)	36(1)	2(1)	19(1)	4(1)
C(12)	167(3)	46(1)	83(2)	10(2)	55(2)	31(1)
C(13)	51(1)	31(1)	28(1)	-2(1)	13(1)	-2(1)
C(14)	66(1)	56(1)	35(1)	-12(1)	17(1)	-17(1)
N(1)	61(1)	31(1)	31(1)	-4(1)	17(1)	-1(1)
N(2)	116(2)	37(1)	75(2)	-8(1)	16(1)	1(1)
O(1)	155(2)	43(1)	154(2)	17(1)	49(2)	-2(1)
O(2)	149(2)	48(1)	155(2)	-33(1)	51(2)	6(1)
O(3)	113(1)	53(1)	29(1)	5(1)	24(1)	6(1)
O(4)	119(1)	33(1)	51(1)	-1(1)	33(1)	9(1)
O(5)	52(1)	60(1)	42(1)	-7(1)	22(1)	-13(1)
O(6)	50(1)	50(1)	32(1)	-8(1)	15(1)	-12(1)
S	60(0)	32(0)	30(0)	0(0)	17(0)	-5(0)

H(2)	929(3)	687(1)	821(4)
H(3)	942(2)	582(1)	821(3)
H(5)	556(2)	579(1)	938(3)
H(6)	574(3)	682(1)	933(4)
H(91)	930(3)	375(1)	769(4)
H(92)	846(3)	389(1)	583(4)
H(93)	894(3)	444(1)	725(4)
H(101)	562(3)	403(1)	475(4)
H(102)	573(3)	463(1)	608(4)
H(103)	491(3)	410(1)	603(4)
H(121)	776(4)	243(2)	1188(6)
H(122)	685(3)	283(1)	1277(4)
H(123)	817(5)	297(2)	1326(7)
H(141)	800(3)	590(1)	1401(4)
H(142)	803(2)	534(1)	1493(3)
H(143)	950(3)	556(1)	1493(4)

3.6.3 (c)

H(2)	9(1)
H(3)	5(1)
H(5)	6(1)
H(6)	8(1)
H(91)	8(1)
H(92)	8(1)
H(93)	11(1)
H(101)	9(1)
H(102)	11(1)
H(103)	9(1)
H(121)	14(1)
H(122)	8(1)
H(123)	16(2)
H(141)	9(1)
H(142)	4(1)
H(143)	8(1)

3.6.3 (d)

Table 3.6.4 (a,b,c)

(a) Interatomic distances ($\mathring{A}$) with e.s.d.'s in parentheses. The hydrogen atoms are numbered according to the atoms to which they are attached.

(b) Interbond angles (degrees) with e.s.d.'s (degrees) in parentheses.

(c) Torsion angles (degrees) with e.s.d.'s (degrees) in parentheses. A torsion angle A-B-C-D is considered to be positive if when viewed down the B-C bond the A-B bond will eclipse the C-D bond when rotated less than 180° in a clockwise direction.

C(1)	C(2)	1.371(4)	C(8)	C(11)	1.427(2)
C(1)	C(6)	1.366(4)	C(8)	S	1.724(2)
C(1)	N(2)	1.463(3)	C(9)	S	1.784(3)
C(2)	C(3)	1.375(3)	C(10)	S	1.793(2)
C(3)	C(4)	1.393(3)	C(11)	O(3)	1.216(2)
C(4)	C(5)	1.390(3)	C(11)	O(4)	1.347(2)
C(4)	N(1)	1.403(2)	C(12)	O(4)	1.427(3)
C(5)	C(6)	1.387(3)	C(13)	O(5)	1.195(3)
C(7)	C(8)	1.424(2)	C(13)	O(6)	1.331(2)
C(7)	C(13)	1.525(3)	C(14)	O(6)	1.448(3)
C(7)	N(1)	1.289(2)	N(2)	O(1)	1.216(4)
N(2)	O(2)	1.213(4)			

3.6.4 (a)

C(2) - H(2)	0.851(30)	C(10) - H(102)	0.956(30)
C(3) - H(3)	0.966(23)	C(10) - H(103)	0.845(33)
C(5) - H(5)	1.064(24)	C(12) - H(121)	0.830(39)
C(6) - H(6)	0.826(27)	C(12) - H(122)	0.929(33)
C(9) - H(91)	0.838(24)	C(12) - H(123)	0.953(43)
C(9) - H(92)	0.926(28)	C(14) - H(141)	0.909(27)
C(9) - H(93)	1.072(31)	C(14) - H(142)	0.883(22)
C(10) - H(101)	0.950(31)	C(14) - H(143)	0.945(24)

3.6.4 (a) (continued)

C(6)	C(1)	C(2)	121.39(19)	N(2)	C(1)	C(2)	118.95(23)
C(3)	C(2)	C(1)	119.39(22)	N(2)	C(1)	C(6)	119.65(23)
C(5)	C(6)	C(1)	119.84(22)	O(1)	N(2)	C(1)	118.33(26)
O(2)	N(2)	C(1)	118.95(26)	C(4)	C(3)	C(2)	120.46(20)
C(5)	C(4)	C(3)	119.33(17)	N(1)	C(4)	C(3)	117.49(17)
N(1)	C(4)	C(5)	123.06(18)	C(6)	C(5)	C(4)	119.58(20)
C(7)	N(1)	C(4)	122.87(15)	C(13)	C(7)	C(8)	117.04(14)
N(1)	C(7)	C(8)	122.36(15)	C(11)	C(8)	C(7)	121.27(15)
S	C(8)	C(7)	121.30(12)	N(1)	C(7)	C(13)	120.59(15)
O(5)	C(13)	C(7)	123.97(16)	O(6)	C(13)	C(7)	110.75(15)
S	C(8)	C(11)	116.90(13)	O(3)	C(11)	C(8)	125.22(17)
O(4)	C(11)	C(8)	113.85(16)	C(9)	S	C(8)	107.18(10)
C(10)	S	C(8)	108.30(9)	C(10)	S	C(9)	101.45(10)
O(4)	C(11)	O(3)	120.91(17)	C(12)	O(4)	C(11)	116.64(18)
O(6)	C(13)	O(5)	125.11(16)	C(14)	O(6)	C(13)	115.50(15)
O(2)	N(2)	O(1)	122.73(23)				

C(6)	C(1)	C(2)	C(3)	-0.6(3)	N(2)	C(1)	C(2)	C(3)	-179.7(2)
C(2)	C(1)	C(6)	C(5)	0.4(4)	N(2)	C(1)	C(6)	C(5)	179.5(2)
C(2)	C(1)	N(2)	O(1)	176.1(3)	C(2)	C(1)	N(2)	O(2)	-3.8(4)
C(6)	C(1)	N(2)	O(1)	-3.0(4)	C(6)	C(1)	N(2)	O(2)	177.1(3)
C(1)	C(2)	C(3)	C(4)	-0.0(3)	C(2)	C(3)	C(4)	C(5)	0.9(3)
C(2)	C(3)	C(4)	N(1)	177.0(2)	C(3)	C(4)	C(5)	C(6)	-1.0(3)
N(1)	C(4)	C(5)	C(6)	-176.9(2)	C(3)	C(4)	N(1)	C(7)	131.5(2)
C(5)	C(4)	N(1)	C(7)	-52.6(3)	C(4)	C(5)	C(6)	C(1)	0.4(3)
C(13)	C(7)	C(8)	C(11)	-19.1(2)	C(13)	C(7)	C(8)	S	169.5(1)
N(1)	C(7)	C(8)	C(11)	162.4(2)	N(1)	C(7)	C(8)	S	-9.0(2)
C(8)	C(7)	C(13)	O(5)	-71.1(2)	C(8)	C(7)	C(13)	O(6)	113.5(2)
N(1)	C(7)	C(13)	O(5)	107.4(2)	N(1)	C(7)	C(13)	O(6)	-68.0(2)
C(8)	C(7)	N(1)	C(4)	173.6(2)	C(13)	C(7)	N(1)	C(4)	-4.9(3)
C(7)	C(8)	C(11)	O(3)	-0.6(3)	C(7)	C(8)	C(11)	O(4)	-178.9(2)
S	C(8)	C(11)	O(3)	171.2(2)	S	C(8)	C(11)	O(4)	-7.2(2)
C(7)	C(8)	S	C(9)	61.3(2)	C(7)	C(8)	S	C(10)	-47.4(2)
C(11)	C(8)	S	C(9)	-110.4(2)	C(11)	C(8)	S	C(10)	140.9(1)
C(8)	C(11)	O(4)	C(12)	177.2(2)	O(3)	C(11)	O(4)	C(12)	-1.3(3)
C(7)	C(13)	O(6)	C(14)	174.4(1)	O(5)	C(13)	O(6)	C(14)	-0.9(3)

Table 3.6.5

A. Selected intramolecular non-bonded distances (< 4.0 Å).

C(3) .... C(7)	3.47	C(9) .... N(1)	3.17
C(4) .... C(13)	2.83	C(10) ... N(1)	3.09
C(4) .... O(6)	3.05	C(10) ... O(5)	3.23
C(5) .... C(7)	3.03	C(11) ... C(13)	2.89
C(5) .... C(13)	2.98	C(11) ... O(5)	3.31
C(5) .... O(5)	3.26	C(11) .... S	2.69
C(5) .... O(6)	3.36	C(12) .... O(3)	2.62
C(6) .... O(1)	2.72	C(13) .... O(3)	2.63
C(7) .... C(9)	3.37	C(14) .... O(5)	2.66
C(7) .... C(10)	3.28	N(1) .... S	3.04
C(7) .... C(14)	3.70	O(3) .... O(5)	2.94
C(7) .... O(3)	2.88	O(3) .... O(6)	3.12
C(8) .... C(12)	3.64	O(4) .... S	2.77
C(8) .... O(5)	3.14		
C(8) .... O(6)	3.38		

B. Selected intermolecular distances (< 4.0 Å)

C(1) .... N(2)^{i}	4.0	C(9) .... C(14)^{v}	3.44
C(1) .... O(1)^{i}	3.53	C(9) .... O(3)^{iii}	3.15
C(1) .... O(2)^{ii}	3.56	C(9) .... O(6)^{v}	3.20
C(3) .... C(14)^{iii}	3.35		
C(7) .... O(5)^{iv}	3.28		

Roman numeral superscripts refer to the following equivalent positions relative to the molecule at (x,y,z):

(i) x, 3/2 - y, - 1/2 + z

(ii) x, 3/2 - y, 1/2 + z

(iii) x, y, -1 + z

(iv) 1 - x, 1 - y, 2 - z

(v) 2 - x, 1 - y, 2 - z

Table 3.6.5 (continued)

Table 3.6.6

LEAST-SQUARES PLANES

Planes are in the form of $AX + BY + CZ - D = 0$ where X, Y and Z refer to an orthogonalized set of axes, D is the perpendicular distance from the plane to the origin and A, B and C refer to the components of unit vector normal to the best plane. An asterisk denotes atoms used to define the plane.

A. (1) Equation of the plane

$-0.2071X + 0.0140Y - 0.9782Z + 7.2122 = 0$

$\chi^2 = 24.11$ with three degrees of freedom.

The deviations (Å) of the atoms from the plane are:

C(1)*	-0.005(2)	N(1)	0.062(1)
C(2)*	0.002(2)	N(2)	0.001(2)
C(3)*	0.003(2)	O(1)	0.068(3)
C(4)*	-0.005(2)	O(2)	-0.057(3)
C(5)*	0.005(2)		
C(6)*	0.001(2)		

(2) Equation of the plane

$0.8859X - 0.0044Y + 0.4638Z - 7.5015 = 0$

The deviations (Å) of the atoms from the plane are:

C(4)*	0.0	C(11)	0.232(2)
C(7)*	0.0	C(13)	0.112(2)
N(1)*	0.0	S	-0.536(1)
C(8)	-0.135(2)		

(3) Equation of the plane

$0.1493X - 0.0074Y + 0.9888Z - 7.0925 = 0$

The deviations (Å) of the atoms from the plane are:

N(2)*	0.0	C(2)	-0.084(2)
O(1)*	0.0	C(6)	0.058(2)
O(2)*	0.0	N(1)	-0.099(1)
C(1)	-0.002(2)		

(4) Equation of the plane

$0.9969X - 0.0358Y + 0.0706Z - 4.7266 = 0$

The deviations (Å) of the atoms from the plane are:

C(11)*	0.0	O(4)*	0.0
C(12)*	0.0	O(3)	-0.023(2)

(5) Equation of the plane

$-0.0722X + 0.8554Y - 0.5128Z - 4.9721 = 0$

The deviations (Å) of the atoms from the plane are:

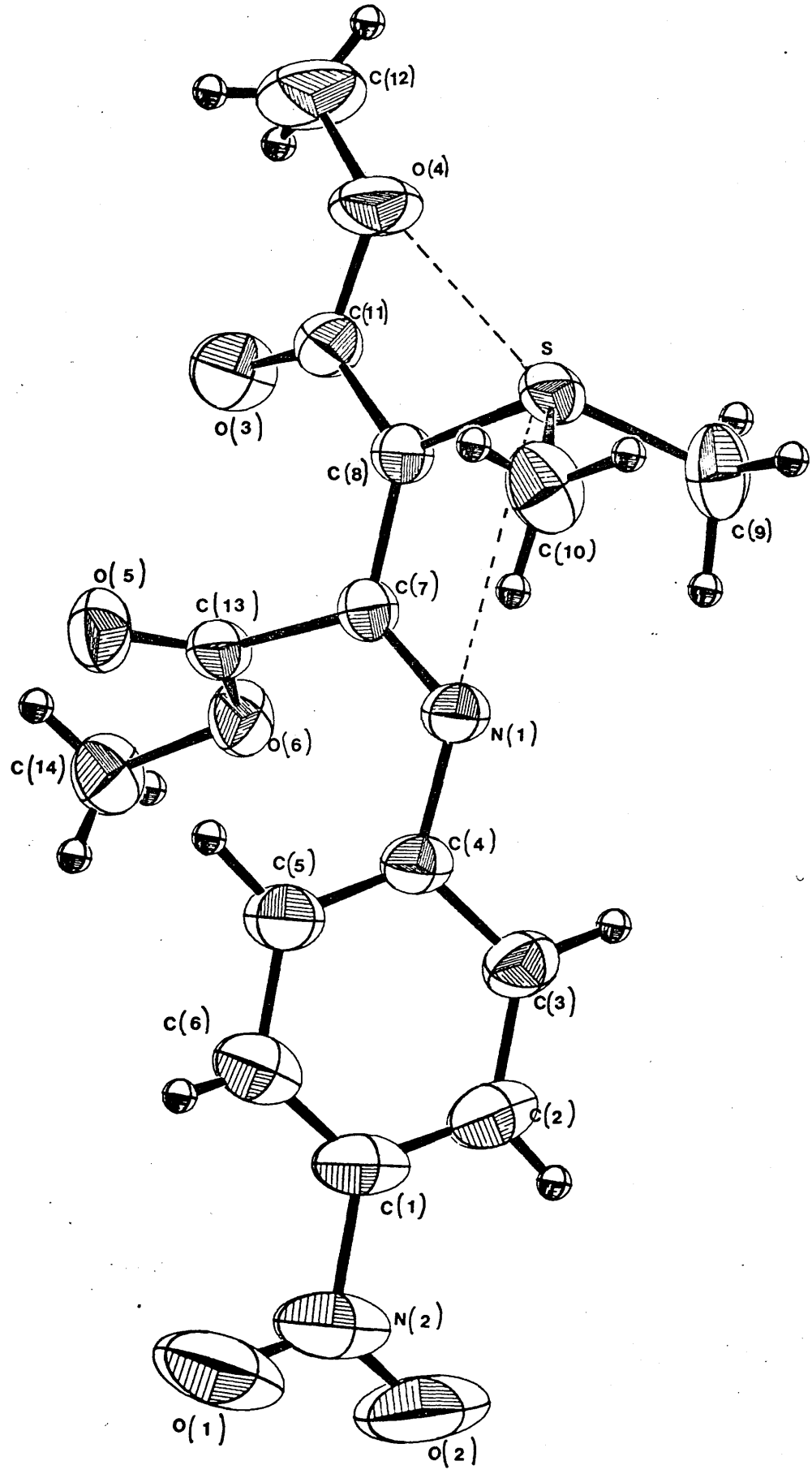
C(13)*	0.0	O(6)*	0.0
C(14)*	0.0	O(5)	-0.016(1)

B. The angle between planes (1) and (2) is 50.4°, between (1) and (3), 3.4° between (2) and (3), 53.8°, and between (4) and (5) 82°.

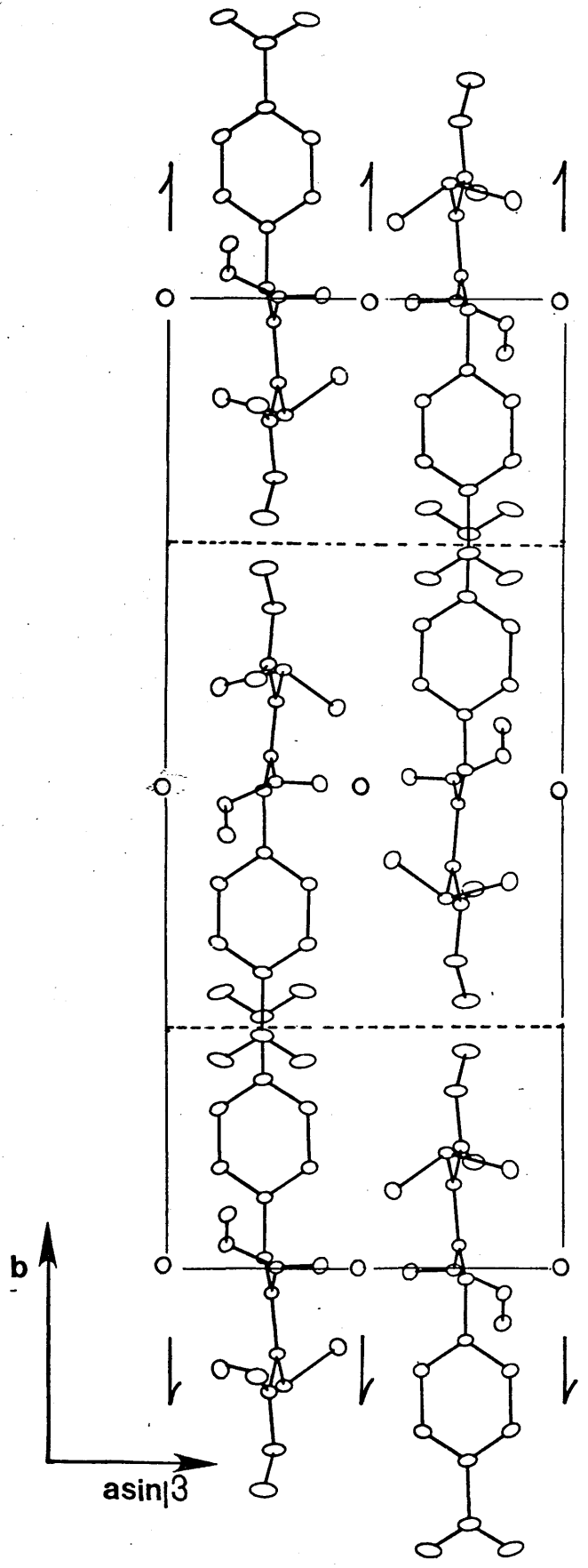
Figure 3.6.1 (a and b)

(a) A general view of VI giving the atomic numbering scheme. Hydrogen atoms are numbered according to the atoms to which they are bonded.

(b) The molecular packing of VI viewed along the short c-axis.


C(12)
O(4)
C(11)
O(3)
S
C(8)
C(10)
C(9)
O(5)
C(13)
C(7)
O(6)
N(1)
C(14)
C(4)
C(5)
C(3)
C(6)
C(2)
C(1)
N(2)
O(1)
O(2)

(a)



(b)

Discussion of VI.

The crystal structure analysis of VI reveals a characteristic molecular geometry similar to the one established for the stabilized ylides previously described (sections 3.3 to 3.5). The bonding system and bond angles around the central framework of the molecule are given in Figure 3.6.2. Thus the carbon atoms of the central C-C bond possess near-trigonal geometry and the C(7) - C(8) bond [1.424(2) Å] is considerably shortened[67,68] (Table 3.6.4). Furthermore, the carbonyl bond [C(11) - O(3)] of the stabilizing methoxycarbonyl-group is slightly longer [1.216(2) Å] than the corresponding bond [C(13) - O(5)] of length 1.195(3) Å, and the imino nitrogen to carbon bond [C(7) - N(1)] is nearly a perfect double bond[56] [1.289(2) Å]. There are therefore clear indications, in keeping with the evidence already mentioned for the other betaines, of delocalization of the formal negative charge on N(1) into the methoxycarbonyl group geminal to the 'onium' species. A similar pattern of delocalization is suggested by the length of 1.427(2) Å for the C(8) - CO bond. The C - CO_2Me bond, not adjacent to the 'onium' moiety, is 1.525(3) Å while the torsion angle for this bond is 113.5(2)° [-113.5(2)° for the mirror imaged molecule] . As has been suggested before, this latter phenomenon of $C(sp^2)$ - $C(sp^2)$ bond lengthening can plausibly be attributed to the intramolecular overcrowding in the molecule. The S - C(8) bond [1.724(2) Å] compares well with similar bonds in molecules III (A, B), IV and V (this thesis), while the N(1) - C(4)

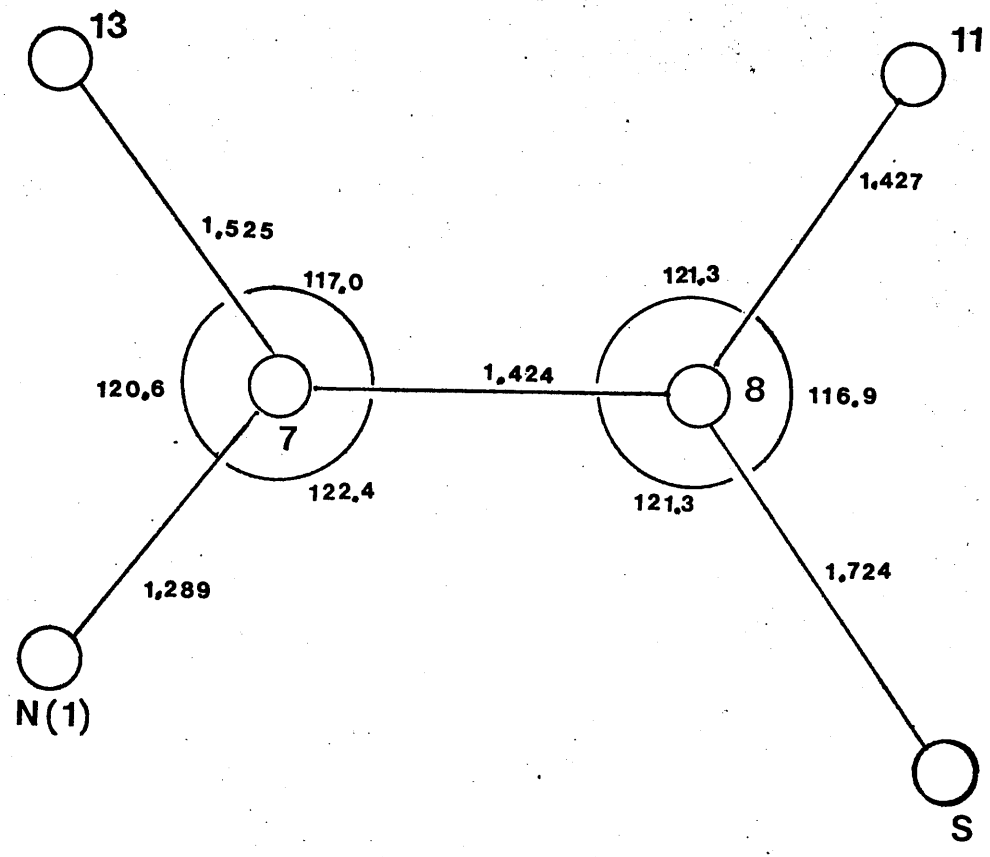
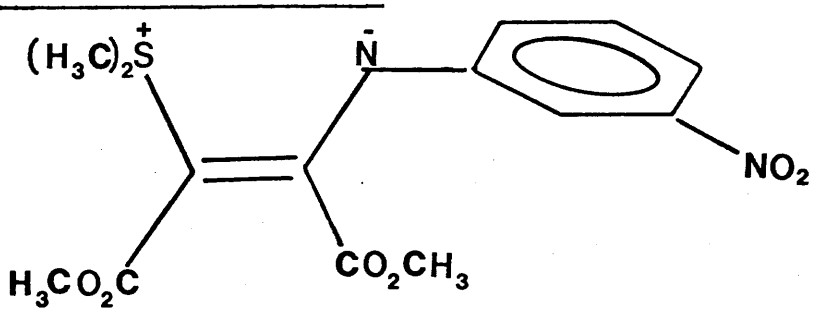

13
11
1,525
1,427
117,0
121,3
120,6
1,424
8
116,9
7
122,4
121,3
1,289
1,724
N(1)
S

Figure 3.6.2

bond [1.403(2) Å] suggests no appreciable perturbation of electron density into the ring system. Further, to support this, is the large torsional movement exhibited by the aromatic ring along the N(1) - C(4) bond (c.a 53°) [Tables 3.6.4(c) and 3.6.6]. A reflection of the internal strain in this molecule is also given by the values for i) the exocyclic valency angle N(1) - C(4) - C(5) [123.1(2)°] ii) the valency angle C(7) - N(1) - C(4) [122.9(1)°] and iii) the unequal angles at the central framework of the molecule (Table 3.6.4). Further features of the molecular geometry are the approximately pyramidal arrangement around the sulphur atom (average pyramidal angle, 105.6°) and the staggered position of the methyl groups with respect to the C-C central bond (Table 3.6.4).

Close intramolecular contacts are noted and listed in Table 3.6.5. The molecular packing viewed along the c-axis is shown in Figure 3.6.1(b). Of the intermolecular contacts (Table 3.6.5) several are shorter than the van der Waals distances given by Pauling[50] (1967) (3.40 Å for O ... C_{methyl} and 4.0 Å for C_{methyl} .... C_{methyl}) and these, too, are listed in Table 3.6.5.

3.7 Experimental and Results for VII.



VII

Dimethylsulphonium-2-(3-nitrophenylimino)-1,2-bismethoxycarbonylethylide.

Preparation of Crystals

The corresponding N-aryl-sulphimide was prepared first (see 'Preparation for I'), and the betaine was then prepared by a procedure similar to that described by Hayashi and Swern[34] (1974). Few crystallizations from ethanol followed by a crystallization from benzene produced pure yellow, parallel piped-shaped crystals. The structure was substantiated by a mass spectrum analysis: m/e, 340(M^+), 278($M^+ - (CH_3)_2S$) and 281($M^+ - CO_2CH_3$).

N-aryl-sulphimide + $H_3CO_2C - C \equiv C - CO_2CH_3$ ⟶ VII

Crystal Data

Molecular Formula	$C_{14}H_{16}N_2O_6S$
Molecular Weight	340.2 a.m.u.
Crystal System	Monoclinic
Unit Cell Dimensions	$a = 13.870(2)$ Å
	$b = 8.522(1)$ Å
	$c = 13.971(3)$ Å
	$\beta = 105.47(1)^\circ$
Unit Cell Volume	$V = 1591.55$ Å^3
Number of Molecules per Unit Cell	$Z = 4$
Calculated Density	$D_c = 1.42$ g.cm^{-3}
Number of Molecules per Asymmetric Unit	$N = 1$
Space Group	$P2_1/c$ (C_{2h}^5, No.14)

Equivalent Positions	x,y,z
	-x, 1/2 + y, 1/2 - z
Linear Absorption Coefficient	$\mu = 2.24\ cm^{-1}$
Number of Electrons per Unit Cell	F(000) = 712

Data Collection

Diffractometer Used	Enraf-Nonius CAD-4
Radiation Used	$M_o - K_\alpha$, $\overline{\lambda} = 0.7114\ \text{Å}$
Filter	Graphite Monochromator
	$\cos^2 2\theta_m = 0.960$
Upper Limit for Data Collection	$2\theta_{max} = 56^\circ$
Number of Observed	
Independent Reflections	m = 2133
Unobserved Cut-Off	$2.0\ \sigma_I$
Number of Parameters Refined	n = 273
Number of Reflections per	
Parameter	m/n = 7.8

Structure Determination and Refinement

The coordinates of 16 out of 23 nonhydrogen atoms were obtained from an E-map calculated with the set of phases having the highest combined figure of merit produced by the 'MULTAN' direct phasing program (version 1976) for the space group $P2_1/c$. Normalized structure factors were calculated with an overall isotropic temperature factor of $3.27\ \text{Å}^2$ (= B) and an overall scale factor determined by Wilson's plot.

726 triplet relationships which were produced from 185 reflections with $|E| > 1.7$ were used (8 reflections per nonhydrogen atom and 3.9 triplet relationships per reflection).

The atoms located by 'MULTAN' were assigned isotropic thermal parameters of B = 4.0 (U = 0.051) and were refined by one cycle of isotropic least-squares calculation. A subsequent calculation of the electron density distribution revealed the sites for all the nonhydrogen atoms. R and R_w at this stage were 0.331 and 0.317 respectively. The various parameters used with 'MULTAN' are outlined in Table 3.7.1. The positions of the hydrogen atoms were located in a difference map after cycle 8 and their positional and isotropic thermal parameters were allowed to vary during the last 6 cycles of the least-squares. A weighting scheme of the form $w = 1/\sigma^2(F_o)$ which provided an approximately flat distribution of $w\Delta^2$ with $|F_o|$ was employed and the refinement converged at R = 0.034 and R_w = 0.047. All parameter shifts were smaller than 0.89 σ, the average shift/error being equal to 0.2 and the standard deviation of an observation of unit weight was equal to 1.5143. No absorption correction was applied and a final Δ F synthesis revealed no errors in the model. The course of the refinement is summarized in Table 3.7.2. A listing of the observed and calculated structure factors with the appropriate phases is given in the supplement to this thesis. The crystal and molecular structure together with a numbering scheme are shown in Figures 3.7.1(a) and 3.7.1(b). The atomic coordinates and thermal parameters, bond lengths, valency angles and torsion angles with e.s.d.'s and other relevant data are given in Tables 3.7.3 to 3.7.6.

Table 3.7.I

SUMMARY OF THE CONDITIONS (INCLUDING VARIOUS FIGURES OF INTEREST) ASSOCIATED WITH SOLVING THE STRUCTURE OF VII.

In this table:

1. NE - is the number of the largest $|E|$'s chosen to define the structure.
2. NSRT - is the number of Σ_2 relationships to be retained.
3. NSRTT - is the total number of Σ_2 relationships.
4. PROB - is the probability acceptance limit chosen for Σ_1.
5. NSPEC - is the number of special phases (permutations restricted to ϕ_{spec}, $\phi_{spec} + 180^{\circ}$).

   NGEN - is the number of general phases (phase permutation 45°, 135°, 225°, 315°)

   NANY - is the number of phases of either sort.
6. NSET - is the total number of phase sets that have been developed.
7. PUB - is the published phase.
8. NAT - is the number of nonhydrogen atoms in the asymmetric unit.
9. ABS FOM, PSI ZERO, RESID and CFOM are all figures of merit.

$C_{14}H_{16}N_2O_6S$, $P2_1/c$, NAT = 23

PARAMETERS		STARTING SET TYPE	hkl	PHI	PUB	RESULTS PHASE SET CONSIDERED	FIGURES OF MERIT ABS FOM	PSI ZERO	RESID	TOTAL NUMBER OF CORRECT PEAKS FOUND IN E-MAP
SIGMA - 2		SIGMA - 1	16,0,-12	360*	360	Max	1.2891	239.8	40.89	16
NE(|E| > 1.70)	185					Min	0.7416	169.3	20.60	
NSRT	726	Origin defining phases	3,1,-2	360	360	CFOM8 = 2.3755	1.2891	213.3	20.60	
NSRTT	not known		5,5,-3	360	360					
CONVERGE			9,4,-8	360	360					
PROB	0.95	Permuted phases	8,4,-6	180 360	180					
NSPEC, NGEN, NANY	4,0,0		6,7,-9	180 360	180					
FASTAN			4,8,-7	180 360	180					
NSET	16		4,3,-4	180 360	360					

*For space group $P2_1/c$ in general: $\phi(h,k,l) = \phi(-h,k,-l) + \pi(k + l)$.

Table 3.7.2

PROGRESS OF LEAST-SQUARES REFINEMENT

CYCLES	PARAMETERS REFINED	R	R_w
0	none	0.331	0.317
5	x,y,z, $U_{(iso)}$ for C, N, O, and S atoms; scale factor; unit weights; full-matrix.	0.117	0.117
3	x,y,z, U_{ij} for C, N, O, and S; scale factor; unit weights; full matrix.	0.061	0.076
6	x,y,z, U_{ij} for C, N, O and S; x,y,z, $U_{(iso)}$ for H atoms; scale factors; weights from counting statistics; block diagonal.	0.034	0.047

Table 3.7.3(a,b,c,d)

(a) Fractional atomic coordinates ($\times 10^4$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM X/A Y/B Z/C

(b) Anisotropic thermal parameters ($\mathring{A}^2$, $\times 10^3$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}

(c) Fractional atomic coordinates ($\times 10^3$) of hydrogen atoms, with e.s.d.'s in parentheses. The hydrogens are numbered according to the atoms to which they are attached.

(d) Isotropic thermal parameters ($\mathring{A}^2$, $\times 10^2$) of hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM $U_{(iso)}$.

C(1)	0007(2)	1238(3)	8143(2)
C(2)	0100(2)	2180(3)	8960(2)
C(3)	0804(2)	3360(2)	9226(2)
C(4)	1461(1)	3595(2)	8640(1)
C(5)	1366(2)	2656(3)	7798(2)
C(6)	0653(2)	1497(3)	7562(2)
C(7)	2821(1)	5059(2)	9629(1)
C(8)	3497(1)	6347(2)	9779(1)
C(9)	3475(2)	6704(3)	7737(2)
C(10)	2199(2)	8503(3)	8493(2)
C(11)	4306(1)	6514(2)	10663(2)
C(12)	5675(2)	8085(3)	11515(2)
C(13)	2907(1)	3913(2)	10482(1)
C(14)	3408(3)	1316(3)	10960(2)
N(1)	2156(1)	4833(2)	8792(1)
N(2)	-0597(2)	1951(3)	9578(2)
O(1)	-1188(2)	0864(3)	9375(2)
O(2)	-0556(2)	2824(3)	10268(2)
O(3)	4529(1)	5562(2)	11331(1)
O(4)	4808(1)	7879(2)	10694(1)
O(5)	2558(1)	4090(2)	11169(1)
O(6)	3345(1)	2613(2)	10284(1)
S	3439(0)	7718(1)	8859(0)

C(1)	54(1)	44(1)	60(1)	-8(1)	-5(1)	-5(1)
C(2)	45(1)	44(1)	53(1)	-6(1)	6(1)	1(1)
C(3)	48(1)	38(1)	44(1)	-5(1)	7(1)	-2(1)
C(4)	46(1)	33(1)	39(1)	2(1)	4(1)	4(1)
C(5)	56(1)	47(1)	42(1)	9(1)	8(1)	2(1)
C(6)	64(1)	47(1)	49(1)	7(1)	-1(1)	-10(1)
C(7)	41(1)	34(1)	40(1)	1(1)	17(1)	2(1)
C(8)	40(1)	38(1)	44(1)	-1(1)	13(1)	8(1)
C(9)	75(2)	77(2)	53(1)	8(1)	33(1)	18(1)
C(10)	61(1)	53(1)	72(2)	15(1)	11(1)	13(1)
C(11)	38(1)	40(1)	47(1)	1(1)	16(1)	1(1)
C(12)	56(1)	69(2)	59(1)	-17(1)	5(1)	-7(1)
C(13)	43(1)	41(1)	39(1)	-6(1)	10(1)	2(1)
C(14)	126(3)	44(1)	61(2)	2(2)	5(2)	15(1)
N(1)	47(1)	42(1)	42(1)	-5(1)	11(1)	5(1)
N(2)	59(1)	71(1)	75(2)	-25(1)	18(1)	-5(1)
O(1)	101(2)	121(2)	121(2)	-74(2)	45(1)	-31(2)
O(2)	110(2)	110(2)	104(2)	-51(1)	64(1)	-39(1)
O(3)	56(1)	54(1)	50(1)	-5(1)	5(1)	11(1)
O(4)	52(1)	48(1)	58(1)	-13(1)	2(1)	5(1)
O(5)	63(1)	69(1)	44(1)	-5(1)	25(1)	5(1)
O(6)	74(1)	41(1)	46(1)	9(1)	16(1)	8(1)
S	45(0)	42(0)	52(0)	-5(0)	11(0)	14(0)

H(1)	-049(2)	049(3)	799(2)
H(3)	081(2)	400(3)	980(2)
H(5)	185(2)	282(3)	740(2)
H(6)	056(2)	093(3)	698(2)
H(91)	352(2)	753(3)	729(2)
H(92)	413(3)	615(4)	787(3)
H(93)	288(2)	608(4)	754(2)
H(101)	171(2)	771(3)	831(2)
H(102)	216(2)	914(4)	793(2)
H(103)	211(2)	916(4)	902(2)
H(121)	605(3)	904(5)	1136(3)
H(122)	546(2)	840(4)	1205(2)
H(123)	615(2)	712(3)	1160(2)
H(141)	367(3)	051(5)	1065(3)
H(142)	389(3)	152(5)	1155(3)
H(143)	271(3)	102(6)	1091(3)

3.7.3 (c)

H(1)	7(1)
H(3)	6(1)
H(5)	6(1)
H(6)	7(1)
H(91)	7(1)
H(92)	12(1)
H(93)	10(1)
H(101)	8(1)
H(102)	9(1)
H(103)	11(1)
H(121)	14(1)
H(122)	10(1)
H(123)	8(1)
H(141)	14(1)
H(142)	13(1)
H(143)	18(2)

3.7.3 (d)

Table 3.7.4(a,b,c)

(a) Interatomic distances ($\mathring{A}$) with e.s.d.'s in parentheses. The hydrogen atoms are numbered according to the atoms to which they are attached.

(b) Interbond angles (degrees) with e.s.d.'s (degrees) in parentheses.

(c) Torsion angles (degrees) with e.s.d.'s (degrees) in parentheses. A torsion angle A-B-C-D is considered to be positive if when viewed down the B-C bond the A-B bond will eclipse the C-D bond when rotated less than 180° in a clockwise direction.

C(1)	C(2)	1.373(3)	C(8)	C(11)	1.437(2)
C(1)	C(6)	1.378(4)	C(8)	S	1.723(2)
C(2)	C(3)	1.382(3)	C(9)	S	1.802(3)
C(2)	N(2)	1.470(4)	C(10)	S	1.788(3)
C(3)	C(4)	1.392(3)	C(11)	O(3)	1.213(3)
C(4)	C(5)	1.400(3)	C(11)	O(4)	1.351(3)
C(4)	N(1)	1.407(3)	C(12)	O(4)	1.433(3)
C(5)	C(6)	1.374(3)	C(13)	O(5)	1.195(3)
C(7)	C(8)	1.423(3)	C(13)	O(6)	1.327(3)
C(7)	C(13)	1.520(3)	C(14)	O(6)	1.441(3)
C(7)	N(1)	1.296(2)	N(2)	O(1)	1.219(3)
N(2)	O(2)	1.208(4)			

3.7.4 (a)

C(1) - H(1)	0.917(27)	C(10) - H(102)	0.947(32)
C(3) - H(3)	0.975(24)	C(10) - H(103)	0.959(36)
C(5) - H(5)	0.987(28)	C(12) - H(121)	1.015(43)
C(6) - H(6)	0.919(27)	C(12) - H(122)	0.917(36)
C(9) - H(91)	0.954(28)	C(12) - H(123)	1.041(27)
C(9) - H(92)	0.993(36)	C(14) - H(141)	0.934(45)
C(9) - H(93)	0.965(30)	C(14) - H(142)	0.927(34)
C(10) - H(101)	0.944(28)	C(14) - H(143)	0.991(49)

3.7.4 (a) (continued)

C(6)	C(1)	C(2)	117.76(22)	C(3)	C(2)	C(1)	123.41(21)
N(2)	C(2)	C(1)	118.72(21)	C(5)	C(6)	C(1)	120.85(22)
N(2)	C(2)	C(3)	117.85(20)	C(4)	C(3)	C(2)	118.29(19)
O(1)	N(2)	C(2)	118.08(23)	O(2)	N(2)	C(2)	119.28(23)
C(5)	C(4)	C(3)	118.84(19)	N(1)	C(4)	C(3)	123.34(18)
N(1)	C(4)	C(5)	117.51(18)	C(6)	C(5)	C(4)	120.84(21)
C(7)	N(1)	C(4)	122.81(17)	C(13)	C(7)	C(8)	117.98(17)
N(1)	C(7)	C(8)	122.03(18)	C(11)	C(8)	C(7)	122.40(18)
S	C(8)	C(7)	121.04(15)	N(1)	C(7)	C(13)	119.98(18)
O(5)	C(13)	C(7)	125.76(19)	O(6)	C(13)	C(7)	108.57(16)
S	C(8)	C(11)	116.39(15)	O(3)	C(11)	C(8)	125.16(19)
O(4)	C(11)	C(8)	113.02(18)	C(9)	S	C(8)	108.47(11)
C(10)	S	C(8)	108.50(11)	C(10)	S	C(9)	100.23(13)
O(4)	C(11)	O(3)	121.82(19)	C(12)	O(4)	C(11)	116.58(18)
O(6)	C(13)	O(5)	125.34(20)	C(14)	O(6)	C(13)	117.10(19)
O(2)	N(2)	O(1)	122.62(26)				

C(6)	-	C(1)	-	C(2)	-	C(3)	-0.1(4)	C(6)	-	C(1)	-	C(2)	-	N(2)	178.5(2)
C(2)	-	C(1)	-	C(6)	-	C(5)	0.2(4)	C(1)	-	C(2)	-	C(3)	-	C(4)	-0.8(3)
N(2)	-	C(2)	-	C(3)	-	C(4)	-179.4(2)	C(1)	-	C(2)	-	N(2)	-	O(1)	4.7(4)
C(1)	-	C(2)	-	N(2)	-	O(2)	-176.2(2)	C(3)	-	C(2)	-	N(2)	-	O(1)	-176.6(2)
C(3)	-	C(2)	-	N(2)	-	O(2)	2.5(3)	C(2)	-	C(3)	-	C(4)	-	C(5)	1.5(3)
C(2)	-	C(3)	-	C(4)	-	N(1)	175.0(2)	C(3)	-	C(4)	-	C(5)	-	C(6)	-1.5(3)
N(1)	-	C(4)	-	C(5)	-	C(6)	-175.3(2)	C(3)	-	C(4)	-	N(1)	-	C(7)	56.6(3)
C(5)	-	C(4)	-	N(1)	-	C(7)	-129.9(2)	C(4)	-	C(5)	-	C(6)	-	C(1)	0.7(4)
C(13)	-	C(7)	-	C(8)	-	C(11)	5.9(3)	C(13)	-	C(7)	-	C(8)	-	S	-179.0(1)
N(1)	-	C(7)	-	C(8)	-	C(11)	-173.0(2)	N(1)	-	C(7)	-	C(8)	-	S	2.2(3)
C(8)	-	C(7)	-	C(13)	-	O(5)	82.2(3)	C(8)	-	C(7)	-	C(13)	-	O(6)	-104.2(2)
N(1)	-	C(7)	-	C(13)	-	O(5)	-98.9(3)	N(1)	-	C(7)	-	C(13)	-	O(6)	74.7(2)
C(8)	-	C(7)	-	N(1)	-	C(4)	-177.9(2)	C(13)	-	C(7)	-	N(1)	-	C(4)	3.2(3)
C(7)	-	C(8)	-	C(11)	-	O(3)	4.3(3)	C(7)	-	C(8)	-	C(11)	-	O(4)	-174.9(2)
S	-	C(8)	-	C(11)	-	O(3)	-171.0(2)	S	-	C(8)	-	C(11)	-	O(4)	9.8(2)
C(7)	-	C(8)	-	S	-	C(9)	-52.8(2)	C(7)	-	C(8)	-	S	-	C(10)	55.2(2)
C(11)	-	C(8)	-	S	-	C(9)	122.6(2)	C(11)	-	C(8)	-	S	-	C(10)	-129.4(2)
C(8)	-	C(11)	-	O(4)	-	C(12)	-175.3(2)	O(3)	-	C(11)	-	O(4)	-	C(12)	5.5(3)
C(7)	-	C(13)	-	O(6)	-	C(14)	-174.0(2)	O(5)	-	C(13)	-	O(6)	-	C(14)	-0.4(3)

Table 3.7.5

A. Selected intramolecular non-bonded distances (<4.0 Å).

C(3) ... C(7)	3.06	C(11) ... C(13)	2.91
C(3) ... C(13)	3.01	C(11) ... O(5)	3.40
C(3) ... O(2)	2.71	C(11) ... S	2.69
C(4) ... C(13)	2.82	C(12) ... O(3)	2.65
C(4) ... O(6)	3.10	C(13) ... O(3)	2.65
C(5) ... C(7)	3.47	N(1) ... S	3.02
C(7) ... C(9)	3.32	O(3) ... O(5)	2.96
C(7) ... C(14)	3.67	O(3) ... O(6)	3.14
C(7) ... O(3)	2.91	O(4) ... S	2.76
C(8) ... C(12)	3.65	O(5) ... C(14)	2.69
C(8) ... O(5)	3.24		
C(8) ... O(6)	3.28		
C(9) ... N(1)	3.08		
C(10) .. N(1)	3.16		
C(10) .. C(7)	3.34		

B. Selected intermolecular distances (<4.0 Å)

C(1) ... C(4)^{i}	3.57	C(9) ... C(14)^{iii}	3.56
C(1) ... C(5)^{i}	3.65	C(9) ... O(3)^{v}	3.34
C(6) ... C(10)^{ii}	3.36	C(12) .. C(14)^{vi}	3.73
C(6) ... O(2)^{iii}	3.25		
C(9) ... C(12)^{iv}	3.88		

Roman numeral superscripts refer to the following equivalent positions relative to the molecule at (x,y,z):

(i) $-x, -1/2 + y, 3/2 - z$

(ii) $x, -1 + y, z$

(iii) $x, 1/2 - y, -1/2 + z$

(iv) $x, 3/2 - y, -1/2 + z$

(v) $1 - x, 1 - y, 2 - z$

(vi) $1 - x, 1/2 + y, 5/2 - z$.

Table 3.7.5 (continued)

Table 3.7.6

LEAST-SQUARES PLANES

Planes are in the form of $AX + BY + CZ - D = 0$ where X, Y and Z refer to an orthogonalized set of axes, D is the perpendicular distance from the plane to the origin and A, B and C refer to the components of unit vector normal to the best plane. An asterisk denotes atoms used to define the plane.

A. (1) Equation of the plane

$0.5151X - 0.6530Y + 0.5552Z - 3.8361 = 0$

$\chi^2 = 33.34$ with three degrees of freedom.

The deviations (Å) of the atoms from the plane are:

C(1)*	0.004(2)	N(1)	-0.100(2)
C(2)*	0.000(2)	N(2)	-0.027(2)
C(3)*	-0.006(2)	O(1)	0.042(3)
C(4)*	0.008(2)	O(2)	-0.100(3)
C(5)*	-0.006(2)		
C(6)*	-0.001(2)		

(2) Equation of the plane

$0.7501X - 0.5867Y - 0.3052Z + 6.2440 = 0$

The deviations (Å) of the atoms from the plane are:

C(4)*	0.0	C(11)	0.104(2)
C(7)*	0.0	C(13)	0.074(2)
N(1)*	0.0	S	-0.154(1)
C(8)	-0.044(2)		

(3) Equation of the plane

$-0.5310X + 0.6023Y - 0.5961Z + 4.3504 = 0$

The deviations (Å) of the atoms from the plane are:

N(2)*	0.0	C(3)	-0.096(2)
O(1)*	0.0	C(1)	0.056(2)
O(2)*	0.0	N(1)	-0.074(2)
C(2)	-0.022(2)		

(4) Equation of the plane

$0.7642X + 0.3380Y + 0.5493Z - 8.9755 = 0$

C(13)*	0.0	O(5)	-0.007(2)
C(14)*	0.0		
O(6)*	0.0		

(5) Equation of the plane

$0.7379X - 0.4149Y - 0.5323Z + 8.4704 = 0$

The deviations (Å) of the atoms from the plane are:

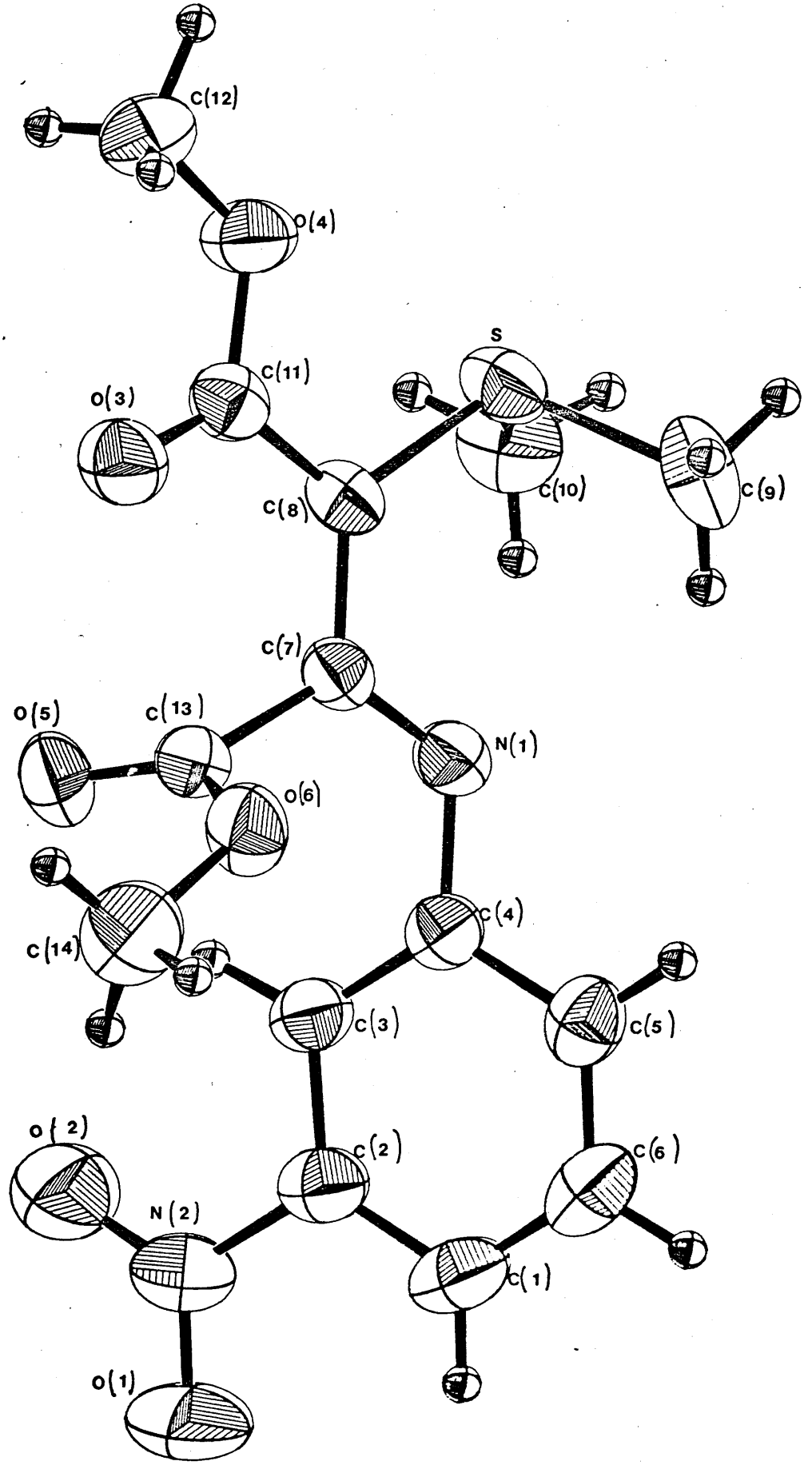
C(11)*	0.0	O(3)	-0.098(2)
C(12)*	0.0		
O(4)*	0.0		

B. The angle between planes (1) and (2) is 53.1°, between (1) and (3) 3.8°, between (2) and (3) 56.9° and between (4) and (5) 82.4°.

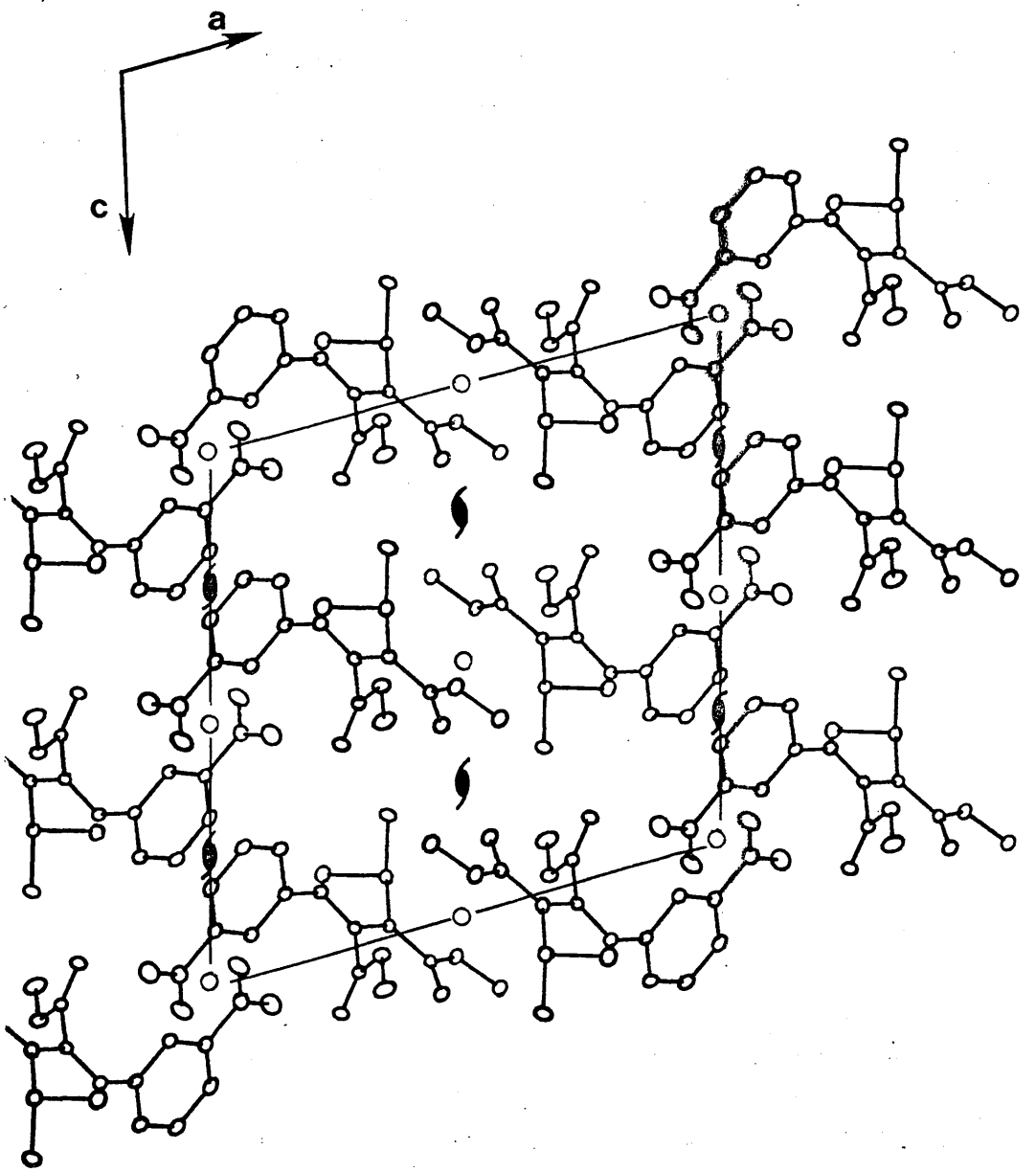
Figure 3.7.1 (a and b)

a. A general view of VII giving the atomic numbering scheme. Hydrogen atoms are numbered according to the atoms to which they are bonded.

b. The molecular packing of VII viewed along the short b-axis.


C(12)
O(4)
S
C(11)
O(3)
C(10)
C(9)
C(8)
C(7)
O(5)
C(13)
N(1)
O(6)
C(4)
C(14)
C(3)
C(5)
O(2)
C(2)
C(6)
N(2)
C(1)
O(1)

(a)



(b)

3.III Discussion of VII and VI

The almost identical geometry of molecules VII and VI becomes evident from a comparison of the corresponding bond lengths, valency and dihedral angles (Tables 3.6.4 and 3.7.4). The main geometrical characteristics of both molecules are summarized in Table 3.III.1. Thus the 'through conjugation' pattern at the central bond system is observed and the two methoxycarbonyl groups in each molecule, though tilted with respect to each other (c.a. 80°), are very nearly planar (Table 3.III.1 Section 5). This latter observation is probably a result of smaller steric requirements of the $-CO_2M_e$ groups compared to the bulky benzoyl groups in betaines III, IV and V (3.3, 3.4 and 3.5) in which the planarity is destroyed.

3.8 Overall Aspects of Ylides I to VII

From the structure analyses of the two N-arylsulphimides (iminosulphuranes) I and II (this thesis) it can be concluded that i) the sulphimides do reveal great similarity to sulphur-carbon ylides which is reflected in a trigonal arrangement (sp^2 hybridization) of nitrogen in S-N ylides and of carbon in S-C ylides, ii) the relatively unhindered geometry of the sulphimides (I and II) can account for the high reactivity exhibited towards a variety of reagents[25] (Gilchrist, 1977) whereby the molecules can react either as strong nucleophiles (e.g. with electrophilic acetylenes to form the 'delocalized sulphur-betaines')[33] (Gilchrist et al, 1976) or as electrophiles in hydrolytic reactions[25] (e.g. basic hydrolysis to form the sulphoxide and amine). The same similarity was

Table 3.III.1

No.	STRUCTURE VII	STRUCTURE VI
1	N(1) - C(7) - C(8) - S 2.2(3)	N(1) - C(7) - C(8) - S -9.0(2)
2	C(8) - C(7) - C(13) - O(6) -104.2(2)	C(8) - C(7) - C(13) - O(6) 113.5(2)
3	C(7) - C(13) - O(6) - C(14) -174.0(2)	C(7) - C(13) - O(6) - C(14) 174.4(1)
4	C(7) - C(8) - C(11) - O(4) -174.9(2)	C(7) - C(8) - C(11) - O(4) -178.9(2)
5	C(8) - C(11) - O(4) - C(12) -175.3(2)	C(8) - C(11) - O(4) - C(12) 177.2(2)
6	C(4) - N(1) - C(7) - C(8) -177.9(2)	C(4) - N(1) - C(7) - C(8) 173.6(2)
7	C(3) - C(4) - N(1) - C(7) 56.6(3)	C(5) - C(4) - N(1) - C(7) -52.6(3)
8	C(11) - C(8) - S 116.4(1)	C(11) - C(8) - S 116.9(1)
9	C(8) - C(7) - C(13) 118.0(2)	C(8) - C(7) - C(13) 117.0(1)
10	C(7) - N(1) - C(4) 122.8(2)	C(7) - N(1) - C(4) 122.9(1)
11	N(1) - C(4) - C(3) 123.3(2)	N(1) - C(4) - C(5) 123.1(2)
12	C(7) - C(13) 1.520(3) Å	C(7) - C(13) 1.525(3) Å

shown to exist in iminophosphoranes (e.g. A) (Hewlins, 1971)[80] and in phosphorus ylides whereby from the crystal structure analysis of A the trigonal arrangement of the nitrogen atom was revealed (the valency angle P-N-C being equal to 124.2°). Although the coplanarity of the aromatic ring and the P,N,C plane (in A) has been previously assumed (Schuster, 1967)[81] the latter analysis showed the p-bromophenyl ring to be tilted at 35° to the P, N, C plane. Nevertheless this latter observation does not appear to increase significantly the steric hindrance and like the iminosulphuranes (I and II), the iminophosphorane (A) can react either as a nucleophile [e.g. with electrophilic acetylenes to form the related 'delocalized phosphorus-betaines' [82] (B)] or as an electrophile (e.g. in hydrolysis).

A similar system containing the Ph_3 P = N - Ar system has also been described by Cameron and Prout (1969)[83] (C). As in the case of the two sulphimides where the S-N bond appears to have been significantly shortened (1.622 - 1.640 Å) with respect to Pauling's sum of covalent radii (1.74 Å)[50], the P-N bond (1.567 in A) appears to have been shortened to a relatively larger degree than the S-N bond (the sum of Pauling's covalent radii for P-N bond, corrected for electronegativity is 1.77 Å). However the different substituents on the sulphur and phosphorus atoms render difficult any direct comparison of these bonds as was previously noted by Johnson and Amel (1968)[84].

Unlike the N-arylsulphimides (I and II) the stabilized betaines

(structures III to VII) are not as reactive, a fact which has been rationalized in terms of a decreased basicity due to delocalization patterns and increased steric influence affecting the nucleophilicity of the nitrogen atom (3.11).

A few conformational features needed to reduce internal strain in those molecules were also described for a number of similar 'phosphorus betaines' [molecule B and molecule D (Gilardi and Karle, 1972)[85]]. Thus (i) out of plane torsion (S-C-C-N) is observed in the 'sulphur betaines' (-12° to 13°) and is also observed in B (15.5°, calculated by Karle from the coordinates given by Mak and Trotter[82]) and in D (-37°) for the P-C-C-N chain of atoms. This twisting has been suggested to originate (3.3) from the close contacts S ... C(benzoyl ring) or S ... O(methoxy), but deformations due to short contacts of the kind $-S(CH_3)_2$ ... N cannot be excluded.

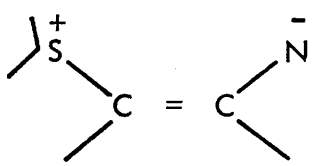
(ii) The benzoyl or methoxycarbonyl groups which are not attached to the C-S or C-P bonds are significantly rotated about the C-CO bonds (-90° to -114° in the 'sulphur betaines' and -69° in D). A similar twist of the methyl ester group occurs also in molecule B.

(iii) The ring systems attached to the iminonitrogen are in all cases rotated by $40-60^{\circ}$. In molecule D the corresponding torsion angle is equal to -61°.

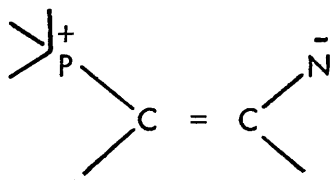
(iv) The valency angles at the C-C central framework of the 'sulphur and phosphorus betaines' appear to be significantly unequal (sections 3.3 - 3.7 and ref. 85).

(v) The C(central) - C(carbonyl) bond length (which is not attached to the C-S bond) is significantly lengthened in all the betaines (III to VII) (1.520 Å - 1.549 Å) though in the case of molecule D the corresponding bond length is only 1.507(9) Å. The bond lengthening is thought to be a result of the overcrowding in such molecules.

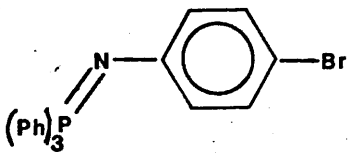
All other bonds involved in the 'through conjugation' effect are similar in all the molecules that were investigated. All examples which were found to possess the systems



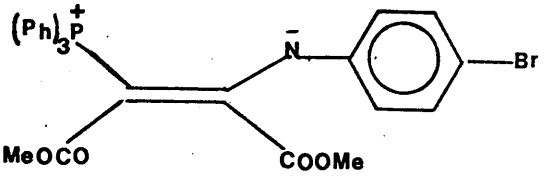
or



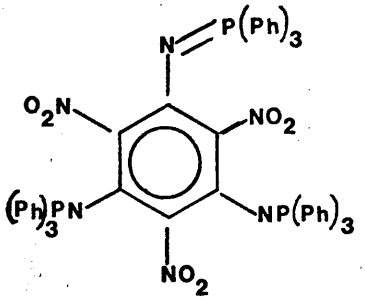
(E^{70}, F^{86}, G^{69} and H^{87}) exhibit similar patterns of delocalization and hence comparable bond lengths. The P-C bonds (e.g. 1.753 Å in D) and the S-C bonds [e.g. 1.736(3) in IV] are significantly shortened compared to Pauling's sum of covalent radii (corrected for electronegativity) (1.84 Å and 1.81 Å for P-C and S-C bonds respectively) though here too, direct comparison of the bonds is not feasible[84].



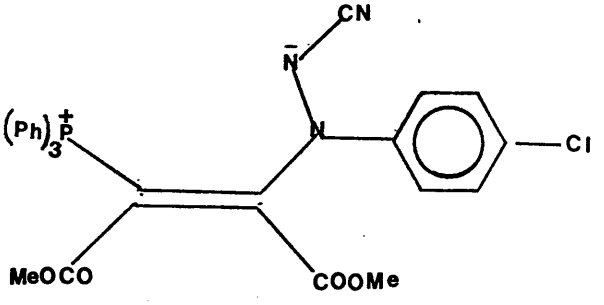
A



B



C



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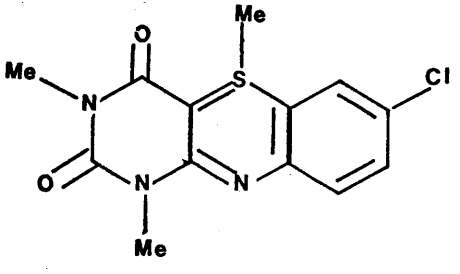

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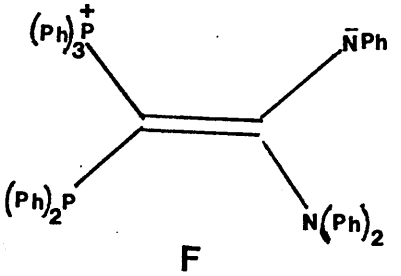

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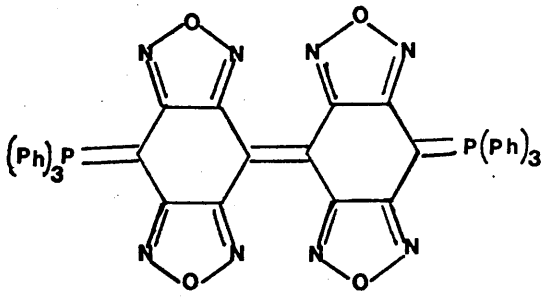
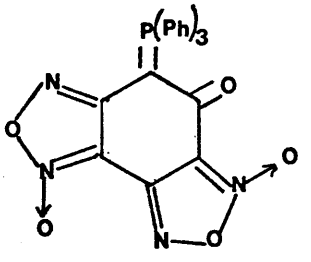


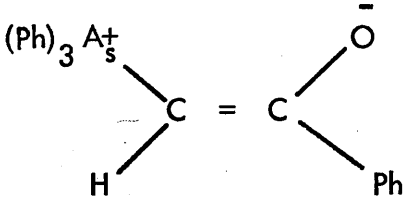
G



H

CHAPTER 4

THE CRYSTAL AND MOLECULAR STRUCTURE OF A BETAINE OF THE FORM

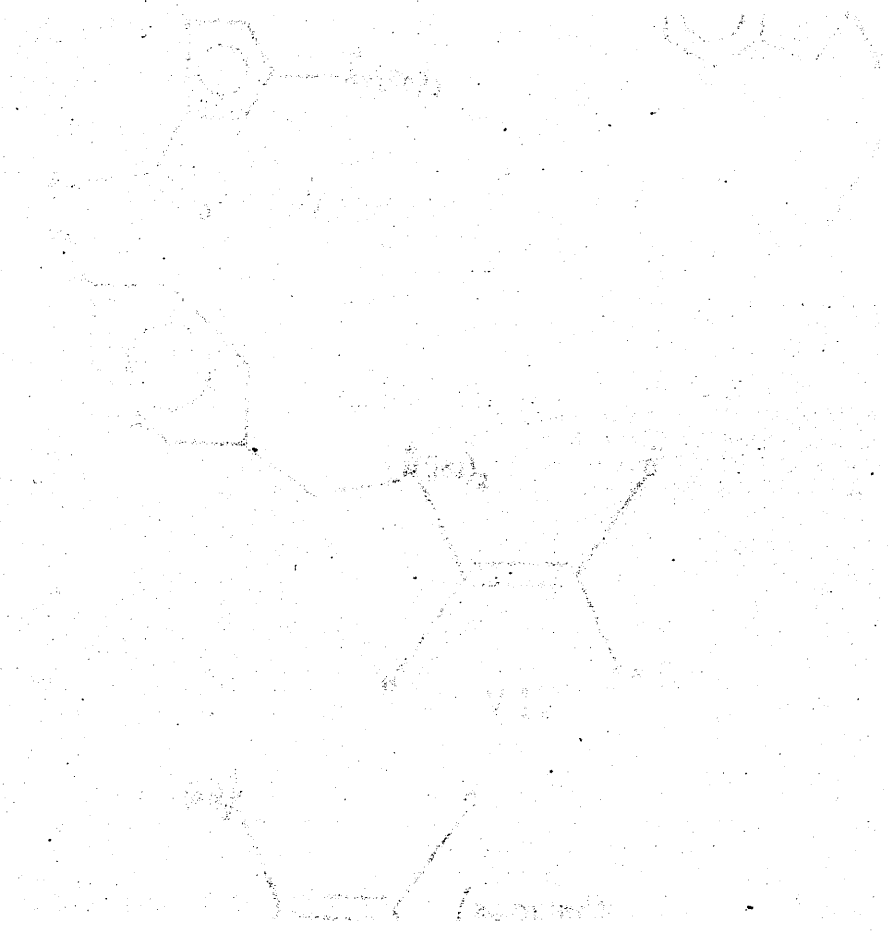


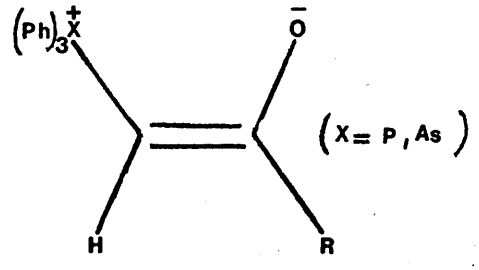
4.1 Introduction

The structures of β -ketostabilized ylides (I, R = Ph, p - $CH_3C_6H_4$, Me, p-$O_2NC_6H_4$ etc.) as well as of ester ylides (I, R = OMe) have been thoroughly investigated by the proton nuclear magnetic resonance technique[88] (Dale and Frϕyen, 1970 and references cited therein). As a result it was established that whereas the spectra of ester ylides (phosphorus, arsenic and sulphur ylides) and that of II (formylmethylidene triphenylphosphorane[89]) showed temperature dependence (cis/trans equilibria) there was no sign of internal rotation along the central C-C bond in the case of the β -ketostabilized ylides. Furthermore, on the bases of infrared data[88] the β -keto ylides were shown to exhibit a pronounced 'through conjugation effect' [ν_{CO} (cm^{-1}) = 1500 - 1540 for X = As and 1500 - 1582 for X = P] compared to the ester ylides [ν_{CO} (cm^{-1}) = 1585 - 1640 for X = As and 1565 - 1635 for X = P] . In similar - β carbonyl sulphonium ylides[90] (III) charge delocalization onto the oxygen atom was also found to be important [ν_{CO}(cm^{-1}) = 1470 - 1505] . Although X-ray analyses for several carbonyl stabilized arsonium ylides have been reported[91,92] (IV and V) [Ferguson and Rendle 1975, 1976 and references cited therein] no crystallographic work has been known to be carried out on phenacyl arsonium ylides (β - ketostabilized). Since spectroscopic data for the latter has been accumulated[88,93] and structural work for a few related carbonyl-stabilized ammonium ylides[94] (VI and VII) [Bailey, Hull, Kersting and Morrison, 1971] and phosphonium ylides[78-79] (VIII) [Speziale and Ratts, 1965 and Stephens,

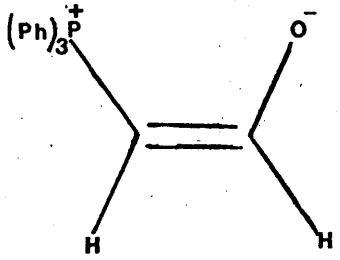
1965)] has been done, an X-ray structural study aiming at investigating the configurational characteristic and nature of stabilization in the arsonium ylide I(X = As, R = $-C_6H_5$) was initiated.

It should be noted that crystallographic and spectroscopic work concerning carbonyl-stabilized cyclic ylides (sulphonium and phosphonium) is also known to have been carried out[70,73,87,95-97]. However the X-ray analysis technique has been applied only for the compounds cited in references 70, 73, 87.

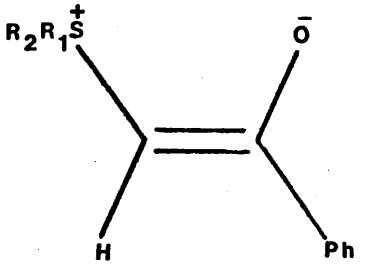




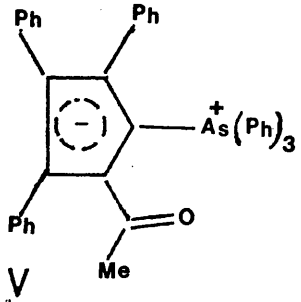
I



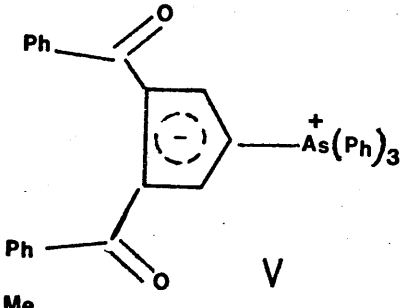
II



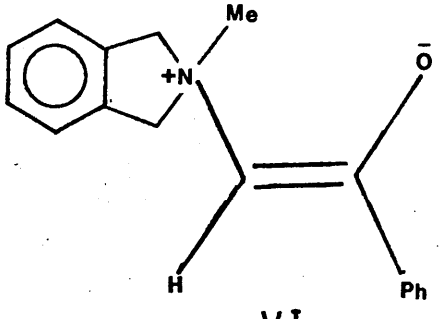
III



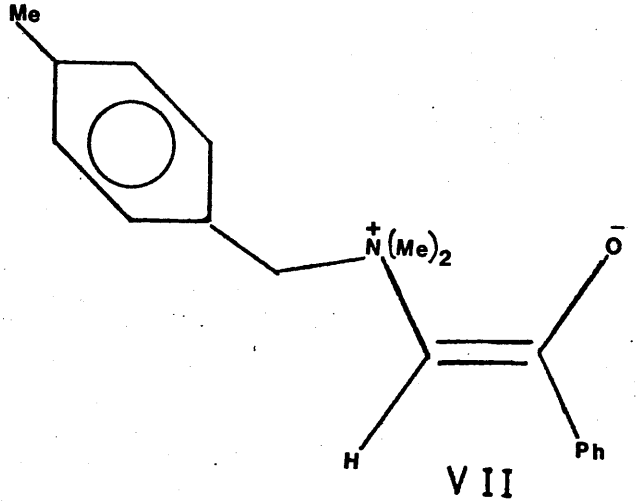
IV



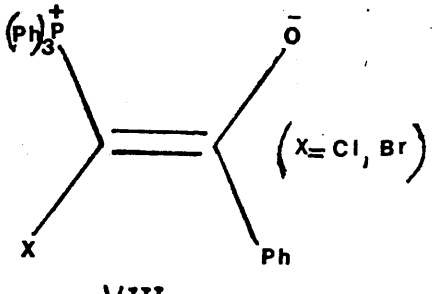
V



VI

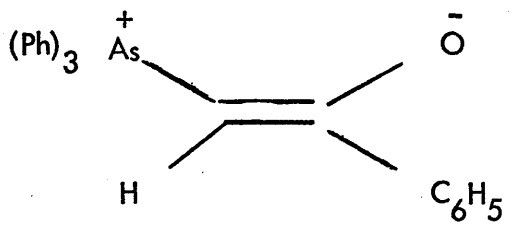


VII



VIII

Experimental and Results for I



I

Triphenylarsoniumphenacylide

Crystal Data

Molecular Formula	$C_{26}H_{21}OAs$
Molecular Weight	424.39 a.m.u.
Crystal System	Monoclinic
Unit Cell Dimensions	a = 19.343(2) Å
	b = 11.103(3) Å
	c = 23.859(3) Å
	β = 126.55(1)°
Unit Cell Volume	V = 4116.37 Å^3
Number of Molecules per Unit Cell	Z = 8
Calculated Density	D_c = 1.37 g.cm^{-3}
Number of Molecules per Asymmetric Unit	N = 2
Space Group	P2/c (C_{2h}^4, No.13)
Equivalent Positions	x,y,z
	-x, y, 1/2 - Z
Linear Absorption Coefficient	μ = 16.58 cm^{-1}
Number of Electrons per Unit Cell	F(000) = 1744

Data Collection

Diffractometer Used	Enraf-Nonius CAD-4
Radiation Used	$M_0 - K_\alpha$, $\overline{\lambda} = 0.7114$ Å
Filter	Graphite Monochromator
	$\cos^2 2\theta_m = 0.960$
Upper Limit for Data Collection	$2\theta_{max} = 50^\circ$
Number of Observed Independent Reflections	m = 3483
Unobserved Cut-Off	$2.0\ \sigma_I$
Number of Parameters Refined	n = 674
Number of Reflections per Parameter	m/n = 5.2

Structure Determination and Refinement

Systematic absences in the diffraction data (hol absent when l is odd) suggested the possible space groups Pc or P2/c. The N(Z) cumulative probability distribution and the distribution of $|E|$'s for the complete data set pointed towards a centric space group. A listing of 'average values' given in Table 4.1.1 seems to support this assumption.

The structure was solved in space group P2/c by application of the multisolution tangent formula technique using the computer program 'MULTAN'. The 400 highest normalized structure factors with $|E| > 1.83$ were used to generate 4000 Σ_2 relationships (7.1 $|E|$ values per atom and 10 Σ_2 relationships per $|E|$). Origin defining reflections and those constituting the starting set were chosen automatically by the program

and led to a successful phase determination. A three dimensional Fourier synthesis using the 400 normalized structure factors revealed the positions of 17 atoms in the asymmetric unit, while the missing atoms were subsequently located by successive 2 cycles of isotropic full matrix least-squares and a difference electron density calculation. The structure was further refined by 18 cycles of least-squares calculations minimizing the function $\sum w(|F_o| - |F_c|)^2$ and finally converged when R and R_w were 0.033 and 0.038 respectively. The standard deviation of an observation of unit weight was equal to 5.3487. Hydrogen atoms were located after cycle 14 and consequently their positional and isotropic thermal parameters were allowed to vary in the last 6 cycles of the refinement. The weighting scheme used, of the form $w = 1/\sigma^2(F_o)$ based on counting statistics, provided an approximately constant distribution of $\overline{w\Delta^2}$ with increasing $|F|$'s and hence was considered to be adequate. No absorption correction was applied and there were no significant residual peaks in the final difference Fourier map, the highest one being of $0.34\, e\text{Å}^{-3}$. The average and maximum values of the shift/σ for the atomic parameters in the last cycle of refinement were 0.07 and 0.42 respectively for all atoms. The various parameters used with MULTAN the transformation of phases from the 'MULTAN hemisphere of reflections' to the reflections in the data set collected ($\pm$h, -k, l) and the various stages in the least-squares refinement are all given in Tables 4.1.2 and 4.1.3.

A listing of the observed and calculated structure amplitudes with the appropriate phases is given in the supplement to this thesis. The scattering factors used for the atoms C, O and As were those given by Cromer and Mann (1968) and the one for H were those given by Stewart et al (1965). The crystal and molecular structure together with a numbering scheme are given in Figures 4.1.1(a) and 4.1.1(b). The atomic coordinates and thermal parameters, bond lengths, valency angles and torsion angles with e.s.d.'s and other relevant data are given in Tables 4.1.4 to 4.1.7.

Table 4.1.1

STATISTICAL ANALYSIS OF AVERAGE VALUES FOR CENTRIC AND ACENTRIC SPACE GROUPS.

EXPRESSION	EXPERIMENTAL VALUES	THEORETICAL VALUES	
		CENTRIC	ACENTRIC
$\overline{\text{MOD (E)}}$	0.824	0.798	0.886
$\overline{E^3}$	1.479	1.596	1.329
$\overline{E^4}$	2.486	3.0	2.0
$\overline{E^5}$	4.594	6.383	3.323
$\overline{E^6}$	9.164	15.0	6.0
$\overline{\text{MOD}(E^2 - 1)}$	0.903	0.968	0.736
$\overline{(E^2 - 1)^2}$	1.486	2.0	1.00

Table 4.1.2

SUMMARY OF THE CONDITIONS (INCLUDING VARIOUS FIGURES OF INTEREST) ASSOCIATED WITH SOLVING THE STRUCTURE OF I.

In this table:

1. NE - is the number of the largest $|E|$'s chosen to define the structure.
2. NSRT - is the number of Σ_2 relationships to be retained.
3. NSRTT - is the total number of Σ_2 relationships.
4. PROB - is the probability acceptance limit chosen for Σ_1.
5. NSPEC - is the number of special phases (permutations restricted to ϕ_{spec}, $\phi_{spec} + 180^\circ$).

   NGEN - is the number of general phases (phase permutation 45°, 135°, 225°, 315°).

   NANY - is the number of phases of either sort.
6. NSET - is the total number of phase sets that have been developed.
7. PUB - is the published phase.
8. NAT - is the number of nonhydrogen atoms in the asymmetric unit.
9. ABS FOM, PSI ZERO, RESID and CFOM are all figures of merit.

$C_{26}H_{21}OAs$, P2/c, NAT = 56

PARAMETERS		STARTING SET TYPE	hkl	PHI	PUB	RESULTS PHASE SET CONSIDERED	FIGURES OF MERIT ABS FOM	PSI ZERO	RESID	TOTAL NUMBER OF CORRECT PEAKS FOUND IN E-MAP
SIGMA - 2		SIGMA - 1	20,0,-14*	180	180	Max	1.2442	3.6	43.9	17
NE(|E| > 1.83)	400		2,0,-18	180	180	Min	0.6680	1.5	14.73	
NSRT	4000	Origin	17,6,-11	360	360	CFOM5 = 2.2208	1.2442	3.2	14.73	
NSRTT	7004	defining	3,2,-2	360	360					
CONVERGE		phases	12,1,-20	360	360					
PROB	0.95	Permuted	2,5,11	180 360	360					
NSPEC, NGEN, NANY	5,0,0	phases	13,1,0	180 360	360					
FASTAN			6,2,0	180 360	180					
NSET	32		6,4,-5	180 360	360					
			5,5,9	180 360	360					

*For space group P2/c in general, $\phi(h,k,l) = \phi(\bar{h},k,\bar{l}) + \pi l$. Therefore $\phi(2\ 0,0\ -14) = \phi(-20,0,14)$, etc.

Table 4.1.3

PROGRESS OF LEAST-SQUARES REFINEMENT

CYCLES	PARAMETERS REFINED	R	R_w
2	x,y,z $U_{(iso)}$ for only 17 non hydrogen atoms (out of 56); scale factor; unit weights; full matrix.	0.267	0.362
6	x,y,z,$U_{(iso)}$ for C, O, As atoms; scale factor; unit weights; block diagonal.	0.067	0.073
6	x,y,z,U_{ij}, for C, O, As atoms; scale factor; unit weights; block diagonal.	0.048	0.055
4	x,y,z,U_{ij} for C, O, As atoms; Hydrogen atoms - contributing to the structure factor calculations but their positional and thermal parameters not varied; scale factor; block diagonal; unit weights.	0.037	0.040
6	x,y,z U_{ij} for C, O, As atoms; x,y,z,$U_{(iso)}$ for H atoms; scale factor; weights from counting statistics; cycles 3 and 4 with damping factor of 0.8 and cycles 5 and 6 with damping factor of 0.5.	0.033	0.038

Table 4.1.4(a,b,c,d)

(a) Fractional atomic coordinates ($\times 10^4$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM X/A Y/B Z/C

(b) Anisotropic thermal parameters (Å^2, $\times 10^3$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}

(c) Fractional atomic coordinates ($\times 10^3$) of hydrogen atoms with e.s.d.'s in parentheses. The hydrogens are numbered according to the atoms to which they are attached.

(d) Isotropic thermal parameters (Å^2, $\times 10^2$) of hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM $U_{(iso)}$.

C(1)	-0969(3)	-2941(5)	0761(3)
C(2)	-0533(4)	-2709(5)	0484(3)
C(3)	0008(3)	-1739(5)	0705(2)
C(4)	0102(3)	-0966(4)	1205(2)
C(5)	-0334(3)	-1209(4)	1488(3)
C(6)	-0867(3)	-2186(5)	1263(3)
C(7)	2221(4)	0946(6)	3872(3)
C(8)	1666(6)	1775(6)	3438(4)
C(9)	1207(5)	1642(5)	2717(3)
C(10)	1357(3)	0683(5)	2461(2)
C(11)	1928(4)	-0185(6)	2908(3)
C(12)	2361(4)	-0043(6)	3621(3)
C(13)	-1086(4)	3673(5)	0259(3)
C(14)	-1408(3)	2542(6)	0164(3)
C(15)	-0869(3)	1583(5)	0533(3)
C(16)	0006(3)	1778(4)	0992(2)
C(17)	0324(3)	2918(5)	1080(3)
C(18)	-0226(4)	3863(5)	0704(3)
C(19)	3856(4)	0391(6)	0864(4)
C(20)	4112(4)	-0314(6)	1429(4)
C(21)	3553(3)	-0513(5)	1603(3)
C(22)	2750(3)	-0016(4)	1221(2)
C(23)	2506(3)	0682(5)	0645(3)
C(24)	3061(4)	0877(5)	0469(3)
C(25)	2177(3)	-0204(4)	1447(2)
C(26)	1483(3)	0545(4)	1180(2)
O(1)	2373(2)	-1024(3)	1885(2)
AS(1)	0793(0)	0464(0)	1469(0)
C(27)	5524(4)	8640(5)	0979(3)
C(28)	5816(3)	7987(5)	1573(3)
C(29)	5426(3)	6911(5)	1518(3)
C(30)	4740(3)	6497(4)	0870(3)
C(31)	4452(3)	7173(5)	0281(3)
C(32)	4854(4)	8231(6)	0343(3)
C(33)	6536(4)	2246(6)	2122(3)

C(34)	6547(4)	3084(6)	1708(3)
C(35)	5877(4)	3884(6)	1329(3)
C(36)	5203(3)	3878(4)	1370(2)
C(37)	5210(4)	3067(6)	1806(3)
C(38)	5882(4)	2262(6)	2178(3)
C(39)	2539(3)	5069(5)	1573(3)
C(40)	2607(4)	4031(5)	1300(3)
C(41)	3110(3)	4003(5)	1063(3)
C(42)	3556(3)	5014(5)	1118(2)
C(43)	3482(3)	6069(5)	1388(3)
C(44)	2958(3)	6089(5)	1605(3)
C(45)	1258(4)	3839(5)	-2744(3)
C(46)	0958(3)	4615(6)	-2483(3)
C(47)	1485(3)	4941(5)	-1786(2)
C(48)	2308(3)	4475(4)	-1341(2)
C(49)	2580(3)	3690(5)	-1618(3)
C(50)	2057(4)	3383(5)	-2317(3)
C(51)	2871(3)	4891(4)	-0592(2)
C(52)	3638(3)	4306(4)	-0112(2)
O(2)	2626(2)	5777(3)	-0427(2)
AS(2)	4239(0)	4935(0)	0772(0)

4.1.4 (a) (continued)

C(1)	58(4)	39(3)	67(4)	-1(3)	25(3)	16(3)
C(2)	63(4)	45(3)	42(3)	4(3)	22(3)	-1(3)
C(3)	47(3)	48(3)	37(3)	5(3)	21(3)	5(2)
C(4)	39(3)	36(3)	37(3)	8(2)	19(2)	5(2)
C(5)	63(4)	38(3)	65(4)	-3(3)	44(3)	-1(3)
C(6)	65(4)	53(4)	73(4)	-2(3)	47(3)	5(3)
C(7)	86(5)	97(5)	44(4)	-21(4)	36(4)	-6(3)
C(8)	185(8)	52(4)	73(5)	10(5)	87(6)	-4(4)
C(9)	141(6)	53(4)	58(4)	31(4)	62(4)	15(3)
C(10)	43(3)	54(4)	35(3)	-7(3)	23(3)	-2(3)
C(11)	88(4)	89(5)	52(4)	31(4)	41(4)	11(3)
C(12)	83(4)	128(6)	50(3)	37(4)	40(3)	26(4)
C(13)	78(4)	51(4)	60(4)	32(3)	32(3)	17(3)
C(14)	48(4)	74(5)	67(4)	19(3)	19(3)	11(3)
C(15)	46(3)	48(3)	55(3)	8(3)	23(3)	5(3)
C(16)	43(3)	40(3)	36(3)	10(2)	24(3)	7(2)
C(17)	45(3)	52(4)	53(4)	6(3)	20(3)	9(3)
C(18)	83(4)	35(3)	76(4)	5(3)	39(4)	5(3)
C(19)	85(5)	82(5)	105(5)	0(4)	78(4)	-4(4)
C(20)	54(4)	96(5)	104(5)	22(4)	52(4)	9(4)
C(21)	55(4)	67(4)	65(4)	13(3)	39(3)	8(3)
C(22)	38(3)	43(3)	44(3)	5(2)	24(2)	-4(3)
C(23)	51(3)	52(3)	54(3)	3(3)	33(3)	-3(3)
C(24)	68(4)	65(4)	68(4)	9(3)	50(3)	4(3)
C(25)	42(3)	38(3)	39(3)	1(2)	21(2)	-5(2)
C(26)	42(3)	43(3)	43(3)	10(3)	25(2)	12(2)
O(1)	62(2)	61(2)	61(2)	21(2)	40(2)	23(2)
AS(1)	37(0)	38(0)	38(0)	5(0)	22(0)	4(0)
C(27)	64(4)	53(4)	118(5)	-10(3)	60(4)	-12(3)
C(28)	50(3)	70(4)	76(4)	-7(3)	36(3)	-27(3)
C(29)	46(3)	67(4)	51(4)	-3(3)	27(3)	-8(3)
C(30)	38(3)	52(3)	51(3)	4(2)	27(3)	-2(3)
C(31)	54(4)	69(4)	51(4)	-6(3)	26(3)	3(3)
C(32)	85(5)	71(5)	79(5)	-8(4)	49(4)	14(3)
C(33)	59(4)	86(5)	62(4)	39(4)	19(3)	17(3)

C(34)	64(4)	118(6)	78(5)	39(4)	45(4)	22(4)
C(35)	63(4)	91(5)	71(4)	26(4)	45(4)	23(4)
C(36)	45(3)	51(3)	34(3)	7(3)	19(3)	0(3)
C(37)	55(4)	81(5)	69(4)	11(3)	32(3)	27(4)
C(38)	69(4)	89(5)	79(5)	16(4)	32(4)	39(4)
C(39)	52(3)	96(4)	56(3)	0(3)	37(3)	0(3)
C(40)	60(4)	77(4)	69(4)	-9(3)	41(4)	0(3)
C(41)	53(4)	53(4)	64(4)	-6(3)	33(3)	-6(3)
C(42)	38(3)	59(3)	34(3)	9(3)	19(2)	2(3)
C(43)	47(3)	65(4)	41(3)	0(3)	23(3)	-3(3)
C(44)	55(4)	76(4)	56(4)	9(3)	35(3)	-11(3)
C(45)	63(4)	77(4)	41(3)	-17(3)	25(3)	-12(3)
C(46)	44(3)	90(5)	49(3)	5(3)	17(3)	3(3)
C(47)	45(3)	59(3)	44(3)	0(3)	22(3)	-1(3)
C(48)	39(3)	43(3)	36(3)	-9(2)	23(2)	-5(2)
C(49)	47(3)	75(4)	36(3)	7(3)	19(3)	-2(3)
C(50)	78(4)	60(4)	48(4)	-9(3)	39(3)	-14(3)
C(51)	46(3)	43(3)	39(3)	2(2)	26(2)	1(2)
C(52)	51(3)	49(3)	34(3)	4(3)	22(3)	-8(2)
O(2)	61(2)	62(2)	46(2)	18(2)	28(2)	-5(2)
AS(2)	39(0)	49(0)	33(0)	5(0)	18(0)	0(0)

4.1.4 (b) (continued)

H(1)	-122(3)	-353(4)	070(2)
H(2)	-062(2)	-321(3)	016(2)
H(3)	035(2)	-151(3)	057(2)
H(5)	-019(3)	-068(4)	188(2)
H(6)	-115(3)	-234(4)	142(2)
H(7)	246(3)	099(5)	436(3)
H(8)	164(3)	246(4)	362(3)
H(9)	089(3)	222(4)	244(2)
H(11)	197(3)	-087(4)	273(2)
H(12)	265(3)	-067(5)	386(3)
H(13)	-141(2)	422(3)	002(2)
H(14)	-199(3)	240(4)	-012(2)
H(15)	-105(3)	075(4)	050(2)
H(17)	086(2)	304(3)	135(2)
H(18)	001(2)	459(3)	077(2)
H(19)	419(3)	055(5)	078(3)
H(20)	457(3)	-059(4)	170(2)
H(21)	368(2)	-104(3)	197(2)
H(23)	191(3)	101(4)	037(2)
H(24)	284(3)	140(4)	007(2)
H(26)	133(2)	110(3)	089(2)
H(27)	587(2)	933(3)	107(2)
H(28)	636(3)	818(5)	204(3)
H(29)	561(3)	639(4)	192(2)
H(31)	397(3)	685(4)	-013(2)
H(32)	462(3)	871(4)	-008(2)
H(33)	705(3)	173(4)	239(2)
H(34)	703(3)	305(4)	169(2)
H(35)	586(3)	439(4)	107(3)
H(37)	473(3)	312(5)	178(3)
H(38)	585(3)	175(4)	243(2)
H(39)	212(3)	503(4)	168(3)
H(40)	228(3)	333(4)	128(2)
H(41)	310(3)	332(5)	086(3)
H(43)	372(3)	677(4)	135(2)

H(44)	288(2)	680(3)	176(2)
H(45)	086(3)	362(5)	-324(3)
H(46)	041(3)	492(4)	-272(2)
H(47)	129(3)	544(4)	-159(2)
H(49)	308(2)	343(3)	-135(2)
H(50)	222(3)	278(4)	-248(2)
H(52)	387(2)	364(3)	-018(2)

4.1.4 (c) (continued)

H(1)	6(1)	H(44)	4(1)
H(2)	5(1)		
H(3)	5(1)	H(45)	11(2)
H(5)	7(2)		
H(6)	7(2)	H(46)	7(1)
H(7)	10(2)		
H(8)	9(2)	H(47)	6(1)
H(9)	5(1)		
H(11)	9(2)	H(49)	2(1)
H(12)	9(2)		
H(13)	4(1)	H(50)	8(2)
H(14)	8(2)		
H(15)	8(2)	H(52)	3(1)
H(17)	2(1)		
H(18)	5(1)		
H(19)	9(2)		
H(20)	8(2)		
H(21)	5(1)		
H(23)	6(1)		
H(24)	6(1)		
H(26)	2(1)		
H(27)	5(1)		
H(28)	10(2)		
H(29)	7(2)		
H(31)	5(1)		
H(32)	8(2)		
H(33)	8(2)		
H(34)	6(1)		
H(35)	9(2)		
H(37)	10(2)		
H(38)	8(2)		
H(39)	8(2)		
H(40)	8(2)		
H(41)	10(2)		
H(43)	7(2)		

Table 4.1.5 (a,b,c)

(a) Interatomic distances ($\mathring{A}$) with e.s.d.'s in parentheses. The hydrogen atoms are numbered according to the atoms to which they are attached.

(b) Interbond angles (degrees) with e.s.d.'s (degrees) in parentheses.

(c) Torsion angles (degrees) with e.s.d.'s (degrees) in parentheses. A torsion angle A-B-C-D is considered to be positive if when viewed down the B-C bond the A-B bond will eclipse the C-D bond when rotated less than 180° in a clockwise direction.

C(1) - C(2)	1.370(12)	C(27) - C(28)	1.378(10)
C(1) - C(6)	1.376(10)	C(27) - C(32)	1.359(7)
C(2) - C(3)	1.370(8)	C(28) - C(29)	1.377(9)
C(3) - C(4)	1.391(8)	C(29) - C(30)	1.384(6)
C(4) - C(5)	1.384(11)	C(30) - C(31)	1.383(8)
C(4) - AS(1)	1.924(5)	C(30) - AS(2)	1.932(5)
C(5) - C(6)	1.366(7)	C(31) - C(32)	1.368(9)
C(7) - C(8)	1.322(9)	C(33) - C(34)	1.364(11)
C(7) - C(12)	1.354(11)	C(33) - C(38)	1.349(12)
C(8) - C(9)	1.397(10)	C(34) - C(35)	1.374(8)
C(9) - C(10)	1.343(10)	C(35) - C(36)	1.367(11)
C(10) - C(11)	1.372(7)	C(36) - C(37)	1.368(10)
C(10) - AS(1)	1.944(5)	C(36) - AS(2)	1.929(4)
C(11) - C(12)	1.388(9)	C(37) - C(38)	1.380(8)
C(13) - C(14)	1.360(9)	C(39) - C(40)	1.368(9)
C(13) - C(18)	1.355(8)	C(39) - C(44)	1.367(9)
C(14) - C(15)	1.379(8)	C(40) - C(41)	1.387(12)
C(15) - C(16)	1.379(7)	C(41) - C(42)	1.373(8)
C(16) - C(17)	1.368(7)	C(42) - C(43)	1.384(9)
C(16) - AS(1)	1.919(4)	C(42) - AS(2)	1.933(7)
C(17) - C(18)	1.378(7)	C(43) - C(44)	1.386(11)
C(19) - C(20)	1.372(11)	C(45) - C(46)	1.376(11)
C(19) - C(24)	1.349(8)	C(45) - C(50)	1.345(8)
C(20) - C(21)	1.388(13)	C(46) - C(47)	1.385(7)
C(21) - C(22)	1.364(7)	C(47) - C(48)	1.383(6)
C(22) - C(23)	1.392(8)	C(48) - C(49)	1.373(9)
C(22) - C(25)	1.507(10)	C(48) - C(51)	1.508(6)
C(23) - C(24)	1.383(11)	C(49) - C(50)	1.383(7)
C(25) - C(26)	1.372(7)	C(51) - C(52)	1.382(6)
C(25) - O(1)	1.263(6)	C(51) - O(2)	1.253(7)
C(26) - AS(1)	1.834(7)	C(52) - AS(2)	1.835(5)

C(1) - H(1)	0.776(44)	C(27) - H(27)	0.952(42)
C(2) - H(2)	0.879(46)	C(28) - H(28)	0.998(42)
C(3) - H(3)	0.928(58)	C(29) - H(29)	0.982(49)
C(5) - H(5)	0.992(51)	C(31) - H(31)	0.934(34)
C(6) - H(6)	0.861(68)	C(32) - H(32)	0.976(51)
C(7) - H(7)	0.964(61)	C(33) - H(33)	0.988(45)
C(8) - H(8)	0.888(56)	C(34) - H(34)	0.961(63)
C(9) - H(9)	0.862(37)	C(35) - H(35)	0.815(62)
C(11) - H(11)	0.894(57)	C(37) - H(37)	0.902(72)
C(12) - H(12)	0.869(48)	C(38) - H(38)	0.849(59)
C(13) - H(13)	0.816(35)	C(39) - H(39)	0.995(74)
C(14) - H(14)	0.915(47)	C(40) - H(40)	0.985(56)
C(15) - H(15)	0.978(48)	C(41) - H(41)	0.890(58)
C(17) - H(17)	0.851(33)	C(43) - H(43)	0.935(53)
C(18) - H(18)	0.896(40)	C(44) - H(44)	0.923(44)
C(19) - H(19)	0.803(75)	C(45) - H(45)	0.980(51)
C(20) - H(20)	0.782(41)	C(46) - H(46)	0.920(45)
C(21) - H(21)	0.958(45)	C(47) - H(47)	0.949(57)
C(23) - H(23)	0.989(42)	C(49) - H(49)	0.832(31)
C(24) - H(24)	0.970(45)	C(50) - H(50)	0.906(59)
C(26) - H(26)	0.841(35)	C(52) - H(52)	0.935(41)

4.1.5 (a) (continued)

C(6) - C(1) - C(2)	119.56(57)	C(3) - C(2) - C(1)	120.71(52)
C(5) - C(6) - C(1)	120.70(68)	C(4) - C(3) - C(2)	119.65(60)
C(5) - C(4) - C(3)	119.48(49)	AS(1) - C(4) - C(3)	120.01(45)
AS(1) - C(4) - C(5)	120.46(35)	C(6) - C(5) - C(4)	119.87(52)
C(10) - AS(1) - C(4)	106.18(22)	C(16) - AS(1) - C(4)	106.41(23)
C(26) - AS(1) - C(4)	115.91(23)	C(12) - C(7) - C(8)	120.13(59)
C(9) - C(8) - C(7)	121.02(70)	C(11) - C(12) - C(7)	120.05(61)
C(10) - C(9) - C(8)	119.50(62)	C(11) - C(10) - C(9)	119.80(50)
AS(1) - C(10) - C(9)	122.42(41)	AS(1) - C(10) - C(11)	117.77(42)
C(12) - C(11) - C(10)	119.42(61)	C(16) - AS(1) - C(10)	107.43(22)
C(26) - AS(1) - C(10)	116.46(24)	C(18) - C(13) - C(14)	120.10(59)
C(15) - C(14) - C(13)	120.61(64)	C(17) - C(18) - C(13)	120.19(55)
C(16) - C(15) - C(14)	119.27(53)	C(17) - C(16) - C(15)	119.67(49)
AS(1) - C(16) - C(15)	121.07(37)	AS(1) - C(16) - C(17)	119.16(45)
C(18) - C(17) - C(16)	120.12(59)	C(26) - AS(1) - C(16)	103.72(24)
C(24) - C(19) - C(20)	120.58(82)	C(21) - C(20) - C(19)	119.66(74)
C(23) - C(24) - C(19)	119.62(58)	C(22) - C(21) - C(20)	121.10(55)
C(23) - C(22) - C(21)	117.80(60)	C(25) - C(22) - C(21)	119.44(47)
C(25) - C(22) - C(23)	122.74(53)	C(24) - C(23) - C(22)	121.23(57)
C(26) - C(25) - C(22)	118.35(44)	O(1) - C(25) - C(22)	118.29(51)
O(1) - C(25) - C(26)	123.34(59)	AS(1) - C(26) - C(25)	121.77(39)
C(32) - C(27) - C(28)	120.43(60)	C(29) - C(28) - C(27)	119.56(55)
C(31) - C(32) - C(27)	120.67(59)	C(30) - C(29) - C(28)	120.00(51)
C(31) - C(30) - C(29)	119.53(53)	AS(2) - C(30) - C(29)	120.70(40)
AS(2) - C(30) - C(31)	119.61(41)	C(32) - C(31) - C(30)	119.80(54)
C(36) - AS(2) - C(30)	105.25(25)	C(42) - AS(2) - C(30)	109.22(25)
C(52) - AS(2) - C(30)	114.18(23)	C(38) - C(33) - C(34)	118.83(66)
C(35) - C(34) - C(33)	120.21(78)	C(37) - C(38) - C(33)	121.60(65)
C(36) - C(35) - C(34)	120.93(62)	C(37) - C(36) - C(35)	118.68(58)
AS(2) - C(36) - C(35)	119.11(41)	AS(2) - C(36) - C(37)	122.08(55)
C(38) - C(37) - C(36)	119.66(75)	C(42) - AS(2) - C(36)	108.45(24)
C(52) - AS(2) - C(36)	106.90(22)	C(44) - C(39) - C(40)	120.19(67)

C(41) - C(40) - C(39)	120.15(61)		C(43) - C(44) - C(39)	120.43(56)	
C(42) - C(41) - C(40)	119.69(55)		C(43) - C(42) - C(41)	120.23(61)	
AS(2) - C(42) - C(41)	118.13(45)		AS(2) - C(42) - C(43)	121.59(47)	
C(44) - C(43) - C(42)	119.24(56)		C(52) - AS(2) - C(42)	112.42(26)	
C(50) - C(45) - C(46)	119.81(51)		C(47) - C(46) - C(45)	120.00(59)	
C(49) - C(50) - C(45)	120.29(61)		C(48) - C(47) - C(46)	120.75(56)	
C(49) - C(48) - C(47)	117.61(44)		C(51) - C(48) - C(47)	118.94(49)	
C(51) - C(48) - C(49)	123.39(50)		C(50) - C(49) - C(48)	121.53(57)	
C(52) - C(51) - C(48)	120.03(47)		O(2) - C(51) - C(48)	118.09(46)	
O(2) - C(51) - C(52)	121.88(43)		AS(2) - C(52) - C(51)	114.05(39)	
As(1) - C(26) - H(26)	112(3)		As(2) - C(52) - H(52)	118(2)	
C(25) - C(26) - H(26)	126(3)		C(51) - C(52) - H(52)	128(2)	

4.1.5 b (continued)

C(6) - C(1) - C(2) - C(3)	0.6(9)	C(2) - C(1) - C(6) - C(5)	-0.2(10)
C(1) - C(2) - C(3) - C(4)	-1.5(9)	C(2) - C(3) - C(4) - C(5)	2.0(8)
C(2) - C(3) - C(4) - AS(1)	-175.3(4)	C(3) - C(4) - C(5) - C(6)	-1.6(8)
AS(1) - C(4) - C(5) - C(6)	175.7(5)	C(3) - C(4) - AS(1) - C(10)	-144.2(4)
C(3) - C(4) - AS(1) - C(16)	101.6(5)	C(3) - C(4) - AS(1) - C(26)	-13.1(5)
C(5) - C(4) - AS(1) - C(10)	38.5(5)	C(5) - C(4) - AS(1) - C(16)	-75.7(5)
C(5) - C(4) - AS(1) - C(26)	169.6(4)	C(4) - C(5) - C(6) - C(1)	0.7(9)
C(12) - C(7) - C(8) - C(9)	1.0(13)	C(8) - C(7) - C(12) - C(11)	0.5(11)
C(7) - C(8) - C(9) - C(10)	-2.8(12)	C(8) - C(9) - C(10) - C(11)	3.1(10)
C(8) - C(9) - C(10) - AS(1)	-176.8(6)	C(9) - C(10) - C(11) - C(12)	-1.6(10)
AS(1) - C(10) - C(11) - C(12)	178.2(5)	C(9) - C(10) - AS(1) - C(4)	-116.3(6)
C(9) - C(10) - AS(1) - C(16)	-2.7(6)	C(9) - C(10) - AS(1) - C(26)	113.0(6)
C(11) - C(10) - AS(1) - C(4)	63.9(5)	C(11) - C(10) - AS(1) - C(16)	177.5(5)
C(11) - C(10) - AS(1) - C(26)	-66.8(5)	C(10) - C(11) - C(12) - C(7)	-0.2(11)
C(18) - C(13) - C(14) - C(15)	1.7(10)	C(14) - C(13) - C(18) - C(17)	-2.0(10)
C(13) - C(14) - C(15) - C(16)	-1.1(10)	C(14) - C(15) - C(16) - C(17)	0.6(9)
C(14) - C(15) - C(16) - AS(1)	-175.6(5)	C(15) - C(16) - C(17) - C(18)	-0.8(9)
AS(1) - C(16) - C(17) - C(18)	175.5(5)	C(15) - C(16) - AS(1) - C(4)	-3.2(5)
C(15) - C(16) - AS(1) - C(10)	-116.6(5)	C(15) - C(16) - AS(1) - C(26)	119.6(5)
C(17) - C(16) - AS(1) - C(4)	-179.4(4)	C(17) - C(16) - AS(1) - C(10)	67.2(5)
C(17) - C(16) - AS(1) - C(26)	-56.7(5)	C(16) - C(17) - C(18) - C(13)	1.5(10)
C(24) - C(19) - C(20) - C(21)	-1.0(11)	C(20) - C(19) - C(24) - C(23)	1.3(11)
C(19) - C(20) - C(21) - C(22)	-0.1(11)	C(20) - C(21) - C(22) - C(23)	0.9(9)
C(20) - C(21) - C(22) - C(25)	-177.0(6)	C(21) - C(22) - C(23) - C(24)	-0.6(9)
C(25) - C(22) - C(23) - C(24)	177.3(5)	C(21) - C(22) - C(25) - C(26)	162.8(5)
C(21) - C(22) - C(25) - O(1)	-15.6(8)	C(23) - C(22) - C(25) - C(26)	-15.0(8)
C(23) - C(22) - C(25) - O(1)	166.6(5)	C(22) - C(23) - C(24) - C(19)	-0.5(10)
C(22) - C(25) - C(26) - AS(1)	-175.5(4)	O(1) - C(25) - C(26) - AS(1)	2.8(8)
C(25) - C(26) - AS(1) - C(4)	-68.4(5)	C(25) - C(26) - AS(1) - C(10)	57.6(5)
C(25) - C(26) - AS(1) - C(16)	175.3(4)	C(32) - C(27) - C(28) - C(29)	0.3(10)
C(28) - C(27) - C(32) - C(31)	0.7(11)	C(27) - C(28) - C(29) - C(30)	-0.6(10)
C(28) - C(29) - C(30) - C(31)	-0.1(9)	C(28) - C(29) - C(30) - AS(2)	175.3(5)

C(29) - C(30) - C(31) - C(32)	1.0(9)	AS(2) - C(30) - C(31) - C(32)	-174.4(5)
C(29) - C(30) - AS(2) - C(36)	-41.7(5)	C(29) - C(30) - AS(2) - C(42)	74.6(5)
C(29) - C(30) - AS(2) - C(52)	-158.6(5)	C(31) - C(30) - AS(2) - C(36)	133.7(5)
C(31) - C(30) - AS(2) - C(42)	-110.0(5)	C(31) - C(30) - AS(2) - C(52)	16.8(6)
C(30) - C(31) - C(32) - C(27)	-1.3(11)	C(38) - C(33) - C(34) - C(35)	-3.5(11)
C(34) - C(33) - C(38) - C(37)	2.8(11)	C(33) - C(34) - C(35) - C(36)	1.7(11)
C(34) - C(35) - C(36) - C(37)	0.8(10)	C(34) - C(35) - C(36) - AS(2)	-175.2(5)
C(35) - C(36) - C(37) - C(38)	-1.4(10)	AS(2) - C(36) - C(37) - C(38)	174.5(5)
C(35) - C(36) - AS(2) - C(30)	-48.8(5)	C(35) - C(36) - AS(2) - C(42)	-165.5(5)
C(35) - C(36) - AS(2) - C(52)	73.0(5)	C(37) - C(36) - AS(2) - C(30)	135.4(5)
C(37) - C(36) - AS(2) - C(42)	18.6(6)	C(37) - C(36) - AS(2) - C(52)	-102.9(5)
C(36) - C(37) - C(38) - C(33)	-0.4(11)	C(44) - C(39) - C(40) - C(41)	1.0(10)
C(40) - C(39) - C(44) - C(43)	-2.6(10)	C(39) - C(40) - C(41) - C(42)	1.4(10)
C(40) - C(41) - C(42) - C(43)	-2.1(9)	C(40) - C(41) - C(42) - AS(2)	-179.4(5)
C(41) - C(42) - C(43) - C(44)	0.5(9)	AS(2) - C(42) - C(43) - C(44)	177.6(5)
C(41) - C(42) - AS(2) - C(30)	176.9(5)	C(41) - C(42) - AS(2) - C(36)	-68.9(5)
C(41) - C(42) - AS(2) - C(52)	49.1(5)	C(43) - C(42) - AS(2) - C(30)	-0.3(5)
C(43) - C(42) - AS(2) - C(36)	113.9(5)	C(43) - C(42) - AS(2) - C(52)	-128.1(5)
C(42) - C(43) - C(44) - C(39)	1.9(9)	C(50) - C(45) - C(46) - C(47)	1.2(10)
C(46) - C(45) - C(50) - C(49)	0.0(10)	C(45) - C(46) - C(47) - C(48)	-1.5(9)
C(46) - C(47) - C(48) - C(49)	0.5(8)	C(46) - C(47) - C(48) - C(51)	177.7(5)
C(47) - C(48) - C(49) - C(50)	0.6(9)	C(51) - C(48) - C(49) - C(50)	-176.4(5)
C(47) - C(48) - C(51) - C(52)	169.7(5)	C(47) - C(48) - C(51) - O(2)	-10.8(8)
C(49) - C(48) - C(51) - C(52)	-13.3(8)	C(49) - C(48) - C(51) - O(2)	166.1(5)
C(48) - C(49) - C(50) - C(45)	-0.9(9)	C(48) - C(51) - C(52) - AS(2)	179.9(4)
O(2) - C(51) - C(52) - AS(2)	0.5(7)	C(51) - C(52) - AS(2) - C(30)	-70.7(5)
C(51) - C(52) - AS(2) - C(36)	173.3(4)	C(51) - C(52) - AS(2) - C(42)	54.4(5)

4.1.5 (c) (continued)

Table 4.1.6

A. Selected intramolecular non-bonded distances (<4.0 Å).

C(3) ... C(26)	3.46	C(30) ... O(2)	3.44
C(4) ... C(11)	3.55	C(31) ... C(51)	3.54
C(4) ... C(15)	3.24	C(31) ... C(52)	3.42
C(4) ... O(1)	3.67	C(31) ... O(2)	3.26
C(5) ... C(10)	3.38	C(37) ... C(41)	3.48
C(3) ... O(1)	3.76	C(37) ... C(42)	3.37
C(9) ... C(16)	3.31	C(38) ... C(40)	3.60
C(9) ... C(17)	3.50	C(41) ... C(52)	3.53
C(10) ... O(1)	3.55	C(41) ... O(2)	3.66
C(11) ... O(1)	3.17	C(42) ... C(51)	3.46
C(17) ... C(26)	3.37	C(42) ... O(2)	3.11
C(21) ... O(1)	2.79	C(43) ... O(2)	3.61
C(23) ... C(26)	2.93	C(47) ... O(2)	2.78
O(1) ... As(1)	3.07	C(49) ... C(52)	2.97
O(1) ... H(11)	2.57	O(2) ... As(2)	2.86
O(1) ... H(21)	2.41	O(2) ... H(31)	2.56
C(29) ... C(36)	3.39	O(2) ... H(47)	2.44
C(30) ... C(35)	3.40	H(23) ... H(26)	2.10
C(30) ... C(43)	3.36	H(52) ... H(49)	2.24
C(30) ... C(51)	3.66		

B. Selected intermolecular distances (<4.0 Å)

C(13) ... $O(2)^{i}$	3.29
C(14) ... $O(2)^{i}$	3.34

Roman numeral superscripts refer to the following equivalent positions relative to the molecule at (x,y,z) (i) -x, 1 - y, -z.

Table 4.1.6 (continued)

Table 4.1.7

LEAST-SQUARES PLANES

Planes are in the form of $AX + BY + CZ - D = 0$ where X, Y and Z refer to an orthogonalized set of axes, D is the perpendicular distance from the plane to the origin and A, B and C refer to the components of unit vector normal to the best plane. An asterisk denotes atoms used to define the plane.

A. (I) Equation of the plane

$$-0.4219X + 0.5574Y - 0.7150Z + 1.6183 = 0$$

$\chi^2 = 6.89$ with 3 degrees of freedom.

The deviations (Å) of the atoms from the plane are:

C(1)*	0.002(6)	C(5)*	-0.005(5)
C(2)*	0.004(6)	C(6)*	-0.001(6)
C(3)*	-0.009(5)	As (1)	0.125(1)
C(4)*	0.008(5)		

(2) Equation of the plane

$$-0.8725X - 0.4856Y - 0.0537Z - 0.1483 = 0$$

$\chi^2 = 7.09$ with 3 degrees of freedom.

The deviations (Å) of the atoms from the plane are:

C(7)*	-0.005(9)	C(11)*	0.003(8)
C(8)*	-0.009(11)	C(12)*	0.006(8)
C(9)*	0.018(9)	As(1)	-0.066(1)
C(10)*	-0.008(6)		

(3) Equation of the plane

$0.6580X - 0.1608Y - 0.7356Z + 2.6365 = 0$

$\chi^2 = 3.52$ with 3 degrees of freedom.

The deviations (Å) of the atoms from the plane are:

C(13)*	-0.008(7)	C(17)*	-0.003(6)
C(14)*	0.005(7)	C(18)*	0.008(7)
C(15)*	-0.001(6)	As (1)	0.117(1)
C(16)*	0.001(5)		

(4) Equation of the plane

$0.0132X + 0.8135Y + 0.5814Z - 1.3888 = 0$

$\chi^2 = 4.37$ with 3 degrees of freedom.

The deviations (Å) of the atoms from the plane are:

C(19)*	0.008(6)	C(23)*	-0.001(5)
C(20)*	-0.002(7)	C(24)*	-0.004(5)
C(21)*	-0.005(6)	As (1)*	0.659 (1)
C(22)*	0.005(5)		

(5) Equation of the plane

$0.8668X - 0.4879Y - 0.1028Z - 3.1829 = 0$

$\chi^2 = 1.92$ with 3 degrees of freedom.

The deviations (Å) of the atoms from the plane are:

C(27)*	0.001(8)	C(31)*	-0.006(7)
C(28)*	-0.000(7)	C(32)*	0.006(9)
C(29)*	0.002(7)	As (2)	0.148(1)
C(30)*	0.002(6)		

(6) Equation of the plane

$-0.0501X - 0.6495Y - 0.7587Z + 5.2051 = 0$

$\chi^2 = 22.59$ with 3 degrees of freedom.

The deviations (Å) of the atoms from the plane are:

C(33)*	0.018(6)	C(37)*	-0.009(6)
C(34)*	-0.016(7)	C(38)*	-0.008(6)
C(35)*	-0.003(6)	As(2)	0.167(1)
C(36)*	0.009(5)		

(7) Equation of the plane

$0.2975X - 0.2740Y + 0.9146Z - 1.999 = 0$

$\chi^2 = 22.17$ with 3 degrees of freedom.

The deviations (Å) of the atoms from the plane are:

C(39)*	0.012(5)	C(43)*	0.003(5)
C(40)*	0.003(6)	C(44)*	-0.015(6)
C(41)*	-0.014(6)	As(2)	-0.035(1)
C(42)*	0.008(5)		

(8) Equation of the plane

$0.6005X + 0.7711Y - 0.2118Z - 8.1988 = 0$

$\chi^2 = 4.25$ with 3 degrees of freedom.

The deviations (Å) of the atoms from the plane are:

C(45)*	0.003(7)	C(49)*	-0.006(6)
C(46)*	-0.009(7)	C(50)*	0.005(6)
C(47)*	0.005(6)	As(2)	-0.022(1)
C(48)*	0.001(5)		

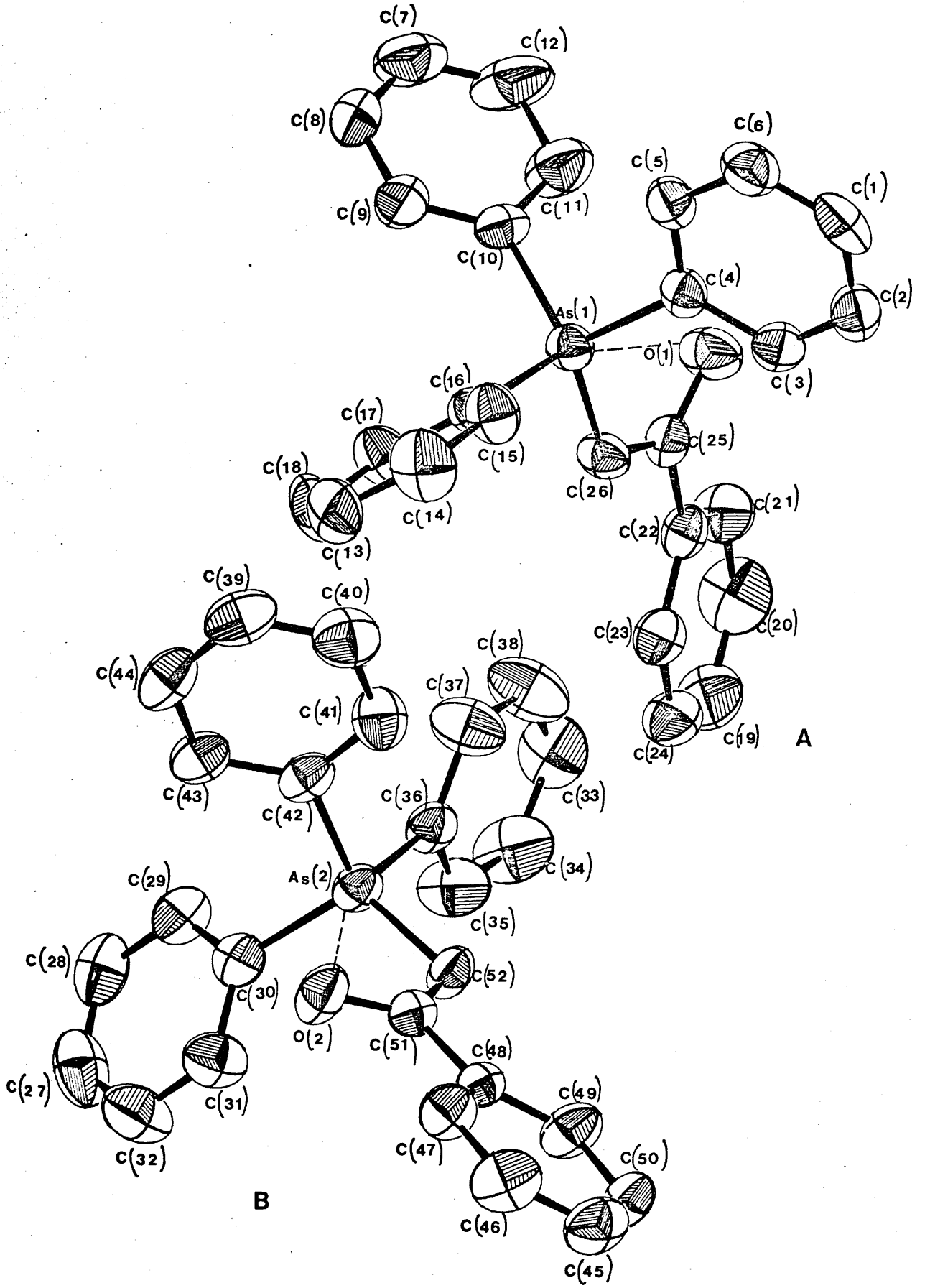
B. The angles between the different planes are:

(1) and (2)	82.2°
(1) and (3)	80.9°
(2) and (3)	117.2°
(5) and (6)	69.4°
(5) and (7)	72.7°
(6) and (7)	122.1°

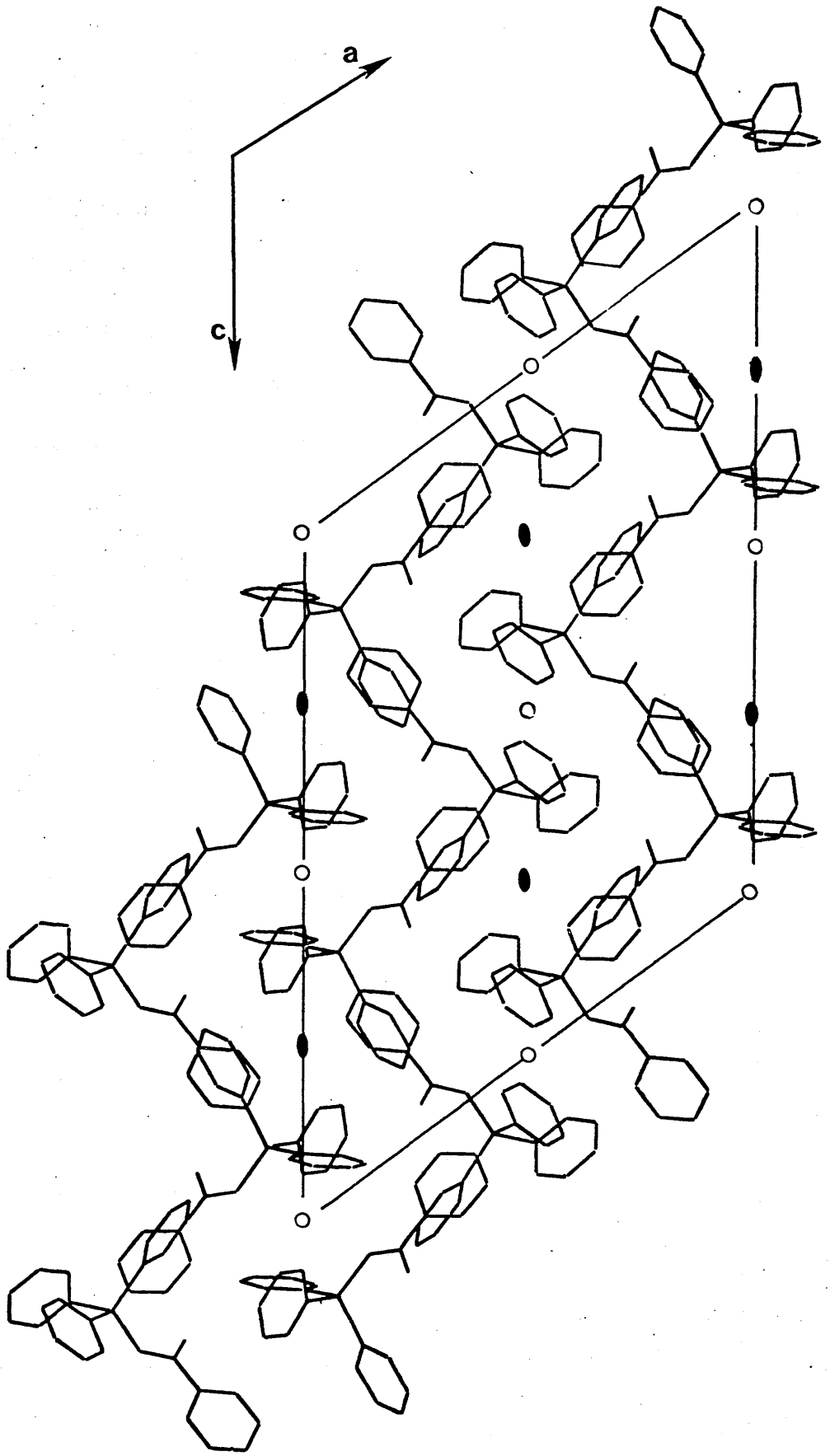
Figure 4.1.1 (a and b)

(a) A general view of I giving the atomic numbering scheme.

(b) The molecular packing of I viewed along the b-axis.


C(7)
C(12)
C(8)
C(6)
C(5)
C(1)
C(9)
C(11)
C(10)
C(4)
C(2)
As(1)
O(1)
C(3)
C(16)
C(17)
C(25)
C(15)
C(18)
C(26)
C(21)
C(14)
C(22)
C(13)
C(39)
C(40)
C(23)
C(20)
C(38)
C(44)
C(37)
C(41)
C(24)
C(19)
A
C(43)
C(36)
C(33)
C(42)
C(34)
As(2)
C(29)
C(35)
C(28)
C(52)
C(30)
O(2)
C(51)
C(48)
C(27)
C(49)
C(31)
C(47)
C(50)
C(32)
B
C(46)
C(45)

(a)



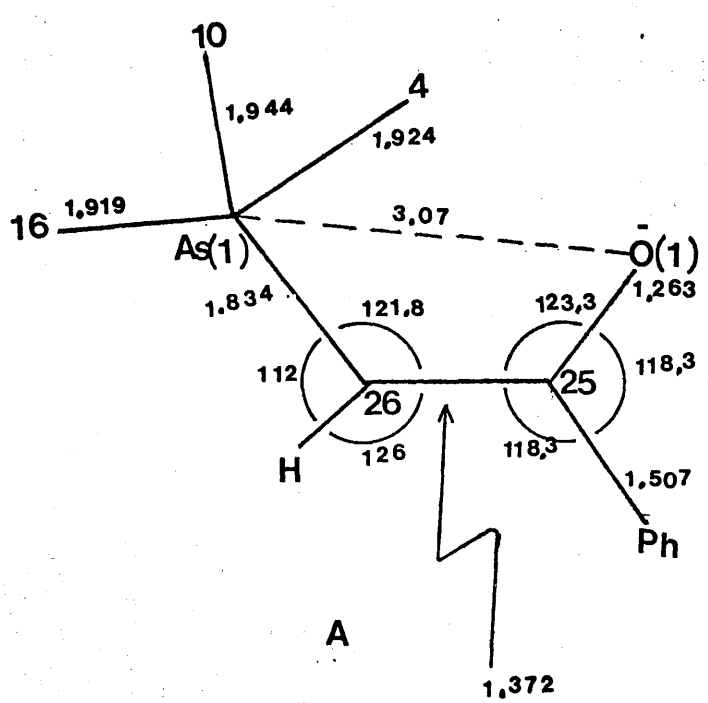
(b)

Discussion of I

The main features of the molecular geometry including pertinent bond lengths and angles for the two molecules (A and B) in the asymmetric unit are shown in Figures 4.1.1(a) and 4.1.2.

In both molecules the bonded atoms As, C, C, O are coplanar [dihedral angles, 2.8(8)° and 0.5(7)° for A and B respectively] though in molecule A the C(benzoyl ring) atom deviates from the plane formed by these atoms [C(22) - C(25) - C(26) - As(1) is equal to -175.5(4)°] while in molecule B it does not [C(48) - C(51) - C(52) - As(2) is equal to 179.9(4)°]. The near trigonal geometry at the central C-C bond (Figure 4.1.2 and Table 4.1.5), its corresponding shortening [1.372(7) Å in A and 1.382(6) Å in B] with respect to the expected[67] $C_s p^2 - C_s p^2$ single bond length (1.48 Å in butadiene and biphenyls) and the lengthened C-O bonds [1.263(6) Å] in A and [1.253(7) Å] in B seem to support the existence of a 'through conjugation' effect whereby a negative charge formally located on the carbon atom [C(26) and C(52) in A and B respectively] is delocalized towards the carbonyl oxygen atom. Similar patterns of conjugation have been observed before with phosphonium and ammonium ylides[94,78-79] (as has been mentioned in the introduction to section 4.1 - compounds VI, VII and VIII).

The expected trans position of the phenyl group with respect to the triphenylarsonium moiety is observed though the planarity of the benzoyl group is not retained [C(23) - C(22) - C(25) - C(26) in A


10
1,944
4
1,924
16
1,919
As(1)
3,07
O(1)
1,834
121,8
123,3
1,263
112
26
25
118,3
H
126
118,3
1,507
Ph
A
1,372

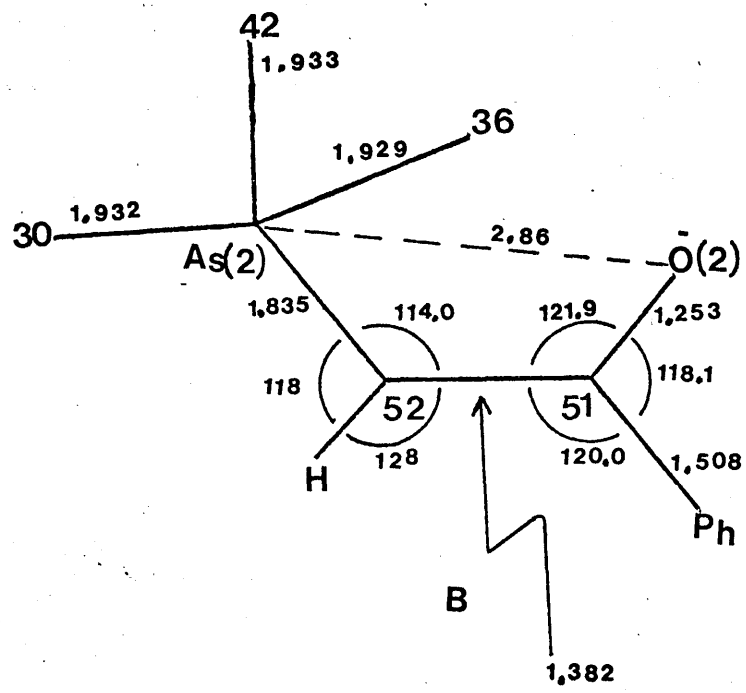

42
1,933
36
1,929
30
1,932
As(2)
2,86
O(2)
1,835
114,0
121,9
1,253
118
52
51
118,1
H
128
120,0
1,508
Ph
B
1,382

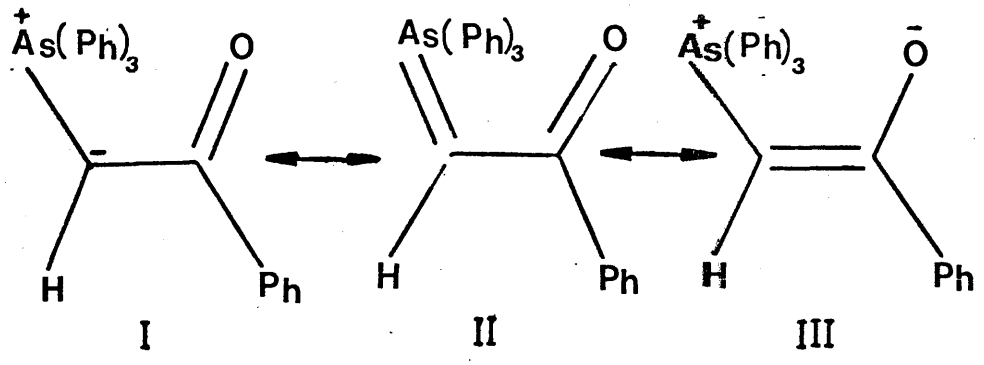
Figure 4.1.2

and C(49) - C(48) - C(51) - C(52) in B are equal to -15.0(8)° and -13.3(8)° respectively] due to repulsions between the -CH-hydrogen and the ortho-hydrogen atom of the benzoyl ring.

The three phenyl rings bonded to the arsenic atoms in molecules A and B are arranged in the favoured regular 'propeller' conformation. However an outstanding difference is exhibited between the two molecules in which the propeller type conformation in B seems to indicate an arrangement in the opposite sense [Table 4.1.5(c)] . This observation is also manifested by slightly different intramolecular contacts (Table 4.1.6). While in molecule A the C(11) ... O(1) distance is 3.17 Å, in molecule B the corresponding distances O(2) ... C(43) and O(2) ... C(41) are equal to 3.61 Å and 3.66 Å respectively [the expected separation from van der Waals' contact is 3.40 Å] . An examination of the molecular model and the latter differences in the C ... O distances would suggest that the shorter As(2) ... O(2) contact (2.86 Å) as compared to As(1) ... O(1) (3.07 Å) (Figure 4.1.2) and the pronounced decrease (from a normal trigonal angle) of the valency angle As(2) - C(52) - C(51) [114.0(4)°] as compared to the angle As(1) - C(26) - C(25) [121.8(4)°] might be ascribed to the different 'propeller' arrangements which in B seems to interfere minimally with the $As^{+} \ldots \bar{O}$ interaction [the sum of the appropriate van der Waals' radii for As and O is 3.40 Å, and a typical covalent As - O distance is equal to 1.70(1) Å [98] (Ferguson and Macaulay, 1968)] . As has already been observed[91] (Ferguson and Rendle, 1975, compound IV

in the introduction to section 4.1) the interaction between the arsenic and oxygen atoms results in a distortion of the tetrahedral arrangement around the arsenic atom towards a rather trigonal-bipyramidal configuration with atoms C(4), C(10) and C(26) in molecule A, C(30), C(42) and C(52) in molecule B in the equatorial positions and atoms O(1) and C(16), O(2) and C(36) in A and B respectively in the axial positions.

The fact that the valency angles C-As -C (whereby the carbon atoms are the ones in the equatorial positions) are splayed out and the As - C(Ph) bonds are slightly longer compared to the quoted[99] (Palenik, 1966) $C(sp^2)$ - arsonium bond length of 1.897(9) Å is also a reflection of the type of distortion postulated for this compound ('tetrahedral' towards 'trigonal-bipyramidal'). The arsonium - C (ylide) bond lengths [1.834(7) Å and 1.835(5) Å in A and B respectively] are not only shorter than the expected length for $C(sp^2)$ - As but are significantly shorter than similar bonds found in related systems, [1.881(4) Å][91] and [1.868(5) Å][92]. An appreciable double-bond character between the ylide carbon and the arsenic atom cannot be supported on the basis of the present analysis (as was in the cases of S-C and S-N bonds, overall discussion 3.1 and section 3.3 in this thesis) though the best approximation to the molecular structure (valence bond notation) might contain both polar and covalent contributions as is indicated by the following formulae:



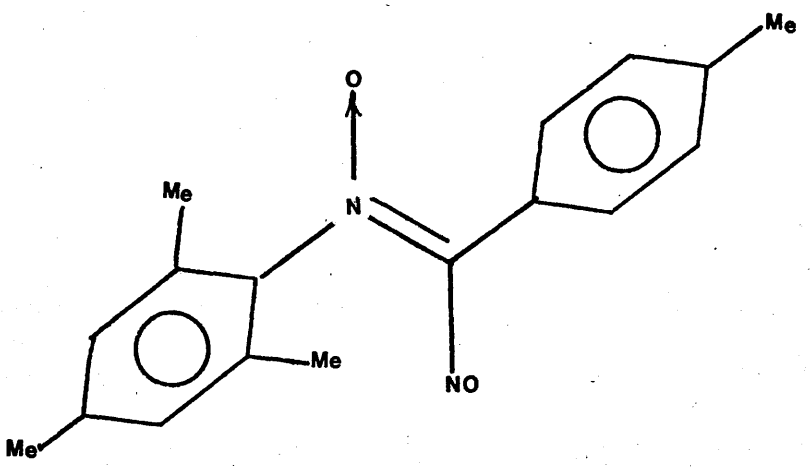
Later ^{13}C nuclear magnetic resonance studies carried out on this molecule[93] (Frøyen and Morris, 1976) do seem to support the presence of high electron density on the sp^2 hybridised ylide carbon (enhanced shielding) and therefore attributing 'weight' to the resonance structure I.

It is interesting to note the consistent difference, in the C-O and C(central) - C(central) bonds, between the carbonyl-stabilized ammonium ylide[94] (structure VII, in the introduction to section 4.1) and the arsenic ylide (bonds taken as weighted means). Though only differences of 2.8 σ are observed it is possible that the delocalization in the ammonium system as compared with the arsenic one is further enhanced, thus reflecting the only possible 'route' for conjugation - from the formally negative ylide carbon atom to the carbonyl oxygen.

Apart from the geometrical features mentioned already for the arsenic ylide, the rigorous planarity of the phenol rings (Table 4.1.7) and the slight offset of the arsenic atoms from the least-squares planes of the rings should be noted. Selected intra- and inter-molecular contacts are listed in Table 4.1.6.

The molecular packing is of a 'herring-bone' arrangement and the closest As ... As contacts are equal to 7.18 Å [As(1) ... As(1)] .

THE CRYSTAL AND MOLECULAR STRUCTURE OF A NITROSO-IMINE N-OXIDE OF THE FORM

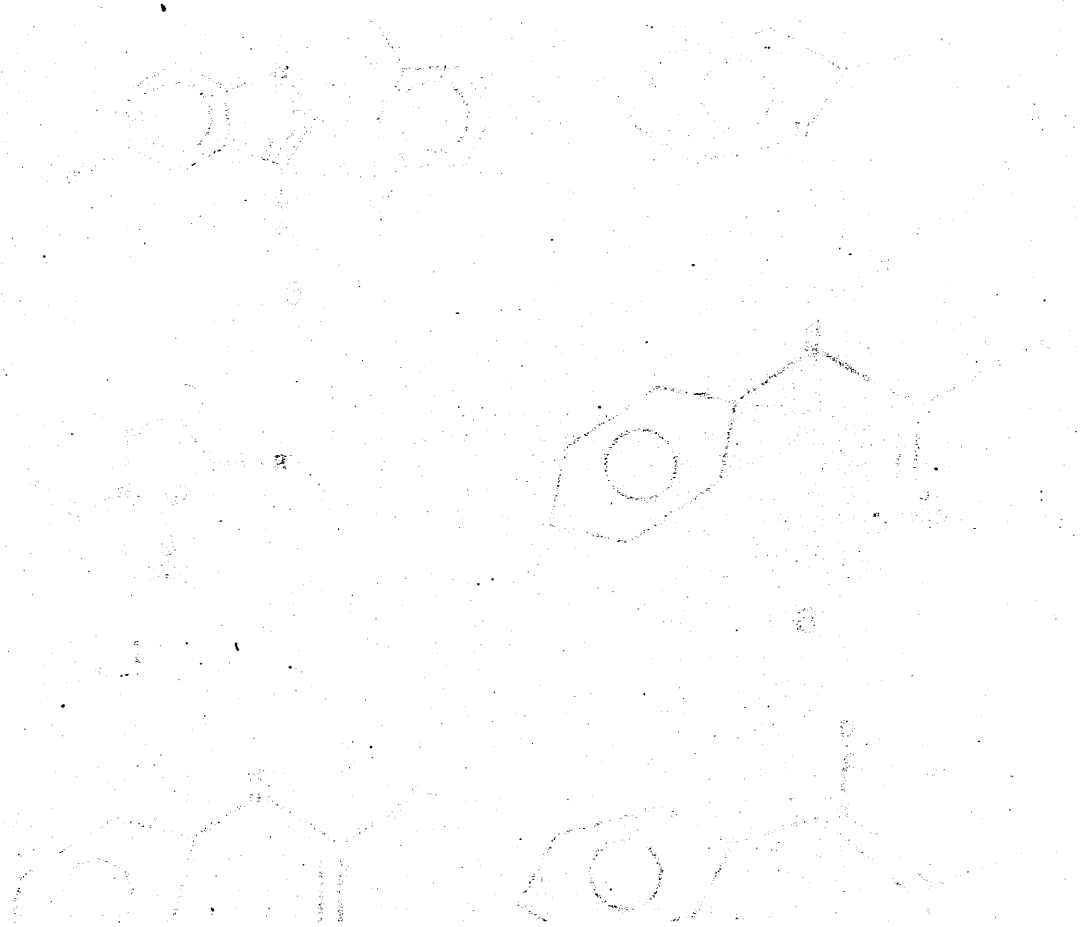


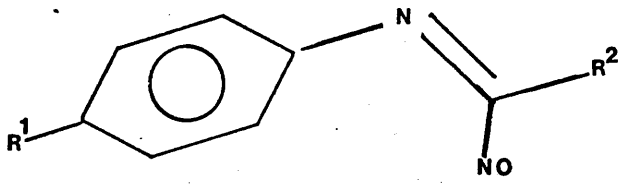
4.2 Introduction

The C-nitroso-imines (I) have been invoked as intermediates (though short lived) in a number of chemical reactions. The intermediacy of these compounds (I) seems to account for not only the formation of 1,2,4-benzoxadiazines[100,101] (2) (Gilchrist et al, 1976 and Cameron and Freer, 1976) from N-aryl-S,S-dimethylsulphimides (3) and nitrile oxides (4), but also for the formation of 1,2,4-benzoxadiazines and benzimidazole 3-oxides (5) from the reaction of 2,6-disubstituted benzonitrile oxides with N-arylsulphimides (Shiraishi, Shigemoto and Ogawa, 1978)[102]. Mechanisms[103] for the reaction of the 2-pyridylsulphimides (6) with nitrile oxides to form (7) (Gilchrist et al, 1976), and for the oxidation of N-phenyl benzamidoxime (8) to the O-benzoyl derivative of the oxime[104] (9) (Boyer and Frints, 1968) also depend upon the intermediacy of such derivatives. It is interesting to note that previous work[105] (Kirby and Sweeny, 1973) has indicated the possibility of intercepting such C-nitroso imine intermediates (through the work on related intermediates, RCONO) and thus provided further evidence for their existence.

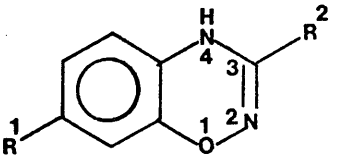
The cyclization that was shown before to take place with C-nitroso-imines also takes place with C-nitroso-imine N-oxides. Thus compound (10) has been isolated[106] from the reaction of nitrosobenzene with benzonitrile oxide (Minisci, Galli, and Quilico, 1963) but was reported to cyclize exothermically to 1-hydroxy 2-phenylbenzimidazole 3-oxide (11).

In view of these cyclizations, it is clear that the presence of substituents in the aromatic ring of the nitroso derivative will affect the stability of the intermediate product. Thus compound (12) is stable and does not cyclize to form the benzimidazole[106] (the ortho positions are not available for cyclization). By analogy the C-nitroso-imine N-oxide (13) was expected to be stable and indeed it has proved possible to investigate its geometrical features by the X-ray analysis at room temperature.





1



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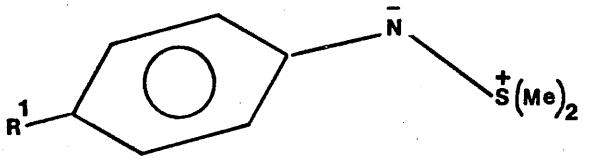

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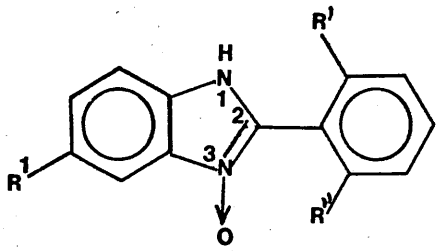

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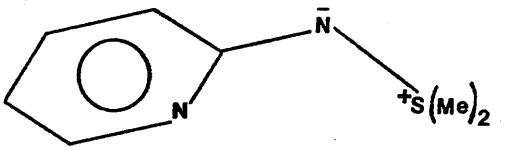

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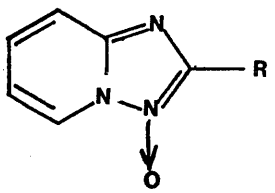

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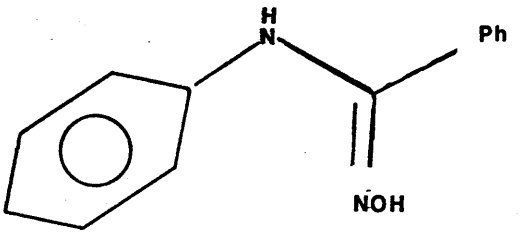

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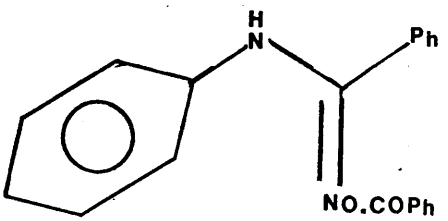

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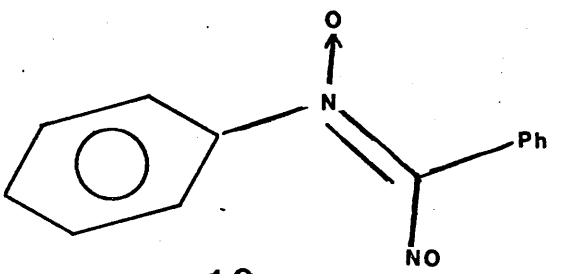

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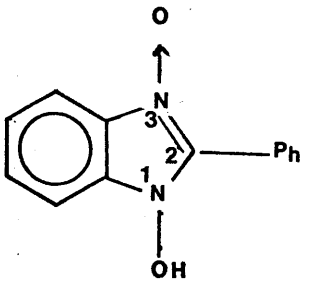

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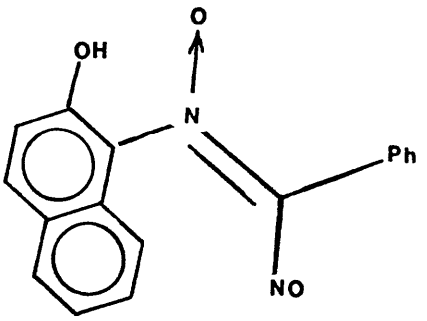

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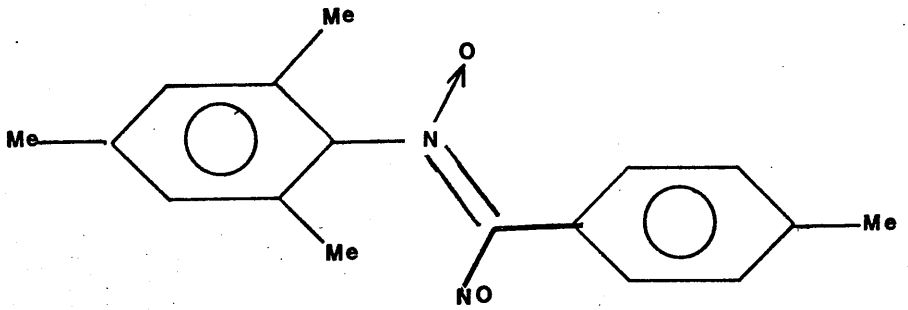
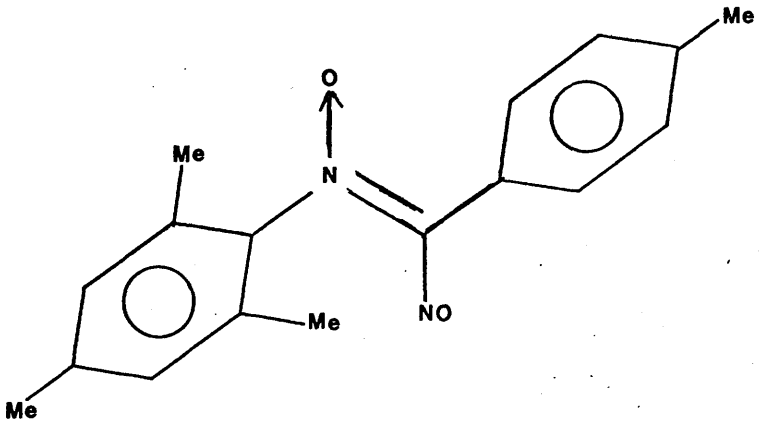


13

Experimental and Results for II



II

N-[2,4,6-trimethylphenyl] α -nitroso-4-methylbenzaldimine-N-oxide.

Crystal Data

Molecular Formula	$C_{17}H_{18}N_2O_2$
Molecular Weight	282.35 a.m.u.
Crystal System	Monoclinic
Unit Cell Dimensions	a = 8.192 (2) Å
	b = 10.912(2) Å
	c = 9.890(2) Å
	β = 118.23(4)°
Unit Cell Volume	V = 778.92 Å^3
Number of Molecules per Unit Cell	Z = 2
Calculated Density	D_c = 1.20 g.m^{-3}
Number of Molecules per Asymmetric Unit	N = 1
Space Group	$P2_1$ (C_2^2, No.4)
Equivalent Positions	x,y,z
	-x, 1/2 + y, -z

Linear Absorption Coefficient	$\mu = 0.74\ cm^{-1}$
Number of Electrons per Unit Cell	$F(000) = 300$

Data Collection

Diffractometer Used	Hilger and Watts Y290
Radiation Used	$M_0 - K_\alpha$, $\overline{\lambda} = 0.71069\ \text{Å}$
Filter	Graphite Monochromator
	$\cos^2 2\theta_m = 0.970$
Upper Limit for Data Collection	$2\theta_{max} = 54^\circ$
Number of Observed Independent Reflections	$m = 1295$
Unobserved Cut-off	$2.5\ \sigma_I$
Number of Parameters Refined	$n = 230$
Number of Reflections per Parameter	$m/n = 5.6$

Structure Determination and Refinement

Systematic absences in the diffraction data (hkl absent when h + l is odd, and oko absent when k is odd) suggested the possible space groups $B2_1$ or $B2_1/m$ (with a = 8.192 Å, b = 10.912 Å, c = 17.467 Å and $\beta = 93.82^\circ$). The data collection was carried out in the 'B'-centered setting and thereafter the primitive unit cell was chosen by the transformation

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \bar{a} \\ \bar{b} \\ \bar{c} \end{pmatrix} = \begin{pmatrix} \bar{a}' \\ \bar{b}' \\ \bar{c}' \end{pmatrix} .$$

This meant a change by the same transformation matrix of the l indices to $l' = (l - h)/2$. A statistical analysis provided by 'MULTAN' and based only on the observed reflections indicated a centrosymmetric space group but since the calculated specific density of the crystal (D_c), based on 2 molecules per unit cell was equal to 1.20 $g.cm^{-3}$ the noncentrosymmetric space group was tried first though a possibility of the molecule possessing a mirror plane of symmetry did exist.

The structure was solved in space group $P2_1$ by the application of direct methods ('MULTAN' - version 1974). 20 nonhydrogen atoms (out of 21) were located in the E-map derived from the best set of phases and the site of the missing carbon atom was revealed by a difference electron density synthesis. The calculated R and R_w at this stage were 0.269 and 0.251 respectively. The various parameters used with 'MULTAN' are outlined in Table 4.2.1.

The crystal structure was fully refined to convergence during 18 cycles of block diagonal least-squares, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. The refinement of the atomic positional and anisotropic thermal parameters for C, N and O and positional and isotropic thermal parameters for the hydrogen atoms that were resolved, led to a conventional R factor of 0.054 and a weighted R of 0.072. Towards the latter stages of the refinement a weighting scheme of the form $w^{-1} = 0.1801 + 0.0537|F_o| + 0.0040|F_o|^2$ was used instead of unit weights which were employed initially. A final difference map was featureless, the maximum electron density being equal to 0.19 e $\mathring{A}^{-3}$.

The refinement was assumed complete when the average and maximum values of the shift/ σ for the atomic parameters in the last least-squares cycle were 0.03 and 0.13 respectively for the non-hydrogen atoms and 0.07 and 0.32 respectively for the hydrogen atoms. No absorption correction was applied and the final standard deviation of an observation of unit weight was equal to 3.8437.

In all structure-factor calculations the atomic scattering factors used for C, N and O were those given by Cromer and Mann (1968), and for hydrogen those given by Stewart et al (1965). Final values of the observed and calculated structure factors including the phases, are given in the supplement to this thesis. A perspective view of the molecule together with the numbering scheme is illustrated in Figure 4.2.1(a). The molecular arrangement viewed along the a-axis is shown in Figure 4.2.1(b). The atomic coordinates and thermal parameters, bond lengths, valency angles and torsion angles with e.s.d.'s and other relevant data are given in Tables 4.2.3 to 4.2.6.

Table 4.2.I

SUMMARY OF THE CONDITIONS (INCLUDING VARIOUS FIGURES OF INTEREST) ASSOCIATED WITH SOLVING THE STRUCTURE OF II.

In this table:

1. NE - is the number of the largest $|E|$'s chosen to define the structure.
2. NSRT - is the number of Σ_2 relationships to be retained.
3. NSRTT - is the total number of Σ_2 relationships.
4. PROB - is the probability acceptance limit chosen for Σ_1.
5. NSPEC - is the number of special phases (permutations restricted to ϕ_{spec}, $\phi_{spec} + 180^{\circ}$).

   NGEN - is the number of general phases (phase permutation 45°, 135°, 225°, 315°).

   NANY - is the number of phases of either sort.
6. NSET - is the total number of phase sets that have been developed.
7. PUB - is the published phase.
8. NAT - is the number of nonhydrogen atoms in the asymmetric unit.
9. ABS FOM, PSI ZERO, RESID and CFOM are all figures of merit.

$C_{17}H_{18}N_2O_2$, $P2_1$, NAT = 21

PARAMETERS		STARTING SET TYPE	hkl	PHI	PUB	RESULTS PHASE SET CONSIDERED	FIGURES OF MERIT ABS FOM	PSI ZERO	RESID	TOTAL NUMBER OF CORRECT PEAKS FOUND IN E-MAP
SIGMA - 2		SIGMA - 1	-	-	-	Max	1.3027	145.2	37.49	20
NE	200					Min	0.8817	65.57	26.14	
NSRT	2000	Origin defining phases	8,0,-5	360	360	CFOM 22 = 2.3006	1.1189	66.6	28.98	
NSRTT	not known		1,1,1	360	342					
CONVERGE			1,0,-8	360	360					
PROB	0.95	Permuted phases	3,0,-4	180 360	360					
NSPEC, NGEN, NANY	2,2,0		3,5,-7	±45 ±135	206					
FASTAN			7,0,-5	180 360	360					
NSET	32		4,6,2	±45 ±135	165					

Table 4.2.2

PROGRESS OF LEAST-SQUARES REFINEMENT ('y' coordinate of atom C8 is fixed)

CYCLES	PARAMETERS REFINED	R	R_w
0	none	0.269	0.251
5	$x,y,z,U_{(iso)}$ for C, N, and O atoms; scale factor; full matrix; unit weights.	0.149	0.149
3	x,y,z,U_{ij} for C, N and O atoms; scale factor; full matrix; unit weights.	0.100	0.114
3	x,y,z,U_{ij} for C, N and O atoms. H atoms included in the structure factor calculations as fixed contributors; counting loss correction; weighting scheme; full matrix.	0.061	0.085
7	x,y,z,U_{ij} for atoms C, N and O; $x,y,z,U_{(iso)}$ for only 10 hydrogen atoms (located from Fourier maps); block diagonal; scale factor; weighting scheme.	0.054	0.072

Table 4.2.3 (a,b,c,d)

(a) Fractional atomic coordinates (x 10^4) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM X/A Y/B Z/C

(b) Anisotropic thermal parameters ($\AA^2$, x 10^3) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}

(c) Fractional atomic coordinates (x 10^3) of hydrogen atoms with e.s.d.'s in parentheses. The hydrogens are numbered according to the atoms to which they are attached.

(d) Isotropic thermal parameters ($\AA^2$, x 10^2) of hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM $U_{(iso)}$.

C(1)	3865(7)	7494(6)	-2069(5)
C(2)	4158(8)	6497(5)	-1154(7)
C(3)	3574(7)	6487(4)	-0052(5)
C(4)	2715(5)	7503(5)	0150(4)
C(5)	2475(7)	8524(5)	-0731(5)
C(6)	3038(7)	8503(6)	-1853(5)
C(7)	0254(5)	6640(4)	2468(4)
C(8)	1043(6)	5721	3562(5)
C(9)	0432(7)	5607(5)	4634(5)
C(10)	-0929(7)	6359(5)	4635(5)
C(11)	-1679(6)	7242(5)	3520(5)
C(12)	-1099(5)	7428(4)	2418(5)
C(13)	2108(6)	7492(4)	1346(4)
C(14)	4528(10)	7503(8)	-3270(7)
C(15)	2485(8)	4871(6)	3557(6)
C(16)	-1563(10)	6181(7)	5837(7)
C(17)	-1937(7)	8430(5)	1247(6)
N(1)	0806(5)	6719(4)	1262(4)
N(2)	2799(5)	8224(4)	2636(4)
O(1)	-0004(5)	5993(4)	0157(4)
O(2)	4035(6)	8950(4)	2753(4)

C(1)	71(3)	88(3)	60(2)	-30(3)	46(2)	-21(2)
C(2)	90(4)	66(3)	97(3)	-16(3)	72(3)	-23(3)
C(3)	77(3)	51(3)	75(3)	-8(2)	51(3)	-7(2)
C(4)	47(2)	55(2)	46(2)	-8(2)	25(2)	-6(2)
C(5)	62(3)	65(3)	65(3)	10(2)	33(2)	13(2)
C(6)	70(3)	100(4)	59(3)	-9(3)	30(2)	25(3)
C(7)	47(2)	48(2)	53(2)	-2(2)	30(2)	-4(2)
C(8)	48(2)	58(2)	57(2)	5(2)	28(2)	1(2)
C(9)	73(3)	64(3)	58(3)	3(2)	36(2)	8(2)
C(10)	70(3)	64(3)	70(3)	-12(2)	50(3)	-10(2)
C(11)	53(2)	65(3)	73(3)	-2(2)	43(2)	-10(2)
C(12)	45(2)	47(2)	58(2)	1(2)	25(2)	1(2)
C(13)	51(2)	52(2)	52(2)	-6(2)	33(2)	-6(2)
C(14)	120(5)	157(6)	95(4)	-73(5)	87(4)	-48(4)
C(15)	88(4)	84(3)	83(3)	32(3)	54(3)	15(3)
C(16)	115(5)	110(5)	100(4)	-1(4)	85(4)	-1(4)
C(17)	63(3)	64(3)	81(3)	12(2)	29(3)	18(2)
N(1)	52(2)	55(2)	46(2)	-9(2)	27(2)	-9(1)
N(2)	61(2)	75(3)	65(2)	-17(2)	37(2)	-23(2)
O(1)	93(2)	92(2)	69(2)	-41(2)	56(2)	-30(2)
O(2)	90(2)	94(3)	94(2)	-45(2)	54(2)	-38(2)

H(21)	480(8)	581(6)	-120(7)
H(31)	379(5)	570(4)	065(4)
H(51)	210(7)	927(5)	-033(5)
H(61)	286(6)	915(4)	-246(4)
H(91)	098(7)	508(5)	555(6)
H(111)	-255(6)	769(4)	346(5)
H(141)	594	743	-269
H(142)	400	682	-395
H(143)	500(9)	829(6)	-324(7)
H(151)	193	448	253
H(152)	330(9)	544(6)	334(7)
H(153)	306(9)	444(6)	454(8)
H(161)	-141(9)	527(5)	626(7)
H(162)	-028	624	693
H(163)	-238	672	594
H(171)	-150	863	043
H(172)	-164	928	182
H(173)	-327	835	067

4.2.3 (c)

H(21)	11(2)
H(31)	5(1)
H(51)	7(1)
H(61)	5(1)
H(91)	8(2)
H(111)	7(1)
H(141)	5
H(142)	5
H(143)	12(2)
H(151)	5
H(152)	11(2)
H(153)	12(2)
H(161)	10(2)
H(162)	5
H(163)	5
H(171)	5
H(172)	5
H(173)	5

Table 4.2.4 (a,b,c)

(a) Interatomic distances (Å) with e.s.d.'s in parentheses. The hydrogen atoms are numbered according to the atoms to which they are attached.

(b) Interbond angles (degrees) with e.s.d.'s (degrees) in parentheses.

A torsion angle A-B-C-D is considered to be positive if when viewed down the B-C bond the A-B bond will eclipse the C-D bond when rotated less than 180° in a clockwise direction.

C(1)	C(2)	1.362(8)	C(8)	C(9)	1.375(8)
C(1)	C(6)	1.362(9)	C(8)	C(15)	1.503(8)
C(1)	C(14)	1.521(11)	C(9)	C(10)	1.385(8)
C(2)	C(3)	1.382(10)	C(10)	C(11)	1.372(7)
C(3)	C(4)	1.377(7)	C(10)	C(16)	1.519(11)
C(4)	C(5)	1.370(7)	C(11)	C(12)	1.394(8)
C(4)	C(13)	1.484(7)	C(12)	C(17)	1.501(7)
C(5)	C(6)	1.388(9)	C(13)	N(1)	1.331(6)
C(7)	C(8)	1.390(5)	C(13)	N(2)	1.380(6)
C(7)	C(12)	1.385(7)	N(1)	O(1)	1.256(5)
C(7)	N(1)	1.465(7)	N(2)	O(2)	1.247(6)

C(2) - H(21)	0.934(71)	C(15) - H(151)	0.994(6)
C(3) - H(31)	1.062(42)	C(15) - H(152)	1.007(77)
C(5) - H(51)	1.015(56)	C(15) - H(153)	0.979(67)
C(6) - H(61)	0.887(42)	C(16) - H(161)	1.063(59)
C(9) - H(91)	0.982(52)	C(16) - H(162)	1.096(5)
C(11) - H(111)	0.844(52)	C(16) - H(163)	0.935(8)
C(14) - H(141)	1.025(7)	C(17) - H(171)	1.048(7)
C(14) - H(142)	0.964(8)	C(17) - H(172)	1.060(6)
C(14) - H(143)	0.938(71)	C(17) - H(173)	0.967(5)

4.2.4 (a) (continued)

C(6)	- C(1)	- C(2)	119.05(54)	C(14)	- C(1)	- C(2)	120.54(61)
C(3)	- C(2)	- C(1)	120.85(55)	C(14)	- C(1)	- C(6)	120.35(57)
C(5)	- C(6)	- C(1)	121.12(55)	C(4)	- C(3)	- C(2)	119.94(45)
C(5)	- C(4)	- C(3)	119.48(45)	C(13)	- C(4)	- C(3)	119.73(42)
C(13)	- C(4)	- C(5)	120.77(45)	C(6)	- C(5)	- C(4)	119.51(52)
N(1)	- C(13)	- C(4)	121.05(38)	N(2)	- C(13)	- C(4)	125.95(43)
C(12)	- C(7)	- C(8)	123.08(41)	N(1)	- C(7)	- C(8)	117.82(40)
C(9)	- C(8)	- C(7)	117.37(41)	C(15)	- C(8)	- C(7)	121.32(44)
N(1)	- C(7)	- C(12)	118.98(37)	C(11)	- C(12)	- C(7)	116.36(41)
C(17)	- C(12)	- C(7)	123.06(43)	C(13)	- N(1)	- C(7)	122.23(35)
O(1)	- N(1)	- C(7)	115.62(40)	C(15)	- C(8)	- C(9)	121.30(38)
C(10)	- C(9)	- C(8)	122.27(43)	C(11)	- C(10)	- C(9)	118.07(50)
C(16)	- C(10)	- C(9)	119.92(49)	C(16)	- C(10)	- C(11)	122.00(55)
C(12)	- C(11)	- C(10)	122.82(50)	C(17)	- C(12)	- C(11)	120.58(46)
N(2)	- C(13)	- N(1)	112.99(39)	O(1)	- N(1)	- C(13)	122.14(39)
O(2)	- N(2)	- C(13)	114.40(41)				

C(6)	C(1)	C(2)	C(3)	2.1(9)	C(14)	C(1)	C(2)	C(3)	179.4(6)
C(2)	C(1)	C(6)	C(5)	-0.7(9)	C(14)	C(1)	C(6)	C(5)	-178.0(6)
C(1)	C(2)	C(3)	C(4)	-1.3(9)	C(2)	C(3)	C(4)	C(5)	-1.0(8)
C(2)	C(3)	C(4)	C(13)	-179.3(5)	C(3)	C(4)	C(5)	C(6)	2.4(8)
C(13)	C(4)	C(5)	C(6)	-179.3(5)	C(3)	C(4)	C(13)	N(1)	-64.0(6)
C(3)	C(4)	C(13)	N(2)	114.8(6)	C(5)	C(4)	C(13)	N(1)	117.7(5)
C(5)	C(4)	C(13)	N(2)	-63.5(7)	C(4)	C(5)	C(6)	C(1)	-1.6(9)
C(12)	C(7)	C(8)	C(9)	-0.0(7)	C(12)	C(7)	C(8)	C(15)	178.9(5)
N(1)	C(7)	C(8)	C(9)	-176.1(4)	N(1)	C(7)	C(8)	C(15)	2.9(6)
C(8)	C(7)	C(12)	C(11)	-1.2(7)	C(8)	C(7)	C(12)	C(17)	179.4(4)
N(1)	C(7)	C(12)	C(11)	174.7(4)	N(1)	C(7)	C(12)	C(17)	-4.7(7)
C(8)	C(7)	N(1)	C(13)	-97.4(5)	C(8)	C(7)	N(1)	O(1)	81.3(5)
C(12)	C(7)	N(1)	C(13)	86.4(5)	C(12)	C(7)	N(1)	O(1)	-94.8(5)
C(7)	C(8)	C(9)	C(10)	0.7(7)	C(15)	C(8)	C(9)	C(10)	-178.3(5)
C(8)	C(9)	C(10)	C(11)	0.0(8)	C(8)	C(9)	C(10)	C(16)	179.3(5)
C(9)	C(10)	C(11)	C(12)	-1.5(8)	C(16)	C(10)	C(11)	C(12)	179.2(5)
C(10)	C(11)	C(12)	C(7)	2.1(7)	C(10)	C(11)	C(12)	C(17)	-178.5(5)
C(4)	C(13)	N(1)	C(7)	176.5(4)	C(4)	C(13)	N(1)	O(1)	-2.1(7)
N(2)	C(13)	N(1)	C(7)	-2.5(6)	N(2)	C(13)	N(1)	O(1)	178.9(4)
C(4)	C(13)	N(2)	O(2)	0.4(7)	N(1)	C(13)	N(2)	O(2)	179.3(4)

Table 4.2.5

A. Selected intramolecular non-bonded distances (< 4.0 Å).

C(3) ... N(1)	3.11	C(5) ... O(2)	3.09
C(3) ... O(1)	3.08	C(7) ... N(2)	2.65
C(4) ... O(1)	2.77	C(8) ... C(13)	3.33
C(4) ... O(2)	2.77	C(8) ... N(2)	3.41
C(5) ... N(2)	3.23	C(8) ... O(1)	3.07

B. Selected intermolecular distances (< 4.0 Å).

C(1) ... $C(9)^{i}$	3.76	C(6) ... $C(9)^{iv}$	3.68
C(1) ... $C(17)^{ii}$	3.60	C(8) ... $C(14)^{v}$	3.64
C(2) ... $C(17)^{ii}$	3.62	C(9) ... $C(14)^{v}$	3.64
C(3) ... $C(17)^{iii}$	3.58	C(14) ... $C(15)^{vi}$	3.66

Roman numeral superscripts refer to the following equivalent positions relative to the molecule at (x,y,z):

(i) x,y,z-1	(iv) -x, 1/2 + y, -z
(ii) 1 + x, y, z	(v) x, y, 1 + z
(iii) x, y-1, z	(vi) 1 - x, 1/2 + y, -z

Table 4.2.6

LEAST-SQUARES PLANES

Planes are in the form of $AX + BY + CZ - D = 0$ where X, Y and Z refer to an orthogonalized set of axes, D is the perpendicular distance from the plane to the origin and A, B and C refer to the components of unit vector normal to the best plane. An asterisk denotes atoms used to define the plane.

A.

(1) Equation of the plane

$0.6538X + 0.3548Y + 0.6684Z - 4.4095 = 0$

$\chi^2 = 19.99$ with 3 degrees of freedom. The deviations (Å) of the atoms from the plane are:

C(1)*	-0.011 (6)	C(5)*	0.014 (5)
C(2)*	0.013 (6)	C(6)*	-0.003 (6)
C(3)*	0.001 (5)	C(13)	-0.008 (4)
C(4)*	-0.009 (4)	C(14)	0.015 (7)

(2) Equation of the plane

$-0.4742X - 0.6400Y - 0.6045Z + 5.4904 = 0$

$\chi^2 = 11.34$ with 3 degrees of freedom. The deviations (Å) of the atoms from the plane are:

C(7)*	0.001 (4)	C(12)*	-0.008 (4)
C(8)*	0.003 (3)	C(15)	0.038 (6)
C(9)*	-0.006 (5)	C(16)	0.0 (7)
C(10)*	-0.003 (5)	C(17)	-0.025 (6)
C(11)*	0.011 (5)	N(1)	0. (4)

(3) Equation of the plane

$0.5259X - 0.6890Y + 0.4989Z + 4.4719 = 0$

$\chi^2 = 7.61$ with 2 degrees of freedom. The deviations (Å) of the atoms from the plane are:

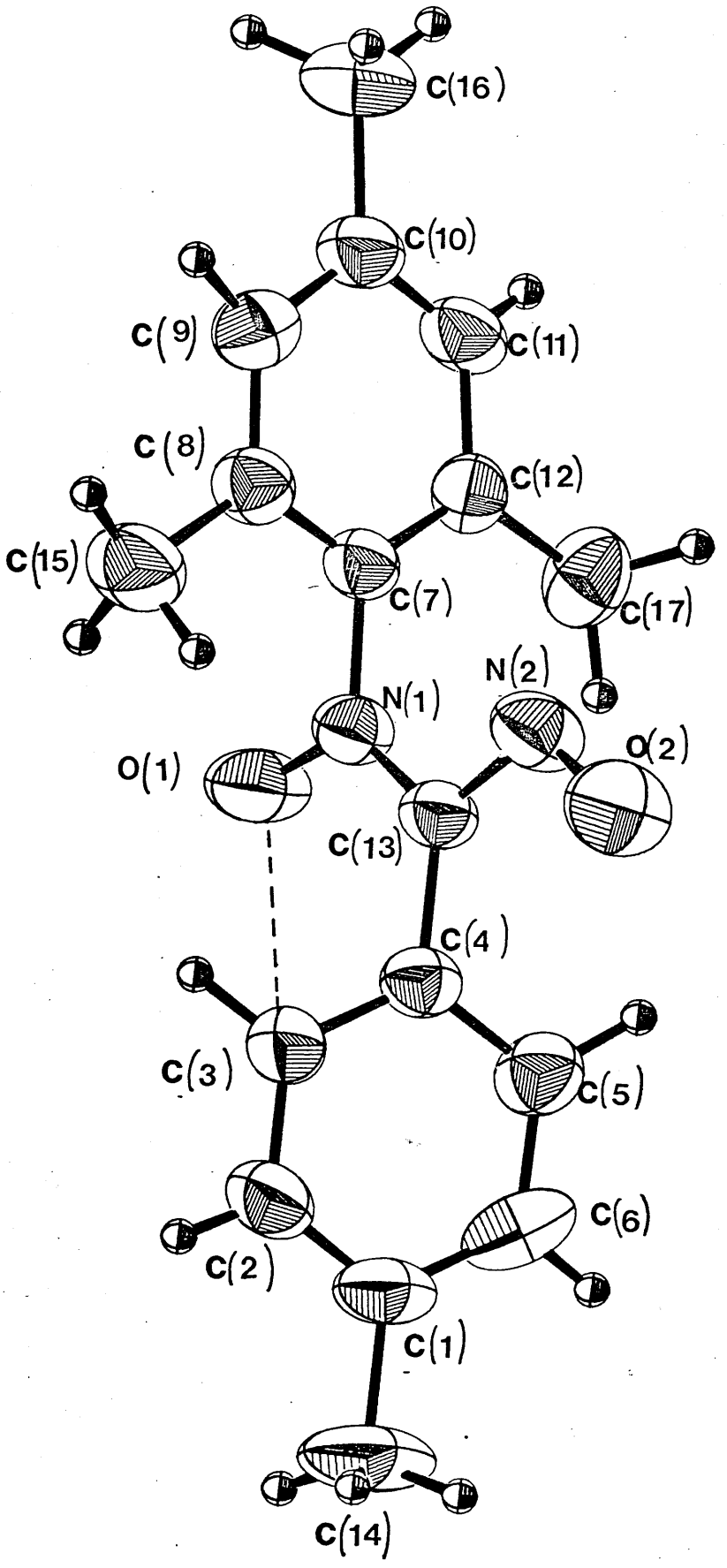
C(13)*	0.002 (5)	O(1)*	-0.005 (4)
N(1)*	0.007 (4)	O(2)*	0.002 (4)
N(2)*	-0.007 (4)		

B. The angle between planes (1) and (2) is 19.8°, between (2) and (3) is 83.7° and between (1) and (3) is 64.3°.

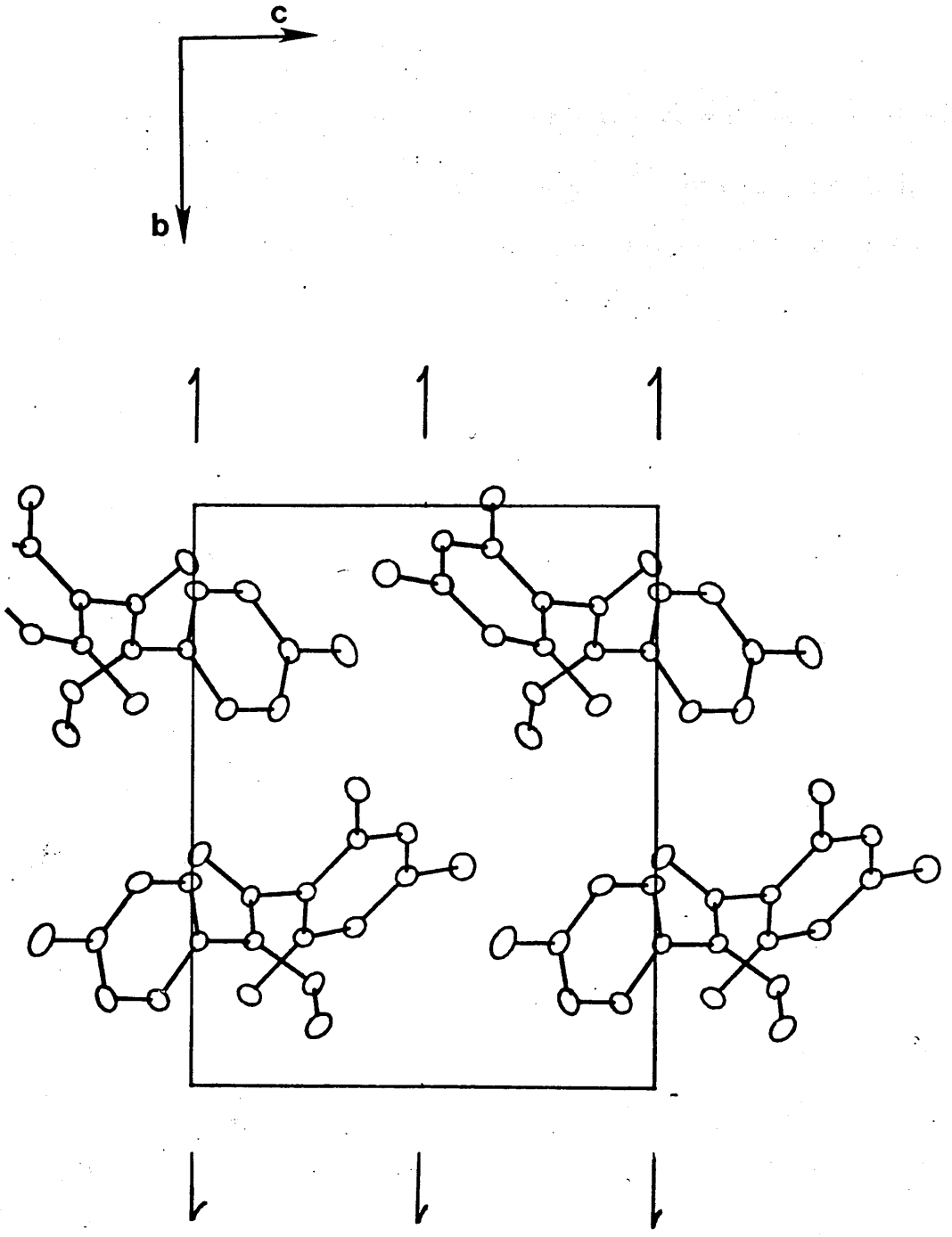
Figure 4.2.1 (a and b)

(a) A general view of II giving the atomic numbering scheme. Hydrogen atoms are numbered according to the atoms to which they are bonded.

(b) The molecular packing of II viewed along the short a-axis.


C(16)
C(10)
C(9)
C(11)
C(8)
C(12)
C(15)
C(7)
C(17)
N(2)
N(1)
O(1)
O(2)
C(13)
C(4)
C(3)
C(5)
C(6)
C(2)
C(1)
C(14)

(a)



(b)

Discussion of II

The crystal structure determination of the C-nitroso-imine N-oxide II reveals a transoid arrangement of the -N = C - N = 0 group of atoms [Figure 4.2.1 (a) and Table 4.2.4 (c)]. The bonded atoms O(1), N(1), C(13), N(2) and O(2) are experimentally coplanar with dihedral angles of N(1) - C(13) - N(2) - O(2) [179.3 (4)°] and N(2) - C(13) - N(1) - O(1) [178.9 (4)°] (χ^2 for the least-squares plane is equal to 7.61 with 2 degrees of freedom). However, coplanarity between the O-N = C-N = 0 and the aryl groups is not attained due to steric hindrance, and thus the torsion angles C(3) - C(4) - C(13) - N(1) and C(12) - C(7) - N(1) - C(13) are equal to -64.0 (6)° and 86.4 (5)° respectively (the angle between the least-squares planes of the rings is equal to 19.8°). The central N(1) - C(13) bond length of 1.331 (6) Å compares with the partial $N(sp^2)$ - $C(sp^2)$ double bond quoted for formamide[56] [1.322 (3) Å] and although the C(13) - N(2) bond [1.380 (6) Å] has not been significantly shortened with respect to the typical $C(sp^2)$ - $N(sp^2)$ single bond [taken as 1.391 (2) Å, section 3.1 this thesis], the two N-O bonds [1.256 (5) Å and 1.247 (6) Å] do seem to possess partial double-bond character and therefore support the suggestion of a 'through conjugation' effect whereby a negative charge [formally located on atom O(1)] delocalizes towards the oxygen atom O(2). A length of 1.265 (8) Å, ascribed to a similar partial double bond (N-O) provides further evidence for the existence of the delocalized system postulated[107]. [From Pauling's sum of covalent radii corrected

for electronegativity, the N-O single bond is equal to 1.44 Å and the N = O double bond - to 1.20 Å. In formamidoxime[108] and N,N-dimethylacetamidoxime[109] the single N-O bonds are quoted as 1.414 (9) Å and 1.430 Å respectively] .

The close non-bonded intramolecular contacts observed and listed in Table 4.2.5 and the unequal angles at the C(13) atom [113.0 (4)°, 125.9 (4)° and 121.0 (4)°] and the N(1) atom [115.6 (4)°, 122.2 (3)° and 122.1 (4)°] do reflect an appreciable degree of configurational strain in the molecule though the non-bonded separations seem to be almost maximized by the nearly perpendicular arrangement of the rings with respect to the O-N = C-N = 0 group of atoms (Table 4.2.6).

It has been noted previously[102] by Shiraishi et al (1978) that for C-nitroso-imines a coplanar configuration of the nitroso and the aryl group attached to the carbon atom is favoured on the basis of possible interaction between the two groups whereby the -N = C-N = 0 moeity is in the cisoid form and the aryl group attached to the nitrogen atom is tilted with respect to it (Figure 4.2.2).

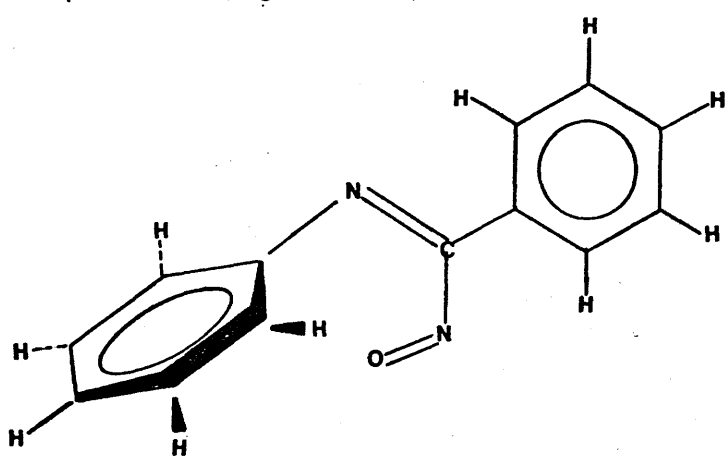


Figure 4.2.2.

This could account for the exclusive production of one cyclization product (1,2,4-benzoxadiazine) when the ortho-positions (2,6) on the aryl ring attached to the carbon atom are not substituted. In the case of C-nitroso-imine-N-oxides, the additional $\overset{+}{N} - \overline{O}$ bond introduces new non-bonded repulsions which presumably cause the two groups (O-N = C-N = 0 and the ring attached to the C-atom) to deviate significantly from coplanarity. That these interactions (introduced by the $\overset{+}{N} - \overline{O}$ bond) are quite considerable is indicated by the short O(1) ... C(3) (3.08 Å) contact found for molecule II (present analysis) and since this is a nearly maximized separation a much shorter separation would be invoked for a case where the two groups are coplanar. An examination of a molecular model shows that an angle of 30° between the groups would result in a separation of ~2.5 Å between O(1) and C(3) and ~ 2 Å between O(1) and H(33).

Once coplanarity is lost, the cisoid form of the O = N-C = N-O group cannot be exclusively preferred to the transoid form and hence two cyclization products are expected (1,2,4-benzoxadiazines and benzimidazole 3-oxides). Evidence to support this is given in the introduction to this section where compound (10) cyclizes to give compound II (the benzimidazole 3-oxide) and as mentioned by Gilchrist et al[100] the 3-phenyl-1,2,4-benzoxadiazine is also formed (these observations are unpublished).

It appears therefore that rationalization of the reaction products from cyclization of C-nitroso-imine-N-oxides can be given in terms of steric factors as for the similar cases of C-nitroso-imines, and in particular for the case where the aryl ring attached to the carbon atom is disubstituted at the ortho-positions[102].

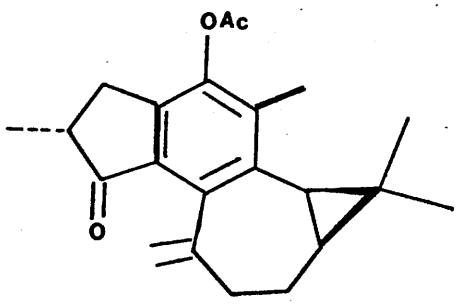
Selected intermolecular contacts are given in Table 4.2.5 though none are unusually short.

CHAPTER 5

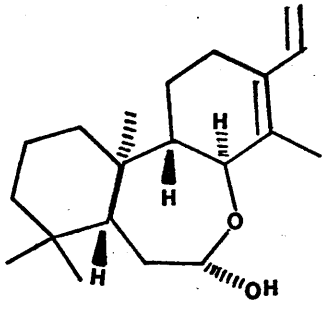
STRUCTURAL STUDIES OF THREE NATURAL PRODUCTS

THE CRYSTAL AND MOLECULAR STRUCTURE OF TWO DITERPENOIDS OF THE FORM

I.



II.

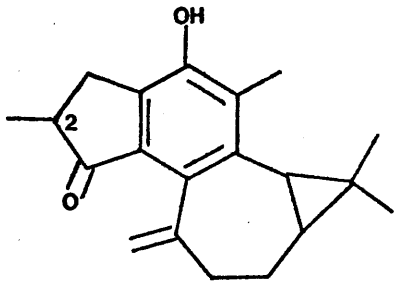


5.1 Introduction

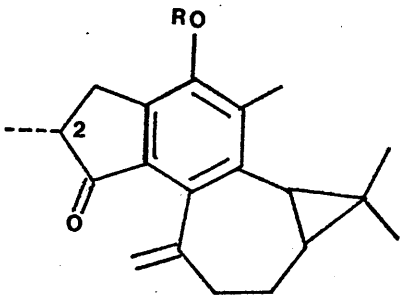
The plant family 'Euphorbiaceae'[110] produces a range of diterpenoids based on the cembrene[110] and casbene[110] (4) skeleton. Some of these compounds exhibit cocarcinogenic activity (e.g. lathyrol), whereas others (e.g. jatrophone[111] and jatrophatrione[112]) are tumour-inhibitors. Connolly et al[113] (1979) has isolated, from the roots of Jatropha gossypiifolia (Euphorbiaceae), two new diterpenoids, jatropholone A (1), $C_{20}H_{24}O_2$ and its C-2 epimer jatropholone B (2).

jatropholone A $\overset{\text{base}}{\rightleftharpoons}$ jatropholone B

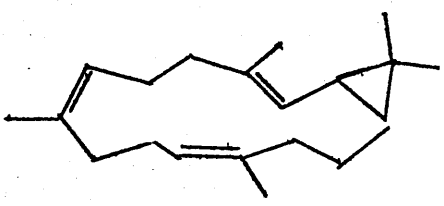
Spectroscopic examinations[113] of these compounds readily revealed their functionality which included a tricarbocyclic system in addition to a fully substituted cresol ring. Furthermore, the indication of the existence of a cyclopropane ring suggested that the jatropholones were based on a cyclized casbene skeleton[114]. Since there was insufficient evidence to prove unambiguously the detailed structures of the two diterpenoids, jatropholone B acetate (3) was submitted for an X-ray analysis which established structure (2) for this derivative. The jatropholones represent a new skeletal type of diterpenoids, closely related to crotofolin A[115] (5). Their absolute configuration has not been established.



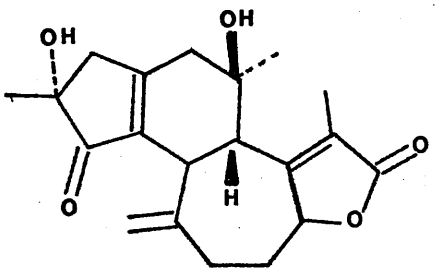
1



2 (R = H)
3 (R = Ac)

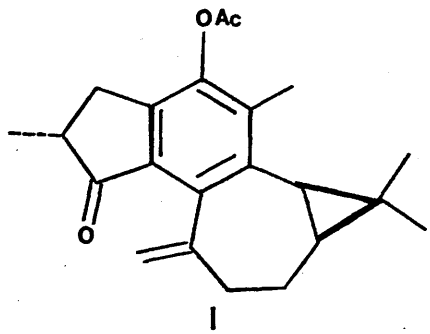


4



5

Experimental and Results for I



I

Jatropholone B

Crystal Data

Molecular Formula	$C_{22}H_{26}O_3$
Molecular Weight	338.48 a.m.u.
Crystal System	Orthorhombic
Unit Cell Dimensions	a = 12.389(2) Å
	b = 17.875(3) Å
	c = 8.708 (1) Å
Unit Cell Volume	V = 1928.73 $Å^3$
Number of Molecules Per Unit Cell	Z = 4
Calculated Density	D_c = 1.17 $g.cm^{-3}$
Number of Molecules Per Asymmetric Unit	N = 1
Space Group	$P2_12_12_1$ (D_2^4, No.19)
Equivalent Positions	x,y,z
	1/2 - x, - y, 1/2 + z
	1/2 + x, 1/2 - y, - z
	-x, 1/2 + y, 1/2 - z

Linear Absorption Coefficient	$\mu = 0.71\ cm^{-1}$
Number of Electrons Per Unit Cell	$F(000) = 728$

Data Collection

Diffractometer Used	Hilger and Watts Y290
Radiation Used	$M_0 - K_\alpha$, $\overline{\lambda} = 0.71069\ \text{Å}$
Filter	Graphite Monochromator
	$\cos^2 2\theta_m = 0.970$
Upper Limit for Data Collection	$2\theta_{max} = 58^\circ$
Number of Observed	
Independent Reflections	$m = 1766$
Unobserved Cut-Off	$2.5\ \sigma_I$
Number of Parameters Refined	$n = 331$
Number of Reflections Per	
Parameter	$m/n = 5.3$

Structure Determination and Refinement

The conditions h = 2n, k = 2n and l = 2n limiting respectively the hoo, oko and ool reflections in the diffraction data determined the space group to be $P2_12_12_1$ (D_2^4, No.19). The direct-methods program 'MULTAN' (Version 1974) was used to calculate phases for the highest 250 $|E|$ values (10 $|E|$ values per nonhydrogen atom). 2000 Σ_2 relationships were used (8 relationships per one $|E|$ value), and the phase set with the largest combined figure of merit (out of 32 sets produced from 2 special and 2 general reflections) was selected to give a calculated E-map which revealed the positions of a 13-atom fragment (including the fully substituted benzene ring). Alternate least-squares

refinements with variable isotropic thermal parameters and difference Fourier calculations yielded the coordinates of the missing 12 nonhydrogen atoms. The conventional discrepancy factor and weighted R factor at this stage were 0.202 and 0.265 respectively.

The crystal structure was refined during 17 cycles of block-diagonal least-squares calculations minimizing the sum of the weighted squares of the residual $[\ \Sigma w(|F_o| - |F_c|)^2]$ to a final conventional R of 0.035 and weighted R_w of 0.046. All calculated shifts were < 0.09, the average shift/error being equal to 0.02 and the final value for the standard deviation of an observation of unit weight(s) amounted to 3.464. A detailed description of the different stages of the refinement is given in Table 5.1.1.

The H atoms were located on difference electron-density maps evaluated at intermediate stages of the least-squares refinement of the structural parameters. In the final 7 cycles of the least-squares calculations, positional parameters for all the atoms, anisotropic thermal vibration parameters for the nonhydrogen atoms and isotropic thermal vibration parameters for the H atoms were varied.

The quantities $w = (0.4291 - 0.0400 |F_o| + 0.0045 |F_o|^2)^{-1}$ and $w = 1/0.5187$ for $|F_o| > \overline{|F_o|}_{min}$ and $|F_o| < \overline{|F_o|}_{min}$ respectively (where $\overline{|F_o|}_{min} = 2.7$) were used to weight the least-squares differences for the observed data. The final analysis of the average $w\Delta^2$ as a function of $|F_o|$ indicated the use of a proper weighting scheme for

this data.

There were no significant residual peaks in the final difference Fourier map, the highest peak showing an electron density of 0.20 $e\text{Å}^{-3}$, and no absorption correction was applied.

The scattering factors for O and C atoms were taken from Cromer and Mann (1968) and those for H were from Stewart et al (1965).

Final values for the observations, calculated structure amplitudes and phases are given in the supplement to this thesis.

Figure 5.1.1(a) is an 'ORTEP' drawing (Johnson, 1965) indicating the numbering scheme and illustrating the 50% probability ellipsoids for the nonhydrogen atoms and the overall molecular conformation.

Figure 5.1.1(b) represents a packing diagram viewed along the c-axis and shows the arrangement of the molecules in the unit cell.

Final atomic coordinates and their e.s.d.'s estimated from the inverse of the least-squares matrix together with the different thermal parameters are given in Tables 5.1.2(a) to 5.1.2(d). Tables 5.1.3 to 5.1.6 list bonded and non-bonded distances with e.s.d.'s and other relevant molecular dimensions.

Table 5.1.1

PROGRESS OF LEAST-SQUARES REFINEMENT

CYCLES	PARAMETERS REFINED	R	R_w
0	none	0.202	0.265
4	$x,y,z,U_{(iso)}$ for C, O; scale factor; full matrix; unit weights.	0.174	0.217
4	Counting loss correction to 14 reflections; x,y,z,U_{ij} for C, O; scale factor; block diagonal; unit weights.	0.096	0.107
2	As above, but including 22 H atoms in the structure factor calculations as fixed contributors.	0.061	0.065
3	x,y,z,U_{ij} for C, O; $x,y,z,U_{(iso)}$ for 26 H atoms; scale factor; block diagonal; unit weights.	0.046	0.047
2	As in the last 3 cycles of refinement but with applying a weighting scheme.	0.038	0.051
2	As in the last 2 cycles of refinement but with partial shifts of 0.5 and excluding 3 reflections from the calculation (appeared to be affected by extinction)	0.035	0.046

Table 5.1.2 (a,b,c,d)

(a) Fractional atomic coordinates ($\times 10^4$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM X/A Y/B Z/C

(b) Anisotropic thermal parameters ($\AA^2$, $\times 10^3$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}

(c) Fractional atomic coordinates ($\times 10^3$) of hydrogen atoms with e.s.d.'s in parentheses. The hydrogens are numbered according to the atoms to which they are attached.

(d) Isotropic thermal parameters ($\AA^2$, $\times 10^2$) of hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM $U_{(iso)}$.

C(1)	8582(2)	10222(2)	8478(3)
C(2)	7721(2)	9794(2)	7658(4)
C(3)	7974(3)	8962(2)	7557(4)
C(4)	9111(2)	8819(1)	7049(3)
C(5)	9562(2)	9306(1)	5811(3)
C(6)	9741(2)	9033(1)	4326(3)
C(7)	9447(2)	8305(1)	3640(3)
C(8)	9969(2)	8268(2)	2036(3)
C(9)	10353(3)	9061(2)	1695(3)
C(10)	10241(2)	9467(1)	3209(3)
C(11)	10568(2)	10179(1)	3579(3)
C(12)	10424(2)	10472(1)	5048(3)
C(13)	9874(2)	10039(1)	6145(3)
C(14)	9668(2)	10342(1)	7729(3)
C(15)	8921(2)	11001(2)	8036(3)
C(16)	9732(3)	8303(2)	7686(4)
C(17)	10877(4)	7694(2)	2065(4)
C(18)	12081(2)	10604(2)	2152(4)
C(19)	12382(3)	11088(2)	0827(4)
C(20)	10894(3)	11224(2)	5448(4)
C(21)	8347(3)	11396(2)	6739(4)
C(22)	9249(3)	11528(2)	9315(4)
O(1)	8883(2)	7820(1)	4177(2)
O(2)	11005(1)	10635(1)	2410(2)
O(3)	12657(2)	10226(2)	2906(4)

5.1.2 (a)

C(1)	61(1)	70(2)	39(1)	4(1)	4(1)	-6(1)
C(2)	54(1)	89(2)	66(2)	-4(1)	10(1)	-9(2)
C(3)	83(2)	88(2)	66(2)	-30(2)	22(2)	-12(2)
C(4)	80(2)	50(1)	38(1)	-8(1)	2(1)	-4(1)
C(5)	47(1)	53(1)	38(1)	4(1)	0(1)	1(1)
C(6)	48(1)	53(1)	38(1)	6(1)	-1(1)	2(1)
C(7)	63(1)	56(1)	45(1)	6(1)	-8(1)	-2(1)
C(8)	77(2)	74(2)	39(1)	13(2)	-10(1)	-9(1)
C(9)	85(2)	73(2)	39(1)	18(2)	6(1)	2(1)
C(10)	49(1)	56(1)	38(1)	13(1)	1(1)	4(1)
C(11)	44(1)	57(1)	47(1)	9(1)	8(1)	11(1)
C(12)	45(1)	50(1)	52(1)	8(1)	4(1)	1(1)
C(13)	42(1)	51(1)	40(1)	4(1)	0(1)	-1(1)
C(14)	50(1)	56(1)	40(1)	4(1)	-8(1)	-4(1)
C(15)	60(1)	63(1)	43(1)	10(1)	0(1)	-4(1)
C(16)	127(3)	63(2)	53(2)	0(2)	6(2)	7(1)
C(17)	124(3)	80(2)	70(2)	30(2)	12(2)	-5(2)
C(18)	55(1)	75(2)	69(2)	15(1)	18(1)	13(2)
C(19)	71(2)	85(2)	78(2)	2(2)	30(2)	11(2)
C(20)	70(2)	57(2)	80(2)	-7(1)	11(2)	-5(1)
C(21)	76(2)	86(2)	55(2)	29(2)	0(1)	2(2)
C(22)	104(2)	69(2)	56(2)	5(2)	0(2)	-17(1)
O(1)	100(1)	64(1)	62(1)	-17(1)	0(1)	-6(1)
O(2)	55(1)	66(1)	58(1)	11(1)	16(1)	18(1)
O(3)	58(1)	162(3)	135(2)	31(2)	24(1)	74(2)

H(11)	863(2)	1012(2)	956(4)
H(21)	696(3)	986(2)	819(4)
H(22)	763(3)	1001(2)	668(3)
H(31)	752(3)	876(2)	688(4)
H(32)	786(3)	872(2)	850(5)
H(81)	939(3)	815(2)	131(4)
H(91)	1107(3)	901(2)	143(5)
H(92)	994(3)	927(2)	097(4)
H(141)	1029(2)	1035(1)	837(3)
H(161)	941(3)	797(2)	845(5)
H(162)	1055(3)	823(2)	738(5)
H(171)	1058(3)	718(2)	226(4)
H(172)	1152(3)	789(2)	282(5)
H(173)	1123(3)	773(2)	113(4)
H(191)	1202(4)	1161(3)	106(7)
H(192)	1209(5)	1084(3)	-012(8)
H(193)	1313(3)	1111(2)	075(5)
H(201)	1165(4)	1125(2)	528(5)
H(202)	1071(5)	1162(3)	477(7)
H(203)	1076(5)	1141(3)	638(7)
H(211)	827(3)	1107(2)	581(5)
H(212)	764(3)	1156(2)	694(5)
H(213)	878(4)	1194(2)	649(5)
H(221)	859(3)	1184(2)	967(5)
H(222)	990(3)	1197(2)	898(4)
H(223)	949(3)	1121(2)	1013(5)

H(11)	7(1)
H(21)	9(1)
H(22)	7(1)
H(31)	7(1)
H(32)	11(1)
H(81)	8(1)
H(91)	9(1)
H(92)	9(1)
H(141)	5(1)
H(161)	11(1)
H(162)	10(1)
H(171)	9(1)
H(172)	11(1)
H(173)	8(1)
H(191)	15(2)
H(192)	19(3)
H(193)	11(1)
H(201)	12(1)
H(202)	15(2)
H(203)	17(2)
H(211)	10(1)
H(212)	10(1)
H(213)	11(1)
H(221)	12(1)
H(222)	9(1)
H(223)	11(1)

Table 5.1.3 (a,b,c)

(a) Interatomic distances (Å) with e.s.d.'s in parentheses. The hydrogen atoms are numbered according to the atoms to which they are attached.

(b) Interbond angles (degrees) with e.s.d.'s (degrees) in parentheses.

(c) Torsion angles (degrees) with e.s.d.'s (degrees) in parentheses.

A torsion angle A-B-C-D is considered to be positive if when viewed down the B-C bond the A-B bond will eclipse the C-D bond when rotated less than 180° in a clockwise direction.

C(1)	- C(2)	1.495(4)	C(8)	- C(17)	1.522(5)
C(1)	- C(14)	1.511(3)	C(9)	- C(10)	1.511(4)
C(1)	- C(15)	1.505(4)	C(10)	- C(11)	1.374(4)
C(2)	- C(3)	1.521(5)	C(11)	- C(12)	1.393(3)
C(3)	- C(4)	1.499(5)	C(11)	- O(2)	1.412(3)
C(4)	- C(5)	1.494(3)	C(12)	- C(13)	1.406(3)
C(4)	- C(16)	1.324(4)	C(12)	- C(20)	1.507(4)
C(5)	- C(6)	1.400(3)	C(13)	- C(14)	1.503(3)
C(5)	- C(13)	1.396(3)	C(14)	- C(15)	1.521(4)
C(6)	- C(7)	1.478(4)	C(15)	- C(21)	1.510(4)
C(6)	- C(10)	1.390(3)	C(15)	- C(22)	1.515(4)
C(7)	- C(8)	1.541(4)	C(18)	- C(19)	1.491(5)
C(7)	- O(1)	1.207(3)	C(18)	- O(2)	1.354(3)
C(8)	- C(9)	1.525(4)	C(18)	- O(3)	1.181(4)

5.1.3 (a)

C(1) - H(11)	0.964(31)	C(17) - H(172)	1.091(41)
C(2) - H(21)	1.054(36)	C(17) - H(173)	1.028(34)
C(2) - H(22)	0.941(31)	C(19) - H(191)	1.056(51)
C(3) - H(31)	0.894(33)	C(19) - H(192)	1.001(67)
C(3) - H(32)	0.939(43)	C(19) - H(193)	0.925(42)
C(8) - H(81)	0.979(34)	C(20) - H(201)	0.948(47)
C(9) - H(91)	0.922(38)	C(20) - H(202)	0.947(53)
C(9) - H(92)	0.893(35)	C(20) - H(203)	0.896(64)
C(14) - H(141)	0.955(24)	C(21) - H(211)	1.000(41)
C(16) - H(161)	0.981(41)	C(21) - H(212)	0.943(39)
C(16) - H(162)	1.059(39)	C(21) - H(213)	1.141(42)
C(17) - H(171)	0.996(34)	C(22) - H(221)	1.040(44)
C(22) - H(223)	0.962(44)		

5.1.3 (a) (continued)

C(14) - C(1) - C(2)	120.16(22)	C(15) - C(1) - C(2)	123.42(23)
C(3) - C(2) - C(1)	112.37(25)	C(15) - C(1) - C(14)	60.60(17)
C(13) - C(14) - C(1)	119.73(20)	C(15) - C(14) - C(1)	59.50(17)
C(14) - C(15) - C(1)	59.89(17)	C(21) - C(15) - C(1)	119.52(24)
C(22) - C(15) - C(1)	117.56(23)	C(4) - C(3) - C(2)	112.20(26)
C(5) - C(4) - C(3)	117.73(23)	C(16) - C(4) - C(3)	122.77(28)
C(16) - C(4) - C(5)	119.45(28)	C(6) - C(5) - C(4)	121.48(21)
C(13) - C(5) - C(4)	119.97(20)	C(13) - C(5) - C(6)	118.45(21)
C(7) - C(6) - C(5)	129.93(22)	C(10) - C(6) - C(5)	121.47(22)
C(12) - C(13) - C(5)	120.57(21)	C(14) - C(13) - C(5)	118.87(20)
C(10) - C(6) - C(7)	108.57(20)	C(8) - C(7) - C(6)	107.50(21)
O(1) - C(7) - C(6)	128.16(23)	C(9) - C(10) - C(6)	112.54(22)
C(11) - C(10) - C(6)	118.95(21)	O(1) - C(7) - C(8)	124.32(24)
C(9) - C(8) - C(7)	105.52(22)	C(17) - C(8) - C(7)	108.90(24)
C(17) - C(8) - C(9)	113.55(27)	C(10) - C(9) - C(8)	104.37(21)
C(11) - C(10) - C(9)	128.51(23)	C(12) - C(11) - C(10)	121.70(22)
O(2) - C(11) - C(10)	118.54(21)	O(2) - C(11) - C(12)	119.66(21)
C(13) - C(12) - C(11)	118.66(22)	C(20) - C(12) - C(11)	119.82(23)
C(18) - O(2) - C(11)	118.25(21)	C(20) - C(12) - C(13)	121.47(23)
C(14) - C(13) - C(12)	120.47(21)	C(15) - C(14) - C(13)	122.94(20)
C(21) - C(15) - C(14)	121.09(23)	C(22) - C(15) - C(14)	116.61(23)
C(22) - C(15) - C(21)	112.68(25)	O(2) - C(18) - C(19)	110.53(25)
O(3) - C(18) - C(19)	127.69(28)	O(3) - C(18) - O(2)	121.77(29)

C(14) - C(1) - C(2) - C(3)	71.0(3)	C(15) - C(1) - C(2) - C(3)	143.7(3)
C(2) - C(1) - C(14) - C(13)	0.8(4)	C(2) - C(1) - C(14) - C(15)	113.8(3)
C(15) - C(1) - C(14) - C(13)	-113.0(2)	C(2) - C(1) - C(15) - C(14)	-108.6(3)
C(2) - C(1) - C(15) - C(21)	2.4(4)	C(2) - C(1) - C(15) - C(22)	145.1(3)
C(14) - C(1) - C(15) - C(21)	111.0(3)	C(14) - C(1) - C(15) - C(22)	-106.3(3)
C(1) - C(2) - C(3) - C(4)	-46.8(3)	C(2) - C(3) - C(4) - C(5)	-40.2(4)
C(2) - C(3) - C(4) - C(16)	137.3(3)	C(3) - C(4) - C(5) - C(6)	-108.4(3)
C(3) - C(4) - C(5) - C(13)	75.3(3)	C(16) - C(4) - C(5) - C(6)	74.0(4)
C(16) - C(4) - C(5) - C(13)	-102.3(3)	C(4) - C(5) - C(6) - C(7)	7.1(4)
C(4) - C(5) - C(6) - C(10)	-174.8(2)	C(13) - C(5) - C(6) - C(7)	-176.5(2)
C(13) - C(5) - C(6) - C(10)	1.6(3)	C(4) - C(5) - C(13) - C(12)	171.9(2)
C(4) - C(5) - C(13) - C(14)	-4.6(3)	C(6) - C(5) - C(13) - C(12)	-4.5(3)
C(6) - C(5) - C(13) - C(14)	179.0(2)	C(5) - C(6) - C(7) - C(8)	-172.9(2)
C(5) - C(6) - C(7) - O(1)	8.8(5)	C(10) - C(6) - C(7) - C(8)	8.8(3)
C(10) - C(6) - C(7) - O(1)	-169.5(3)	C(5) - C(6) - C(10) - C(9)	179.9(2)
C(5) - C(6) - C(10) - C(11)	0.3(4)	C(7) - C(6) - C(10) - C(9)	-1.7(3)
C(7) - C(6) - C(10) - C(11)	178.7(2)	C(6) - C(7) - C(8) - C(9)	-12.3(3)
C(6) - C(7) - C(8) - C(17)	109.9(3)	O(1) - C(7) - C(8) - C(9)	166.1(3)
O(1) - C(7) - C(8) - C(17)	-71.7(4)	C(7) - C(8) - C(9) - C(10)	10.9(3)
C(17) - C(8) - C(9) - C(10)	-108.2(3)	C(8) - C(9) - C(10) - C(6)	-6.2(3)
C(8) - C(9) - C(10) - C(11)	173.4(2)	C(6) - C(10) - C(11) - C(12)	0.8(4)
C(6) - C(10) - C(11) - O(2)	-175.6(2)	C(9) - C(10) - C(11) - C(12)	-178.7(2)
C(9) - C(10) - C(11) - O(2)	4.8(4)	C(10) - C(11) - C(12) - C(13)	-3.7(4)
C(10) - C(11) - C(12) - C(20)	173.8(2)	O(2) - C(11) - C(12) - C(13)	172.7(2)
O(2) - C(11) - C(12) - C(20)	-9.8(4)	C(10) - C(11) - O(2) - C(18)	-89.0(3)
C(12) - C(11) - O(2) - C(18)	94.5(3)	C(11) - C(12) - C(13) - C(5)	5.5(3)
C(11) - C(12) - C(13) - C(14)	-178.0(2)	C(20) - C(12) - C(13) - C(5)	-171.9(2)
C(20) - C(12) - C(13) - C(14)	4.6(4)	C(5) - C(13) - C(14) - C(1)	-45.9(3)
C(5) - C(13) - C(14) - C(15)	-116.9(3)	C(12) - C(13) - C(14) - C(1)	137.6(2)
C(12) - C(13) - C(14) - C(15)	66.6(3)	C(1) - C(14) - C(15) - C(21)	-108.4(3)
C(1) - C(14) - C(15) - C(22)	107.9(3)	C(13) - C(14) - C(15) - C(1)	107.7(3)
C(13) - C(14) - C(15) - C(21)	-0.7(4)	C(13) - C(14) - C(15) - C(22)	-144.4(2)
C(19) - C(18) - O(2) - C(11)	176.9 (2)	O(3) - C(18) - O(2) - C(11)	- 2.4 (4)

5.1.3 (c)

Table 5.1.4

A. Selected intramolecular non-bonded distances (<4.0 Å).

C(2) ... C(16)	3.65	C(12) ... O(3)	3.37
C(2) ... C(21)	3.07	C(13) ... C(16)	3.39
C(3) ... C(6)	3.57	C(14) ... C(20)	2.96
C(4) ... C(7)	3.14	C(13) ... C(21)	3.12
C(4) ... O(1)	3.09	C(15) ... C(20)	3.35
C(5) ... C(15)	3.68	C(16) ... O(1)	3.34
C(5) ... O(1)	3.13	C(16) ... H(32)	2.54
C(6) ... C(16)	3.20	C(17) ... O(1)	3.09
C(7) ... C(16)	3.54	C(17) ... H(91)	2.43
C(9) ... C(18)	3.51	C(18) ... C(20)	3.41
C(9) ... O(2)	2.99	C(20) ... C(21)	3.36
C(10) .. C(17)	3.41	C(20) ... O(2)	2.85
C(10) .. C(18)	3.19	C(22) ... H(11)	2.64
C(10) .. O(3)	3.30	C(22) ... H(141)	2.61
C(12) .. C(15)	3.34		
C(12) .. C(21)	3.39		

B. Selected intermolecular distances (<4.0 Å).

C(5) ... C(19)^{i}	3.85	C(17) ... C(22)^{iii}	3.78
C(8) ... C(16)^{ii}	3.80	C(19) ... O(1)^{iv}	3.47
C(9) ... C(16)^{ii}	3.82	C(19) ... O(3)^{v}	3.46

Romal numeral superscripts refer to the following equivalent positions relative to the molecule at (x,y,z):

(i) 5/2 - x, 2 - y, 1/2 + z

(ii) x, y, z - 1

(iii) 2 - x, y - 1/2, 3/2 - z.

(iv) 2 - x, 1/2 + y, 1/2 - z

(v) 5/2 - x, 2 - y, z - 1/2

Table 5.1.4 (continued)

Table 5.1.5

LEAST – SQUARES PLANES

Planes are in the form of AX + BY + CZ - D = 0 where X, Y and Z refer to an orthogonalized set of axes, D is the perpendicular distance from the plane to the origin and A, B and C refer to the components of unit vector normal to the best plane. An asterisk denotes atoms used to define the plane.

A.

(I) Equation of the plane

$$-0.8875X + 0.3556Y - 0.2931Z + 6.0696 = 0$$

χ^2 = 295.14 with 3 degrees of freedom.

C(5)*	-0.013 (2)	C(4)	-0.142 (3)
C(6)*	-0.004 (2)	C(7)	0.032 (3)
C(10)*	0.008 (2)	C(9)	0.013 (3)
C(11)*	0.006 (2)	C(14)	0.040 (2)
C(12)*	-0.024 (2)	C(20)	-0.166 (3)
C(13)*	0.025 (2)	O(2)	0.114 (2)

(2) Equation of the plane

$$0.3207X + 0.6564Y + 0.6828Z + 18.1723 = 0$$

χ^2 = 32.75 with one degree of freedom.

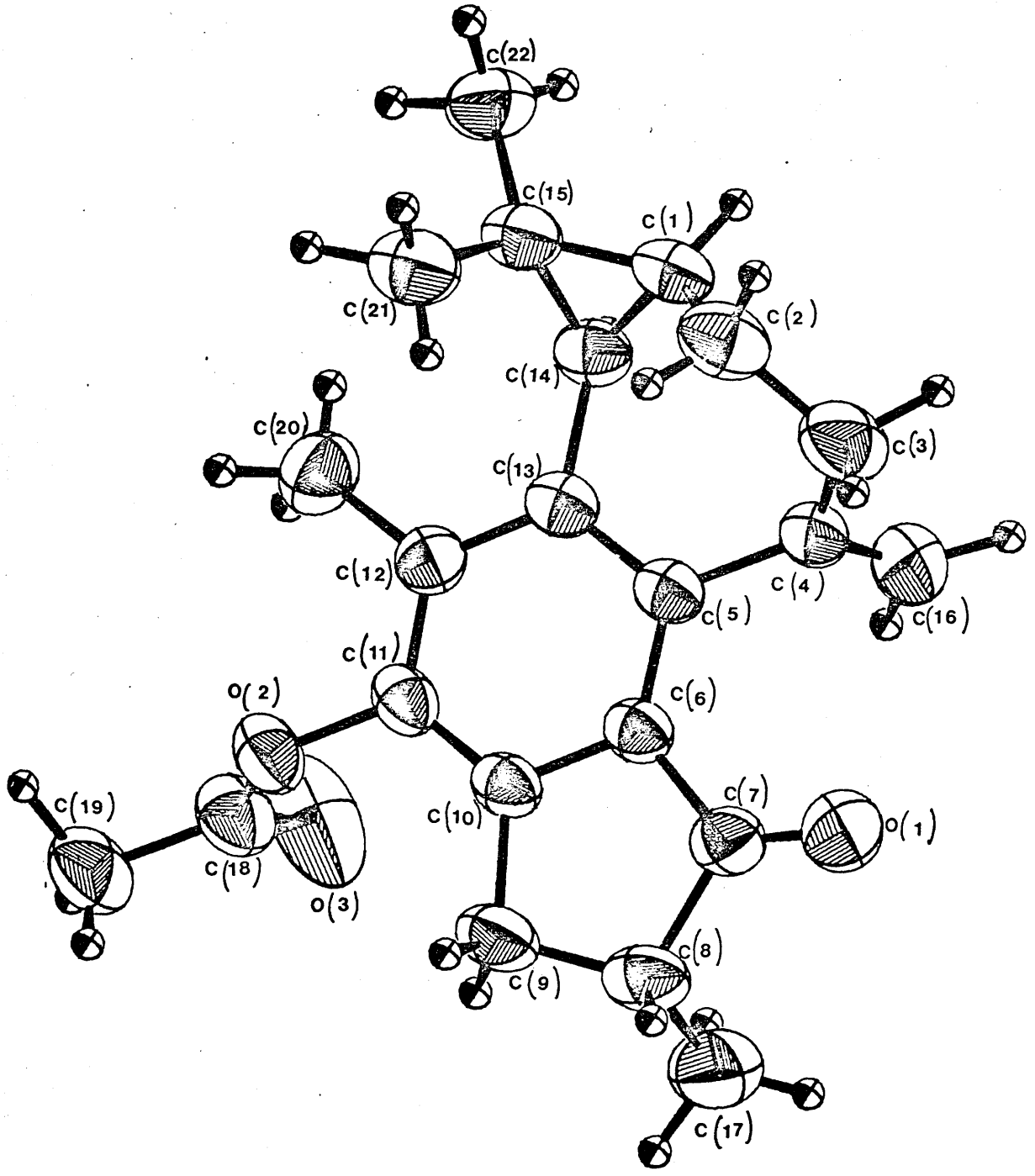
C(3)*	0.006 (3)	C(5)*	0.003 (2)
C(4)*	-0.012 (2)	C(16)*	0.008 (2)

B. The angle between planes (I) and (2) is 75.5°.

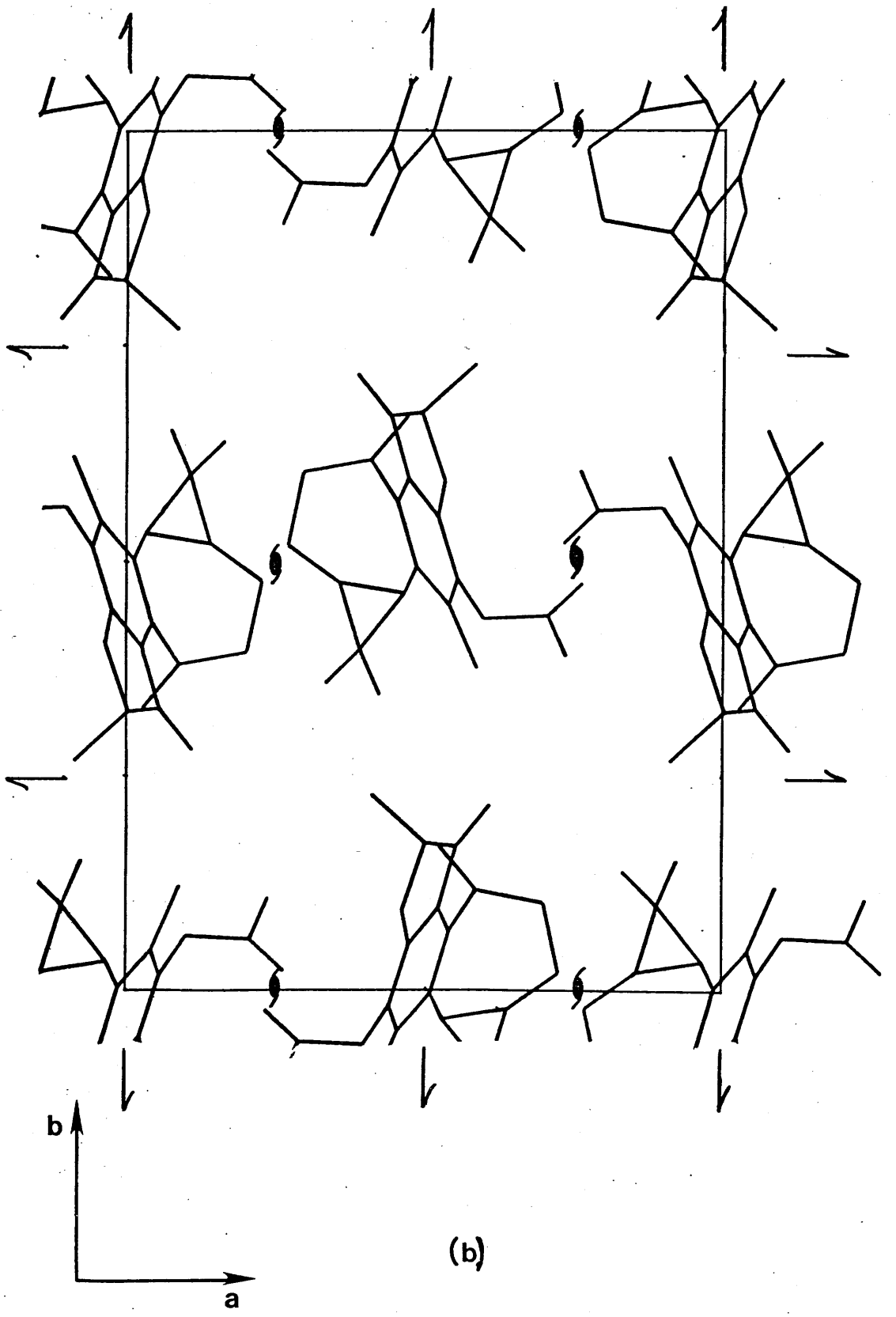
Figure 5.1.1 (a and b)

(a) A general view of I giving the atomic numbering scheme. Hydrogen atoms are numbered according to the atoms to which they are bonded.

(b) The molecular packing of I viewed along the c-axis.


C(22)
C(15)
C(1)
C(21)
C(2)
C(14)
C(20)
C(3)
C(13)
C(12)
C(4)
C(5)
C(16)
C(11)
O(2)
C(6)
C(19)
C(10)
C(7)
O(1)
C(18)
O(3)
C(8)
C(9)
C(17)

(a)



(b)

Discussion of I

The main features of the conformation and geometries of I are illustrated in Figures 5.1.1 (a) and 5.1.2 (a and b) and in Table 5.1.6.

The seven-membered ring possesses essentially a twisted-boat conformation indicated by its dihedral angles [Figure 5.1.2(b) and Table 5.1.6] and confirmed by an inspection of a Dreiding stereomodel of I. The deviations from the calculated dihedral values for cycloheptane[116,117] (Hendrickson, 1961, 1967) suggest a high degree of flattening in the seven-membered ring compared to cycloheptane, an effect which can presumably be ascribed to the presence of three adjacent sp^2 hybridized centers and a cyclopropane ring.

	Dihedral Angles						
	w_1	w_2	w_3	w_4	w_5	w_6	w_7
Seven-membered ring in I	-40.2	75.3	-4.6	-45.9	0.8	71.0	-46.8
Cycloheptane[116,117]	-45.4	64.4	17.9	-74.6	17.9	64.4	-45.4

Table 5.1.6

The five-membered ring, in which one torsion angle has a value of almost zero [C(7) - C(6) - C(10) - C(9) is equal to -1.7 (3)°] as a result of fusion to the benzene ring, adopts a conformation which approximates to an envelope[118] form, though the degree of flattening is

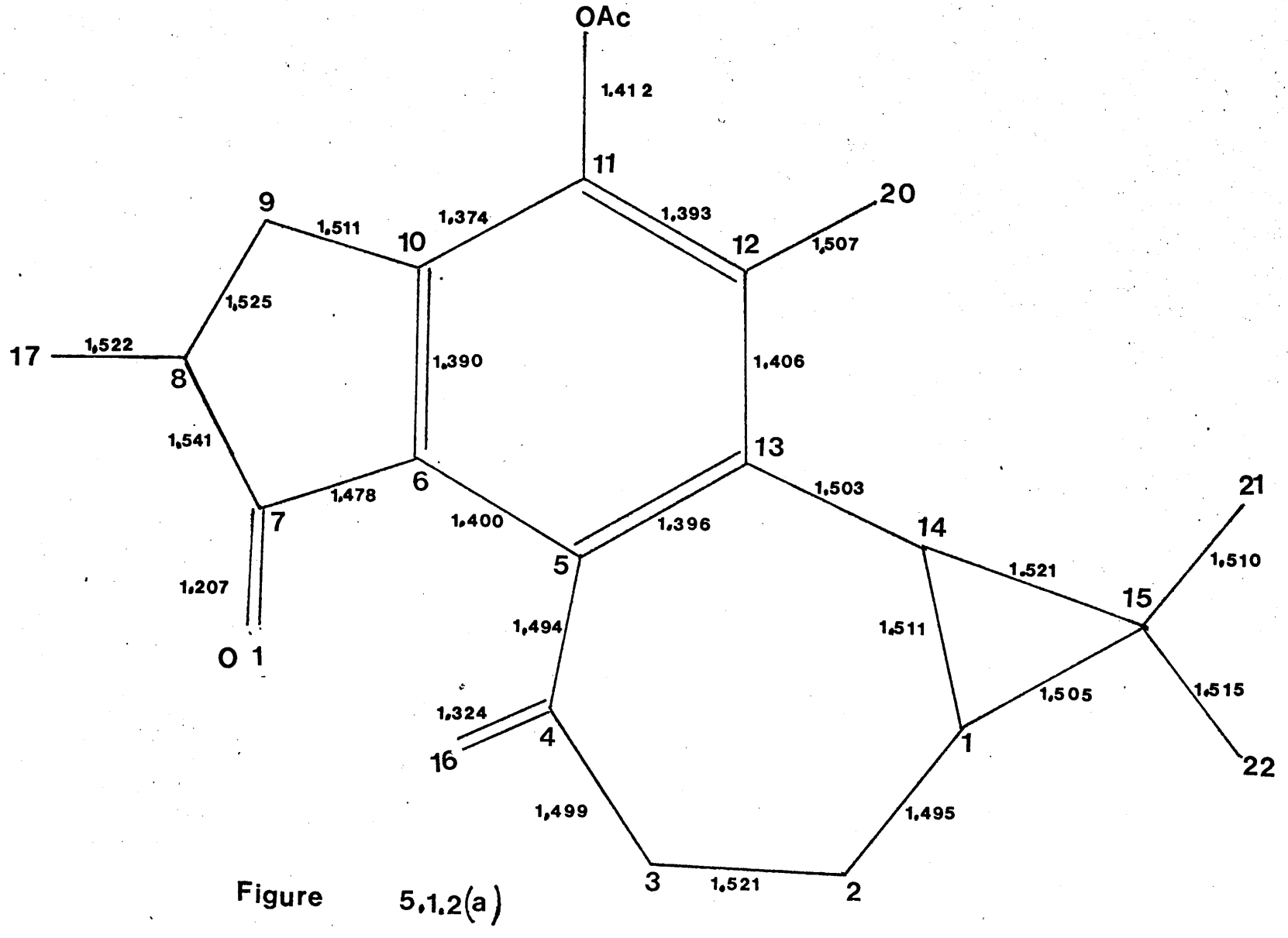

OAc
1.412
11
9
1.511
10
1.374
1.393
12
20
1.507
1.525
17
1.522
8
1.390
1.406
1.541
13
6
1.503
21
1.478
7
1.400
1.396
14
1.521
1.510
1.207
5
15
1.494
1.511
O 1
1.324
1.505
1.515
4
1
16
22
1.499
1.495
3
1.521
2

Figure 5,1,2(a)

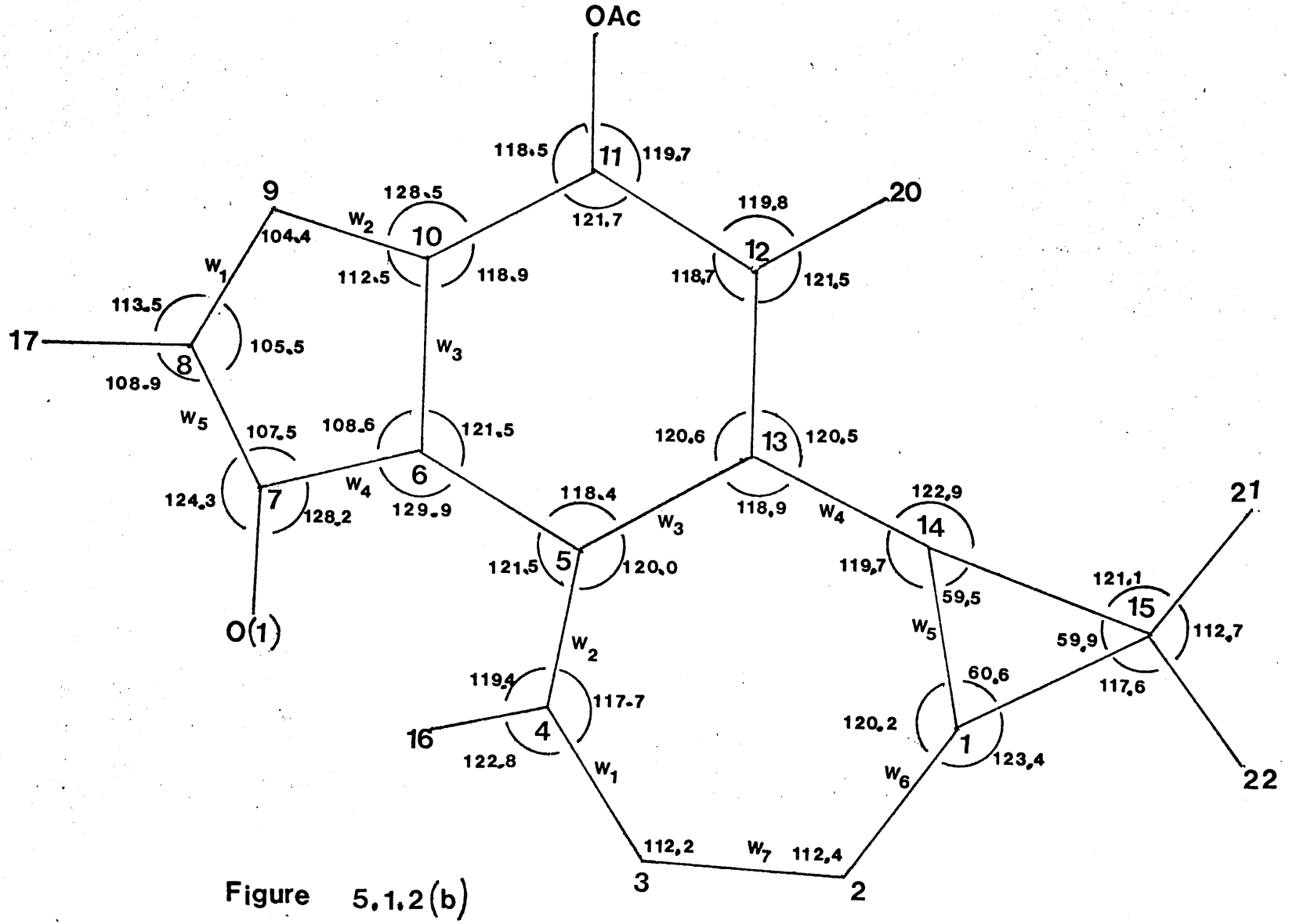

OAc
11
118.5
119.7
121.7
9
128.5
W2
104.4
10
W1
112.5
118.9
12
119.8
20
118.7
121.5
113.5
17
105.5
W3
8
108.9
W5
107.5
108.6
121.5
120.6
13
120.5
6
W4
124.3
7
128.2
129.9
118.4
W3
118.9
W4
122.9
14
21
121.5
5
120.0
119.7
59.5
121.1
15
O(1)
W5
59.9
112.7
W2
60.6
119.4
117.7
117.6
120.2
16
4
1
123.4
122.8
W1
W6
22
112.2
W7
112.4
3
2

Figure 5.1.2(b)

even greater than for cyclopentene[119] due to the presence of the carbonyl group (w_1, w_2, w_3, w_4 and w_5 are respectively equal to 10.9, -6.2, -1.7, 8.8 and -12.3° while the theoretical values for cyclopentene are 24, -15, 0, 15 and -24° [Table 5.1.3 (c) and Figure 5.1.2 (b)]. The unusual tricyclic carbon skeleton of I in which the cyclopropane ring is attached to a π -bonding substituent (benzene ring) is interesting since the validity of the Walsh[120] model (Walsh, 1949) for the bonding in cyclopropane is confirmed[121] (Bar and Bernstein, 1977). In the Walsh model interaction between the ring and the substituent is favoured for the so called 'bisecting' orientation when the appropriate orbitals are parallel. The angle between the interacting orbitals is essentially equivalent to the angle between the C(1) - C(15) vector and the normal to the phenyl ring (Table 5.1.5). Calculations based on simple geometrical considerations shows this angle to be equal to 83.7° which do suggest a 'perpendicular' rather than a 'bisecting' arrangement, with no possible significant overlap. Thus the expected symmetrical cyclopropyl ring is observed and may be considered to be, within experimental error, an equilateral triangle with internal angles of 60.6 (2)°, 59.9 (2)° and 59.5 (2)° and bond lengths of 1.521 (4) Å, 1.505 (4) Å and 1.511 (3) Å [mean value of 1.512 (4) Å]. However it should be noted that work done by Lauher and Ibers[122] (1975), seems to indicate some inconsistency with the already known structural model for cyclopropanes.

An additional feature of the conformation of I is the transoid arrangement of the three membered ring with respect to the C(4) - C(16) double bond which seems to provide adequate intramolecular separations, thus preventing the otherwise expected repulsive intereactions in the cisoid form between C(21) (methyl) and the atoms C(3), C(4), C(5) and C(16) [from a model, the expected C(methyl) ... C contacts in the cisoid form are found to be $< 2.7\,\text{Å}$] . Also of interest are the perpendicular orientations of the acetate group and of the C(4) - C(16) double bond relative to the phenyl ring [C(10) - C(11) - O(2) - C(18) and C(16) - C(4) - C(5) - C(6) are equal to -89.0 (3)° and 74.0 (4)° respectively] . The latter angle indicates a lack of conjugation between the aromatic ring and the adjacent C-C double bond [the C(4) - C(16) bond length is 1.324 (4) Å which compares well with the $C(sp^2)$ - $C(sp^2)$ double bond of length 1.337 (5) in ethylene[68]] .

The benzene ring itself is planar to within 0.025 Å . The deviations of the ring atoms and of the phenyl-bonded substituent atoms from the least-squares plane (of the ring) do not seem to indicate the existence of any significant pattern though they possibly do reflect the crowding of the fully substituted cresol ring.

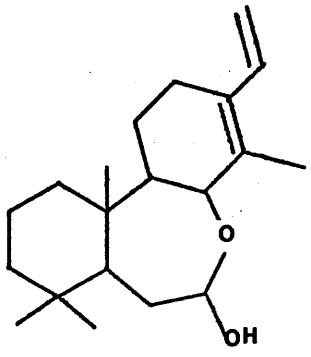
Other features of the molecular geometry are comparable with literature values for similar bonding situations.

The packing of the molecules does not appear to possess any unusually short intermolecular distances and their separations are governed by the van der Waals forces.

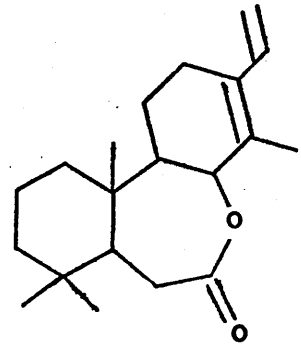
5.2 Introduction for Diterpenoid II

Extract of the roots of the Indian plant Acacia Jacquemontii has produced a new diterpenoid (I), $C_{20}H_{32}O_2$, which was later formulated as a cassane[123](5). Spectroscopic investigations[124] (Murray et al, 1979) revealed the functional groups which included a tricyclic skeleton with a conjugated diene system, a vinyl group and a vinyl methyl group, a cyclic hemiacetal and three tertiary methyl groups. However, attempts aimed at chemically interrelating the diene and hemiacetal functions proved to be fruitless. The oxidation product of (I), the lactone (2), seemed to be completely resistant to hydrolysis, and efforts to effect selective allylic oxidation of the dienediol (3) [the reductive ring opening product of (I)] did not produce the expected conjugated dienone.

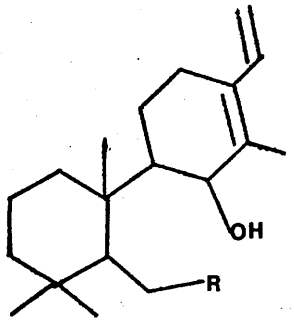
In order to confirm the structure (I) an X-ray analysis has been undertaken. The results do clearly establish the existence of the unique seven-membered hemiacetal ring B and allow the relative stereochemistry to be determined (4).



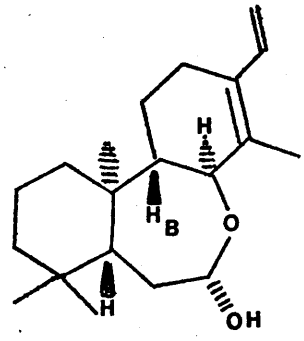
1



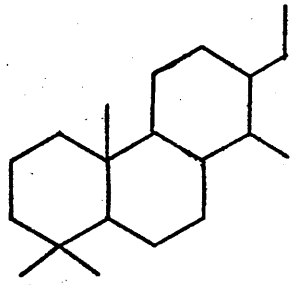
2



3 R = CH_2OH

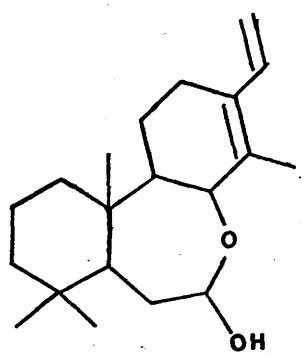


4



5

Experimental and Results for II



II

Crystal Data

Molecular Formula	$C_{20}H_{32}O_2$
Molecular Weight	304.52 a.m.u.
Crystal System	Orthorhombic
Unit Cell Dimensions	a = 10.336(2) Å
	b = 24.230(5) Å
	c = 7.308(1) Å
Unit Cell Volume	V = 1830.20 Å^3
Number of Molecules Per Unit Cell	Z = 4
Calculated Density	D_c = 1.11 g.cm^{-3}
Number of Molecules Per Asymmetric Unit	N = 1
Space Group	$P2_12_12_1$ (D_2^4, No.19)

Equivalent Positions	x,y,z
	1/2 - x, - y, 1/2 + z
	1/2 + x, 1/2 - y, - z
	-x, 1/2 + y, 1/2 - z
Linear Absorption Coefficient	$\mu = 0.65\ cm^{-1}$
Number of Electrons Per Unit Cell	F(000) = 672

Data Collection

Diffractometer Used	Hilger and Watts Y290
Radiation Used	$M_0 - K\alpha$, $\overline{\lambda} = 0.71069\ \text{Å}$
Filter	Graphite Monochromator
	$\cos^2 2\theta_m = 0.970$
Upper Limit for Data Collection	$2\theta_{max} = 54^\circ$
Number of Observed Independent Reflections	m = 896
Unobserved Cut-Off	$2.5\ \sigma_I$
Number of Parameters Refined	n = 199
Number of Reflections per Parameter	m/n = 4.5

Structure Determination and Refinement

The space group $P2_12_12_1$ was determined uniquely from the systematic absences in the diffraction data (hoo absent when h = 2n + 1, oko absent when k = 2n + 1 and ool absent when l = 2n + 1).

The structure was solved by application of the multi-solution direct methods program 'MULTAN' (Version 1974). The largest 250 $|E|$ values with $|E| > 1.18$ were chosen to define the structure (11.4 E's per atom) and 2000 Σ_2 relationships were retained (8 relationships per one $|E|$ value). Thirty-two sets were produced out of which the set with the highest combined figure of merit allowed calculation of an E-map which revealed 21 out of 22 non hydrogen atoms in the asymmetric unit. The missing atom was located from a difference Fourier synthesis phased on the known atoms. The R factor and R_w at this stage were 0.243 and 0.264 respectively. A summary of the various parameters used with 'MULTAN' is outlined in Table 5.2.1.

Positional and thermal vibration parameters as well as the scale parameter were refined to convergence during a course of 14 cycles of full matrix least-squares calculations where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. After the last cycle no shifts were larger than 0.09σ, the standard deviation of an observation of unit weight was 1.5638 and the quantities R and R_w were 0.078 and 0.10 respectively. A summary of the least-squares refinement is given in Table 5.2.2.

A difference Fourier synthesis at the end of the 9th cycle of refinement revealed the positions of 23 out of 32 hydrogen atoms.

Although some diffused maxima occurred in positions stereochemically acceptable for the undetermined hydrogen atoms it was not possible to determine their coordinates and a theoretical calculation based on the nonhydrogen atoms was used in order to deduce the missing positions.

At this stage the following weighting scheme was introduced: $w = (a + b|F_o| + c|F_o|^2)^{-1}$ and the final values for the parameters a,b and c which minimised the variation of $\overline{w\Delta^2}$ as a function of $|F_o|$ were a = 4.441, b = -0.2985 and c = 0.0138. In the range where $|F_o| < |F_o|_{min}$ ($|F_o|_{min} = 5$) the polynomial obtained from curve fitting may not be appropriate and so weights equal to 1/2.6179 were used.

The final three-dimensional difference Fourier synthesis revealed no errors in the model, the highest peak being equal to 0.32 e Å^{-3}.

Scattering factors for C and O atoms were taken from Cromer and Mann (1968) and those for H atoms from Stewart et al (1965).

Final values for the calculated and observed structure factor amplitudes and the appropriate phases are given in the supplement to this thesis.

Figure 5.2.1(a) is an ORTEP drawing of the molecule showing the atomic numbering and Figure 5.2.1(b) is a packing diagram viewed along $\bar{c}$. Final atomic coordinates, thermal parameters and e.s.d.'s (derived from the inverse of the least-squares matrix) are listed in Table 5.2.3. Tables 5.2.4 and 5.2.5 list the bond lengths valence angles and other relevant intra- and inter-molecular data.

Table 5.2.I

SUMMARY OF THE CONDITIONS (INCLUDING VARIOUS FIGURES OF INTEREST ASSOCIATED WITH SOLVING THE STRUCTURE OF II).

In this table:

1. NE - is the number of the largest $|E|$'s chosen to define the structure.
2. NSRT - is the number of Σ_2 relationships to be retained.
3. NSRTT - is the total number of Σ_2 relationships.
4. PROB - is the probability acceptance limit chosen for Σ_1.
5. NSPEC - is the number of special phases (permutations restricted to ϕ_{spec}, $\phi_{spec} + 180^\circ$).

   NGEN - is the number of general phases (phase permutation 45°, 135°, 225°, 315°).

   NANY - is the number of phases of either sort.
6. NSET - is the total number of phase sets that have been developed.
7. PUB - is the published phase.
8. NAT - is the number of nonhydrogen atoms in the asymmetric unit.
9. ABS FOM, PSI ZERO, RESID and CFOM are all figures of merit.

$C_{20}H_{32}O_2$, $P2_12_12_1$, NAT = 22.

PARAMETERS		STARTING SET TYPE	hk l	PH l	PUB	RESULTS PHASE SET CONSID-ERED	FIGURES OF MERIT ABS FOM	PSI ZERO	RESID	TOTAL NUMBER OF CORRECT PEAKS FOUND IN E-MAP
SIGMA - 2		SIGMA - 1	-	-	-	Max	1.3622	354.6	49.56	21
NE(|E| > 1.18)	250					Min	0.7264	151.3	40.48	
NSRT	2000	Origin	0,7,3	90	90	CFOM10 = 2.6855	1.3013	195.8	40.48	
NSRTT	not known	defining	1,11,0	90	90					
CONVERGE		phases	0,4,3	360	360					
PROB	0.95	Permuted	3,8,0	±90	270					
NSPEC, NGEN, NANY	2,2,0	phases	0,5,3	±90	90					
FASTAN			2,3,1*	±45 ±135	89					
NSET	32		4,1,2	±45 ±135	129					

*The enantiomorph is fixed by the 2,3,1 reflection.

Table 5.2.2

PROGRESS OF LEAST-SQUARES REFINEMENT

CYCLES	PARAMETERS REFINED	R	R_w
0	none	0.243	0.264
6	$x,y,z,U_{(iso)}$ for C, O; scale factor; full-matrix; unit weights.	0.156	0.162
3	x,y,z,U_{ij} for C, O; scale factor; full-matrix; unit weights	0.106	0.121
3	x,y,z,U_{ij} for C, O with 32 H atoms as fixed contributors to the structure factor calculations (U_{iso} = 0.051 A^2); scale factor; full-matrix; weighting scheme.	0.081	0.104
2	As in the last 3 cycles of the refinement, but excluding 10 reflections which appeared to be affected by extinction.	0.078	0.10

Table 5.2.3 (a,b,c)

(a) Fractional atomic coordinates ($\times 10^4$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM X/A Y/B Z/C.

(b) Anisotropic thermal parameters ($\mathring{A}^2 \times 10^3$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}

(c) Fractional atomic coordinates ($\times 10^4$) of hydrogen atoms with e.s.d.'s in parentheses. The hydrogens are numbered according to the atoms to which they are attached.

C(1)	8657(12)	1673(5)	10146(13)
C(2)	7917(12)	2207(4)	10188(14)
C(3)	6620(13)	2174(5)	9322(16)
C(4)	6717(14)	1977(5)	7289(14)
C(5)	7538(10)	1452(4)	7102(12)
C(6)	7714(10)	1280(4)	5042(13)
C(7)	7487(10)	0672(5)	4776(13)
C(8)	9407(10)	0488(4)	6621(11)
C(9)	9355(9)	0836(4)	8399(13)
C(10)	8872(10)	1446(4)	8145(13)
C(11)	10670(11)	0784(5)	9395(15)
C(12)	10978(11)	0194(5)	9897(15)
C(13)	10855(10)	-0189(4)	8283(15)
C(14)	10149(11)	-0039(4)	6778(13)
C(15)	11484(11)	-0717(5)	8444(18)
C(16)	12161(15)	-0916(6)	9819(23)
C(17)	10017(13)	-0407(6)	5101(15)
C(18)	5323(14)	1850(5)	6707(19)
C(19)	7172(15)	2482(5)	6181(16)
C(20)	9932(12)	1794(4)	7260(16)
O(1)	8105(7)	0340(3)	6128(8)
O(2)	8010(8)	0548(3)	3002(8)

C(1)	89(9)	57(7)	22(5)	1(7)	-4(6)	-5(5)
C(2)	86(8)	55(7)	27(5)	-4(7)	-2(7)	-21(6)
C(3)	81(9)	76(9)	51(8)	18(7)	6(7)	-18(7)
C(4)	86(9)	66(9)	28(6)	6(8)	7(6)	1(6)
C(5)	53(6)	54(7)	19(5)	-9(6)	3(5)	-6(5)
C(6)	64(7)	60(7)	23(6)	6(6)	1(5)	7(5)
C(7)	62(7)	67(8)	20(5)	-1(6)	5(5)	6(5)
C(8)	48(6)	51(6)	15(4)	-1(5)	5(4)	-8(4)
C(9)	40(6)	37(6)	30(6)	1(5)	-1(5)	-4(4)
C(10)	54(7)	53(7)	20(5)	-13(5)	-8(5)	-16(5)
C(11)	52(7)	62(8)	49(7)	-7(6)	0(6)	-16(6)
C(12)	71(8)	78(8)	40(7)	9(7)	0(7)	-2(7)
C(13)	44(6)	58(7)	49(7)	-6(6)	22(6)	6(6)
C(14)	59(7)	54(7)	26(5)	-17(6)	1(5)	-9(6)
C(15)	59(8)	63(8)	68(9)	13(7)	4(7)	3(8)
C(16)	93(11)	90(10)	99(12)	14(8)	-44(10)	11(10)
C(17)	98(10)	117(11)	30(7)	24(9)	-21(7)	-6(8)
C(18)	100(10)	75(9)	57(8)	23(8)	-9(9)	3(8)
C(19)	121(11)	59(8)	38(6)	4(8)	6(8)	13(6)
C(20)	66(8)	52(7)	52(8)	-17(6)	25(7)	-9(6)
O(1)	61(5)	53(4)	22(3)	-13(4)	-1(3)	1(3)
O(2)	87(6)	62(5)	21(4)	-18(4)	2(4)	0(4)

H(11)	8115	1362	10909
H(12)	9592	1724	10909
H(21)	7813	2580	11364
H(22)	8328	2590	10000
H(31)	6171	1846	10000
H(32)	6102	2606	9640
H(51)	7020	1124	7727
H(61)	6919	1497	4545
H(62)	8823	1276	5000
H(71)	6505	0630	4939
H(81)	10000	0786	5455
H(91)	8465	0683	9091
H(111)	10883	1097	10345
H(112)	11487	0970	8636
H(121)	10487	0177	10909
H(122)	12178	0240	10000
H(151)	11325	-1093	7482,
H(161)	12329	-1379	10000
H(162)	12339	-0687	10994
H(171)	9131	-0489	4545
H(172)	10276	-0267	4091
H(173)	10703	-0565	5455
H(181)	4584	2207	6716
H(182)	5276	1755	5350
H(183)	4956	1525	7397
H(191)	7634	2559	5000
H(192)	6461	2873	5909
H(193)	8076	2706	6818
H(201)	10697	1855	8636
H(202)	10503	1548	6364
H(203)	9354	2165	6364
H(02)	7903	0128	3182

Table 5.2.4(a,b,c)

(a) Interatomic distances ($\mathring{A}$) with e.s.d.'s in parentheses. The hydrogen atoms are numbered according to the atoms to which they are attached.

(b) Interbond angles (degrees) with e.s.d.'s (degrees) in parentheses.

(c) Torsion angles (degrees) with e.s.d.'s (degrees) in parentheses.

A torsion angle A-B-C-D is considered to be positive if when viewed down the B-C bond the A-B bond will eclipse the C-D bond when rotated less than 180° in a clockwise direction.

C(1)	C(2)	1.501(16)	C(8)	C(9)	1.550(13)
C(1)	C(10)	1.578(14)	C(8)	C(14)	1.493(14)
C(2)	C(3)	1.485(18)	C(8)	O(1)	1.438(12)
C(3)	C(4)	1.564(16)	C(9)	C(10)	1.571(14)
C(4)	C(5)	1.534(17)	C(9)	C(11)	1.547(15)
C(4)	C(18)	1.534(20)	C(10)	C(20)	1.527(15)
C(4)	C(19)	1.541(17)	C(11)	C(12)	1.510(17)
C(5)	C(6)	1.572(13)	C(12)	C(13)	1.506(16)
C(5)	C(10)	1.576(14)	C(13)	C(14)	1.368(15)
C(6)	C(7)	1.504(16)	C(13)	C(15)	1.441(16)
C(7)	O(1)	1.427(12)	C(14)	C(17)	1.523(16)
C(7)	O(2)	1.437(12)	C(15)	C(16)	1.316(21)

C(1) - H(11)	1.093(11)	C(15) - H(151)	1.163(13)
C(1) - H(12)	1.122(12)	C(16) - H(161)	1.143(14)
C(2) - H(22)	1.031(11)	C(16) - H(162)	1.038(16)
C(3) - H(31)	1.046(13)	C(17) - H(171)	1.021(13)
C(3) - H(32)	1.198(13)	C(17) - H(172)	0.856(12)
C(5) - H(51)	1.062(10)	C(17) - H(173)	0.846(13)
C(6) - H(61)	1.041(11)	C(18) - H(181)	1.154(13)
C(6) - H(62)	1.147(11)	C(18) - H(182)	1.019(14)
C(7) - H(71)	1.027(11)	C(18) - H(183)	1.008(13)
C(9) - H(91)	1.113(9)	C(19) - H(191)	1.004(12)
C(11) - H(111)	1.052(11)	C(19) - H(193)	1.176(14)
C(11) - H(112)	1.106(11)	C(20) - H(202)	1.064(12)
C(12) - H(121)	0.898(11)	O(2) - H(02)	1.031(7)

5.2.4 (a) (continued)

C(10) - C(1) - C(2)	113.03(84)	C(3) - C(2) - C(1)	113.96(96)
C(5) - C(10) - C(1)	108.76(83)	C(9) - C(10) - C(1)	105.31(77)
C(20) - C(10) - C(1)	107.48(86)	C(4) - C(3) - C(2)	111.30(104)
C(5) - C(4) - C(3)	111.95(92)	C(18) - C(4) - C(3)	105.34(105)
C(19) - C(4) - C(3)	105.98(95)	C(18) - C(4) - C(5)	109.19(96)
C(19) - C(4) - C(5)	116.27(104)	C(6) - C(5) - C(4)	111.65(81)
C(10) - C(5) - C(4)	116.70(87)	C(19) - C(4) - C(18)	107.47(102)
C(10) - C(5) - C(6)	111.05(82)	C(7) - C(6) - C(5)	111.45(82)
C(9) - C(10) - C(5)	110.18(79)	C(20) - C(10) - C(5)	114.68(83)
O(1) - C(7) - C(6)	113.19(82)	O(2) - C(7) - C(6)	105.32(81)
O(2) - C(7) - O(1)	109.72(83)	C(8) - O(1) - C(7)	116.84(74)
C(14) - C(8) - C(9)	114.73(76)	O(1) - C(8) - C(9)	108.25(74)
C(10) - C(9) - C(8)	115.08(76)	C(11) - C(9) - C(8)	108.64(79)
O(1) - C(8) - C(14)	106.66(78)	C(13) - C(14) - C(8)	124.20(90)
C(17) - C(14) - C(8)	113.14(88)	C(11) - C(9) - C(10)	114.29(79)
C(20) - C(10) - C(9)	109.96(82)	C(12) - C(11) - C(9)	112.11(90)
C(13) - C(12) - C(11)	112.00(93)	C(14) - C(13) - C(12)	120.76(98)
C(15) - C(13) - C(12)	116.41(101)	C(15) - C(13) - C(14)	122.80(104)
C(17) - C(14) - C(13)	122.65(99)	C(16) - C(15) - C(13)	128.88(125)

C(10)	C(1)	C(2)	C(3)	58.0(13)	C(2)	C(1)	C(10)	C(5)	-49.1(11)
C(2)	C(1)	C(10)	C(9)	-167.2(9)	C(2)	C(1)	C(10)	C(20)	75.6(11)
C(1)	C(2)	C(3)	C(4)	-57.1(13)	C(2)	C(3)	C(4)	C(5)	50.2(13)
C(2)	C(3)	C(4)	C(18)	168.7(10)	C(2)	C(3)	C(4)	C(19)	-77.6(12)
C(3)	C(4)	C(5)	C(6)	-175.9(9)	C(3)	C(4)	C(5)	C(10)	-46.7(13)
C(18)	C(4)	C(5)	C(6)	67.8(12)	C(18)	C(4)	C(5)	C(10)	-162.9(9)
C(19)	C(4)	C(5)	C(6)	-53.9(13)	C(19)	C(4)	C(5)	C(10)	75.3(13)
C(4)	C(5)	C(6)	C(7)	-134.0(9)	C(10)	C(5)	C(6)	C(7)	93.8(10)
C(4)	C(5)	C(10)	C(1)	45.4(12)	C(4)	C(5)	C(10)	C(9)	160.3(9)
C(4)	C(5)	C(10)	C(20)	-75.0(12)	C(6)	C(5)	C(10)	C(1)	174.9(8)
C(6)	C(5)	C(10)	C(9)	-70.2(10)	C(6)	C(5)	C(10)	C(20)	54.5(11)
C(5)	C(6)	C(7)	O(1)	-45.0(11)	C(5)	C(6)	C(7)	O(2)	-164.8(8)
C(6)	C(7)	O(1)	C(8)	-42.9(11)	O(2)	C(7)	O(1)	C(8)	74.4(10)
C(14)	C(8)	C(9)	C(10)	166.2(8)	C(14)	C(8)	C(9)	C(11)	36.6(11)
O(1)	C(8)	C(9)	C(10)	-74.8(9)	O(1)	C(8)	C(9)	C(11)	155.6(8)
C(9)	C(8)	C(14)	C(13)	-6.8(14)	C(9)	C(8)	C(14)	C(17)	171.7(9)
O(1)	C(8)	C(14)	C(13)	-126.6(10)	O(1)	C(8)	C(14)	C(17)	51.8(11)
C(9)	C(8)	O(1)	C(7)	97.9(9)	C(14)	C(8)	O(1)	C(7)	-138.2(8)
C(8)	C(9)	C(10)	C(1)	169.8(8)	C(8)	C(9)	C(10)	C(5)	52.6(10)
C(8)	C(9)	C(10)	C(20)	-74.7(10)	C(11)	C(9)	C(10)	C(1)	-63.5(10)
C(11)	C(9)	C(10)	C(5)	179.4(8)	C(11)	C(9)	C(10)	C(20)	52.0(11)
C(8)	C(9)	C(11)	C(12)	-60.0(11)	C(10)	C(9)	C(11)	C(12)	170.0(9)
C(9)	C(11)	C(12)	C(13)	51.6(12)	C(11)	C(12)	C(13)	C(14)	-19.7(15)
C(11)	C(12)	C(13)	C(15)	162.0(10)	C(12)	C(13)	C(14)	C(8)	-2.8(16)
C(12)	C(13)	C(14)	C(17)	178.9(10)	C(15)	C(13)	C(14)	C(8)	175.4(10)
C(15)	C(13)	C(14)	C(17)	-2.9(17)	C(12)	C(13)	C(15)	C(16)	0.1(20)
C(14)	C(13)	C(15)	C(16)	-178.3(14)					

Table 5.2.5

A. Selected intramolecular non-bonded distances (< 4.0 Å).

C(1) ... C(11)	3.05	C(6) ... C(20)	3.07
C(1) ... C(20)	2.50	C(8) ... C(20)	3.24
C(2) ... C(19)	3.10	C(9) ... C(20)	2.54
C(2) ... C(20)	3.15	C(10) .. C(19)	3.38
C(3) ... C(18)	2.46	C(11) ... C(20)	3.00
C(3) ... C(19)	2.48	C(12) ... C(15)	3.90
C(4) ... C(20)	3.35	C(12) ... C(16)	2.95
C(5) ... C(18)	2.50	C(15) ... C(17)	2.97
C(5) ... C(19)	2.61	C(17) ... O(1)	2.78
C(5) ... C(20)	2.61	C(17) ... O(2)	3.47
C(6) ... C(18)	3.08	C(19) ... C(20)	3.40
C(6) ... C(19)	3.08		

B. Selected intermolecular distances (< 4.0 Å).

C(16) ... $C(18)^{i}$	3.69	O(1) ... $H(02)^{i}$	2.15
O(1) ... $O(2)^{i}$	2.80	O(2) ... $O(1)^{ii}$	2.80

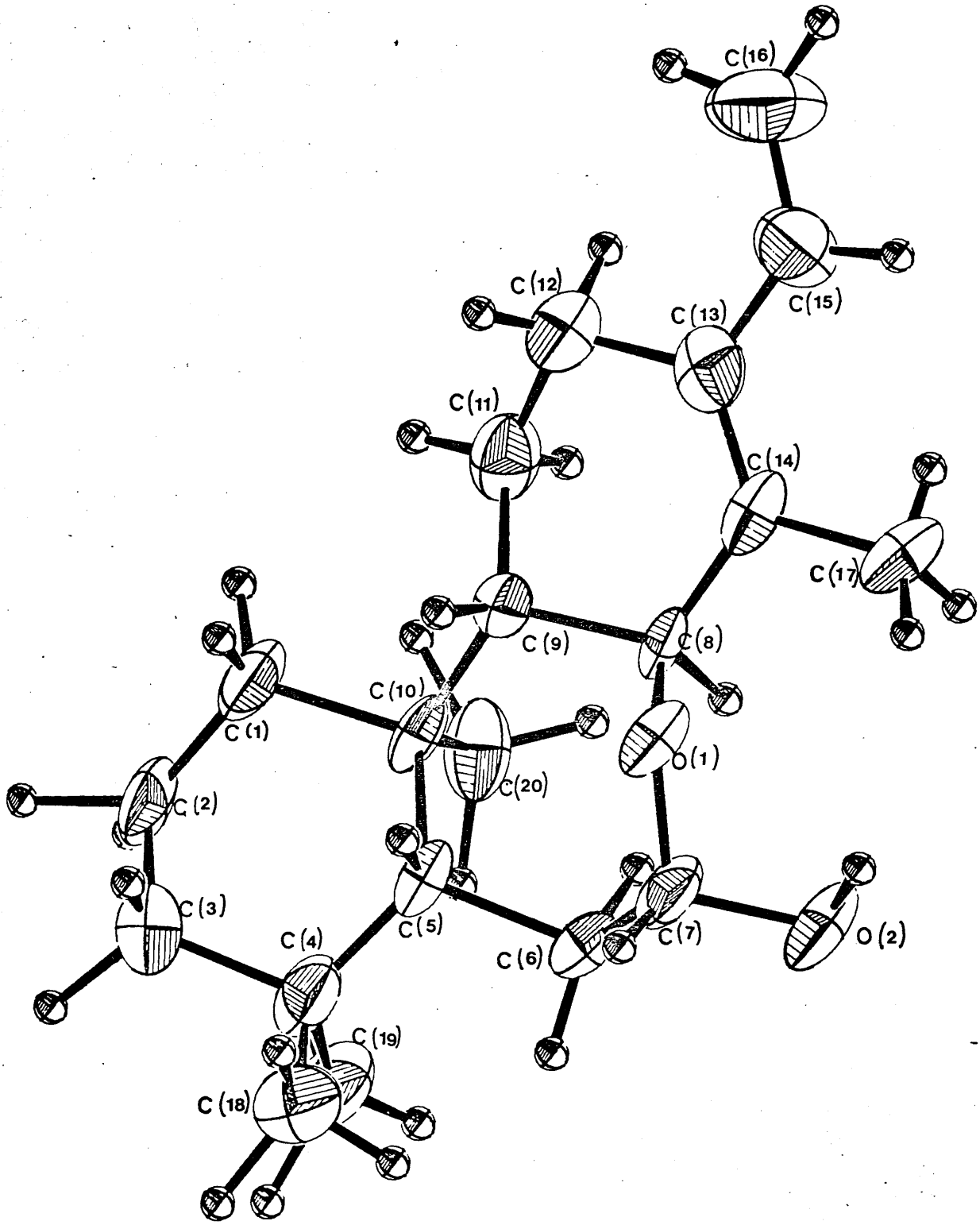
Roman numeral superscripts refer to the following equivalent positions relative to the molecule at (x,y,z):

(i) 3/2 - x, - y, 1/2 + z (ii) 3/2 - x, - y, -1/2 + z.

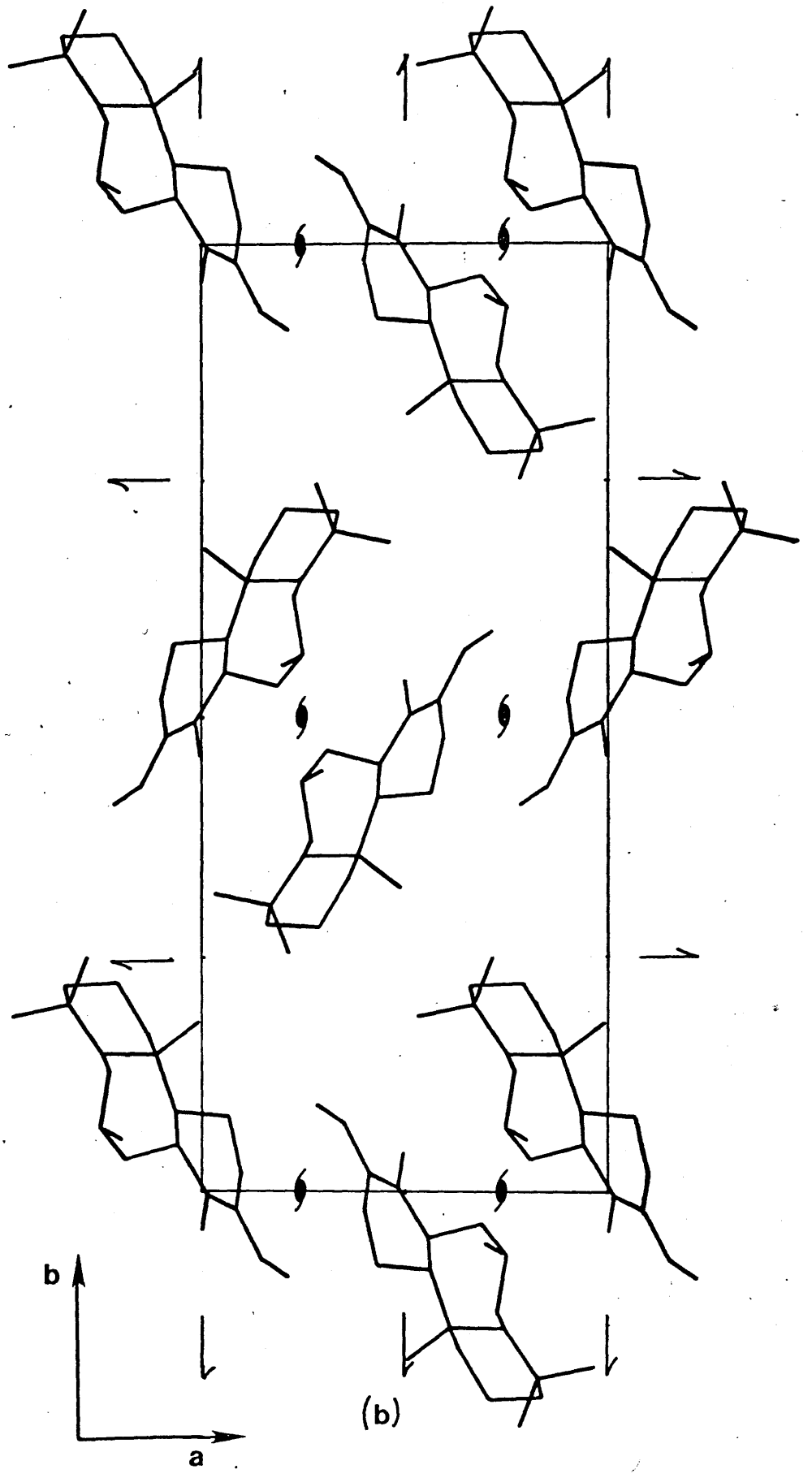
Figure 5.2.1 (a and b)

(a) A general view of II giving the atomic numbering scheme. Hydrogen atoms are numbered according to the atoms to which they are bonded.

(b) The molecular packing of II viewed along the c-axis.


C(16)
C(12)
C(13)
C(15)
C(11)
C(14)
C(17)
C(9)
C(8)
C(10)
C(1)
O(1)
C(20)
C(2)
C(3)
C(4)
C(5)
C(6)
C(7)
O(2)
C(19)
C(18)

(a)



(b)

Discussion of II

The more important features of the molecular geometry are shown in Figures 5.2.1(a) and 5.2.2 (a and b). The stereochemistry of the ring-fusion can be described as a 'trans-anti-trans' with regard to the A/B, A/C and B/C ring junctions respectively.

The six-membered ring, A, adopts a 'chair' conformation while the seven-membered ring, B, which possesses the hemiacetal group adopts a 'twist-chair' conformation [Table 5.2.4(c)]. The latter seems to agree with evidence from studies on cycloheptanes which provide support for the 'twist-chair' form as the most stable cycloheptane conformation[116,117,125] (Hendrickson, 1961, 1967 and Pauncz and Ginsburg, 1960). Ring C exhibits the normal 'half-chair' conformation dominated by the two trigonal carbon atoms C(14) and C(13) and with atoms C(8), C(12), C(13) and C(14) closely coplanar. (Geometrical values for an ideal cyclohexene were given by Corey and Sneen[126], 1955).

Despite the relatively high standard deviations in the bond lengths (Table 5.2.4) which render difficult any direct comparison, it appears as if several $C(sp^3)$ - $C(sp^3)$ bonds do deviate systematically from the accepted value[1.543(1)]. Thus the bonds C(1) - C(10), C(5) - C(10), C(9) - C(10) and C(3) - C(4) [1.58(1), 1.58(1), 1.57(1) and 1.56(2) respectively] are all longer than the quoted value for the C-C single bond and it seems significant that all of these bonds are attached to at least one of the two fully substituted carbon atoms, C(4) and C(10).

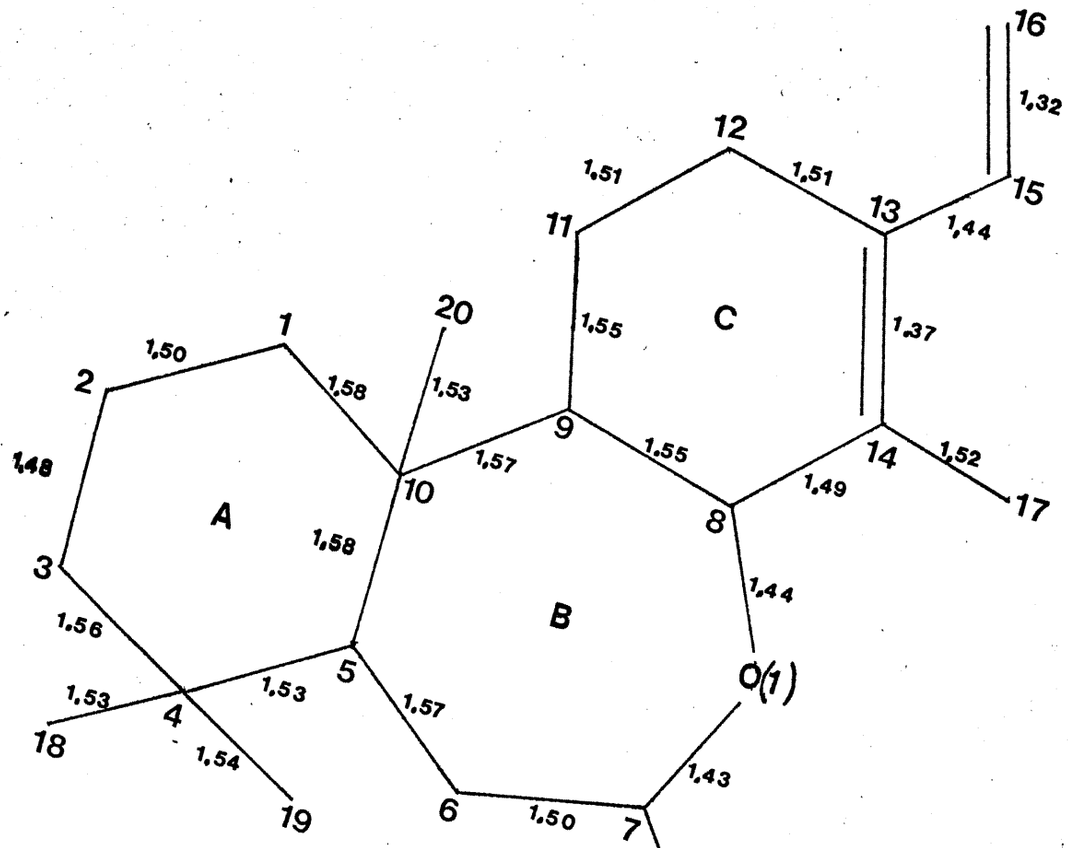

16
1,32
12
1,51
1,51
15
11
13
1,44
20
1
C
1,55
1,37
1,50
2
1,58
1,53
9
1,55
14
1,52
1,48
1,57
1,49
17
A
10
8
1,58
3
1,44
B
1,56
O(1)
5
1,53
1,53
1,57
4
18
1,54
1,43
19
6
1,50
7
1,44
O(2)

Figure 5.2.2(a)

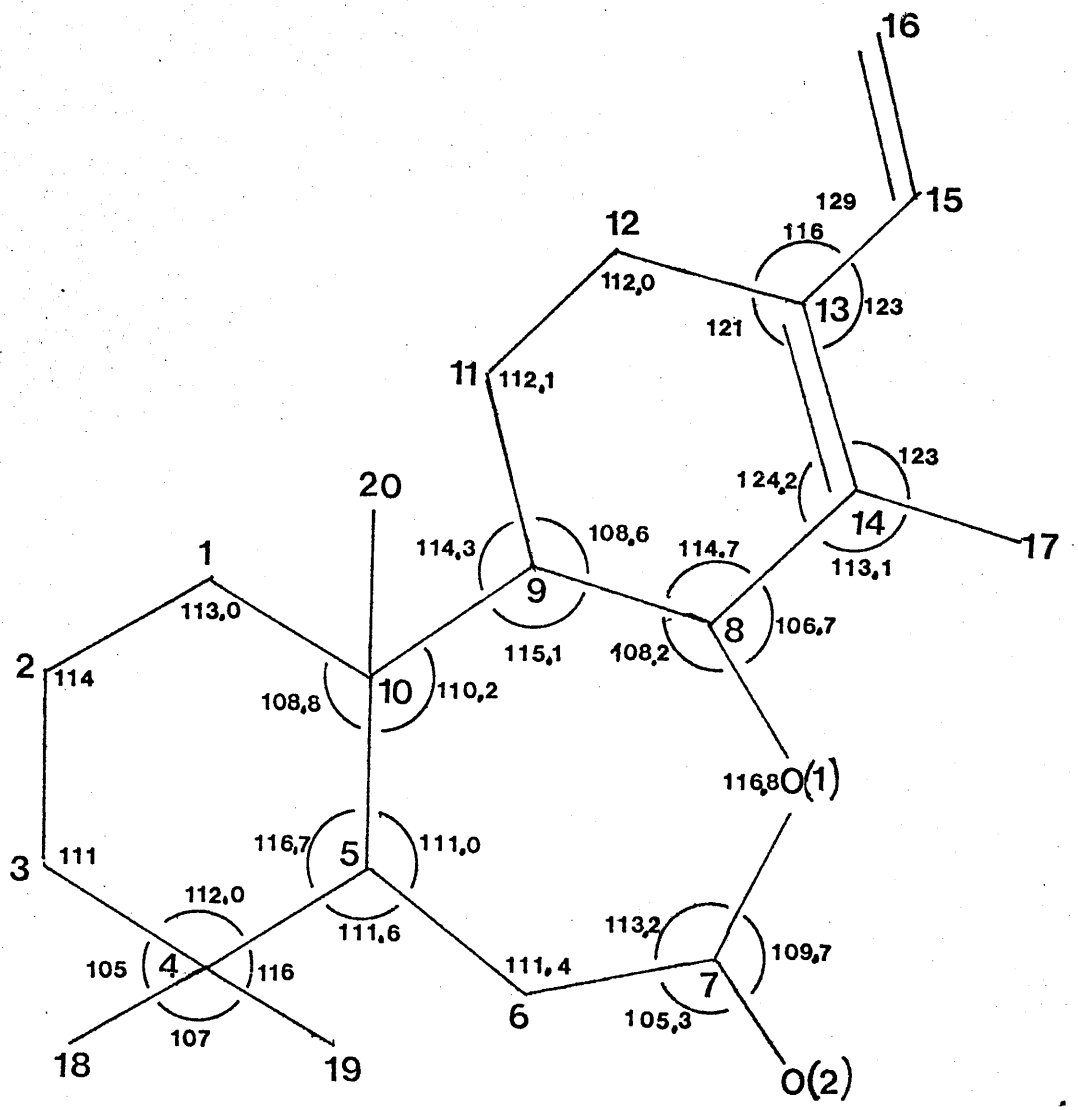

16
15
129
116
12
112,0
13
123
121
11
112,1
20
123
124,2
14
17
113,1
1
114,3
108,6
114,7
9
8
106,7
113,0
115,1
108,2
2
114
10
110,2
108,8
116,8
O(1)
3
111
116,7
5
111,0
112,0
111,6
113,2
109,7
105
4
116
111,4
7
6
105,3
107
18
19
O(2)

Figure 5,2,2 (b)

Similar trends in the $C(sp^3) - C(sp^3)$ bond lengths, attributed to steric factors have been previously observed with other molecules[127-130] (Hall and Maslem, 1965, Cesar and Grant, 1965, Muir and Sim, 1968 and Cox and Sim, 1978).

The crystal structure reveals fairly short intermolecular O ... O contacts [O(1) ... $O(2)^{i}$ and O(2) ... $O(1)^{ii}$ are both equal to 2.80 Å] which might indicate that the molecules are hydrogen bonded such that each molecule from one column is hydrogen bonded to two molecules from a second column, the columns themselves extending along the c-axis and the molecules, connected by the appropriate two-fold axis parallel to $\bar{c}$ (Figure 5.2.3).

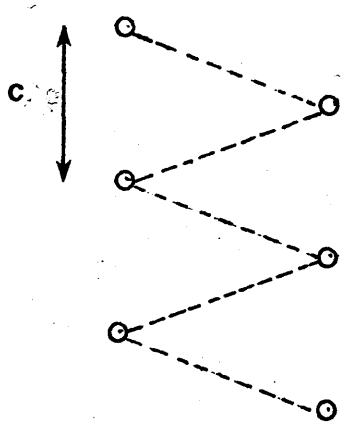
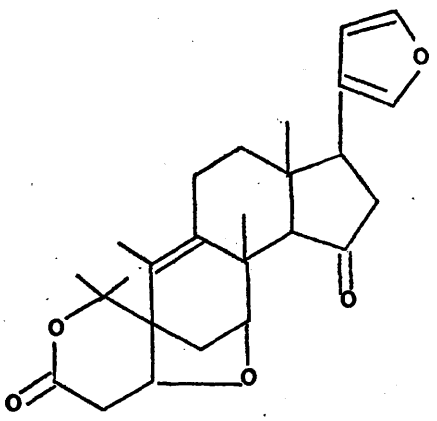


Figure 5.2.3.

The O-H ... O angle has been calculated to be equal to 118° but since the positions of the H atoms have not been determined accurately the significance of this angle is doubtful though it clearly deviates from 180°.

Other features of the molecular geometry are the coplanar diene system [Table 5.2.4(c)] and the unequal angles around atoms C(13), C(14) and C(15) which presumably reflect the strain created by the coplanar arrangement and by the eclipsing of atoms C(15) and C(17).

THE CRYSTAL AND MOLECULAR STRUCTURE OF A TETRANORTRITERPENOID OF THE FORM



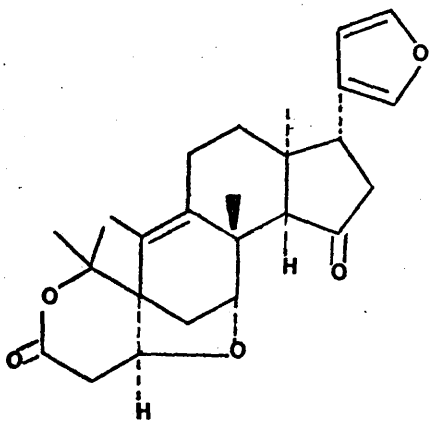
5.3 Introduction

A new tetranortriterpenoid, $C_{26}H_{32}O_5$, which has been extracted from the bark of Carapa procera (Meliaceae) was shown by the X-ray crystallographic technique to possess a spiro-lactone structure (I).

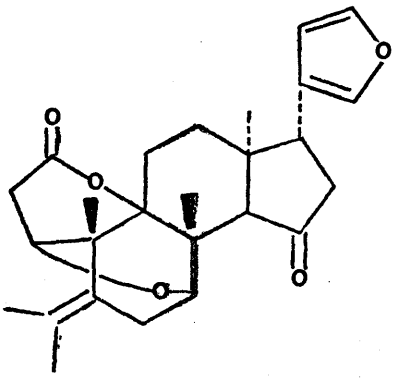
The spectroscopic characteristics of (I) (Connolly et al, 1979)[131] revealed the β -substituted furan, three tertiary methyl groups, a cyclopentanone ring, a tetrasubstituted double bond, a δ -lactone group and a cyclic ether attached to two secondary carbon atoms. This data also indicated that the molecule had a tricarbocyclic skeleton and as a result of a close examination of the ^1H n.m.r. spectrum structure (2) was suggested.

Since a chemical investigation was not possible, mainly due to lack of material, the structure has been fully substantiated by the X-ray analysis though the absolute configuration has not been determined.

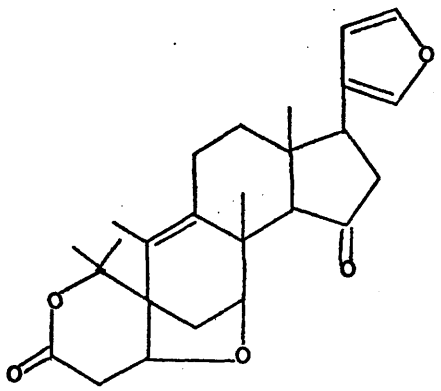
The latter was assumed to be as in (I) by analogy with other similar molecules. It is interesting to note that two compounds, recently described, have been shown to possess a similar ring A spiro lactone (Austin[132] and Andibenin[133]).



1



2



III

Crystal Data

Molecular Formula	$C_{26}H_{32}O_5$
Molecular Weight	424.58 a.m.u.
Crystal System	Orthorhombic
Unit Cell Dimensions	a = 9.608 (2) Å
	b = 22.359 (5) Å
	c = 10.202 (2) Å
Unit Cell Volume	V = 2191.63 Å^3
Number of Molecules Per Unit Cell	Z = 4
Calculated Density	D_c = 1.29 g.cm^{-3}
Number of Molecules Per Asymmetric Unit	N = 1
Space Group	$P2_12_12_1$ (D_2^4, No.19)

Equivalent Positions	x,y,z
	1/2 - x, - y, 1/2 + z
	1/2 + x, 1/2 - y, - z
	- x, 1/2 + y, 1/2 - z
Linear Absorption Coefficient	$\mu = 0.83\ cm^{-1}$
Number of Electrons Per Unit Cell	F(000) = 912

Data Collection

Diffractometer Used	Enraf-Nonius CAD-4
Radiation Used	$M_0 - K_\alpha$, $\overline{\lambda} = 0.7114\ \text{Å}$
Filter	Graphite Monochromator
	$\cos^2 2\theta_m = 0.960$
Upper Limit for Data Collection	$2\theta_{max} = 56^\circ$
Number of Observed Independent Reflections	m = 1050
Unobserved Cut-Off	$2.0\ \sigma_I$
Number of Parameters Refined	n = 125
Number of Reflections Per Parameter	m/n = 8.4

Structure Determination and Refinement

The structure was solved in space group $P2_12_12_1$ by standard direct methods using 'MULTAN' (Version 1976) to phase the 200 $\lfloor E \rfloor$ values greater than 1.32 (6.5 $\lfloor E \rfloor$ values per atom). Four permuted phases produced 64 phase sets out of which that with the highest combined figure

of merit clearly revealed a recognizable molecular fragment of 21 non-hydrogen atoms (out of 31). This fragment was further extended by successive Fourier syntheses until the whole molecular structure became apparent. At this stage a structure-factor calculation indicated an R and R_w (weighted) of 0.362 and 0.455 respectively.

The various parameters used with 'MULTAN' are summarized in Table 5.3.1.

The structure was then refined during 10 cycles of full-matrix least-squares calculations, minimizing the function $\sum w(|F_o| - |F_c|)^2$, to a residual R, R_w and S (S≡ standard deviation of an observation of unit weight) of 0.084, 0.102 and 3.1848 respectively. Atom types were assigned on the basis of bond distances and thermal parameters during the stage of the isotropic refinement. The weights applied to the observations in the different stages of the refinement were of the form $w = 1/\sigma^2(F_o)$ based on counting statistics and provided an approximately flat distribution of $\overline{w\Delta^2}$ with increasing $|F_o|$ at the end of the refinement. No attempt was made to vary the thermal parameters of the non-hydrogen atoms anisotropically since this would have resulted in a rather small ratio of m/n (= 3.75).

The hydrogen atoms were introduced in their geometrically calculated positions with C-H bond lengths equal to 1.0 Å and thermal parameters of $U = 0.051\ \text{Å}^2$, but their positional parameters and isotropic thermal vibrations were not allowed to vary during the refinements.

No absorption correction was applied and the refinement was terminated when all parameter shifts were equal to or less than 0.05 of their corresponding standard deviations. A final ΔF synthesis showed no deviations greater than 0.53 e $\mathring{A}^{-3}$.

Scattering factors for O and C atoms were taken from Cromer and Mann (1968) and those for H were from Stewart et al. (1965).

Final values for the observed calculated structure amplitudes and phases are given in the supplement to this thesis. Figure 5.3.1(a) is an ORTEP drawing indicating the numbering scheme used, and Figure 5.3.1(b) shows the arrangement of the molecules in the unit cell viewed along the a-axis.

Final atomic coordinates and their e.s.d.'s estimated from the inverse of the least-squares matrix together with the different thermal parameters are given in Table 5.3.3, and Tables 5.3.4 and 5.3.5 list bond lengths, valence angles and other relevant intra- and intermolecular data.

Table 5.3.I

SUMMARY OF THE CONDITIONS (INCLUDING VARIOUS FIGURES OF INTEREST) ASSOCIATED WITH SOLVING THE STRUCTURE OF III.

In this table:

1. NE - is the number of the largest $|E|$'s chosen to define the structure.
2. NSRT - is the number of Σ_2 relationships to be retained.
3. NSRTT - is the total number of Σ_2 relationships.
4. PROB - is the probability acceptance limit chosen for Σ_1.
5. NSPEC - is the number of special phases (permutations restricted to ϕ_{spec}, $\phi_{spec} + 180^\circ$).

   NGEN - is the number of general phases (phase permutation 45°, 135°, 225°, 315°).

   NANY - is the number of phases of either sort.
6. NSET - is the total number of phase sets that have been developed.
7. PUB - is the published phase.
8. NAT - is the number of nonhydrogen atoms in the asymmetric unit.
9. ABS FOM, PSI ZERO, RESID and FOM are all figures of merit.

$C_{26}H_{32}O_5$, $P2_12_12_1$, NAT = 31

PARAMETERS		STARTING SET TYPE	hkl	PHI	PUB	RESULTS PHASE SET CONSIDERED	FIGURES OF MERIT ABS FOM	PSI ZERO	RESID	TOTAL NUMBER OF CORRECT PEAKS FOUND IN E-MAP
SIGMA - 2		SIGMA - 1	-	-	-	Max	1.6534	232.7	46.98	21
NE(| E|> 1.32)	200					Min	0.9488	97.86	28.74	
NSRT	2000	Origin	2,19,1*	45	31	CFOM45 = 2.6393	1.4257	102.91	28.74	
NSRTT	2575	defining	0,1,2	90	90					
CONVERGE		phases	5,15,0	90	90					
PROB	0.95	Permuted	0,0,2	180 360	180					
NSPEC, NGEN, NANY	2,2,0	phases	6,13,0	180 360	180					
FASTAN			1,4,4	++ 45 ++ 135	58					
NSET	64		7,3,3	++ 45 ++ 135	220					

* The enantiomorph is fixed by the 2,19,1 reflection.

Table 5.3.2

PROGRESS OF LEAST-SQUARES REFINEMENT

CYCLES	PARAMETERS REFINED	R	R_w
0	none	0.362	0.455
6	$x,y,z,U_{(iso)}$ for C, O; scale factor; full-matrix; unit weights.	0.110	0.134
4	As above but with 32 geometrically calculated H atoms as fixed contributors to the structure factor calculations; weighting scheme.	0.084	0.102

Table 5.3.3 (a,b,c)

(a) Fractional atomic coordinates ($\times 10^4$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM X/A Y/B Z/C

(b) Isotropic thermal parameters ($\mathring{A}^2$, $\times 10^3$) of non-hydrogen atoms with e.s.d.'s in parentheses. The table shows:

ATOM $U_{(iso)}$

(c) Fractional atomic coordinates ($\times 10^4$) of hydrogen atoms (calculated positions). The hydrogens are numbered according to the atoms to which they are attached.

C(1)	0878(12)	9142(5)	− 1048(13)
C(2)	2336(14)	9361(6)	− 0636(13)
C(3)	2861(14)	9857(5)	− 1451(12)
C(4)	0483(12)	10239(5)	− 1523(11)
C(5)	0002(11)	9586(4)	− 1822(11)
C(6)	0370(12)	9400(5)	− 3243(12)
C(7)	0300(12)	8707(5)	− 3056(12)
C(8)	-1266(11)	8518(4)	− 3012(10)
C(9)	-2087(11)	8951(4)	− 2164(10)
C(10)	-1555(12)	9447(5)	− 1621(11)
C(11)	-3562(11)	8735(4)	− 1951(12)
C(12)	-3536(12)	8161(5)	− 1167(12)
C(13)	-2739(11)	7668(5)	− 1839(11)
C(14)	-1343(12)	7878(5)	− 2397(11)
C(15)	-1029(12)	7401(5)	− 3460(11)
C(16)	-2348(14)	7095(5)	− 3824(13)
C(17)	-3533(11)	7393(4)	− 3025(11)
C(18)	-2425(14)	7168(5)	− 0846(13)
C(19)	-2360(14)	9822(5)	− 0661(12)
C(20)	-4738(12)	7015(5)	− 2700(11)
C(21)	-4848(15)	6408(6)	− 2575(14)
C(22)	-6129(15)	7222(6)	− 2530(14)
C(23)	-6919(15)	6737(6)	− 2270(14)
C(24)	0395(14)	10476(6)	− 0151(15)
C(25)	-0165(16)	10689(6)	− 2512(15)
C(26)	-1771(12)	8534(5)	− 4465(11)
O(1)	-6217(12)	6271(5)	− 2288(11)
O(2)	0104(9)	7284(4)	− 3930(9)
O(3)	0996(8)	8622(3)	− 1848(8)
O(4)	4100(11)	9930(4)	− 1742(11)
O(5)	1979(9)	10272(3)	− 1931(9)

C(1)	42(3)
C(2)	53(4)
C(3)	47(3)
C(4)	38(3)
C(5)	32(3)
C(6)	37(3)
C(7)	35(3)
C(8)	28(3)
C(9)	27(3)
C(10)	36(3)
C(11)	37(3)
C(12)	42(3)
C(13)	35(3)
C(14)	35(3)
C(15)	38(3)
C(16)	51(3)
C(17)	33(3)
C(18)	50(3)
C(19)	51(4)
C(20)	39(3)
C(21)	60(4)
C(22)	59(4)
C(23)	62(4)
C(24)	60(4)
C(25)	63(4)
C(26)	38(3)
O(1)	88(3)
O(2)	59(3)
O(3)	46(2)
O(4)	74(3)
O(5)	47(2)

H(1)	0323	9044	−0243
H(021)	3002	9021	−0701
H(022)	2292	9504	0297
H(61)	1324	9539	−3501
H(62)	−0324	9550	−3892
H(7)	0774	8505	−3805
H(111)	−4018	8662	−2819
H(112)	−4101	9045	−1459
H(121)	−4510	8024	−1030
H(122)	−3082	8244	−0307
H(14)	−0637	7842	−1679
H(161)	−2278	6659	−3601
H(162)	−2522	7141	−4782
H(17)	−3880	7741	−3538
H(181)	−3320	7006	−0487
H(182)	−1854	7333	−0108
H(183)	−1900	6838	−1284
H(191)	−2610	9551	0084
H(192)	−3223	9951	−1125
H(193)	−1962	10192	−0250
H(21)	−4072	6114	−2685
H(22)	−6454	7646	−2593
H(23)	−7940	6752	−2091
H(241)	0977	10202	−0388
H(242)	−0597	10445	0100
H(243)	0710	10891	0020
H(251)	−1205	10668	−2444
H(252)	0127	10579	−3419
H(253)	0142	11107	−2317
H(261)	−1218	8246	−5007
H(262)	−1672	8945	−4834
H(263)	−2769	8412	−4434

Table 5.3.4. (a,b,c)

(a) Interatomic distances ($\mathring{A}$) with e.s.d.'s in parentheses.

(b) Interbond angles (degrees) with e.s.d.'s (degrees) in parentheses.

(c) Torsion angles (degrees) with e.s.d.'s (degrees) in parentheses.

A torsion angle A-B-C-D is considered to be positive if when viewed down the B-C bond the A-B bond will eclipse the C-D bond when rotated less than 180° in a clockwise direction.

C(1)	- C(2)	1.542(18)	C(9)	- C(10)	1.341(15)
C(1)	- C(5)	1.522(16)	C(9)	- C(11)	1.513(15)
C(1)	- O(3)	1.425(14)	C(10)	- C(19)	1.504(17)
C(2)	- C(3)	1.476(18)	C(11)	- C(12)	1.513(15)
C(3)	- O(4)	1.237(17)	C(12)	- C(13)	1.506(16)
C(3)	- O(5)	1.348(15)	C(13)	- C(14)	1.531(16)
C(4)	- C(5)	1.562(15)	C(13)	- C(17)	1.557(16)
C(4)	- C(24)	1.499(19)	C(13)	- C(18)	1.538(16)
C(4)	- C(25)	1.555(18)	C(14)	- C(15)	1.551(16)
C(4)	- O(5)	1.498(14)	C(15)	- C(16)	1.487(18)
C(5)	- C(6)	1.549(16)	C(15)	- O(2)	1.218(15)
C(5)	- C(10)	1.541(16)	C(16)	- C(17)	1.551(17)
C(6)	- C(7)	1.563(15)	C(17)	- C(20)	1.471(15)
C(7)	- C(8)	1.564(15)	C(20)	- C(21)	1.369(17)
C(7)	- O(3)	1.415(14)	C(20)	- C(22)	1.424(18)
C(8)	- C(9)	1.519(14)	C(21)	- O(1)	1.381(19)
C(8)	- C(14)	1.565(14)	C(22)	- C(23)	1.350(19)
C(8)	- C(26)	1.560(16)	C(23)	- O(1)	1.240(18)

5.3.4 (a)

C(5) - C(1) - C(2)	115.92(94)	O(3) - C(1) - C(2)	110.03(94)
C(3) - C(2) - C(1)	113.27(107)	O(3) - C(1) - C(5)	106.20(96)
C(4) - C(5) - C(1)	110.16(91)	C(6) - C(5) - C(1)	100.62(87)
C(10) - C(5) - C(1)	109.59(88)	C(7) - O(3) - C(1)	110.60(82)
O(4) - C(3) - C(2)	124.31(117)	O(5) - C(3) - C(2)	120.46(113)
O(5) - C(3) - O(4)	115.23(108)	C(4) - O(5) - C(3)	117.99(89)
C(24) - C(4) - C(5)	119.67(99)	C(25) - C(4) - C(5)	111.09(95)
O(5) - C(4) - C(5)	105.96(83)	C(6) - C(5) - C(4)	111.46(87)
C(10) - C(5) - C(4)	116.77(87)	C(25) - C(4) - C(24)	110.78(100)
O(5) - C(4) - C(24)	107.27(92)	O(5) - C(4) - C(25)	99.99(91)
C(10) - C(5) - C(6)	107.00(88)	C(7) - C(6) - C(5)	98.18(85)
C(9) - C(10) - C(5)	118.83(95)	C(19) - C(10) - C(5)	118.24(94)
C(8) - C(7) - C(6)	108.23(84)	O(3) - C(7) - C(6)	102.64(84)
O(3) - C(7) - C(8)	113.13(90)	C(9) - C(8) - C(7)	110.10(82)
C(14) - C(8) - C(7)	107.71(84)	C(26) - C(8) - C(7)	105.39(87)
C(14) - C(8) - C(9)	109.28(85)	C(26) - C(8) - C(9)	111.44(85)
C(10) - C(9) - C(8)	124.37(95)	C(11) - C(9) - C(8)	111.37(83)
C(26) - C(8) - C(14)	112.78(83)	C(13) - C(14) - C(8)	118.09(89)
C(15) - C(14) - C(8)	109.86(88)	C(11) - C(9) - C(10)	124.19(97)
C(19) - C(10) - C(9)	122.29(103)	C(12) - C(11) - C(9)	109.33(89)
C(13) - C(12) - C(11)	112.87(98)	C(14) - C(13) - C(12)	112.98(87)
C(17) - C(13) - C(12)	113.16(90)	C(18) - C(13) - C(12)	109.34(95)
C(17) - C(13) - C(14)	105.14(88)	C(18) - C(13) - C(14)	107.18(91)
C(15) - C(14) - C(13)	102.70(85)	C(18) - C(13) - C(17)	108.75(86)
C(16) - C(17) - C(13)	102.60(88)	C(20) - C(17) - C(13)	115.92(94)
C(16) - C(15) - C(14)	108.99(97)	O(2) - C(15) - C(14)	126.60(104)
O(2) - C(15) - C(16)	124.41(106)	C(17) - C(16) - C(15)	107.26(96)
C(20) - C(17) - C(16)	116.72(91)	C(21) - C(20) - C(17)	130.69(111)
C(22) - C(20) - C(17)	125.40(101)	C(22) - C(20) - C(21)	103.78(109)
O(1) - C(21) - C(20)	108.19(115)	C(23) - C(22) - C(20)	106.88(113)
C(23) - O(1) - C(21)	109.60(114)	O(1) - C(23) - C(22)	111.47(129)

C(5) - C(1) - C(2) - C(3)	-21.9(15)	O(3) - C(1) - C(2) - C(3)	98.6(12)
C(2) - C(1) - C(5) - C(4)	-24.4(13)	C(2) - C(1) - C(5) - C(6)	93.4(11)
C(2) - C(1) - C(5) - C(10)	-154.1(10)	O(3) - C(1) - C(5) - C(4)	-146.9(9)
O(3) - C(1) - C(5) - C(6)	-29.2(11)	O(3) - C(1) - C(5) - C(10)	83.3(11)
C(2) - C(1) - O(3) - C(7)	-124.9(10)	C(5) - C(1) - O(3) - C(7)	1.3(12)
C(1) - C(2) - C(3) - O(4)	-145.8(13)	C(1) - C(2) - C(3) - O(5)	34.5(16)
C(2) - C(3) - O(5) - C(4)	4.8(16)	O(4) - C(3) - O(5) - C(4)	-174.9(10)
C(24) - C(4) - C(5) - C(1)	-61.1(13)	C(24) - C(4) - C(5) - C(6)	-171.9(10)
C(24) - C(4) - C(5) - C(10)	64.7(14)	C(25) - C(4) - C(5) - C(1)	167.8(10)
C(25) - C(4) - C(5) - C(6)	57.0(12)	C(25) - C(4) - C(5) - C(10)	-66.4(12)
O(5) - C(4) - C(5) - C(1)	60.1(11)	O(5) - C(4) - C(5) - C(6)	-50.7(11)
O(5) - C(4) - C(5) - C(10)	-174.1(9)	C(5) - C(4) - O(5) - C(3)	-52.6(12)
C(24) - C(4) - O(5) - C(3)	76.3(12)	C(25) - C(4) - O(5) - C(3)	-168.1(10)
C(1) - C(5) - C(6) - C(7)	42.9(10)	C(4) - C(5) - C(6) - C(7)	159.7(9)
C(10) - C(5) - C(6) - C(7)	-71.5(10)	C(1) - C(5) - C(10) - C(9)	-70.5(13)
C(1) - C(5) - C(10) - C(19)	100.5(11)	C(4) - C(5) - C(10) - C(9)	163.4(10)
C(4) - C(5) - C(10) - C(19)	-25.6(14)	C(6) - C(5) - C(10) - C(9)	37.8(13)
C(6) - C(5) - C(10) - C(19)	-151.2(10)	C(5) - C(6) - C(7) - C(8)	76.5(10)
C(5) - C(6) - C(7) - O(3)	-43.3(10)	C(6) - C(7) - C(8) - C(9)	-43.4(11)
C(6) - C(7) - C(8) - C(14)	-162.5(8)	C(6) - C(7) - C(8) - C(26)	76.9(10)
O(3) - C(7) - C(8) - C(9)	69.6(11)	O(3) - C(7) - C(8) - C(14)	-49.5(11)
O(3) - C(7) - C(8) - C(26)	-170.1(9)	C(6) - C(7) - O(3) - C(1)	27.1(11)
C(8) - C(7) - O(3) - C(1)	-89.3(11)	C(7) - C(8) - C(9) - C(10)	4.7(14)
C(7) - C(8) - C(9) - C(11)	-172.3(9)	C(14) - C(8) - C(9) - C(10)	122.8(11)
C(14) - C(8) - C(9) - C(11)	-54.2(11)	C(26) - C(8) - C(9) - C(10)	-111.9(12)
C(26) - C(8) - C(9) - C(11)	71.1(11)	C(7) - C(8) - C(14) - C(13)	160.8(9)
C(7) - C(8) - C(14) - C(15)	-82.0(10)	C(9) - C(8) - C(14) - C(13)	41.2(12)
C(9) - C(8) - C(14) - C(15)	158.4(9)	C(26) - C(8) - C(14) - C(13)	-83.4(11)
C(26) - C(8) - C(14) - C(15)	33.9(12)	C(8) - C(9) - C(10) - C(5)	-1.9(16)
C(8) - C(9) - C(10) - C(19)	-172.6(10)	C(11) - C(9) - C(10) - C(5)	174.7(10)
C(11) - C(9) - C(10) - C(19)	4.1(17)	C(8) - C(9) - C(11) - C(12)	65.2(11)
C(10) - C(9) - C(11) - C(12)	-111.9(12)	C(9) - C(11) - C(12) - C(13)	-59.9(12)

C(11) - C(12) - C(13) - C(14)	45.6(13)	C(11) - C(12) - C(13) - C(17)	-73.7(12)
C(11) - C(12) - C(13) - C(18)	164.9(9)	C(12) - C(13) - C(14) - C(8)	-37.3(13)
C(12) - C(13) - C(14) - C(15)	-158.3(9)	C(17) - C(13) - C(14) - C(8)	86.6(11)
C(17) - C(13) - C(14) - C(15)	- 34.4(10)	C(18) - C(13) - C(14) - C(8)	-157.8(9)
C(18) - C(13) - C(14) - C(15)	81.2(10)	C(12) - C(13) - C(17) - C(16)	159.5(9)
C(12) - C(13) - C(17) - C(20)	- 72.1(12)	C(14) - C(13) - C(17) - C(16)	35.8(11)
C(14) - C(13) - C(17) - C(20)	164.2(9)	C(18) - C(13) - C(17) - C(16)	-78.7(11)
C(18) - C(13) - C(17) - C(20)	49.6(12)	C(8) - C(14) - C(15) - C(16)	-106.3(10)
C(8) - C(14) - C(15) - O(2)	74.1(14)	C(13) - C(14) - C(15) - C(16)	20.2(12)
C(13) - C(14) - C(15) - O(2)	-159.5(11)	C(14) - C(15) - C(16) - C(17)	2.0(13)
O(2) - C(15) - C(16) - C(17)	-178.4(11)	C(15) - C(16) - C(17) - C(13)	- 23.0(12)
C(15) - C(16) - C(17) - C(20)	-150.8(10)	C(13) - C(17) - C(20) - C(21)	- 96.1(15)
C(13) - C(17) - C(20) - C(22)	88.8(14)	C(16) - C(17) - C(20) - C(21)	25.0(18)
C(16) - C(17) - C(20) - C(22)	-150.2(12)	C(17) - C(20) - C(21) - O(1)	-178.5(11)
C(22) - C(20) - C(21) - O(1)	- 2.6(14)	C(17) - C(20) - C(22) - C(23)	178.7(12)
C(21) - C(20) - C(22) - C(23)	2.5(15)	C(20) - C(21) - O(1) - C(23)	1.8(16)
C(20) - C(22) - C(23) - O(1)	-1.5(16)	C(22) - C(23) - O(1) - C(21)	- 0.1(17)

5.3.4 (c) (continued)

Table 5.3.5

A. Selected intramolecular non-bonded distances (<4.0 Å).

C(1) ... C(19)	3.48	C(12) ... C(20)	3.21
C(1) ... C(24)	3.15	C(12) ... C(22)	3.54
C(2) ... C(24)	3.15	C(14) ... O(3)	2.85
C(3) ... C(24)	3.05	C(15) ... C(18)	3.03
C(4) ... C(19)	3.02	C(15) ... C(26)	2.82
C(6) ... C(25)	3.02	C(16) ... C(18)	3.04
C(6) ... C(26)	3.09	C(16) ... C(21)	3.12
C(7) ... C(15)	3.21	C(16) ... C(26)	3.33
C(7) ... O(2)	3.31	C(17) ... C(26)	3.39
C(8) ... O(2)	3.20	C(18) ... C(20)	2.94
C(10) ... C(24)	3.32	C(18) ... C(21)	3.38
C(10) ... C(25)	3.21	C(19) ... C(24)	3.07
C(10) ... C(26)	3.55	C(19) ... C(25)	3.43
C(11) ... C(19)	3.00	C(26) ... O(2)	3.37
C(11) ... C(26)	3.12		

B. Selected intermolecular distances (<4.0 Å).

C(17) ... $O(2)^{i}$	3.45	C(23) ... $C(26)^{i}$	3.39
C(21) ... $C(26)^{i}$	3.54	C(26) ... $O(1)^{ii}$	3.38
C(22) ... $C(26)^{i}$	3.55		

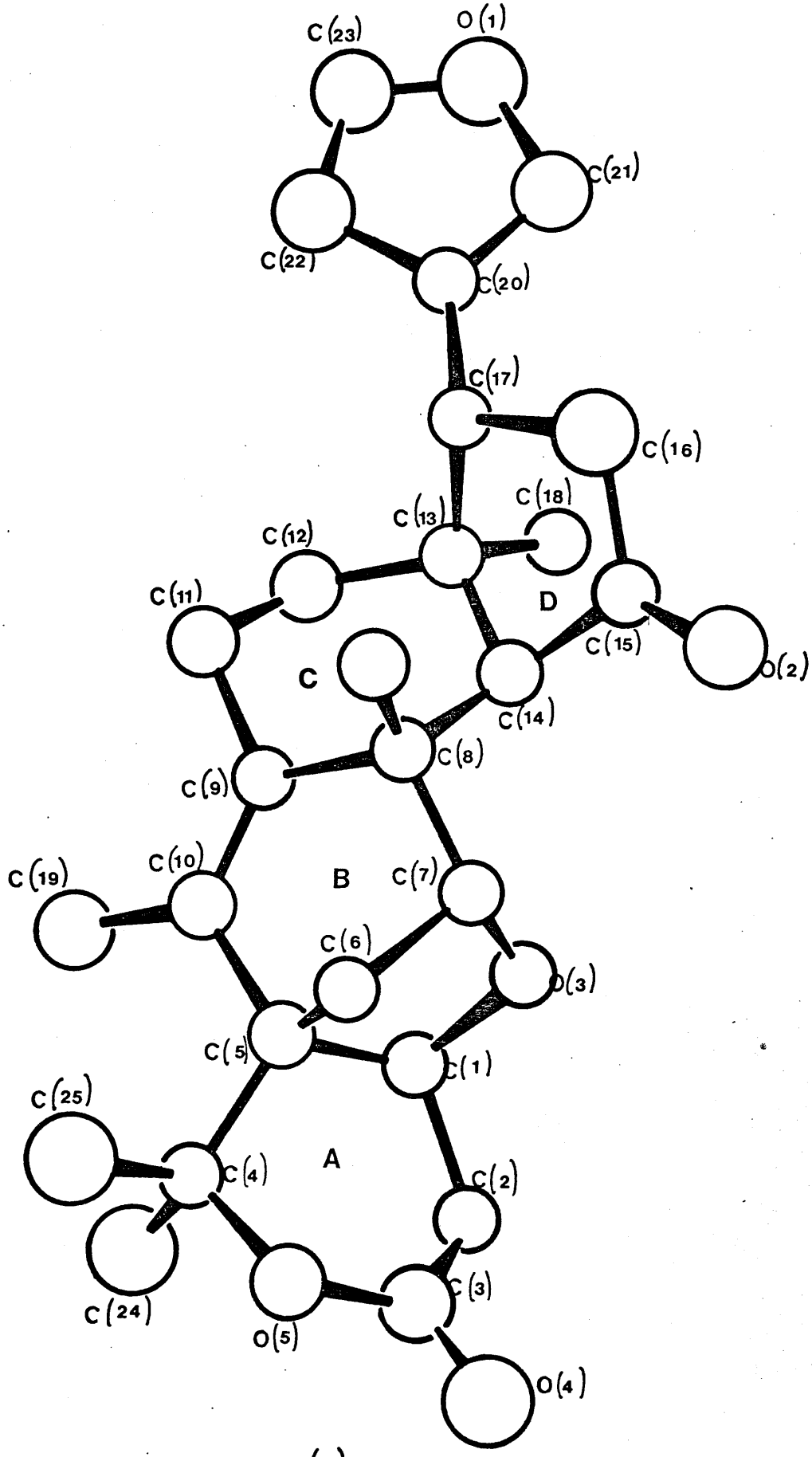
Roman numeral superscripts refer to the following equivalent positions relative to the molecule at (x,y,z):

(i) $x - 1/2, 3/2 - y, 1 - z$ (ii) $0.5 + x, 3/2 - y, 1 - z$.

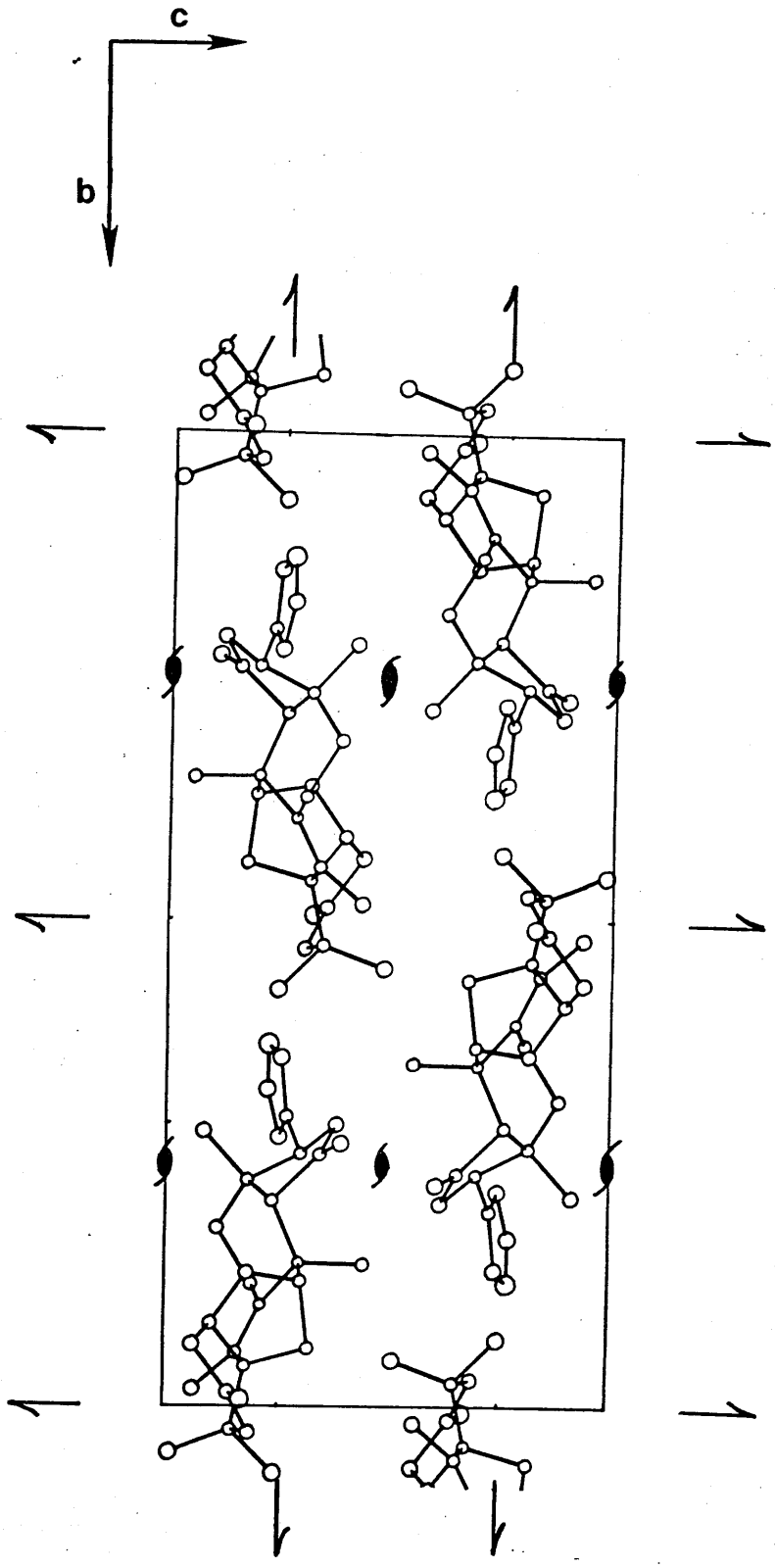
Figure 5.3.1 (a and b)

(a) A general view of III giving the atomic numbering scheme.

(b) The molecular packing of III viewed along the short a-axis.


C(23)
O(1)
C(21)
C(22)
C(20)
C(17)
C(16)
C(18)
C(13)
C(12)
C(11)
D
C
C(15)
O(2)
C(14)
C(8)
C(9)
C(10)
C(19)
B
C(7)
C(6)
O(3)
C(5)
C(1)
C(25)
A
C(4)
C(2)
C(3)
C(24)
O(5)
O(4)

(a)



(b)

Discussion of III

The stereochemistry of the structure can be seen clearly from Figure 5.3.1(a).

Apart from being cis-fused to the cyclohexane ring (C), the cyclopentanone ring (D) is 'enveloped-shaped' with atoms C(14), C(15), C(16) and C(17) being coplanar [the dihedral angle C(14) - C(15) - C(16) - C(17) is equal to $2(1)^{\circ}$].

Noteworthy and although in contrast with the conformation just mentioned is the fact that cyclopentanone has been found to exist predominantly in the half-chair conformation in the gas phase with no envelope conformation detected[134,135] [Kim and Gwinn, 1969; Allinger, Tribble and Miller, 1972]. The six-membered ring (C) and the cyclohexene ring (B) adopt chair-like and half-chair conformations respectively, in which coplanarity of atoms C(5), C(8), C(9) and C(10) is achieved by the presence of the two trigonal carbon atoms C(9) and C(10). The stereochemistry of the fusion at the junction which involves the one trigonal carbon atom approximates to a quasi-trans fusion[119] indicated by the corresponding 'torsion angles of junction' [C(14) - C(8) - C(9) - C(11) and C(7) - C(8) - C(9) - C(10) are equal to -54° and 5° respectively].

The 'skew-boat' form of the spiro-lactone ring (A) is readily revealed by an examination of the Dreiding stereomodel of III.

The bond lengths and angles (Table 5.3.4) show no significant anomalies and they do seem to be consistent with the formulation given for III (Introduction, 5.3) though due to the early termination of the least-squares refinement a meaningful discussion and comparison of the bond lengths is not feasible.

Distances which seem to represent short intra- and intermolecular contacts are listed in Table 5.3.5. However the molecular packing [Figure 5.3.1(b)] seems to be dominated by van der Waals forces.

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EXPERIMENTAL DATA FOR COMPOUNDS DESCRIBED IN THE THESIS:

STRUCTURAL STUDIES OF YLIDES AND RELATED DERIVATIVES,

AND OF

SEVERAL NATURAL PRODUCTS.

by

ABRAHAM MALTZ

Chemistry Department

January, 1979.

List of Contents

Data for

Data for S,S-Dimethyl-N-m-nitrophenylsulphimide.

Crystal Data

$C_8H_{10}N_2O_2S$, M = 198.24; orthorhombic,

a = 13.663(3)Å, b = 13.850(3)Å, c = 5.008(1)Å,

V = 947.74Å^3; D_c = 1.39 g.cm^{-3}, Z = 4; F(000) = 416;

space group $P2_12_12_1$ (D_2^4, No.19); $M_0 - K_\alpha$ radiation, λ = 0.7107Å,

$\mu(M_0 - K_\alpha)$ = 2.96 cm^{-1}.

0,0,L

2	298	293	180

0,1,L

1	158	156	270
2	255	254	90
3	57	56	90
4	139	145	90
5	62	65	270
6	75	74	270

0,2,L

0	0*	3	180
1	772	864	180
2	142	147	180
3	45	46	180
4	107	109	0
6	42	41	180
7	18*	15	180

0,3,L

1	331	326	90
2	228	235	270
3	177	184	90
4	91	93	90
6	42	43	270

0,4,L

0	234	222	180
1	81	79	180
2	56	54	180
3	158	156	0
4	204	206	0
5	164	169	180

0,5,L

1	19	18	90
2	139	134	270
3	250	257	90
4	149	148	90
5	169	174	270

0,6,L

0	297	290	180
1	263	261	180
2	48	46	180
3	117	121	0
4	172	174	180
5	86	85	180

0,7,L

1	33	35	90
2	59	61	90
3	257	256	90
4	158	154	270
5	102	103	270

0,8,L

0	310	308	180
1	212	217	180
2	60	61	0
3	131	130	0
4	26	26	180
5	28	27	180

0,9,L

1	140	133	270
2	17	15	270
3	118	113	270
4	146	147	270
6	50	52	90

0,10,L

0	359	354	180
1	81	82	180
2	122	117	0
3	29	30	0
4	90	92	180

0,11,L

3	47	48	270
4	52	52	270

0,12,L

0	147	145	180
2	146	151	0
3	33	29	180
5	33	32	0

0,13,L

1	47	49	270
2	112	116	90
3	59	59	270
4	38	36	270

0,14,L

0	40	44	180
1	192	195	0
2	76	78	0
3	25	30	180
4	38	33	180

0,15,L

1	41	41	90
2	50	46	90

0,16,L

0	108	105	0
1	77	77	0
3	42	42	180

0,17,L

1	31	34	90
3	23	25	270

0,18,L

0	39	39	0
1	51	49	0

1,0,L

1	224	225	90
3	336	327	270
4	73	72	180
5	67	68	90
6	62	63	0

1,1,L

0	97	111	90
1	325	319	251
2	436	442	292
3	209	203	70
4	112	111	121
5	103	104	192
7	39	38	356

1,2,L

0	117	119	270
1	606	636	98
2	174	167	265
3	66	65	318
4	110	110	87
5	91	90	30
6	47	49	317

1,3,L

0	458	482	90
1	267	265	20
2	100	101	317
3	84	83	78
4	116	117	200
5	76	75	193

1,3,L

6	58	59	330

1,4,L

0	451	480	90
1	294	287	37
2	295	288	297
3	80	77	215
4	86	87	171
5	33	35	333
6	49	48	309

1,5,L

0	49	48	90
1	311	308	235
2	151	143	54
3	187	180	68
4	121	121	166
5	33	32	262
6	56	59	357

1,6,L

0	224	226	90
1	417	408	321
2	249	251	292
3	138	136	196
4	103	104	85
5	87	87	23

1,7,L

0	325	312	270
1	72	73	347
2	182	177	31
3	50	52	21
4	85	87	150
5	75	76	323
6	59	60	351

1,8,L

0	64	64	90
1	171	164	245
2	117	114	222
3	128	126	112
4	78	80	79
5	47	46	309
6	56	56	208

1,9,L

0	37	31	90
1	115	114	281
2	106	109	83
3	91	92	140
4	80	75	231
5	54	53	339
6	38	42	78

1,10,L

0	182	180	90
1	121	120	251
2	83	84	188
3	86	88	93
4	27	29	33
5	48	45	277
6	34	29	135

1,11,L

0	102	101	270
1	78	78	315
2	51	51	96
3	85	82	171
4	47	47	305
5	69	70	35

1,12,L

0	49	48	270
1	171	171	240
2	31	30	161
3	83	84	75
4	66	68	337

1,13,L

0	120	123	270
1	39	36	107
2	128	128	127
3	65	67	211
4	49	51	329

1,14,L

0	58	55	270
1	35	34	257
2	105	107	64
3	65	69	37
4	32	34	290

1,15,L

1	54	54	87
2	48	48	255
3	83	81	269
4	29	30	307

1,16,L

0	104	104	270
1	22	25	17
2	68	69	141
4	43	43	279

1,17,L

1	52	52	77
3	28	31	188

1,18,L

0	54	57	270
1	38	37	96
2	47	46	117

1,19,L

0	35	35	90
1	42	43	87

2,0,L

0	131	130	180
1	162	162	90
2	231	222	0
3	51	52	90
4	31	29	0
5	119	118	270
6	26	25	180
7	48	47	90

2,1,L

0	675	816	180
1	953	1136	149
2	165	159	95
3	166	158	321
4	110	115	103
5	44	43	248
6	52	55	208

2,2,L

0	451	483	0
1	356	372	110
2	205	198	147
3	154	155	112
4	111	112	314
5	55	56	232

2,3,L

0	321	332	180
1	239	241	53
2	312	310	319
3	205	202	34
4	198	198	155
5	128	130	217

2,3,L

6	36	36	352

2,4,L

0	150	143	0
1	368	369	259
2	90	85	33
3	141	145	51
4	123	124	251
5	86	87	251
6	64	64	96

2,5,L

0	257	262	180
1	76	72	286
2	110	109	101
3	105	107	78
4	222	222	198
6	37	36	4

2,6,L

0	69	66	0
1	198	195	193
2	265	257	114
3	45	44	111
4	226	228	273
5	59	58	179
6	58	57	88

2,7,L

0	246	244	180
1	165	164	42
2	275	268	346
3	104	109	208
4	62	63	217
5	43	44	337

2,8,L

0	344	339	180
1	160	156	207
2	53	55	95
3	226	221	270
4	54	55	240
5	52	54	75
6	56	56	47

2,9,L

0	116	115	180
1	239	235	348
2	91	92	3
3	55	51	146
4	23	26	196
5	41	41	327

2,10,L

0	74	75	180
1	65	62	342
2	107	107	307
3	73	76	353
4	34	32	120
5	78	77	91
6	18	25	121

2,11,L

1	194	194	349
2	91	98	23
3	97	98	175
4	55	57	322
5	34	33	359

2,12,L

0	24	22	180
1	110	109	6
2	46	42	10
3	50	50	266
4	50	49	136
5	47	49	80

2,13,L

0	98	98	0
1	107	109	342
2	84	82	201
3	63	63	188
4	47	46	324

2,14,L

0	31	33	0
1	99	99	104
2	24	22	317
3	41	40	248
4	43	42	92

2,15,L

0	133	134	0
2	80	82	147
3	40	39	228
4	28	27	3

2,16,L

1	27	27	19
2	43	43	297
3	46	44	198

2,17,L

0	51	47	0
1	44	44	152
2	75	76	179

2,18,L

2	22	20	217

2,19,L

1	33	35	167

3,0,L

1	265	259	270
2	305	297	0
3	173	163	90
4	82	86	180
5	49	51	90
6	73	74	0

3,1,L

0	282	297	90
1	358	358	77
2	421	417	304
3	125	125	33
4	101	99	74
5	37	39	300
6	51	53	245

3,2,L

0	131	121	270
1	598	607	346
2	271	260	45
3	185	178	142
4	100	99	183
5	40	43	1
6	86	85	354

3,3,L

0	321	338	90
1	375	385	297
2	332	331	256
3	218	216	112
4	61	61	141
5	84	85	271
6	25	28	143

3,4,L

0	504	535	90
1	298	194	13

3,4,L

2	219	212	124
3	129	128	205
4	40	41	230
5	119	119	2
6	26	23	357

3,5,L

0	37	35	90
1	322	331	260
2	326	310	179
3	187	182	115
4	78	78	50
5	61	62	3
6	11*	8	131

3,6,L

1	54	51	68
2	51	53	112
3	11*	18	303
4	47	46	263
5	110	113	331

3,7,L

0	108	113	270
1	243	237	251
2	222	216	69
3	229	229	90
4	60	63	329
5	74	74	232
6	52	53	182

3,8,L

0	25	20	90
1	104	106	72
2	39	39	17
3	144	143	193
5	43	42	21
6	59	61	157

3,9,L

0	109	108	270
1	51	53	241
2	223	225	84
3	33	37	120
4	51	51	258

3,10,L

0	202	205	270
1	71	71	292
2	96	91	163
3	76	78	226
4	93	94	356

3,11,L

0	220	220	270
1	95	98	208
2	117	121	78
3	68	68	298
4	90	88	280

3,12,L

0	52	52	270
1	164	166	128
2	102	104	178
3	41	42	338
4	48	49	19
5	30	30	197

3,13,L

0	86	85	270
1	103	100	38
2	95	97	26
3	76	74	291
4	34	35	230
5	41	38	120

3,14,L

1	28	30	197
2	67	64	254
3	48	47	354

3,15,L

0	89	90	270
1	96	98	94
2	28	33	159
3	33	34	254

3,16,L

0	28	30	90
2	21	20	342

3,17,L

0	66	63	90
1	82	81	102
2	24	25	249
3	74	72	322

3,18,L

0	50	47	90

4,0,L

0	337	355	180
1	105	106	90
2	138	140	0
3	69	73	90
4	130	126	180
5	66	65	270
6	56	57	180

4,1,L

0	161	172	180
1	234	228	96
2	45	43	122
3	121	116	353
4	87	84	243
5	76	74	153
6	76	75	55

4,2,L

0	439	433	180
1	147	146	298
2	366	352	328
3	223	225	134
4	94	92	223
5	71	71	268
6	56	54	55

4,3,L

0	219	227	180
1	394	391	209
2	77	75	329
3	208	201	287
4	76	77	231
5	52	55	101
6	51	52	94

4,4,L

0	147	145	180
1	125	130	9
2	292	275	110
3	115	115	179
4	118	122	254
5	67	69	356
6	35	36	75

4,5,L

0	319	312	180
1	213	203	86
2	287	285	45
3	101	101	268
4	113	112	188
5	72	74	103

4,6,L

0	158	162	0
1	162	156	358
2	122	113	346
3	183	185	219
4	40	40	351
5	64	66	27
6	26	27	44

4,7,L

0	222	208	180
1	126	126	82
2	80	76	316
3	166	169	272
4	31	34	172
5	53	54	30
6	26	23	315

4,8,L

0	174	173	0
1	207	206	347
2	152	152	193
3	21	20	163
4	61	59	315
5	14*	11	37
6	42	44	113

4,9,L

0	144	149	180
1	184	182	347
2	169	169	316
3	116	117	144
4	45	42	83
5	78	78	67

4,10,L

0	245	244	0
1	79	80	28
2	84	85	137
3	72	73	232
4	47	48	331
5	39	40	90

4,11,L

0	212	210	0
1	135	135	342
2	76	76	145
3	62	56	150
4	61	58	97

4,12,L

0	49	47	0
1	58	57	177
2	145	144	168
3	34	32	315
4	38	38	8
5	36	37	119

4,13,L

0	74	74	0
1	46	46	59
2	41	40	234
3	33	35	155
4	44	46	81
5	34	33	329

4,14,L

0	29	28	0
1	30	30	148
2	34	34	224
3	62	60	330

4,15,L

1	41	41	277
2	65	69	226
4	59	57	40

4,16,L

1	80	82	168
2	41	40	259
3	51	48	15

4,17,L

0	32	32	0
2	30	29	185
3	24	22	65

4,18,L

0	32	24	180
1	45	46	199
2	30	28	2

4,19,L

0	41	38	0

5,0,L

1	296	286	270
2	249	236	0
3	176	174	90
4	56	55	180
5	82	80	270

5,1,L

0	298	299	270
1	332	325	359
2	133	126	179
3	125	123	140
4	63	62	54
5	116	114	357

5,2,L

0	322	321	90
1	177	180	277
2	130	133	110
3	232	227	109
4	87	90	257
6	46	42	88

5,3,L

0	118	115	90
1	222	212	29
2	404	405	176
3	73	75	157
4	80	80	12
5	52	52	15
6	70	70	190

5,4,L

0	76	74	270
1	318	312	239
2	419	424	94
3	161	157	61
4	104	105	307
6	11*	14	43

5,5,L

0	115	109	90
1	311	302	210
2	46	45	231
3	82	84	10
4	98	94	318
5	23	23	256
6	85	85	175

5,6,L

0	322	328	270
1	25	28	106
2	245	239	81
3	143	142	285
4	56	56	264
5	37	40	183
6	29	25	156

5,7,L

1	106	108	221
3	110	109	200
4	32	33	28
5	42	41	115
6	51	48	170

5,8,L

0	150	144	270
1	176	182	72
2	198	201	112
3	87	88	257
4	84	83	265
6	16*	14	359

5,9,L

0	125	125	270
1	54	54	130
2	156	155	181
3	38	35	33
4	84	87	351
5	71	74	212

5,10,L

0	50	50	270
1	226	229	103
2	92	94	245
3	167	167	265
4	38	37	287

5,11,L

0	113	116	90
1	144	141	132
2	78	77	4
3	87	90	5
5	57	56	183

5,12,L

0	67	69	270
1	66	63	36
2	91	91	302
3	56	56	264
4	48	48	83
5	45	47	82

5,13,L

0	29	26	270
1	32	32	281
2	61	59	7
3	73	73	346

5,14,L

0	62	61	90
1	97	96	90
2	65	64	275
3	28	27	233
4	22	28	91

5,15,L

0	28	29	270
1	20	19	55
2	34	35	25
3	25	26	336
4	59	58	142

5,16,L

0	127	125	90
2	52	51	288
3	35	33	27

5,17,L

0	15*	12	270
1	43	39	359
2	32	31	328

5,18,L

0	39	38	90
1	36	39	246

6,0,L

0	49	53	180
1	76	72	90
2	189	190	0
3	61	59	270
4	155	153	180
5	59	59	90
6	47	49	0

6,1,L

0	172	168	0
1	139	131	20
2	167	162	73
3	76	74	179
4	100	100	314
5	23	19	342
6	63	65	99

6,2,L

0	366	362	180
1	242	236	292
2	116	118	353
3	140	141	240
4	95	98	119
5	59	59	43
6	18	19	281

6,3,L

0	32	27	180
1	294	285	10
2	62	57	104
3	100	102	267
4	111	115	276
5	62	62	73
6	28	29	110

6,4,L

0	52	48	180
1	391	390	11
2	182	182	328
3	126	125	147
4	135	129	115
5	37	38	59
6	40	40	282

6,5,L

0	255	249	0
1	40	40	129
2	86	87	230
3	125	125	263
4	139	139	13
5	54	56	92

6,6,L

0	119	113	0
1	132	134	30
2	73	72	237
3	187	190	191
4	20	22	21
5	59	62	316

6,7,L

0	75	79	0
1	59	64	194
2	123	122	218
3	24	23	170
4	43	44	122
5	52	55	92

6,8,L

0	62	62	180
1	186	187	21
2	81	83	195
3	69	73	156

6,8,L

4	116	121	28
5	38	36	53

6,9,L

0	181	188	0
1	173	177	179
2	64	68	183
3	57	59	325
4	56	58	59
5	43	42	101

6,10,L

0	230	232	0
1	72	71	308
2	164	163	169
3	59	61	45
4	39	39	12
5	47	45	261

6,11,L

0	179	176	180
1	95	92	125
2	43	41	241
3	46	44	337
4	53	52	109
5	8*	15	206

6,12,L

0	129	130	0
1	117	117	166
2	68	67	198
4	28	25	293

6,13,L

0	46	46	0
1	38	37	215
2	57	55	271
3	32	32	27
4	28	33	112

6,14,L

1	88	89	218
2	37	42	146
3	56	56	40

6,15,L

0	29	33	180
1	44	43	259
2	40	39	1
3	46	47	68

6,16,L

1	38	36	212
3	30	33	17

6,17,L

0	33	33	180
2	45	47	42

6,18,L

0	7*	5	180
1	40	43	181

7,0,L

1	34	31	270
2	67	67	180
3	94	97	90
4	161	156	0
6	55	55	180

7,1,L

0	50	52	270
1	168	163	339
2	204	197	91
3	112	112	216
4	81	84	296
5	45	44	58
6	36	33	106

7,2,L

0	175	169	270
1	130	125	186
2	182	178	135
3	182	186	56
4	75	78	1
5	81	83	211
6	70	69	185

7,3,L

0	221	208	270
1	60	64	88
2	224	223	93
3	148	151	295
4	47	44	255
5	38	35	72

7,4,L

0	158	149	90
1	146	143	291
2	100	101	81
3	114	115	311
4	87	90	251
5	98	96	176

7,5,L

0	223	219	270
1	288	286	97
2	49	49	240
3	143	143	250
4	51	51	171
5	31	34	65
6	35	35	183

7,6,L

0	265	251	270
1	93	94	248
2	136	134	82
3	16	16	252
5	46	43	169

7,7,L

0	75	76	90
1	217	219	90
2	85	85	246
3	70	71	296
4	51	51	2
6	25	20	207

7,8,L

0	56	54	270
1	157	155	110
2	25	24	274
3	109	108	334
5	31	33	191

7,9,L

0	224	230	90
1	141	143	161
2	167	171	267
3	102	104	293
5	23	21	118

7,10,L

0	94	98	90
1	71	73	290
2	86	82	8
3	64	65	307
4	72	72	212
5	40	41	130

7,11,L

1	61	62	257
2	86	86	279
3	49	52	35
4	84	83	67

7,12,L

0	27	27	270
1	89	87	46
2	65	63	306
3	50	51	270
4	52	52	157

7,13,L

0	39	37	90
1	35	34	353
2	53	53	284
3	51	53	120
4	44	45	111

7,14,L

0	34	35	90
1	60	61	102
2	36	36	327
3	43	44	142
4	43	46	148

7,15,L

0	83	85	90
1	67	65	299
3	46	46	93

7,16,L

0	29	32	90
1	28	28	355
2	50	48	267
3	42	44	182

7,17,L

1	62	58	254

8,0,L

0	211	204	0
1	59	54	270
2	151	153	0
3	80	78	270
4	46	41	0
5	71	73	90
6	18	18	180

8,1,L

1	282	278	1
2	47	46	233
3	93	94	192
4	56	53	74
5	69	69	338

8,2,L

0	98	96	0
1	46	40	65
2	73	70	185
3	162	160	236
4	29	27	139
5	83	81	119
6	38	38	276

8,3,L

0	464	469	0
1	108	106	8
2	123	125	166
3	199	195	111
4	94	95	21
5	36	36	329
6	33	28	213

8,4,L

0	142	143	0
1	50	53	111
2	40	36	234
3	85	86	301
4	110	111	74
5	30	31	131
6	37	37	301

8,5,L

0	253	259	0
1	20	20	206
2	140	144	141
3	85	79	178
4	52	51	322
5	20	22	277

8,6,L

0	145	143	180
1	60	62	197
2	93	90	213
3	98	101	85
4	100	103	102
6	52	54	264

8,7,L

0	126	128	0
1	140	140	111
2	212	217	221
3	87	87	4
4	112	115	0
5	43	42	186

8,8,L

0	99	108	180
1	86	90	188
2	28	30	353
3	76	74	75
4	47	45	44
5	56	55	272

8,9,L

0	49	47	0
1	138	138	234
2	57	55	216
3	73	73	18
4	18	20	217
5	49	48	212

8,10,L

0	90	89	180
1	58	58	55
2	70	69	291
3	44	39	66
4	41	37	158
5	52	50	262

8,11,L

1	191	190	185
2	47	47	114
3	51	49	357
5	22	20	143

8,12,L

0	20	24	0
1	71	73	262
3	54	55	92

8,13,L

0	157	155	180
1	49	48	196
2	72	71	14
3	59	60	332

8,14,L

0	28	28	180
1	28	29	243

8,14,L

2	28	31	65

8,15,L

0	47	45	180
2	49	51	39
3	26	28	331

8,16,L

0	41	41	0
1	28	27	16
2	39	38	35

8,17,L

0	33	32	180

9,0,L

1	21	23	90
2	206	205	180
3	94	91	270
4	89	85	0
6	25	29	180

9,1,L

0	164	161	270
1	219	217	113
2	152	154	65
3	103	101	15
4	78	77	236
5	74	73	179

9,2,L

1	206	201	94
2	87	88	273
3	100	100	303
4	35	33	71
5	50	52	117

9,3,L

0	21	18	90
1	132	134	66
2	45	44	66
3	83	81	257
4	95	97	209
5	45	47	155
6	42	42	27

9,4,L

0	112	117	90
1	74	70	111
2	106	104	283
3	55	58	164
4	59	57	37
5	20	21	225
6	45	40	210

9,5,L

0	66	63	270
1	142	144	116
2	32	29	60
3	105	108	287
4	48	47	156
5	32	27	56

9,6,L

0	195	193	90
1	21	23	40
2	132	129	254
3	84	88	338
4	40	43	78
5	61	60	178

9,7,L

0	102	102	90
1	123	120	80
2	130	129	323
3	50	49	283
4	38	39	178
5	31	30	11

9,8,L

0	110	116	90
1	146	148	256
2	71	73	313
3	45	47	51
4	83	84	174
5	35	34	205

9,9,L

1	55	53	328
2	44	43	258
3	57	54	200
4	68	69	118
5	42	43	62

9,10,L

1	67	71	264
2	80	82	351
3	33	37	53
4	50	50	111

9,11,L

2	72	72	283
3	32	30	181
4	47	45	97

9,12,L

0	69	69	270
1	56	56	253
3	71	72	105

9,13,L

0	153	159	90
1	40	41	267
2	33	32	273
3	61	59	138

9,14,L

0	14*	15	90
1	49	50	336
2	36	35	130

9,15,L

0	0*	9	270
1	71	71	270
2	48	43	212

9,16,L

0	56	58	270
1	24	27	238
2	36	35	102

10,0,L

0	394	400	0
1	50	49	270
2	156	155	180
4	68	63	0

10,1,L

0	57	57	0
1	112	111	64
2	159	160	165
3	32	36	150
4	107	107	90
5	31	32	260
6	47	48	273

10,2,L

0	142	142	0
1	169	169	175

10,2,L

2	108	108	119
3	89	85	29
4	85	84	346
5	27	26	138

10,3,L

0	87	90	0
1	75	79	114
2	165	165	280
3	24	20	53
4	54	56	98
5	45	46	321

10,4,L

1	182	185	169
2	86	88	138
3	95	91	302
5	41	39	193

10,5,L

0	27	23	180
1	45	43	156
2	67	67	193
3	137	138	88
4	25	28	42
5	64	63	208

10,6,L

0	22	20	180
1	191	196	168
2	88	87	279
3	59	56	35
4	29	25	163
5	42	44	185

10,7,L

1	40	38	323
2	94	96	60
3	51	46	84
4	73	72	276
5	62	63	251

10,8,L

0	137	140	180
1	110	111	250
3	76	77	20
4	50	51	188
5	35	32	210

10,9,L

0	31	28	0
1	41	42	249
2	37	39	193
3	15*	21	65
4	65	62	262

10,10,L

0	113	110	180
1	46	47	145
2	68	71	34
3	31	32	26
4	41	38	203

10,11,L

0	38	37	180
1	28	27	247
2	43	48	56
4	48	49	282

10,12,L

0	107	110	180
1	39	38	3
2	101	99	345
3	31	31	266
4	26	25	173

10,13,L

0	47	44	180
2	23	23	80
3	50	49	312

10,14,L

1	93	93	12
2	51	50	346
3	24	28	173

10,15,L

1	27	26	314
2	32	31	350

11,0,L

1	202	208	90
2	174	174	0
3	116	119	270
4	34	35	180
5	60	58	90

11,1,L

0	69	67	90
1	140	139	239
2	143	143	311
3	88	86	13
4	24	23	149
5	46	45	145

11,2,L

0	142	146	90
1	93	94	46
2	85	87	249
3	37	38	241
4	22	26	122
5	24	25	58

11,3,L

0	19	18	90
1	63	64	314
3	17	14	104
4	20	28	133
5	40	46	190

11,4,L

0	205	212	90
1	62	64	86
2	99	97	268
3	55	57	281
4	58	61	130
5	29	31	53

11,5,L

0	37	35	90
1	31	28	229
2	30	30	245
3	101	102	55
4	38	44	176

11,6,L

0	106	104	90
1	100	104	312
2	120	122	290
3	58	59	171
4	36	33	82
5	46	45	326

11,7,L

1	70	72	264
2	66	67	35
3	56	58	155
4	74	77	170
5	36	33	27

11,8,L

1	34	34	221
2	72	68	207
3	58	58	116
4	63	64	65

11,9,L

1	61	63	318
2	53	54	61
3	56	58	183

11,10,L

1	59	58	260
3	63	62	91

11,11,L

0	38	41	270
2	23	23	54
3	44	42	163

11,12,L

1	75	78	281
3	40	40	133

11,13,L

0	68	68	270
1	24	28	14
2	37	34	116

11,14,L

0	101	102	270
1	63	62	245
2	49	45	108

11,15,L

1	31	29	136

12,0,L

0	97	100	0
1	84	84	90
2	57	58	180
3	72	71	90
4	26	26	180
5	63	61	270

12,1,L

0	97	101	180
1	160	159	142
2	94	93	3
3	83	83	344
4	38	37	146
5	30	27	162

12,2,L

0	104	105	0
1	149	150	203
2	54	53	249
3	60	58	135
4	65	65	343
5	24	26	288

12,3,L

0	108	108	180
1	50	52	196
2	56	55	337
3	50	48	351
4	51	50	129
5	39	41	249

12,4,L

0	85	84	180
1	56	58	232
2	39	37	110
3	83	86	57
5	40	40	210

12,5,L

0	177	182	180
1	30	32	145
2	106	106	3
3	60	62	114
4	39	39	192

12,6,L

0	36	40	0
1	29	29	148
2	68	70	85
3	55	54	300
4	73	73	270
5	42	36	200

12,7,L

0	80	77	180
1	34	38	344
2	23	22	338
4	51	49	226

12,8,L

0	70	72	180
1	67	71	160
2	28	23	77
3	58	55	274
4	48	45	210

12,9,L

0	22	20	180
1	48	46	31
2	66	67	18
3	29	30	173
4	33	33	242

12,10,L

0	26	28	180
2	50	53	8
3	42	40	283
4	18	16	236

12,11,L

0	21	23	180
1	75	76	332
3	39	36	286

12,12,L

0	53	52	180
1	54	53	16
3	28	28	266

12,13,L

0	74	71	0
1	76	74	356

12,14,L

1	24	25	318

12,15,L

0	35	38	0

13,0,L

1	151	151	270
2	62	62	0
3	21	23	90
4	20	23	180
5	37	39	90

13,1,L

0	72	73	90
1	58	57	12
2	115	113	265

13,1,L

3	38	38	88
4	52	49	83

13,2,L

0	141	142	270
1	75	75	56
2	67	65	47
4	78	76	141

13,3,L

0	85	87	90
1	115	114	267
2	42	43	273
3	89	87	92
4	46	48	140

13,4,L

0	105	103	90
2	35	37	28
3	34	33	110
4	30	30	263

13,5,L

1	117	118	272
2	43	43	204
3	62	59	146

13,6,L

0	19	17	90
1	38	36	309
2	36	35	127
3	44	46	205

13,7,L

1	86	83	247
2	64	66	113
3	80	78	73
4	44	43	336

13,8,L

0	42	41	270
1	37	38	335
2	64	63	171

13,9,L

0	64	65	270
1	27	30	216
2	48	46	61
3	24	21	35
4	32	38	258

13,10,L

0	17	19	270
1	32	31	205
2	27	26	198
3	28	28	225

13,11,L

0	111	110	180
1	75	75	314
0	61	59	270
2	71	69	106

13,12,L

0	44	43	270

13,13,L

0	49	52	270
1	34	33	90
2	17*	22	81

13,14,L

1	28	30	112

14,0,L

2	48	51	0
3	41	42	90
4	37	33	180

14,1,L

0	36	37	180
1	76	79	197
2	54	52	94
3	31	29	353
4	51	50	330

14,2,L

0	111	110	180
1	75	75	314
2	56	55	356
3	36	32	150
4	29	31	207

14,3,L

0	125	125	180
1	31	30	143
2	47	47	15
3	56	54	358
4	42	46	219

14,4,L

1	97	97	31
2	58	57	71
3	38	37	152

14,5,L

0	29	33	0
2	70	70	8
3	42	41	267
4	40	40	203

14,6,L

1	46	43	342
3	57	56	207
4	32	29	215

14,7,L

0	105	110	180
2	42	41	330
3	36	38	232
4	34	31	146

14,8,L

2	16*	17	184
3	14*	17	197

14,9,L

0	24	22	180
1	49	53	358
2	43	46	313
3	44	44	197

14,10,L

1	46	46	7
3	33	30	273

14,11,L

1	52	50	11
2	50	48	221

14,12,L

0	79	78	0
1	24	21	184
2	45	44	164

14,13,L

0	28	30	0

15,0,L

1	38	38	270
2	38	36	0
3	48	44	90

15,1,L

0	36	37	270
1	40	42	65
3	46	43	126
4	32	33	111

15,2,L

1	73	74	289
2	60	58	90
3	78	77	102

15,3,L

0	96	98	90
1	70	70	15
2	39	40	223
3	50	48	185
4	38	38	328

15,4,L

0	87	89	270
1	26	25	280
2	82	80	115
3	30	29	172
4	24	25	303

15,5,L

0	31	31	270
1	64	62	244
2	39	39	175
3	26	27	53
4	24	21	7

15,6,L

0	69	69	270
1	22	23	231
2	69	67	98
3	33	36	332

15,7,L

3	14*	17	47

15,8,L

0	57	57	270
1	35	37	96
2	49	47	42
3	35	34	275

15,9,L

1	38	40	212
2	35	36	143

15,10,L

1	62	61	83

15,11,L

1	28	26	95

16,0,L

0	36	40	180
1	25	25	90
2	78	78	0
3	40	38	270

16,1,L

2	37	36	86
3	37	38	252

16,2,L

0	50	53	180

16,3,L

0	92	94	0
1	60	62	37

16,4,L

1	66	62	334
2	51	49	351
3	53	51	188

16,5,L

0	21	18	0
3	34	33	219

16,6,L

1	47	53	32
2	32	33	177
3	36	34	158

16,8,L

0	35	32	0
1	36	57	1

16,9,L

0	26	25	0
2	35	33	241

16,10,L

0	57	57	0

17,0,L

1	12*	10	270
2	9*	2	0
3	41	39	90

17,1,L

0	36	33	270
1	32	31	27
2	30	28	98

17,2,L

1	22	26	296
2	41	41	173

17,3,L

0	43	46	270
1	31	29	117
2	58	57	129

17,4,L

1	44	45	221
2	24	27	110

17,5,L

1	67	68	106

17,6,L

1	28	31	61
2	47	47	50

17,8,L

1	33	32	128

17,9,L

0	54	55	90

18,1,L

1	47	48	24

18,1,L

2 25 29 202

18,2,L

0 25 23 0
2 34 36 306

18,3,L

0 43 41 0
1 31 27 343

18,4,L

1 20 20 184
2 30 29 149

18,5,L

0 35 33 270

0 47 48 0

19,1,L

Data for S,S-Dimethyl-N-p-nitrophenylsulphimide

Crystal Data

$C_8H_{10}N_2O_2S$, M = 198.24; monoclinic,

a = 4.811(1)Å, b = 9.874(2)Å, c = 19.947(4)Å,

β = 97.45(3)°, V = 939.6Å^3; D_c = 1.40 g.cm^{-3},

Z = 4; F(000) = 416; space group $P2_1/c$ (C_{2h}^5, No.14);

M_0 - K_α radiation, λ = 0.7107Å, μ (M_0 - K_α) = 2.98 cm^{-1}.

0,0,L

2	313	-309
4	540	-564
10	551	530
12	227	-218
14	193	-187
18	83	88

0,1,L

1	30	22
2	209	201
3	71	-65
4	230	237
5	248	250
6	145	-141
7	168	165
8	82	81
10	482	474
11	120	-119
13	111	-106
14	118	-113
15	76	80
16	176	-176
22	80	69
24	68	-48

0,2,L

2	57	-55
3	159	157
4	526	543
5	245	-245
6	280	275
7	154	-153
8	165	-164
9	46	44
10	261	-254
11	382	383
14	280	278
15	75	-86
16	130	-129
17	85	-78
22	84	92

0,3,L

1	202	-194
3	57	47
4	85	-83
6	416	398
7	32	-32
8	294	290
9	119	-112
10	182	-180
12	166	-164
13	83	91
14	144	-146
16	229	227
17	82	74

0,4,L

0	56	-49
1	52	55
2	250	-234
3	293	-289
5	423	409
6	200	-192
8	208	198
9	80	-89
10	165	164
11	181	-177
13	132	-138
14	128	-129
15	244	248
18	114	102
22	90	-90

0,5,L

1	251	241
5	274	-266
6	285	-277
7	260	-260
8	151	-156
9	132	136
10	89	81
11	173	171
12	106	112
14	102	104
16	172	-179
19	76	61
20	67	73

0,6,L

0	202	-205
1	56	43
2	82	74
6	258	257
7	178	-181
8	152	-163
10	86	-81
11	116	111
15	76	-69
16	67	60
17	131	-133
19	118	117

0,7,L

1	116	-111
2	180	-181
4	68	-52
5	177	175
6	145	151
7	95	91
9	78	-64
10	66	-60
11	97	-96
16	103	110
19	71	-68

0,8,L

4	59	-58
7	202	196
10	64	-46
11	91	-80
13	67	-46
17	103	105

0,9,L

1	119	125
2	182	179
3	78	-82
5	99	-101
9	71	61
13	82	-95
17	70	52

0,10,L

0	74	-77
2	81	85
3	164	158
5	71	-72
7	97	-98
11	79	67

0,11,L

1	104	-113
3	113	117
9	91	-84
13	101	91

1,0,L

-24	88	-84
-20	140	143
-14	94	-91
-12	136	130
-10	186	-181
-8	57	33
-6	60	63
-4	447	467
0	143	142
4	383	-379
6	233	239
8	230	223
10	133	-139
12	317	-328
16	311	321

1,1,L

-22	70	-68
-18	84	84
-14	239	-246
-12	177	-182
-10	97	-73
-9	268	258
-8	742	759
-6	85	86
-5	55	52
-4	534	-552
-3	55	64
-2	396	-400
-1	85	-90
0	244	-239
1	442	440
3	701	-733
4	41	50
5	185	-180
6	402	-408
7	120	118
9	154	151
10	134	137
11	49	58
13	138	-141
14	176	-176
16	164	-161
18	197	194
20	71	59

1,2,L

-20	133	-148
-19	87	84
-16	122	122
-15	92	-97
-14	83	89
-13	69	-65
-12	154	-157
-11	72	-74
-10	133	-134
-9	214	-200
-8	257	258
-7	104	106
-6	325	330
-5	345	334
-4	328	-325
-3	278	269
-2	315	-315
-1	367	391
0	488	-498
1	175	-172
3	84	75
18	178	-180
5	327	-318
7	165	161
8	372	-371
9	97	105
12	291	297
13	113	-128
15	148	-148
16	69	-79
17	148	147
20	65	47

1,3,L

-18	111	-117
-17	69	62
-16	126	-114
-15	61	-67
-14	99	96
-13	152	153
-12	193	190
-11	106	-109
-10	93	-87
-9	171	-165
-8	312	-302
-6	70	-80
-5	236	-223
-4	263	256
-3	179	171
-2	63	68
-1	190	-194
0	99	-89
1	154	-154
2	259	249
3	605	605
4	154	153
5	289	273
6	168	164
7	293	-273
8	242	-237
9	140	-144
10	215	-217
12	93	81
13	174	179
16	149	144
17	94	-103
18	129	-135

1,4,L

-24	73	-54
-20	104	108
-19	93	-72
-17	129	-135
-16	92	-82
-15	219	230
-14	217	-217
-13	111	117
-12	214	220
-10	152	155
-9	267	-275
-8	164	-161
-7	243	-233
-6	445	-426
-5	243	229
-4	100	82
-3	163	163
-2	294	285
0	51	58
1	299	-277
2	521	-508
3	82	81
6	79	90
7	46	20
8	341	329
10	65	66
11	65	-53
12	109	-113
13	122	127

1,5,L

-16	190	186

-14	242	-252
-13	144	-148
-11	105	101
-8	172	177
-7	131	-135
-6	125	114
-4	404	-394
-3	43	52
-2	146	141
-1	137	141
0	89	90
1	134	-136
2	66	-61
3	146	-146
4	259	-254
7	194	193
8	53	39
9	66	59
10	172	183
11	63	-49
12	59	-16
13	88	-91
17	70	68

1,6,L

-20	73	-50
-17	129	118
-15	77	-70
-14	186	182
-13	188	-188
-12	87	-84
-11	134	133
-10	72	-60
-9	254	265

-7	154	152
-6	57	57
-5	294	-287
-4	59	43
-3	374	-378
-2	80	-88
-1	205	199
0	50	-45
2	111	112
4	70	76
5	90	-109
7	67	73
8	168	-165

1,7,L

-18	71	-49
-17	67	-61
-15	120	121
-14	120	121
-11	85	-94
-8	73	-76
-7	162	167
-5	161	160
-4	185	180
-3	155	-159
-1	188	-194
0	191	-189
1	64	71
2	69	-77
3	151	148
6	59	76
7	83	-67
9	139	-132
10	112	-121

1,8,L

-17	92	-67
-13	87	95
-9	116	-114
-6	61	-45
-5	90	77
-3	171	171
-2	103	-94
-1	111	-106
0	255	256
3	65	-15
5	100	110
6	93	-86
8	66	65
9	143	-148
19	92	-73

1,9,L

-17	70	-55
-11	108	104
-5	67	-60
-1	228	232
1	135	-139
3	80	-78
5	91	-61
7	68	83
9	105	121
11	100	-96
13	74	-60

1,10,L

-11	78	-70

0	71	-87
1	95	99
5	144	-139
9	106	90

1,11,L

-22	96	96
-20	74	93
-18	196	-197
-16	80	-72
-14	164	166
-12	273	276
-8	72	-86
-6	281	-277
-4	128	125
-2	151	-151
0	33	34
2	83	-81
8	243	228
10	182	-184

1,12,L

3	74	-78
5	121	121

2,0,L

-18	71	77
-16	164	-160
-14	144	-149
-13	58	-33
-12	246	251
-11	75	77
-10	333	338
-9	73	-76
-7	266	258
-6	433	-434
-5	75	77
-4	209	-215
-3	284	-271
-2	378	376
-1	133	-132
0	225	231
1	312	-316
3	209	193
4	426	-424
6	61	-45
7	216	210
8	242	246
9	74	-63
12	151	-152
14	91	-88
17	81	75

2,1,L

14	121	119
16	84	82
20	94	-109

2,1,L

18	216	213
19	80	-80
20	110	-92

2,2,L

-22	75	-73
-20	69	-74
-18	101	106
-17	69	-86
-16	72	66
-15	183	-182
-13	131	128
-12	145	-150
-11	74	85
-10	54	53
-9	53	77
-7	129	123
-6	112	103
-5	132	-130
-4	250	-238
-3	237	223
-2	83	70
0	222	209
1	53	-50
2	127	129
3	213	210
4	206	-206
5	328	-324
6	167	-167
7	203	-198
8	81	-70
9	93	85
10	234	229
11	66	65
12	93	78
14	109	-114

2,3,L

-25	72	51
-20	100	-93
-18	63	-60
-17	81	81
-15	101	92
-14	277	277
-13	160	-162
-12	134	-136
-11	52	-60
-10	193	-197
-8	179	-178
-7	56	-51
-6	480	485
-5	44	-56
-4	465	461
-3	41	39
-2	425	-399
-1	218	217
0	222	-217
1	162	164
2	210	-212
3	130	125
4	563	561
5	239	-237
6	155	-160
7	132	-124
8	101	-109
9	70	62

2,4,L

-17	80	-83
-15	144	-143
10	66	-70
12	92	87
15	111	-106
16	66	-67
19	88	70

2,5,L

-18	75	-63
-15	82	91
-14	184	-198
-13	136	-143
-12	159	163
-8	80	-89
-6	73	73
-5	194	197
-4	128	130
-3	204	-189
-2	148	141
-1	128	-128
0	210	-208
1	101	102
2	342	-343
3	95	-102
4	398	406
5	176	177
6	156	156
10	189	-194
12	90	-98
14	99	101

2,6,L

-14	64	61
-12	236	-236
-9	73	94
-8	114	112
-7	142	-147
-6	58	54
-5	207	-215
-4	77	-81
-2	151	-155
-1	182	181
-13	142	144
-12	91	-93
-11	169	168
-10	138	145
-9	106	-119
-7	205	-214
-6	182	-182
-4	124	-122
-3	236	240
-2	148	147
-1	124	135
0	231	235
1	204	-207
2	137	-140
3	102	-102
4	110	-116
5	243	239
8	142	145
9	114	-109
11	100	-96
12	103	-118
15	108	106

2,7,L

-21	69	-51
-17	74	74
-11	165	-167
-9	174	178
-7	94	100
-3	115	-115
-2	93	-98
-1	167	-167
0	101	99
1	294	301
3	109	-107
5	103	-103
7	78	-87
9	108	110
11	138	144
12	89	78

2,8,L

-15	81	86
-12	129	128
-11	88	-100
-9	85	-92
-8	63	-67
1	65	42
2	279	291
3	75	-77
4	125	-132
7	119	110
11	92	-80
12	65	82
13	70	-55

2,9,L

-8	71	61
0	117	-116
1	103	-91
2	68	86
5	94	88
11	74	-104

2,10,L

-15	79	-75
-11	70	66
-1	85	94
3	81	-70
5	85	-85

2,11,L

1	71	74

3,0,L

-18	81	-56
-14	171	172
-12	108	108
-7	96	92
-5	144	150
-1	114	-119
1	99	-104
2	97	-111
3	85	100
7	84	-94
13	77	75

3,1,L

-10	201	-285
-8	198	-203
-6	77	75
-4	142	146
-2	139	-140
0	75	-85
2	87	87
4	252	253
8	81	-78
10	182	-179
12	98	111
14	89	94
20	89	-96
22	70	58
-26	93	-65
-16	144	-149
-13	161	162
-12	338	348
-11	123	-137
-8	223	-220
-6	166	-169
-4	126	122
-3	63	63
-2	351	350
-1	110	-110
0	305	-302
1	93	98
2	149	-151
6	214	219
9	93	86
12	68	-89

3,1,L			-13	151	-152	5	99	108	-6	105	-97	7	87	-89	-18	72	-47	-18	77	77
			-11	147	152	6	61	51	-5	64	-60				-14	99	88	-4	84	-97
16	70	60	-9	129	134	7	159	-161	-4	71	-51	3,9,L			-8	111	-117	0	129	130
			-8	199	206	8	94	-91	-3	135	136				-7	78	82	3	71	-81
3,2,L			-7	91	-94	10	74	-73	-2	71	71	-9	142	-133	-4	125	128	6	119	-117
			-4	222	-233	11	70	64	0	101	93	-5	72	87	0	215	-209	8	74	70
-22	70	-62	-3	65	-72	14	97	99	3	161	-159	9	68	-71	3	68	72			
-20	71	54	-2	246	-250				4	169	-172				4	134	141	4,4,L		
-18	124	125	-1	172	171	3,5,L			7	125	141	3,10,L			5	63	-49			
-17	89	70	2	252	255				11	67	-79				6	113	115	-16	106	103
-12	245	-235	3	238	-238	-19	67	-54	14	77	-78	-3	95	79	8	83	-82	-13	97	-92
-10	256	254	4	80	89	-15	91	96				1	102	-90				-9	79	60
-8	113	119	5	104	98	-11	78	-60	3,7,L						4,2,L			-8	109	114
-7	97	-108	6	196	-198	-9	72	-68				3,11,L						-5	153	-156
-5	110	111	8	93	-94	-7	60	73	-19	70	85				-21	72	63	-2	168	-160
-4	186	-184	10	95	111	-6	116	-122	-13	82	-82	-9	79	58	-12	108	115	-1	69	63
-3	173	177	12	83	89	-5	76	74	-12	66	-40				-11	122	120	5	101	-100
-2	66	-43	20	85	76	-4	130	143	-10	129	-122	4,0,L			-10	174	178	12	69	75
-1	110	-98				-2	138	139	-9	76	65				-9	159	-163			
0	189	186	3,4,L			-1	80	-78	-8	66	50	-20	112	-100	-8	118	-111	4,5,L		
1	158	-159				1	105	-109	-6	82	94	-16	82	96	-6	177	-177			
3	89	-78	-20	78	-65	3	193	196	-5	96	-98	-10	427	-419	-2	139	146	-18	73	-55
4	144	-133	-18	99	-116	4	251	-262	4	71	81	-8	178	178	0	92	77	-14	71	88
6	80	-73	-14	65	56	6	225	235	5	94	-104	-6	146	146	1	119	-118	-6	67	60
8	105	108	-12	119	119	9	113	-109	7	109	102	-2	72	-71	2	118	-124	-4	113	107
9	85	86	-11	97	-98	10	63	-42	9	87	81	0	154	-159	3	61	58	0	106	-99
10	124	126	-10	89	-84	13	96	107	15	74	-49	2	259	262	4	133	-138	6	99	99
12	87	-89	-7	80	81							6	136	-142	5	86	76			
14	64	-82	-4	204	204	3,6,L			3,8,L			8	124	-121	6	139	143	4,6,L		
			-3	134	-134							10	80	72	9	65	-52			
3,3,L			-1	82	-90	-15	72	-56	-10	138	-142	12	73	61	12	84	-88	-16	73	-71
			0	154	-154	-13	78	64	-7	116	123	16	68	-61	16	75	72	-15	70	41
-16	94	95	1	89	95	-10	73	74	-3	91	-100							-5	72	77
-15	85	-83	2	133	-138	-9	68	68	2	105	105	4,1,L			4,3,L			-2	73	88
-14	94	-98	4	150	148	-7	151	-150	3	86	95									

4,6,L

-1	83	-81
5	69	51
9	107	-100

4,7,L

-17	71	-54
-8	97	89
-4	94	-80
8	68	78

4,8,L

-3	69	-61
-1	93	84

4,9,L

-8	71	-64
-7	69	67
-3	69	-63
3	76	67

4,10,L

-7	82	-65

5,0,L

-14	82	-65
-10	88	82
-8	112	112
-4	122	-118
0	74	64
2	93	99
6	149	-143

5,1,L

-18	80	-67
-8	113	-107
-7	73	63

-6	104	111
-2	83	-77
8	129	-123

5,2,L

-12	73	46
-8	152	-149
-6	78	59
-4	74	60
2	103	-103
4	81	85
7	73	-84
10	70	-61

5,3,L

-14	80	-69
-10	95	84
-6	73	-86
-2	85	82
8	69	75

5,4,L

-12	84	-70
-8	109	103
-4	76	-47
-2	72	-44

5,5,L

-14	97	79
-12	70	-53
-9	80	54
-6	72	78
-11	75	-64

5,6,L

-9	70	-48

5,8,L

-1	80	66

6,0,L

0	80	56

6,3,L

-12	72	63
-6	78	-80
-4	76	77

Data for Dimethylsulphonium 1,2-dibenzoyl-2-(phthalimidoimino) ethylide

Crystal Data

$C_{26}H_{20}N_2O_4S$, M = 456.52; orthorhombic,

a = 13.548(3)Å, b = 29.591(5)Å, c = 12.418(2)Å,

V = 4978.36Å^3; D_c = 1.30 g.cm^{-3}; Z = 8 with two molecules per asymmetric unit; F(000) = 2032; space group $P2_12_12_1$ (D_2^4, No.19);

M_0 - Kα radiation, λ = 0.7107Å, μ (M_0 - Kα) = 1.61 cm^{-1}.

0,-40,L

2	76	63	180

0,-39,L

1	142	121	90
3	104	105	90

0,-37,L

1	77	66	270
7	97	99	270

0,-36,L

0	125	101	180

0,-35,L

9	62*	85	90

0,-34,L

0	144	154	0
2	114	98	0
6	0*	28	0

0,-33,L

1	96	108	270

0,-32,L

0	129	124	180
2	140	131	180
10	117	92	180

0,-31,L

1	88	98	90
5	93	87	90
6	142	132	90
8	133	113	90

0,-30,L

2	203	204	0
4	133	135	0
8	110	100	0
10	123	136	0

0,-29,L

6	184	178	270

0,-28,L

0	309	305	180
1	71	45	0
2	302	304	180
3	158	175	0
6	99	102	180
8	190	191	180
9	104	103	0

0,-27,L

1	189	178	90
2	166	184	90
3	88	83	270
4	74	80	90
5	102	79	270

0,-26,L

0	283	286	0
2	107	93	0
3	142	102	180
5	153	169	180
6	79	84	0
8	234	248	0
9	134	132	180

0,-25,L

1	71	108	270
3	173	163	270
5	76	82	90
6	61	39	270
10	37*	67	90

0,-24,L

2	351	360	180
3	123	141	0
4	131	133	180
6	69	86	180
7	114	138	0
8	216	206	180
9	93	86	0

0,-23,L

1	212	217	270
2	276	265	270
3	197	185	270
4	210	210	270

0,-22,L

0	403	366	0
2	575	594	0
4	377	372	0
5	121	120	180
8	113	118	0
13	0*	8	180

0,-21,L

1	59	49	90
2	206	214	90
4	95	93	270
5	201	226	90
6	295	296	90
8	107	128	270
12	99	103	90

0,-20,L

0	68	77	180
2	336	327	180
3	140	121	180
4	360	360	180
6	139	152	180
10	207	203	180
12	77	62	0

0,-19,L

2	88	64	90
3	280	265	270
4	283	253	270
6	172	175	90
8	104	142	270
12	122	131	270

0,-18,L

0	185	181	0
1	113	127	180
2	76	59	180
4	133	141	0
6	166	152	0
7	73	47	180
8	135	151	0
10	99	81	0
11	104	122	180

0,-17,L

1	407	389	90
2	97	85	270
3	225	235	90
4	191	200	90
5	258	272	90
6	156	176	270
7	133	129	90
8	129	113	90
9	53*	104	90
10	124	113	90

0,-16,L

1	108	111	180
2	300	305	180
4	533	543	180
6	306	310	180
8	70	49	180
10	286	289	0

0,-15,L

1	149	157	270
2	902	913	270
3	103	98	270
5	278	262	270
7	109	116	270
9	136	133	270
10	569	565	270
11	43*	65	90
12	177	168	270

0,-14,L

0	596	623	180
1	210	198	0
2	393	346	180
3	183	178	0
4	362	375	0
5	84	79	0
8	297	286	0
9	116	118	180
10	330	322	180
11	45*	65	0

0,-13,L

1	76	85	270
2	516	502	90
3	99	107	270
4	141	124	270
7	214	191	90
8	77	90	90
9	117	142	90
10	527	517	90
12	258	253	90
14	73	64	90

0,-12,L

0	1678	1636	0
1	373	348	180
2	104	88	0
3	112	97	0
4	325	328	0
5	204	215	180
6	66	62	0
7	99	99	180
8	267	256	180
9	131	141	0
10	67	75	0
12	118	126	0

0,-11,L

1	198	195	270
2	157	180	270
3	283	306	270
4	294	273	270
5	177	167	270
6	81	86	90
9	0*	70	270
10	153	155	270
11	69	90	270
12	285	258	270
14	67	61	270

0,-10,L

0	1318	1351	180
1	163	189	0
2	879	888	0
3	62	28	0
4	126	143	0
5	224	201	180
6	242	246	180
7	214	225	0
8	125	127	180
12	106	92	180

0,-9,L

1	283	294	90
2	211	185	90
3	168	144	90
4	811	788	90
6	152	134	270
7	253	256	90
8	457	453	90
10	192	185	90
12	355	348	90

0,-8,L

1	187	216	0
2	157	135	0
3	55	31	0
4	160	148	180
5	351	334	180
6	254	239	0
8	423	414	0
9	122	128	180
10	162	170	0
12	168	172	0
13	93	102	180

0,-7,L

1	48*	64	90
2	1419	1463	270
3	104	121	270
4	990	975	270
5	272	240	270
6	269	264	270
8	474	466	270
10	176	166	270
11	87	74	270
12	219	197	270

0,-6,L

0	424	440	0
1	33*	10	181
2	2564	2605	180
3	270	248	0
5	92	83	180
6	540	590	180
7	129	113	0
8	401	382	180
9	62	77	0
10	400	404	180
12	203	223	180
16	65*	65	180

0,-5,L

1	74	88	270
2	502	524	90
3	224	197	90
4	481	512	270
5	78	93	90
6	699	689	90
8	276	242	270
10	115	96	90
12	73	85	270
14	0*	26	90
17	0*	36	90

0,-4,L

0	794	775	180
1	0*	87	0
2	88	106	180
4	959	971	180
5	205	193	180
6	210	208	0
8	262	275	0
10	428	442	0
11	86	75	180
12	298	309	0
14	88	92	180
15	35*	5	0

0,-3,L

2	614	657	90
3	95	56	90
4	296	247	90
5	175	159	270
6	420	411	90
7	196	181	90
8	173	165	90
10	177	170	270
14	103	99	270

0,-2,L

0	1907	2079	180
1	0*	81	0
2	2208	2269	180
3	144	151	0
4	481	463	0
5	155	148	180
7	69	41	0
8	151	106	180
10	425	440	180
12	139	140	180

0,-1,L

2	2116	2119	270
3	88	27	270
6	125	152	90
7	151	161	90
8	100	99	90
10	112	99	90
11	39*	26	90
13	63*	56	90
14	0*	80	90

0,0,L

2	358	336	0
4	286	277	0
6	163	157	180
8	266	265	0
10	584	568	0
12	70	85	180
14	113	119	0

1,-40,L

1	53*	60	79

1,-38,L

0	52*	22	90
3	0*	35	185
4	51*	49	45

1,-37,L

3	56*	56	155

1,-36,L

7	0*	43	348

1,-35,L

0	150	143	90

1,-34,L

0	108	89	90
2	101	103	66
5	59*	65	148
8	0*	33	45

1,-32,L

0	142	155	270
2	125	116	292

1,-31,L

3	119	111	30
7	104	100	79

1,-30,L

0	111	111	90
4	107	95	33

1,-29,L

0	0*	64	270
2	160	174	263
3	213	218	240
6	141	136	299
8	112	104	290

1,-28,L

0	266	276	270
1	27*	30	92
5	42*	44	59
9	124	112	236
10	60*	69	252

1,-27,L

0	156	153	90
1	241	263	49
2	181	161	64
4	100	100	41
5	127	146	121
6	165	158	126
8	84	93	68

1,-26,L

0	205	193	90
1	95	101	181
2	234	234	39
3	173	178	291
4	197	194	41
5	111	109	40
6	147	128	200
7	102	137	43
9	119	119	46
11	113	110	64

1,-25,L

1	88	84	83
2	148	163	145
3	184	185	79
4	243	228	232
5	116	120	308
6	68	95	288
7	99	100	250
8	119	116	222
9	112	122	229
10	108	93	187

1,-24,L

0	160	143	90
1	285	276	192
2	131	119	263
3	187	173	171
5	89	79	302
6	150	140	226
7	104	123	226
8	26*	45	53
11	15*	93	226

1,-23,L

0	189	189	90
1	130	129	224
2	153	140	62
3	139	130	88
4	212	224	12
5	51*	91	332
6	180	170	75
7	71	48	145
8	125	125	97
9	118	109	69
10	126	144	44
13	100	89	104

1,-22,L

1	356	349	30
2	185	206	145

1,-22,L

3	248	252	59
4	80	114	342
5	225	208	4
7	113	117	106
10	118	119	272
11	75	68	85

1,-21,L

0	285	293	270
1	78	84	283
2	220	209	332
3	293	289	231
4	326	323	292
5	291	290	18
6	103	98	223
7	148	122	251
8	120	118	310
9	132	126	350
10	136	136	236

1,-20,L

0	166	181	270
1	140	136	226
2	313	294	356
3	226	226	186
5	200	206	218
6	114	87	301
7	181	169	250
8	115	122	334
9	138	144	207
11	122	113	240
15	64*	42	244

1,-19,L

0	65	24	90
1	252	262	139
2	194	208	127
3	282	286	144
4	150	147	2
5	156	145	142
6	173	176	125
7	221	229	136
11	94	105	141
12	101	99	12

1,-18,L

0	60	33	90
1	168	173	11
2	355	358	263
3	563	560	4
4	80	83	207
5	289	277	12
6	98	91	192
7	386	410	13
8	141	101	255
9	90	61	73
10	166	155	98
11	138	161	38
14	80	54	102

1,-17,L

0	249	248	270
1	274	290	333
2	399	390	290
3	438	426	37
4	203	222	250
5	290	312	324
6	119	112	278
7	238	238	285
8	199	192	199
9	131	123	240
13	49*	55	296

1,-16,L

0	535	504	90
1	376	384	149
2	312	295	85
3	493	488	167
5	388	384	190
6	169	187	100
7	248	240	193
8	348	340	101
9	168	171	202
10	117	97	350
11	0*	96	167
12	102	106	304
13	77	72	230
14	0*	75	278

1,-15,L

0	61	55	270
1	349	341	195
2	344	376	96
3	241	238	272
4	242	239	108
5	235	218	88
6	264	265	65
7	161	169	157
8	469	451	60
9	160	169	194
10	221	221	341
14	54*	52	308

1,-14,L

0	198	197	90
1	178	200	60
2	441	448	196
3	204	190	173
4	77	86	41
5	212	240	342
6	235	217	279
7	314	302	354
8	420	419	293
9	309	297	27
10	144	154	286
12	117	129	169

1,-13,L

0	181	191	90
1	496	486	324
2	440	434	60
3	250	210	38
5	418	412	45
6	253	244	259
7	239	237	357
8	289	269	255
9	208	216	323
10	343	352	201
11	74	74	283
13	0*	26	81

1,-12,L

0	70	91	90
1	541	525	189
2	488	482	336
3	637	650	162
4	103	110	66
5	518	495	134
6	67	89	154
7	96	101	190
8	104	106	76
9	281	283	223
10	264	260	154
11	160	155	261
13	94	97	182

1,-11,L

0	68	63	270
1	1189	1177	210
2	354	309	213
3	621	648	166
4	395	332	347
5	721	693	218
6	67	41	152
7	68	72	130
8	204	216	147
9	121	122	90
10	253	236	57
11	63	72	213

1,-10,L

1	1302	1325	349
2	346	327	165
3	770	740	356
4	271	247	355
5	745	740	340
6	200	189	207
7	101	123	52
8	262	244	186
9	92	95	359
10	186	185	272
11	168	167	29
12	104	118	66
13	101	92	332

1,-9,L

0	419	414	270
1	461	486	1
2	601	638	1
3	324	311	3
4	496	517	192
5	345	348	69
6	304	322	327
7	175	174	336
8	157	149	25
9	53*	67	91
10	201	212	321
11	173	165	32
15	83	75	80

1,-8,L

1	747	774	269
2	296	296	330
3	625	646	166
4	234	238	122
5	317	297	15
6	147	140	63
7	385	377	184
8	221	225	55
9	96	93	72
10	263	273	42
11	189	196	196
12	103	107	344

1,-7,L

0	251	257	90
1	882	911	89
2	155	142	279
3	165	168	210
4	345	297	45
5	61	44	241
6	261	233	130
7	324	301	217
10	180	165	160
11	132	131	172
12	86	97	202

1,-6,L

0	298	268	270
1	154	112	138
3	148	135	20
4	518	519	280
5	351	356	358
6	364	337	232
7	305	300	342
8	174	159	341
9	128	139	280
10	78	54	143
15	78	93	306

1,-5,L

0	106	130	90
1	281	304	56
2	372	379	259
3	540	557	42
4	473	431	286
5	562	533	31
6	281	308	21
7	258	265	53
8	158	165	218
9	126	121	36
10	122	117	96
12	174	176	333
13	113	93	100

1,-4,L

0	257	248	270
1	600	629	198
2	1105	1091	102
3	903	930	134
4	60	58	343
5	693	674	158
6	189	189	345
7	360	396	109
8	78	103	132
9	189	175	143
10	178	198	243
11	103	113	52
12	91	101	39
13	137	136	116

1,-3,L

2	711	717	108
3	715	719	266
4	334	359	218
5	793	894	213
6	187	149	160
7	355	355	270
9	179	159	232
10	108	112	282
13	193	193	260

1,-2,L

1	577	610	188
2	1112	1154	213
3	364	365	292
4	261	265	76
5	887	894	327
6	156	155	58
7	185	156	212
8	182	180	266
9	80	105	264
10	162	154	51
12	143	139	239
13	145	139	315

1,-1,L

2	1971	2041	350
4	202	232	164
5	693	627	70
6	268	236	151
7	175	184	287
8	79	85	324
9	36*	48	302
10	33*	51	123
11	150	139	71
12	114	108	332

1,0,L

1	788	845	90
2	1564	1587	0
3	348	371	90
5	511	552	90
6	429	398	180
7	214	181	270
10	51*	23	180
11	136	127	90

2,-38,L

0	114	87	180

2,-35,L

0	74	73	0
7	60*	43	184
8	0*	29	234

2,-34,L

2	106	93	188
4	79	53	160

2,-32,L

0	72	88	0
2	94	80	325

2,-31,L

1	124	113	257
2	99	101	39
3	67	82	200
5	60*	60	236

2,-30,L

3	0*	54	245

2,-29,L

0	129	112	180
1	246	251	87
2	212	213	216
4	0*	83	242
6	127	126	168
7	0*	111	47

2,-28,L

0	164	183	0
1	102	102	325
5	126	117	33
8	79	88	101
10	103	88	66

2,-27,L

0	282	285	0
1	258	272	248
2	108	101	32
3	104	117	283
4	242	242	355
5	152	133	251
6	106	158	26
7	97	89	229
9	121	110	273
10	96	92	11
12	64*	37	106

2,-26,L

0	221	238	180
1	135	151	186
2	132	120	246
3	237	227	152
4	125	90	160
5	170	177	96
10	94	119	258
11	42*	67	65

2,-25,L

2	174	185	28
3	316	304	151
4	480	488	182
5	197	198	74
6	163	177	178
7	70*	145	32
9	132	128	83
11	110	83	42
12	66*	42	240

2,-24,L

0	130	129	180
1	189	192	270
3	223	187	312
4	167	176	241
5	88	98	20
6	104	126	93
7	136	122	212
8	77	63	112
10	77	70	63

2,-23,L

0	77	73	0
1	164	178	253
2	133	132	49
3	126	86	156
5	219	218	290
6	205	204	1
7	155	143	262
8	70	74	353
9	76	84	259

2,-22,L

0	98	75	0
1	251	246	48
2	131	115	79
3	107	89	119
4	152	168	316
5	171	178	80
6	115	111	58
8	123	104	206
9	79	64	20
11	62*	46	264

2,-21,L

0	348	330	180
1	439	408	87
2	189	191	221
3	186	192	32
5	104	98	36
6	326	340	185
7	157	167	103
8	123	117	192

2,-20,L

0	114	85	0
1	137	160	202
2	291	281	295
3	97	97	316
4	106	103	224
5	122	131	226
6	135	107	283
7	245	231	226
8	104	101	122
9	177	178	178
10	80	79	281

2,-19,L

0	397	400	0
1	0*	74	273
2	343	336	21
3	178	175	181
4	102	81	134
5	106	81	318
6	128	105	27
7	117	125	213
8	117	115	79
9	105	98	96
12	134	102	34

2,-18,L

0	186	178	180
1	330	333	174
2	243	231	306
3	165	161	121
4	318	324	56
5	188	192	93
6	174	167	358
7	141	178	24
8	268	285	74
9	164	144	342
11	136	125	50
12	94	85	80
13	46*	70	29

2,-17,L

0	172	162	180
1	71	53	43
2	322	307	131
3	171	183	67
4	165	163	209
5	352	348	81
6	111	108	313
7	163	161	273
8	139	154	326
9	0*	136	203

2,-17,L

10	105	131	50

2,-16,L

0	62	80	180
1	334	327	348
2	284	295	117
3	271	262	282
4	99	85	253
5	286	279	335
6	275	287	224
7	40*	80	246
8	225	215	227
9	164	163	150
11	26*	92	184
12	165	149	282
13	107	108	217

2,-15,L

0	94	83	180
1	282	287	200
2	148	137	1
3	355	334	287
4	455	434	343
5	331	334	251
6	135	140	157
8	148	129	187
9	134	135	357
11	75	104	332

2,-14,L

0	198	185	180
1	137	137	118
2	510	479	81
3	333	304	2
4	168	148	228
5	258	250	135
6	159	145	71
7	83	76	120
8	165	179	25
9	328	329	7
10	111	123	75
11	221	205	12
12	133	136	78
13	102	92	16

2,-13,L

0	1234	1243	180
1	516	519	294
2	927	917	348
3	673	695	262
4	208	220	152
5	84	101	164
6	456	432	183
7	122	110	93
9	144	122	156
10	200	213	209
12	55*	158	347

2,-12,L

1	934	902	179
2	656	674	229
3	133	120	274
4	589	541	270
5	182	173	195
6	457	421	267
7	125	135	220
8	114	100	163
9	193	189	201
10	125	130	143
11	196	199	188
14	147	130	260

2,-11,L

0	246	231	0
1	506	520	71
2	404	375	127
3	762	695	83
4	197	184	210
5	238	247	23
6	447	414	13
7	142	156	343
8	275	279	205
9	136	144	75
10	73	56	191
11	159	152	89
12	115	96	186

2,-10,L

0	367	363	0
1	585	629	31
2	185	151	69
3	154	162	160
4	568	592	50
5	426	407	33
6	365	360	92
7	204	186	339
8	112	130	346
9	108	100	269
10	86	67	267
11	146	153	335
14	154	132	86
16	85	80	81

2,-9,L

0	241	249	0
1	686	721	91
2	434	408	25
3	58	86	301
4	353	342	352
5	178	178	183
6	256	268	117
8	306	308	2
9	201	194	253
10	311	320	21
11	125	139	248
13	80	78	267
15	35*	57	252

2,-8,L

0	99	110	180
1	238	255	318
2	243	225	107
4	330	293	249
5	151	143	15
6	246	232	92
7	277	290	189
8	99	108	250
9	128	110	138
10	83	84	242
11	227	221	180
12	90	82	270
13	66	71	185
14	119	103	253

2,-7,L

0	2146	2246	180
1	175	170	155
2	196	168	124
3	734	686	92
4	514	523	197
5	146	199	76
6	204	206	186
7	214	192	93
8	115	101	12
9	99	109	39
10	143	131	180
11	40*	63	323

2,-6,L

0	951	995	0
1	594	538	188
2	563	556	84
3	173	186	312
4	306	304	305
5	300	304	191
6	258	234	25
7	56	48	115
8	92	101	76
9	168	176	2
10	222	225	59
12	193	203	89

2,-6,L

13	72	76	36
14	82	77	26

2,-5,L

0	1525	1491	0
1	1653	1607	226
2	1192	1214	353
3	684	733	286
4	134	159	287
5	686	616	277
6	289	281	5
7	269	299	250
8	96	99	351
9	249	248	269
11	131	122	166
13	129	125	256

2,-4,L

0	136	137	0
1	905	928	40
2	1018	1066	219
3	222	207	66
4	91	96	252
5	71	81	31
6	317	297	225
7	111	123	201
8	246	238	239
9	253	243	162
10	193	200	269
11	125	99	356
12	150	147	257

2,-3,L

0	992	973	0
1	991	1023	90
2	1541	1512	171
3	599	574	80
4	296	319	213
5	182	205	57
6	435	466	169
7	326	318	73
8	433	415	173
9	388	410	76
11	164	173	102
12	170	178	176
13	104	97	65

2,-2,L

0	198	217	180
1	98	105	293
2	1228	1300	274
3	875	878	190
4	282	265	72
5	643	623	354
6	311	307	69
7	441	411	353
8	467	454	73
9	285	291	348
13	100	93	359

2,-1,L

1	666	670	264
2	745	778	61
3	952	969	301
4	586	630	334
5	489	474	103
6	285	289	166
7	317	338	236
8	505	480	355
9	317	315	260
10	212	215	357
11	183	200	282
12	114	128	1

2,0,L

0	0*	42	0
1	275	304	90
2	75	71	0
3	185	173	90
4	158	172	180
5	241	234	270
6	181	180	0
7	96	108	270
8	290	276	180
9	82	51	90
11	88	95	90
12	148	120	180
13	108	132	270

3,-39,L

5	82	82	264

3,-37,L

0	97	107	270

3,-36,L

1	56*	62	110
2	45*	42	227

3,-35,L

0	91	99	90

3,-34,L

1	114	116	184
4	38*	42	124

3,-33,L

0	87	58	270
2	127	123	269

3,-32,L

1	101	113	324
3	86	113	20

3,-31,L

0	42*	21	270
8	59*	67	3

3,-30,L

1	193	196	116
2	127	128	240
4	94	90	244
5	100	95	218
11	0*	26	267

3,-29,L

1	128	136	187

3,-28,L

1	186	188	355
2	0*	61	318
3	111	136	11
5	91	78	346
6	88	78	57
9	54*	51	30

3,-27,L

0	304	294	90
3	118	144	9
4	96	83	187
5	123	122	341
6	86	112	281
7	96	95	92

3,-26,L

0	35*	41	90
1	140	141	222
2	122	132	21
3	123	133	150
4	180	181	300
5	197	211	191
6	121	143	183
7	62*	58	220

3,-26,L

9	90	73	202
12	111	104	189

3,-25,L

1	105	87	179
2	182	190	357
3	125	129	109
4	156	162	69
5	86	90	296
6	100	100	184
11	69	40	154

3,-24,L

0	128	125	90
1	136	154	162
2	150	172	131
3	84	107	355
4	223	220	100
5	268	258	25
6	164	177	56
7	135	142	38
8	89	73	14
10	97	89	1
12	97	100	21
14	83	66	32

3,-23,L

0	225	229	270
1	242	259	339
2	280	277	243
4	301	308	222
5	97	99	190
6	145	140	299
8	151	147	342
9	191	190	13
10	70	55	85

3,-22,L

1	156	156	141
2	405	404	224
3	145	148	269
4	167	166	273
5	188	189	228
6	176	169	180
7	128	123	169
10	112	120	162
12	92	64	233

3,-21,L

0	86	86	90
1	262	256	146
3	107	114	162
4	304	293	109
5	203	205	212
6	286	283	79
7	89	123	352
8	181	172	139
9	189	193	209
11	86	94	203
13	95	104	216

3,-20,L

0	144	157	270
1	251	249	269
2	267	264	12
4	278	306	24
6	109	107	49
7	208	217	310
8	221	245	25
10	50*	51	356

3,-19,L

0	388	395	90
1	209	209	349
2	137	138	319
3	212	213	46
4	243	261	266
5	138	153	155
6	398	408	279
8	95	131	336
9	115	111	125
10	98	95	306
12	36*	59	248
15	0*	36	61

3,-18,L

1	121	141	91
2	291	295	240
3	372	370	286
4	274	264	210
5	175	173	116
6	270	268	218
7	284	324	75
8	140	121	208
9	98	100	209
10	85	92	254
12	82	108	195
13	54*	56	216

3,-17,L

1	265	257	174
2	0*	28	172
3	295	293	191
4	644	633	87
6	389	386	111
7	154	143	276
9	194	186	338
11	125	109	212
13	61*	63	190

3,-16,L

0	78	81	270
2	207	231	144
3	265	277	74
4	282	297	75
5	195	179	43
6	304	297	43
7	131	112	161
8	146	159	134
9	115	100	81
10	35*	79	149

3,-15,L

0	293	309	270
1	605	645	13
2	219	225	248
3	241	217	358
4	360	390	256
5	237	235	12
6	406	389	269
7	110	123	57
8	177	166	247
9	181	168	64
10	196	194	265
12	77	76	266

3,-14,L

0	217	213	270
1	658	677	268
2	203	185	162
3	132	155	82
4	319	315	277
5	227	256	297
6	123	117	261
8	150	154	347
9	86	87	359
10	67	76	278
13	84	86	54

3,-13,L

0	834	839	90
1	328	350	333
2	345	377	101
3	242	225	168
4	568	554	84
5	370	378	205
6	301	306	81
7	97	121	128
8	240	250	95

3,-13,L

9	76	94	220
10	85	101	127
11	120	127	234
12	94	94	97

3,-12,L

0	513	497	90
1	189	209	253
2	746	756	24
3	422	414	231
4	512	506	141
5	72	84	220
6	72	92	162
7	225	206	308
9	67	70	318
10	98	100	30
11	141	160	98
12	126	107	34
13	123	114	239

3,-11,L

0	524	511	270
1	217	219	216
2	1288	1324	288
3	193	189	74
4	812	832	247
5	124	105	100
6	427	428	240
7	248	235	192
8	0*	88	336
9	89	116	267
10	62	49	92
11	107	113	5
12	116	122	283
13	139	128	4

3,-10,L

1	644	666	82
2	587	590	244
3	183	168	272
4	479	470	285
5	215	230	314
6	296	281	6
7	137	135	138
8	81	88	132
9	165	166	97
10	69	104	16
12	126	122	249
14	54*	72	328

3,-9,L

0	374	397	270
1	1036	1013	144
2	631	647	88
3	217	200	194
4	415	425	102
5	151	166	236
6	269	275	47
7	84	87	56
8	168	173	83
11	100	117	121
12	129	143	82

3,-8,L

0	754	787	270
1	1034	1035	246
2	528	513	43
3	550	570	136
5	245	219	51
6	411	411	144
7	203	206	215
8	150	160	150
9	105	118	257
11	171	184	271

3,-7,L

1	828	856	344
2	533	555	300
3	511	496	53
4	311	314	245
5	189	194	289
6	403	403	262
7	163	184	335
8	148	136	282
9	0*	47	331
10	107	111	307
11	132	128	275
12	0*	81	266

3,-6,L

0	339	307	270
1	319	342	317
2	634	655	193
3	573	535	287
4	438	442	231
5	222	247	345
6	193	172	223
7	381	397	88
8	404	389	351
9	127	131	261
10	129	140	227
11	273	270	97

3,-5,L

0	1849	1860	90
1	750	782	0
2	202	190	194
3	64	37	356
4	976	945	99
5	152	176	229
6	665	641	87
7	234	241	76
8	260	260	40
9	130	131	240
10	122	145	113

3,-4,L

0	57	29	270
1	164	159	127
3	117	100	90
4	345	338	77
5	223	215	33
6	276	257	125
7	336	333	268
8	489	516	169
9	162	180	106
10	146	133	203
12	95	91	157
14	130	123	170

3,-3,L

0	2578	2704	90
1	1090	1129	27
2	668	685	27
3	448	453	156
4	569	582	252
5	403	422	181
6	564	532	244
7	248	270	306
8	208	210	201
10	130	151	255
11	121	123	31
12	88	109	168
17	27*	43	317

3,-2,L

0	911	943	90
1	1103	1115	280
2	1165	1171	137
3	451	466	262
4	477	458	316
6	441	471	345
7	469	458	71
8	412	365	14
9	120	126	89
10	287	299	358
11	183	185	307
13	95	80	80
14	142	144	10

3,-1,L

1	437	429	70
2	2256	2306	264
3	907	873	183
4	491	495	72
5	98	92	120
6	214	214	32
7	245	236	114
9	243	225	23
10	146	150	18
11	86	107	172

3,0,L

1	2113	2092	270
2	153	125	180
3	170	155	90
4	511	534	180
5	91	100	90
6	793	729	180
7	181	169	270
9	412	411	270
10	270	276	180
11	69	71	90

4,-40,L

0	48*	46	180

4,-39,L

2	150	102	161

4,-38,L

4	132	111	23

4,-36,L

5	0*	36	298

4,-35,L

6	61*	43	200

4,-34,L

1	88	87	70
7	30*	42	79

4,-33,L

3	86	96	317

4,-32,L

7	29*	48	269

4,-31,L

1	17*	40	48

4,-30,L

3	163	155	78
4	57*	56	289
5	82	84	88

4,-29,L

0	111	100	180
3	106	110	310
4	145	106	159
10	51*	26	160

4,-28,L

1	79	90	243
5	92	96	236
7	89	107	279
9	91	87	217

4,-27,L

0	165	137	180
1	132	123	136
3	87	87	108
4	74	79	15
6	119	110	326
7	73	87	26

4,-26,L

1	119	114	77
2	87	96	10
3	113	127	34
5	186	191	70
7	169	177	99
8	38*	43	316

4,-25,L

1	74	98	234
2	143	137	266
3	49*	62	243
5	117	124	234
7	89	138	276
8	0*	57	107

4,-24,L

0	102	107	0
1	130	151	288
2	102	111	19
3	413	420	279
4	171	169	80
5	257	244	277
6	110	98	204
7	161	162	247
8	121	111	53

4,-23,L

0	195	197	0
1	269	258	58
2	283	289	68
3	302	307	15
4	123	133	64
6	102	102	300
7	195	186	176
9	120	110	72

4,-22,L

1	332	325	82
2	385	379	203
3	313	319	89
4	171	183	334
5	147	145	101
6	149	132	268

4,-21,L

0	171	166	180
1	142	191	294
2	350	353	253
3	194	183	256
4	179	182	163
5	106	100	184
6	106	89	264
7	99	105	28
8	207	206	111

4,-20,L

0	190	166	0
2	197	196	121
3	357	348	279
4	193	201	41
5	216	220	74
7	90	86	293
8	173	186	238
9	121	112	279

4,-19,L

0	276	262	180
1	241	236	123
2	254	261	46
3	104	118	97
4	170	180	62
5	179	190	266
6	195	181	284

4,-19,L

7	122	138	4
8	111	87	290
11	102	97	37
12	94	107	15

4,-18,L

0	289	292	180
1	169	142	52
2	185	167	218
3	55	89	80
4	127	161	271
5	121	133	166
6	0*	157	115
7	203	202	146
8	138	131	131
9	232	222	108
14	37*	40	326

4,-17,L

0	226	212	180
1	198	207	216
2	201	194	128
3	184	167	248
4	316	327	210
6	161	171	110
7	243	246	128
8	155	145	346
9	75	82	258
11	120	126	167

4,-16,L

0	140	139	180
1	382	383	305
2	141	152	197
3	302	295	268
4	266	263	48
5	187	194	290
6	210	190	326
7	168	159	7
8	185	188	346
9	31*	22	141

4,-15,L

0	461	467	0
1	445	436	42
2	348	331	63
3	148	134	31
4	199	214	9
5	184	171	63
6	246	246	324
7	106	103	348
8	128	141	259
9	242	249	348
11	209	193	344

4,-14,L

0	302	301	0
2	168	176	252
4	107	115	64
5	198	211	277
6	85	96	96
8	116	128	183
9	98	78	256
11	152	142	213

4,-13,L

0	279	262	180
1	224	223	97
2	260	291	285
3	280	275	2
4	276	276	167
5	273	260	132
6	106	98	231
7	75	76	195
8	131	118	125
9	249	243	175
10	131	137	208
11	148	155	162
13	104	102	151
14	0*	14	292
15	78	84	184

4,-12,L

1	459	487	86
2	185	166	3
3	174	178	180
4	103	123	61
5	485	470	66
6	61	64	236
8	155	160	217
9	78	73	336
13	101	95	45
15	40*	50	18

4,-11,L

1	491	462	223
2	200	193	13
3	97	132	291
5	443	432	328
6	255	254	60
7	117	102	298
8	152	152	42
10	163	168	74
13	136	134	348

4,-10,L

0	559	551	0
1	318	320	282
2	398	396	181
3	669	601	108
4	253	231	189
5	364	383	258
6	159	148	25
7	227	209	257
8	207	200	26
9	138	134	207
11	68	64	133
12	103	122	192
14	69	81	174

4,-9,L

0	241	225	180
1	369	367	39
2	220	230	192
3	934	986	208
4	74	80	41
5	295	290	121
6	131	153	106
7	240	217	154
8	207	179	189
9	161	150	152
10	105	122	276
12	119	132	267
13	173	167	185

4,-8,L

0	86	111	180
1	464	485	110
2	138	129	5
3	612	592	337
4	585	601	16
5	283	281	89
6	226	231	290
7	544	574	84
8	102	116	253
9	228	229	49
11	88	91	340
12	94	81	3
13	140	129	316
14	99	75	324

4,-7,L

0	84	54	180
1	78	67	329
2	449	450	106
3	957	970	333
4	447	423	124
5	184	156	324
6	296	270	275
7	444	432	290

4,-7,L

8	82	85	311
9	196	193	348
10	212	224	308
11	128	139	316
12	99	103	97
13	111	98	29

4,-6,L

0	288	323	180
1	177	172	213
2	764	784	215
3	801	800	262
4	475	463	201
5	593	629	262
6	248	259	159
7	624	645	259
8	262	257	41
9	131	140	241
11	195	201	256
12	93	92	169
13	106	115	89
14	79	86	165

4,-5,L

1	369	379	166
2	847	866	202
3	310	264	73
4	249	246	286
5	507	521	100
7	299	292	105
8	202	190	133
9	106	123	128
10	123	124	189
11	211	228	120

4,-4,L

0	282	261	0
1	485	453	280
2	846	813	133
3	276	293	81
4	262	281	355
5	1061	1037	89
6	131	139	218
7	357	369	89
8	251	257	234
9	210	219	109
10	88	74	200
11	320	319	69
12	69	74	337
14	80	102	345

4,-3,L

0	154	150	180
1	725	742	44
2	499	516	56
3	753	784	203
4	208	188	46
5	477	433	272
6	271	214	296
7	219	217	253
8	230	251	283
10	123	121	61
11	261	267	345
12	89	58	268

4,-2,L

0	626	597	0
1	806	790	225
2	420	409	95
3	810	780	342
4	137	118	351
5	843	837	261
6	243	245	100
7	329	347	269
9	160	161	255
10	54*	68	138
11	125	127	219
14	45*	66	187

4,-1,L

0	945	965	180
1	1358	1380	127
2	618	642	67
3	995	1006	2
4	149	138	3
5	437	454	95
6	201	258	78
7	222	229	116
9	169	179	58
10	97	82	182
11	181	200	176
14	21*	23	212

4,0,L

0	1927	1973	180
1	2692	2722	90
2	499	491	0
4	701	697	0
5	604	635	90
6	218	220	0
7	389	373	90
8	299	287	0
9	168	186	90
10	67	77	180
11	142	166	270
12	117	110	0
13	78	83	90

5,-39,L

1	60*	5	134

5,-38,L

5	77	68	157

5,-37,L

0	0*	18	270
6	86	67	229

5,-35,L

0	71	53	270
2	63*	46	77

5,-34,L

4	36*	34	298

5,-33,L

5	60*	87	323

5,-32,L

0	86	85	90
5	70	71	338

5,-31,L

1	113	124	237
5	87	95	137
7	58*	57	223

5,-29,L

0	101	108	270
1	146	131	23
2	123	128	299
4	82	86	324
7	85	83	8
8	103	100	344
9	53*	28	11

5,-28,L

0	128	111	90
6	57*	52	267
11	34*	22	116

5,-27,L

1	112	127	162
3	104	91	205

5,-27,L

4	113	79	146
6	125	114	146
8	93	105	183

5,-26,L

0	139	153	270
3	101	102	143
4	66	66	56
6	42*	83	123
9	0*	4	196

5,-25,L

1	69	92	276
2	129	139	107
3	261	268	311
5	127	114	12
6	106	120	357
7	119	133	343
8	134	125	306
9	85	75	297

5,-24,L

0	310	305	270
1	195	195	80
3	166	165	120
6	93	79	14
8	98	109	293

5,-23,L

1	224	227	189
2	107	137	155
3	94	79	222
4	185	189	114
5	169	168	114
9	105	101	144
11	94	81	119
12	65*	58	172

5,-22,L

0	445	431	90
1	172	165	301
2	214	235	123
3	275	280	296
4	97	64	171
5	70	101	182

5,-21,L

1	367	362	42
2	263	222	321
3	177	176	330
4	169	191	344
5	132	155	259
7	140	149	66
12	62*	95	358

5,-20,L

0	582	617	270
1	153	169	49
2	301	301	251
3	174	167	156
4	131	147	312
5	69	72	141
7	38*	46	334
8	94	96	280
10	133	135	287
13	91	93	169

5,-19,L

0	294	306	270
1	309	333	240
2	312	334	167
3	183	186	113
4	160	157	212
5	138	139	138
6	106	116	330
7	155	156	243
9	118	116	111
12	120	120	178

5,-18,L

1	306	309	349
2	515	522	93
3	178	206	347
4	314	313	81
5	262	263	346
6	151	159	111
8	63	70	78
12	95	73	103
15	28*	19	332

5,-17,L

1	131	143	328
2	224	208	358
3	179	186	312
5	192	214	296
6	170	159	8
8	144	151	240
9	97	111	319
10	87	101	12

5,-16,L

0	77	89	270
1	379	380	174
2	441	440	277
3	189	188	163
4	339	363	279
5	210	229	183
6	385	377	274
7	326	327	173
8	193	203	287
9	74	77	159

5,-15,L

0	168	172	90
3	76	65	11
4	156	155	166
5	121	125	236
7	143	154	106
8	88	76	247
9	137	138	96
10	53*	87	193
14	58*	67	177

5,-14,L

0	339	334	90
1	249	234	192
2	352	349	79
3	194	214	351
4	335	327	91
6	423	443	93
7	200	202	13
8	374	388	102
9	87	89	310
10	121	105	118
11	159	161	341

5,-13,L

0	216	214	90
1	285	266	121
2	127	137	88
3	77	59	51
4	97	115	86
5	85	86	221
6	231	206	161
7	171	149	338
8	112	130	43
9	38*	29	298
10	75	91	355
11	118	128	282

5,-12,L

0	1069	1008	270
1	168	190	150
2	114	92	108
3	88	99	138
4	649	627	263
5	89	110	196

5,-12,L

6	207	186	256
8	97	108	262
9	114	126	186
10	89	95	262
11	68	74	119

5,-11,L

1	158	123	108
2	244	232	213
3	103	73	267
4	135	146	197
5	259	263	92
7	271	258	271
10	64*	140	30
11	137	138	112

5,-10,L

0	51	15	270
1	646	645	345
2	563	553	84
3	581	577	1
4	461	475	92
5	303	296	340
6	101	121	135
7	127	129	256
8	107	132	33
9	239	237	340
10	171	117	101
12	126	140	88

5,-9,L

0	105	100	90
1	437	380	93
2	71	77	312
3	206	208	320
4	621	600	9
5	333	334	276
6	156	120	45
7	378	375	100
8	131	142	207
9	136	124	102
10	368	370	183
11	104	106	53
12	144	146	159

5,-8,L

0	150	134	270
1	287	270	164
2	590	651	281
3	220	223	139
4	130	112	14
5	318	317	193
6	385	357	293
7	98	92	158
8	224	233	272
9	163	171	167
10	236	250	258

5,-7,L

0	315	316	270
1	438	461	260
2	380	378	192
3	96	121	47
5	176	159	98
6	190	180	282
7	152	147	310
8	467	503	0
9	92	109	71
10	345	377	339
11	193	188	272
12	154	181	2

5,-6,L

0	705	714	90
1	261	261	319
2	824	779	93
3	145	148	67
4	130	108	303
5	90	98	175
6	215	208	109
8	224	231	67
9	144	142	121
10	193	217	60

5,-5,L

0	256	260	90
1	505	494	85
2	490	481	10
3	1098	1065	278
4	185	195	182
5	414	382	96
6	195	211	197
7	209	210	89
8	455	470	179
9	216	217	250
10	290	277	176
11	178	181	84
12	79	121	190

5,-4,L

0	1470	1473	270
2	566	612	281
3	591	603	184
4	80	76	355
6	143	135	178
7	175	160	181
8	204	211	227
9	156	153	347

5,-3,L

1	340	363	273
2	931	894	166
3	295	296	59
4	230	237	221
5	174	173	267
6	365	333	354
7	262	261	268
8	305	317	345
10	209	205	7
11	124	137	269
14	52*	50	3

5,-2,L

0	467	449	90
1	336	329	321
2	251	265	291
3	165	171	129
4	861	882	82
5	276	276	350
6	158	172	301
7	105	129	8
8	119	117	73
9	223	226	14
10	98	110	271
11	93	90	355
14	0*	26	24
16	43*	47	288

5,-1,L

0	68	54	270
1	172	177	148
2	238	209	99
3	1012	1048	88
4	293	298	354
5	417	426	262
6	344	353	168
7	131	123	100
8	137	148	172
9	210	206	71
10	185	192	161
11	127	142	272
13	163	134	93
16	110	103	177

5,0,L

1	61	50	270
3	338	322	90
4	135	56	180
5	267	269	270
8	49*	48	180

5,0,L

11	132	154	270
15	0*	6	270

6,-38,L

2	0*	29	25

6,-37,L

0	85	76	180

6,-34,L

0	0*	12	180
3	52*	59	329

6,-33,L

1	45*	49	304

6,-32,L

2	49*	36	292
4	41*	46	347
5	91	72	97

6,-31,L

2	0*	23	343

6,-29,L

0	240	246	180

1	0*	123	254
2	161	156	146

6,-28,L

2	180	160	93

6,-27,L

1	138	136	30
2	112	118	332
4	97	130	350
6	146	151	291
8	94	88	319
9	40*	17	82

6,-26,L

1	94	126	347
3	187	196	286
4	141	162	212
5	135	161	299
9	99	85	19

6,-25,L

2	194	185	276
3	184	178	256
5	188	192	287
6	80	64	159
9	80	79	291
12	38*	31	175

6,-24,L

0	107	100	0
1	218	239	337
5	147	131	95
10	72	71	2

6,-23,L

1	315	298	149
2	163	164	75
3	115	110	287
4	191	182	58
5	126	121	88
6	63	58	13
11	72	70	167

6,-22,L

0	547	542	180
2	421	457	97
3	149	156	122
4	255	258	127
5	160	165	272
8	0*	18	187

6,-21,L

0	432	436	180
1	383	406	284
2	312	316	203
3	128	129	49
4	121	138	291
7	59*	78	238

6,-20,L

0	415	449	0
2	472	474	334
4	148	170	270
6	146	142	2
7	180	182	82
8	158	155	345
12	69	73	302

6,-19,L

1	437	427	86
2	232	196	331
3	252	258	143
6	85	100	53
7	140	139	109
9	60*	55	183
11	123	107	131

6,-18,L

1	136	144	343
2	204	225	122
4	177	168	172
5	74	72	116
6	149	146	166
8	57*	109	250
9	96	101	154
12	59*	60	125

6,-17,L

0	306	291	180
1	241	280	247
2	195	182	331
3	158	151	286

5	197	195	313
7	154	156	41
9	115	107	17
13	41*	64	34

6,-16,L

1	212	211	201
2	65	86	8
3	134	122	294
6	76	110	14
7	320	281	279
9	140	152	338

6,-15,L

1	116	123	9
2	159	172	205
5	90	99	47
6	106	127	268
7	107	121	280
8	110	105	102
9	120	117	159
10	80	98	19

6,-14,L

1	56*	143	280
2	68	94	93
3	69	102	131
4	174	152	113
6	131	110	233
7	200	206	69
8	199	211	130

6,-14,L

9	139	116	183
10	105	105	121
13	75	66	127

6,-13,L

0	284	299	0
1	251	255	300
2	259	264	339
3	153	129	138
4	255	265	303
5	80	84	270
7	83	99	259
8	212	223	270
9	177	188	320

6,-12,L

1	244	241	344
2	293	300	253
3	236	218	279
5	266	274	22
6	120	111	304
7	144	145	18
10	127	136	279
11	104	110	313
14	0*	46	306

6,-11,L

0	217	180	180
1	281	287	150
2	264	283	131
3	280	265	239
4	147	142	132
5	355	377	143
6	285	295	103
7	262	258	168
8	165	189	126
9	105	114	292
10	132	139	128

6,-10,L

0	83	72	180
1	409	386	122
2	351	323	74
3	231	255	132
4	142	139	145
5	257	268	144
6	217	223	82
7	253	274	173
8	199	199	8
9	300	316	84
10	174	179	4
11	0*	141	183

6,-9,L

0	237	207	180
1	340	310	30
2	197	186	242
3	187	182	50
4	291	267	313
5	115	110	81
6	332	335	318
7	178	185	54
8	320	325	13
9	322	324	111
10	207	206	329

6,-8,L

0	285	287	0
1	256	288	19
2	97	104	283
3	316	335	267
4	196	175	200
5	188	177	233
6	219	222	226
7	153	164	258
8	283	284	175
9	296	304	282
10	0*	135	213
11	178	186	13
12	58*	102	275

6,-7,L

0	118	97	180
1	89	95	88
2	331	345	143
3	361	361	286
4	139	140	124
5	131	130	38
6	264	286	163
7	195	187	285
8	336	343	183
9	0*	125	280
10	187	194	120
11	181	162	120
12	99	108	49
13	0*	9	145

6,-6,L

0	58	39	180
1	213	216	78
2	506	485	69
3	238	261	173
4	178	184	50
5	53	98	326
6	282	270	310
7	336	339	84
8	216	206	339
9	197	201	155
11	201	215	188

6,-5,L

0	273	280	0
1	262	275	111
2	268	243	277
3	271	251	28
4	460	467	323
5	104	91	177
6	325	319	38
7	302	325	112
8	245	258	333
9	238	232	355
11	93	89	308

6,-4,L

0	448	447	180
1	651	615	255
2	317	323	356
3	756	770	294
4	555	557	201
5	99	113	336
6	225	214	124
7	263	279	263
8	145	132	207
9	335	337	350
10	143	159	156
13	98	97	357
15	0*	25	194

6,-3,L

0	377	377	180
1	394	391	311
2	304	325	236
3	658	688	240
4	224	204	173
5	285	280	249
6	156	175	189
7	228	230	260
8	328	320	165
9	192	188	233
10	126	120	207

6,-2,L

0	494	470	0
1	244	275	44
2	677	693	7
3	240	229	60
4	55	58	75
5	430	404	99
6	191	185	2
7	258	250	102

6,-2,L

8	170	169	22
9	148	188	91
10	118	125	22
12	0*	9	235

6,-1,L

0	380	372	0
1	249	232	293
2	960	986	339
3	610	592	123
4	431	422	37
5	159	145	25
6	195	169	0
7	130	142	88
8	170	174	3
9	231	222	96
10	112	111	2

6,0,L

0	343	343	180
1	596	574	90
2	896	885	180
3	631	642	270
4	658	653	180
5	141	149	90
6	72	82	180
7	113	119	270
8	91	86	180
9	318	319	270
11	93	92	270

7,-32,L

0	118	111	90
1	104	86	100
6	88	77	113

7,-30,L

0	143	136	270
2	82	87	193

7,-29,L

3	86	50	105
5	0*	46	359

7,-28,L

2	158	159	73
7	74	70	108

7,-27,L

0	101	100	270
4	93	65	94
7	51*	36	308

7,-26,L

1	126	148	93
4	188	190	243
6	121	128	293

7,-25,L

1	164	177	184
2	93	96	313
4	98	98	301
6	92	71	274

7,-24,L

1	117	121	273
2	129	136	40
3	124	131	224
4	94	86	117
5	65	101	148
7	140	142	100
9	97	99	107

7,-23,L

1	318	322	351
2	169	162	245
4	172	176	103
13	53*	25	358

7,-22,L

0	232	231	270
1	320	326	264
4	123	134	300
6	160	160	312
7	132	132	262
9	43*	53	284
12	54*	40	8

7,-21,L

0	298	312	90
1	319	324	187
2	151	145	18
3	101	104	274
4	198	204	280
6	131	134	251
7	159	161	166
9	84	108	158
11	120	112	163

7,-20,L

0	318	321	90
1	289	291	71
2	208	200	28
3	340	360	100
4	189	191	181
5	97	90	299
8	70	80	123
10	35*	63	76

7,-19,L

1	229	210	19
2	145	151	259
3	288	279	9
4	224	204	104
5	194	188	359
6	172	187	97
7	197	199	0
9	142	141	337
11	129	133	350

7,-18,L

1	153	147	279
2	150	131	12
3	54*	68	315
4	107	144	338
5	86	118	228
7	127	126	280
10	74	81	278

7,-17,L

0	532	548	90
1	353	354	184
2	233	212	299
3	293	294	180
5	267	263	167
6	267	269	289
7	127	123	132
9	189	181	169
11	96	95	135
13	100	84	150

7,-16,L

0	63	97	90
1	66	63	66
2	113	107	92
4	133	112	183
5	178	176	91
6	160	168	183

7,-15,L

1	248	231	22
2	204	213	79
3	342	358	341

7,-15,L

4	130	115	113
5	196	206	1
6	168	167	91
7	253	186	329
9	129	129	329
10	128	117	227
13	0*	102	353

7,-14,L

2	107	111	288
6	36*	74	244
10	51*	60	352

7,-13,L

1	500	502	180
2	102	109	78
3	437	423	188
4	361	386	277
5	200	210	153
7	215	219	187
11	129	130	184
13	86	97	182

7,-12,L

0	65	83	220
2	147	145	207
5	170	170	224
6	181	190	16
8	207	205	14
9	102	87	99
11	89	100	281

7,-11,L

1	761	728	358
2	173	158	269
3	527	545	0
4	522	512	105
5	419	427	354
7	152	100	0
8	76	77	244
9	135	78	35
11	161	161	1

7,-10,L

1	110	89	194
2	74	56	117
3	106	105	120
4	134	131	348
5	237	241	117
7	203	192	248
8	176	185	191
11	96	112	89
12	112	98	333

7,-9,L

0	93	79	270
1	550	569	185
2	407	410	284
3	377	387	189
4	333	343	269
5	286	286	178
6	325	312	276
9	120	92	154
11	177	182	173

7,-8,L

0	142	142	90
1	124	121	17
2	410	408	1
3	394	393	281
4	210	202	182
6	276	275	9
7	242	241	99
8	100	86	283
9	257	265	262
12	85	78	174

7,-7,L

0	88	101	90
1	595	563	0
2	311	312	98
3	75	77	49
4	218	233	63
6	308	304	86
7	183	173	349
9	204	203	6
10	81	107	277

7,-6,L

1	524	485	245
2	220	207	44
3	457	445	84
5	123	128	226
6	250	247	186
8	123	129	138
9	334	357	89
10	100	122	5

7,-5,L

0	848	853	90
1	690	676	182
2	263	231	105
3	195	194	180
4	187	195	88
5	131	124	356
6	191	189	231
7	249	245	166
9	196	204	208
10	87	85	65
11	45*	23	157

7,-4,L

0	85	108	270
1	230	231	71
2	684	681	187
3	364	343	64
4	419	375	203
5	49*	63	144
6	280	294	357
7	212	215	281
9	318	331	279
10	102	105	141
11	150	182	272
15	108	95	266

7,-3,L

0	475	425	270
1	330	312	183
2	321	304	303
3	322	322	357
4	365	396	86
5	350	349	343
7	268	275	17
8	317	314	91
9	197	199	17

7,-2,L

0	123	108	90
1	149	143	309
2	382	337	5
3	210	207	58
4	270	281	324
5	273	273	108
6	319	340	166
7	122	139	105
8	359	368	200
9	153	154	90
11	206	201	88
13	66	75	76

7,-1,L

0	95	91	90
1	182	190	327
2	122	138	38
3	252	232	351
4	545	529	270
5	364	352	186
6	203	208	261

8,-12,L

1	180	166	73
2	192	205	318
3	277	313	41
5	48*	52	41
6	218	234	88
8	122	121	7
9	134	126	181
14	92	99	114

8,-11,L

0	572	600	0
1	60	54	329
3	76	102	332
4	164	163	78
6	111	139	104
7	97	107	208
8	78	92	177
9	137	131	184

8,-10,L

0	256	271	0
1	322	307	183
2	170	164	313
3	289	260	263
4	190	199	287
5	86	77	187
6	202	206	302
14	90	103	285

8,-9,L

0	620	585	180
1	287	290	253
2	285	288	190
3	75	70	42
4	214	223	270
5	185	192	259
6	238	246	211
8	93	101	224
9	51*	61	357

8,-8,L

0	379	360	180
1	93	115	40
2	306	316	172
3	136	136	99
4	170	173	84
5	88	87	302
6	143	154	188
7	135	132	62
8	241	262	128
12	100	101	108

8,-7,L

0	494	520	0
1	212	208	327
2	734	732	9
3	172	169	122
4	116	117	80
5	166	144	64
6	286	273	342
8	207	209	38
10	107	99	73
12	103	104	35

8,-6,L

1	373	363	207
2	293	277	327
4	183	190	330
5	0*	68	294
6	175	164	327
7	123	114	316
8	283	284	268
10	169	160	301
12	133	122	296

8,-5,L

0	202	196	180
1	118	114	105
2	321	333	180
3	119	98	106
4	533	561	180
5	191	197	61
6	179	172	209
7	149	155	48
8	99	99	229
10	181	200	227
12	178	178	209
13	86	84	88

8,-4,L

1	280	280	190
2	175	180	242
3	83	89	50
4	351	344	172
5	108	98	104
6	334	366	145
7	106	118	109
8	82	82	98
10	204	199	116

8,-3,L

0	319	333	0
1	249	236	165
2	150	149	307
3	163	163	321
4	425	439	329
5	90	96	139
6	318	313	5
7	265	271	262
10	218	221	39
12	115	137	19

8,-2,L

0	575	519	0
1	408	379	26
2	80	98	355
3	375	362	198
4	504	515	46
5	154	159	327
6	269	277	311
7	157	138	289
8	187	225	74
9	113	121	197
10	189	195	293

8,-1,L

0	921	866	180
1	325	319	298
2	370	374	166
3	153	163	158
4	282	306	149
5	178	184	58
6	421	403	188
8	155	143	140
9	113	106	224
12	110	123	190
14	49*	75	198

8,0,L

0	711	731	180
1	182	177	270
2	207	198	180
3	156	153	90
5	130	138	90
6	270	273	180
11	36*	61	90

9,-33,L

5	58*	64	118

9,-31,L

7	49*	12	301

9,-29,L

2	121	102	129
3	109	116	46
8	0*	38	61

9,-28,L

1	76	79	284
8	16*	24	189

9,-27,L

5	85	83	217

9,-26,L

0	80	99	90

9,-25,L

4	127	111	119
7	94	73	37
8	87	94	37

9,-24,L

0	116	75	270
2	189	186	265

9,-23,L

2	186	147	17
3	152	136	151
5	107	108	212

9,-22,L

0	258	272	90
1	218	232	189
2	186	182	81
3	90	96	209
10	130	129	76

9,-21,L

1	102	109	42
3	163	177	49
4	127	141	351

9,-20,L

1	160	158	14
3	313	325	342
4	171	167	239
5	144	143	23
10	98	74	222

9,-19,L

1	259	260	109
2	101	95	258
3	176	194	230
4	120	110	213
9	116	129	242

9,-18,L

3	195	185	175
5	252	266	179
6	112	119	35

9,-17,L

0	132	143	270
1	163	157	355
4	143	158	29
5	115	121	57
7	120	123	59
8	0*	21	321
9	122	125	68

9,-16,L

0	241	251	270
1	111	106	311
2	183	183	246
3	26*	20	1
4	120	107	266
5	370	349	7
6	138	123	252
7	99	115	339
8	200	142	236
9	122	116	5

9,-15,L

1	133	137	199
2	186	221	130
3	224	214	124
4	127	99	167
5	112	120	196
7	156	144	230
9	140	145	232

9,-14,L

0	127	111	270
1	309	317	167
2	311	313	88
3	230	223	206
4	230	232	198
5	236	247	191
6	143	159	104
7	332	343	185
9	151	154	153

9,-13,L

0	84	76	90
2	216	221	228
3	205	201	289
5	183	189	291
9	96	110	41
11	65*	82	61

9,-12,L

1	268	263	1
2	242	245	289
3	322	322	11
4	154	155	264
5	220	213	27
7	211	221	16
8	50*	39	62

9,-11,L

0	175	190	90
1	240	221	114
2	321	325	10
3	116	123	292
4	166	89	133
5	144	153	113
8	123	116	325
10	88	81	183

9,-10,L

0	628	636	90
1	136	174	216
3	330	322	160
4	234	229	77
5	195	210	198
10	105	111	50

9,-9,L

0	438	421	270
1	97	110	300
2	235	225	198
3	225	222	38
4	154	159	270
5	81	86	86
6	105	109	331
8	112	110	166

9,-8,L

0	442	466	270
1	138	164	18
2	216	211	285
3	365	373	344
4	185	187	276
5	263	253	357
6	140	155	220
7	142	151	3
9	140	130	358
10	92	102	289

9,-7,L

1	74	85	44
2	221	231	40
3	158	154	116
4	97	92	199
5	143	145	123
6	84	83	90
7	191	189	126
8	136	128	130
9	111	110	138
12	67	56	24

9,-6,L

0	221	222	90
1	339	345	178
2	112	103	70
3	249	227	222
4	61	66	66
5	132	138	212
6	127	130	134
7	192	226	191
8	175	185	66
9	112	106	168

9,-5,L

0	86	79	90
1	82	71	52
3	151	153	302
4	293	289	336
5	316	320	257
6	253	263	107
7	354	363	285
8	205	203	345
9	72	89	40
11	99	99	283

9,-4,L

0	419	411	90
1	141	148	10
2	118	98	304
3	158	168	21
4	179	181	163
5	274	265	38
6	72	89	319
7	124	134	80
8	150	145	257

9,-3,L

0	161	167	270
1	253	256	130
2	69	70	89
3	141	114	94
4	124	136	217
5	281	271	124
6	104	104	60
7	133	143	54
8	52*	94	15
9	95	89	321
15	108	97	92

9,-2,L

0	315	298	270
1	148	145	192
2	86	80	108
3	133	152	250
4	332	335	238
5	383	361	173
6	73	79	75
7	110	101	330
8	231	232	112
12	78	76	133

9,-1,L

0	121	133	270
1	224	250	292
2	126	117	177
3	356	391	266
5	228	244	286
6	113	129	164
8	313	320	180
9	79	79	217
11	48*	38	184

9,0,L

1	51*	58	90
2	100	82	0
5	177	171	90
6	97	92	0
7	187	189	270
8	236	215	0
12	35*	45	0

10,-31,L

2	30*	36	296
7	0*	23	274

10,-30,L

0	120	120	0
1	99	93	258

10,-28,L

7	30*	64	69

10,-26,L

0	123	106	0
5	164	147	262

10,-25,L

3	58*	54	207

10,-24,L

0	169	173	180
2	0*	11	325
7	96	89	78

10,-23,L

1	56*	67	18
3	102	119	163
4	53*	57	265
9	38*	7	151

10,-22,L

0	123	118	0
1	170	173	244
2	107	73	325
3	158	163	243
5	72	64	268
6	58*	91	13

10,-21,L

0	196	206	0
1	150	134	0
2	139	144	66

10,-20,L

0	169	158	180
1	288	281	91
2	86	86	161
3	116	129	41
6	102	106	163

10,-19,L

1	181	169	0
5	59*	76	219

10,-18,L

0	134	142	180
1	114	121	317
2	117	103	315
3	187	181	296
4	124	112	335
6	137	131	354
7	118	120	251

10,-17,L

3	114	115	184
4	142	160	35
5	97	76	44
6	96	97	354

10,-16,L

2	146	149	3
3	141	162	154
4	173	167	182
7	187	202	98
8	64	71	2
9	26*	27	67
11	59*	37	50

10,-15,L

0	0*	2	0
2	72	71	313
3	173	192	337
4	174	180	100
6	186	188	131
7	103	96	212
8	73	72	233
12	97	95	277

10,-14,L

0	109	117	180
1	94	85	103
2	200	216	196
3	148	150	49
4	108	116	332
7	113	103	216

10,-13,L

1	161	167	106
2	218	230	103
3	170	184	35
6	164	159	330
7	163	165	21
8	89	83	46
9	121	113	8
10	164	157	84
12	112	102	89

10,-12,L

2	330	339	19
3	220	212	282
4	117	131	58
5	93	76	102
6	136	137	173

10,-11,L

0	164	147	180
1	133	161	341
2	254	251	277
3	171	158	198
5	106	132	209
6	156	149	245
7	230	222	188
9	187	175	201
10	169	176	268

10,-10,L

0	99	98	180
2	223	253	202
3	83	109	87
4	208	206	188
5	131	115	112
6	151	152	335
7	63	63	142
8	159	161	209
10	133	137	207

10,-9,L

1	138	134	186
3	145	151	169
4	101	116	82
5	227	231	24
6	107	117	63
9	124	117	41
10	119	125	93
11	70	61	23
12	86	81	82

10,-8,L

1	101	108	270
5	107	123	272
8	95	98	23
9	133	124	263
10	134	133	46

10,-7,L

1	144	137	203
5	181	175	233
6	110	118	139
8	73	80	303
10	59*	53	282

10,-6,L

0	322	320	180
1	195	192	88
2	73	84	245
3	102	117	90
4	84	114	314
5	354	352	82
8	79	78	174
9	108	114	84
10	119	120	205

10,-5,L

0	144	114	180
1	360	383	17
2	129	113	115
3	167	185	52
4	144	129	72
5	181	164	36
6	66	71	193

10,-4,L

0	616	601	0
1	125	131	286
2	470	474	3
3	374	383	272
4	70	102	30
5	406	422	269
6	135	147	52
7	202	185	273
8	174	155	15
9	98	88	276
10	170	184	359
11	87	84	273

10,-3,L

0	141	152	0
1	317	309	337
2	198	176	25
3	175	162	243
5	207	194	320
6	120	147	228
7	229	229	196
8	106	104	331
9	72	68	211
14	47*	38	233

10,-2,L

0	642	614	180
1	375	370	81
2	577	575	177
3	464	461	89
5	51*	87	80
6	195	207	337
7	156	165	96
8	241	252	186
10	107	142	162
13	100	97	87

10,-1,L

1	179	181	144
2	215	220	194
3	155	139	24
4	154	155	309
5	141	137	103
6	149	139	23
11	59*	55	57

10,0,L

0	222	222	0
1	417	411	270
2	533	541	0
3	306	327	270
4	157	154	180
5	227	231	270
6	371	375	180
7	123	136	90
8	168	166	0
10	97	95	0
11	82	88	270
13	150	161	270

11,-33,L

0	34*	4	270

11,-31,L

2	0*	61	345

11,-30,L

1	95	98	1
2	75	84	34

11,-29,L

4	91	62	190

11,-27,L

4	44*	57	33

11,-26,L

1	76	89	1

11,-25,L

7	65*	68	149

11,-24,L

2	0*	43	103
3	71	69	142
5	96	108	212

11,-23,L

5	52*	11	346

11,-22,L

1	113	124	351

11,-21,L

0	133	139	270
6	65*	77	275

11,-20,L

0	102	93	90
2	126	144	184
4	113	114	84

11,-19,L

0	80	84	90
1	151	151	333
2	146	145	95
4	154	165	103
6	117	126	74
7	0*	36	293
10	125	99	38

11,-18,L

0	135	149	270
1	97	95	290
2	151	151	232
4	126	125	218
6	134	150	315

11,-17,L

0	318	320	270
1	80	85	22
2	200	206	276
4	134	137	264
6	156	151	254
8	106	98	240
10	112	97	255

11,-16,L

0	235	235	90
2	96	106	45
3	157	159	118
5	96	95	274
6	128	140	140

11,-15,L

0	230	243	90
1	225	231	176
2	112	111	60
4	223	211	70
5	125	116	24
6	178	176	81
8	186	170	67

11,-14,L

0	121	122	270
1	112	118	26
2	159	137	255
3	104	109	349
4	143	88	197
6	169	174	301
8	125	140	303
9	31*	44	32

11,-13,L

0	123	125	270
1	132	125	4
2	161	161	252
3	131	135	344
4	107	120	256
5	109	118	209
6	232	234	260
8	224	229	254
10	101	90	252

11,-12,L

0	128	120	90
1	91	122	72
2	155	142	69
3	137	123	276
4	206	211	24
6	165	151	78
8	209	214	119

11,-11,L

0	212	221	90
1	101	112	242
2	208	206	91
6	145	143	92
7	106	104	332
8	45*	172	71

11,-10,L

0	248	242	270
1	120	126	296
2	125	106	313
3	162	166	200
5	81	81	331

11,-10,L

7	115	97	226
10	79	77	256

11,-9,L

0	177	182	270
1	163	175	0
2	288	286	256
3	139	151	109
4	153	188	323
5	33*	107	15
6	119	113	257
7	109	108	140
8	142	139	289

11,-8,L

1	177	184	152
2	201	203	96
3	184	200	89
4	142	118	23
5	72	95	167

11,-7,L

0	216	224	90
1	185	181	190
2	239	247	102
3	147	151	240
4	152	158	137
6	94	71	90
7	117	114	120
8	173	187	120
11	40*	52	72
12	48*	32	143

11,-6,L

0	289	289	270
2	231	216	239
3	106	85	309
4	103	100	255
7	115	108	342
8	191	144	223
10	134	128	186
12	22*	69	161
14	60*	59	170

11,-5,L

0	308	310	270
1	75	84	194
2	126	135	321
3	168	165	340
4	147	143	252
6	135	145	312
7	96	95	343
10	87	95	312
11	0*	5	306
14	51*	44	343

11,-4,L

0	195	200	90
1	191	198	15
2	133	143	39
3	108	85	234
4	141	196	62
6	137	130	89

11,-3,L

0	103	91	90
1	247	247	333
2	66*	167	180
3	107	94	124
4	254	255	116
5	142	114	142
6	178	165	53

11,-2,L

0	142	130	270
1	187	193	232
2	265	200	172
3	154	140	261
4	355	367	180
5	115	128	348
6	131	147	319
14	64*	62	171

11,-1,L

1	115	116	146
2	0*	80	321
3	184	191	82
4	218	218	3
6	74	140	288

11,0,L

1	187	196	90
2	190	195	0
3	322	316	90
4	417	432	0
6	105	113	0
7	63	98	90
8	136	123	180
9	131	138	90

12,-29,L

3	96	78	86

12,-27,L

1	114	106	293

12,-25,L

1	0*	138	102

12,-23,L

3	230	164	273
8	0*	32	78

12,-22,L

2	57*	54	26
3	0*	7	141

12,-21,L

9	80	84	85

12,-20,L

2	61*	64	162
4	85	80	204

12,-19,L

0	150	144	180
1	116	100	275
5	95	101	246

12,-18,L

1	61*	73	212
2	0*	33	50
4	94	87	52
11	57*	32	358

12,-17,L

1	0*	101	91
3	188	181	86

12,-16,L

0	125	123	180
1	131	145	191
2	65	82	211
4	126	110	246
7	87	79	172
9	167	151	179
11	133	140	183

12,-15,L

2	43*	35	263

12,-15,L

3	104	91	239
11	62*	63	89

12,-14,L

0	102	117	0
2	148	146	54
4	125	122	20
11	154	145	0

12,-13,L

6	98	101	6
11	0*	61	270

12,-12,L

2	109	134	205
3	163	166	180

12,-11,L

0	221	188	180
2	194	180	337

12,-10,L

2	103	99	25
3	101	124	6
5	122	126	359

12,-9,L

1	244	244	269
2	86	92	171
3	121	100	281
5	147	151	278
7	135	164	260
8	43*	72	126

12,-8,L

0	108	93	180
9	145	135	173

12,-7,L

0	0*	73	180
1	396	392	96
2	85	82	191
3	228	235	99
5	111	114	120
7	198	201	98

12,-6,L

1	103	95	340
6	42*	50	262
7	125	137	10
9	133	141	357

12,-5,L

0	189	178	180
1	108	114	271
2	204	201	2
3	296	304	274
5	209	213	268
7	128	126	301

12,-4,L

1	80	102	11
3	179	185	1
5	142	142	193
6	59*	56	268
7	144	144	182

12,-3,L

1	215	202	86
2	95	101	4
3	202	215	65
5	173	147	91
7	226	226	80
9	90	100	106

12,-2,L

1	289	240	166
2	42*	29	275
3	176	165	183
6	87	81	79

12,-1,L

0	112	104	0
1	643	601	266
2	347	362	180
3	12*	44	222
4	79	78	189
5	265	267	254
7	187	192	270
9	194	199	268

12,0,L

1	71	90	270
3	45*	11	90
4	0*	6	180

13,-26,L

3	22*	56	197

13,-25,L

7	37*	30	225

13,-24,L

7	69*	45	329

13,-22,L

5	95	129	137

13,-21,L

4	103	92	105

13,-19,L

2	117	105	270
4	142	156	270

13,-18,L

4	123	119	250

13,-17,L

2	130	122	85

13,-16,L

0	28*	25	90
7	0*	115	335

13,-15,L

2	52*	62	295

13,-14,L

0	143	114	270
1	81	73	199
6	0*	54	301

13,-13,L

0	133	119	90
1	79	79	318
2	145	160	74
6	113	98	53

13,-12,L

0	201	220	90
1	146	151	341
2	178	188	106
3	118	115	54

13,-11,L

0	258	267	220
1	103	111	165
2	177	171	275
3	133	136	142
4	144	148	284
6	119	114	236
11	68*	38	249

13,-10,L

0	190	195	270
1	138	122	186
2	165	165	258
4	172	166	247
6	90	91	298
8	67	62	25

13,-9,L

0	183	177	90
1	165	174	331
2	174	195	106
3	102	102	354
4	167	158	112
5	95	114	12
7	155	135	339
9	44*	72	59
10	66*	64	87

13,-8,L

1	193	193	68
2	153	150	34
4	157	174	62

13,-7,L

1	175	178	137
4	112	101	260
5	158	165	171
6	122	119	223
8	127	125	253

13,-6,L

1	11*	53	288
3	51*	37	282
5	106	120	191
6	131	138	324

13,-5,L

4	81	103	56
5	125	123	349
6	156	168	17
8	108	108	31

13,-4,L

0	61	51	270
1	81	88	191
2	85	81	27
4	155	135	111
6	100	128	149
8	114	110	164

13,-3,L

0	86	75	90
1	140	142	20
2	88	86	282
3	169	182	178
4	103	102	259
6	167	123	224
7	177	179	181
10	55*	62	154

13,-2,L

0	110	113	90
2	113	133	288
3	153	146	239
4	77	63	278
7	126	126	188
8	125	89	353
10	67*	83	28

13,-1,L

1	105	133	243
2	160	153	64
3	172	180	309

13,0,L

1	247	249	90
3	120	124	90
4	117	132	0
6	142	150	180

14,-24,L

3	0*	43	266

14,-21,L

4	53*	50	232

14,-20,L

0	108	103	180

14,-19,L

5	89	93	342

14,-17,L

2	106	107	243
7	80	59	133

14,-13,L

1	42*	41	149

14,-12,L

1	138	120	276

14,-11,L

1	88	83	295
5	82	94	319
7	88	86	352

14,-10,L

1	117	118	100
2	89	97	215
4	114	118	209
6	99	95	172
9	69	56	287

14,-9,L

3	102	108	54
5	103	111	152
6	99	101	97
7	89	85	159

14,-8,L

2	113	96	10
4	196	194	4
5	107	89	77
9	59*	70	101

14,-7,L

3	91	101	1
6	88	102	274

14,-6,L

2	102	128	179
3	101	75	205
4	289	290	170
5	161	174	268
6	120	124	156

14,-5,L

3	128	138	181
5	103	99	118
6	109	101	60
8	122	121	89

14,-4,L

0	107	108	0
2	177	172	359
3	148	150	98
4	276	268	355
5	193	203	91
6	184	173	353
7	97	98	85

14,-3,L

2	160	155	95
7	69	88	297
8	166	166	261

14,-2,L

0	165	170	180
2	129	118	182
3	227	219	285
4	204	193	180
6	181	163	179
7	107	117	272
9	65*	37	249

14,0,L

0	112	110	0
1	72	76	90
2	140	130	0
3	278	278	90
4	122	124	0
5	94	89	90
6	135	136	0

15,-24,L

0	18*	10	270

15,-23,L

2	0*	21	112

15,-22,L

1	32*	43	11

15,-21,L

5	42*	11	332

15,-20,L

1	84	93	208

15,-18,L

1	115	113	5
3	150	157	354

15,-16,L

3	125	123	170
4	0*	24	326

15,-15,L

1	72	78	244
3	88	84	131
7	104	66	136

15,-14,L

3	80	73	350
5	145	143	352
7	141	121	4

15,-12,L

0	99	114	90
1	173	178	196
3	99	85	179
7	115	117	178

15,-11,L

1	112	133	116
8	63*	48	4
9	27*	17	249

15,-10,L

1	130	120	41
3	169	164	13

15,-8,L

0	120	106	270
1	68*	98	209
3	132	130	187
5	97	87	177

15,-7,L

1	100	92	155
4	85	95	159

15,-6,L

0	132	136	90
1	168	197	12
3	98	107	7
5	149	147	357

15,-5,L

3	61*	76	329
6	57*	46	182
9	146	128	87

15,-4,L

0	84	79	270
1	137	132	204
3	116	108	195

15,-3,L

2	49*	62	203
3	67	43	171

15,-2,L

2	110	112	91

15,-1,L

0	38*	16	90
3	87	85	92
5	111	94	61

16,-22,L

2	37*	40	107

16,-19,L

2	74	58	354

16,-18,L

1	66*	49	57

16,-13,L

4	0*	34	321

16,-11,L

3	104	78	77
6	58*	61	163

16,-10,L

0	28*	31	0

16,-8,L

4	75	80	249

16,-7,L

2	49*	45	109
6	121	125	179

16,-6,L

2	108	101	93

16,-5,L

2	83	88	1
4	123	122	13
6	170	146	352

16,-4,L

1	62*	53	34
6	63*	72	218

16,-3,L

0	100	110	180
4	129	132	175
6	151	130	172
8	64*	70	180

16,-1,L

0	220	196	0
1	96	92	261
2	159	158	352
3	124	120	285
4	120	109	384
6	121	115	353

16,0,L

2	81	66	180
4	91	74	180
6	84	62	180

17,-17,L

0	155	141	90

17,-15,L

0	141	135	270
1	91	90	5
2	92	90	259

17,-14,L

2	0*	19	266

17,-13,L

1	167	160	181

17,-12,L

2	51*	13	51

17,-11,L

0	76	73	270
1	145	143	356
3	113	119	359

17,-9,L

0	142	153	90

17,-8,L

1	93	110	268

17,-7,L

0	191	184	270
1	114	108	342
4	57*	50	334

17,-6,L

4	41*	15	153
5	49*	55	74

17,-5,L

1	120	82	172
6	57*	16	178

17,-4,L

4	39*	61	355

17,0,L

2	144	134	180
4	0*	100	180
5	55*	23	90
6	91	83	0

18,-10,L

3	71	52	195

18,-9,L

3	81	49	164

18,-7,L

3	0*	38	286

18,-6,L

1	95	98	264

18,-5,L

1	86	71	98
2	47*	58	186
4	46*	34	188

18,-4,L

1	94	71	85
2	66*	51	181
5	87	85	90

18,-2,L

1	72	44	247
4	64*	60	344
5	87	73	263

18,-1,L

2	65*	36	187

18,0,L

2	55*	57	180
3	88	67	90
4	82	58	180

Data for Dimethylsulphonium 1,2-dibenzoyl-2-(4-chlorophenylimino) ethylide

Crystal Data

$C_{24}H_{20}ClNO_2S$, M = 421.95; monoclinic,

a = 8.157(2)Å, b = 16.741(3)Å, c = 15.859(3)Å, β = 103.15(3)°,

V = 2108.86Å^3; D_c = 1.33 g.cm^{-3}, Z = 4; F(000) = 880;

space group $P2_1/c$ (C_{2h}^5, No.14); $M_o - K_\alpha$ radiation, λ = 0.7107Å,

$\mu(M_o - K_\alpha)$ = 2.94 cm^{-1}.

0,0,L

-16	162	160
-14	161	-160
-12	71	74
-10	295	298
-8	550	523
-6	226	233
-4	796	824
-2	349	349
2	349	349
4	796	824
6	225	233
8	543	523
10	284	298
12	95	74
14	153	-160
16	154	160
18	81	77

0,1,L

-21	48*	-59
-19	116	117
-13	64	-65
-11	160	-157
-9	206	209
-8	194	195
-7	207	-200
-6	493	-482
-5	141	-151
-4	106	-98
-3	1030	1086
-2	114	-114
1	55*	-195
2	108	114
3	1032	1086
4	103	98
5	151	-151
6	497	482
7	210	-200
8	188	-195
9	206	209
11	149	-157
14	0*	20
19	125	117
21	77	-59

0,2,L

-19	98	-91
-17	66	58
-16	63	-56
-15	181	-175
-14	115	-112
-13	111	109
-12	170	-173
-10	79	80
-9	141	-145
-8	103	-109
-7	556	551
-6	431	-428
-5	490	492
-4	1295	-1360
-3	680	690
-2	747	-783
-1	304	318
0	0*	109
1	305	-318
2	739	-783
3	681	-690
4	1284	-1360
5	482	-492
6	435	-428
7	550	-551
8	115	-109
9	141	145
12	178	-173
13	122	-109
14	132	-112
15	181	175
16	34*	-56

0,3,L

-19	52*	51
-14	100	-99
-13	277	-277
-12	360	-365
-10	198	193
-8	169	171
-7	395	-384
-6	346	332
-5	836	-834
-4	848	862
-3	697	-690
-2	435	-438
-1	344	341
1	348	341
2	433	438
3	693	-690
4	834	-862
5	830	-834
6	339	-332
7	397	-384
8	174	-171
10	191	-192
12	360	365
13	282	-277

0,4,L

-19	0*	41
-18	113	117
-17	99	98
-15	117	124
-13	71	73
-11	181	188
-10	78	72
-9	14*	23
-8	380	376
-7	336	340
-6	153	-160
-5	159	-153
-4	267	-274
-3	246	246
-2	237	239
-1	607	613
0	292	289
1	601	-613
2	237	239
3	238	-246
4	271	-274
5	155	153
6	163	-160
7	332	-340
8	370	376
11	175	-188
13	76	-73
15	119	-124
17	92	-98
18	108	117

0,5,L

-14	127	-133
-13	66	-50
-12	153	142
-11	480	484
-10	139	-142
-9	487	495
-8	31*	25
-7	93	96
-6	112	-107
-5	486	481
-4	225	223
-3	731	-750
-2	309	-314
-1	672	673
1	669	673
2	311	314
3	728	-750
4	233	-223
5	493	481
6	117	107
7	90	96
9	489	495
12	139	-142
14	119	133

0,6,L

-15	0*	-50
-13	253	-256
-12	303	-304
-11	502	-514
-9	88	88
-8	440	438
-6	414	-417
-4	522	-519
-3	321	-314
-2	127	-128
-1	96	98
0	586	-597
1	97	-98
2	129	-128
3	314	314
4	514	-519
6	406	-417
8	442	438
9	87	-88
11	496	514
12	314	-304
13	246	256
16	146	-160
19	52*	42

0,7,L

-14	103	-96
-13	227	-232
-12	192	200
-11	234	236
-8	101	-91
-6	90	-75
-5	261	-189
-4	105	99
-3	301	-302
-1	579	580
1	578	580
3	297	-302
4	98	-99
5	174	-189
6	90	75
7	58	-44
8	91	91
10	52*	69
11	244	236
12	196	-200
13	229	-232
14	89	96
18	77	-80

0,8,L

-14	53*	-48
-13	140	137
-10	275	281
-9	409	403
-8	161	155
-7	160	-166
-6	80	80
-5	83	88
-4	260	-252
-3	297	-292
-1	271	-269
0	230	240
1	262	269
3	296	292
4	252	-252
5	94	-88
6	75	80
7	174	166
8	146	155

0,8,L

9	401	-403
10	288	281
13	130	-137

0,9,L

-17	35*	47
-16	82	75
-12	134	125
-9	289	287
-8	179	173
-7	278	279
-6	283	287
-5	229	-232
-4	248	-245
-3	48*	-57
-2	148	149
1	60	73
2	146	-149
4	248	245
5	229	-232
6	276	-287
7	279	279
8	184	-173
9	275	287
12	134	-125

0,10,L

-16	0*	43
-14	109	-113
-12	75	-66
-11	69	-63
-10	278	285
-8	132	-143
-7	57*	-61
-5	132	-121
-4	131	-131
-3	133	-128
-1	191	-191
0	463	462
1	195	191
2	40*	38
3	127	128
4	136	-131
5	122	121
7	50*	61
8	151	-143
10	282	285
11	19*	63
12	62	-66
13	104	107
14	115	-113
17	0*	30
19	0*	14

0,11,L

-15	52*	-32
-14	25*	44
-11	246	-241
-9	228	235
-7	111	-112
-6	170	-173
-5	460	-468
-4	94	-99
-3	198	-196
-2	242	-238
-1	66	56
2	248	238
3	202	-196
4	108	99
5	458	-468
6	167	173
7	101	-112
8	83	77
9	238	235
11	239	-241

0,12,L

-8	179	-167
-4	107	-118
-3	194	-212
-2	237	-239
-1	79	82
0	282	295
1	82	-82
2	240	-239
3	215	212
4	118	-118
8	163	-167
17	98	-84

0,13,L

-12	100	-101
-11	94	-103
-9	122	126
-8	77	99
-6	98	-102
-5	149	-145
-4	67	60
-2	242	-244
-1	193	212
1	210	212
2	243	244
4	54*	-60
5	140	-145
6	99	102
8	91	-99
9	120	126
11	119	-103
12	98	101
13	103	-96
15	67	-70

0,14,L

-9	109	-100
-8	139	136
-7	183	190
-5	76	-70
-2	352	355
0	285	284
2	348	355
6	32*	-15
7	183	-190
8	124	136
9	118	100
10	35*	47
12	56*	-61
17	39*	-59

0,15,L

-10	137	129
-5	129	119
-4	88	100
-2	70	-81
-1	242	251
1	251	251
2	98	81
4	98	-100
5	119	119
10	117	-129
11	77	69
12	93	84
15	14*	35

0,16,L

-7	148	146
-6	153	-151
6	154	-151
7	148	-146
9	21*	-29

0,17,L

-8	0*	49
-6	161	154
-3	254	-260
1	57*	60
3	251	-260
6	152	-154
7	19*	-20
12	56*	41
14	0*	46

0,18,L

-9	87	102
-4	69	-74
-3	135	140
0	100	-121
3	132	-140

0,19,L

-6	94	97
-2	89	-74
2	74	74
6	108	-97

0,20,L

6	64	59

0,21,L

9	51*	57

0,22,L

-2	42*	-43
0	76	71
5	0*	2

0,23,L

3	29*	-7

1,0,L

-22	56*	38
-16	167	170
-10	229	-235
-8	117	-120
-6	129	141
-4	555	-542
-2	274	-278
0	869	898
2	413	420
4	1051	1112
6	239	-234
8	479	-500
10	233	236
12	133	-147
14	96	110

1,1,L

-16	151	160
-15	248	247
-13	188	189
-12	123	-130
-11	202	-209
-10	39*	65
-8	444	-423
-7	242	243
-6	363	-363
-5	283	285
-4	78	-73
-3	38*	30
-2	222	-222
-1	534	-551
0	210	-211
1	230	-237
2	539	550
3	1021	1070
4	187	182

1,1,L

5	98	82
6	230	224
7	346	330
8	226	-230
9	255	-236
10	387	-394
13	100	99
14	129	-133
15	159	-159

1,2,L

-19	0*	-24
-18	111	-110
-15	241	-238
-13	231	238
-11	172	-175
-10	91	-98
-9	106	-119
-8	347	-335
-7	236	234
-6	647	661
-4	564	-570
-3	1048	1082
-2	1302	-1341
-1	1227	1283
0	841	-870
1	293	299
2	744	754
3	897	934
4	997	1030
6	50	-46
8	77	-74

1,3,L

-21	48*	34
-20	31*	37
-16	129	140
-15	50*	71
-14	123	-133
-13	169	-179
-12	330	-337
-11	251	-251
-10	144	151
-8	123	-125
-7	80	-88
-6	484	474
-5	259	277
-4	375	369
-3	741	-752
-2	728	-731
-1	1147	1185
0	1055	1094
1	471	-482
2	188	-178
3	691	702
4	423	-427
5	283	-293
6	271	284
7	158	-177
8	244	-245
9	275	-275
10	157	-151

1,4,L

9	450	451
10	80	67
12	254	253
15	132	131

12	176	172
14	173	-180
16	76	94
18	98	71
21	42*	40

-16	0*	37
-14	115	107
-13	333	332
-11	70	-76
-10	429	-435
-9	153	-154
-8	103	118
-7	363	-354
-6	524	516
-5	116	-119
-4	618	615
-3	248	251
-2	201	203
-1	475	473
0	828	-846
1	672	-703
2	422	433
3	360	363
5	227	227
6	410	-420
7	419	-428
8	431	-443

10	213	-215
11	335	-338
13	115	107
16	127	-117
17	68	-49

1,5,L

-21	42*	-14
-14	95	104
-13	170	-172
-12	187	-201
-9	117	-121
-8	260	-263
-7	446	433
-4	227	-229
-3	688	-683
-2	97	-108
-1	710	-714
0	237	-233
1	180	-176
3	71	-78
4	656	-656
5	488	497
6	225	-227
7	783	-789
8	285	-278
10	127	-143
11	200	207
12	317	-322
13	115	116
15	46*	20
18	106	106

1,6,L

-14	192	191
-13	117	-114
-12	105	-96
-10	151	-155
-9	113	120

-8	289	286
-7	68	55
-6	274	257
-5	624	592
-4	697	694
-3	149	151
-2	530	-517
0	72	-81
1	80	-85
2	329	336
3	88	-95
4	99	-94
5	79	-77
6	146	-155
7	72	76
8	180	186
9	155	-146
10	232	-230
11	158	154
12	197	197
13	105	118
16	101	-93
19	47*	-17

1,7,L

-17	88	74
-12	246	255
-10	151	-160
-9	273	-264
-8	234	229
-7	299	303
-5	278	282
-4	82	71
-3	136	121

-2	592	579
0	47*	58
1	145	-142
3	272	273
4	522	511
5	254	266
6	93	87
7	345	-359
8	327	332
9	74	-79
10	207	209
11	231	240
13	195	191
15	130	138
19	52*	-9

1,8,L

-15	136	131
-14	84	67
-12	79	-82
-10	71	-79
-9	90	-92
-7	347	-340
-6	429	418
-5	332	322
-4	105	-100
-3	365	-343
-2	204	-204
-1	603	-585
0	234	-237
1	151	159
3	598	-597
4	157	157
5	276	277

6	328	-321
7	144	151
8	94	87
9	307	-310
10	216	220
11	144	-144
12	211	211
14	178	176
16	51*	-25

1,9,L

-15	94	95
-14	49*	50
-12	127	-136
-11	191	-201
-9	54*	-58
-7	316	317
-5	66	74
-4	337	-334
-3	84	-87
-2	443	436
-1	463	-454
0	593	-577
1	194	-192
2	77	71
3	332	330
4	118	126
5	102	96
6	281	-277
7	109	-103
9	204	-207
10	229	226

1,9,L

12	155	-148
13	141	143
14	118	122

1,10,L

-14	102	-100
-13	66	-58
-8	234	-238
-6	286	276
-5	180	170
-4	51	32
-3	138	-136
-2	123	-137
-1	178	-181
3	364	-356
4	165	165
5	292	290
6	169	-173
7	315	324
8	274	-276
9	111	116
12	103	-101
17	29*	-29

1,11,L

-15	123	105
-14	104	95
-13	110	112
-12	104	119
-11	208	-201
-8	58*	-67
-7	99	113
-6	95	102
-5	176	171
-4	237	241
-3	125	134
-2	107	-91
-1	262	-260
0	67	-63
1	148	145
3	142	140
4	216	213
5	157	-152
6	218	217
7	132	-129
9	98	-104
10	136	134
13	107	108
15	159	-161

1,12,L

-13	114	117
-10	173	-175
-8	105	-105
-7	186	195
-6	180	192
-4	287	-275
-3	58	54
-2	185	-191
-1	134	127
0	137	-136
1	255	-251
4	348	366
7	13*	31
8	215	-194
10	86	87
11	108	-109
13	82	81
16	75	49

1,13,L

-12	66	-61
-9	168	-167
-8	103	-104
-6	127	-129
-5	23*	27
-4	245	241
-3	85	-84
-2	314	-312
-1	246	-252
0	147	-137
1	110	107
2	164	-167
3	339	341
4	240	-244
8	93	-93
14	91	-88
15	60*	-51

1,14,L

-14	123	109
-13	82	80
-9	144	-147
-8	34*	46
-7	113	106
-6	100	88
-5	80	-76
1	247	-237
2	105	98
3	98	94
4	115	117
5	0*	-46
10	120	-123
11	108	-97
12	110	97
14	27*	-52
15	54*	74

1,15,L

-9	162	-152
-8	176	-182
-7	100	85
-5	211	204
-4	252	244
-3	142	-137
-1	116	-122
2	115	-118
3	183	184
4	90	94
5	64	66
6	126	126
8	76	-80
10	127	-140

1,16,L

-10	95	-88
-6	84	-80
-5	90	88
-3	84	81
-2	63	-58
-1	151	158
0	118	-116
1	189	191
2	115	118
4	111	98
5	78	78
12	75	78
15	27*	43

1,17,L

-14	17*	12
-13	0*	-28
-10	78	-89
-9	130	-125
-2	103	105
0	56*	-55
4	164	162
5	105	109
7	107	-104
12	0*	-25

1,18,L

-11	29*	-2
-7	126	-124
-4	126	135
0	84	-82
2	31*	34
3	137	-136
9	138	-152

1,19,L

-12	58*	47
-10	115	-109
-5	116	103
12	47*	-53

1,20,L

-1	0*	-33

1,21,L

3	0*	9

1,22,L

-6	38*	58

1,23,L

-4	29*	-15

2,0,L

-18	137	128
-14	175	-173
-12	192	188
-8	418	-420
-6	49*	-63
-4	336	-343
-2	1350	1406
0	1809	-1866
2	963	-968
4	413	-403
6	114	-102
8	500	-497
10	176	-173
12	494	-500

2,1,L

-18	0*	-6
-17	152	-139
-16	252	264
-14	107	103
-13	180	184
-10	220	217
-8	385	-376
-7	178	-185
-6	246	236
-5	62	-70
-4	126	114
-3	942	939
-1	572	-550
0	140	-140
1	682	694
2	32*	36
3	450	-451
4	421	410
6	75	68
7	801	784
8	212	-210
10	213	-207
12	176	193
13	124	121
14	176	-177

2,2,L

-19	48*	65
-17	89	-85
-15	140	-134

2,2,L

-14	126	-135
-13	152	148
-12	417	409
-10	97	93
-8	55	-61
-7	336	332
-6	122	-116
-5	608	-599
-4	324	306
-2	424	422
0	193	-188
1	472	473
2	252	-267
3	152	-142
4	822	823
5	522	-524
6	598	601
7	120	101
8	224	232
9	263	271
10	211	209
11	300	-301
13	86	81
16	122	131

2,3,L

-20	32*	2
-18	41*	-45
-17	0*	15
-13	126	130
-12	66	-82
-11	65	-67
-10	351	359
-9	75	-60
-7	290	-300
-6	464	458
-5	56	-59
-4	44*	59
-3	147	-139
-2	772	757
-1	1021	1024
0	375	-367
1	486	-497
2	57	-66
3	240	-233
4	185	177
5	180	177
6	532	527
7	317	311
8	270	-263
10	260	263
11	192	-194
14	159	-158

2,4,L

-20	95	66
-16	85	-84
-15	94	-82
-11	133	-122
-9	233	-216
-8	654	-627
-7	318	-291
-6	760	-747
-5	646	-636
-4	735	718
-3	280	-278
-2	351	336
-1	280	-289
0	1334	-1333
1	370	361
2	114	-99
3	446	428
4	726	-743
5	91	-101
6	250	251
9	71	86
10	295	-299
11	115	-102
12	72	-70
15	77	56
17	70	-52
20	104	-96

2,5,L

-20	72	-42
-15	192	-186
-13	116	114
-12	97	-95
-11	131	138
-9	270	-275
-8	307	-305
-7	136	131
-5	508	-489
-3	442	-419
-2	88	90
-1	56	61
0	422	413
1	817	-813
3	235	-230
6	108	106
7	259	-249
8	69	-70
10	89	-102
11	178	-175
13	178	-184
14	107	-112
15	100	88

2,6,L

-14	0*	88
-13	213	-210
-12	88	81
-11	219	228
-10	182	174
-8	39*	-50
-7	132	138
-6	394	-386
-5	167	156
-4	729	708
-3	170	156
-2	682	677
-1	289	286
0	431	416
1	244	229
2	400	387
3	72	-60
4	186	-182
5	114	-112
6	584	588
8	159	169
10	270	-268
11	112	-111
12	174	168
13	159	-156
16	121	102
18	120	103
19	117	-99

2,7,L

-21	74	58
-15	155	-148
-13	230	227
-12	73	76
-11	191	185
-10	124	-131
-9	258	-244
-8	100	103
-6	255	-265
-5	409	394
-4	380	-374
-3	884	845
-2	309	299
-1	409	398
0	407	-390
1	424	-427
2	138	-119
4	202	203
5	252	256
6	190	-190
7	16*	-3
8	173	181
9	106	-98
10	85	-80
11	161	-162
13	59*	-73
14	32*	-33
15	216	205

2,8,L

-15	116	117
-11	163	154
-10	211	209
-9	168	-166
-8	0*	3
-7	86	-99
-6	52*	-68
-5	147	153
-4	118	117
-3	53	-69
-2	319	311
0	170	162
1	316	316
2	245	-260
3	420	-406
4	74	-64
5	53	55
6	165	-177
7	100	-105
8	173	176
9	126	130
10	149	-130

2,9,L

-17	122	-110
-10	96	98
-8	148	149
-7	443	-433
-6	120	-124
-5	109	-101
-3	240	250
-2	213	213
-1	146	-138
0	134	-128
1	161	-151
3	88	-89
4	95	-93
6	247	-241
7	305	321
8	105	115
9	246	-253
11	127	-121
12	212	222
14	138	140

2,10,L

-18	54*	52
-17	73	75
-15	37*	-71
-14	0*	-98
-13	113	103
-12	304	311
-11	181	176
-10	214	-208
-9	211	207
-8	163	-164
-5	212	211
-4	126	-120
-2	150	152
-1	165	164
0	101	-80
2	469	-480
3	313	-319
4	163	169
7	126	118

2,10,L

8	100	-90
9	174	182
11	71	66
12	173	-186
16	112	72

2,11,L

-17	85	-73
-11	95	100
-9	95	95
-7	230	-239
-5	65	-68
-4	107	-109
-3	477	485
-1	228	-210
2	97	-65
3	275	-282
6	167	-142
7	328	337
8	84	-76
12	49*	-37
13	0*	158
16	0*	-24

2,12,L

-15	0*	-105
-12	59*	73
-10	108	-118
-9	181	-167
-7	15*	-52
-5	240	-245
-4	132	-128
-3	166	146
-2	112	112
0	178	-157
1	110	-112
4	147	148
5	227	-239
6	176	181
8	87	95
10	82	85
12	113	-107
13	96	94

2,13,L

-18	67	-53
-16	49*	31
-14	80	-87
-11	170	162
-10	170	183
-7	202	-209
-3	209	210
0	312	317
2	74	-122
4	130	-121
6	100	103
7	171	165
8	71	72
13	0*	-7

2,14,L

-15	0*	-37
-5	89	-76
-4	163	167
2	267	-277
3	234	246
5	97	-103
6	65	78
10	125	-128

2,15,L

-15	0*	-40
-11	106	118
-10	76	69
-3	119	105
-2	77	134
-1	101	101
1	214	-216
2	74	-73
3	84	-113
4	82	-79
8	86	-98

2,16,L

-7	71	-75
-6	177	-183
-4	143	144
-1	85	71
1	65	65
2	0*	184
6	111	120
8	74	86
10	74	-52

2,17,L

-12	95	83
-11	0*	47
-5	65	-80
-4	75	-75
-1	92	103
1	205	-197

2,18,L

-7	91	-79
-4	56*	52
4	110	-98
9	0*	-3
11	29*	53

2,19,L

-11	47*	-23
-10	45*	-50
-7	91	-86
-4	85	-74
-2	104	90
6	61*	-74
11	18*	-25

2,20,L

-9	54*	-23
-2	114	112
2	101	-88
3	0*	-46

2,21,L

-3	108	91
2	26*	-12

2,22,L

-2	69*	81

2,23,L

-2	56*	22

3,0,L

-18	266	249
-16	99	104
-12	191	-183
-8	302	314
-6	399	394
-4	606	-603
-2	448	441
0	752	730
2	202	210
4	83	74
6	201	-203
8	398	397
10	137	155
12	103	98

3,1,L

-16	124	137
-13	79	-90
-12	99	114
-10	63	-65
-9	186	193
-8	112	-111
-7	448	-433
-6	567	549
-5	146	-152
-4	191	182
-3	144	-151
-2	311	316
-1	371	-362
0	796	770
1	652	656
2	121	109
3	314	-304
4	606	585
5	110	-106
6	186	187
8	83	-89
10	285	293
11	223	219
12	130	147
17	109	87

3,2,L

-22	96	-81
-17	113	-114
-12	142	-140
-11	74	-90
-9	457	453
-8	419	411
-7	344	334
-6	274	-266
-5	152	-145
-4	627	-616
-3	713	703
-2	102	90
-1	172	-184
0	702	702
1	396	389
2	127	140
4	165	-164
5	188	-183
6	296	-296
8	139	132
10	252	258
11	343	-352
12	184	-169
13	91	88
15	134	-139

3,3,L

-15	63	-73
-14	190	-200
-13	120	-116
-12	98	117
-11	55	-54
-9	168	165
-8	310	-317
-6	237	237
-5	170	-177
-3	195	-191
-2	126	-112
-1	137	-129
0	212	214
1	385	382
2	380	-376
3	298	-294
4	151	141
5	181	-188
6	188	176
7	324	-313

3,3,L

8	104	-108
9	71	88
10	127	126
11	57*	-59
16	65	53
17	42*	-67

3,4,L

-13	117	-114
-12	131	-127
-11	301	-309
-10	240	242
-8	211	208
-6	157	-149
-5	537	-513
-4	88	74
-3	55	62
-2	583	-576
-1	848	-847
0	230	239
2	177	-158
3	357	343
4	639	-633
5	281	-270
7	83	83
8	132	-128
11	67	77
14	165	-151
16	56*	78
17	47*	-77

3,5,L

-17	134	125
-15	92	-97
-14	111	-107
-13	63	68
-12	104	110
-11	179	181
-10	247	-240
-9	256	258
-8	95	103
-7	493	499
-6	131	-128
-5	181	-176
-4	162	164
-3	130	-140
-2	143	-140
-1	507	498
0	693	669
1	385	387
2	314	-305
3	236	239
5	343	-338
8	97	101
9	371	375
10	117	110
11	57*	-51
12	96	111
13	79	-73
14	0*	22
16	79	77

3,6,L

-13	83	-103
-12	305	-304
-11	174	165
-10	253	262
-9	75	-72
-7	236	235
-6	378	-373
-4	531	-523
-3	76	-69
-2	96	98
-1	239	-232
0	192	181
1	157	-155
2	420	403
4	247	-256
5	196	203
6	183	180
7	171	-184
8	248	-261
9	46*	-53
10	103	97
14	115	-109

3,7,L

-21	41*	-35
-15	104	-111
-14	156	157
-12	152	-113
-11	123	-130
-10	132	132
-9	116	-120
-8	157	154
-7	204	224
-6	284	-280
-4	116	-109
-2	141	-139
-1	110	-106
0	432	-431
1	264	265
2	173	179
4	203	-192
5	78	-84
6	147	-152
8	138	152
9	266	265
10	254	-266
13	167	-174
16	116	-133

3,8,L

-14	166	-171
-13	180	-182
-12	101	-100
-10	224	237
-9	269	-276
-8	251	256
-7	72	79
-6	134	-127
-5	126	121
-4	113	-97
-3	350	-360
-2	208	-223
-1	355	346
0	474	471
1	180	172
2	47*	51
3	75	66
4	76	-70
5	110	103
6	105	-104
7	193	-189
8	85	83
11	249	257
12	132	116
15	115	108

3,9,L

-9	283	282
-8	293	296
-7	73	-76
-5	105	-102
-4	212	203
-3	195	-193
-2	194	194
-1	217	220
0	86	-91
1	450	457
2	278	277
3	98	-105
4	0*	-5
5	97	-95
10	244	-249
11	33*	36
13	145	-137

3,10,L

-15	0*	-8
-13	122	131
-12	117	125
-11	173	188
-10	163	-148
-9	144	145
-8	153	165
-5	101	106
-4	151	-148
-2	106	107
-1	113	107
1	122	121
2	69	73
3	98	97
5	90	80
6	220	-220
10	95	91
12	123	-127
13	128	-129

3,11,L

-14	0*	53
-13	223	-214
-12	127	-140
-9	251	250
-8	80	95
-6	108	94
-5	83	-97
-4	235	-235
-3	352	-355
-2	234	-229
-1	58	-51
1	68	70
2	62	67
3	244	-242
5	351	-356
9	84	-87
11	213	211

3,12,L

-13	109	-108
-9	31*	-34
-8	165	158
-7	0*	-78
-5	118	-118
-3	157	165
-2	69	74
-1	238	-239
0	143	153
1	72	-78
2	34*	-7
3	134	127
4	30*	-58
5	251	-258
7	109	-97
8	144	119
9	91	-89
12	80	-92

3,13,L

-11	62	-56
-9	118	108
-6	139	136
-5	50*	-41
-4	263	-267
-3	189	-186
-2	115	-127
-1	168	171
0	248	234
1	277	286
2	223	-232
3	98	112
4	64	50

3,13,L

5	106	-103
6	103	91
8	36*	-70

3,14,L

-13	22*	5
-12	109	-105
-11	90	-96
-9	130	139
-7	86	101
-5	88	-87
-2	133	-138
-1	292	-291
3	212	207
7	33*	37
10	120	106

3,15,L

-17	39*	43
-8	55*	44
-7	118	116
-6	102	113
-5	159	-151
-1	101	99
0	100	104
2	100	98
8	121	-102
9	152	152

3,16,L

-9	72	80
-2	123	-122
0	191	190
2	197	194
4	123	-122

3,17,L

-13	37*	14
-7	82	90
-6	71	63
-1	70	85
0	27*	-57
1	102	-110
2	147	139

3,18,L

-10	68	54
-4	55*	-68
-3	122	-116
4	159	-151
10	0*	32

3,19,L

-12	97	-94
0	98	-104
2	122	116
6	14*	-37

3,22,L

-2	51*	35
-1	0*	-3

4,0,L

-14	233	222
-12	150	-151
-10	426	-433
-8	105	116
-6	99	99
-4	684	-621
-2	99	-77
0	508	-501
2	98	100
4	713	730
6	197	-198
8	187	189
12	259	259
14	200	197

4,1,L

-19	51*	-25
-16	39*	44
-15	169	171
-11	263	260
-10	80	-70
-9	145	-139
-8	115	-118
-7	137	-134
-6	105	110
-5	507	514
-4	261	-261
-3	381	-372
-2	86	87
-1	457	-444

0	109	-115
2	71	78
3	84	-89
4	48*	41
5	241	237
6	64	-64
7	141	-146
9	223	-231
10	313	316
12	101	-99
13	92	-91
14	126	115

4,2,L

-20	40*	-23
-15	119	120
-14	277	282
-13	91	81
-11	218	-215
-10	130	-135
-9	300	301
-7	291	-291
-6	223	217
-5	260	257
-4	62	66
-3	274	265
-1	275	258
0	141	-155
1	128	135
2	126	126
3	76	71
4	103	112
5	101	98
6	197	-201

7	325	327
8	53*	-56
9	79	-78
10	185	-173
13	81	90
14	98	96
16	63*	-73
17	42*	60

4,3,L

-17	20*	28
-15	85	96
-14	84	-97
-13	128	-142
-12	221	222
-10	225	-225
-9	139	-140
-8	257	-250
-7	125	126
-4	203	-207
-3	81	74
-2	348	-328
-1	304	-297
0	288	281
2	100	-118
3	441	433
4	273	269
5	235	231
6	182	-183
7	209	-210
8	30*	-56
16	65	76

4,4,L

-18	106	-105
-17	33*	-14
-11	136	-158
-10	195	-202
-9	85	85
-8	76	-74
-7	208	-210
-6	536	526
-5	98	98
-4	339	333
-3	380	377
-2	701	-682
0	312	298
1	119	-103
2	129	-118
3	201	201
4	300	294
6	246	245
7	293	288
8	166	-175
9	109	-99
10	73	47
15	105	-94

4,5,L

-13	66	46
-12	68	-72
-11	184	-187
-10	244	-252
-7	119	114
-6	66	-70
-4	155	-136
-3	281	276

-1	107	105
0	224	227
1	398	-407
2	102	-114
3	468	480
4	215	-212
5	113	-119
6	282	-273
7	125	-134
9	127	145
10	31*	38
12	103	-108
13	178	177
15	52*	28
17	61*	-49

4,6,L

-19	60*	-8
-18	65*	-52
-16	129	130
-12	143	-147
-10	74	87
-9	142	-153
-8	296	-297
-7	114	-104
-6	367	365
-5	127	128
-4	175	180
-3	120	123
-2	508	-495
-1	176	-168
0	119	125
1	459	-452
2	93	-89

4,6,L

4	74	63
5	120	115
7	169	-171
8	341	-336
9	251	-253
10	201	-200

4,7,L

-14	149	151
-13	118	116
-11	275	-278
-10	123	128
-9	105	-101
-8	96	95
-7	160	162
-5	167	160
-4	278	278
-2	276	-271
-1	280	-284
0	163	171
1	231	-227
2	238	230
3	220	221
4	109	-112
6	164	168
7	117	-110
8	115	122
9	129	120
13	96	77
14	82	-71

4,8,L

-9	42*	-57
-8	120	109
-7	71	79
-6	271	270
-5	45*	25
-4	88	91
-3	160	-135
-2	183	-171
-1	364	357
0	119	-106
1	194	-196
3	85	-83
4	124	128
5	151	154
8	83	-91
9	129	132
12	108	107

4,9,L

-15	97	102
-12	37*	-24
-10	97	-118
-9	71	-65
-6	16*	1
-5	314	323
-4	374	388
0	327	-325
1	137	128
2	179	176
5	275	278
6	130	128
7	152	-143

9	121	-118

4,10,L

-14	105	90
-13	107	105
-12	81	-88
-11	88	102
-10	264	-251
-8	70	-68
-5	209	-222
-3	111	-111
-1	48*	-45
0	344	-356
1	126	-130
2	256	267
3	98	-87
4	151	146
5	115	123
6	185	-180
14	106	96

4,11,L

-16	79	88
-13	101	-107
-12	73	84
-8	62	50
-6	117	119
-5	371	369
-4	163	165
-3	436	-431
-2	115	-115
-1	141	-134
1	116	-106

3	17*	47
5	103	103
9	205	-198
11	145	142

4,12,L

-14	118	112
-12	86	88
-11	96	-103
-10	62	-61
-5	157	162
-3	238	233
-2	274	278
0	130	-121
4	136	143
9	92	-89
13	40*	19

4,13,L

-9	111	-113
-8	182	-178
-5	152	165
-3	103	-105
-1	132	-134
0	111	-105
1	165	173
2	209	-204
3	169	170
4	86	85
5	86	93
7	82	-86
8	83	-89
9	95	-89

12	164	-158
14	55*	51

4,14,L

-12	57*	-61
-11	112	-110
-7	0*	-54
-2	115	-124
-1	155	-147
0	169	-166
7	125	120
8	81	-90
9	88	-75
13	32*	-10

4,15,L

-13	89	85
-12	75	76
-11	72	-71
-9	90	-82
-7	57*	1
-4	89	81
-1	172	-168
0	51*	72
1	190	-186
13	36*	51

4,16,L

-8	80	-106
-6	126	130
-5	125	128
-3	79	91

-2	105	-91
0	110	98
1	41*	-10
7	55*	61
8	159	-148

4,17,L

-14	94	111
-13	88	74
-10	66	-50
-3	92	100
0	76	-77
3	143	138
6	78	80

4,18,L

-11	35*	-3
-4	89	92
7	77	-79

4,19,L

-10	0*	-28
-4	109	115
5	0*	12

4,20,L

-5	34*	8

4,21,L

-3	0*	-38

5,0,L

-18	98	-95
-16	207	-207
-14	183	-185
-6	685	-673
-4	140	-131
0	430	-431
6	88	-100
8	225	224
10	170	-166
14	27*	14
16	111	-100

5,1,L

-12	92	113
-11	173	162
-9	84	-89
-8	73	63
-7	75	76
-5	116	106
-4	172	-166
-1	258	260
0	436	-410
1	213	-202
2	131	-138
3	294	-302
5	248	249
7	153	161
9	86	71
12	138	-149
13	96	-112

5,2,L

-12	391	397
-10	150	141
-9	132	132
-7	452	-442
-6	150	-153
-5	77	76
-4	417	398
-3	259	-242
-2	275	271
-1	100	-88
0	153	-160
1	318	314
2	275	-273
3	241	-237
4	227	-232
5	176	-184
7	181	182
8	105	99
9	147	-141
10	172	-174
11	105	97
16	42*	16
17	79	63

5,3,L

-15	58*	77
-12	261	262
-11	130	147
-10	132	-126
-9	79	61
-8	151	157
-7	74	68

-6	191	186
-5	273	-251
-4	309	-301
-3	116	107
-2	443	439
-1	152	148
0	102	-94
1	138	-144
2	144	137
3	153	123
4	544	545
7	137	165
8	132	-133
10	96	89
12	134	-130
13	0*	-8
14	124	124

5,4,L

-15	107	103
-14	75	-91
-12	69	102
-11	219	217
-8	286	-288
-7	182	-185
-6	108	-109
-5	112	96
-4	44*	-38
-3	54	41
-2	151	154
1	385	389
2	187	-190
4	54*	19
6	257	256

5,5,L

7	307	313
8	159	151
9	68*	143
10	121	117
12	175	-183
16	99	87

-17	88	-102
-16	36*	-25
-12	133	-132
-11	87	-96
-10	76	71
-8	80	-99
-7	253	-250
-6	139	-140
-5	245	-254
-4	292	-285
-3	265	260
-2	95	82
0	145	-154
1	360	-349
2	78	-77
5	304	-301
7	74	91
9	129	-141
13	135	136

5,6,L

-15	85	-83
-14	116	-110
-11	175	-181
-9	287	-290

-8	315	-315
-7	164	-165
-6	156	152
-5	196	-189
-4	180	173
-3	266	-259
-2	250	250
0	406	410
1	187	-189
2	190	-183
4	136	139
5	141	-141
6	141	149
7	111	-113
14	79	-69

5,7,L

-16	16*	-1
-13	64	70
-10	146	126
-9	48*	62
-8	121	-129
-7	201	-203
-6	251	-254
-5	167	-160
-4	85	87
-3	259	259
-2	178	-182
-1	218	224
0	84	69
3	69	62
4	162	-163
6	151	145
7	126	125

10	96	108
11	149	-158

5,8,L

-17	61*	46
-15	103	-114
-13	132	134
-11	81	84
-9	262	265
-8	67	-74
-7	388	386
-6	115	115
-5	97	89
-4	93	-100
-3	109	112
-2	293	283
-1	568	570
0	185	-191
1	118	-117
4	130	-124
5	13*	33
6	45*	57
9	160	198

5,9,L

-19	0*	-14
-12	69	-41
-11	128	116
-10	150	147
-9	169	-174
-8	72	-79
-7	256	-263
-6	94	95

-4	522	504
-3	262	267
-1	138	145
1	162	-173
2	150	141
3	218	-206
4	193	-156
5	0*	112
12	119	123

5,10,L

-10	0*	-64
-6	150	-157
-5	175	-184
-3	209	-217
-1	151	162
1	118	-132
2	64	79
3	72	-64
4	106	-99
5	104	-103
7	139	-122
8	176	186
10	87	-79
11	50*	-47
13	0*	14

5,11,L

-11	244	245
-5	93	88
-4	0*	-43
-2	114	96
-1	101	94

0	24*	-33
1	121	-120
2	183	-151
3	127	-126
5	256	262
6	73	-74
9	138	97

5,12,L

-12	66	87
-10	63	91
-6	173	-173
-5	99	102
-2	145	141
0	195	-191
1	140	150
2	125	-124
3	147	-158
4	97	-92
6	38*	-48
8	77	88

5,13,L

-10	55*	29
-9	29*	-64
-4	93	-100
-2	138	139
3	144	-144
4	147	155
6	115	-118
10	50*	61

5,14,L

-5	26*	-33
-2	57*	63
1	130	126
3	89	-77
7	145	147

5,15,L

-16	0*	-54
-15	114	-113
-9	47*	46
-7	62	-51
-5	59*	-46
-4	119	-111
-3	119	106
-2	108	106
0	0*	25
2	60*	-59
6	93	-92
7	136	130

5,16,L

-4	0*	-14
1	33*	16
2	96	-96

5,17,L

-10	81	73
-9	43*	41
-6	123	-127
7	23*	22

5,18,L

-1	95	100
7	15*	-17

5,19,L

-4	31*	39
-2	55*	-13
0	40*	68

5,20,L

-6	51*	-72
-5	81	-74
-2	101	96

5,21,L

-1	65	42

6,0,L

-18	72	56
-12	182	-185
-10	240	243
-8	308	304
-6	318	-317
-4	143	139
-2	170	-174
2	657	673
4	134	-144
6	71	-63
8	107	108
10	0*	-59

14	0*	-92

6,1,L

-15	132	-140
-12	206	211
-11	138	-126
-10	35*	-48
-8	161	161
-7	115	111
-4	157	159
-3	294	-303
-1	298	287
0	132	-128
1	134	-152
3	256	-262
4	225	228
6	156	160
8	242	246
9	131	125
11	113	99

6,2,L

-17	32*	-17
-13	126	-140
-12	122	-116
-8	225	223
-7	0*	-79
-5	0*	31
-3	197	-203
-2	116	-113
-1	71	60
0	145	-146
1	268	269

2	114	105
3	126	-126
4	288	-295
6	199	-207
8	44*	-70
9	0*	-44
10	102	98
11	155	151

6,3,L

-17	55*	58
-16	65	-42
-10	158	-155
-9	164	175
-8	131	113
-7	83	82
-5	71	-83
-4	90	-70
-2	215	215
-1	89	76
0	267	-265
1	186	194
2	103	115
3	105	113
4	160	181
5	153	-140
6	34*	-52
8	126	120
9	106	-106

6,4,L

-15	95	85
-13	96	100

-11	212	218
-10	113	124
-9	74	68
-8	105	102
-4	179	-183
-3	272	-273
-2	85	95
-1	308	-309
0	273	273
2	34*	48
3	270	-271
7	69	-53
10	138	132
12	114	-123

6,5,L

-15	47*	51
-11	107	-96
-10	218	212
-9	256	260
-8	148	157
-7	136	138
-4	22*	-102
-3	128	125
-2	56*	60
-1	283	-282
0	81	-88
1	409	402
2	172	-166
3	102	105
5	162	-164
7	109	104
9	61*	-57
13	128	122

6,6,L

-20	36*	-41
-18	74	88
-17	29*	51
-16	85	76
-15	66	-68
-14	103	-111
-11	168	-163
-10	153	-159
-9	188	-187
-8	58	-69
-7	67	76
-6	56*	-60
-4	323	-329
-3	77	-73
-1	156	-164
0	158	148
1	105	104
2	131	-110
3	131	124
4	142	160
8	82	-91
10	231	239

6,7,L

-16	0*	22
-12	113	-102
-11	72	-53
-10	101	114
-9	74	80
-8	105	-97
-7	118	-120
-6	140	-141

-5	347	-352
-4	147	-151
-3	187	-182
-1	161	-156
1	364	372
4	91	-92
5	131	-117
8	123	-123
11	106	-109

6,8,L

-13	44*	56
-12	47*	-78
-7	216	214
-4	173	-182
-3	134	123
-2	143	-139
0	121	-128
1	56*	-56
2	88	82
3	195	202
11	0*	-125
12	51*	59

6,9,L

-17	22*	53
-9	55*	-73
-6	160	170
-5	64	-82
-4	79	75

6,9,L

-3	138	-144
-2	70	57
-1	82	76
0	243	251
2	83	87
5	86	-75
7	79	-71
8	183	-185
9	78	66

6,10,L

-14	104	60
-13	72	-67
-12	69	-52
-11	75	-83
-10	87	63
-8	261	267
-4	143	144
0	207	212
1	116	133
2	260	253
3	227	229
4	57*	-43
6	49*	37
12	42*	46
13	63*	44

6,11,L

-12	68	-79
-10	85	-75
-7	243	249
-4	157	-163
-2	0*	87
-1	142	135
0	81	-74
1	56*	66
2	146	-140
3	70	-62
4	91	75

6,12,L

-13	74	-67
-12	94	-87
-5	81	78
-4	117	112
-2	152	-153
-1	127	-133
4	144	-153
6	115	-122
7	85	-80
10	124	-102

6,13,L

-13	79	-90
-11	106	-107
-10	86	-80
-8	145	156
-4	84	-94
-3	117	-116
2	60	52
3	68	-75
5	132	-131
6	91	-97
8	35*	47

6,14,L

-15	34*	49
-12	48*	-8
-4	86	-95
-1	57*	-36
4	0*	23
9	44*	-52

6,15,L

-8	100	110
-5	0*	6
-3	88	84
0	0*	-77
1	100	98
4	54*	63
7	87	64
8	14*	34

6,16,L

-10	65	-72
-9	31*	-12
-6	63*	80
-4	105	-100
-3	93	-92
3	0*	25
6	58*	-59

6,17,L

-9	79	79
-3	49*	20
6	58*	56

6,19,L

3	91	91

7,0,L

-14	171	179
-10	61	56
-8	49*	-25
-6	149	148
-4	234	239
-2	55*	-42
2	203	222
6	217	206
8	274	-278
10	180	-172
12	24*	40

7,1,L

-14	198	134
-13	106	59
-12	122	130
-9	133	-121
-8	118	110
-2	44*	-30
0	221	-225
1	125	-114
2	39*	37
7	233	-230
8	195	193
11	96	-105

7,2,L

-16	0*	-57
-13	137	-149
-12	259	-280
-11	173	175
-10	98	-102
-7	60	64
-6	139	133
-5	143	131
-4	18*	24
-3	77	-70
-2	141	-148
-1	234	246
0	203	-195
1	94	91
3	0*	-81
5	144	152
6	40*	57
11	146	165
12	112	113
14	75	65

7,3,L

-16	64*	-74
-14	78	90
-12	125	-122
-10	149	-153
-8	52*	43
-7	152	-143
-6	76	-103
-5	110	111
-4	90	93
0	234	-237

7,4,L

-14	122	119
-12	143	148
-11	129	127
-7	73	-77
-6	126	127
-5	0*	72
-3	185	-180
-2	109	114
-1	120	-122
0	150	151
1	188	-193
3	201	-191
4	231	230
5	108	90
7	98	-96
9	123	-121

7,5,L

-19	0*	-13
-17	10*	-32
-11	95	-92
-9	118	103
-8	73	72
-6	102	94
1	74	75
3	159	165
4	238	-236
5	117	136
6	198	-206
8	148	155
10	99	-98

7,6,L

-10	113	-116
-8	92	-73
-7	67	78
-6	58	-42
-4	92	-99
-3	399	391
-2	34*	-44
-1	72	77
0	255	-252
1	93	100
2	140	-140
4	131	111
5	38*	40
6	74	-113
11	0*	-11

7,7,L

-16	0*	39
-14	0*	-2
-8	49*	-64
-7	132	-129
-6	141	156
-5	96	72

7,7,L

-3	116	-121
-2	108	-123
-1	132	-131
0	232	229
2	0*	-24
7	103	93
10	0*	22

7,8,L

-13	41*	54
-7	73	-105
-5	266	-256
-3	140	140
-2	150	-163
-1	286	-304
0	111	-82
1	232	-232
2	78	-81
4	110	116
8	75	-56
9	17*	-27
11	118	-118
12	64*	82

7,9,L

-8	78	-79
-7	69	72
-5	151	146
-3	61	-64
-2	119	-125
0	138	154

1	85	-96
3	80	83
6	62*	76
8	135	-127

7,10,L

-12	44*	-66
-6	80	-87
-4	133	138
-3	159	157
1	64	80
3	102	106
6	127	117
10	74	-69

7,11,L

-14	86	74
-9	152	-147
-7	106	97
1	76	-61
2	31*	36
3	114	116
4	75	64
6	113	119
7	127	-129
8	39*	30

7,12,L

-5	75	82
-4	75	124
0	51*	45
3	38*	-17

6	96	94

7,13,L

-9	86	-73
-8	0*	45
-6	105	-92
-2	86	83
0	83	-97

7,14,L

-5	107	108
-4	48*	66
1	13*	-14
6	96	-73
8	0*	-39

7,15,L

-4	91	71
-1	0*	-54

7,16,L

-10	86	-93
1	65	-40
5	10*	-24

7,17,L

-7	56*	-47
-6	59*	40
-3	65*	69

7,18,L

-3	51*	43
1	0*	-54

8,0,L

-8	297	-314
-6	114	-117
2	131	-134
6	140	147
8	144	-152
10	140	-146

8,1,L

-7	62	52
-6	93	-92
-5	207	-211
-2	99	-95
-1	124	108
0	136	-136
3	112	118
4	85	-77
9	103	120
10	86	-81

8,2,L

-13	158	-165
-11	98	95
-10	112	109
-7	113	104
-6	30*	9
-1	175	170

0	151	146
1	0*	-7
2	132	-121
6	118	118
7	143	-149
8	118	135

8,3,L

-14	0*	64
-11	104	114
-8	86	81
-5	41*	35
-4	240	247
-3	78	90
-2	104	114
4	154	-158
5	34*	71
10	87	-80

8,4,L

-5	39*	-43
-4	113	-117
-3	135	-126
-2	258	260
2	94	-106
7	0*	-22

8,5,L

-13	125	-121
-11	88	101
-6	124	-129
-5	123	124

-3	33*	-40
-2	85	-79
-1	195	-199
6	72	-70

8,6,L

-12	80	55
-9	63	52
-4	122	-122
-3	137	139
-2	174	164
0	82	-85
4	109	103
9	72	-35

8,7,L

-17	42*	-4
-13	64	-71
-7	291	-228
-6	104	117
-2	67	-85
0	94	104
1	80	-71
3	124	-122
4	102	106
7	69	74

8,8,L

-12	0*	-4
-9	120	115
-5	100	-113
7	79	75

9	58*	-36

8,9,L

-14	102	-84
-11	75	62
-5	87	-73
-1	88	97
0	43*	52
1	96	-102
9	106	87

8,10,L

-16	70	61
-15	0*	3
-12	0*	23
-10	108	95
-9	103	102
-8	76	-87
-2	84	-81
1	41*	-18
4	102	-109

8,11,L

-5	71	-74
-3	98	75
-1	83	83
1	118	-112
7	52*	-35

8,12,L

-9	53*	-12
-5	52*	-51
-3	86	-95

8,13,L

-10	75	78
2	58*	58
3	41*	21
4	85	-75
5	92	70

8,14,L

-12	46*	22
-10	0*	-27
3	0*	-29

8,15,L

-7	100	-95
-1	36*	31
2	75	56
3	81	-88

8,16,L

-7	0*	14
-1	54*	43

9,0,L

-16	72	84
-8	158	-165
-2	212	-221
4	72	-56

9,1,L

-16	42*	7
-12	52*	-42
-11	56*	-70
-7	67	76
-6	111	-118
-5	156	-164
-2	100	-107
2	90	80
4	0*	-37

9,2,L

-12	42*	59
-10	64	71
-9	88	-113
-8	89	91
-7	67	75
-3	97	-102
-2	53*	-33
0	136	139
1	116	-125
7	107	-107

9,3,L

-12	40*	-41
-7	67	63
-6	123	-125
-4	153	159
-1	53*	0
3	88	59
5	64*	60

9,4,L

-7	112	115
-3	142	-146
6	102	-102

9,5,L

-16	74	59
-6	48*	-53
2	54*	61
3	62*	-65

9,6,L

-16	0*	1
-13	59*	65
-12	47*	47
-10	65	-46
-8	103	110
-5	141	139
2	140	121
5	10*	-54

9,7,L

-13	0*	-32
-9	47*	-52
-4	114	-125
3	81	-88
7	63*	-69

9,8,L

-15	38*	34
-9	0*	17
-7	84	-83
-2	40*	-56
1	153	161
3	75	82
6	48*	-52

9,9,L

-8	62*	-64
-3	0*	-1
4	32*	53

9,10,L

-6	85	99
0	109	93
5	58*	-64

9,11,L

-3	59*	49
-1	36*	-3

9,13,L

-10	69*	78

10,0,L

-10	128	-113
-8	115	-115
-6	78	77
4	76	78

10,1,L

-11	72	-73
-10	73	75
-1	53*	-53
5	89	-79

10,2,L

-12	47*	66
-4	58*	51
1	0*	-96

10,3,L

-9	43*	-40
-8	76	-72
-2	122	-107
4	115	-84
5	0*	66

10,4,L

-9	43*	-24
-7	22*	18
-6	69	-84
-5	0*	-37
0	85	-83
4	64*	-30

10,5,L

-6	66	66
-3	111	-106
0	0*	63
2	107	97

10,6,L

-12	0*	-20
-7	0*	-29
-4	92	81
0	135	-124
4	25*	10

10,7,L

-4	62*	-78
4	31*	8

10,8,L

-7	121	-98
-4	77	89
3	0*	-33

10,9,L

-7	53*	-21
-1	65*	-72
1	45*	26

10,10,L

-5	20*	27
-1	100	-101

10,11,L

-6	55*	-43
-3	69*	88

11,1,L

-8	69*	-52
-7	86	-87
-3	0*	6

11,2,L

-5	88	-92

11,3,L

-2	31*	-66

11,4,L

-6	41*	-3
-3	111	115

Data for Dimethylsulphonium 1,2-dibenzoyl-2-(2-pyridylimino) ethylide

Crystal Data

$C_{23}H_{20}N_2O_2S$, M = 388.49; monoclinic,

a = 8.092(2)Å, b = 16.365(3)Å, c = 15.068(3)Å, β = 92.50(3)°,

V = 1993.49Å^3; D_c = 1.29 g.cm^{-3}, Z = 4; F(000) = 816;

space group $P2_1/n$; M_o - K_α radiation, λ = 0.7107Å,

μ (M_o - K_α) = 1.73 cm^{-1}.

-10,-7,L

-2	0*	23

-10,-4,L

-6	0*	-44

-10,-3,L

-5	54*	69
0	0*	-107

-10,-2,L

-5	51*	-63

-10,0,L

-1	0*	0

-9,-10,L

-5	0*	-21

-9,-9,L

-3	29*	41

-9,-6,L

-2	96	-104

-9,-4,L

-9	48*	-18
-3	122	127
-1	80	-92

-9,-3,L

-3	80	-92

-9,-2,L

-9	41*	-59
-6	0*	-73
-4	50*	-33

-9,-1,L

-10	0*	16
0	141	-158

-9,0,L

-11	78	-83
-7	177	175
-1	148	160

-8,-12,L

-1	116	-125

-8,-11,L

-9	46*	-16
-4	48*	-88

-8,-8,L

-2	159	170

-8,-7,L

-8	92	-96
-7	85	-74
0	106	-122

-8,-5,L

-12	68*	3
-9	128	120
-5	118	-128
-1	152	156

-8,-4,L

-6	80	97
-2	100	-101

-8,-3,L

-12	9*	-59
-6	113	106

-8,-2,L

-11	58*	83
-9	78	76
-8	0*	37
-7	128	-134
-3	121	109

-8,-1,L

-5	132	143
-4	109	-113
0	141	151

-8,0,L

-8	83	82
-4	105	-109

-7,-16,L

-1	53*	35

-7,-15,L

0	0*	-32

-7,-14,L

-3	107	-110

-7,-11,L

-1	112	112

-7,-9,L

-3	131	-147
0	122	128

-7,-8,L

-7	174	-188

-4 97 125

-7,-7,L

-5	119	114
-2	141	-135
-1	54*	-36

-7,-6,L

-8	158	166
-4	221	-230
-3	73	89

-7,-5,L

-4	148	161
0	88	-91

-7,-4,L

-14	45*	6
-12	0*	-32
-10	53*	-67
-9	64*	-79
-7	113	125
-4	124	133

-7,-3,L

-1	85	88

-7,-2,L

-14	0*	-13

-7 49* 57

-2 105 -91

-7,-1,L

-9	133	123
-1	120	116

-7,0,L

-7	133	-141
-1	248	-245

-6,-17,L

-2	48*	4

-6,-16,L

-2	50*	-66

-6,-13,L

-11	44*	39

-6,-10,L

-6	163	169
-4	117	114

-6,-9,L

-6	72	75
-3	133	132
-1	107	99

-6,-8,L

-7	92	-77
-4	175	-188
-3	192	179
-2	80	-84
0	126	-135

-6,-7,L

-11	44*	-55
-10	41*	-18
-5	58*	-32
-4	144	-137
-3	179	185
-2	84	-92
0	213	229

-6,-6,L

-10	82	84
-8	98	101
-5	221	-224
-3	130	138
-2	198	197
-1	184	-195
0	127	136

-6,-5,L

-5	169	183
-1	264	-260

-6,-4,L

-12	72	-64
-8	190	159
-7	192	184
-6	131	-128
0	0*	24

-6,-3,L

-10	144	148
-8	183	-170
-6	314	-323
-5	163	171
-4	104	109
-3	132	-127
-2	278	276
0	111	-127

-6,-2,L

-7	86	75
-5	100	96
-3	233	-232
-1	71	81

-6,-1,L

-13	41*	-42
-12	42*	-33
-9	177	176
-6	96	101
-5	228	-234
-3	154	-149
-1	224	217

-6,0,L

-10	139	-148
-9	0*	0
-8	184	-183
-6	443	459
-4	163	136
-2	262	-250
0	205	-201

-5,-17,L

0	70*	-45

-5,-15,L

-7	62*	52
-4	74	-62

-5,-14,L

-2	76	-75

-5,-13,L

-8	93	105
-6	109	127
0	63*	54

-5,-12,L

-8	77	86
-7	103	-110

-5,-11,L

-8	0*	21
-5	183	187
-1	239	-260

-5,-10,L

-5	186	197
-2	98	114
0	100	104

-5,-9,L

-8	146	-153
-5	221	231
-4	274	276

-5,-8,L

-11	110	-124
-8	102	-112
-3	353	-355
-1	66	-63

-5,-7,L

-9	151	128
-6	141	-136
-4	162	177
-3	222	-224
-2	140	131
-1	131	139
0	207	-223

-5,-6,L

-6	213	226
-4	135	129
-2	236	-230
0	247	-253

-5,-5,L

-9	49*	41
-8	84	-85
-6	162	162
-5	245	-262
-2	195	-183
-1	300	297
0	71	65

-5,-4,L

-7	154	-160
-6	215	-222
-5	117	129
-4	163	-159
-3	216	233
-2	139	148

-5,-3,L

-9	202	207
-8	251	255
-6	74	78
-5	118	131
-4	141	-145
-3	181	175
-2	172	-170
-1	143	-139
0	146	142

-5,-2,L

-11	134	122
-9	128	-127
-8	226	212
-6	47*	69
-5	119	-121
-4	121	-117
-2	186	193
-1	119	129

-5,-1,L

-17	0*	-42
-14	47*	-24
-8	129	-116
-7	224	-220
-6	116	-108
-4	102	103

-5,0,L

-15	91	-87
-7	338	332
-3	159	167
-1	353	-347

-4,-19,L

-2	68*	-43

-4,-16,L

-2	33*	3
0	174	167

-4,-15,L

-10	82	72
0	186	-178

-4,-14,L

-8	74	-68

-4,-13,L

-7	117	129
-1	159	163
0	168	168

-4,-12,L

-12	33*	78
-1	203	-209

-4,-11,L

-7	80	86
-6	177	171
-2	170	-182

-4,-10,L

-11	52*	46
-9	113	116

-5 54* -49
-3 154 165
-1 139 131

-4,-9,L

-6	0*	-27
-4	130	126
-3	210	225
-1	125	-141

-4,-8,L

-12	142	-129
-6	127	-139
-4	195	-204
-3	134	-141
-2	199	201
0	109	99

-4,-7,L

-9	110	-107
-7	140	-125
-6	216	-214
-5	128	-122
-4	213	211
-3	174	177
-2	246	255
-1	158	-162

-4,-6,L

-11	137	145
-7	261	262

-4,-6,L

-6	191	194
-5	246	257
-3	265	-274

-4,-5,L

-9	319	322
-6	219	-240
-5	294	-300
-4	182	-179
-3	80	77
-2	180	-176
-1	176	165
0	91	-114

-4,-4,L

-9	303	-308
-8	355	-353
-7	239	-241
-6	154	155
-5	297	-278
-4	440	442
-3	269	267
-1	366	368
0	236	-227

-4,-3,L

-18	61*	-15
-9	224	228
-8	194	185
-7	48*	-47
-6	377	384
-4	92	-98
-3	421	-426
-1	381	375
0	271	272

-4,-2,L

-11	180	184
-10	109	105
-9	139	137
-8	276	276
-7	127	-128
-4	530	-495
-3	559	548
-2	185	-172
-1	186	172

-4,-1,L

-13	107	112
-10	199	-198
-9	190	-192
-7	148	138
-6	142	134
-5	308	294
-4	269	-253
-2	342	-336
-1	316	-294
0	197	-191

-4,0,L

-15	0*	0
-12	175	-178
-10	106	95
-6	271	-249
-4	557	-531
-2	544	520
0	866	813

-3,-20,L

-2	40*	-47

-3,-17,L

-10	47*	-52

-3,-16,L

-8	44*	77
-4	143	-128
-3	118	131

-3,-15,L

-9	34*	-22
-7	97	-91

-3,-14,L

-1	120	-127

-3,-13,L

-14	0*	-27
-10	89	80
-2	205	215
-1	148	140

-3,-12,L

-8	106	-107
-3	156	-162
-2	246	-243
0	109	-119

-3,-11,L

-4	133	-120
-2	163	-152
0	94	-98

-3,-10,L

-13	92	-88
-10	15*	-7
-7	183	-181
-6	136	147
-5	169	177
-4	238	236
-3	182	185
-1	192	168
0	179	-189

-3,-9,L

-15	63*	-25
-6	182	188
-4	129	125
-3	87	-89

-3,-8,L

-11	156	175
-9	125	139
-7	208	-197
-5	93	-96
-4	392	-405
-3	37*	-69

-3,-7,L

-12	130	-99
-10	150	-147
-7	199	-199
-6	220	218
-5	274	264
-3	361	370
-2	223	-237
-1	243	-246

-3,-6,L

-13	99	98
-11	96	-91
-9	179	-184
-8	208	214
-6	155	148
-5	238	230
-4	281	-281
-3	331	341
-2	164	167
-1	90	-104
0	90	101

-3,-5,L

-10	262	253
-7	143	-138
-6	345	-342
-5	199	-184
-4	287	280
-3	182	-189
-2	284	279
-1	236	-239
0	292	-297

-3,-4,L

-18	0*	27
-13	177	159
-11	110	-96
-10	98	94
-9	94	-96
-7	111	106
-6	317	-319
-5	164	152
-3	456	-470
-2	126	-116
-1	450	-441
0	270	285

-3,-3,L

-19	77	-62
-15	142	149
-14	61*	-89
-11	315	-307
-9	112	99
-7	255	260
-6	299	-290
-5	330	-340
-4	171	160
-3	328	344
-1	771	771
0	94	-102

-3,-2,L

-12	135	121
-11	149	145
-10	209	231
-8	87	-87
-6	155	-141
-5	190	197
-4	520	507
-3	159	-148
-2	455	424

-3,-1,L

-13	46*	-83
-12	144	177
-11	224	-220
-10	225	-219
-9	124	120
-7	130	138
-6	103	119
-3	233	-226
-2	374	-358
-1	831	-770

-3,0,L

-13	315	-327
-11	217	180
-7	149	-142

-3,0,L

-5	465	-451
-3	346	340
-1	1009	950

-2,-20,L

-3	78	-89

-2,-18,L

-1	79	89

-2,-17,L

-3	158	-143

-2,-15,L

-1	137	136

-2,-14,L

-13	0*	-19
-5	167	-174
-4	182	-183
0	228	230

-2,-13,L

-9	96	-88
-6	216	-215

-2,-12,L

-9	118	-138
-8	167	191
-7	106	102

-2,-11,L

-10	147	145
-8	189	198
-7	109	-112
-6	193	-193
-4	89	90
-3	101	-97

-2,-10,L

-13	52*	4
-6	128	-116
-4	193	182
-2	171	154
0	152	-159

-2,-9,L

-17	0*	-3
-15	52*	62
-13	93	-92
-12	136	-142
-11	226	-210
-4	84	78
-2	121	-111
-1	178	192
0	107	-109

-2,-8,L

-12	170	177
-6	141	-146
-5	120	-134
-4	150	170
-3	141	147
-2	118	-122
-1	353	347
0	307	-328

-2,-7,L

-12	142	129
-7	241	237
-6	175	176
-4	198	-201
-3	281	269
-2	334	-353
0	218	216

-2,-6,L

-13	218	-227
-9	216	220
-7	191	-173
-5	105	99
-4	107	-122
-3	141	147
-2	98	88
0	388	417

-2,-5,L

-12	83	90
-10	180	-185
-9	106	-87
-8	255	-258
-5	91	-84
-4	304	306
-3	440	465
-2	237	228
-1	302	-314

-2,-4,L

-12	195	-200
-10	80	70
-9	163	-168
-8	297	306
-7	151	134
-5	148	-142
-4	371	-396
-3	813	-818
-2	166	162
-1	270	265
0	318	333

-2,-2,L

-14	145	94

-2,-3,L

-8	186	188
-6	264	-262
-5	133	142
-4	170	-168
-3	98	-85
-2	882	870
-1	379	-390
0	124	128

-2,-2,L

-16	0*	11
-13	107	103
-10	19*	29
-9	190	-181
-8	155	-148
-7	161	168
-6	99	95
-5	292	275
-4	382	-363
-3	266	255
-2	501	-494
-1	241	-251
0	343	339

-2,-1,L

-14	66*	-64
-11	189	-179
-10	139	-118
-9	95	104
-7	137	134
-6	153	153
-5	545	-522
-3	512	-494
-2	1006	984
-1	650	619
0	812	-782

-2,0,L

-12	89	-94
-10	132	157
-8	114	-111
-6	466	460
-4	183	188
-2	396	383
0	435	417

-1,-20,L

-5	0*	-23

-1,-19,L

-3	0*	21

-1,-18,L

-1	125	-116

-1,-17,L

-6	101	-85
-2	63*	67

-1,-16,L

-13	69*	17
-8	82	-89
-4	74	67
0	175	-168

-1,-15,L

-11	63*	-66
-7	195	193

-1,-14,L

-8	131	-145
-5	123	-118
-3	113	106
-2	58*	49
-1	137	159

-1,-13,L

-3	162	-167
-2	281	-282

-1,-12,L

-7	90	-77
-6	199	207
-5	122	-122
-4	260	-247
-2	106	-105
0	79	82

-1,-11,L

-7	168	-179
-6	189	178
-5	319	309
-3	152	161
-2	35*	-63
-1	315	-308

-1,-10,L

-4 179 -168
-2 61 55
0 181 192

-1,-9,L

-12 106 -117
-11 54* -36
-6 218 -220
-5 0* -4
-4 197 -185
-2 372 384
-1 239 -238
0 47* 44

-1,-8,L

-9 180 -180
-7 232 221
-5 427 445
-3 120 -125
-2 168 -154
-1 384 -390
0 116 -126

-1,-7,L

-11 174 -164
-10 172 159
-8 58* -21
-7 134 125
-5 210 -209
-4 498 499

-3 109 83

-1,-6,L

-7 136 -139
-6 60 -85
-4 470 462
-3 134 -148
-2 165 -162
0 310 -335

-1,-5,L

-17 64* -58
-14 123 127
-10 276 -274
-7 155 -149
-6 143 -132
-5 380 -389
-4 281 -285
-2 434 -464
-1 335 347
0 263 265

-1,-4,L

-15 0* 53
-12 98 -118
-9 277 288
-7 219 -207
-6 456 -459
-5 436 416
-3 704 744
-1 160 169
0 442 481

-1,-3,L

-12 192 200
-11 138 161
-9 117 128
-8 214 204
-7 148 123
-6 117 107
-5 223 236
-4 213 224
-3 181 -192
-2 420 -434

-1,-2,L

-13 106 89
-11 82 102
-10 139 -117
-9 126 -126
-8 134 144
-7 451 -451
-6 346 348
-5 255 -247
-3 788 -820
-2 1180 1226
-1 117 -131

-1,-1,L

-14 223 -227
-12 118 109
-8 72 -72
-7 437 -423
-5 328 -347
-3 547 559

-2 915 920
-1 228 237
0 411 -419

-1,0,L

-13 137 146
-9 210 -211
-7 237 216
-5 431 423
-3 225 199
-1 692 643

0,-16,L

-9 74 -53
-5 110 101
-4 120 -121
0 131 119

0,-15,L

-15 44* 37

0,-14,L

-13 0* -10
0 155 152

0,-13,L

-11 102 -89
-6 118 -114
-3 224 -225
-2 181 -174

-1 110 114

0,-12,L

-9 231 205
-7 116 -113
-6 100 -88
0 292 -290

0,-11,L

-10 152 -142
-9 186 212
-4 237 254
-3 114 -119

0,-10,L

-13 90 -82
-10 159 -146
-9 153 152
-6 215 217
-5 137 -141
-4 202 -225
-2 107 104
0 259 248

0,-9,L

-12 54* 71
-10 215 212
-9 131 -123
-8 161 149
-7 259 -263
-3 223 243

-1 353 -344

0,-8,L

-9 283 -280
-8 228 235
-5 153 167
-4 105 -114
-3 306 -301

0,-7,L

-12 162 -169
-11 116 118
-6 205 -218
-5 243 240
-4 97 100
-3 370 362
-2 632 638
-1 370 373

0,-6,L

-10 105 -98
-5 216 218
-4 388 405
-3 174 -170
-2 125 -124
-1 253 261
0 1014 -1038

0,-5,L

-15 129 124
-11 264 -263

-9 119 127
-7 322 320
-6 144 -135
-5 764 -790
-4 252 -263
-3 437 -446
-2 125 -141

0,-4,L

-12 245 246
-9 191 -183
-8 160 -171
-7 212 -220
-4 297 310
-3 370 375
-2 519 542
-1 361 363
0 532 -572

0,-3,L

-10 184 -189
-9 88 81
-8 140 -147
-7 343 340
-6 721 734
-5 324 -325
-4 305 -335
-3 354 -368
-2 586 -621
-1 892 921

0,-2,L

-9	329	323
-8	208	230
-7	104	113
-6	156	-157
-5	282	-284
-4	224	-234
-3	1120	1168
-2	1040	-1093
-1	567	625
0	354	-426

0,-1,L

-19	0*	-7
-18	0*	30
-11	159	148
-10	163	-172
-9	216	-220
-8	215	-195
-6	350	349
-5	183	182
-4	334	-345
-3	119	111

0,0,L

-14	168	185
-12	330	-314
-10	96	98
-8	149	145
-4	800	-808

1,-19,L

-6	0*	31

1,-17,L

-1	59*	-100

1,-16,L

0	179	168

1,-15,L

0	85	92

1,-14,L

-9	113	-111
-4	222	-230
-2	188	-174

1,-13,L

-10	75	66
-6	244	-248
-2	168	182
0	18*	77

1,-12,L

-8	161	-141
-6	110	144
-5	223	235
-4	118	127
-3	213	-197
-1	328	-314
0	86	-82

1,-11,L

-11	122	-115
-7	196	199
-6	178	-184
-5	272	-251
-3	288	-286

1,-10,L

-9	81	-68
-8	187	-201
-5	89	-109
-4	192	193
-3	185	195
-2	66	-58
-1	210	198
0	202	-191

1,-9,L

-16	78	-64
-12	77	72
-10	118	-113
-7	215	205
-6	175	171
-4	140	144
-2	618	-617
-1	170	-183

1,-8,L

-11	223	233
-9	265	263
-6	238	239
-5	277	-264
-2	442	-421
-1	372	366
0	127	126

1,-7,L

-12	163	-162
-11	113	114
-8	171	175
-7	484	-469
-6	268	259
-4	578	579
-2	224	-209
-1	242	-235

1,-6,L

-10	204	-195
-9	163	-164
-8	282	268
-7	381	-379
-6	98	-108
-5	149	141
-4	37*	-48
-3	395	389
-2	475	468
-1	143	139
0	334	335

1,-5,L

-16	67*	85
-10	249	263
-4	818	-800
-3	291	298
-2	141	-145
0	269	265

1,-4,L

-13	246	251
-10	151	122
-9	149	-148
-6	407	-395
-5	548	562
-4	344	-359
-3	136	-140
-2	378	-398
-1	894	-884
0	474	-481

1,-3,L

-14	167	-160
-13	78	120
-9	224	-227
-7	166	187
-6	101	-115
-4	255	-267
-3	635	658
-2	1572	1615
-1	260	273
0	975	-984

1,-2,L

-14	111	-104
-10	290	287
-8	128	-139
-7	127	-146
-6	291	-304
-4	28*	31
-3	206	-217
-2	1146	1144
-1	557	-552

1,-1,L

-14	57*	35
-12	269	255
-11	207	-203
-10	162	-170
-8	481	-507
-7	671	675
-5	211	209
-4	511	539
-3	339	-359
-2	94	-128
-1	297	-289
0	421	-418

1,0,L

-13	108	-107
-9	304	309
-7	190	174
-5	297	-332
-3	733	773
-1	814	804

2,-20,L

-7	0*	1
-1	0*	-34

2,-17,L

-12	40*	30
-9	32*	7
-7	49*	14
-3	142	-126

2,-16,L

-1	166	163

2,-15,L

-12	76*	86
-6	105	106
-4	90	87
0	81	-80

2,-14,L

-4	117	-114
-3	161	-154
-2	148	-143
0	236	230

2,-13,L

-7	99	-93
-3	192	190

2,-12,L

-8	0*	93
-6	254	255
-5	264	250
-4	147	-119

2,-11,L

-8	273	266
-6	228	-235
-5	151	-158
-4	272	-258

2,-10,L

-16	0*	-10
-13	39*	36
-9	120	-106
-8	228	-220
-7	192	-193
-4	197	-191
-1	214	-213
0	162	-159

2,-9,L

-12	84	-77
-11	127	-135
-10	0*	-3
-9	143	-117
-7	330	317
-6	113	130
-5	98	130
-4	147	141
-3	239	-246
0	112	109

2,-8,L

-16	56*	-22
-14	92	-80
-11	172	186
-10	155	156
-9	227	229
-6	175	-153
-5	165	-170
-4	374	358
-3	319	317
-2	434	433
-1	161	166
0	316	-328

2,-7,L

-17	29*	-12
-11	164	-148
-10	158	-148
-8	97	-101
-7	212	199
-5	71	79
-4	246	-247
-3	78	-95
-2	198	-198
-1	405	-380
0	233	-217

2,-6,L

-13	219	-217
-11	270	-271
-8	224	178
-7	174	162
-6	182	-188
-4	65	-59
-3	267	-265
-1	351	343
0	419	418

2,-5,L

-13	155	160
-12	199	189
-10	109	-114
-8	167	-172
-7	133	-135
-5	41*	-83
-4	389	384
-3	507	500
-2	829	823
-1	580	-562

2,-4,L

-10	183	-191
-8	279	284
-7	93	109
-6	398	396
-5	262	-255
-4	435	-425
-3	510	-496
-2	560	-544
-1	373	368
0	340	333

2,-3,L

-13	117	-122
-12	96	-109
-11	131	134
-10	191	189
-7	164	-169
-5	260	-233
-2	803	-770
-1	164	163
0	139	-127

2,-2,L

-15	0*	-34
-14	89	99
-9	358	-349
-8	126	107
-7	263	260
-6	219	-237
-5	553	572
-3	272	-280
-1	331	333
0	362	337

2,-1,L

-16	73*	99
-15	180	190
-14	171	172
-13	106	-135
-8	68	65
-7	241	231
-5	135	140
-3	830	-808
-2	590	545
-1	1706	1600
0	839	783

2,0,L

-14	153	-125
-8	204	-217
-6	380	-372
-4	587	607
-2	851	-848
0	450	417

3,-21,L

0	0*	-32

3,-18,L

-1	94	-100

3,-16,L

-9	87	-77

3,-14,L

-6	0*	-82
-2	79	-78

3,-13,L

-2	137	-143
-1	62*	43

3,-12,L

-8	189	198
-6	151	151
-1	189	195
0	116	119

3,-11,L

-16	0*	8
-13	64*	-76
-5	128	141
-1	81	-65
0	106	-98

3,-10,L

-16	0*	-32
-8	124	-136
-7	208	-197
-6	130	-127
-5	172	180
-4	160	-153
-3	158	-152
-2	163	-157
-1	236	-236
0	196	189

3,-9,L

-15	0*	14
-7	252	267
-6	126	-136
-4	109	-93
-3	103	-101
-2	228	204
-1	153	-162

3,-8,L

-10	275	276
-5	353	353
-4	324	327
-2	90	-94
-1	81	-97

3,-7,L

-11	210	-195
-9	141	-145
-6	134	-116
-4	203	190
-2	304	300
-1	146	-134

3,-6,L

-9	219	227
-8	136	-114
-6	71	-66
-5	342	-313
-4	209	-215
-3	230	-224
-2	121	120
-1	91	81
0	96	-100

3,-5,L

-12	159	143
-11	0*	37
-8	297	-302
-7	92	-89
-6	240	240
-4	296	297
-3	257	228
-2	126	-137
-1	140	134
0	315	-297

3,-4,L

-14	73	61
-6	248	272
-5	439	-429
-4	293	274
-3	215	231
-1	181	188
0	294	-285

3,-3,L

-15	136	-147
-13	115	-122
-9	113	119
-8	320	-308
-7	307	-292
-6	122	125
-5	467	-441
-3	354	363
-1	379	-361
0	116	-102

3,-2,L

-16	78	-96
-15	116	-110
-14	151	155
-8	156	174
-6	262	258
-4	162	155
-3	306	307
-2	128	-127
-1	333	-336

3,-1,L

-16	0*	39
-12	107	-104
-11	149	150
-10	130	123
-8	188	165
-7	137	-134
-5	110	114
-4	149	-132
-3	319	319
-2	90	94

3,0,L

-13	278	281
-11	87	83
-9	536	-524
-7	636	-620
-5	543	570
-3	952	932
-1	676	-625

4,-16,L

-1	98	-102
0	147	167

4,-15,L

-2	95	107
0	175	178

4,-14,L

-10	119	112

4,-13,L

-1	161	168
0	158	-168

4,-12,L

-9	153	150
-7	0*	-48
-6	106	-99
-1	246	238
0	122	-122

4,-11,L

-12	92	103
-8	191	-190
-5	131	-155
-3	109	-111
-2	28*	44
-1	101	-109

4,-10,L

-6	179	197
-5	53*	-50
0	88	86

4,-9,L

-7	171	-158
-3	367	364
-2	125	-116

4,-8,L

-15	0*	-50
-8	186	201
-6	126	115
-4	238	-221
-3	171	158
-2	290	-278
0	110	99

4,-7,L

-7	178	167
-6	167	-157
-4	159	-158
-2	189	187

4,-6,L

-10	180	-171
-9	128	-138
-7	140	-120
-5	212	215

-4	181	207
-3	105	-104
-1	146	-124

4,-5,L

-13	108	90
-8	100	110
-6	132	116
-4	206	-221
-3	446	-439
-2	281	265
-1	142	-143
0	122	114

4,-4,L

-6	274	-267
-3	329	-298
-1	480	451
0	260	-227

4,-3,L

-11	142	-153
-7	168	168
-6	146	161
-3	502	-485
-1	417	367
0	285	-273

4,-2,L

-15	152	150
-6	118	139

-4	109	80
-3	193	-191
-1	274	264

4,-1,L

-10	0*	14
-9	135	133
-7	256	-251
-6	268	253
-3	140	156
-2	207	-178
0	197	190

4,0,L

-8	141	141
-4	417	-409
0	880	813

5,-19,L

0	0*	-31

5,-15,L

-2	0*	25

5,-14,L

-2	0*	-139

5,-12,L

-12	48*	-37

-9	59*	-60
-5	58*	143
-4	83	72
-3	100	-106
-2	191	178
-1	209	-210
0	7*	0

5,-11,L

-3	236	-231
0	119	108

5,-10,L

-7	65*	-89
-6	99	-88
-5	0*	-51

5,-9,L

-8	103	-92
-7	137	131
-6	112	112
-4	131	114
-2	194	-213
-1	92	94
0	100	-97

5,-8,L

-14	94	84

5,-8,L

-9	129	135
-5	184	-173
-2	164	-157
-1	279	267

5,-7,L

-11	137	137
-5	216	-198
-4	162	158
0	227	-223

5,-6,L

-16	63*	-69
-6	113	116
-5	78	75
-3	216	203
-2	98	-104
-1	88	90
0	263	253

5,-5,L

-8	156	172
-6	151	-156
-5	125	130
-4	400	-385
-3	290	298
-2	90	88

5,-4,L

-7	104	-110
-6	154	-158
-5	133	134
-3	162	166
-2	192	-183
-1	552	-546
0	34*	-8

5,-3,L

-12	101	-120
-7	199	224
-6	98	-109
-4	0*	-14
-3	56*	-80
-2	166	152
-1	224	-216
0	159	142

5,-2,L

-9	86	-80
-6	180	-210
-4	375	392
-2	115	114
-1	59*	63

5,-1,L

-8	177	-181
-6	119	125
-5	104	106
-4	382	392
-2	115	-107
-1	439	-414

5,0,L

-15	39*	-63
-13	155	-149
-5	393	-400
-1	150	140

6,-17,L

-7	39*	40

6,-14,L

-11	41*	-41

6,-13,L

-7	40*	-41
-2	72	68
-1	105	101

6,-12,L

-11	0*	19
-4	80	78

6,-11,L

-4	148	-135

6,-10,L

-7	101	-115
-6	160	-146
-3	153	170

6,-9,L

-10	0*	44
-7	168	166
-6	106	96
-2	0*	-38

6,-8,L

-5	173	-168
-4	110	104
-2	219	211
0	131	-135

6,-7,L

-11	113	-114
-9	169	-154
-8	122	-140
-5	149	138
-3	219	-226
0	225	-229

6,-6,L

-5	70	66
-4	250	-241
-1	197	185
0	137	136

6,-5,L

-9	156	175
-8	166	-177
-4	97	-109
-3	284	274
-2	196	190
-1	118	127

6,0,L

-14	129	-128
-12	92	-97
-8	47*	-53
-6	272	-291
-2	151	160
0	213	-200

6,-4,L

-17	0*	23
-10	175	-189
-6	257	270
-4	212	-223
-3	161	-153
-2	410	-387

6,-3,L

-8	152	148
-7	167	-161
-6	166	161
-5	131	-107
-4	230	-230
0	142	127

6,-2,L

-5	214	220
-4	187	176
-3	185	176
-2	167	159
-1	217	-198

6,-1,L

-6	147	-220
-5	113	124
-4	261	-265
-3	186	-195

7,-17,L

-3	58*	-48

7,-16,L

0	74*	-69

7,-15,L

-8	26*	22

7,-14,L

-5	58*	-37

7,-13,L

-4	0*	97

7,-12,L

-4	65*	-25
-1	52*	47

7,-10,L

-3	45*	25
-1	98	-88

7,-9,L

-3	76	-60
0	115	128

7,-8,L

-7	77	-56
-5	58*	87

7,-7,L

-9	96	-100

7,-6,L

-15	0*	5
-6	161	-158
-2	154	137

7,-5,L

-10	120	135
-4	196	208
-2	70	-51
0	71	-91

7,-4,L

-5	263	-262
-4	166	170
-2	247	-245
0	98	-112

7,-3,L

-8	156	-165
-6	0*	-176
-5	0*	-25
-4	120	111
-1	245	210

7,-2,L

-5	167	180
-4	144	131
-2	204	-203

7,-1,L

-8	122	139
-6	59*	84
-4	147	-151
-1	42*	56

7,0,L

-11	0*	138
-10	0*	0
-7	239	-258
-3	119	134

8,-15,L

-2	65*	4

8,-14,L

-6	0*	-18
0	0*	-1

8,-13,L

-5	62*	66

8,-12,L

-4	58*	-28

8,-11,L

-6	91	-85
-1	56*	-58

8,-10,L

-7	39*	62

8,-9,L

-9	0*	71
-5	114	-91

8,-8,L

-2	98	-62
-1	64*	-62

8,-7,L

0	121	122

8,-6,L

0	40*	-35

8,-5,L

-12	83	-76
-3	169	-153

8,-4,L

-13	0*	-15
0	63*	-72

8,-3,L

-4	65*	74

8,-2,L

-9	0*	-50
-1	164	134
0	70*	90

8,-1,L

-14	50*	-35
-8	133	101
-4	87	-92
-2	97	-98
0	198	-151

8,0,L

-2	163	-155

9,-8,L

-8	44*	-63

9,-7,L

-2	0*	12
0	0*	31

9,-5,L

-4	62*	-76

9,-4,L

-1	51*	-84

9,-3,L

-3	72*	-104

9,-2,L

-2	156	149

9,-1,L

-4	94	96
-3	0*	-118
0	207	-158

9,0,L

-7	107	132

10,-8,L

-3	0*	-37
-2	90	95

10,-6,L

-4	83	-62

Data for Dimethylsulphonium-2-(4-nitrophenylimino)-1,2-bismethoxy-carbonylethylide

Crystal Data

$C_{14}H_{16}N_2O_6S$, M = 340.2; monoclinic,

a = 9.698(1)Å, b = 22.545(2)Å, c = 7.744(1)Å,

β = 108.49(1)°, V = 1605.76Å^3; D_c = 1.41 g.cm^{-3},

Z = 4; F(000) = 712; space group $P2_1/c$ (C_{2h}^5, No.14);

M_0 - Kα radiation, λ = 0.7114Å, μ (M_0 - Kα) = 2.23 cm^{-1}.

-13,0,L		
2	52	-54
6	55	-52

-13,1,L		
1	43	37

-13,2,L		
6	38	-45

-13,7,L		
4	48	-41

-13,8,L		
2	36	-31

-12,0,L		
2	46	43
4	51	-46
6	51	52

-12,1,L		
5	36	-32
7	44	-44

-12,2,L		
3	42	-43
5	65	63

-12,3,L		
1	33	-30
3	21	19
5	30	-26

-12,4,L		
0	45	41
2	47	-39

-12,5,L		
0	37	-36
3	32	28

-12,6,L		
3	57	60
4	30	25
5	60	-53
7	48	49

-12,7,L		
4	30	-26

-12,8,L		
0	46	-40
2	47	44
3	31	28
5	36	-36
6	55	53

-12,10,L		
1	44	42
6	43	37

-12,14,L		
3	40	39

-12,15,L		
3	36	25

-11,0,L		
2	24	26

-11,1,L		
0	40	-41
1	68	-65
2	45	47
3	54	49
4	68	-66
5	108	-111
6	58	57
7	70	71

-11,2,L		
4	43	40
7	53	-52

-11,3,L		
0	41	-40
1	44	40
2	69	67
4	71	-69
5	43	-41
6	92	89
7	54	-49

-11,4,L		
2	70	-70
4	43	48
6	41	32

-11,5,L		
1	64	64
3	35	-37
4	79	77
7	47	-46

-11,6,L		
2	28	-36
3	29	-33
4	30	16
7	54	50

-11,7,L		
3	25	24
4	85	80
6	38	-29
7	43	51

-11,9,L		
1	38	-38
2	32	35
3	62	57
4	34	-32
5	67	-69
6	43	45
7	64	63

-11,11,L		
0	29	-27
2	70	66
4	65	-65
6	71	70

-11,12,L		
4	51	46

-11,13,L		
1	66	66
7	73	-69

-11,14,L		
2	51	-45
4	29	23
5	55	-48
6	32	28

-11,15,L		
4	70	60

-11,16,L		
2	58	-51
5	57	-51

-11,18,L		
3	24	-21

-10,0,L		
0	88	-98
2	48	-49
4	63	64
6	76	-75

-10,1,L		
0	38	36
2	86	91
7	101	102

-10,2,L		
0	42	-40
1	143	-154
3	46	40
4	72	-76
5	67	-64
7	97	96
8	41	-41
9	81	-83

-10,3,L		
1	62	-58
2	79	80
3	58	70
4	35	28
6	47	45
7	43	43

-10,4,L		
0	50	-46
1	37	-32
2	112	107
4	140	-142
6	109	112
8	109	-110
9	35	-34

-10,5,L		
1	35	-38
2	52	44
3	46	52
4	28	24

-10,6,L		
1	77	77
2	75	72
3	102	-103
4	56	-51

-10,6,L

5	122	122
6	53	51
7	86	-87
8	49	-51
9	56	60

-10,7,L

3	39	32
9	47	-39

-10,8,L

0	56	54
1	47	43
3	51	-50
4	40	35
5	71	70
6	68	-68
7	59	-61

-10,9,L

4	31	-27

-10,10,L

5	46	-54
6	36	-35

-10,11,L

2	43	40
4	36	-33

-10,12,L

1	52	-49
2	56	53
4	93	-87
6	53	48
8	48	-45

-10,13,L

1	50	-55
2	54	56
6	33	30

-10,14,L

3	89	-91
4	31	-33
7	82	-84

-10,15,L

3	42	-38

-10,16,L

0	41	41
3	76	-73
4	90	89
5	65	60

-10,17,L

3	45	-47
6	46	-42

-10,18,L

1	69	-68

-10,20,L

1	38	-30
2	32	34

-10,21,L

1	54	-52

-9,0,L

0	123	-130
2	193	207
4	66	-69
6	79	-79

-9,1,L

0	122	120
1	97	98
2	79	-72
3	145	-150
5	239	247
6	78	-80
7	91	-92
8	41	39
9	43	43

-9,2,L

0	119	-115
1	50	52
2	68	72
4	37	-47
5	52	59
6	40	-33

-9,3,L

0	102	97
2	74	-75
5	53	50
6	137	-136
7	89	88
8	29	22
9	83	-82

-9,4,L

0	39	-35
1	56	53
2	40	43
3	50	49
4	32	-35
5	60	63
6	57	-48

-9,5,L

4	105	-104
7	100	95
9	110	-110

-9,6,L

0	66	-64
2	51	52
3	46	46
4	48	-48
5	41	38
7	53	-51
8	35	31

-9,7,L

1	56	59
2	30	23
3	135	-136
4	52	-55
5	82	84
6	74	69
7	65	-68
8	63	-60
9	35	35

-9,8,L

0	90	-90
1	44	40
2	44	48
4	43	-43
5	37	29
7	34	-30

-9,9,L

1	120	116
2	71	-76
3	146	-142
4	106	111
5	119	117
6	37	-41
7	112	-117
9	70	71

-9,10,L

0	47	-47
1	106	110
2	56	58
3	101	-104
4	29	-20
5	57	49
6	88	-87

-9,11,L

1	47	-52
2	108	-104
3	38	-38
4	77	76
5	58	58
6	81	-81
8	46	44
9	48	-53

-9,12,L

2	38	38
5	53	58
6	103	-104

-9,13,L

1	42	-42
2	46	-48
3	37	35
4	83	-92
5	36	-27
7	73	72

-9,14,L

1	31	-35
3	62	66
6	61	-56

-9,15,L

0	29	-22
1	37	36
3	36	-36
4	130	-127
5	38	34
8	54	-49

-9,16,L

0	62	-57
2	38	35
8	40	36

-9,17,L

2	41	-41
3	113	-111
5	82	81

-9,17,L

6	31	-31
7	60	-61

-9,18,L

1	41	41
2	72	67
3	40	-34
4	35	36
7	23	-23

-9,19,L

0	58	60
1	71	-70
2	52	-50
3	45	-45
4	50	49
5	23	23
6	43	-42

-9,20,L

4	41	42

-9,21,L

0	37	38
1	45	-45
3	40	38

-9,22,L

2	52	-43
3	56	49

-9,23,L

1	40	36
2	46	42

-8,0,L

0	277	269
2	87	-80
4	184	-184
6	186	179

-8,1,L

0	133	-127
1	145	-148
2	173	-171
3	143	144
6	124	124
7	84	-83
9	87	-88

-8,2,L

0	92	90
1	268	275
2	49	-53
3	76	82
4	143	153
6	92	95
7	215	-225
9	114	119

-8,3,L

0	80	-82
1	167	170
2	59	-51
3	155	-171
4	33	-19
5	71	-67
6	50	50
8	36	-37

-8,4,L

0	102	106
1	55	47
2	129	-129
3	64	69
4	208	210
6	65	-65
7	54	-52

-8,5,L

0	88	89
1	203	211
2	70	-71
3	96	-101
4	71	71
5	37	-34
6	95	-100
7	33	34

-8,6,L

0	94	91
1	87	-83
2	77	-80
3	88	91
5	75	-73
7	86	89
8	25	-30
9	87	-89

-8,7,L

0	125	126
2	97	-95
3	92	85
4	47	52
5	84	-84
6	64	-68
8	24	21

-8,8,L

0	41	46
2	29	-30
4	57	-49
5	58	-54
6	87	86
8	88	-84

-8,9,L

1	91	-94
3	72	69
5	135	-143

-8,10,L

0	83	82
2	95	-93
3	128	-133
5	109	113
7	68	-65
9	124	126

-8,11,L

0	43	-38
2	50	-42
3	38	42
4	35	-40
6	43	38

-8,12,L

0	94	98
1	73	78
2	165	-166
3	56	63
4	111	103
7	77	-75
8	73	76
9	86	82

-8,13,L

1	78	84
2	155	-159
3	69	-67
4	45	43
5	39	-38

-8,14,L

1	45	-46
2	89	-83
3	130	132
4	85	84
5	57	-58
7	75	74

-8,15,L

0	46	46
2	107	-114
3	66	71
4	81	76
5	43	-45
6	51	-52
7	69	68

-8,16,L

0	28	-29
1	23	-20
3	76	72
4	80	-75
7	39	42
8	58	-61

-8,17,L

1	46	-42
3	183	178
7	89	86

-8,18,L

1	60	59
2	38	-38
4	58	-56
7	74	-79

-8,19,L

0	29	-33
3	92	88
4	36	-34
6	90	90
7	49	50

-8,20,L

1	52	45
2	85	-80
4	82	85
6	69	-71

-8,21,L

1	90	87
6	27	28

-8,22,L

2	65	-62
3	39	41
4	85	77
5	75	-70
6	42	-36

-8,24,L

3	28	30

-8,25,L

3	51	51

-7,0,L

0	348	371
2	195	-205
4	101	105
6	108	113
8	33	-26

-7,1,L

0	48	-30
1	38	-33
2	30	15
3	139	144
4	94	102
5	178	-181
7	103	-106
8	65	-65
9	54	55

-7,2,L

0	173	178
1	248	-256
3	36	39
5	262	-270
6	51	53
7	87	88
8	34	-35

-7,3,L

0	26	25
1	39	28
3	33	-23
4	64	65
5	90	86
6	55	54
7	177	-181
9	128	123

-7,4,L

0	101	-109
1	119	-121
2	89	93
3	109	-109
4	149	-162
5	165	-172
6	187	189
7	43	-37
8	89	-88

-7,5,L

1	33	-28
2	36	-33
3	47	-41
4	151	146
5	114	107
6	66	-62
7	126	-130
8	81	85
9	153	152

-7,6,L

0	29	-29
1	131	128
2	21	23
3	189	-195
4	55	-56
6	95	92
7	45	-46

-7,7,L

0	50	49
1	151	-164
3	98	99
4	40	33
6	115	-114
8	60	60

-7,8,L

0	92	90
1	45	38
2	160	-163
3	47	-43
4	33	32
5	30	32
8	60	60

-7,9,L

1	196	-194
2	80	74
3	113	108
4	27	-30
5	68	-71
7	62	63

-7,10,L

0	85	86
1	228	-232
2	35	-45
3	225	240
4	33	-30
5	83	-81
6	98	99
9	95	-96

-7,11,L

0	21	22
2	54	55
3	33	35
4	28	36
5	62	-64
7	103	-109
9	145	142

-7,12,L

0	73	-76
1	134	-137
2	60	57
4	155	-148
5	80	-90
6	204	211
7	37	39
8	90	-92

-7,13,L

4	228	239
6	41	-36
7	123	-123
8	56	52
9	130	125

-7,14,L

0	48	-49
2	87	90
3	168	-176
4	134	-137
6	82	85
7	34	-34
8	66	-65

-7,15,L

3	94	93
4	194	199
5	30	-34
8	101	99

-7,16,L

0	44	46
1	64	62
3	148	-152
6	57	-61
7	38	-43

-7,17,L

1	104	-110
2	62	60
3	138	141
4	66	-69
5	66	-65
7	53	55

-7,18,L

1	81	-81
2	66	-62
3	89	84
6	51	48
7	49	42

-7,19,L

0	44	-40
1	45	49
2	43	44
3	119	115
4	40	-43
5	37	-38
6	35	26
7	46	-48
8	56	-54

-7,20,L

0	86	-88
2	36	34
4	85	-84
5	83	-80
6	107	104
7	67	65

-7,21,L

0	63	-62
4	72	68
5	52	51
6	60	-57

-7,22,L

1	69	72
2	119	113
3	77	-80
4	93	-85
5	38	35
6	34	38

-7,23,L

1	67	-65
2	29	-22
4	38	37
6	92	-88

-7,24,L

0	46	44
1	39	39
3	50	-47
5	75	75

-7,25,L

3	63	66
5	40	-47

-7,26,L

2	51	-49

-7,27,L

2	39	39

-6,0,L

0	280	-280
2	61	-52
4	303	316
6	208	-211
8	128	-128

-6,1,L

0	211	211
1	472	491
2	56	65
3	390	-386
4	151	153
5	182	194
6	279	-274
7	37	36

-6,2,L

0	102	-106
1	292	-286
2	114	-102
3	59	-58
4	40	39
6	248	-259
7	238	243
9	105	-107

-6,3,L

0	217	231
1	87	-100
2	79	-82
3	162	172
4	189	185
5	98	96
6	266	-265
7	76	79
8	72	77
9	75	-81

-6,4,L

0	102	-102
1	36	-29
2	48	-46
3	55	60
4	51	46
5	53	-55
6	169	-168
8	102	106

-6,5,L

0	102	-102
1	150	-157
2	175	186
4	133	-138
5	101	-102
6	103	109
7	26	27
8	37	-41
9	62	-62

-6,6,L

1	159	-146
2	30	-24
3	88	-78
4	174	164
6	126	-127
7	57	-56
8	124	125
9	72	76

-6,7,L

0	189	-201
1	93	92
2	181	191
3	206	-210
4	161	-158
5	117	120
6	154	161
7	31	-29
8	67	-66

-6,8,L

0	81	-88
3	29	11
4	121	110
5	47	-42
6	162	-163
7	41	36
8	102	94

-6,9,L

1	298	302
2	65	-65
3	326	-330
5	294	299
6	27	-25
7	62	-58
8	105	107
9	55	54

-6,10,L

0	113	-106
1	142	-131
2	44	41
3	168	177
5	149	-155
7	99	98
9	123	-126

-6,11,L

0	111	116
1	43	48
2	145	-151
3	45	-52
4	162	172
6	131	-134
7	100	103
8	105	105

-6,12,L

0	147	-152
1	136	-132
2	71	73
3	21	10
5	40	-38
7	113	113
8	44	-56
9	64	-60

-6,13,L

1	153	-157
2	151	153
3	133	132
6	46	-53
7	101	105
8	34	-42
9	69	-68

-6,14,L

0	109	-107
1	60	63
2	53	47
3	49	47
6	52	-53
7	50	-49
8	46	47

-6,15,L

0	121	-118
1	101	103
2	179	185
3	178	-179
4	98	-102
6	100	102
7	38	-36
8	89	-88

-6,16,L

0	126	-133
1	76	-81
2	101	100
3	67	-66
4	155	150
5	39	41
6	49	-49
8	99	97

-6,17,L

0	91	87
1	106	103
2	155	158
3	268	-265
4	39	36
5	69	68
6	45	-47
7	142	-141

-6,18,L

0	79	88
1	61	-64
2	115	115
5	31	-39
7	85	84

-6,19,L

0	79	72
2	79	-80
3	121	-118
4	90	90
5	23	-22
6	125	-123
8	66	68

-6,20,L

0	43	42
1	45	-39
2	107	103
4	84	-82
6	46	43
7	71	74

-6,21,L

1	95	-98
2	57	-58
3	63	61
5	53	-54

-6,22,L

2	60	63
3	46	-47
4	41	-39
5	41	40
7	31	-31

-6,23,L

0	72	-69
2	71	70
4	86	-84
5	29	34
6	64	63

-6,24,L

3	40	-37
6	49	-47

-6,25,L

1	71	69
3	86	-86
5	82	77

-6,26,L

0	66	-64
2	32	28
4	54	52

-6,27,L

0	74	70
3	64	-60
4	49	50

-6,28,L

1	27	-28
2	46	45

-5,0,L

0	291	-297
2	131	-142
4	359	-361
6	78	79
8	101	-102

-5,1,L

0	442	-448
1	33	21
2	36	29
3	48	30
5	106	-107
6	60	59
7	87	87
8	50	42

-5,2,L

0	84	79
1	480	471
2	92	104
3	390	-390
4	44	-42
5	341	343
6	82	-81
7	98	-98
9	82	83

-5,3,L

0	307	-302
1	384	-391
2	124	-131
3	73	72
4	199	-201
5	172	-175
6	46	42
7	178	184
9	88	-85

-5,4,L

0	307	323
2	135	-152
3	36	26
4	394	393
5	222	217
6	400	-404
7	118	120
8	159	163
9	40	31

-5,5,L

0	77	61
1	407	-403
2	90	-93
3	178	171
4	358	-344
5	33	-35
6	51	45
7	148	153
9	111	-111

-5,6,L

0	42	44
1	555	-556
2	213	-202
3	570	558
4	174	168
5	101	-111
6	72	-76
7	146	146
8	37	30
9	73	-69

-5,7,L

0	53	-54
1	75	66
3	311	300
4	46	-44
5	64	-57
6	67	72

-5,8,L

0	141	-136
1	83	-81
2	222	241
3	141	143
4	42	-44
5	198	-194
6	197	199
7	68	72
8	170	-177

-5,9,L

0	69	-63
2	146	148
4	87	-88
5	58	60
6	48	-45
8	40	-33

-5,10,L

0	87	-88
1	278	282
2	32	-29
3	140	-139
4	67	-70
5	137	144
6	104	103
7	98	-100
8	64	-65
9	111	108

-5,11,L

0	246	-238
1	113	111
2	149	150
3	59	60
4	67	-71
7	115	113
8	85	-86
9	124	-122

-5,12,L

0	168	175
1	259	265
2	80	-88
3	31	-27
4	165	166
5	55	60
6	207	-209
7	67	-59
8	109	106

-5,13,L

0	63	-64
1	32	-40
3	67	-65
4	204	-203
5	70	-67
6	40	34
7	114	117
8	61	-64
9	82	-80

-5,14,L

0	104	101
1	53	-57
2	40	-38
3	238	242
4	149	146
5	40	-38
6	150	-153
7	112	109
8	66	61
9	70	-70

-5,15,L

1	207	-212
3	142	-147
4	196	-195
5	27	29
8	44	-43

-5,16,L

0	43	-43
1	281	-280
2	208	209
3	350	354
4	153	-152
5	42	41
6	78	80
7	73	73
8	84	-90

-5,17,L

0	181	176
1	120	125
2	85	-79
3	31	30
4	114	-118
7	52	-56
9	35	38

-5,18,L

0	66	-64
1	104	104
2	52	-49
3	98	-102
4	47	-53
5	32	38
6	82	89
7	83	-81
8	115	-111

-5,19,L

0	103	-100
2	57	58
3	111	-106
7	66	61
8	46	41

-5,20,L

0	112	110
1	50	46
2	45	-48
3	61	-62
4	79	77
5	99	99
6	80	-78
7	92	-87

-5,21,L

0	55	55
1	69	71
4	58	-58
5	44	-39
6	52	47
7	38	41
8	37	34

-5,22,L

0	42	38
1	72	-78
2	116	-111
3	60	62
4	93	88
5	62	-59

-5,23,L

0	55	58
1	23	19
6	65	62
7	33	-34

-5,24,L

0	63	-64
1	78	-77
3	85	80
4	24	-28
5	79	-76
6	79	78

-5,25,L

4	58	54

-5,26,L

0	37	-36
2	120	120
5	54	53

-5,27,L

0	65	59
4	35	-34

-5,28,L

0	51	46
2	57	-54
3	30	-27
4	31	37

-5,29,L

0	26	28
1	27	26

-4,0,L

0	166	184
2	194	190
4	61	62
6	69	68
8	170	168

-4,1,L

0	197	-191
1	797	-796

-4,4,L

0	36	-29
2	288	280
3	395	396
4	266	-267
5	296	-293
6	241	235
7	31	33
8	76	-74

-4,2,L

0	46	-53
1	417	413
2	324	331
3	32	-24
4	145	-144
5	87	81
6	211	211
7	162	-160
8	91	99

-4,3,L

0	220	-225
1	25	-13
2	403	389
3	192	-174
4	311	-311
6	349	359
7	206	-214
8	168	-176
9	85	88

-4,4,L

0	36	-29
1	111	114
2	221	222
3	159	-153
4	349	-331
6	159	162
7	27	-18

-4,5,L

0	42	40
1	27	-14
2	251	-242
4	178	173
5	296	298
7	145	-144
8	70	73
9	116	118

-4,6,L

0	99	-109
1	508	486
2	105	102
3	282	265
4	247	-243
5	53	-47
6	62	62
8	47	-43
9	36	-37

-4,7,L

0	37	-33
1	52	38
2	298	-273
3	58	62
4	162	157
5	177	-179
6	139	-146
8	145	147

-4,8,L

0	151	166
1	219	-213
2	77	-75
5	31	32
6	70	73
7	61	72
9	36	26

-4,9,L

0	221	-224
1	331	-331
2	111	96
3	430	418
4	87	-87
5	247	-253
6	141	138
7	58	48
8	115	-116
9	84	-89

-4,10,L

0	81	67
1	134	144
2	88	90
3	111	-111
4	110	110
9	79	77

-4,11,L

0	219	-222
1	112	117
2	282	299
3	101	-114
4	306	-303
5	104	98
6	226	230
7	117	-128
8	194	-192

-4,12,L

1	157	144
2	204	206
3	89	-99
4	70	-68
5	43	42
6	71	68
7	42	-39

-4,13,L

1	269	278
2	68	-70
3	195	-191
4	72	-68
5	143	150
7	193	-201
9	95	94

-4,14,L

0	19	-18
1	66	63
3	250	-250
4	81	-83
6	91	90
9	66	-64

-4,15,L

0	194	195
1	179	-191
2	34	-42
3	244	245
4	141	152
5	229	231
6	171	-172
7	67	-66
8	98	98

-4,16,L

0	338	341
1	268	272
2	197	-201
3	204	206
4	321	-315
5	175	-178
7	103	-98

-4,17,L

0	134	-134
1	53	-51
2	351	-354
3	181	180
4	57	-61
5	88	-80
6	151	153
7	139	132

-4,18,L

0	176	-181
1	84	88
2	221	-228
3	122	124
4	125	127
5	83	-84
6	40	-37
7	54	-50

-4,19,L

0	110	-114
1	122	130
2	154	158
3	73	-72
4	88	-88
6	119	115
8	99	-98

-4,20,L

0	138	-143
2	47	-50
4	22	-21

-4,21,L

1	187	192
2	58	59
3	171	-176
5	108	105
7	62	-66
8	52	-48

-4,22,L

1	27	-32
3	58	-58
4	71	-70
5	51	50
7	58	62

-4,23,L

0	77	81
2	167	-163
4	115	119
5	33	30
6	78	-78

-4,24,L

1	76	76
6	47	41

-4,25,L

1	42	-47
3	97	97
4	52	48
5	56	-62

-4,26,L

0	121	120
1	65	-58
2	55	-53
4	38	-37
5	45	-45

-4,27,L

0	69	-68
2	36	-29
3	100	94
4	53	-51

-4,28,L

0	60	-57
1	65	59
3	75	68

-4,29,L

1	136	128
3	70	-67

-4,30,L

0	54	-51

-3,0,L

0	26	-18
2	84	83
4	308	319
6	239	-251
8	180	179

-3,1,L

0	715	709
1	450	-479
2	127	-132
3	62	-63
5	55	-54
6	83	-85
7	185	191
8	48	48

-3,2,L

0	175	-170
1	746	-745
2	464	-468
3	455	449
4	66	-66
6	96	92
7	103	110
8	44	53
9	161	-167

-3,3,L

0	382	369
1	453	436
2	178	171
3	336	323
4	264	259
5	133	-127
6	85	82
7	61	-66
8	80	83

-3,4,L

0	172	-178
1	61	64
2	189	-179
3	134	-117
4	404	-389
5	59	-57
6	557	563
7	70	-70
8	207	-210
9	38	-33

-3,5,L

0	457	-453
1	434	406
2	293	300
3	167	170
4	476	452
5	247	-239
6	228	220
7	107	-109
8	105	-107

-3,6,L

0	231	235
1	647	642
2	272	278
3	687	-660
4	64	64
5	76	85
6	51	57
7	91	-90
8	128	-120
9	136	139

-3,7,L

0	175	-160
1	192	205
2	369	370
3	267	-247
4	94	-90
5	71	64
6	65	63
8	107	-111
9	80	-80

-3,8,L

0	264	279
1	187	174
2	238	-245
3	142	-136
4	181	179
5	198	202
6	296	-300
7	102	-105
8	147	149
9	36	39

-3,9,L

1	100	102
2	133	-120
3	230	235
5	91	-88
6	29	29
8	29	24
9	44	-40

-3,10,L

0	189	184
1	66	-59
3	42	41
4	170	172
5	229	-233
6	182	-186
7	44	42
8	70	67
9	108	-106

-3,11,L

0	488	478
1	149	-146
2	196	-201
3	32	-31
4	27	31
5	90	-90
6	84	-79
8	74	74
9	64	61

-3,12,L

1	198	-193
2	45	-46
3	114	-104
4	165	-162
6	157	150
8	110	-109
9	26	-29

-3,13,L

0	54	46
2	142	139
3	169	165
5	39	-39
6	36	47

-3,14,L

0	63	71
1	46	47
2	206	-208
3	305	-304
4	131	-130
5	111	98
6	190	193
7	162	-159
8	45	-31
9	57	49

-3,15,L

0	174	-174
1	287	300
2	161	160
3	113	114
4	31	34
5	59	-63
6	170	177
7	119	-121
8	48	-44

-3,16,L

0	198	200
1	212	216
2	392	-403
3	413	-415
4	243	250
5	127	-135
7	34	-31
8	125	128
9	80	83

-3,17,L

0	216	-217
1	29	-36
2	79	83
3	165	-169
4	231	238
5	75	77
6	67	66
8	111	-119

-3,18,L

0	103	112
1	156	-158
2	62	62
3	90	93
4	158	160
5	90	-91
6	186	-188
7	134	134
8	113	107

-3,19,L

0	220	220
1	45	-35
2	153	-157
3	108	110
6	83	-87

-3,20,L

0	73	-81
3	95	99
4	41	-39
5	65	-63
6	52	51
7	52	47

-3,21,L

0	91	-96
1	146	-146
3	45	45
6	34	-27

-3,22,L

1	98	101
2	87	88
3	43	-41
4	61	-61
5	89	86
6	58	59

-3,23,L

0	60	-62
2	101	98
4	38	-44

-3,24,L

0	111	115
1	75	79
2	91	-91
3	67	-63
4	43	43
5	63	57
6	109	-102

-3,25,L

1	58	56
2	60	59
3	62	-65
4	53	-49
5	73	74

-3,26,L

0	83	85
1	80	-72
2	140	-138
3	82	78
5	49	-56

-3,27,L

2	44	-43
4	108	104
5	50	-45

-3,28,L

2	60	61
5	93	-90

-3,29,L

1	66	-67
2	39	-35

-3,30,L

0	36	-41
1	41	40
2	53	47

-2,0,L

0	2508	-2842
2	915	919
4	395	-372
6	198	193
8	203	-206

-2,1,L

0	319	332
1	983	1003
2	516	501
3	38	30
4	200	200
5	274	274
6	195	-201
7	39	-37
8	77	77

-2,2,L

0	35	9
1	95	-86
2	239	246
3	159	-158
4	206	-199
6	45	-43
8	155	-155
9	65	69

-2,3,L

0	384	392
1	71	-66
2	215	-218
3	68	72
4	125	115
5	74	71
6	324	-338
7	196	206
8	140	148

-2,4,L

1	377	392
2	115	-114
3	89	81
4	230	226
5	101	99
6	52	-45
8	52	-56

-2,5,L

0	308	312
1	126	-118
2	372	348
3	247	-214
4	183	-183
5	146	-140
6	77	-72
7	102	104
8	122	-126

-2,6,L

0	25	-32
1	105	-110
2	106	-102
3	94	-92
4	60	-62
5	29	21
6	67	69
7	42	31

-2,7,L

0	230	223
1	49	-47
2	199	187
3	377	-357
4	72	55
5	146	137
6	127	138
8	163	-162
9	50	44

-2,8,L

0	577	-571
1	159	164
2	565	523
3	263	-245
4	418	-400
5	176	169
6	71	62
7	104	-108
8	94	-93

-2,9,L

0	153	154
2	217	-205
3	263	-262
4	167	161
5	126	128
6	95	-84
7	60	-56
8	97	100
9	82	82

-2,10,L

0	570	-560
1	182	181
2	198	197
3	88	-91
4	255	-255
5	249	251
7	85	-88
8	45	-45

-2,11,L

0	80	72
1	85	78
2	177	-176
3	189	185
4	295	293
5	152	-159
6	177	-180
7	32	37
8	181	181
9	76	-77

-2,12,L

0	155	177
1	143	-144
2	181	-187
3	235	-223
4	119	119
5	73	78
6	181	-185
8	59	52
9	66	67

-2,13,L

1	265	-265
3	209	203
4	34	-26
5	49	-46
6	51	46
7	85	89
9	90	-84

-2,14,L

0	185	186
1	106	-117
3	203	201
4	171	167
5	73	-62
6	89	-93
8	44	-49
9	59	59

-2,15,L

0	63	-66
1	37	45
2	39	-40
3	205	-201
4	255	-266
5	166	-164
6	81	88
7	32	32
8	100	-95
9	43	53

-2,16,L

0	293	-297
1	115	-115
2	209	218
3	199	-204
4	244	246
5	138	134
6	151	152
7	135	131
8	69	-67

-2,17,L

0	105	111
2	209	216
3	196	-194
4	69	71
5	85	77
6	248	-246
7	99	-96
8	36	-26

-2,18,L

0	112	-106
2	297	300
3	304	-310
4	154	-153
5	167	164
6	86	85
8	66	68

-2,19,L

0	79	81
1	274	-281
2	43	-52
3	64	67
4	101	98
6	115	-116
8	88	85

-2,20,L

0	163	166
1	64	70
2	46	-44
4	92	89
5	55	55
6	43	-46
7	72	-76
8	117	110

-2,21,L

0	63	-61
1	198	-212
2	38	36
3	140	137
5	89	-87
7	46	51
8	44	44

-2,22,L

0	102	106
1	65	-62
2	70	-78
3	108	107
4	103	105
5	65	-61
6	41	-45

-2,23,L

0	85	-92
2	151	154
4	77	-80
6	98	99

-2,24,L

0	47	-50
1	94	-95
2	67	60
3	58	53
6	26	-18
7	51	52

-2,25,L

1	33	34
3	90	-92
5	63	64

-2,26,L

0	96	-100
1	93	90
2	121	120
5	83	80
6	39	38

-2,27,L

3	65	-70
5	57	-49

-2,28,L

0	40	38
3	111	-104
5	64	61

-2,29,L

1	131	-121
3	54	51

-2,30,L

0	65	60

-2,31,L

0	77	-72
2	64	60

-1,0,L

0	98	-84
2	852	822
4	114	116
6	123	127
8	47	-49

-1,1,L

0	54	56
1	76	74
2	618	585
3	371	-346
4	492	-476
5	210	208
6	149	146
7	40	-41
8	78	-75

-1,2,L

0	109	-117
1	191	182
2	166	-176
3	350	317
4	274	254
7	77	-80
9	81	80

-1,3,L

0	871	-879
1	547	535
2	230	231
3	774	-730
4	194	-159
5	286	280
6	34	26
8	134	-142

-1,4,L

0	29	36
1	206	-195
2	314	315
3	520	488
4	398	378
5	119	109
6	449	-460
7	40	38
8	103	104

-1,5,L

0	825	841
1	1227	1248
2	355	-350
3	361	-349
4	112	-96
5	352	348
6	310	-303
8	96	100

-1,6,L

0	108	-113
1	277	269
2	210	-200
3	299	274
4	147	-122
5	31	21
6	144	-146
8	51	43
9	102	-102

-1,7,L

0	929	935
1	91	-97
2	951	-875
3	119	-121
4	374	354
5	93	-86
6	206	-203
8	127	128

-1,8,L

0	140	-149
1	195	-190
3	54	57
4	68	-63
5	20	-13
6	112	117
8	105	-106
9	47	42

-1,9,L

0	52	-51
1	300	278
2	70	-78
3	178	-160
5	98	-100
7	47	40
8	60	-61
9	36	-24

-1,10,L

0	208	-213
1	269	266
2	72	56
3	230	-225
4	46	-40
5	91	81
9	150	145

-1,11,L

0	349	-378
1	211	-211
2	172	172
3	367	-381
4	215	-228
5	163	158
6	111	107
8	83	-81

-1,12,L

0	160	-173
1	123	-126
2	68	-76
3	317	318
4	190	185
6	169	-162
7	39	38
8	151	148
9	43	42

-1,13,L

0	44	42
1	218	218
2	348	-339
3	371	-366
4	58	55
5	109	103
6	59	-59
8	46	36

-1,14,L

0	123	-132
1	118	-122
2	138	131
3	316	311
4	176	173
6	134	-145
7	106	110
8	45	41

-1,15,L

0	481	483
1	45	-47
2	377	-380
3	37	43
4	105	105
6	184	-189
7	164	162
8	83	81
9	41	-46

-1,16,L

0	136	-142
1	25	-15
3	232	236
4	126	-133
5	165	168
8	107	-106
9	50	-54

-1,17,L

0	46	-46
2	193	-196
3	241	244
5	113	-116
6	35	-23
7	92	92
8	77	77

-1,18,L

0	25	-29
1	113	112
2	114	119
3	68	-73
5	105	103
7	117	-121
8	60	-57

-1,19,L

0	128	-129
1	63	59
2	195	200
3	67	-69
4	147	-154
6	145	140
8	63	-67

-1,20,L

1	79	-94

-1,20,L

2	61	67
4	113	113
6	102	-98

-1,21,L

0	236	259
1	165	173
2	44	43
3	74	-71
4	114	-111
5	78	76
7	34	-24

-1,22,L

1	119	-127
2	158	-170
3	96	89
4	69	76
5	101	-100
6	49	-53

-1,23,L

0	92	94
1	83	87
2	146	-146
4	77	74
6	38	-40

-1,24,L

0	82	-83
2	38	40
3	28	29
5	75	-75
6	88	82

-1,25,L

0	78	79
1	143	-140
2	43	-45
3	70	70
5	125	-120

-1,26,L

0	58	-61
3	34	-34

-1,27,L

0	119	-109
2	81	82
4	86	-87

-1,28,L

2	27	-30
5	58	56

-1,29,L

1	79	78
2	53	49
3	75	-70

-1,30,L

1	61	-57

-1,31,L

0	182	174

0,0,L

2	744	-721
4	66	-67
6	347	-356
8	171	177

0,1,L

1	925	-897
2	1707	-1763
3	351	349
4	317	-311
6	234	238
7	188	-199

0,2,L

0	553	576
1	72	72
2	292	-272
3	640	619
4	374	366
5	405	-409
6	84	87
7	27	23
9	50	-51

0,3,L

1	253	244
2	153	-161
3	123	116
4	114	-108
5	236	-233
6	193	191
7	130	-138

0,4,L

0	123	-137
1	550	-554
2	194	203
3	122	-108
4	204	-208
5	309	-316
6	273	278
8	87	-83

0,5,L

1	155	-155
2	311	-306
3	175	175
4	97	90
5	107	-109
6	62	-67
7	48	50
8	127	127

0,6,L

0	254	-246
1	105	-91
2	101	-94
3	442	-445
4	52	-48
5	135	149
6	143	145
7	129	-117
9	59	58

0,7,L

1	780	-753
2	117	-117
3	437	414
4	55	-54
5	37	4
6	164	-173
7	45	38
8	89	87

0,8,L

0	695	674
1	65	64
2	1065	-1019
3	457	431
4	382	367
5	42	-40
8	132	133

0,9,L

1	85	86
2	332	325
3	51	53
4	100	94
5	116	-119
8	76	-79

0,10,L

0	1238	1208
1	663	-635
2	379	-386
3	84	90
4	51	52
5	172	-175
7	123	127
8	34	38
9	60	-59

0,11,L

1	762	-713
2	46	-46
3	146	133
4	41	-33
5	134	135
6	92	96
7	55	-62
8	76	-73
9	83	80

0,12,L

0	22	-16
1	69	69
2	284	288
3	562	547
4	332	-336
5	119	-123
6	196	198
8	121	-120
9	55	-55

0,13,L

1	67	80
2	137	-118
3	110	107
4	94	89
5	178	-190
6	23	25
8	59	60
9	39	37

0,14,L

0	150	-141
1	105	124
2	91	96
3	195	-197
4	212	-218
5	74	70
6	119	124
7	69	-74
8	54	-50

0,15,L

2	36	-47
3	231	230

0,15,L

4	193	201
5	74	-74
7	44	42
8	109	113
9	75	-75

0,16,L

0	147	144
2	184	-184
3	83	-90
4	37	-44
6	126	-124
7	111	-109
8	46	37

0,17,L

1	103	-111
3	271	274
4	50	-54
6	116	111
7	79	74
8	49	49

0,18,L

0	335	340
2	306	-316
3	269	269
4	32	29
5	120	-120
6	65	-64

0,19,L

1	121	127
3	101	112
4	77	-80
6	80	84

0,20,L

0	181	-186
1	50	-57
3	101	103
4	143	-132
5	94	-93
6	108	112
8	113	-110

0,22,L

0	139	-155
1	138	142
2	119	114
3	41	-48
4	78	-77
5	77	72
6	79	81
7	25	-34

0,23,L

4	22	20
5	66	-66
6	78	-78
7	65	64

0,24,L

0	87	90
1	78	76
2	59	-59
3	94	-117
5	85	83

0,25,L

3	71	101
5	59	-58
6	37	35

0,26,L

0	74	87
1	78	-82
2	138	-135
4	53	51
5	87	-85

0,28,L

1	38	-35
3	54	59
4	49	-49

0,30,L

0	66	-63

0,31,L

2	44	-46

1,0,L

2	1396	-1366
4	132	-128
6	121	129
8	48	51

1,1,L

1	314	324
2	613	-612
3	220	196
4	817	807
5	147	157
6	142	-141
7	207	-213

1,2,L

1	86	83
2	302	299
3	435	-426
4	55	-53
5	127	-119
6	105	-113

1,3,L

1	411	-399
2	201	-208
3	321	319
4	402	388
6	166	-167
8	70	72

1,4,L

1	117	112
2	83	69
3	180	-175
4	212	-211
5	135	-134
6	74	78
7	51	-49

1,5,L

1	921	-918
2	272	250
3	57	60
5	241	-254
6	174	169
8	68	-67

1,6,L

1	670	-683
2	492	469
3	39	40
4	49	41
5	155	-155
7	92	93
8	46	43

1,7,L

1	258	259
2	771	746
3	76	-69
4	356	-359
5	151	151
6	192	189
7	120	-122
8	81	-82
9	64	60

1,8,L

2	289	278
3	43	-50
4	85	-92
5	177	-180
6	81	-82
7	94	92
8	68	69
9	74	-70

1,9,L

1	237	-242
2	122	-126
3	266	-261
4	99	-96
5	300	314
6	33	-28
7	128	-122
8	139	142
9	97	96

1,10,L

1	364	-375
2	159	-143
3	161	160
4	43	-41
6	95	93
9	108	-108

1,11,L

1	212	182
2	276	-293
3	342	333
4	321	319
6	170	-171
7	63	-63
8	140	133
9	49	49

1,12,L

1	125	136
2	45	-46
3	284	-282
4	141	-138
5	92	-96
6	192	191
8	48	-45

1,13,L

1	299	-302
2	304	300
3	272	274
4	195	195
7	77	73
8	82	-77

1,14,L

2	66	70
3	62	-55
4	175	-176
5	139	-139
6	55	58

1,15,L

2	372	376
3	174	-175
5	95	88
6	140	142
7	68	-74
8	100	-95

1,16,L

1	19	-12
2	352	349
5	92	-95
8	57	58

1,17,L

1	137	144
2	221	224
3	276	-280
5	90	88
7	164	-163

1,18,L

4	119	-119
6	52	51
7	76	76

1,19,L

2	235	-237
3	48	52
4	217	222
5	45	-41
6	130	-131
7	101	-93

1,20,L

1	158	176
3	98	-104
4	113	-113
6	65	63

1,21,L

1	121	-132
2	124	-128
3	70	64
4	133	131
5	77	-74

1,22,L

1	69	78
2	200	205
3	112	-111
4	46	-45

1,23,L

1	86	-88
2	90	89
3	53	-61
4	102	-94
5	61	64
6	29	29

1,24,L

1	73	-79
2	54	59
4	61	-54

1,25,L

1	101	108
3	70	-69
5	149	143

1,26,L

2	87	85
4	23	-25

1,27,L

2	82	-87
4	70	72

1,29,L

1	48	-80
3	65	65

1,30,L

1	54	69

2,0,L

2	103	-95
4	176	162
6	167	164
8	179	-195

2,1,L

1	747	746
2	711	714
3	171	-184
4	173	167
5	358	-372
6	164	-167
7	215	222
8	48	-47

2,2,L

1	277	-283
2	211	-211
3	634	-628
4	63	-62
5	383	395
6	214	-217
7	70	73
9	89	91

2,3,L

1	92	88
2	265	-269
3	126	-125
4	70	-71
5	138	136
6	88	-85
7	97	96
9	45	-42

2,4,L

1	153	-144
2	573	-562
4	379	377
5	224	229
6	356	-359
7	73	75
8	141	145
9	34	29

2,5,L

1	285	282
2	72	-72
3	51	-55
4	141	-143
5	148	153
6	88	87
9	26	-31

2,6,L

1	349	-363
2	275	-277
3	344	345
4	336	340
5	220	-232
6	157	-156
7	167	161
9	61	-63

2,7,L

1	220	222
2	183	169
5	31	-21
6	114	115
7	81	82

2,8,L

2	510	493
3	75	-68
5	119	-122
6	36	34
7	49	41
8	113	-116
9	40	-41

2,9,L

1	54	26
2	209	200
3	62	68
4	179	-175
6	57	55
7	118	119
9	61	-55

2,10,L

1	270	275
2	116	112
3	78	74
4	103	95
5	84	79
6	27	27
7	142	-147

2,11,L

1	690	668
2	245	243
3	165	-158
4	86	-82
5	131	-132
7	65	65
9	49	-30

2,12,L

2	354	-348
3	256	-252
4	331	329
5	79	80
6	165	-164
8	94	92

2,13,L

1	218	226
2	64	57
3	266	-272
4	38	-40

2,13,L

5	121	125
6	76	-76
8	74	-75

2,14,L

1	130	-132
2	135	-140
3	259	260
4	171	165
5	79	-71
6	143	-141
7	125	126
8	71	70

2,15,L

1	170	161
2	98	-98
3	192	-195
4	131	-130
8	43	-48

2,16,L

1	77	-72
2	73	70
3	116	119
5	45	-42
6	69	70
7	108	105

2,17,L

1	23	18
2	129	128
3	138	-143
4	41	-32
5	62	-59

2,18,L

2	214	220
3	166	-162
5	71	74
6	68	64

2,19,L

1	34	-36
2	169	171
3	139	-137

2,20,L

2	71	-76
3	78	-79
4	135	137
5	82	80
6	77	-76

2,21,L

1	137	141
2	31	38
3	116	-116
4	45	44
5	58	62
6	29	-32

2,22,L

1	101	-106
2	109	-104
3	66	68
4	52	51
5	62	-61
6	71	-65

2,23,L

1	77	81
2	80	-80
3	80	-78
4	48	47
5	41	41

2,24,L

1	94	-93
2	65	62
3	96	95
5	69	-67

2,26,L

1	63	62
2	101	99
5	76	71

2,27,L

1	38	37
4	42	-36

2,28,L

3	60	-61
4	52	54

2,29,L

3	40	-45

3,0,L

2	258	243
4	81	81
8	44	-47

3,1,L

1	504	-485
2	255	272
3	225	212
4	322	-323
5	206	-211
6	69	72
7	185	191

3,2,L

1	286	292
2	229	209
3	292	295
4	34	-30
6	129	131
9	74	-80

3,3,L

1	407	-412
2	275	263
3	65	-66
4	196	-190
5	51	-54
6	106	105
8	66	-66

3,4,L

1	183	180
2	291	291
3	100	96
4	62	-69
5	72	67

3,5,L

1	173	-156
2	41	44
4	65	-56
5	87	89
6	84	-79
7	40	-38
9	66	66

3,6,L

1	261	265
2	215	-194
3	61	-65
4	162	-162
5	232	240
7	74	-74

3,7,L

1	168	-164
2	333	-338
3	301	285
4	78	81
5	197	-196
6	72	-73
7	66	64
8	67	65

3,8,L

1	157	144
2	166	-154
3	69	-67
5	142	138
6	37	43

3,9,L

1	86	-84
2	141	140
3	217	218
4	78	-75
5	235	-236
6	92	92
7	80	79
8	91	-93

3,10,L

1	166	-162
2	91	97
5	52	-48
7	80	84
8	47	-39

3,11,L

1	62	-64
2	178	180
4	264	-257
5	28	27
6	148	144
8	98	-96

3,12,L

1	118	106
2	237	240
3	110	117
4	48	49
5	40	39
8	53	-48

3,13,L

1	55	55
2	102	-92
3	108	-104
4	157	-157
5	85	80
6	44	-48
7	79	-77
8	46	44

3,14,L

1	298	312
3	94	-95
4	94	93
5	110	111
7	71	-68

3,15,L

1	190	-190
2	117	-117
3	48	56
4	34	-30
6	119	-117
7	29	27
8	47	47

3,16,L

2	191	-194
4	38	40
5	91	88
7	72	-66

3,17,L

1	54	-47
3	204	200
4	107	-109
5	61	-57
7	105	103

3,18,L

1	39	-41
2	255	-254
3	96	96
5	23	-34
6	40	-31

3,19,L

1	40	40
2	154	160
3	58	-58
4	133	-131
6	86	86
7	58	57

3,20,L

1	193	-200
3	92	95
4	46	-39

3,21,L

1	94	99
2	60	65
3	63	-62
4	49	-48
5	46	45

3,22,L

2	59	-62
5	60	59

3,23,L

2	86	-83
4	70	71

3,24,L

1	42	39
2	86	-83
3	30	-28
4	65	61

3,25,L

1	53	-55
3	86	84
5	88	-84

3,26,L

1	37	-39
2	44	-44
4	59	56

3,27,L

2	78	76
4	52	-56

3,28,L

1	115	-114
3	58	56

3,29,L

1	86	80
2	26	23

4,0,L

2	129	131
4	54	-54
6	46	-46
8	145	154

4,1,L

1	72	-57
2	59	-64
3	236	-247
4	36	35
5	188	193
6	54	53
7	70	-76
8	54	47

4,2,L

1	44	-44
2	234	227
3	92	92
4	122	-126
5	92	-90
6	125	123
8	42	47

4,3,L

1	228	-228
2	45	40
3	114	119
4	147	156
5	38	-44
6	84	87
7	32	-33

4,4,L

1	67	67
2	365	356
3	83	-83
4	247	-241
5	41	-36
6	170	172
8	50	-52

4,5,L

1	472	-459
2	22	18
3	148	150
4	54	60
5	54	-56
6	90	88

4,6,L

1	346	336
2	266	264
3	39	-36
4	78	-78
5	143	145
6	61	58

4,7,L

7	111	-111

4,8,L

1	77	73
2	59	-66
5	59	57
6	52	-53
7	52	-43
8	65	62

4,9,L

1	135	146
2	194	-197
3	117	-118
4	81	84
5	87	89
6	56	-51
7	115	-116

4,10,L

1	159	158
2	44	48
4	49	-49
5	84	-89
6	39	-39
7	46	47

4,11,L

1	133	-128
2	128	-136
4	63	57

4,12,L

2	171	163
3	53	-56
4	165	-163
5	35	-33
6	54	54

4,13,L

1	201	-202
2	87	83
3	154	165
4	39	-27
5	81	-79
6	55	61

4,14,L

2	37	-29
3	309	-306
4	127	-122
5	51	50
6	28	29
7	54	-57

4,15,L

2	133	138
3	103	101
5	134	134
6	96	92

4,16,L

1	111	109
4	52	-46
6	82	-75
7	72	-71

4,17,L

1	153	157
2	308	-301
3	49	-46
5	123	123
6	57	56
7	63	-56

4,18,L

2	158	-154
3	135	137
4	97	94
5	73	-71

4,19,L

1	107	108
2	123	-121
3	40	40
4	68	66
6	37	-27

4,20,L

1	44	43
3	44	46
4	41	-42
5	47	-47
6	33	35

4,21,L

1	90	-93
2	38	39
3	95	94
5	34	-43

4,22,L

1	65	65
3	40	-44
4	42	-42

4,23,L

1	86	-88
2	91	89
4	65	-60

4,24,L

1	49	56
2	75	-68

4,25,L

1	83	79
2	45	34
4	27	21

4,26,L

1	57	-47
2	51	-50

4,27,L

2	117	-109

5,0,L

2	261	268
4	52	-58
8	56	-52

5,1,L

1	252	256
2	37	36
5	111	114
6	55	-54

5,2,L

1	141	145
2	106	-106
3	196	-204
5	118	119
7	69	-68

5,3,L

1	278	276
2	32	15
3	141	146
4	40	-41
6	77	-82

5,4,L

1	121	135
2	379	-380
3	98	-97
4	35	37
5	40	-40
6	34	36

5,5,L

1	168	167
2	38	-28
4	99	98
5	71	-68
6	30	24
7	33	27
8	39	-43

5,6,L

1	36	-21
3	36	34
4	47	43
5	198	-205
7	33	36

5,7,L

1	72	-80
2	67	69
3	270	-250
4	88	93
5	51	49
8	29	-31

5,8,L

1	212	-211
2	100	102
4	106	-111

5,9,L

1	55	-54
2	98	-105
3	42	-35
4	112	116
5	46	45

5,10,L

1	176	183
3	116	-124
4	35	-29
5	124	128
7	86	-82

5,11,L

1	28	24
2	43	-41
3	48	55
4	99	101
5	53	-50

5,12,L

1	36	-30
2	202	-203
3	118	-123
4	61	62
5	74	68
6	79	-75

5,13,L

1	39	42
2	58	52
3	112	119
5	67	-66

5,14,L

1	248	-243
2	114	-121
3	58	55
5	43	-46
7	43	43

5,15,L

1	133	139
2	37	37
3	113	108
5	37	-34
7	45	-48

5,16,L

1	57	61
2	37	38
3	56	-61
4	40	-37
5	131	-131
6	73	73

5,17,L

1	118	-118
2	60	-60
3	117	-108
4	124	126

5,18,L

1	63	66
2	202	205
3	120	-124
4	51	49

5,19,L

1	127	-128

5,20,L

1	132	133
2	70	-72
3	59	-60

5,20,L

4	83	81
5	47	44

5,21,L

1	64	-66
3	28	30

5,22,L

1	45	-43
2	61	-57
3	38	42
4	56	57
5	26	-35

5,23,L

2	57	55

5,24,L

1	43	-42
2	70	64
3	59	56

5,28,L

1	106	102

6,0,L

2	89	-89

6,1,L

2	83	79
3	90	94
4	55	-59
7	42	43

6,2,L

1	37	-39
2	47	-39
3	52	60
4	52	55

6,3,L

1	231	234
2	42	47
3	155	-161
4	91	-94
5	73	71

6,4,L

1	43	-28
3	72	71
4	53	54
5	43	38

6,5,L

1	402	407
2	58	-60
3	157	-160
4	59	58
5	89	89
6	109	-112

6,6,L

1	37	-30
2	22	9
3	44	-45
4	43	-48
5	22	-19
6	33	-27

6,7,L

1	81	-87
2	143	-150
3	40	45
4	93	91
6	82	-81

6,8,L

1	18	9
3	30	-23

6,9,L

1	156	-162
2	40	39
3	84	81
5	83	-86
7	57	57

6,10,L

1	81	-81
2	29	-36

6,11,L

2	50	45
3	42	-45
4	54	-50

6,12,L

2	34	-28
3	55	58

6,13,L

1	83	89
2	127	-133
3	165	-166
5	58	52

6,14,L

1	48	46
2	68	63
3	165	160
4	57	59
6	36	34

6,15,L

1	126	125
2	134	-137
3	63	-60
4	53	52
5	122	-123
6	80	-78

6,16,L

1	51	-42
3	66	-69
4	56	54
5	79	77
6	52	49

6,17,L

1	132	-136
2	140	141
3	109	109
4	46	48
5	84	-80

6,18,L

2	109	109
3	80	-79
5	50	46

6,19,L

1	64	-67
2	87	82
3	39	35
4	53	-51

6,20,L

1	31	-29
2	46	44

6,21,L

1	52	52
3	51	-48

6,23,L

2	55	-57

6,25,L

1	78	-73

7,0,L

2	85	-89
4	143	143
6	76	-73

7,1,L

1	35	28
2	47	-51
3	90	-90
5	37	-40
7	42	-43

7,2,L

1	226	-231
3	120	123
4	69	71
5	125	-131
7	51	50

7,3,L

1	38	-17
2	99	-95
3	61	-65

7,4,L

1	132	-135
2	117	114
3	24	26

7,5,L

4	90	-95
5	29	29

7,6,L

1	53	51
2	69	-68
3	56	-53
5	100	106

7,7,L

1	57	57
2	37	-24
3	38	42
4	73	-77

7,8,L

2	184	-183
4	103	104

7,9,L

1	70	70

7,10,L

1	91	-94
2	42	-41
3	150	154
4	58	56
5	73	-74

7,11,L

1	47	-44
3	54	-53
4	30	29

7,12,L

1	91	-89
2	135	134
3	137	137
4	43	-41
5	51	-44

7,13,L

3	26	-29

7,14,L

1	61	64
2	81	78
4	35	-34

7,15,L

1	34	30
3	43	-44
4	41	-38

7,16,L

2	78	-70
5	78	75

7,17,L

1	107	109
4	59	-63

7,18,L

1	46	-45
2	97	-97
3	64	64

7,19,L

1	42	46

7,20,L

1	112	-109
2	42	42
3	56	50
4	43	-40

7,24,L

1	49	47
2	39	-40

8,0,L

2	76	76
4	82	-83

8,1,L

1	163	-166
2	106	-105
5	63	63

8,2,L

1	65	61
2	28	-20

8,3,L

1	147	-145
2	55	-50
3	89	92
4	67	70
5	65	-60

8,4,L

1	41	-28
2	41	-39
4	29	25

8,5,L

1	178	-179
2	86	88
3	95	95
4	34	-24
5	84	-86
6	45	48

8,6,L

1	94	-99
2	30	19
5	27	-28

8,7,L

1	46	-41
2	91	97
4	72	-69
6	50	48

8,8,L

1	46	-39
2	43	44

8,9,L

1	46	40
5	59	59

8,10,L

1	23	32
3	43	-42
4	28	-29

8,11,L

1	121	-118
2	41	-38
3	52	54
4	36	38
5	25	26

8,13,L

1	98	-97
2	60	64
3	97	98
5	25	-9

8,14,L

1	54	-57
2	36	-28

8,15,L

2	111	108

8,16,L

2	43	37
4	58	-57

8,17,L

1	46	51
3	48	-45

8,19,L

2	69	-64

8,20,L

1	47	46

8,21,L

2	41	-35

9,0,L

2	53	-56
4	106	-108

9,1,L

3	56	58

9,2,L

1	98	101
3	72	-76

9,4,L

3	28	-23
4	29	29

9,5,L

1	58	-58
2	44	43
5	41	-46

9,6,L

1	35	-33

9,7,L

2	105	99

9,8,L

2	71	73
4	24	-23

9,9,L

3	51	-48

9,10,L

1	98	98
2	74	73

9,11,L

9,12,L

2	68	-67
3	47	-49

9,13,L

1	74	66
3	36	-36

9,16,L

2	60	60

9,17,L

1	48	-50

9,19,L

2	34	33

9,20,L

1	59	57

9,21,L

1	37	33

10,0,L

2	80	-81
4	91	89

10,1,L

1	66	75
2	62	59

10,3,L

2	50	46

10,4,L

1	38	36
4	39	-37

10,5,L

1	41	39

10,6,L

1	71	76

10,7,L

1	33	28

10,8,L

2	59	-58

10,10,L

1	47	-39

10,11,L

1	68	65

10,13,L

1	32	31

10,14,L

1	55	56

10,16,L

1	34	38
2	53	-51

11,0,L

2	54	59

11,2,L

2	32	35

11,3,L

1	54	-51
2	29	-22

11,5,L

1	48	-43

11,8,L

1	28	28

11,9,L

2	30	-33

11,10,L

1	37	37

11,11,L

1	51	-52
2	39	-41

11,13,L

1	65	-55

12,6,L

1	25	-29

Data for Dimethylsulphonium-2-(3-nitrophenylimino)-1,2-bismethoxy-carbonylethylide

Crystal Data

$C_{14}H_{16}N_2O_6S$, M = 340.2; monoclinic,

a = 13.870(2)Å, b = 8.522(1)Å, c = 13.971(3)Å, β = 105.47(1)°,

V = 1591.55Å^3; D_c = 1.42 g.cm^{-3}, Z = 4; F(000) = 712;

space group $P2_1/c$ (C_{2h}^5, No.14); M_0 - $K\alpha$ radiation, $\mu(M_0 - K\alpha)$ = 2.24 cm^{-1}.

λ = 0.7114Å.

-18,0,L

4	62	-58

-18,2,L

5	46	40

-17,0,L

2	103	97
4	90	90

-17,1,L

2	83	-77
4	80	-78
5	67	-63
8	89	83

-17,2,L

1	59	55
5	44	43
7	42	39

-17,3,L

8	64	-60

-17,4,L

6	48	-39

-16,0,L

2	95	-98
12	109	109

-16,1,L

1	38	38
2	148	147
10	61	62
11	63	-66

-16,2,L

4	59	-55
5	58	-57
10	44	42

-16,3,L

2	77	-76
6	119	113
8	47	49
10	69	-62

-16,4,L

4	80	80

-15,0,L

2	217	-215
4	53	-51
6	87	90
8	107	109
10	91	-93
12	84	-96

-15,1,L

1	55	59
3	60	57
6	78	78
7	71	-68
8	65	-64
10	72	-68
11	58	65

-15,2,L

3	49	48
5	89	88
8	103	-99

-15,3,L

4	80	-80
6	59	-61

-15,4,L

5	107	-103
7	64	-59
12	64	-59

-15,5,L

4	51	49
6	58	54
7	54	57

-15,6,L

1	77	-74
6	68	-64

-14,0,L

2	72	70
6	76	-80
10	69	68

-14,1,L

1	101	-101
2	119	123
3	109	-106
4	91	-90
6	47	-53
11	58	60
12	70	-70

-14,2,L

3	97	-98
4	104	101
6	122	121
7	66	68
9	53	52
10	92	-89
12	52	-47

-14,3,L

4	107	102
5	62	58
6	55	-56
8	142	-136

-14,4,L

1	38	-46
2	67	68
4	58	-61
6	112	-108
10	98	88

-14,5,L

2	58	-56
4	89	-87
10	70	68

-14,6,L

1	84	80
5	84	-81
6	66	57

-14,7,L

1	85	-82
5	61	59

-13,0,L

2	43	-45
4	38	-37
10	66	76
12	96	94
14	96	90

-13,1,L

2	279	273
4	52	58
5	96	96
6	56	-57
8	68	-71
9	50	-56
10	160	163
11	97	-99
12	84	85

-13,2,L

4	65	-60
5	49	51
6	70	-70
8	90	92
9	118	-124
10	59	61
14	70	-65

-13,3,L

2	121	-122
4	144	-147
5	77	-79
8	80	73
11	65	64

-13,4,L

3	71	-67
4	165	170
6	109	111

-13,5,L

1	58	-55
2	64	64
7	61	-59
9	115	-110
11	87	-86

-13,6,L

3	61	56
4	97	-87
6	59	-55
7	54	-59
8	88	85
9	51	49
11	75	71

-13,7,L

1	76	74
2	43	-31
8	48	-45

-12,0,L

2	50	-50
4	195	-194
6	99	-104
8	88	89
10	90	98
14	59	-57

-12,0,L

16	69	66

-12,1,L

3	127	-133
5	78	83
6	154	152
7	109	113
8	54	-63
10	203	-197

-12,2,L

1	171	171
2	85	88
3	125	-120
4	201	206
5	131	-130
6	84	-85
8	149	-149
12	87	90
13	72	69

-12,3,L

1	130	125
2	71	-68
3	216	222
4	86	-85
5	44	48
6	31	30
8	71	68
10	103	99
11	62	-61

-12,4,L

2	107	-106
3	83	82
4	110	-112
5	51	-56
6	85	86
9	56	49
11	81	77
13	58	-60

-12,5,L

2	103	-98
3	137	-136
4	98	101
5	127	-121
9	90	94
10	68	-70
13	89	-84
14	68	63

-12,6,L

4	75	76
5	45	45
6	127	-122
8	106	-108
12	67	66

-12,7,L

3	73	74
5	88	89

-12,8,L

1	78	76
5	64	-62

-11,0,L

2	164	163
6	45	-50
10	86	90

-11,1,L

2	61	56
4	56	-63
6	62	-61
7	92	-95
8	138	135
11	71	71
12	50	-52

-11,2,L

2	161	-164
3	118	-112
4	111	108
5	186	-174
6	248	255
7	93	94
9	155	152
10	207	-209
11	91	94
12	84	-91
13	79	-81

-11,3,L

2	63	60
3	63	61
4	91	88
6	60	58
8	204	-208
9	82	82
10	129	-126
11	80	80
14	51	49

-11,4,L

1	73	-77
2	81	78
3	35	36
4	107	-110
5	168	164
6	199	-199
7	40	42
8	96	-98
9	50	-50
13	87	83

-11,5,L

1	84	86
2	95	-104
3	75	79
4	119	-118
5	65	-59
8	176	185
9	70	79
10	83	84

-11,6,L

1	52	57
4	49	45
7	56	-57
8	57	-64

-11,7,L

1	79	-80
3	143	-143
4	73	64
7	88	82

-11,8,L

1	50	-47
3	54	61
9	58	-56

-10,0,L

2	243	-250
4	261	256
6	259	269
8	253	-255
10	154	-154
12	140	146
14	80	89
16	54	51

-10,1,L

1	85	85
2	254	265
3	146	-151
4	220	223
5	61	-59
8	120	-119
9	73	79
10	145	144
12	163	169
16	104	-100

-10,2,L

1	111	111
2	186	194
3	129	134
4	71	70
5	154	-157
7	128	-128
8	62	60
9	128	-130
12	128	-133
14	66	-65
16	57	-52

-10,3,L

1	79	85
2	280	-284
3	216	219
4	197	-202
5	158	-168
6	154	157
7	69	-69
8	83	86
9	79	-84

-10,4,L

1	80	-88
2	91	-93
3	54	-60
5	165	166
7	243	243
8	159	161
9	150	154
11	64	-66
12	82	85
13	62	-64

-10,5,L

1	172	-178
2	177	182
3	103	-109
4	143	152
6	150	-152
7	128	-128
9	74	-78
13	74	69

-10,6,L

3	59	61
4	57	-54
6	55	62
7	130	-131
8	57	60

-10,6,L

9	61	-57
11	69	67
12	87	-87
13	95	88
14	57	-58

-10,7,L

1	42	45
2	72	-72
4	61	-65
6	90	84
7	37	-36
10	65	-60
11	66	65
12	102	-92

-10,8,L

1	59	-63
4	52	49

-9,0,L

2	52	-45
4	406	-393
6	115	-116
8	216	226

-9,1,L

1	80	74
2	235	-231
4	99	-71
5	176	169
6	162	159
7	60	54
8	40	43
9	95	-94
10	112	-125
11	65	-67
12	76	-76
13	54	-56

-9,2,L

1	142	-147
2	168	173
3	58	-57
4	31	43
5	87	92
6	109	-106
8	167	-173
9	84	-83
10	129	127
12	106	110
13	41	48

-9,3,L

1	205	-202
2	282	289
3	256	263
4	68	-75
5	111	118
6	98	-103
7	216	-219
8	107	105
9	215	-217
10	135	138
13	102	101
14	128	-125

-9,4,L

1	57	61
2	94	-97
3	78	71
4	169	-176
5	116	116
8	353	354
9	89	-89
12	141	-133
16	84	79

-9,5,L

3	126	-133
4	140	144
5	77	-86
7	65	65
9	50	48

-9,6,L

1	108	-111
3	127	-129
8	72	-70
11	111	-107
12	71	66

-9,7,L

2	122	130
3	88	87
5	74	72
6	59	-60

-9,8,L

1	64	61
2	70	-69
5	46	-50
9	51	54

-9,9,L

1	65	58
8	79	-72

-8,0,L

4	243	-252
6	346	-349
8	184	-179
10	287	292
14	57	-55
16	71	-71
18	98	93

-8,1,L

1	126	128
2	77	-83
3	62	-62
4	347	-341
5	153	-150
7	53	-54
8	207	212
9	36	-42
10	84	86
12	48	-53

-8,2,L

1	74	75
2	41	39
3	204	206
4	115	114
5	162	-160
6	238	242
7	153	-145
8	40	36
9	194	-196
10	136	-140
11	121	125

-8,3,L

1	85	-92
3	71	-82
4	180	187
5	307	300
6	267	276
7	267	274
10	288	-287
11	141	-139

-8,4,L

1	59	-69
3	88	90
4	115	-119
5	154	151
6	587	-601
8	250	-251
9	164	163
12	96	97

-8,5,L

3	114	114
4	76	-77
7	68	73
9	162	165
10	56	52
11	143	140

-8,6,L

1	236	255
5	180	-183
6	214	227
7	92	-97
9	77	78
12	50	-50
13	101	-101
14	72	68

-8,7,L

1	56	-53
2	86	-96
3	72	-74
4	59	51
7	81	73
8	61	-57
11	94	-92
12	102	95

-8,8,L

1	100	-101
5	100	94
9	97	-98

-8,9,L

6	41	41
8	67	72

-8,10,L

3	33	-28

-7,0,L

2	297	-301
4	63	-61
6	372	361
8	140	-142
10	266	-265
12	125	-122
14	124	123
16	66	69

-7,1,L

1	165	-177
2	514	511
3	96	-89
5	55	59

-7,1,L

6	72	-76
8	119	-114
9	89	90
10	205	221
11	161	170
12	150	157
13	57	62
16	56	-47

-7,2,L

1	236	228
2	444	430
3	72	79
4	39	-50
5	296	-298
6	291	-293
9	78	-77
10	59	56
14	129	-130
17	43	-41

-7,3,L

2	107	-102
3	240	-231
5	329	-342
7	52	-45
10	219	-219
12	72	-69
16	88	89

-7,4,L

1	233	233
2	163	-166
3	102	-107
4	288	287
5	128	133
6	135	139
7	183	179
9	101	103
11	55	-57
12	109	106
13	115	-114
16	88	-89

-7,5,L

1	78	-94
2	85	84
3	138	-152
4	220	227
5	97	96
6	66	-69
7	220	217
8	217	-218
11	141	-136
12	115	117
15	76	69
16	83	-80

-7,6,L

1	60	-51
2	192	195
5	67	-65
7	127	-128
14	88	-76

-7,7,L

1	83	89
2	148	-151
4	77	-78
5	99	-105
7	72	-77
8	71	73
9	119	121
11	87	95
12	80	-77

-7,8,L

3	68	-67
4	98	92
7	84	84
8	110	-112

-7,9,L

1	68	-63
2	89	89
5	44	37
7	65	63

-7,10,L

3	67	62

-6,0,L

2	760	-751
4	477	-468
6	160	150
8	170	165
10	140	142
12	78	-84
18	36	-40

-6,1,L

1	357	362
2	300	-310
4	373	-365
5	437	-433
6	288	-259
7	148	-143
8	177	-180
9	141	151
10	149	-146
11	152	153
12	92	93
13	124	-126
16	76	77

-6,2,L

1	77	70
2	189	-182
3	199	200
4	483	478
5	234	226
6	330	328
7	96	91
8	212	-209
9	103	-109
10	194	-190
11	128	-130
12	247	253
14	132	135
15	49	50
18	61	-57

-6,3,L

2	242	260
4	137	-134
6	259	-256
7	92	-94
8	153	158
10	201	201
11	187	-196
14	85	-77

-6,4,L

4	120	-125
5	161	-167
6	121	124
7	77	-78
8	186	188
11	87	86
12	124	-113
15	51	-54

-6,5,L

1	118	116
5	235	-245
6	285	289
8	71	-69
9	72	73
10	184	-185
12	105	-103
14	101	99

-6,6,L

1	195	-199
4	146	143
5	52	61
7	149	-149
8	107	107
9	57	-50

-6,7,L

1	69	-73
3	152	155
5	173	174
6	75	-70
7	161	-167
8	107	111
9	233	-238
10	59	62

-6,8,L

2	34	36
3	89	90
4	66	-72
6	59	55
11	77	76

-6,9,L

3	103	-106
4	51	-52
5	79	-83
9	74	77

-6,10,L

6	66	-58
7	62	61

-5,0,L

4	576	-562
6	78	-75
8	131	-132
10	380	396
14	117	-127
18	83	77

-5,1,L

1	375	-367
2	311	-312
3	175	-178
4	484	-473
5	388	378
6	386	-352
7	230	225
8	380	374
9	201	-207
10	313	310
12	127	127
14	127	-136
15	53	-48
17	57	-63

-5,2,L

1	152	-149
2	191	-190
3	344	-339
4	87	-90
5	352	-334
6	30	-37
8	345	348
9	182	-177
13	85	87
14	88	89
15	92	86
16	107	107

-5,3,L

1	168	173
2	290	295
3	82	82
4	586	594
6	170	155
7	147	-152
8	203	-195
9	61	58
10	138	-135
11	73	-71
12	51	-49
14	57	-62
16	66	-60

-5,4,L

1	150	-152
2	77	89
4	234	-225
5	142	144
6	342	-349
8	187	-184
9	116	-106
11	92	-92
13	90	89

-5,5,L

1	155	157
2	52	48
3	524	531
4	432	-443
5	158	161
6	189	-189
8	81	84
9	80	78
10	131	136
11	142	144
13	66	68
15	103	-104
16	82	74

-5,6,L

1	182	192
2	178	-181
5	96	-103
6	259	266
8	86	90
9	162	171
10	101	-100
12	67	-68
13	73	-79
14	88	80
15	81	-78

-5,7,L

2	123	-124
3	118	-116
4	87	97
5	41	-47
8	56	-68
9	103	-110
11	57	-45
13	59	-54

-5,8,L

1	131	-135
4	92	-97
5	102	101
6	71	-76
7	43	44
9	132	-131
10	63	58
11	60	-59

-5,9,L

1	93	88
3	121	117
4	72	70
7	64	-62

-5,10,L

1	71	72
2	78	-79
3	59	-65
5	69	-76

-4,0,L

2	53	-52
4	782	-727
6	162	156
8	140	132
10	83	-84
14	69	-67
18	59	-60

-4,1,L

1	150	-153
2	393	403
3	245	235
4	227	234
5	530	503
6	303	-293
7	154	152
8	389	-378
12	315	321
13	113	119
14	68	63
15	90	90

-4,2,L

2	76	72
3	290	287
4	60	59
6	168	-159
7	81	-75
9	49	47
10	55	60
11	110	108
12	137	-139
14	116	-117
15	119	-118
18	78	76

-4,3,L

1	506	-504
2	573	-571
3	92	-86
4	742	-730
5	122	-121
6	150	142
7	117	-122
8	193	192
9	80	73
10	100	-97
11	156	158
12	153	-148
14	67	68
15	100	-98
16	85	84

-4,4,L

1	135	-110
2	72	69
3	253	-264
5	161	-154
6	107	111
8	62	-60
10	117	-122
14	125	121
16	32	34

-4,5,L

1	63	59
2	256	246
4	222	215
5	62	59
7	88	91
8	64	61
11	87	-82

-4,6,L

1	99	-99
2	112	116
3	208	219
4	137	-144
5	166	168
6	245	-260
7	191	-185
9	117	-115
10	60	64
11	48	46
13	73	76
14	95	-90

-4,7,L

1	106	105
2	87	-86
3	53	52
4	114	-118
5	39	46
7	78	84

-4,8,L

1	48	-52
3	149	-150
4	59	59
7	211	201
8	124	-121
9	75	72
11	100	-105

-4,9,L

1	155	-159
2	50	47
3	126	-125
4	70	65
5	88	85

-4,10,L

1	86	90
2	71	67
7	58	-56

-3,0,L

2	622	629
4	709	698
6	87	91
8	357	348
10	88	91

-3,0,L

12	185	-189
14	352	-357

-3,1,L

1	34	-28
2	1767	-1848
3	360	-345
4	761	-741
5	156	-142
7	258	257
8	95	94
9	42	52
10	347	-357
11	54	53
12	126	119
14	78	69
15	64	62
18	63	-62

-3,2,L

1	797	806
2	168	162
3	595	-570
4	363	357
5	28	-34
6	48	-35
7	457	440
8	407	-390
9	372	362
11	50	-52
12	160	167
13	74	-68
14	150	150
17	67	62

-3,3,L

1	161	-161
2	156	164
3	305	-319
4	225	240
5	134	141
6	145	135
7	101	-90
8	116	-110
9	155	-160
10	118	125
11	180	-184
12	138	143
13	110	112

-3,4,L

1	178	187
2	384	376
3	134	134
4	122	-124
5	430	-428
7	145	-145
8	192	204
10	89	95
12	74	-72
13	72	-72
14	90	-83

-3,5,L

2	179	-178
3	224	-224
4	215	205
5	113	-116
7	116	121
8	190	-187
9	75	83
10	69	-64
11	62	-65
13	81	-87
14	69	69

-3,6,L

1	184	-181
3	191	-194
4	290	300
7	141	137
8	80	-81
10	54	64
12	101	103
15	70	66

-3,7,L

1	74	-71
2	118	134
4	81	94
5	122	-122
7	76	-77
9	131	-132
10	55	53

-3,8,L

1	119	124
2	89	90
3	81	86
5	56	-56
7	103	-106
9	53	39

-3,9,L

2	85	-98
3	166	-163
5	67	-64
9	145	142
10	117	-115

-3,10,L

7	67	70

-3,11,L

1	59	-48
3	102	97

-2,0,L

2	286	-293
4	149	136
6	153	-153
8	455	-454
12	326	341
14	97	100
18	59	-52

-2,1,L

1	709	710
2	798	771
3	694	674
4	195	192
5	109	-95
6	527	-524
7	57	-52
8	237	241
9	67	66
10	180	174
11	98	-98
13	247	-248
15	70	-74
17	54	52
18	53	50

-2,2,L

1	471	-459
2	824	-835
4	202	204
5	45	-40
6	922	851
7	122	128
8	280	275
10	41	-43
12	55	-50
14	117	118
16	52	54

-2,3,L

2	324	321
3	387	-374
4	219	222
5	180	-177
6	462	438
7	56	-59
8	94	73
9	58	58
10	115	-113

-2,4,L

1	482	-485
2	470	482
3	390	-387
4	41	-37
5	215	222
6	436	-426
8	119	-120
9	238	-220
10	66	-69
11	78	-83
13	107	104
16	60	-53

-2,5,L

1	259	258
2	144	-140
3	191	188
4	310	-313
5	66	-60
6	173	-181
7	139	-131
8	132	130
10	204	204
11	64	63
12	48	-47
13	102	94
14	72	-68

-2,6,L

1	284	283
2	152	-157
3	279	280
4	55	-61
6	157	158
8	94	101
9	77	69
10	65	71
11	92	91
14	73	65

-2,7,L

1	174	-172
3	100	-96
4	68	63
7	129	135
8	79	-80
10	71	-71
11	144	-144
13	135	-130
14	49	42

-2,8,L

1	236	-241
2	139	-135

-2,8,L		
3	52	-58
5	77	77
6	72	-68
10	58	49
12	81	82

-2,9,L		
1	194	194
6	59	52
7	107	-100
8	79	74

-2,10,L		
1	137	133
5	100	-95
6	59	61
7	77	-74

-2,11,L		
3	47	-44

-1,0,L		
2	805	-804
4	1219	1244
6	312	331
8	64	-63
10	230	-221
12	56	61
14	60	-58

18	40	-41

-1,1,L		
1	425	428
2	484	480
3	160	154
4	226	232
5	488	459
7	51	46
8	287	-283
10	155	160
11	50	-48
12	173	167
14	44	39
16	89	-92

-1,2,L		
1	194	-197
2	452	466
3	380	393
4	444	-455
5	452	421
6	400	-390
7	115	-109
8	328	-308
10	85	87
11	102	106
13	126	126
15	106	-109

-1,3,L		
1	274	277
2	33	-27
3	88	94
4	498	-494
5	376	-359
6	137	135
7	120	110
8	306	298
9	130	115
10	78	-85
11	56	55
12	157	-153
15	62	-59
16	102	101

-1,4,L		
1	178	184
2	369	-364
4	62	-58
5	176	-174
6	181	183
7	79	79
8	154	155
10	63	-66
11	74	-74
12	48	-52
13	98	-95
14	141	134
15	53	58

-1,5,L		
1	133	-139
3	89	92
4	339	330
5	128	131
6	89	91
7	94	95
8	100	-104
9	68	81
12	66	63
13	95	-96
16	80	-75

-1,6,L		
1	134	-128
2	127	-127
3	147	143
4	195	-195
6	93	-93
7	39	-31
10	61	-66
11	67	72
13	46	53

-1,7,L		
1	189	201
2	190	-200
3	270	280
4	112	-115
6	48	48
7	182	-179
8	50	54
9	71	71
11	147	150

-1,8,L		
1	612	-611
1	115	117
2	242	-230
3	55	-53
6	93	98
9	73	75
10	111	-105
11	83	-75

-1,9,L		
1	68	-64
2	66	64
5	60	63
6	50	-51
10	65	61

-1,10,L		
2	74	68
3	100	95
7	85	-77

0,0,L		
2	1066	1076
4	729	-704
6	486	-469
8	330	344
10	108	-105
12	274	-276
14	99	-94

0,1,L		
1	374	-357
2	207	211
2	129	129
3	107	-114
4	76	-76
5	120	123
6	211	208
7	287	-278
8	142	-122
9	152	-148
10	377	-387
11	218	216
12	284	-293
13	90	90
16	90	88

0,2,L		
0	1380	-1454
1	264	272
2	230	-224
3	312	-315
4	196	-172
5	650	629
6	223	205
7	323	297
8	21	-29
9	114	111
10	62	-71
11	57	58
13	73	73
15	66	-63

0,3,L		
3	546	511
4	40	-29
5	385	360
6	191	-181
7	149	-140
8	157	141
9	63	-49
10	159	156
12	83	84
13	115	119
14	71	-61
15	52	57

0,4,L		
1	48	-52
2	216	227
3	115	119
4	55	-55
5	87	-87
7	107	-116
8	166	166
9	155	-156
10	102	98
12	166	-169
14	85	-80

0,5,L		
1	183	190
2	121	-122
3	126	-115
4	149	-152
5	291	-284

0,5,L

7	81	76
12	58	-49
14	62	55

0,6,L

0	68	-73
1	102	-110
2	59	-60
3	120	118
4	95	102
5	111	104
7	130	134
8	75	-73
10	76	-75
11	116	-116
12	107	105
15	74	70

0,7,L

1	284	-284
2	279	280
3	60	-57
4	212	214
5	212	214
6	109	-107
8	65	64
10	89	87
13	47	43

0,8,L

0	216	235
1	41	-40
3	206	-209
7	92	-88
8	56	54
11	69	61
12	80	-73

0,9,L

1	75	79
3	116	-116
4	64	-68
5	160	-162
8	77	-75
9	69	66

0,10,L

0	61	-64
1	62	-55
2	38	45
5	90	86
7	145	136
8	72	-65

0,11,L

3	48	43

1,0,L

0	63	-61
2	303	320
4	48	-45
6	321	-301
8	199	-190
10	262	264
12	59	65

1,1,L

0	112	112
1	246	245
2	584	553
3	172	-168
4	50	-55
5	120	-123
7	114	-106
8	151	-142
9	74	-75
10	272	283
11	115	-121
12	129	130
13	49	-52
15	31	-36

1,2,L

1	733	726
2	397	-399
3	138	-129
4	50	44
5	243	-225
6	265	240
8	184	175
9	65	-65
11	56	-51
16	51	47

1,3,L

0	302	-310
1	49	52
2	138	-144
3	404	-377
4	692	663
5	149	-126
6	501	486
7	114	106
8	91	-91
9	50	-47
10	272	-278
12	46	47
14	95	98
15	107	116

1,4,L

0	229	-229
1	182	168
2	517	513
3	93	86
4	360	360
5	30	-36
6	195	-196
8	228	-235
10	85	85
11	117	-119
12	63	62
13	67	-69
14	77	-77
15	83	83
16	142	-135

1,5,L

1	289	-287
2	83	-71
3	85	85
4	227	-232
5	56	-47
6	140	-150
7	59	-50
10	56	52
14	52	-45

1,6,L

0	112	113
1	118	117
2	169	172
3	160	164
5	167	-170
6	80	87
7	115	-124
8	225	223
9	227	228
11	165	164

1,7,L

0	65	66
1	85	-82
2	91	-93
3	210	-208
4	167	168
5	117	115
6	61	62
8	82	-78
9	64	-66
10	76	-69
11	119	-114

1,8,L

1	163	-168
2	51	-50
3	122	-119
4	67	-67
5	130	128
6	43	-47
7	97	101
9	74	-73
10	81	80
11	41	-47

1,9,L

2	84	86
3	97	97
4	51	-50
7	57	-59
9	49	-50

1,10,L

1	93	92
5	80	-80
6	55	50

1,11,L

3	61	-56

2,0,L

0	98	96
2	202	202
4	339	340
8	304	-296
10	118	-115
14	102	112
16	97	98

2,1,L

0	546	-557
1	256	257
2	1903	1983
3	511	-508
4	614	621
5	165	151
6	392	390
8	308	-305
10	110	-101
11	48	-51
12	59	63
16	82	-79

2,2,L

0	655	-676
1	1131	1127
2	184	-180
3	374	-369
4	155	-151
5	190	-176
6	365	-362

2,2,L			8	68	66	4	74	-76	3,0,L			12	109	111	3	124	122	6	40	45
			13	84	-82	5	123	132				14	121	116	4	219	-219	7	79	-78
9	81	-82	14	109	108	6	93	87	0	986	1037				5	254	-267			
10	146	145				7	31	40	2	449	444	3,3,L			8	108	106	3,9,L		
11	79	-87	2,5,L			8	86	82	4	103	97				9	206	205			
12	58	55				9	135	131	6	94	-105	0	262	252	10	126	-130	0	53	-42
13	138	140	0	50	38	12	88	-86	10	260	267	1	220	209	11	53	52	2	81	-71
14	55	-60	2	214	201				14	189	-179	2	116	113	13	71	-73	3	105	-106
15	45	48	3	95	-93	2,8,L			16	61	-52	3	537	512				4	70	-69
			4	393	385							4	255	-256	3,6,L			5	91	-92
2,3,L			6	112	-117	0	191	-189	3,1,L			5	155	155				6	48	50
			7	52	48	1	204	204				6	49	48	0	157	-165	9	95	88
0	167	171	8	121	-119	2	101	-105	0	313	330	7	96	97	2	205	-204			
1	55	58	9	57	-56	3	131	-130	2	166	-159	10	51	57	4	150	148	3,10,L		
2	62	-57	11	123	-124	4	44	42	3	726	-696				6	39	-42			
3	481	477	12	113	113	5	196	-187	4	426	-425	3,4,L			7	114	-115	3	69	-64
4	443	-430				6	64	59	5	410	-377				8	111	-112			
5	65	-64	2,6,L			8	67	-70	6	124	-112	0	119	131	10	83	-80	3,11,L		
6	308	-310				9	123	118	9	207	209	1	92	-83						
7	150	146	0	67	66				10	225	-230	2	132	125	3,7,L			1	59	-58
8	87	86	1	181	-181	2,9,L			12	112	-114	3	316	314						
10	166	169	2	199	201							4	345	-344	0	45	-52	4,0,L		
12	63	-68	3	219	221	0	124	-119	3,2,L			6	50	47	2	63	66			
13	65	-68	4	92	91	8	43	-39				7	111	-114	3	45	40	0	143	-150
14	43	-40	5	279	286	9	83	-76	0	749	-745	8	136	135	4	146	149	2	115	119
			6	286	-300				1	153	152	9	98	-94	5	215	215	8	329	-333
2,4,L			7	75	-70	2,10,L			2	745	-718	10	69	-71	9	87	-96	10	28	-30
			8	69	-81				3	124	117	12	104	-100	10	95	92			
1	235	-231	9	105	-100	2	59	-63	4	388	363	15	60	-63				4,1,L		
2	192	-182	11	38	-39	3	79	76	5	26	10				3,8,L					
3	267	-276							6	87	87	3,5,L						0	72	76
4	170	-171	2,7,L			2,11,L			8	344	-357				0	177	182	1	456	-453
5	65	-76							9	155	146	0	316	316	1	80	82	2	173	172
6	285	279	1	120	125	1	86	82	10	254	-267	1	210	213	2	98	100	3	254	-255
7	138	141	2	133	-140				11	118	116	2	277	-273	3	130	133			

4,1,L

4	133	131
5	253	246
6	127	115
7	160	-157
8	96	101
9	74	-79
10	101	112
11	72	71
13	69	75

4,2,L

0	648	627
1	482	500
2	345	-347
3	284	282
4	309	-299
5	216	-222
6	212	205
7	168	-174
8	492	499
9	204	-214
10	63	56
12	169	-177

4,3,L

0	536	-535
1	384	-365
2	434	-435
3	200	203
4	146	-139
5	115	-110
6	267	270
7	92	91
10	56	-56
14	63	66

4,4,L

1	189	-193
2	428	425
3	299	-297
4	67	66
5	80	83
6	259	-254
7	144	152
9	79	84
11	44	-45
12	71	74

4,5,L

0	213	204
1	145	137
2	221	218
3	116	116
5	142	-149
6	425	-435
7	312	-326
9	78	-80
13	85	83
14	72	-66

4,6,L

0	73	74
1	127	132
2	74	-75
4	129	130
6	255	259
12	69	-60

4,7,L

3	241	-248
4	89	89
5	80	-89
6	72	74
7	118	115
8	62	-64
9	93	89
12	53	-52

4,8,L

0	60	-59
1	189	-185
4	39	35
5	45	42
6	39	38
8	50	-46
9	55	-51

4,9,L

1	62	52
3	129	129
7	62	-65

4,10,L

0	109	104
1	66	61

5,0,L

0	385	-387
2	1116	-1100
4	374	-348
6	483	489
8	227	232
10	109	-107
14	92	96

5,1,L

0	29	-23
1	568	548
2	405	409
3	117	109
4	257	264
5	34	28
6	60	62
7	78	-81
8	175	-181
9	32	33
10	59	-53
12	92	96
13	44	-48
14	65	61

5,2,L

0	129	126
2	236	231
3	31	30
4	75	76
5	148	-143
6	125	-125
7	130	-128
8	149	-151
9	85	-83
10	90	96
11	93	104

5,3,L

0	112	-103
1	411	-386
2	247	-241
3	355	339
4	497	-498
6	112	112
7	65	-69
8	159	154
9	111	-119
12	55	-58
14	34	-31

5,4,L

0	73	-70
2	127	-123
3	208	-206
5	40	-47
6	66	64
7	110	117
8	288	290
9	101	99

5,5,L

1	224	-232
3	336	-345
4	343	344
6	92	-86
9	40	-39
11	79	-73
12	66	61

5,6,L

0	111	102
1	172	-174
2	218	211
3	61	63
4	96	-101
6	163	-163
7	138	-140
8	48	-53
9	73	-75

5,7,L

0	82	77
1	175	177
3	157	158
4	137	-137
5	73	77
7	76	-75
10	25	29

5,8,L

7	61	60
9	56	52

5,9,L

1	70	-67
3	55	-50
5	70	71

6,0,L

0	280	280
2	604	579
4	196	183
6	187	-192
8	57	63
10	203	210
12	65	-65
14	109	-105

6,1,L

0	371	359
1	157	151
2	250	-246
3	208	-216
4	167	-176
5	69	-65
6	148	154
8	65	69
10	108	-114
12	124	-122

6,2,L

0	679	-657
1	155	-151

6,2,L

2	93	-95
3	180	-189
4	64	64
5	102	101
6	57	56
7	274	277
8	155	-153
9	111	-109
10	55	-55
14	37	41

6,3,L

0	291	-307
1	352	-333
2	292	296
5	421	429
6	123	-130
7	367	364
10	82	82
11	124	-127
12	102	99
14	52	-53

6,4,L

0	309	300
2	140	141
3	157	-149
4	163	-166
5	128	-134
6	397	-408
9	146	155
10	45	42

6,5,L

0	94	-95
1	121	115
2	149	-145
3	107	107
4	175	180
5	67	-73
8	106	-110
9	52	54

6,6,L

0	218	-227
1	53	53
2	172	-177
3	72	-70
5	22	-33
6	55	61
8	79	-81
11	83	-79

6,7,L

0	119	-124
1	79	-86
2	56	-57
4	74	67
5	56	54
10	56	56

6,8,L

0	175	176
1	141	145
2	52	56
3	92	91
7	83	-77
8	42	41

6,9,L

1	111	103
4	82	-83
5	60	-55

7,0,L

0	315	-338
2	121	-117
4	60	-62
8	236	-254

7,1,L

0	331	327
1	69	-70
2	561	545
4	301	-286
5	57	60
6	259	-259
9	59	69
10	170	180
11	62	69

7,2,L

0	400	408
1	73	-66
2	211	192
3	254	254
4	134	130
5	88	-86
6	139	142
8	43	51
9	153	-155
10	87	-85
12	63	-63

7,3,L

0	94	-91
1	61	62
2	157	-159
3	78	-85
5	152	-157
6	180	180
8	135	133
9	62	61
10	127	-129

7,4,L

0	242	-249
1	207	-211
2	87	-83
4	235	238
5	310	325
6	75	-76
7	75	76
8	45	-41
12	94	93

7,5,L

0	110	111
2	77	-78
4	133	-129
5	114	-113
6	69	-66
10	50	51

7,6,L

1	102	104
3	56	56
4	122	-126
5	130	-136
6	81	84
7	146	-158
9	68	68
11	62	58

7,7,L

2	56	-55
3	79	-84
9	48	40

7,8,L

1	111	-110
4	70	68
7	71	68
8	89	-81

7,9,L

2	43	44

7,10,L

0	51	47
1	80	76

8,0,L

0	103	-96
2	288	-289
4	127	-122
6	132	135
8	77	73
10	67	68
12	72	-71

8,1,L

0	483	-476
1	125	122
2	80	79
3	90	87
4	243	248
5	84	91
6	107	112
7	70	-69
8	174	-179
9	106	-109
12	104	104

8,2,L

0	60	62
1	96	99
2	230	239
3	223	224
4	93	87
5	68	76
6	69	-67
8	57	-50
9	83	-80
12	53	53

8,3,L

0	69	75
2	193	-197
3	98	-97
4	206	-218
5	162	-162
6	89	-91
8	103	106
9	79	82

8,4,L

1	249	255
2	75	-74
3	52	-54
4	154	153
5	190	-201
6	161	160
8	98	99
9	96	92

8,5,L

0	99	-92

8,5,L

1	28	-29
4	245	244
5	130	-138
6	221	224
10	66	-57

8,6,L

0	153	-159
1	224	-239
5	81	89
7	74	-81

8,7,L

0	92	93
2	58	-59
4	81	-84
6	75	-83
7	110	-106

8,8,L

0	72	68
1	42	46
2	79	-76
6	98	86
7	66	65

9,0,L

0	430	416
2	58	-58
4	380	-374
6	48	55
8	114	121
10	194	197

9,1,L

0	193	197
1	88	83
3	62	59
4	118	-121
5	43	-49
7	87	-90
9	63	-65
10	94	-93
11	52	53

9,2,L

0	138	-141
1	30	-32
2	185	-183
3	211	-209
4	76	79
5	109	-108
6	98	97
7	85	89
10	160	-157

9,3,L

0	88	-94
1	60	60
2	218	226
3	270	275
4	252	253
5	144	154
7	67	-63

9,4,L

0	87	82
1	86	-83
3	81	77
4	136	-134
5	99	98
6	118	-119
8	48	43
10	47	42

9,5,L

3	69	72
4	167	-166
8	53	55
9	60	65

9,6,L

0	83	-87
2	101	-99
5	50	55

9,7,L

1	95	-92
5	90	87
6	79	-88
7	33	40

9,8,L

1	52	-51
2	78	77

9,9,L

1	93	89

10,0,L

0	412	-411
2	185	183
6	115	-128
8	210	-218
10	48	47

10,1,L

2	154	151
3	46	-47
6	138	-133
7	104	110
8	62	-65
12	109	110

10,2,L

0	282	270
7	59	61
8	70	71

10,3,L

0	184	182
1	112	-112
2	94	-96
3	153	-161
6	88	83
8	44	-43
10	86	-89

10,4,L

1	82	84
2	130	131
4	74	73
6	50	-49
7	47	47
8	80	-75
10	52	-42

10,5,L

0	152	-156
2	112	114
3	220	219
4	33	40
5	116	123
6	41	-39

10,6,L

0	57	62
1	61	55
3	61	58
4	135	-127
6	33	-39
7	86	-83
8	77	77

10,7,L

2	110	-110
3	42	-48
6	36	29
7	78	76

10,8,L

1	67	-57
3	53	-53

11,0,L

0	73	72
2	87	-87
4	65	-66

11,1,L

0	103	-102
1	138	-142
2	67	-64
3	98	-100
4	46	44
10	103	-106

11,2,L

0	68	77
1	129	131
2	220	224
3	50	54
4	92	87
6	74	-78
8	62	-66

11,3,L

0	122	123
4	218	-216
6	65	-62
7	59	-60
8	75	76
10	48	49

11,4,L

4	56	-46
6	87	87
8	104	101

11,5,L

0	56	-58
2	67	67
3	109	-107
4	165	163

11,6,L

1	112	-115
2	83	80
3	42	-49
4	127	125
5	64	61

11,8,L		
1	56	59

12,0,L		
0	115	117
2	70	71
10	85	74

12,1,L		
0	89	88
1	85	87
2	95	-98
8	97	94
10	56	-58

12,2,L		
0	242	-237
1	84	-86
2	245	-238
3	49	-54
5	82	-85
6	119	121
9	54	48

12,3,L		
2	79	79
3	101	-98
4	47	43

12,4,L		
1	107	104
2	177	177
3	74	77
6	73	-70
7	70	-76

12,5,L		
1	124	123
2	123	-120
3	40	46
4	70	-64
5	52	-52

12,6,L		
2	67	-65

12,7,L		
1	106	-99

12,8,L		
1	28	-33

13,0,L		
0	100	-105
2	133	-131
8	42	-45

13,1,L		
2	105	98
3	63	60
5	46	42
6	79	-81
8	42	-42

13,2,L		
0	110	112
4	129	-126
8	61	63

13,4,L		
0	102	-97
3	78	-77
6	86	-79
7	72	69

13,5,L		
2	75	70
3	76	76
6	76	-69

13,6,L		
0	61	66
1	57	54

14,0,L		
0	290	279

14,1,L		
0	169	-163
1	53	-55
4	70	67
6	64	60

14,2,L		
0	96	-90
2	58	49
5	66	61

14,3,L		
0	101	96
4	118	-120
6	85	-84

14,4,L		
2	77	-69

14,6,L		
0	67	65
1	85	-84

15,0,L		
0	122	118
2	165	149
6	104	-100

15,1,L		
0	60	52

15,2,L		
0	78	-77
2	48	-42
3	58	-55

15,3,L		
0	74	-72
1	65	-64

15,4,L		
2	80	76

16,0,L		
0	89	-82
4	88	85

16,1,L		
0	95	-89
1	45	38
2	79	75

16,2,L		
1	61	60
2	41	-38

16,4,L		
0	74	-66

17,1,L		
0	74	-71

Data for Triphenylarsoniumphenacylide

Crystal Data

$C_{26}H_{21}OAs$, M = 424.39; monoclinic,

a = 19.343(2)Å, b = 11.103(3)Å, c = 23.859(3)Å, β = 126.55(1)°,

V = 4116.37Å^3; D_c = 1.37 g.cm^{-3}, Z = 8 with two molecules per asymmetric unit; F(000) = 1744; space group P2/c (C_{2h}^4, No.13);

$Mo - K_\alpha$ radiation, $\mu(Mo - K_\alpha)$ = 17.58 cm^{-1}, λ = 0.7107Å.

-22,-3,L

16	325	-306

-22,-2,L

18	324	283

-22,-1,L

12	460	440
16	421	-395

-22,0,L

10	290	-237
18	391	371
22	408	-398

-21,-5,L

13	314	272
18	225	215

-21,-4,L

12	325	280

-21,-3,L

13	278	258
17	211	-210
18	332	327
21	170	126
22	203	-154

-21,-2,L

8	296	-259
12	428	386
13	174	186
24	315	304

-21,-1,L

14	397	-364
18	501	505
22	353	-327

-21,0,L

10	338	331
12	441	414
24	323	309

-20,-6,L

13	275	281

-20,-5,L

9	151	-181
18	167	-153
19	282	304

-20,-4,L

13	228	239
14	284	-290
18	343	290
19	305	274
20	163	132
23	290	-271

-20,-3,L

8	272	-261
9	222	-197
12	326	287
13	161	138
15	201	-239
20	330	-342
24	301	272

-20,-2,L

12	204	-197
14	529	-526
18	415	409

-20,-1,L

6	394	-361
8	332	-303
10	406	385
12	243	228
20	380	-363
24	387	351

-20,0,L

4	308	333
14	742	-731
18	634	636

-19,-7,L

12	190	-192

-19,-6,L

14	168	197
15	283	-293
18	234	-237
19	271	262

-19,-5,L

9	268	-281
11	160	96
14	350	-342
19	304	314

-19,-4,L

8	312	-284
12	296	276
15	248	-217
16	216	191
19	348	347

-19,-3,L

10	213	246
12	289	-301
14	371	-365
21	183	-194

-19,-2,L

6	292	-275
8	377	-340
9	277	-286
20	581	-586
22	266	-236
24	340	340

-19,-1,L

10	384	382
14	549	-530
18	402	387
24	192	95
26	267	-255

-19,0,L

2	289	248
6	349	-349
8	418	-391
10	308	295
12	193	213
16	357	348
20	593	-609
22	286	-255
24	401	407
26	261	217

-18,-7,L

7	225	-189
8	187	-167
10	314	-321
11	367	347

-18,-6,L

8	229	189
21	311	-269

-18,-5,L

9	157	-191
11	400	389
14	224	227
15	293	-317
19	234	250
21	227	-216

-18,-4,L

9	335	-316
11	204	183
14	243	-242
15	197	-206
21	338	-336
22	333	290

-18,-3,L

2	283	291
4	250	247
6	143	-116
8	259	-242
11	344	338
12	239	-234
16	430	419
20	422	-430
25	190	170

-18,-2,L

8	355	365
10	534	510
12	205	-213
14	375	-355
22	366	399
26	291	-304

-18,-1,L

2	426	412
6	487	-480
8	199	-180
10	249	260
16	593	565
20	589	-578

-18,0,L

8	346	351
10	653	633
12	331	-330
14	547	-562
22	422	427
24	157	150
26	295	-314

-17,-8,L

10	293	-296
11	279	260

-17,-7,L

15	295	-283
17	228	223

-17,-6,L

7	296	-311
10	334	-315
11	523	531
14	294	303
15	325	-351
16	249	212
17	185	215
22	294	-254

-17,-5,L

1	284	-295
2	359	-362
4	224	-229
5	311	326
8	286	267
10	279	242
11	241	251
12	330	281
13	279	-258
15	319	-309
16	422	-424
17	341	361
18	171	-203
21	320	-299
22	209	197

-17,-4,L

1	196	-229
2	279	301
10	401	-407
11	427	408
12	341	-352
15	245	-247
16	454	442
18	207	225
21	320	-330

-17,-3,L

1	368	-365
4	229	-204
5	246	222
8	330	323
10	242	256
11	164	189
14	138	-175
15	184	-185
22	524	511
24	297	268
26	262	-244

-17,-2,L

2	604	584
4	194	211
6	262	-253
7	211	-224
11	401	409
12	506	-488
14	238	224
16	626	610
20	336	-343
25	225	191

-17,-1,L

8	380	374
10	537	546
14	470	-475
22	546	535
24	265	243
26	212	-205

-17,0,L

2	609	579
4	243	241
8	211	-244
12	463	-462
14	337	357
16	579	545
20	393	-380
24	212	-226
26	219	-233

-16,-8,L

14	176	-180
16	404	-396

-16,-7,L

4	227	238
7	304	-302
8	170	-178
11	200	221
18	382	359

-16,-6,L

1	319	-308
2	293	-276
3	380	351
7	384	-385
11	412	404
12	258	253
13	301	-244
16	402	-412
17	349	358
18	221	-248
24	162	150

-16,-5,L

3	309	329
7	274	-300
8	236	-238
13	291	-285
16	350	339
17	284	316
18	387	359

-16,-4,L

1	330	-314
3	322	333
4	303	-298
7	213	-256
8	257	258
13	556	-553
16	365	-381
17	436	425
18	548	-571
21	251	-268
22	364	375
23	200	177

-16,-3,L

2	435	401
3	298	316
4	490	498
7	335	-337
9	191	184
10	279	-262
12	358	-350
13	263	-274
16	570	564
17	276	283
18	236	269
19	137	-169
20	192	-210
23	237	266
24	214	-154
26	295	-280

-16,-2,L

4	314	-326
6	561	-562
8	346	341
10	748	750
17	181	167
18	305	-318
22	505	506
24	351	352

-16,-1,L

2	612	610
3	330	335
4	276	286
6	413	-427
7	253	-270
10	266	-237
12	586	-589
14	275	271
16	764	736
20	147	-174
24	374	-377
26	330	-377
28	377	365

-16,0,L

2	259	247
4	279	-280
6	772	-766
8	404	390
10	884	911
12	219	-246
14	274	-242
18	323	-304
22	506	484
24	321	306

-15,-9,L

9	228	169
12	360	316
16	236	-226

-15,-8,L

3	188	178
4	340	321
6	258	253
7	228	-166
18	399	373

-15,-7,L

3	296	264
7	290	-292
8	183	-188
10	197	204
11	225	236
13	251	-223
16	198	-213

-15,-6,L

3	292	295
4	290	271
7	420	-423
8	189	-216
11	189	138
13	171	-158
16	197	207
18	329	352
19	274	-277
24	157	-215

-15,-5,L

4	436	-453
5	163	180
6	239	-247
7	303	-314
9	417	449
13	278	-282
17	387	402
18	315	-316
22	244	239
23	166	162

-15,-4,L

2	166	189
4	287	294
6	247	271
10	154	-173
12	602	-606
14	169	-168
16	282	280
17	437	439
18	216	222
21	147	-170
24	311	-309

-15,-3,L

4	648	-646
5	374	-384
6	406	-412
8	614	630
9	416	405
10	219	205
13	319	-323
17	361	368
18	685	-697
19	241	-285
22	430	446
24	210	218

-15,-2,L

2	461	453
3	355	368
6	126	35
7	566	-580
8	434	436
10	222	-219
12	853	-829
16	482	490
20	133	166
24	340	-353
26	192	-220

-15,-1,L

2	404	381
4	795	-835
6	844	-866
8	761	792
10	591	599
14	333	322
17	179	199
18	661	-660
22	302	283

-15,0,L

2	355	354
8	575	566
10	280	-290
12	827	-815
14	361	364
16	500	492
24	467	-461
26	280	-281
28	295	306

-14,-10,L

8	286	-275
10	217	202
12	333	300

-14,-9,L

3	246	221
4	328	301
6	302	312
18	317	316

-14,-8,L

8	286	-280
9	228	207
10	282	262
12	237	209
13	283	-291
20	271	-248

-14,-7,L

3	347	347
4	397	378
6	434	450
7	374	-367
9	322	322
13	200	-195
15	207	162
18	295	289

-14,-6,L

4	320	-347
6	450	-463
8	402	-405
9	244	266
11	339	333
13	255	-269
14	269	263
20	198	-214
23	199	210

-14,-5,L

3	312	280
5	190	-217
6	424	447
7	384	-380
9	419	423
10	441	-465
12	438	-410
13	376	-380
14	198	204
19	290	-308
20	435	436
21	137	-120
24	294	-299
26	184	-154

-14,-4,L

3	339	365
4	371	-378
5	277	-287
8	244	-226
9	830	842
11	181	-195
12	274	278
13	631	-649
14	545	551
17	330	350
18	615	-606
19	344	-347
20	213	-165
23	230	222

-14,-3,L

6	760	747
7	527	-529
8	777	801
9	320	321
10	673	-685
12	576	-574
13	221	-231
17	369	365
19	374	-384
20	418	451
21	240	-243
24	325	-317

-14,-2,L

4	765	-747
5	149	-201
6	336	-367
8	202	216
9	452	482
11	260	253
12	263	261
13	330	-324
14	548	563
18	796	-781
19	304	-334
23	341	331
26	249	236

-14,-1,L

3	205	215
4	335	-326
6	604	628
8	755	774
10	756	-774
12	802	-813
20	525	509
24	315	-322

-14,0,L

2	238	248
4	1034	-1018
8	582	592
12	339	328
14	686	689
18	805	-804
28	309	295

-13,-10,L

10	239	231
14	503	-483

-13,-9,L

6	302	-306
8	327	-310
9	216	223
20	309	-323

-13,-8,L

1	255	265
2	213	-210
3	238	253
4	380	400
6	203	249
14	552	-565
15	357	336
18	307	259

-13,-7,L

5	263	-280
6	423	-414
8	400	-403
9	309	308
12	480	471
14	260	260
19	234	-216
20	273	-240

-13,-6,L

1	393	412
2	211	-206
3	404	400
5	547	-544
6	370	395
9	408	401
11	235	-263
12	289	-281
15	412	440
19	468	-447
20	154	187

-13,-5,L

5	330	-340
6	386	-398
8	442	-418
9	476	488
11	319	-297
12	811	809
13	268	-256
14	498	483
15	330	361
20	262	-246

-13,-4,L

2	272	-284
5	307	-311
6	842	852
8	845	880
9	571	568
10	605	-619
11	279	-270
12	603	-615
13	550	-549
15	343	350
17	308	318
19	379	-398
20	432	429
22	357	378
24	215	-241
26	234	-231

-13,-3,L

1	455	446
3	217	247
4	310	-316
5	511	-504
6	237	-254
8	280	-293
9	595	612
10	371	-339
12	484	483
13	455	-457
14	849	838
15	460	464
16	301	-284
18	626	-649
19	412	-445
21	282	295
23	218	226
26	371	395

-13,-2,L

1	268	234
2	406	-417
3	390	399
4	309	-308
5	328	-352
6	943	940
8	686	699
9	552	579
10	653	-647
11	203	-235
12	517	-523
13	309	-310
19	300	-308
20	718	727
22	335	329
24	409	-394
26	264	-238

-13,-1,L

2	424	427
4	634	-656
5	151	-128
6	335	-336
8	168	-168
9	202	236
10	474	-466
11	205	-207
12	389	369
14	745	773
18	634	-640
19	241	-242
21	340	342
23	249	239
26	284	285
28	288	278

-13,0,L

2	299	-299
4	354	-352
6	855	830
8	486	531
10	423	-437
20	872	864
22	429	459
24	458	-449

-12,-11,L

10	372	361

-12,-10,L

2	334	351
6	439	-443
8	246	-255
10	307	308
16	270	234

-12,-9,L

10	414	403
12	297	-271
14	556	-544
15	156	191
18	234	218

-12,-8,L

1	284	272
2	279	269
4	315	318
5	411	-421
6	354	-349
8	209	-211
9	337	346
10	259	292
16	321	304
19	242	-226
20	371	-393
21	214	208

-12,-7,L

1	272	282
5	281	-288
7	316	345
10	314	341
11	293	-290
14	596	-575
15	295	323
19	249	-241

-12,-6,L

1	402	405
2	413	414
4	150	143
5	507	-531
6	223	-245
8	492	-499
9	365	372
10	233	-204
12	540	541
14	147	137
15	260	258
21	249	193
22	178	-212

-12,-5,L

1	424	441
2	371	-388
4	297	-287
5	420	-428
7	398	427
8	571	581
9	178	184
11	524	-523
12	588	-590
13	344	-325
14	493	-493
15	409	420
20	275	273

-12,-4,L

1	404	404
2	322	337
5	630	-640
7	452	486
8	279	-298
9	544	554
10	491	-476
11	663	-647
12	777	776
13	210	-216
14	793	802
15	436	436
16	352	-340
19	198	-229
21	169	116
22	232	-228
26	336	324

-12,-3,L

1	489	494
2	668	-685
3	372	362
4	323	-340
5	595	-628
6	822	851
8	756	794
9	341	343
11	612	-630
12	233	-244
13	322	-316
14	304	-315
15	456	462
16	344	-348
20	455	475
21	144	140
22	318	324
25	166	-181
26	222	-182

-12,-2,L

2	364	385
4	399	-401
5	439	-438
8	405	-423
10	924	-918

-12,-2,L

11	290	-289
12	346	353
13	196	174
14	788	786
15	362	373
18	257	-269
19	336	-309
21	322	330
22	387	-402
24	192	-254
26	420	402

-12,-1,L

1	211	230
2	830	-865
3	168	163
4	181	-197
6	1008	1058
8	510	528
10	412	-411
11	509	-504
13	303	-278
14	214	188
15	290	282
16	767	-755
20	948	958
24	516	-539

-12,0,L

4	881	-879
6	254	-276
8	366	-378
10	689	-709
12	382	381
14	880	863
22	464	-465
26	294	263
28	253	254

-11,-11,L

2	388	381
6	370	-381

-11,-10,L

4	181	-167
6	253	-243
8	387	392
10	432	422
11	208	-200
12	284	-270

-11,-9,L

1	190	222
2	521	509
4	347	367
5	234	-242
6	444	-460
12	344	-323
16	609	578
20	334	-323

-11,-8,L

4	244	-258
6	270	-289
7	242	238
8	405	412
10	450	444
11	541	-530
12	283	-293
14	407	-419
21	236	220

-11,-7,L

1	314	336
2	540	569
4	566	579
5	478	-467
6	375	-351
8	280	-299
9	294	288
15	322	325
16	406	388
17	366	-389
19	298	-302
20	268	-259
21	320	291

-11,-6,L

1	509	526
2	245	-243
3	146	-98
4	329	-326
6	323	-349
7	504	510
8	468	482
10	350	334
11	657	-666
13	254	279
14	481	-471
15	498	508
17	290	-281
20	154	163
21	317	308
25	273	-307

-11,-5,L

1	277	271
2	548	582
3	209	-226
4	323	334
5	735	-768
7	563	572
8	501	-523
10	431	-429
11	683	-646
14	395	387
15	593	600
16	428	430
19	325	-325
22	164	-177

-11,-4,L

1	317	310
2	804	-802
3	219	-221
4	485	-504
5	374	-402
7	428	452
8	517	536
10	491	499
11	658	-652
14	528	-534
15	672	660
16	318	-304
21	281	286
25	263	-271

-11,-3,L

1	479	493
3	336	-339
4	333	359
5	580	-601
6	372	380
7	660	694
8	1005	-1044
9	410	408
10	1022	-1025
11	377	-384
12	331	334
14	817	764
15	599	614
19	295	-285
22	390	-388
25	262	-265
26	369	343

-11,-2,L

1	289	308
2	1101	-1172
4	139	-142
5	668	-677
6	714	753
7	523	525
8	424	409
9	375	374
11	710	-706
12	408	398
14	355	-356
15	465	455
16	985	-966
18	325	332
19	246	-233
20	361	349

-11,-1,L

3	266	-266
4	342	358
5	282	-270
7	547	544
8	864	-890
10	436	-461
11	309	-292
12	257	265
14	772	777
17	252	-258
18	300	310
19	345	-336
20	252	-248
22	462	-470
26	305	302

-11,0,L

2	765	-808
4	505	-499
6	698	722
8	173	205
12	894	870
16	1367	-1352
20	659	671
26	256	249
28	222	-219

-10,-11,L

4	313	-338
8	352	354
10	285	250

-10,-10,L

2	582	608
12	368	-365
16	419	404

-10,-9,L

4	328	-350
6	244	-232
8	537	530
10	313	312
11	368	-339

-10,-8,L

1	266	278
2	488	483
3	219	-226
4	223	245

-10,-8,L

10	340	-314
12	561	-545
13	507	517
14	231	205
16	508	517
17	358	-372
20	227	-222

-10,-7,L

2	255	-251
3	255	-278
4	392	-388
7	517	517
8	322	334
9	187	-211
10	469	464
11	409	-415
12	224	228
13	380	374
15	208	207
17	384	-406
18	296	-313
21	313	342
22	193	229

-10,-6,L

1	393	400
2	505	517
3	520	-558
4	568	595
5	293	-297
7	303	336
8	284	-306
10	634	-658
11	555	-553
12	478	-473
13	554	560
14	351	337
15	360	331
16	653	648
17	469	-483
24	209	-221

-10,-5,L

1	287	294
2	618	-650
3	476	-496
4	642	-677
5	191	-167
7	793	825
8	353	347
9	189	-189
10	687	704
11	631	-639
12	329	323
13	321	334
14	321	-308
15	406	397
16	615	-613
17	527	-531
18	332	-348
20	233	210
21	302	303
22	163	185

-10,-4,L

1	556	567
3	566	-597
4	708	733
5	281	-298
7	1190	1210
8	662	-699
9	199	-214
10	755	-760
11	729	-724
13	351	341
14	566	574
15	290	308
16	470	460
17	758	-752
18	157	161
22	328	-339
23	205	-238

-10,-3,L

1	413	423
2	1036	-1058
3	345	-372
4	773	-792
5	359	-355
6	296	327
7	742	745
8	273	287
10	928	940
11	168	-182
12	582	599
13	404	406
15	487	483
16	995	-1004
18	308	-303
20	250	248

-10,-2,L

1	306	318
3	660	-671
4	1024	1047
5	227	-214
6	1051	1092
7	284	273
8	964	-1010
10	933	-945
11	243	-244
14	510	514
17	519	-518
18	387	403
19	292	-275
20	212	216
21	228	216
22	545	-549

-10,-1,L

2	1086	-1102
4	716	-741
6	695	701
7	316	332
9	368	349
10	289	253
12	563	581
13	237	221
14	485	-485
15	281	269
16	1151	-1137
17	141	-173
19	322	-318
20	308	319
24	225	251
26	276	244

-10,0,L

4	1069	1090
6	331	322
8	935	-956
10	1093	-1084
12	416	421
14	222	213
18	486	491
22	465	-477
24	226	-239

-9,-12,L

4	312	-303
6	251	-232
8	238	256

-9,-11,L

2	325	327
10	236	-214
12	322	-306

-9,-10,L

4	459	-478
6	379	-365
8	359	373
10	371	375
18	346	-333

-9,-9,L

2	258	266
10	462	-465
12	528	-498
13	245	228
14	206	208
16	386	403

-9,-8,L

3	398	-413
4	473	-489
6	289	-292
7	314	330
8	336	341
10	519	541
16	195	-201
17	303	-289
18	466	-449
19	202	188
22	268	268

-9,-7,L

2	193	164
3	437	-469
4	254	251
6	220	252
7	260	289
9	451	-455
10	564	-570
12	311	-304
13	623	629
16	354	337
17	358	-386

-9,-6,L

3	634	-660
6	260	-256
7	714	721
8	317	302
9	154	-145
10	427	461
11	246	-278
12	360	346
13	638	638
16	473	-476
17	411	-426
18	513	-524
19	251	239
21	329	309
22	310	362
23	243	-262

-9,-5,L

1	263	253
2	132	111
3	674	-698
4	515	528
5	162	194
6	303	329
7	593	605

-9,-5,L

9	941	-953
10	488	-488
11	382	-382
12	367	-363
13	417	425
14	195	192
16	407	395
17	527	-532
18	334	339
19	369	387
21	218	184
22	241	-240

-9,-4,L

2	457	-474
3	643	-670
4	332	-355
5	358	371
7	619	639
9	167	-166
10	209	236
11	243	-257
12	675	675
16	810	-850
17	314	-309
18	608	-618
20	343	365
21	255	277

-9,-3,L

2	258	-252
3	526	-522
4	1319	1377
6	1226	1249
8	1390	-1379
9	494	-447
10	914	-921
11	435	-438
13	553	545
16	144	143
17	504	-512
18	733	733
19	335	335
21	453	450
22	544	-561
23	240	-264

-9,-2,L

2	1078	-1087
3	695	-711
4	471	-484
5	631	632
6	160	184
7	739	720
8	337	-330
10	440	459
12	1130	1103
13	201	-188
14	335	-340
16	830	-819
17	315	-325
20	371	354
24	238	255
26	223	246

-9,-1,L

1	116	163
3	331	-350
4	1107	1117
5	330	329
6	1449	1495
8	1224	-1239
9	230	-232
10	1158	-1151
12	465	445
13	290	304
14	390	-395
17	400	-399
18	1133	1134
20	394	398
22	645	-648
24	287	-287

-9,0,L

2	1033	-1057
4	176	-177
6	588	-563
8	1154	-1133
10	1321	1297
12	1312	1282
14	666	-641
16	1112	-1093
26	317	306

-8,-12,L

8	263	274

-8,-11,L

4	425	-450
6	257	-250
8	244	281

-8,-10,L

8	301	309
10	286	-280
12	453	-420
16	238	224

-8,-9,L

1	228	-241
2	324	337
3	236	-231
4	570	-579
8	293	292
14	200	203
15	153	-154
18	397	-373

-8,-8,L

6	523	540
8	404	416
9	539	-538
10	358	-354
11	249	248
12	492	-467
13	403	410

-8,-7,L

2	355	378
3	723	-761
4	507	-539
5	335	330
6	378	-387
7	379	394
9	395	-392
12	256	243
13	399	404
14	447	442
15	243	-218
17	468	-465
18	409	-387
19	273	242
21	188	206
22	273	281

-8,-6,L

3	420	-424
4	207	209
5	366	360
6	597	609
8	180	144
9	727	-751
10	369	-363
12	582	-578
13	394	401
18	311	336
19	300	294
23	293	-283

-8,-5,L

2	214	203
3	412	-434
4	309	-335
5	776	783
6	705	-711
7	862	881
9	476	-492
10	379	363
11	313	-278
12	544	554
13	388	375
15	318	-303
16	359	-345
17	447	-448
18	279	-284
19	216	246
20	215	-223

-8,-4,L

2	123	79
3	357	-362
4	488	492
5	689	711
6	350	355
7	216	228
9	676	-683
10	341	-334
11	392	-367
12	307	-304
13	894	884
14	606	-591
16	433	415
18	601	603
19	334	339
22	333	-337
23	325	-331

-8,-3,L

1	406	-398
2	181	177
3	351	-371
4	585	-608
5	703	713
6	710	-732
8	389	-398
9	682	-685
10	598	604
11	371	-371
12	1168	1138
13	279	259
15	324	-319
16	472	-473
17	221	-210
19	302	309
24	365	364

-8,-2,L

1	200	-192
2	444	-443
3	457	-486
4	1171	1210
6	724	762
7	551	-542
8	219	-227
9	574	-546
12	308	-309

-8,-2,L

13	604	590
14	737	-718
16	484	500
17	452	-449
18	929	910
22	438	-455

-8,-1,L

2	189	-221
4	593	593
6	1387	-1412
7	194	200
8	1519	-1468
9	321	307
10	1464	1415
12	1599	1537
13	662	657
14	955	-955
16	462	-436
20	369	-361
22	336	-322
24	463	456
26	318	312

-8,0,L

4	1400	1444
6	218	241
8	1156	-1142
10	458	438
14	1014	-1019
16	391	390
18	1175	1199
22	470	-510

-7,-12,L

4	339	-299

-7,-11,L

4	193	-199
6	310	292
8	425	424
10	249	-232

-7,-10,L

4	392	-384
10	292	-285
12	213	195
14	439	409
18	298	-279

-7,-9,L

4	129	-152
6	533	537
8	458	448
9	265	-267
10	436	-445
12	565	-538
20	312	329

-7,-8,L

1	295	-293
4	533	-530
5	246	271
9	283	-280
10	242	-239
11	317	307
12	345	331
14	629	635
15	276	-276
18	324	-322

-7,-7,L

3	194	-213
5	425	443
6	663	691
7	384	-387
8	547	565
9	543	-542
11	297	306
12	594	-601
13	413	402
15	175	-189
19	212	239
20	267	244
23	265	-266

-7,-6,L

3	525	-544
4	450	-464
5	206	228
6	215	-238
8	573	-551
9	578	-600
11	413	411
12	517	510
13	494	487
14	546	527
15	617	-610
17	240	-266
18	223	-218
19	455	467
20	265	-262

-7,-5,L

5	574	599
6	540	549
8	634	638
9	331	-327
10	152	-163
12	388	-388
13	557	542
14	517	-521
15	305	-314
18	504	516
23	304	-340

-7,-4,L

1	460	-471
2	281	305
3	445	-468
5	743	755
6	868	-845
7	306	-293
8	1000	-1019
9	878	-869
10	574	562
12	662	659
13	371	369
15	659	-649
16	293	291
19	357	355
20	595	-603
24	219	235

-7,-3,L

2	182	-174
3	362	-367
4	1164	1197
5	195	206
6	283	304
7	362	354
8	703	670
9	495	-473
12	756	-711
13	823	799
14	899	-888
16	404	388
18	572	575
20	148	189
22	169	-163

-7,-2,L

1	368	-373
3	521	-544
4	141	152
5	174	171
6	1635	-1647
7	605	621
8	1049	-1043
9	225	-229
10	803	771
12	636	617
13	442	438
14	486	-462
15	543	-543
16	255	235
17	303	-303
19	293	278
20	780	-807
24	590	625

-7,-1,L

2	741	-775
3	182	-190
4	1026	1077
5	565	579
8	1136	1089
9	264	-271
10	802	750
11	649	645
12	850	-824
13	481	490
14	1466	-1452
16	286	288
18	897	904
21	260	-242
26	236	-265

-7,0,L

2	582	600
4	1346	1345
6	1786	-1761
8	1113	-1105
10	1706	1662
12	1620	1573
14	357	-352
16	194	-221
18	182	163
20	764	-797
22	466	-472
24	524	540
26	311	302

-6,-12,L

6	385	347
8	275	259

-6,-11,L

4	286	-325
8	144	-154
10	320	-297
14	471	437

-6,-10,L

2	275	-279
6	432	432
8	355	343
10	315	-303

-6,-9,L

1	256	-312
8	266	-255
10	463	-465

-6,-9,L

11	297	313
12	379	367
14	521	515
15	231	-235
18	267	-223

-6,-8,L

1	403	-415
2	381	-418
5	281	278
6	614	598
7	224	-210
8	497	487
9	429	-450
11	221	263
13	356	359
16	173	-193
20	357	366

-6,-7,L

1	352	-372
2	149	176
3	194	-203
8	707	-703
10	284	-297
11	322	325
12	470	454
13	262	280
14	755	750
15	433	-437
16	143	-155
17	144	-128
18	228	-204
19	285	272

-6,-6,L

1	477	-500
2	192	-213
5	480	491
6	480	491
8	252	247
9	514	-498
11	201	209
12	429	-430
14	517	-513
15	343	-321
16	358	-372
18	183	179
19	362	382
20	415	410
21	155	-125
22	195	239
23	220	-221

-6,-5,L

1	575	-606
2	387	400
3	454	-464
4	418	426
5	845	833
6	880	-915
7	468	-462
8	611	-628
10	310	306
11	434	423
12	496	495
13	239	237
14	691	672
15	788	-796
16	187	134
17	204	209
18	344	-365
19	212	217
20	410	-438
22	190	-225
23	188	-174

-6,-4,L

1	437	-453
2	195	-213
4	859	834
5	1392	1383
6	479	491
7	664	673
9	737	-741
10	517	520
11	245	277
12	707	-697
13	288	282
14	773	-766
15	563	-578
17	210	244
18	494	504
19	371	378
20	309	295
21	291	-302
22	236	226

-6,-3,L

1	534	-557
2	293	316
3	868	-868
4	484	483
5	222	220
6	1664	-1684
7	593	-569
8	385	-397
9	661	-642
10	221	202
11	541	510
12	479	482
13	123	-114
14	209	208
15	628	-626
16	831	836
17	273	260
18	275	-262
20	613	-616
24	266	293

-6,-2,L

2	465	-483
4	1140	1187
5	365	370
6	541	540
7	308	-300
8	780	756
9	205	212
10	748	722
11	774	739
12	905	-895
14	1252	-1228
15	459	-460
17	205	211
18	525	522
26	323	-323

-6,-1,L

2	927	962
3	624	-615
4	1022	1045
5	1154	-1143
6	1639	-1637
8	1141	-1139
9	617	-588
11	360	367
12	259	235
13	448	441
14	452	447
16	584	584
20	830	-847
22	270	-288
24	535	576
26	183	156

-6,0,L

4	933	936
6	368	-352
8	726	683
10	1352	1306
12	344	-336
14	1532	-1500
18	680	681
22	245	238
26	445	-460

-5,-12,L

10	252	-238

-5,-11,L

2	320	-340
4	257	-277
5	338	306
6	345	334

-5,-10,L

8	317	-302
10	385	-375
12	384	343
14	244	243

-5,-9,L

1	290	-302
2	627	-646
5	290	279
6	613	619
7	150	-112
8	238	199
9	267	-273
10	192	-196
16	472	-462

-5,-8,L

1	352	-363
7	255	-259
8	460	-469
10	547	-540
11	347	349
12	394	388
14	358	357
15	222	-239

-5,-7,L

1	618	-621
2	588	-638
3	572	576
4	403	-410
5	734	734
6	385	385
7	370	-368
8	459	476
9	231	-216
10	228	229
11	425	425
15	396	-405
16	516	-486
20	501	500

-5,-6,L

1	464	-474
2	599	635
6	304	-308
7	470	-467
8	417	-413
9	179	-158
10	454	-447

-5,-6,L

11	714	689
14	541	533
15	361	-356
22	339	-314

-5,-5,L

1	747	-747
2	693	-732
5	1284	1285
7	404	-423
9	314	-316
10	465	457
11	374	378
14	233	-229
15	696	-696
16	284	-273
17	369	367
19	349	379
20	436	470
21	298	-318

-5,-4,L

1	1246	-1275
2	1438	1481
4	307	309
5	480	490
6	602	-612
7	630	-616
8	547	-540
10	119	-112
11	638	628
12	136	-106
14	710	712
15	275	-283
16	278	267
17	206	213
20	362	-352
21	236	-287

-5,-3,L

1	504	-515
2	532	-569
4	1356	1328
5	913	904
6	675	-668
7	615	-626
8	807	792
9	565	-538
10	808	771
11	209	209
12	574	-561
14	920	-949
15	330	-334
17	394	385
19	387	398
20	208	209
21	168	-177
22	425	419

-5,-2,L

1	1108	-1113
2	1454	1489
3	509	-507
4	302	-293
5	425	432
6	825	-815
7	308	-296
8	574	-562
9	173	171
10	175	-187
11	1050	1020
12	486	-485
14	561	555
15	299	-302
16	896	902
18	184	-196
20	733	-752

-5,-1,L

1	772	-798
2	474	-507
3	1352	1397
4	625	-641
7	1339	-1298
8	984	959
9	437	-419
10	1496	1441
11	589	564
12	965	-941
13	445	-421
14	1347	-1318
22	374	385

-5,0,L

2	718	716
4	627	-641
6	633	-615
8	425	-421
10	674	657
12	333	353
14	1033	1024
16	1170	1134
20	659	-651
22	241	-253

-4,-12,L

2	323	-311

-4,-11,L

7	214	-196
8	303	-287

-4,-10,L

1	193	-148
2	446	-479
5	266	274
6	280	282
12	284	287
14	240	-240
16	401	-383

-4,-9,L

1	158	-143
2	273	-271
4	434	428
6	621	619
7	482	-478
8	414	-418
10	467	-461
11	355	347
15	192	-176
18	168	180

-4,-8,L

1	250	-265
2	946	-977
3	390	405
4	412	-409
5	249	238
6	415	400
7	412	-404
9	131	-110
11	276	287
12	609	616
13	277	-286
16	447	-436
17	289	310

-4,-7,L

1	320	-340
4	305	316
7	498	-495
8	588	-597
10	579	-567
11	573	571
15	336	-331
16	293	252

-4,-6,L

1	418	-438
2	738	-778
3	813	817
4	622	-635
5	344	338
6	262	253
7	644	-627
8	621	618
10	497	511
11	368	363
12	441	452
13	645	-647
15	329	-353
16	521	-542
17	427	442
18	142	-140
20	154	219
21	342	-325

-4,-5,L

1	754	-763
2	1282	1330
3	461	469
4	195	193
5	385	394
6	446	-427
7	351	-358
8	358	-370
10	727	-706
11	618	615
12	198	-215
14	268	281
15	195	-196
16	639	633
21	298	-336

-4,-4,L

1	1239	-1259
2	802	-815
3	343	333
4	550	-558
5	709	694
7	224	-227
8	983	975
10	395	405
11	322	323
13	531	-532
14	214	-219
15	271	-282
16	317	-312
17	398	400
18	193	-213
19	261	269
21	298	-324
22	351	377

-4,-3,L

1	356	-363
2	745	782
3	790	765
4	286	293
5	1046	1048
6	369	-366
7	644	-617
8	276	-289
9	379	374
10	145	-158

-4,-3,L

11	553	555
12	800	-769
13	517	-496
14	216	227
15	170	-162
16	918	863
17	227	235
20	350	-363
21	313	-310

-4,-2,L

1	1215	-1260
3	652	706
4	929	-898
5	1014	-994
7	755	-712
8	1209	1179
9	366	363
10	1018	1012
11	507	497
12	782	-758
14	313	-300
18	336	-336
22	426	445
24	210	235

-4,-1,L

1	1384	-1416
2	1790	1877
3	271	265
4	1615	1626
7	1113	-1075
8	142	-155
9	552	-527
10	218	190
11	395	388
12	959	-911
14	379	380
15	333	-348
16	1302	1305
20	444	-452

-4,0,L

2	1679	1683
4	4095	-4134
6	2064	-1994
8	398	383
10	1461	1335
12	1055	-1006
14	445	-439
18	505	-515
22	639	654

-3,-13,L

2	325	-318

-3,-12,L

4	328	301
6	192	175
8	290	-255

-3,-11,L

2	395	-404
12	317	301

-3,-10,L

2	235	-242
4	557	543
6	287	305
8	394	-379

-3,-9,L

2	745	-749
6	335	319
7	178	-176
10	214	215
12	281	243
14	256	-253
16	400	-353

-3,-8,L

2	269	-276
3	414	413
4	575	568
6	479	471
7	496	-491
8	561	-579
9	166	131
10	779	-776
11	428	428
18	339	350

-3,-7,L

1	373	-391
2	683	-729
3	635	625
4	392	-403
7	559	-558
8	358	346
9	417	417
10	609	594
11	383	372
12	628	622
13	510	-513
14	415	-417
16	280	-277
17	364	383

-3,-6,L

2	532	544
3	522	520
4	703	700
5	241	234
7	975	-965
8	447	-439
10	480	-464
11	572	552
13	286	-302
16	550	552
17	265	252
18	361	326

-3,-5,L

1	872	-874
2	653	-661
3	463	472
4	903	-905
7	241	-269
8	491	496
9	387	371
10	354	353
11	394	380
12	488	486
13	805	-801
16	304	-303
17	342	358
18	458	-463
21	246	-249
22	241	263

-3,-4,L

1	439	-440
2	1125	1164
3	1214	1183
4	1161	1155
5	339	331
6	491	-463
7	387	-406
10	484	-490
12	558	-574
13	448	-456
16	709	706
17	371	366
18	303	291
21	236	-269
23	208	224

-3,-3,L

1	612	-602
2	295	287
3	310	301
4	2254	-2242
5	200	190
8	840	804
9	307	-293
10	628	660
11	169	-183
13	371	-372
16	350	-353
17	358	350
18	551	-571
21	268	-248
22	450	479
24	202	252

-3,-2,L

1	1372	-1431
2	3278	3389
3	1728	1750
4	682	717
5	282	280
6	276	278
7	514	-479
8	257	244
9	211	-212
10	764	-756
11	514	494
12	1224	-1208
13	280	-272
14	342	336
16	815	799
17	342	343
24	199	-219

-3,-1,L

2	121	135
3	769	800
4	2248	-2195
5	1473	1463
6	1744	-1671
7	921	-904
8	1275	1221
10	945	907
14	290	299
18	752	-767
19	177	-219
21	179	-171
22	633	645

-3,0,L

2	1775	1822
4	403	-387
6	1076	-1014
8	621	-599
10	420	-425
12	1223	-1210
14	634	615
16	885	885

-2,-13,L

4	271	257

-2,-12,L

3	302	-267
7	205	179
10	227	203

-2,-11,L

4	517	494
8	386	-366

-2,-10,L

2	409	-400
7	182	171
10	294	283
12	357	332

-2,-9,L

1	331	327
3	558	559
4	701	688
6	577	579
7	204	-239
8	279	-293
9	230	242
10	234	-247
13	174	-210
18	382	382

-2,-8,L

2	466	-452
3	334	356
5	270	-272
6	311	-313
7	460	-457
8	382	-383
9	569	572
10	301	292
13	280	-269
16	214	-236
17	177	177

-2,-7,L

3	748	719
4	913	895
5	398	-380
6	220	204
7	732	-706
8	453	-432
9	231	234
10	453	-441
11	219	203
13	216	-204
14	140	-183
18	512	505
19	187	-185

-2,-6,L

3	997	968
4	271	-272
5	271	-261
6	818	-794
7	456	-448
9	728	713
10	525	515
11	177	156
12	533	528
13	524	-552
14	218	-232
18	350	-357
19	248	-259

-2,-5,L

2	313	324
3	1462	1406
4	1062	1022
5	778	-762
6	571	580
7	693	-703
8	542	-527
9	321	326
10	430	-441
11	438	429
12	390	-391
13	400	-413
15	509	522
16	431	437
17	333	347
18	318	313
19	331	-336

-2,-4,L

1	642	-640
2	484	-482
3	450	447
4	680	-662
5	539	-517
6	375	-373
7	298	-298
8	298	289
9	721	726
10	526	526
11	165	154
12	151	172
13	753	-733
16	339	-330
18	492	-491
19	247	-265
22	244	273

-2,-3,L

1	649	689
2	1102	1112
3	1061	1062
5	790	-777
6	566	566
7	761	-750
8	211	222
9	825	798
10	696	-680
12	826	-838
13	586	-589
15	382	409
16	301	294
17	483	491
19	235	-248
21	211	-191

-2,-2,L

1	574	-602
2	989	-1022
3	593	-566
4	239	205
5	314	-311
6	846	-845
7	343	-322
8	1305	1237
9	464	-419
10	1086	1067
11	302	277
12	483	473
14	444	448
16	183	-185
18	650	-656
19	323	-347
22	420	422
23	256	243

-2,-1,L

2	1362	1343
5	460	-454
6	484	474
7	398	-385
8	638	601
9	170	-181
10	1479	-1404
11	250	235
12	797	-780
14	233	231
16	347	337
18	274	267
24	396	-412

-2,0,L

2	87	75
4	3158	-3033
6	2065	-1983
8	514	487
10	993	903
12	443	440
14	489	505
16	316	-338
18	980	-1000
22	410	449

-1,-13,L

3	289	-270

-1,-12,L

4	358	388

-1,-11,L

1	240	-207
8	326	-337
10	299	297
12	262	268

-1,-10,L

3	175	195
4	469	467
9	188	-207
10	374	369
14	340	-312

-1,-9,L

2	254	-237
5	181	-192
9	246	251
12	304	292

-1,-8,L

1	562	571
3	466	443
4	769	763
5	245	-266
6	490	489
12	230	-205
14	362	-345

-1,-7,L

1	261	243
3	482	465
4	430	-433
5	842	-859
6	920	-917
8	580	-595
9	731	732
10	445	428
12	502	493
13	446	-444

-1,-6,L

1	664	642
2	379	-381
3	773	759

-1,-6,L

4	1014	982
5	537	-540
6	236	249
9	462	472
11	595	-600
12	249	-239
15	390	383
18	284	289
19	280	-294

-1,-5,L

1	211	-203
2	286	284
3	232	241
4	312	-338
5	847	-822
6	1284	-1244
8	611	-599
9	946	910
10	361	346
12	524	535
13	406	-415
14	324	320
16	247	-242
18	240	-210

-1,-4,L

1	317	319
3	328	317
4	309	303
5	853	-819
6	557	543
8	827	838
9	916	884
10	387	-389
12	669	-684
13	548	-562
15	486	481
19	403	-390
20	387	394

-1,-3,L

2	1360	1346
4	466	-474
5	201	-203
6	1284	-1274
7	159	144
8	251	226
10	427	435
11	301	-301
13	529	-532
14	468	480
15	173	132
16	257	-233
18	464	-476
19	189	-192

-1,-2,L

1	785	790
2	234	240
3	652	-592
4	141	150
5	388	-403
6	1393	1361
7	348	-339
8	869	835
9	864	828
10	1002	-981
12	1033	-1027
14	216	227
19	192	-227
20	409	443

-1,-1,L

2	1078	1037
3	724	709
4	2304	-2202
5	915	871
6	251	248
8	1595	1482
9	438	437
10	344	-343
12	194	210
13	196	186
14	808	810
18	558	-585

-1,0,L

2	191	203
4	527	545
6	1124	-1074
8	1010	970
10	1662	-1537
12	803	-816
16	342	360
20	390	400

0,-13,L

0	289	-278

0,-12,L

1	255	-254
2	195	203
3	143	-175
4	222	232
6	398	-384
8	160	-231

0,-11,L

0	553	-515
4	393	402
9	203	-183
10	198	187

0,-10,L

0	190	200
2	222	229
6	434	-410
8	368	-362
10	298	328

0,-9,L

0	1158	-1175
2	264	-296
4	532	557
6	259	236
8	202	222
10	429	419
12	331	-339
14	371	-358

0,-8,L

1	475	498
2	328	331
5	599	-596
6	588	-589
8	371	-365
9	407	409
10	349	340

0,-7,L

0	933	-983
1	490	504
4	428	427
5	604	-602
6	381	395
8	332	332
11	255	-268
12	454	-448
14	405	-380

0,-6,L

0	630	633
1	715	689
2	144	164
3	393	388
4	350	-356
5	401	-396
6	748	-733
8	651	-631
9	644	633
10	176	139
12	590	580
13	271	-299
14	320	322

0,-5,L

0	524	-547
1	788	792
2	513	-509
3	561	570
5	333	-329
6	872	844
8	968	966
9	213	201
10	286	-273
11	519	-507
12	669	-687
15	466	462

0,-4,L

0	771	797
1	328	333
2	202	195
3	349	347
4	480	-478
5	803	-804
6	381	-398
8	348	-359
9	764	736
11	340	-336
12	433	436
14	610	600

0,-3,L

0	184	185
2	921	-920
3	1918	1911
4	793	-783
5	460	433
6	1674	1637
8	1179	1148
9	634	639
10	600	-574
11	447	-436
12	556	-555
13	402	-384
16	255	-257
19	279	-294
20	340	351

0,-2,L

0	2819	2913
1	743	739
3	660	-640
4	2267	-2244
5	422	411
6	379	-370
7	295	-285
9	581	566
10	729	-748
11	612	-596
12	471	475
14	917	909

0,-2,L

15	332	363
17	181	-185
18	504	-522

0,-1,L

1	235	237
2	1337	-1289
4	935	-905
5	173	168
6	1261	1228
7	311	-305
8	1000	974
10	622	-612
12	826	-790
16	265	-243
20	613	618

0,0,L

2	236	245
4	4008	-3877
8	459	423
10	1595	-1522
12	453	475
14	1077	1078
18	462	-458

1,-13,L

2	270	263

1,-12,L

0	400	-369

1,-11,L

2	469	502
6	613	-620

1,-10,L

0	625	-641
10	290	290
14	351	-292

1,-9,L

2	713	702
5	224	-211
6	520	-531
10	244	259

1,-8,L

0	715	-728
1	433	445
2	201	-214
4	409	419
5	258	-275
6	433	430
8	245	224
9	429	440
12	280	-279
14	403	-388

1,-7,L

0	307	328
1	951	966
2	798	814
4	251	243
5	826	-805
6	702	-684
8	537	-544
9	687	699
14	290	300
15	283	272
16	250	203
17	250	-268

1,-6,L

0	720	-751
1	764	777
2	356	-362
5	502	-513
6	593	595
7	488	504
8	412	410
9	235	244
11	639	-616
12	412	-395
14	273	-277

1,-5,L

0	497	532
1	849	868
2	742	761
3	453	-429
4	101	129
5	1346	-1340
7	344	349
8	740	-743
9	559	573
11	423	-416
12	443	448
14	404	395
15	404	415

1,-4,L

0	486	-527
1	1193	1193
2	880	-853
4	778	-776
5	761	-763
6	1359	1373
7	405	-399
8	701	693
9	376	385
11	840	-848
14	461	-454
15	290	318
20	369	357

1,-3,L

0	634	646
1	1071	1076
3	168	169
4	287	273
5	481	-466
7	473	457
8	711	-689
9	411	419
10	536	-534
11	463	-458
12	471	470
14	765	763
15	336	343

1,-2,L

0	323	-348
1	1270	1282
2	4006	-3971
3	215	203
4	474	463
5	438	-431
6	2181	2135
8	698	680
10	451	-445
11	573	-578
14	442	-458
16	525	-530
17	195	-241
20	361	371

1,-1,L

0	2675	2799
2	314	-288
3	796	777
4	1733	-1648
5	1109	-1074
6	309	-317
7	203	194
8	1037	-1010
9	434	428
10	708	-702
12	569	560
13	401	404
14	999	1031
15	301	297
18	301	-338

1,0,L

0	246	149
2	1845	-1810
4	172	-172
6	1568	1527
8	1064	1034
10	364	-360
12	177	-202
14	222	-213
16	389	-380
20	534	560

2,-12,L

0	176	-190
2	433	419
6	277	-268

2,-11,L

0	270	-253
3	192	184
8	287	282
10	335	325

2,-10,L

2	665	665
6	466	-470

2,-9,L

0	610	-640
1	206	190
2	220	-231
4	238	-238
6	311	-287
7	380	378
8	416	398
9	153	194
10	428	422
11	319	-328
14	284	-275

2,-8,L

1	512	535
2	1010	1030
4	342	325
5	549	-550
6	636	-633
16	343	320

2,-7,L

0	276	-295
1	533	555
2	254	-262
4	214	-229
7	285	282
8	267	261
10	344	365

2,-7,L

12	241	-233
14	389	-372
16	153	-119

2,-6,L

0	624	635
1	817	819
2	1181	1203
3	598	-586
4	285	304
5	546	-571
6	337	-352
7	621	594
8	802	-818
9	402	402
11	517	-521
14	258	267
15	427	447
17	288	-291

2,-5,L

0	537	-548
1	834	860
2	669	-674
3	725	-699
5	511	-499
6	166	-162
7	474	469
8	274	271
10	326	321
11	815	-824
14	302	-309
15	315	321

2,-4,L

0	352	365
1	1424	1450
2	566	570
3	1174	-1131
4	808	811
5	341	-356
7	733	731
8	899	-911
10	566	-538
11	311	-320
12	453	454
13	407	413

2,-3,L

0	628	-648
1	362	381
2	1459	-1458
3	1280	-1246
5	748	-744
6	1381	1322
7	1603	1591
10	155	182
11	767	-761
12	266	265
14	333	-325
15	478	483
16	336	-337
20	319	316

2,-2,L

0	1612	-1520
1	582	-589
2	231	236
3	630	-620
4	396	411
5	389	363
7	544	539
8	1124	-1133
10	850	-831
12	726	740
13	341	311
14	534	535
17	260	-266

2,-1,L

1	382	369
2	1882	-1854
3	1867	-1828
4	884	-889
5	745	-721
6	1827	1718
8	585	583
9	191	-175
11	324	-329
12	239	243
14	422	-411
16	750	-757
20	441	438

2,0,L

0	797	796
2	2033	2083
4	1391	1392
8	955	-941
10	752	-770
12	793	788
14	537	536

3,-12,L

4	317	-306

3,-11,L

1	198	209
2	486	483

3,-10,L

1	242	277
2	343	348
4	618	-628
6	508	-494
7	223	223
8	592	588
10	237	232

3,-9,L

1	277	236
2	568	576
3	298	-288
10	222	-187
12	274	-259
14	172	169

3,-8,L

4	597	-610
6	395	-396
8	675	649
10	349	349

3,-7,L

1	619	628
2	793	806
3	341	-341
4	424	423
5	501	-507
6	264	-283
7	393	394
10	362	-357
12	215	-203
13	390	365
16	265	261

3,-6,L

0	420	-430
2	361	-368
3	465	-471
4	630	-636
5	210	214
6	352	-358
7	772	759
8	646	631
9	269	-275
10	534	522
11	325	-322

3,-5,L

0	254	287
1	915	917
2	662	679
3	618	-621
4	746	723
5	339	-352
6	302	-301
7	475	491
8	692	-701
9	227	-212
11	369	-377
16	257	271

3,-4,L

0	255	-260
1	444	449
2	1385	-1400
3	1094	-1028
4	593	-571
5	239	-222
6	241	-232
7	778	770
8	242	246
10	503	508
11	636	-629
15	332	360
16	529	-534
17	199	-204

3,-3,L

0	212	-198
1	255	-249
2	136	-128
3	297	-304
4	1457	1422
5	849	811
6	741	746
7	448	438
8	855	-859
9	396	-412
10	794	-761
12	276	259
16	240	240
17	264	-294
18	334	338

3,-2,L

0	228	218
2	1763	-1739
3	1704	-1632
4	563	-560
5	463	-441
6	501	488
7	1277	1262
9	236	243
10	314	308
12	819	797
13	156	150
14	268	-285
16	601	-628

3,-1,L

0	176	-192

3,-1,L

1	299	283
2	344	-343
3	453	-468
4	1572	1563
6	1287	1273
8	1418	-1429
9	554	-551
10	859	-844
12	295	275

3,0,L

2	275	-265
4	1580	-1535
6	451	456
10	388	390
12	578	586
14	394	-387
16	538	-534
18	247	278
20	203	284

4,-11,L

0	391	384
3	145	-105
4	593	-572
8	326	323

4,-10,L

1	256	282
2	298	292
8	262	261
10	279	-291

4,-9,L

0	455	452
1	183	-189
3	536	-546
4	890	-888
6	382	-389
7	292	311
8	554	536

4,-8,L

1	368	385
2	377	390
3	265	-262
6	270	268
8	244	280
9	238	-255
10	497	-501
12	361	-331
13	265	235

4,-7,L

0	585	581
1	184	-183
2	252	-269
3	626	-610
4	842	-829
7	485	492
8	657	675
9	325	-309
13	376	368

4,-6,L

1	194	240
2	453	468
3	573	-599
4	661	663
5	255	-245
6	216	195
7	444	433
9	264	-243
10	487	-460
12	203	-199
13	263	244
14	206	208

4,-5,L

1	304	314
2	389	-397
3	401	-416
4	563	-592
5	436	438
6	423	-431
7	695	740
9	376	-368
10	361	339
11	364	-374
12	463	454
13	369	370
16	279	-300

4,-4,L

0	1108	-1075
1	332	329
2	487	505
3	388	-397
4	1410	1399
6	336	318
7	452	440
8	279	-280
9	790	-805
10	519	-521
11	255	-272
12	357	-348
18	224	240

4,-3,L

0	233	231
1	387	-388
2	1525	-1507
3	950	-944
4	356	-358
5	703	677
6	212	-209
7	838	817
9	127	-158
10	482	479
12	618	637
16	318	-336
17	198	-208

4,-2,L

0	298	-289
1	757	-724
2	215	-213
3	707	-697
4	1152	1170
5	206	192
6	729	720
7	450	464
8	809	-819
9	597	-598
10	722	-737
11	251	-234
12	336	-335
13	488	487
14	192	207
17	295	-286
18	398	396

4,-1,L

1	184	206
2	786	-783
3	290	277
4	579	-558
5	288	-275
6	583	-575
10	1070	1087
12	649	649
14	348	-347
16	354	-348

4,0,L

2	254	-241
4	1304	1284
6	1341	1366
8	1117	-1125
10	842	-831
14	189	-204
18	431	452

5,-12,L

0	263	268
4	286	-269

5,-11,L

4	202	-218

5,-10,L

0	423	443
1	241	-229
4	429	-410
8	246	218

5,-9,L

0	187	233
5	274	281
6	406	405
7	132	-10
8	314	305
9	228	-224
10	420	-426
12	314	-323

5,-8,L

0	496	488
1	297	-289
3	506	-530
4	462	-448
6	194	-195

5,-7,L

3	245	-227
4	210	199
5	401	388
6	649	642
8	239	220
9	477	-460
10	525	-521
12	341	-341
13	319	350

5,-6,L

0	577	570
1	339	-334
2	324	-328
3	545	-562
4	590	-592
5	609	603
6	341	-339
7	326	321
9	454	-451
11	163	153
12	394	393
15	214	-235

5,-5,L

0	490	-493
2	238	235

5,-5,L

3	414	-420
4	590	605
5	606	606
6	548	534
8	197	-194
9	685	-659
10	492	-482
13	287	317

5,-4,L

0	633	621
1	495	-502
2	632	-635
5	614	607
6	365	-367
7	264	264
8	374	-378
9	721	-731
10	341	326
12	493	501
13	252	275
15	190	-221
16	329	-365

5,-3,L

0	1292	-1274
1	925	-909
2	110	-117
3	816	-825
4	1062	1074
5	371	380
6	554	560
7	268	263
9	707	-725
10	469	-464
11	146	-196
12	424	-441
13	497	504
16	157	185

5,-2,L

0	364	373
1	621	-633
2	157	-170
6	514	-524
8	613	-616
9	277	-275
10	990	985
11	413	427
12	656	669
13	329	345

5,-1,L

0	211	-207
2	640	-582
3	538	-527
4	970	1006
6	450	428
8	506	-502
9	357	-342
10	226	-228
13	329	307
14	236	-242
18	427	447

5,0,L

0	204	-194
2	304	-302
6	1167	-1141
8	412	-403
10	1138	1169
12	380	358
16	340	-342

6,-11,L

0	482	459
4	317	-282

6,-10,L

6	400	376
8	275	237

6,-9,L

0	471	466
4	318	-311

6,-8,L

5	398	393
6	417	390
8	201	173
9	322	-340
10	347	-339
12	275	-291

6,-7,L

0	527	528
1	265	-270
3	367	-357
4	412	-408
7	229	-238
11	243	251
12	387	396

6,-6,L

0	283	-302
1	466	-456
2	410	-399
4	200	206
5	379	379
6	418	400
7	245	-248
9	381	-384

6,-5,L

0	422	443
1	363	-365
2	610	595
5	527	540
6	720	-712
8	609	-618
9	231	-205
11	354	336
12	521	522
14	216	207
15	183	-219

6,-4,L

0	1292	-1246
1	509	-504
2	447	-448
4	795	803
5	756	758
6	636	644
9	403	-400
11	215	236
12	288	-280
14	512	-525

6,-3,L

1	907	-898
3	798	-774
4	231	242
5	654	647
6	622	-631
8	782	-780
9	395	-394
10	421	401
12	410	433
13	315	347
15	162	-204

6,-2,L

0	2011	-1989
1	846	-822
3	200	-202
4	1022	1038
9	360	-352
10	355	368
11	291	271
12	330	-317
13	224	213
14	514	-511
16	173	191

6,-1,L

1	515	496
2	481	484
3	198	189
4	539	523
6	1071	-1090
8	462	-467
10	528	528
12	437	461
14	260	-262

6,0,L

0	2310	-2344
2	330	-339
4	1198	1222
6	303	330
10	804	813
12	318	-325
14	581	-583

7,-12,L

0	454	418

7,-11,L

2	348	-346

7,-10,L

0	623	603
4	308	-300

7,-9,L

2	298	-312
4	181	-190
6	530	500

7,-8,L

0	684	694
8	278	-275

7,-7,L

0	385	-382
1	386	-373
2	385	-379
5	332	328
6	303	298
7	215	-215
8	334	337
12	188	-117

7,-6,L

0	518	554
1	620	-636
2	367	378
3	195	164

7,-6,L

5	377	367
6	340	-360
7	333	-325
8	325	-316
11	330	339
12	349	335

7,-5,L

0	496	-515
1	369	-375
2	681	-667
4	252	229
5	559	570
7	194	-210
14	346	-348

7,-4,L

0	180	215
1	606	-605
2	761	750
3	373	-380
4	325	329
5	590	587
6	458	-437
8	352	-378
12	236	248

7,-3,L

3	1483	-1476
4	371	375
5	653	679
6	302	310
7	200	-206
8	541	538
9	132	-168
10	391	397
12	564	-583
14	594	-577

7,-2,L

0	171	206
1	154	-187
2	1094	1059
3	847	-799
4	310	310
5	193	191
6	1052	-1076
8	813	-802
9	257	-268
11	235	215
13	185	190
16	314	330

7,-1,L

0	1514	-1515
2	192	168
3	226	192
4	552	547
5	491	485
6	142	-154
7	287	-300
8	758	759
10	509	502
12	388	-381
14	481	-508

7,0,L

0	397	401
2	1195	1222
4	303	-302
6	1298	-1278
8	565	-581
10	184	205
16	272	298

8,-11,L

0	434	391

8,-10,L

2	524	-510
4	152	-132
6	354	352

8,-9,L

0	334	323
8	259	-265

8,-8,L

0	235	-221
1	240	-219
2	460	-446
3	172	181
5	242	223
6	484	461

8,-7,L

0	322	319
1	160	-174
7	459	-446
8	308	-275
11	415	394

8,-6,L

0	421	-428
1	422	-424
2	416	-400
3	260	257
7	275	-258
8	166	168

8,-5,L

0	450	475
1	574	-589
2	843	855
3	217	219
4	319	322
5	368	351
6	397	-390
7	401	-395
8	341	-362
10	235	-225
11	257	277

8,-4,L

0	826	-853
1	338	-333
2	441	-438
5	530	540
6	246	264
7	217	-230
8	585	564
10	347	342
11	246	250
14	318	-302

8,-3,L

1	449	-448
2	672	699
4	409	409
5	274	304
6	593	-591
7	401	-390
8	328	-354

8,-2,L

0	404	-424
1	144	-142
4	316	-311
5	344	322
7	534	-535
8	669	661
12	411	-390
14	377	-367

8,-1,L

2	907	906
6	988	-1007

8,0,L

2	228	-215
4	228	-234
8	934	919
10	358	352
12	363	-339
14	279	-284

9,-11,L

2	319	-325

9,-10,L

0	154	143

9,-9,L

1	151	-153
2	496	-493
6	239	253

9,-8,L

4	362	349
7	233	-263

9,-7,L

1	360	-332
2	364	-328
3	290	287
4	180	-200
7	171	-176
10	183	188

9,-6,L

0	226	241
1	284	-282
2	332	332
3	389	397
7	399	-410
8	342	-343
10	290	-276
11	322	315

9,-5,L

0	382	-384
1	569	-546
2	316	-299
3	341	330
5	151	173
7	328	-338
8	152	123
10	261	258

9,-4,L

1	362	-359
2	550	564
3	340	339
4	278	271
7	369	-366
8	166	-166

9,-4,L

9	147	127

9,-3,L

0	435	-455
1	553	-556
3	318	322
4	349	-323
5	271	263
8	670	653
10	224	213
11	152	171

9,-2,L

2	1031	1024
3	257	287
4	362	360
6	389	-380
7	571	-570
10	219	-234

9,-1,L

0	246	-262
1	541	-543
2	121	-117
4	579	-585
6	375	-379
8	495	484
10	488	475
12	264	-281

9,0,L

0	650	622
2	823	845
6	550	-543
8	344	363
14	338	324

10,-10,L

2	336	-343

10,-9,L

4	347	329

10,-8,L

2	401	-364

10,-7,L

3	282	271
4	311	302
7	269	-302
8	347	-312

10,-6,L

1	349	-358
3	406	412
7	236	-233
10	268	257

10,-5,L

0	311	287
1	312	-331
2	407	418
3	332	338
4	214	238
7	243	-234
8	221	-200

10,-4,L

1	425	-426
2	319	-322
3	357	340
4	613	-607
8	259	274
9	315	295
10	295	304

10,-3,L

2	541	564
3	507	534
4	428	413
5	235	-235
7	199	-207
12	230	-244

10,-2,L

3	269	293
4	551	-563
6	474	-447
8	490	488
10	280	244

10,-1,L

0	298	280
2	1020	1029
3	171	181
8	134	111
10	266	-269
12	372	-384

10,0,L

4	772	-776
6	742	-779
8	486	518
10	303	302

11,-10,L

0	230	-176

11,-9,L

2	316	-306

11,-8,L

0	358	-357
3	345	309
4	424	387

11,-7,L

3	293	269
3	419	438
4	311	324
7	302	-251

11,-5,L

0	305	289
2	162	-189
3	400	396
4	288	-254
5	261	-282
6	295	-291
9	241	229

11,-4,L

4	279	263
7	183	-153
10	280	-267

11,-3,L

0	323	320
3	328	351
4	650	-641

11,-2,L

2	607	613
3	224	215
6	228	249
8	152	168
10	300	-300

11,-1,L

0	465	473
1	154	-185
4	1073	-1044
8	249	246

11,0,L

2	693	662
6	163	170
10	415	-358

12,-9,L

0	405	-392

12,-7,L

0	495	-503
1	216	213
3	377	373
4	364	349

12,-6,L

5	296	-245
6	268	-256

12,-5,L

3	419	421
6	263	275

12,-4,L

0	514	509
4	404	-394
5	399	-369
6	321	-309
9	257	249

12,-3,L

0	392	-391
3	316	327
6	404	385

12,-2,L

0	763	752
4	501	-508

12,-1,L

1	234	225
2	252	240
4	183	-167
6	390	365
8	193	215
10	252	-242

12,0,L

0	1043	1058
4	753	-758

13,-8,L

1	258	238

13,-7,L

1	164	194

13,-6,L

0	362	-341
1	436	413
3	200	-211

13,-5,L

0	259	244
1	379	368
2	396	407
4	211	-210
5	341	-315
6	361	-338

13,-4,L

1	440	428
6	366	334

13,-3,L

0	554	531
4	353	-326
5	249	-244

13,-2,L

1	286	292
2	417	-419
6	442	423
8	185	200

13,-1,L

0	1031	1031
4	435	-415
6	149	-118

13,0,L

4	328	-318
6	419	436
8	278	270

14,-7,L

0	346	-341
1	240	254

14,-6,L

0	317	310
1	293	288
2	350	370

14,-5,L

1	317	313
2	245	-226

14,-4,L

0	613	596
1	332	337
5	273	-253

14,-3,L

0	310	-306
1	340	309
2	595	-590
6	382	355

14,-2,L

0	686	672
4	268	-271

14,-1,L

2	608	-607
6	400	394

14,0,L

0	879	849

15,-7,L

1	311	280

15,-5,L

0	313	303
1	406	404
2	181	210

15,-4,L

2	379	-354

15,-3,L

0	428	399
1	203	189
4	192	198

15,-2,L

1	182	166
2	628	-613
3	305	-289

15,-1,L

0	411	387
4	294	239

15,0,L

2	674	-637
6	423	396

16,-5,L

2	256	-241

16,-3,L

1	171	155
2	444	-409

16,-2,L

4	296	282

16,-1,L

2	534	-513

16,0,L

4	428	428

17,-1,L

0	257	-239

17,0,L

2	410	-373

18,-2,L

0	364	-330

18,0,L

0	567	-526

Data for N-[2,4,6-trimethylphenyl]α-nitroso-4-methylbenzaldimine-N-oxide

Crystal Data

$C_{17}H_{18}N_2O_2$, M = 282.35; monoclinic,

a = 8.192(2)Å, b = 10.912(2)Å, c = 9.890(2)Å, β = 118.23(4)°;

V = 778.92Å^3; D_c = 1.20 g.cm^{-3}, Z = 2; F(000) = 300;

space group $P2_1$ (C_2^2, No.4); $M_0 - K\alpha$ radiation, $\mu(M_0 - K\alpha)$ = 0.74 cm^{-1}.

λ = 0.7107Å.

0,0,L

4	79	82	0
6	35	32	0
7	46	41	0
8	95	92	0
9	51	50	0
10	14	22	180

0,1,L

-9	104	105	161
-8	52	50	248
-7	82	81	48
-6	108	110	31
-5	53	55	191
-4	66	73	180
-3	144	145	69
-2	104	100	247
-1	322	343	161
1	328	343	341
2	103	100	67
3	146	145	249
4	68	73	0
5	51	55	11
6	110	110	211
7	82	81	228
8	51	50	68
9	103	105	341

0,2,L

-9	55	54	121
-8	66	67	127
-7	44	46	132
-6	65	62	84
-5	81	80	87
-4	27	27	222
-3	67	74	52
-2	472	495	60
1	353	368	200
3	69	74	52
4	26	27	222
5	83	80	87
6	66	62	84
7	42	46	132
8	67	67	127
9	55	54	121

0,3,L

-8	36	35	43
-7	53	55	193
-6	29	27	265
-5	46	45	191
-4	80	78	88
-3	78	78	13
-2	185	191	311
-1	67	70	98
1	67	70	278
2	178	191	131
3	76	78	193
4	75	78	268
5	43	45	11
6	27	27	85
7	51	55	13
8	36	35	223

0,4,L

-8	31	28	277
-7	56	57	212
-6	40	40	19
-5	35	33	356
-4	57	63	169
-3	69	68	40
-1	149	154	193
0	210	220	171
1	150	154	193
2	184	197	150
3	71	68	40
4	60	63	169
5	34	33	356
6	39	40	19
7	54	57	212
8	26	28	277
9	20	20	333

0,5,L

-7	55	49	234
-6	52	52	182
-5	36	37	281
-4	25	16	182
-3	140	137	192
-2	39	37	240
-1	105	101	95
1	104	101	275
2	38	37	60
3	145	137	12
4	23	16	2
5	35	37	101
6	53	52	2
7	55	49	54

0,6,L

-7	26	26	294
-6	45	52	183
-5	62	60	210
-4	82	91	216
-3	93	90	197
-2	96	82	270
-1	51	50	346
0	33	28	147
1	54	50	346
2	100	82	270
3	95	90	197
4	83	91	216
5	63	60	210
6	47	52	183
7	24	26	294
8	19	20	280
9	20	17	243

0,7,L

-9	26	24	300
-7	22	22	2
-6	19	24	341
-5	18	19	107
-4	44	42	316
-3	52	52	277
-2	29	33	115
-1	26	27	256
1	25	27	76
2	29	33	295
3	49	52	97
4	44	42	136
5	19	19	287
6	22	24	161
7	24	22	182
8	14	16	208
9	26	24	120

0,8,L

-8	8*	17	90
-7	30	36	67
-6	33	35	328
-5	33	34	339
-4	37	40	53
-3	38	39	313
-2	21	18	345
-1	41	45	352
0	95	95	346
1	41	45	352
2	20	18	345
3	35	39	313
4	38	40	53
5	33	34	339
6	32	35	328
7	31	36	67

0,9,L

-6	31	31	42
-4	33	32	22
-3	14	13	18
-1	35	35	327
1	35	35	147
4	31	32	202
5	16	19	77
6	29	31	222

0,10,L

-4	21	23	105
-3	34	37	356
-1	51	53	187
0	112	116	183
1	53	53	187
2	10*	8	190
3	35	37	356
4	21	23	105
6	15	10	251

0,11,L

-5	21	21	275
-3	16	14	62
-2	18	20	84
-1	42	40	342
1	43	40	162
2	20	20	264
5	19	21	95

0,12,L

-3	19	15	243
-2	25	25	162
-1	44	43	33
0	76	75	332
1	44	43	33
2	25	25	162
5	0*	6	44

0,13,L

-2	37	36	210

-1	31	30	135
1	30	30	315
2	37	36	30

1,0,L

-10	29	27	180
-9	77	80	0
-8	132	131	0
-7	37	41	180
-6	75	77	180
-5	46	50	0
-4	77	70	0
-3	136	138	180
-2	49	49	180
-1	145	139	180
0	353	342	0
2	454	474	0
3	26	25	180
4	41	39	180
6	43	47	0
7	30	35	0
9	12	14	180
10	36	37	180

1,1,L

-9	54	51	151
-8	90	88	326
-7	49	53	26
-6	129	129	289
-5	89	93	65
-4	236	231	51
-3	77	72	209
-2	213	216	204

-1	234	225	105
0	425	435	354
3	77	74	303
4	64	70	62
5	48	46	267
6	21	24	316
7	24	24	1
8	25	21	215
9	57	55	304
10	25	24	11

1,2,L

-8	113	118	169
-7	35	38	95
-6	163	172	17
-5	52	56	270
-4	100	112	66
-3	298	312	70
-2	181	187	133
-1	189	200	325
0	493	530	75
1	385	397	223
2	304	322	325
3	144	148	293
4	134	121	84
5	77	75	39
6	26	27	253
8	34	33	54
9	18	19	58
10	26	24	322

1,3,L

-11	22	21	274

-9	42	43	184
-8	33	34	96
-7	143	146	139
-6	97	98	108
-5	67	76	221
-4	97	96	300
-2	157	169	164
-1	147	153	22
0	234	236	268
1	460	484	122
3	231	232	343
5	18	18	161
6	33	32	215
8	24	26	103
9	33	32	80
10	23	23	148

1,4,L

-11	15	14	32
-9	14	16	95
-8	18	21	346
-7	35	40	27
-6	79	79	138
-5	111	98	155
-4	51	48	90
-3	180	172	10
-2	119	114	2
-1	33	35	319
0	99	106	146
1	41	44	314
2	344	346	135
3	166	166	150
4	40	42	154
6	27	26	126

7	27	27	190
8	19	18	224
9	22	21	219
10	11*	9	105

1,5,L

-10	9*	10	40
-9	24	24	341
-8	26	24	17
-7	53	50	263
-6	8*	9	228
-5	35	30	287
-4	49	50	183
-3	20	27	68
-2	251	258	2
-1	71	65	174
0	56	55	238
1	23	25	322
2	76	70	255
3	68	69	158
4	41	43	101
5	36	34	60
6	56	57	9
7	49	50	11
9	12	10	43

1,6,L

-9	23	19	85
-8	20	19	176
-7	30	30	236
-6	36	34	240
-5	29	36	173

1,6,L

-4	61	58	256
-3	192	187	189
-2	209	207	177
-1	42	41	272
0	21	21	214
1	55	61	102
3	45	46	353
4	40	34	273
5	42	37	207
6	41	42	171
7	29	31	323
8	15	18	57

1,7,L

-9	24	22	242
-8	39	41	254
-7	40	42	286
-6	39	39	274
-4	30	30	13
-3	61	62	239
-2	88	80	125
-1	83	86	217
0	19	22	263
1	28	27	195
2	20	23	229
3	21	26	286
6	60	61	167
7	27	26	180
8	27	28	282

1,8,L

-8	32	28	323
-7	14	12	327
-6	25	26	248
-5	27	26	244
-4	25	23	14
-3	60	57	302
-1	47	48	177
0	65	61	223
1	69	69	298
2	63	66	273
3	67	70	240
4	17	17	329
5	35	35	356

1,9,L

-8	20	24	80
-7	31	32	50
-6	42	43	34
-4	17	16	2
-3	28	28	315
-2	24	21	0
-1	48	44	339
0	51	55	81
1	112	108	15
2	61	62	17
3	36	39	139
4	34	33	231
5	31	32	350

1,10,L

-6	29	27	15
-5	44	41	39
-3	25	26	329
-2	43	42	23
-1	81	79	335
0	28	25	237
2	29	26	356
3	36	34	46
5	20	16	299

1,11,L

-6	23	26	172
-5	5*	10	197
-4	27	27	89
-2	17	15	149
-1	34	35	21
0	60	56	196
1	73	76	177
2	31	30	223
4	15	11	50

1,12,L

-2	13	19	175
-1	34	28	51
0	17	18	9
1	44	43	85
2	19	18	146

1,13,L

-2	20	18	204
0	15	17	325
1	22	25	316
3	15	16	187

2,0,L

-10	33	28	0
-9	15	15	0
-8	10*	13	180
-7	26	25	0
-6	50	56	0
-5	242	244	180
-4	42	46	0
-3	217	222	0
-2	169	169	0
-1	47	47	180
0	147	130	180
1	178	189	180
2	71	70	180
3	121	136	180
4	137	136	0
5	65	60	0
6	20	20	180
9	14	14	0

2,1,L

-10	36	37	80
-9	56	54	96
-8	26	27	352
-7	20	20	59
-6	72	68	223
-5	303	293	146
-4	96	99	246
-3	111	112	155
-2	284	278	70
-1	94	100	353
0	545	530	192
1	44	45	148
2	172	180	57
3	48	45	175
4	138	138	164
5	23	20	293
6	27	27	51
7	10	10	29
8	17	15	225
9	20	22	230

2,2,L

-11	16	17	107
-10	17	16	153
-9	50	50	50
-8	74	73	83
-7	85	85	304
-6	104	94	301
-5	83	84	326
-4	194	197	52
-3	41	39	168
-2	82	77	101
-1	518	537	74
0	558	545	75
1	143	138	352
2	242	259	358
3	65	74	276
6	26	23	72
7	40	41	50
8	17	16	22

2,3,L

-10	32	33	220
-9	76	75	257
-8	20	16	184

2,3,L

-7	189	191	156
-6	41	45	13
-5	89	92	289
-4	66	70	212
-3	23	27	224
-2	168	159	264
-1	308	310	190
0	52	45	307
1	201	211	57
2	199	205	245
3	133	128	320
4	47	45	321
5	52	56	333
6	35	35	295
7	26	29	250
9	33	34	34

2,4,L

-10	25	28	256
-9	40	40	163
-8	97	99	211
-7	26	31	105
-6	182	189	127
-5	78	86	89
-4	41	32	202
-3	180	183	159
-2	54	47	187
-1	99	95	228
0	157	160	205
1	99	99	261
2	248	252	104
3	79	86	126
4	25	19	132
5	29	28	128
7	48	49	215
8	27	30	174

2,5,L

-11	20	18	2
-10	29	22	316
-9	22	24	246
-8	19	18	46
-7	96	100	314
-6	62	62	333
-5	47	52	140
-4	26	28	119
-2	224	227	359
-1	85	77	10
0	78	79	21
1	89	94	220
2	125	126	308
3	89	90	98
4	35	30	192
5	15	10	270
6	35	38	68
7	19	20	48

2,6,L

-9	27	26	12
-8	52	53	344
-7	47	45	85
-6	32	33	258
-5	20	25	334
-4	26	32	272
-3	91	95	171
-2	73	62	330
-1	141	149	298
0	64	61	185
1	26	27	225
2	75	71	224
4	43	44	121
5	24	25	232
7	38	39	347

2,7,L

-10	25	24	146
-9	26	26	86
-8	33	31	43
-7	27	26	236
-6	23	23	209
-5	40	40	7
-4	47	47	5
-3	43	41	208
-2	97	86	132
-1	65	59	212
0	113	114	31
2	58	51	109
3	63	64	67
4	44	48	58
6	9*	15	124

2,8,L

-9	40	40	150
-7	38	43	260
-6	45	46	255
-5	54	62	241
-3	16	18	313
-2	17	14	202
-1	52	58	153
0	85	84	121
1	22	21	283
2	94	97	229
3	46	50	288
4	46	45	317
6	25	24	214

2,9,L

-9	18	15	259
-8	18	14	90
-6	28	28	147
-5	34	36	187
-4	30	28	251
-1	75	78	264
0	100	99	150
1	42	45	104
2	42	43	202
3	33	34	222
6	13	12	218
7	17	15	286

2,10,L

-6	28	30	40
-5	30	34	34
-3	9*	9	334
-2	32	34	56
-1	59	60	311
0	42	45	306
1	87	88	28
2	37	38	24

2,11,L

-5	41	38	13
-4	20	21	32
-3	21	20	201
-2	23	21	127
-1	29	30	38
0	47	44	268
1	37	36	313
2	18	18	287
4	29	28	313

2,12,L

-5	24	23	132
-2	10*	15	229
1	18	20	203
2	15	17	167
3	26	26	115

2,13,L

-2	16	18	5

3,0,L

-11	25	22	0
-9	24	23	180
-8	46	42	0
-7	23	23	0
-5	134	121	0
-4	549	505	0
-3	102	100	0
-2	137	133	0
-1	186	181	0

3,0,L

0	89	85	0
1	140	141	0
3	26	19	180
4	114	110	0
5	67	66	0
7	17	14	0

3,1,L

-12	15	17	178
-10	22	22	54
-9	34	37	347
-8	31	37	170
-7	41	40	97
-6	68	70	15
-5	236	223	166
-4	284	282	190
-3	201	172	80
-2	40	31	327
-1	62	67	290
0	107	111	287
1	150	159	238
2	128	130	216
3	33	36	202
4	57	62	134
5	37	38	336
8	10*	11	333

3,2,L

-10	28	27	107
-9	85	91	61
-8	59	60	80
-7	26	33	27
-6	107	116	64
-5	60	46	263
-4	174	171	134
-3	75	64	145
-2	58	56	61
-1	205	196	62
0	95	96	48
1	210	217	134
2	149	141	81
3	65	68	53
4	52	49	120
5	62	64	159
7	26	27	102
8	24	16	90

3,3,L

-10	37	40	197
-9	28	29	149
-8	87	93	26
-7	68	76	15
-6	56	59	238
-5	90	89	187
-4	104	100	343
-3	30	29	35
-2	175	167	264
-1	120	112	124
0	217	226	44
1	203	190	58
3	63	59	341
4	48	50	287
5	17	17	328
7	12	15	327
8	19	21	30

3,4,L

-10	17	15	246
-9	30	32	214
-8	93	94	231
-7	50	47	102
-6	133	139	146
-5	18	20	309
-4	139	127	174
-3	165	165	105
-2	15	22	289
-1	305	291	188
0	119	116	162
1	120	124	351
2	67	73	37
3	80	85	227
4	19	22	98
5	24	23	124
7	26	26	256

3,5,L

-10	19	15	246
-8	103	107	198
-7	188	195	206
-6	39	39	42
-5	39	34	54
-4	72	70	287
-3	41	37	189
-2	72	65	101
-1	109	110	193
0	35	39	273
1	145	142	181
2	33	35	41
3	65	69	45
4	33	28	296
5	19	21	83
6	17	18	110
8	22	22	175

3,6,L

-10	28	27	313
-8	62	61	291
-7	23	22	145
-6	75	79	267
-5	17	14	136
-4	37	37	176
-3	35	37	285
-2	51	57	4
-1	38	37	82
0	61	60	318
1	103	102	247
2	163	166	173
3	66	67	270
4	30	30	273
5	14	14	297

3,7,L

-8	67	72	350
-7	68	69	329
-6	65	64	59
-5	35	35	275
-4	26	31	189
-2	68	64	13
-1	24	28	255
0	62	69	3
1	137	146	306
2	52	54	37

3,8,L

-9	46	45	143
-8	52	55	48
-7	21	21	241
-6	34	35	338
-5	38	41	2
-4	27	31	326
-3	47	44	249
-2	54	52	280
-1	27	27	162
0	65	70	123
1	81	77	335
2	41	42	328
3	70	71	49
5	19	20	312
6	15	15	351

3,9,L

-8	48	46	95
-5	15	13	288
-4	26	25	153
-2	22	24	289
-1	30	34	315
0	101	106	118
1	44	45	160
2	50	52	200

3,9,L

3	2*	10	342
6	15	13	311

3,10,L

-8	14	10	9
-6	21	23	114
-5	18	20	220
-4	28	31	170
-3	21	22	158
-1	42	40	307
1	37	36	108
2	19	18	162
5	23	23	157

3,11,L

-7	10*	7	290
-6	13	15	115
-5	22	23	7
-4	22	25	1
-3	13	12	84
-2	21	21	166
1	21	23	31

3,12,L

-6	17	12	182
-4	23	23	337
-3	25	26	31
2	25	21	259

3,13,L

-4	16	17	182
0	14	15	261

4,0,L

-12	32	32	0
-11	10*	12	0
-10	14	17	0
-9	40	42	0
-8	55	53	180
-7	12	8	0
-6	16	20	0
-5	109	119	180
-4	231	196	0
-3	215	192	0
-2	116	101	0
-1	248	225	0
2	50	47	0
7	20	21	0
8	10*	6	0

4,1,L

-10	42	46	154
-9	20	21	191
-8	29	24	126
-7	27	25	349
-6	52	54	126
-5	85	80	61
-4	77	78	9
-3	87	75	316
-2	72	77	207
-1	130	132	76
0	102	106	336
1	18	21	14
2	36	38	310
5	25	28	317

4,2,L

-12	29	27	161
-10	16	19	172
-9	24	25	12
-8	12	16	283
-7	43	43	155
-5	109	100	337
-4	192	187	115
-3	38	28	194
-2	17	15	322
-1	158	148	129
0	90	88	279
1	76	77	283
2	48	49	238
3	35	33	146
4	48	47	54
7	18	19	161

4,3,L

-11	19	17	231
-10	35	36	196
-9	36	38	73
-8	22	22	176
-7	26	23	75
-6	53	57	293
-5	35	35	262
-4	55	55	228
-3	107	111	139
-2	104	98	278
-1	55	63	22
0	53	60	325
1	65	68	191
2	38	43	131
3	49	53	140
4	25	27	168
5	17	19	24
7	0*	9	169

4,4,L

-10	19	19	220
-9	33	33	134
-8	24	20	51
-7	186	184	25
-6	114	116	348
-5	33	36	95
-4	113	117	134
-3	32	39	301
-2	49	51	209
-1	67	68	110
0	85	83	80
1	67	60	117
2	129	136	27
3	30	30	336
4	31	31	165
5	30	28	236

4,5,L

-9	32	30	328
-8	61	61	245
-7	106	109	166
-6	40	36	342
-5	58	59	242
-4	71	69	26
-3	36	38	107
-2	50	52	280
-1	60	65	245
0	30	25	180
1	93	92	173
2	106	103	355
3	101	100	355
4	30	29	74
5	18	17	87
7	7*	10	357

4,6,L

-10	14	12	126
-9	25	25	76
-8	58	57	291
-7	192	200	173
-6	168	173	183
-5	15	15	199
-4	34	36	294
-3	13	12	107
-2	71	74	171
-1	21	20	179
0	45	45	0
1	89	94	178
2	164	165	165
3	57	56	274

4,7,L

-8	40	40	337
-7	61	64	316
-6	67	71	78

4,7,L

-5	97	99	211
-3	37	39	3
-2	28	31	147
-1	42	39	119
0	105	106	27
1	59	54	313
2	68	68	144
3	61	61	194
4	34	36	273
6	17	15	191

4,8,L

-9	26	30	209
-7	36	39	291
-6	90	96	345
-5	20	18	154
-4	45	44	218
-3	30	31	325
-2	22	28	334
-1	46	44	241
0	51	53	265
1	72	73	328
2	41	44	320
3	25	28	4
4	33	32	175
5	8*	10	37

4,9,L

-9	14	11	157
-8	27	28	127
-7	14	13	19

-5	56	61	345
-4	27	29	56
-3	15	19	343
0	28	32	172
3	20	17	288
5	13	11	80

4,10,L

-8	16	15	36
-6	28	27	37
-5	23	24	300
-3	12	11	250
-1	12	12	114

4,11,L

-4	24	26	172
-3	17	16	144
-2	0*	17	273
0	24	24	207
1	22	20	238
3	18	21	85

4,12,L

-3	15	14	48
-2	19	20	57
-1	19	16	22
0	21	22	76
1	17	17	112

5,0,L

-10	25	29	0

-9	111	122	0
-8	22	26	0
-7	41	45	0
-6	16	8	0
-4	35	36	180
-3	47	42	180
-1	190	177	0
0	22	28	0
1	24	25	180

5,1,L

-12	20	17	19
-10	34	40	133
-9	26	29	330
-8	23	19	137
-7	27	26	134
-6	82	78	118
-5	60	62	95
-4	120	108	129
-3	24	24	6
-2	50	49	174
-1	34	42	356
0	141	140	350
1	82	89	89
5	33	36	212

5,2,L

-10	18	21	127
-9	44	47	142
-8	35	38	218
-7	93	96	16
-6	50	52	174
-5	136	119	102

-4	194	185	36
-3	93	85	25
-2	56	48	128
-1	71	63	113
1	61	63	28
2	33	31	328
4	49	50	32

5,3,L

-12	24	25	191
-11	22	22	171
-10	12	13	84
-9	18	18	175
-8	86	84	181
-7	21	23	106
-6	166	163	222
-5	147	135	201
-4	130	121	277
-3	32	21	42
-2	43	42	133
-1	65	63	166
0	48	49	236
1	31	38	292
2	74	82	292
3	91	96	220
5	31	32	29

5,4,L

-12	22	22	223
-8	60	60	186
-7	83	86	133
-6	81	80	353
-5	32	32	98

-4	116	110	204
-3	78	77	252
-2	88	90	98
-1	35	35	134
0	31	39	240
1	62	67	133
2	55	56	95
3	73	66	186
4	39	37	181

5,5,L

-11	26	24	286
-10	20	19	264
-8	29	29	268
-7	43	43	35
-6	210	214	345
-5	68	69	11
-4	65	62	53
-3	81	77	238
-2	71	67	320
-1	54	54	56
0	35	38	275
1	44	50	227
2	69	70	43
3	51	55	16
4	14	14	13
5	10*	9	336

5,6,L

-9	17	17	341
-8	33	37	327
-7	50	52	176

5,6,L

-6	54	51	234
-5	34	32	246
-2	35	36	230
-1	31	25	329
1	50	49	232
2	14	17	10
3	39	41	330

5,7,L

-9	16	15	20
-8	40	44	354
-7	30	32	240
-6	97	99	146
-5	65	70	165
-4	65	68	41
-3	27	28	243
0	43	46	95
1	31	28	119
2	31	33	115
3	36	40	148

5,8,L

-9	18	19	304
-8	21	20	32
-7	14	19	310
-6	43	45	322
-5	43	47	144
-4	32	34	147
-3	17	18	158
-2	32	34	223
-1	17	19	307

0	16	17	15
1	10*	8	310
2	37	39	253
4	26	26	140

5,9,L

-8	18	19	191
-7	21	22	80
-6	6*	5	253
-5	67	73	296
-4	27	27	127
-2	26	23	126
0	8*	16	346
2	0*	4	218
3	33	33	291

5,10,L

-6	25	30	76
-4	58	59	329
-3	31	33	354
-1	17	14	179
1	18	17	73

5,11,L

-5	19	21	71
-4	20	20	229
0	29	25	196
1	0*	14	281

5,12,L

-2	21	17	53

-1	16	17	330

6,0,L

-11	28	30	180
-10	23	22	0
-9	15	19	0
-8	45	52	180
-7	40	43	0
-6	34	28	180
-5	135	137	0
-4	12	7	0
-2	47	42	0
-1	34	37	0
0	77	69	180
1	29	27	180

6,1,L

-10	19	14	124
-9	28	31	341
-8	78	80	23
-7	33	36	271
-6	109	110	178
-5	63	69	27
-4	33	32	241
-3	94	99	201
-2	20	18	158
0	43	42	299
3	45	45	110

6,2,L

-12	29	30	62
-9	16	10	97

-8	28	29	309
-7	75	78	2
-6	83	82	262
-5	134	127	60
-4	115	110	69
-3	120	117	112
-2	21	23	29
-1	48	46	36
0	23	20	35
1	53	52	358
3	40	41	114
4	26	28	66
5	0*	12	229

6,3,L

-9	20	19	226
-8	65	69	144
-7	64	62	48
-6	65	64	270
-5	54	59	148
-4	44	45	20
-3	75	74	46
-1	17	18	314
0	56	60	103
1	39	36	131
2	82	86	321
3	43	41	300
4	24	22	13

6,4,L

-10	18	20	75
-9	16	10	288
-7	115	122	118

-6	71	73	174
-5	140	142	185
-4	56	57	244
-3	20	16	231
-2	27	33	108
-1	30	31	237
1	71	71	116
3	37	40	248

6,5,L

-11	24	27	232
-8	42	41	264
-7	35	37	186
-6	42	38	108
-5	20	24	70
-4	51	56	298
-3	67	73	186
0	36	39	315
2	42	45	135
3	35	38	184

6,6,L

-9	28	29	168
-8	28	22	139
-7	22	23	309
-6	61	65	18
-5	43	37	357
-4	56	57	308
-3	0*	16	291
-2	40	43	161
-1	25	30	208
0	0*	9	253

6,6,L

1	31	29	304
4	20	21	351

6,7,L

-9	13	16	295
-8	18	17	208
-7	26	30	302
-6	38	38	324
-5	27	31	222
-3	53	56	314
-2	56	60	17
-1	15	10	206
0	26	26	235
2	24	24	42

6,8,L

-7	41	40	263
-6	40	40	252
-5	36	36	128
-4	35	39	122
-1	19	20	35
0	20	21	217
1	20	20	219

6,9,L

-8	31	31	18
-7	21	22	44
-5	33	33	325
-4	31	37	112
-3	26	28	154

-2	20	23	166
-1	19	16	142
0	28	29	76

6,10,L

-6	21	24	69
-4	35	35	287
-3	14	17	79
0	18	19	39

6,11,L

-5	30	30	72
-3	9*	9	339

7,0,L

-9	33	32	180
-8	29	28	180
-7	22	25	180
-6	50	50	180
-5	177	169	0
-4	10	8	180
-3	51	52	0
-1	16	17	180
0	13	13	0
2	31	27	180
3	36	36	0
4	30	33	0

7,1,L

-9	15	19	135
-8	38	37	146

-6	122	122	137
-5	82	83	160
-4	63	66	284
-3	31	35	29
-2	23	22	0
-1	33	32	216
0	23	24	205
1	20	22	176
2	40	40	189
3	35	35	158
4	30	29	331

7,2,L

-11	14	18	210
-9	25	27	92
-8	25	28	28
-7	77	74	347
-6	81	77	248
-5	83	81	111
-4	80	78	250
-3	23	22	245
-2	22	18	80
-1	33	33	107
0	15	17	248
1	38	37	338
3	37	38	149
4	18	20	153

7,3,L

-10	25	24	257
-8	32	35	153
-7	59	61	260
-6	100	101	302

-5	59	56	351
-4	25	27	110
-3	28	30	133
0	24	27	118
1	16	9	256
2	29	32	342

7,4,L

-11	28	29	19
-8	26	26	38
-7	69	71	127
-6	33	36	2
-5	19	17	21
-4	35	34	123
-3	38	42	113
-2	58	65	354

7,5,L

-11	42	42	179
-9	22	19	298
-8	24	26	316
-7	13	18	356
-6	37	38	159
-5	33	34	207
-3	38	39	173
-2	24	26	268
-1	20	22	337
2	14	15	42

7,6,L

-6	44	47	144
-5	38	40	123

-4	36	36	24
-3	21	24	177
-2	61	65	169
-1	29	28	221

7,7,L

-10	19	22	23
-7	32	31	78
-6	32	32	48
-5	26	27	22
-4	29	29	0
-3	30	30	325
0	21	15	312

7,8,L

-8	28	28	239
-7	27	20	208
-6	18	20	311
-5	45	46	282
-4	29	30	229
-2	22	28	302
-1	10*	17	18
0	15	14	317
1	17	18	266

7,9,L

-7	13	12	219
-5	13	18	219
-4	17	20	115
-1	13	17	180

7,10,L

-3	12	10	26

8,0,L

-8	43	44	0
-6	39	35	180
-5	194	183	0
-4	58	59	0

8,1,L

-11	34	36	355
-9	17	18	177
-7	9*	12	153
-6	75	72	157
-5	19	18	176
-4	92	86	3
-3	46	46	68
0	20	20	31
2	20	18	198

8,2,L

-10	15	16	145
-7	55	55	85
-6	44	43	75
-5	99	102	131
-4	75	76	194
-3	41	48	13
-2	19	20	308

8,3,L

-10	26	30	202
-7	7*	17	297
-5	45	45	234
-4	25	24	183
-3	31	31	219
-2	17	16	258
-1	24	23	207

8,4,L

-6	19	20	289
-4	25	27	305
-3	35	40	130
-2	23	27	107
-1	19	18	129

8,5,L

-10	29	30	322
-7	24	24	336
-5	29	29	349
-4	21	21	278

8,6,L

-8	24	25	199
-7	21	23	219
-6	34	32	292
-5	23	25	211
-4	12	16	145

8,7,L

-9	18	12	354
-8	16	22	294
-7	8*	17	92
-5	20	20	123
-4	34	35	94
-1	18	22	102

8,8,L

-6	21	21	80
-5	22	20	43
-4	21	20	7
-2	23	22	241

9,0,L

-10	20	23	180
-5	8*	9	0
-4	39	36	180
-3	10*	14	180

9,1,L

-10	27	26	142
-5	6*	9	279
-4	64	70	342
-3	23	22	342
-1	23	21	110

9,2,L

-10	27	27	312
-5	45	47	76
-4	19	21	92
-3	36	39	4
-1	6*	6	54

9,3,L

-6	31	31	139
-4	50	54	116
-3	38	39	155
-2	29	33	333
-1	17	20	293

9,4,L

-9	16	17	167
-7	23	21	6
-4	27	30	299
-3	30	31	121
-2	27	27	160

9,5,L

-9	16	10	282
-7	40	40	10
-3	26	27	298

9,6,L

-8	26	30	165

9,7,L

-6	21	19	233
-5	10*	18	297

10,0,L

-7	23	24	0
-3	22	20	180

10,1,L

-7	14	14	105
-4	31	30	203
-3	8*	9	182

10,2,L

-5	22	21	29

10,3,L

-7	26	25	263
-6	29	31	215
-4	25	27	62

10,4,L

-6	24	25	173
-5	17	16	171

Data for Diterpenoid I (jatropholone)

Crystal Data

$C_{22}H_{26}O_3$, M = 338.48; orthorhombic,

a = 12.389(2)Å, b = 17.875(3)Å, c = 8.708(1)Å, V = 1928.73Å^3;

D_c = 1.17 g.cm^{-3}, Z = 4; F(000) = 728; space group $P2_12_12_1$ (D_2^4, No.19);

$M_0 - K\alpha$ radiation, $\mu(M_0 - K\alpha)$ = 0.71 cm^{-1}. λ = 0.7107Å.

-16,-7,L

0	30	32	0

-16,-6,L

0	41	40	0

-16,-4,L

2	18	17	46

-16,0,L

0	52	49	180
3	0*	6	270

-15,-11,L

0	26	26	90

-15,-9,L

0	38	37	90

-15,-7,L

2	25	24	250
4	46	45	328

-15,-6,L

1	54	52	137
3	29	21	235
4	33	36	136

-15,-5,L

0	39	40	90

-15,-4,L

1	23	25	135
2	0*	5	74
4	54	52	134
5	35	34	129

-15,-3,L

0	42	45	90
3	28	29	309

-15,0,L

1	34	34	90

-14,-12,L

3	11*	3	134

-14,-10,L

0	0*	2	0

-14,-9,L

0	30	25	0

-14,-8,L

3	57	55	186

-14,-7,L

0	65	64	0
3	34	35	309

-14,-6,L

0	65	65	0
1	11*	11	301

-14,-5,L

0	41	38	0
3	26	32	320
4	6*	7	53

-14,-4,L

0	28	27	0
1	41	43	329
3	30	30	154
4	57	54	138
5	13*	15	93

-14,-3,L

5	39	37	331
6	31	25	352

-14,-2,L

0	31	34	180
3	21	24	135
4	47	43	156

-14,-1,L

1	24	20	41
3	26	23	208
4	28	28	231
6	40	37	61

-14,0,L

0	60	62	180
1	31	32	270
3	17	17	90
4	34	32	180

-13,-15,L

1	13*	10	212

-13,-14,L

1	28	24	270
2	29	23	235

-13,-13,L

2	19	18	76

-13,-12,L

1	6*	7	352
2	25	21	255

-13,-10,L

2	29	28	323
4	13*	17	119

-13,-9,L

0	41	44	90
1	32	32	138
3	27	22	81
4	41	40	263
5	24	18	179

-13,-8,L

0	54	53	90
1	53	53	206
3	42	42	331
4	38	37	106
6	23	24	294

-13,-7,L

0	34	30	90
1	55	53	131
2	31	29	250
3	35	38	119
5	41	40	300

-13,-6,L

0	64	64	90
1	58	56	219
2	53	50	194
3	23	26	319

-13,-6,L

4	63	61	116

-13,-5,L

3	40	39	184
5	72	70	320
7	24	25	73

-13,-4,L

0	37	35	90
1	42	43	254
2	41	39	223
4	62	56	120

-13,-3,L

0	21	20	90
2	53	50	40
4	40	42	266
5	59	57	311
7	35	33	61

-13,-2,L

0	19	20	270
1	51	50	261
2	56	50	260
3	47	46	50
4	48	46	67
5	23	23	58
6	26	24	109
7	28	29	193

-13,-1,L

1	51	49	1
2	19	17	92
5	24	25	261

-13,0,L

1	48	49	270
3	0*	1	270
4	60	57	0
5	24	27	90
6	13*	8	0
7	14*	14	270

-12,-17,L

1	42	37	24

-12,-16,L

0	36	34	0

-12,-15,L

2	18	18	229

-12,-14,L

0	25	21	0

-12,-13,L

2	24	24	225

-12,-12,L

1	37	36	335

-12,-11,L

3	36	30	51
4	8*	23	55
6	23	20	217

-12,-10,L

1	41	44	314
2	27	23	47
3	35	35	112
5	32	31	31

-12,-9,L

1	36	38	197
2	47	44	99
3	34	32	243
4	39	40	72
5	24	20	132

-12,-8,L

0	109	108	0
1	34	33	271
2	40	41	283
3	57	61	118

-12,-7,L

1	42	39	196
2	60	62	77
3	82	81	303

-12,-6,L

0	76	77	0
2	14*	19	246

-12,-5,L

1	38	36	197
2	35	37	104
3	65	68	338
5	47	44	319
7	46	47	247

-12,-4,L

0	38	41	180
1	51	52	289
2	18	14	160
3	54	56	127
4	38	38	98
6	36	33	217
7	26	27	325

-12,-3,L

0	15	14	0
4	16	18	177
5	45	48	335

-12,-2,L

0	84	86	180
1	34	35	249
3	30	30	90
4	72	71	117
5	44	44	128
7	41	37	271

-12,-1,L

1	73	72	23
2	55	61	97
3	83	86	195
4	48	49	241
8	16*	7	323

-12,0,L

0	67	69	180
1	33	35	270
5	60	59	90
7	35	30	270

-11,-18,L

1	32	31	210
2	29	32	224

-11,-16,L

2	44	42	192

-11,-15,L

2	56	53	55

-11,-14,L

4	24	21	253

-11,-13,L

2	27	28	104

-11,-12,L

6	13*	17	336

-11,-11,L

0	83	82	90
1	17	17	127
4	15*	18	162

-11,-10,L

0	48	45	90
1	59	60	277
4	34	30	279
7	17	17	196

-11,-9,L

0	153	152	90
1	95	96	155
2	30	31	297
3	30	23	84
6	20	23	221

-11,-8,L

0	14*	15	90
1	113	111	222
2	35	30	59
3	56	58	329
4	28	30	187
5	38	34	307

-11,-7,L

0	39	38	90
1	60	62	158
2	58	59	273
3	47	48	98
5	32	33	265
7	45	44	53
8	26	32	110

-11,-6,L

1	36	36	155
2	76	74	128
3	108	112	320
4	30	32	180
5	26	30	140
6	54	50	90
7	25	30	92

-11,-5,L

0	30	27	90
1	64	62	277
2	77	79	329
3	28	26	91
5	53	56	295
7	30	35	64

-11,-4,L

0	36	39	270
1	113	116	84
2	72	72	114
3	53	59	313
4	32	31	340
5	53	54	116
6	44	44	106
7	33	30	116
8	36	35	107

-11,-3,L

0	32	33	90
2	38	38	353
3	91	93	28
4	49	51	263
5	57	60	264

-11,-2,L

0	55	55	270
1	77	79	67
3	52	50	274
4	39	41	132
5	53	48	112
6	35	35	32

-11,-1,L

0	43	44	90
2	32	30	127
3	59	57	9
4	34	34	331
6	64	68	258

-11,0,L

1	64	64	90
2	33	30	0
3	112	109	270
4	39	38	180
5	62	60	90
6	67	67	0
7	0*	27	270
8	23	21	180

-10,-18,L

0	53	47	0

-10,-17,L

3	46	49	25

-10,-16,L

0	40	41	0

-10,-15,L

2	17	18	321
3	46	43	19

-10,-14,L

1	42	41	210
3	29	29	13

-10,-13,L

4	38	33	183
6	33	34	306

-10,-12,L

0	19	17	180
1	47	45	219
3	42	39	36

-10,-11,L

0	58	56	0
1	35	36	356
2	42	44	151
3	16	14	91
4	28	29	64
6	43	41	264

-10,-10,L

0	37	37	0
1	79	77	244
2	38	37	343
3	31	32	112

-10,-9,L

0	70	70	0
1	43	45	201
3	32	34	332
4	40	39	83

-10,-9,L

6	45	44	208

-10,-8,L

1	59	59	307
2	124	123	328
3	44	42	359
4	36	30	147

-10,-7,L

0	69	69	0
1	43	42	205
2	102	106	97
3	89	94	304
4	59	59	144
5	22	22	65
6	34	30	250
7	37	29	206

-10,-6,L

0	126	128	180
1	25	25	53
2	146	145	334
3	34	33	141
4	55	53	136
8	23	24	198

-10,-5,L

0	52	50	0
1	57	57	276
2	145	148	116
4	73	75	239
5	45	40	275
6	40	39	322
7	32	32	212
9	21	20	301

-10,-4,L

0	94	98	180
1	85	88	28
2	100	107	324
3	146	144	155
4	84	85	159
5	58	59	14
6	35	38	214
7	31	31	274

-10,-3,L

0	31	31	0
1	89	84	16
2	118	121	142
3	56	52	97
4	45	43	246
5	124	126	280
6	77	75	339

-10,-2,L

0	94	95	180
1	61	57	349
2	42	41	201
3	108	106	169
4	69	69	83
5	48	53	101
6	28	30	160
9	40	41	355

-10,-1,L

0	53	51	180
1	112	114	8
2	83	86	112
3	51	51	180
4	77	80	258
5	42	39	293
6	58	59	354
8	15*	14	24

-10,0,L

0	17	16	180
1	100	101	270
2	109	107	180
3	69	69	270
4	107	105	0
5	143	142	90
6	67	69	180
7	22	17	90
9	36	31	90

-9,-19,L

0	33	27	270
2	21	23	25

-9,-18,L

0	22	21	270
1	27	23	162
2	41	36	212
4	19	20	335

-9,-17,L

2	37	37	21
3	11*	11	23
4	26	22	171
5	35	25	79

-9,-16,L

1	38	38	78
2	58	56	198
3	60	56	229
4	24	26	262
6	20	15	144

-9,-15,L

1	24	26	234
2	50	50	30
3	30	29	16
4	16*	15	275
5	34	29	99

-9,-14,L

0	35	33	90
1	73	71	74
2	72	70	211
6	17*	40	257

-9,-13,L

0	47	51	90
1	73	74	251
3	0*	7	178

-9,-12,L

0	32	35	90
1	39	43	301
2	74	76	262
3	29	35	213
4	33	33	91
5	33	36	64

-9,-11,L

1	124	129	266
2	79	78	58
5	53	54	259

-9,-10,L

0	167	171	90
1	116	118	254
2	105	107	318
3	48	50	113
6	38	40	340
7	24	26	2

-9,-9,L

0	37	39	270
1	111	111	221
2	140	141	79

-9,-9,L

3	46	48	78
4	67	72	230
6	41	42	84
9	27	29	200

-9,-8,L

0	126	132	90
1	133	135	263
2	76	79	303
3	42	44	107
4	70	68	143
5	72	77	311
6	41	43	58
7	40	38	66
8	33	32	237

-9,-7,L

0	20	23	270
1	57	59	99
2	48	48	44
3	63	60	155
4	90	93	210
5	82	75	78
6	74	71	70
7	23	25	341
8	34	34	130
9	38	36	220

-9,-6,L

1	105	106	90
2	35	39	140
3	69	70	281
4	59	59	171
5	43	46	337
6	27	29	40
7	80	79	113
9	56	52	314

-9,-5,L

0	98	99	90
1	70	67	130
2	206	203	323
3	35	36	177
4	99	102	196
5	59	59	359
6	37	34	49
7	33	36	35
8	35	37	129
9	22	20	267

-9,-4,L

0	63	61	270
1	128	134	320
2	76	79	144
3	23	23	216
4	48	48	315
5	50	52	20
6	78	79	93
7	49	58	160
8	55	55	59

-9,-3,L

0	66	68	90
1	33	35	67
2	70	74	314
3	83	83	319
4	58	55	285
5	56	59	275
6	44	46	281
7	30	33	105

-9,-2,L

1	99	108	278
3	23	20	272
4	32	26	33
5	38	40	87
6	49	52	95

-9,-1,L

0	91	93	90
1	116	117	349
3	75	76	188
4	110	112	353
5	80	82	337
6	94	91	270
8	31	31	120
10	31	32	237

-9,0,L

2	39	37	180
3	22	21	90
4	27	29	0
5	130	129	90
6	40	38	180
8	20	22	0
9	48	46	270

-8,-19,L

0	21	23	0
2	28	26	34

-8,-18,L

4	16*	21	221

-8,-17,L

0	31	27	0
1	37	34	167
2	25	25	74
3	71	67	25

-8,-16,L

0	19	19	180
3	76	73	204
5	50	44	46

-8,-15,L

2	32	30	299
3	85	86	26

-8,-14,L

1	30	29	270
3	38	33	170
6	21	21	239

-8,-13,L

0	79	73	180
2	55	51	15
3	48	48	13

-8,-12,L

0	33	37	0
1	82	85	248
2	74	71	117
3	50	51	81
4	68	67	33
5	33	33	309

-8,-11,L

0	69	70	0
1	103	100	248
2	87	88	60
3	55	53	108
4	27	27	235
5	47	50	123
6	33	33	207

-8,-10,L

0	141	140	0
1	70	69	254
2	38	40	0
3	48	51	141
4	38	46	114

-8,-10,L

5	81	80	305
6	30	27	174
9	45	49	201

-8,-9,L

0	76	80	0
1	35	37	210
3	48	47	24
4	19	21	157
6	29	34	227
7	51	55	235
9	48	47	1

-8,-8,L

0	36	34	0
1	72	70	304
2	64	66	339
3	18	19	62
4	55	57	156
5	95	96	314
6	54	51	242

-8,-7,L

0	17	18	180
1	115	119	26
2	178	182	122
3	122	124	222
4	26	28	86
5	38	42	54
6	32	32	200
7	82	80	259
9	44	41	27

-8,-6,L

0	24	23	0
1	55	60	166
2	196	197	253
3	135	134	179
4	65	61	6
5	46	47	350
6	88	89	261
9	40	32	293
10	34	35	46

-8,-5,L

0	98	92	0
1	193	195	336
2	239	232	155
3	38	43	125
4	85	84	313
5	56	60	350
6	64	66	185
7	50	52	230

-8,-4,L

0	132	138	0
1	182	186	100
3	111	113	226
5	89	89	43
6	53	54	138
8	30	31	328
9	54	51	264

-8,-3,L

0	199	194	0
1	110	111	343
2	310	309	184
3	57	58	28
4	127	127	21
5	67	68	213
6	47	50	279
7	44	42	283
9	21	18	150

-8,-2,L

0	66	70	0
1	64	68	165
2	192	194	122
3	83	85	309
4	52	46	266
5	133	134	95
6	100	97	102
7	45	46	113
8	23	26	1
9	36	36	354

-8,-1,L

0	96	102	0
1	41	41	294
2	67	63	165
3	126	129	348
4	55	57	71
5	160	160	177
6	100	102	275
7	54	51	357
10	31	32	102

-8,0,L

0	87	92	0
2	113	112	180
3	95	90	270
5	183	186	90
6	69	69	180
7	21	22	270
9	71	67	90

-7,-21,L

1	47	38	142
3	40	34	323

-7,-20,L

4	41	37	13

-7,-19,L

0	41	35	270
5	51	47	69

-7,-18,L

0	23	18	270

-7,-17,L

5	31	30	71
6	27	27	241

-7,-16,L

0	30	28	270
2	44	42	170
3	41	41	183

-7,-15,L

0	31	31	90
2	48	46	3
3	68	61	19
4	38	36	345
7	25	21	177

-7,-14,L

0	78	77	270
1	48	49	298
2	90	87	156
3	80	77	139
4	28	27	247
8	31	25	328

-7,-13,L

0	49	48	90
1	52	53	216
2	31	32	210
3	51	60	288
4	39	39	11
5	37	34	250
7	40	34	81

-7,-12,L

1	60	60	309
2	87	83	55
3	42	43	215
4	52	50	277
5	39	40	126
8	43	32	326
9	40	33	209

-7,-11,L

0	67	66	90
1	86	87	267
2	111	111	95
3	88	90	156
4	33	31	206
5	90	88	310
6	40	39	235

-7,-10,L

0	114	108	270
1	118	117	154
2	153	154	90
3	114	117	288
4	74	77	260
5	52	54	65
6	30	28	9
7	28	30	334

-7,-9,L

[illegible]	[illegible]	41	270
1	146	138	250
2	128	126	89
3	63	64	119
5	54	58	345
6	38	41	101

-7,-8,L

0	35	32	270
1	25	27	34
2	43	41	190
3	106	111	271
4	47	46	111
5	94	97	57
6	42	41	346
8	35	32	197
9	58	60	15

-7,-7,L

0	68	69	90
1	45	43	292
2	72	73	154
3	91	89	160
4	134	137	338
5	87	90	27
6	102	103	122
7	35	35	91
8	32	29	329
10	31	28	127

-7,-6,L

1	43	43	296
2	109	108	292
3	152	160	284
4	39	40	103
5	151	149	50
6	38	38	22
7	27	26	88
8	50	44	166
9	70	64	315
10	29	25	84

-7,-5,L

0	56	55	270
1	145	148	79
2	231	227	269
3	81	80	119
4	62	63	40
5	25	26	293
6	127	125	116
7	58	54	57
9	40	37	213
10	41	36	102

-7,-4,L

1	238	235	319
2	91	87	155
3	139	132	320
4	30	30	259
5	49	47	156
6	64	63	45
7	61	62	178
9	31	31	339

-7,-3,L

0	64	69	270
1	174	171	85
2	67	69	252
3	142	145	302
4	56	56	32
5	91	89	196
6	100	99	243
7	56	62	3
8	10*	14	298
9	79	70	189
10	33	35	134

-7,-2,L

0	76	84	90
1	73	70	331
2	133	134	107
3	165	165	323
4	49	53	82
5	152	155	155
6	87	89	338
7	46	45	27
8	58	57	239

-7,-1,L

0	200	200	90
1	79	84	90
2	66	62	263
3	24	27	3
4	52	53	66
5	51	52	113
6	240	243	273
7	107	105	341
8	35	36	108
9	30	27	225
10	38	39	228

-7,0,L

2	190	195	180
3	94	84	270
4	111	111	180
5	191	182	90
6	50	45	0
7	43	42	90
9	69	68	270
10	39	38	0

-6,-19,L

0	26	27	180

-6,-18,L

3	24	23	15
4	17	17	246
5	22	23	74

-6,-17,L

1	30	28	283
4	52	53	28
6	41	40	274

-6,-16,L

1	48	47	201
4	59	56	205
7	34	31	56

-6,-15,L

1	15	19	48
2	47	48	356
3	98	102	29
4	46	42	33
5	43	48	222
7	22	22	28

-6,-14,L

1	31	31	25
2	107	109	81
3	48	45	202
4	92	88	220
6	35	33	355

-6,-13,L

0	138	138	180
2	92	98	58
3	76	73	359
4	59	55	50
5	27	22	139
7	0*	13	244

-6,-12,L

0	71	69	0
1	140	140	246
2	180	179	80
3	87	82	159
5	22	17	216
6	19	17	298

-6,-11,L

1	55	61	233
2	55	60	44
3	29	27	170
4	86	83	265
6	28	32	157
7	15*	17	201

-6,-10,L

1	117	118	240
2	79	82	18
5	102	105	325
6	57	57	198
7	19	19	23
8	32	34	15

-6,-9,L

0	44	46	0
1	15	15	284
2	35	38	233
3	89	87	41
4	64	59	332
5	63	55	225
6	95	96	210
7	33	36	192
8	45	44	171
9	63	62	342
10	24	21	26

-6,-8,L

0	122	116	180
1	179	165	192
2	48	46	47
3	126	123	345
4	108	108	134
5	66	68	322
6	102	104	265
7	33	30	212
8	67	68	8
10	38	32	136

-6,-7,L

0	58	61	180
1	44	41	243
2	152	147	120
3	161	155	124
4	96	91	323
5	51	53	302
6	114	108	177
7	30	30	204
8	60	59	194
9	36	41	12

-6,-6,L

0	147	145	0
1	157	156	150
2	204	210	237
3	101	100	338
4	50	49	52
5	70	71	138
6	117	119	268
7	109	109	277
8	61	62	89
9	48	48	202

-6,-5,L

0	41	40	0
1	139	139	276
2	307	302	137
3	263	261	83
4	88	84	85
5	133	136	294
6	34	34	142
7	48	50	137
8	61	65	271

-6,-4,L

1	353	364	149
2	172	182	0
3	24	26	244
4	103	95	146
5	63	68	169
6	37	37	252
7	74	74	321
8	34	33	84

-6,-3,L

0	268	270	180
1	128	127	350
2	212	208	183
3	104	106	255
4	51	54	88
5	91	94	134
6	97	96	347
7	47	47	250
8	38	40	294
9	35	36	86
10	45	41	115

-6,-2,L

0	13	12	180
1	337	333	207
2	220	226	13
3	160	156	33
4	223	214	206
5	113	108	78
6	33	37	327
7	80	81	97
8	52	51	108
9	47	44	40
10	0*	7	37
11	21	17	286

-6,-1,L

0	188	192	180
1	263	258	26
2	72	74	44
3	145	136	259
4	56	52	237
5	55	54	20
6	82	82	278
7	76	74	232
8	31	30	170
9	33	28	129

-6,0,L

0	386	394	180

-6,0,L

1	99	97	270
2	97	98	0
4	147	153	180
5	80	86	90
6	126	131	0
9	73	74	90

-5,-21,L

0	35	32	270
4	16*	17	268

-5,-19,L

4	58	54	217
5	56	51	94

-5,-18,L

3	37	39	234
4	32	29	60
7	37	34	95

-5,-17,L

0	18	20	90
3	42	41	63
4	63	58	269
5	38	35	52

-5,-16,L

1	24	19	119
2	53	54	154
3	46	46	226

-5,-15,L

1	14*	16	136
2	44	36	88
3	47	45	359
4	46	48	311

-5,-14,L

0	47	40	90
1	77	77	286
2	81	81	216
3	91	91	212
4	62	64	167
8	38	36	335

-5,-13,L

0	78	79	90
1	81	85	222
2	109	109	68
3	116	118	290
4	99	99	335
7	32	34	357
8	23	24	170

-5,-12,L

0	108	107	90
1	46	42	184
2	72	70	314
3	39	42	173
4	44	45	158
5	22	25	0
7	16	16	85

-5,-11,L

0	131	134	90
1	87	84	215
2	56	58	66
3	30	27	183
4	68	69	185
5	86	89	338

-5,-10,L

0	197	206	270
1	63	65	157
2	113	113	104
3	64	64	254
4	57	57	323
5	129	135	13
6	43	46	92
7	41	46	127
8	30	31	70
9	31	37	341
10	47	53	212

-5,-9,L

0	129	136	270
1	66	65	321
2	93	92	22
3	101	101	356
4	102	107	120
5	36	38	220
6	72	68	109
7	35	35	99
9	42	40	166

-5,-8,L

0	104	102	90
1	108	107	340
4	95	96	339
5	103	99	91
6	52	46	342
8	33	32	233
9	46	47	20
10	62	57	166

-5,-7,L

1	142	151	243
3	96	93	100
4	99	97	36
5	151	152	24
6	79	88	170
7	35	35	182
8	71	67	8
10	24	25	115

-5,-6,L

0	125	125	270
1	68	68	259
2	195	198	253
3	125	123	332
4	35	38	2
5	80	77	106
6	63	66	74
7	28	30	304
8	44	42	175
9	58	63	10

-5,-5,L

2	124	124	269
3	198	202	100
4	140	137	169
5	30	29	308
7	67	69	171
8	39	40	40

-5,-4,L

0	314	327	90
1	414	425	290
2	456	457	192
3	194	185	312
4	49	49	250
5	100	100	279
6	85	88	334
7	59	59	202
8	80	79	185
9	70	71	62
10	47	47	326
11	32	29	286

-5,-3,L

0	340	353	270
1	212	220	156
2	288	290	11
3	67	65	323

-5,-3,L

4	93	92	140
5	104	104	284
6	136	135	308
7	67	71	89
8	56	53	218
9	32	32	197
10	50	45	130

-5,-2,L

0	458	477	90
1	319	329	345
2	410	396	204
3	153	163	107
4	203	196	42
5	61	56	296
6	109	106	327
7	101	101	84
8	66	68	204
9	65	62	237
10	31	34	308

-5,-1,L

0	270	286	270
1	140	140	115
2	71	65	35
3	128	130	259
4	176	180	153
5	120	114	354
6	296	289	286
7	85	82	137
8	29	24	145
9	39	42	323
11	32	33	182

-5,0,L

1	239	239	270
2	42	38	180
3	154	154	90
4	52	51	0
5	98	94	270
6	98	95	0
7	256	255	90
9	111	110	270

-4,-22,L

3	26	25	168

-4,-21,L

4	8*	16	274

-4,-20,L

0	43	42	0
2	31	29	11
6	10*	15	287

-4,-19,L

0	83	83	180
2	29	31	30
5	16*	15	186

-4,-18,L

3	36	38	55
4	45	46	221

-4,-17,L

0	64	60	180
2	47	48	1
3	33	34	203

-4,-16,L

1	49	49	11
4	77	80	208
7	34	38	42

-4,-15,L

1	59	61	100
2	35	39	19
3	72	77	339
4	69	74	38
5	50	51	287

-4,-14,L

0	114	116	180
1	103	111	348
2	137	142	78
3	109	105	197
4	79	78	222
6	38	39	19
7	20	19	89

-4,-13,L

0	30	31	0
2	73	74	91
3	173	173	295
4	86	89	14
5	120	118	67
6	25	26	149

-4,-12,L

0	177	166	0
1	150	146	297
2	117	116	95
3	104	107	175
4	67	66	123
6	71	68	223
7	45	39	261
8	50	49	107

-4,-11,L

1	59	54	120
2	126	128	116
3	137	134	288
4	188	179	291
5	59	60	143
6	73	73	151
7	31	31	34
8	52	44	344

-4,-10,L

0	24	25	0
1	262	258	328
2	30	28	33
3	34	33	22
4	93	92	115
5	64	63	277
6	105	110	217
7	34	34	31
8	32	32	3
10	49	47	225

-4,-9,L

0	56	56	180
1	76	74	108
2	158	157	78
3	51	48	164
4	57	57	334
5	193	186	192
6	158	160	205
7	34	41	4
9	14*	15	338

-4,-8,L

0	119	108	180
1	70	64	124
2	17	18	245
3	56	53	144
4	67	65	242
5	128	124	250
6	136	140	224
7	35	40	45
8	86	86	16
9	65	62	308
10	43	39	123

-4,-7,L

1	246	241	113
2	87	90	354
3	75	66	56
4	44	41	317
5	52	53	329
6	110	109	216
7	49	46	226
8	82	86	163

-4,-6,L

0	291	290	0
1	185	179	83
2	443	442	152
3	99	97	313
4	183	184	329
5	25	29	177
6	70	68	166
7	100	101	267
8	60	65	21
9	28	30	244
11	0*	15	140

-4,-5,L

0	86	81	0
1	147	141	77
2	409	393	164
3	67	72	79
4	197	195	78
5	114	111	319
6	90	91	319
7	111	103	106
8	25	26	148
9	39	38	327

-4,-4,L

0	136	141	0
1	150	154	211
2	239	245	193
3	118	113	264
4	142	146	0
5	98	95	160
6	42	42	324
7	58	54	56
8	66	62	60
10	48	44	320

-4,-3,L

0	168	159	180
1	382	392	321
2	230	222	174
3	208	202	304
4	86	88	84
5	238	228	117
6	131	135	274
7	91	92	105
8	61	64	91
9	53	49	34
10	19	19	126

-4,-2,L

0	789	797	0
1	141	190	47
2	84	79	245
3	219	211	326
4	32	24	223
5	152	151	71
6	160	164	234
7	54	53	121
8	54	54	99
10	26	30	15

-4,-1,L

0	253	251	180
1	277	268	1
2	202	207	131
3	120	111	242
4	170	162	54
5	104	100	120
6	143	144	268
7	52	50	257
8	34	33	160
9	50	53	142

-4,0,L

0	612	613	0
1	171	178	90
2	280	280	180
3	103	98	90
4	63	65	0
5	190	180	90
6	53	54	180
7	35	36	90
8	30	29	0

-3,-23,L

3	11*	14	206

-3,-22,L

3	0*	6	356

-3,-21,L

0	31	34	270
2	19	17	46
4	15*	12	171
5	5*	9	202

-3,-20,L

2	12*	15	271
4	18	25	92

-3,-19,L

0	33	35	90
1	30	29	149
3	13*	18	324
4	39	41	214
5	42	50	116

-3,-18,L

0	37	32	90
1	19	18	286
3	42	39	222
4	44	45	60
7	15*	17	60

-3,-17,L

1	31	34	168
3	53	53	51
4	42	38	274
5	41	38	84

-3,-16,L

0	37	36	270
1	50	53	233
2	107	110	159
3	40	39	257
4	33	35	42
5	27	28	156
8	27	36	23

-3,-15,L

0	76	76	270
1	88	92	269
2	23	24	135
3	77	77	300

-3,-14,L

1	112	111	294
2	45	43	117
3	132	133	211
4	43	42	5
6	23	23	89
9	31	33	141

-3,-13,L

2	181	188	65
3	30	30	313
4	79	80	335
5	77	74	36
6	24	30	236
7	22	23	304
9	21	25	197

-3,-12,L

0	56	53	270
1	23	23	74
2	126	128	80
3	110	108	183
4	92	93	201
5	42	41	23
7	37	36	44

-3,-11,L

0	126	119	90
1	72	73	203
2	22	26	50
4	45	44	50
5	125	131	14
10	28	29	142

-3,-10,L

0	400	406	270
1	166	167	32
2	173	170	93
3	94	94	247
4	98	94	250
5	138	137	63
6	92	94	85
7	55	49	193
10	40	40	209

-3,-9,L

0	61	60	90
1	52	54	21
2	29	28	77
3	93	93	300
4	80	80	61
5	49	49	63
6	61	62	198
7	44	51	20
9	42	43	206
10	43	46	103

-3,-8,L

1	191	196	120
2	139	136	270
3	140	143	319
4	76	77	325
5	116	116	115
6	73	76	27
7	125	130	351
9	27	28	41
10	38	36	182
11	47	54	222

-3,-7,L

0	69	68	90
1	241	246	273
2	240	237	273
3	108	107	280
4	143	142	93
5	156	155	8
6	100	101	162
7	90	92	161
8	103	99	20
9	38	39	234
11	29	28	357

-3,-6,L

0	207	205	270
1	67	69	172
2	140	137	278
3	100	89	342
4	98	95	355
5	108	103	209
6	25	17	150
7	72	78	18
8	26	25	188
9	43	39	14

-3,-5,L

0	113	111	90
1	53	50	244
2	55	53	329
3	204	188	48
4	89	87	173
5	124	123	284
6	29	29	270
7	201	207	158
8	112	107	43
9	52	52	287
10	64	65	224

-3,-4,L

0	90	91	90
1	378	394	285
2	169	164	99
3	82	82	284
4	202	185	252
5	100	100	339
6	66	66	324
8	141	142	230
9	45	45	65

-3,-3,L

0	531	519	270
1	525	515	192
2	59	61	239
3	633	596	54
4	139	136	47
5	131	123	212
6	42	41	98
7	74	72	92
8	29	26	317
9	72	70	265

-3,-2,L

0	851	869	90
1	992	1000	7
2	428	442	214
3	133	125	148
4	172	163	217
5	71	70	265
6	77	81	50
7	141	143	144
8	130	130	288
11	49	50	279

-3,-1,L

0	255	272	90
1	534	522	177
2	231	246	167
3	210	206	298
4	177	174	288
5	66	66	339
6	123	125	245
7	89	82	117
8	112	113	284
9	38	28	273
10	57	57	68
11	27	26	114

-3,0,L

1	489	473	90
2	420	429	0
3	61	59	270
4	38	33	180
5	304	291	270
6	148	149	0
7	247	248	90
8	19	19	0
11	37	34	270

-2,-22,L

4	0*	9	12

-2,-20,L

2	34	30	344
6	33	28	317

-2,-19,L

0	119	115	180
2	48	44	328
6	43	36	298

-2,-18,L

0	72	79	0
1	57	57	328
3	47	47	52

-2,-17,L

2	50	51	30
3	70	67	213
4	46	44	112
5	44	45	318
6	29	29	289

-2,-16,L

1	84	82	13
3	72	74	49
4	41	44	262
5	48	50	220
6	28	26	92

-2,-15,L

0	102	105	0
1	41	41	261
2	91	86	114
3	99	98	286
4	123	121	66
6	38	40	318
7	47	47	121
8	43	40	254

-2,-14,L

0	52	51	180
1	103	97	225
2	126	123	40
3	36	37	96
4	89	84	197
5	45	42	196
6	67	65	133
7	32	31	56

-2,-13,L

0	143	145	0
1	26	24	68
2	57	54	103
3	123	125	292
4	51	51	25
5	34	37	18
6	44	43	238

-2,-12,L

0	136	135	0
1	132	138	194
2	54	57	228
3	51	57	277
4	157	156	151
5	92	92	176
6	41	42	229
7	69	71	310

-2,-11,L

1	110	121	111
2	148	149	153
3	92	96	14
4	112	110	289
5	168	168	275
7	81	83	93
8	46	47	346
9	52	53	271
10	14*	16	192

-2,-10,L

0	133	130	180
1	110	117	219
2	49	55	42
3	140	139	297
4	184	183	158
5	184	190	158
6	45	43	333
7	70	77	3
8	51	53	237

-2,-9,L

0	177	181	0
1	71	66	64
2	100	106	132
3	197	200	127
4	175	179	266
5	234	238	220
6	61	64	181
7	73	77	49
10	43	47	125

-2,-8,L

0	385	387	180
1	138	131	117
2	223	229	315
3	125	127	8
4	153	155	228
5	69	70	268
6	49	43	316
8	17	16	74

-2,-7,L

1	66	66	194
2	120	118	351
3	330	324	33
4	37	39	288
5	73	79	167
6	63	65	149
8	53	58	217

-2,-6,L

0	74	78	0
1	379	389	134
2	119	118	114
3	354	339	356
4	178	185	111
5	60	58	315
6	54	56	135
7	82	83	241
8	102	111	338

-2,-5,L

0	133	139	180
1	284	299	173
2	163	155	151
3	217	205	44
4	99	96	130
5	85	85	220
6	127	127	27
7	157	153	85
8	70	67	269
9	71	68	353

-2,-4,L

0	56	60	180
1	528	537	192
2	421	429	288
3	448	451	326
4	255	233	137
5	119	109	152
6	81	82	271
7	133	133	109
8	102	103	28
9	25	25	252

-2,-3,L

0	349	383	180
1	123	126	359
2	353	359	62
3	308	299	45
4	414	404	149
5	92	92	239
6	157	156	329
7	168	170	112
8	71	72	205
9	73	72	6

-2,-2,L

0	101	108	180
1	889	888	154
2	530	521	353
3	272	268	233
4	246	239	184
5	41	40	167
6	204	202	294
7	87	87	137
8	62	60	74
9	30	27	346

-2,-1,L

1	270	286	180
2	239	248	200
3	367	387	182
4	36	40	217
5	144	141	91
6	165	167	352
7	62	63	201
9	41	40	104
10	19	21	56

-2,0,L

1	21	20	89
2	211	201	0
3	303	314	90
4	197	188	180
5	90	85	90
6	46	49	0
7	128	121	90
8	47	46	180
10	34	31	0

-1,-21,L

4	30	28	167

-1,-20,L

5	26	24	119

-1,-18,L

1	41	38	83
2	47	42	328
4	53	50	81

-1,-17,L

0	73	74	270
1	67	71	189
2	55	60	166
3	66	63	57
4	41	43	212
5	15*	21	101
7	0*	16	181

-1,-16,L

0	131	131	270
2	127	124	115
3	149	146	270
4	45	48	89
5	31	31	160
6	19	22	254

-1,-15,L

0	65	66	270
1	66	68	213
2	98	94	130
3	113	121	341
4	61	64	286
5	60	65	175
6	31	31	78
7	47	57	339
8	38	52	202
9	10*	20	178

-1,-14,L

0	88	89	90
1	76	74	51
2	46	50	132
3	190	197	240
4	94	96	80
5	67	66	81

-1,-13,L

1	44	43	80
2	180	189	129
3	108	112	303
4	175	175	335
5	109	108	37
6	41	45	180
7	33	36	268
8	31	33	216

-1,-12,L

1	80	80	98
2	26	27	259
3	151	153	208
4	150	149	120
5	95	99	357
6	31	34	263
7	62	69	71
9	20	22	105
10	17*	17	248

-1,-11,L

0	87	84	90
1	90	94	52
2	76	76	241
3	168	173	269
4	283	284	12
5	158	166	31
7	23	25	300
8	37	38	149
9	25	28	133
10	46	49	171

-1,-10,L

0	342	331	270
1	132	129	322
2	89	88	358
3	168	167	110
4	84	88	77
5	91	97	48
6	53	56	259
10	34	40	140

-1,-9,L

0	211	214	90
1	108	112	202
2	213	213	261
3	45	43	272
4	114	113	102
5	130	129	54
7	151	147	345
8	16	14	28
9	47	47	188
10	31	33	161
11	37	41	25

-1,-8,L

0	597	580	270
1	370	371	273
2	209	189	276
3	123	115	61
4	170	170	29
5	58	57	157

-1,-8,L

6	50	53	112
7	80	77	334
8	31	32	63
10	24	27	129

-1,-7,L

0	304	324	90
1	329	343	288
2	319	335	272
3	295	287	29
4	320	312	162
5	89	90	157
6	62	60	79
7	99	101	186
9	45	50	223
11	33	32	3

-1,-6,L

0	21	16	270
1	455	467	299
2	257	259	121
3	90	85	158
4	187	182	303
5	187	186	232
6	78	81	202
7	65	61	36
8	118	121	283
11	36	41	70

-1,-5,L

0	203	207	90
1	181	188	273
2	346	348	114
3	239	232	47
4	129	133	285
5	137	139	333
6	117	119	329
7	168	174	178
8	39	40	134
10	47	46	219

-1,-4,L

0	661	666	270
1	283	284	102
2	542	517	96
3	148	139	219
4	346	332	242
5	140	145	59
6	23	27	74
7	97	97	43
8	158	163	270
9	58	59	241
10	0*	6	296

-1,-3,L

0	495	478	270
1	422	408	243
2	350	362	129
3	153	150	70
4	58	55	310
5	36	35	126
6	70	68	353
8	43	40	44
9	26	30	160
11	35	33	185

-1,-2,L

0	374	385	90
1	391	382	300
2	464	440	253
3	201	203	287
4	267	252	240
5	50	46	297
6	51	44	327
7	68	70	93
8	77	79	282
9	33	34	115
10	26	28	49
11	48	46	272

-1,-1,L

0	114	129	90
1	708	707	197
2	189	193	274
3	392	391	237
4	287	275	340
5	256	241	4
6	112	107	170
7	101	95	178
8	50	50	344
9	33	31	58
11	44	42	161

-1,0,L

1	69	71	90
2	558	539	0
4	213	210	0
5	212	203	270
6	94	93	0
7	67	66	90
8	63	63	180
11	40	35	270

0,-21,L

1	18	20	270
6	44	41	270

0,-20,L

0	26	18	180
1	78	74	0
2	35	36	0
3	64	61	180
5	39	35	0
6	23	21	0

0,-18,L

0	152	147	0
1	104	106	0
2	23	24	180
5	48	41	0
6	32	22	180

0,-17,L

1	64	63	90
2	110	110	90
3	59	56	270
4	17	15	90
5	35	34	270
6	63	63	90
7	30	23	270
8	52	56	270

0,-16,L

0	35 .	37	180
1	51	53	0
4	34	32	0
7	10*	8	0
8	30	30	0

0,-15,L

1	65	63	270
2	160	160	90
3	172	171	270
5	65	64	90
8	48	47	270

0,-14,L

0	76	81	180
1	123	124	180
2	101	100	0
3	35	33	180
4	77	77	180
6	54	56	180
9	43	45	0

0,-13,L

3	124	129	270
4	102	107	270
5	46	47	90
6	29	28	270
7	84	75	270

0,-12,L

2	77	75	180
4	95	97	180
6	58	58	180
8	24	25	0

0,-11,L

1	63	59	90
2	41	39	90
4	44	41	90
5	63	67	270
6	57	59	270
7	43	36	90

0,-10,L

0	82	79	0
1	64	69	180
2	31	42	0
3	36	41	180
4	153	149	180
5	169	171	180
6	71	71	180
7	48	48	0

0,-9,L

1	238	232	90
2	110	105	90
3	21	20	90
4	61	55	270
6	57	58	270
7	37	30	270
8	43	40	90
11	22	18	90

0,-8,L

0	82	80	0
1	82	83	0
2	106	106	0
4	143	138	180
5	42	37	0
9	38	40	180

0,-7,L

1	115	107	90
3	112	103	90
4	80	85	90
5	63	62	90
6	23	25	270
7	105	107	270
9	52	60	90

0,-6,L

0	79	78	0
2	144	141	180
3	69	74	180
4	184	182	180
5	59	59	0
6	91	94	0
7	29	34	0
8	125	129	0
10	21	27	180
11	27	27	180

0,-5,L

2	660	642	270
3	239	229	90
5	99	100	270
6	12*	13	270
7	138	142	90
8	34	29	270
9	25	26	90

0,-4,L

0	329	346	180
1	637	659	0
2	253	250	180
3	57	58	0
4	103	97	180
5	185	184	0
7	145	147	180
8	164	168	0
9	24	21	180

0,-3,L

1	143	148	270
2	300	295	270
3	326	332	90
4	611	573	90
5	132	132	270
6	172	159	270
7	259	257	90
8	77	70	270

0,-2,L

1	204	209	180
2	593	580	180
3	679	652	180
4	164	158	0
5	291	281	0
6	61	60	0
7	267	270	180
8	79	80	0
9	53	53	0
10	30	32	180

0,-1,L

1	444	427	270
2	70	70	270
3	164	161	270
4	268	243	90
5	350	345	90
7	105	103	90
8	61	60	270

0,0,L

2	1433	1495	180
4	200	206	0
6	176	169	180
8	88	85	180

Data for Diterpenoid II

Crystal Data

$C_{20}H_{32}O_2$, M = 304.52; orthorhombic,

a = 10.336(2)Å, b = 24.230(5)Å, c = 7.308(1)Å, V = 1830.20Å^3;

D_c = 1.11 g.cm^{-3}, Z = 4; F(000) = 672; space group $P2_12_12_1$ (D_2^4, No.19);

$M_0 - K\alpha$ radiation, μ ($M_0 - K\alpha$) = 0.65 cm^{-1}. λ = 0.7107Å.

0,0,L

2	421	439	0
4	392	554	0

0,1,L

2	131	116	270
3	555	506	90
4	76	58	90
5	82	88	270
6	135	140	270
9	69	87	270

0,2,L

1	865	914	0
2	119	101	0
3	157	117	180
4	138	144	180
5	82	92	180
6	232	233	0
8	39	46	180

0,3,L

1	490	511	270
2	58	66	270
3	136	154	270
4	138	133	90
5	182	184	270
6	232	234	270

0,4,L

1	766	796	180
2	108	104	0
3	630	574	0
4	264	262	180
5	125	118	180
7	49	66	180
9	55	71	0

0,5,L

1	77	54	270
2	641	600	90
3	648	648	90
4	197	180	270
6	68	92	90
8	0	47	90

0,5,L

0	46	50	180
1	46	62	0
2	447	475	180
3	306	287	0
4	172	169	0
7	167	179	180
8	63	22	180

0,7,L

1	99	128	90
2	376	389	90
3	799	784	90
4	0	33	90
6	101	96	90
7	117	120	90
9	67	64	90

0,8,L

0	461	514	180
1	100	92	0
2	161	149	0
4	109	76	180
5	50	42	180
6	12	12	0

0,9,L

1	98	81	270
3	210	211	90
4	89	88	270
5	217	214	90
6	109	95	90

0,10,L

1	99	102	180
3	149	157	0
5	17	17	0
6	71	79	180

0,11,L

1	125	132	90
2	73	82	270
3	57	80	90
4	136	151	270
5	62	59	90
6	109	109	90

0,12,L

0	92	86	0
1	69	63	0
4	76	68	180
5	49	61	0

0,13,L

1	121	115	90
2	298	316	270
3	65	56	90
5	197	198	90
7	39	35	90

0,14,L

0	148	139	0
1	29	7	180
3	55	57	0
6	64	75	0
8	114	114	180

0,15,L

1	282	266	90
2	144	126	270
3	127	124	270

0,16,L

2	140	145	180
5	102	105	0

0,17,L

1	147	148	270
2	71	66	90
3	114	122	270
5	68	88	270

0,18,L

0	129	123	180
1	131	131	180
4	73	89	0

0,19,L

1	80	99	90
2	26	61	90

0,20,L

2	145	208	180

0,21,L

1	36	44	270
2	93	91	90
3	31	44	90

0,22,L

3	66	63	180

0,23,L

5	65	57	270

0,24,L

4	44	45	180

0,26,L

4	31	30	180

0,27,L

2	17	29	90

1,0,L

1	820	815	270
2	552	515	0
5	206	201	90
6	112	111	180
7	122	130	270

1,1,L

1	736	741	286
2	226	216	60
3	45	57	52
4	180	168	205
5	65	57	87

1,2,L

1	743	762	264
2	53	27	212
3	316	272	278
4	159	144	345
5	171	101	136
6	164	162	161
7	132	146	294
9	88	104	200

1,3,L

1	342	377	175
2	176	149	82
3	234	228	2
4	374	358	75
5	195	190	132
6	151	153	47

1,4,L

0	219	240	90
1	567	606	179
2	287	290	334
3	214	223	171
4	252	210	263
5	99	105	142
6	125	130	162
8	55	71	301

1,5,L

0	428	413	270
1	155	153	164
2	237	219	203
3	505	474	291
4	164	155	4
5	180	180	70
6	133	137	56
7	151	161	78

1,6,L

0	163	195	270
1	66	73	231
2	68	62	264
3	382	363	34
5	25	14	25
6	127	132	345

1,7,L

0	126	104	90
2	235	219	162
3	109	115	352
4	73	80	71
5	90	78	62

1,8,L

0	141	131	90
1	457	479	187
2	117	136	319
3	147	133	77
4	0	23	92
6	71	56	341

1,9,L

1	190	190	274
2	262	287	206
3	162	153	270
6	80	92	57

1,10,L

0	216	206	270
1	142	143	177
2	87	110	131
3	62	27	80
4	76	70	215
6	125	140	11
7	81	72	176

1,11,L

0	681	635	90
1	342	377	343
2	156	155	144
4	21	42	115
5	105	106	272
6	79	53	90
7	68	74	357

1,12,L

0	180	145	270
1	205	208	252
2	141	144	84
5	115	103	345
6	66	96	283

1,13,L

0	98	115	90
1	254	245	343
2	93	71	294
3	78	55	286
4	97	102	287
6	64	63	225
7	0	39	348

1,14,L

0	82	98	90
1	221	227	336
2	228	239	142
4	98	89	116
5	204	207	24
6	54	73	349
7	80	84	292

1,15,L

0	95	112	270
1	135	137	268
2	52	52	46
3	115	115	115
4	174	179	253
7	38	50	249

1,16,L

2	157	149	108
3	175	186	179

1,17,L

1	119	109	244
2	156	168	308
3	135	153	24
4	95	92	277
5	92	99	163

1,18,L

1	104	96	154
2	169	180	142
3	177	185	159
4	133	120	81
6	53	57	249

1,19,L

0	67	75	270
1	179	184	131
2	68	70	152
3	152	129	1

1,20,L

1	59	63	32
2	90	87	97
7	55	42	251

1,21,L

0	35	40	270
1	63	78	169
2	159	169	98

1,22,L

0	118	83	270

1,23,L

1	39	47	142

1,24,L

1	95	71	338

1,28,L

2	32	34	342

2,0,L

2	450	450	180
3	90	78	270
4	222	200	180
5	84	62	270
6	81	86	0
9	14	17	270

2,1,L

0	232	254	0
1	380	387	57
2	105	112	90
3	123	95	159
4	167	165	288
5	139	128	23
6	235	241	33
7	47	62	355

2,2,L

0	440	488	0
1	750	775	61
2	301	263	339
3	207	181	290
4	356	346	82
5	153	152	97
6	124	118	348
7	130	135	28

2,3,L

0	801	879	0
1	896	971	89
2	376	382	184
3	349	302	126
4	246	236	218
5	284	282	107
6	172	168	65
7	86	95	17
8	0	37	127

2,4,L

0	183	176	0
1	280	311	67
2	65	78	295
3	197	205	263
4	255	228	9
5	79	67	55
6	161	160	344
7	91	98	9

2,5,L

0	135	161	0
1	485	487	63
2	418	428	154
3	70	88	226
4	258	278	217
7	71	82	13

2,6,L

1	318	312	327
2	165	171	88
3	199	184	175
4	189	178	66
5	85	86	270
6	93	107	336
7	130	146	22

2,7,L

0	231	221	0
1	264	239	187
2	132	144	238
3	113	96	87
4	172	189	157
5	102	108	198
6	103	97	270

2,8,L

1	127	121	176
2	168	168	172
3	268	268	126
6	97	84	266

2,9,L

0	291	331	0
1	198	184	68
2	184	154	204
3	87	61	310
4	74	60	108
6	81	90	251

2,10,L

0	403	427	0
1	426	426	165
2	259	242	139
3	209	180	105
4	98	101	189
6	70	58	306

2,11,L

0	256	220	180
1	205	216	319
2	74	68	63
3	90	77	64
4	136	120	187
5	79	87	230
6	57	70	160

2,12,L

0	294	287	0
1	178	188	249
2	120	121	160
3	93	75	126
4	62	79	291
7	67	67	225

2,13,L

0	47	56	180
2	19	42	9
3	168	176	6
4	73	64	83
5	166	172	268

2,14,L

0	147	150	180
1	96	108	187
3	110	93	67
4	239	233	164
5	80	75	336
6	28	72	127

2,15,L

1	84	98	349
2	157	136	142
3	120	128	273

2,16,L

0	0	29	0
1	145	133	193
2	120	126	254
3	161	165	7
4	147	142	106
5	91	98	87

2,17,L

0	79	79	180
1	166	187	57
2	226	238	106
3	53	53	89
4	152	165	237
5	84	80	137
6	81	78	93

2,18,L

1	98	88	320
2	98	97	247
3	155	162	263

2,19,L

1	84	85	281
2	127	116	94
6	32	6	331

2,20,L

1	37	54	252
2	121	113	3
6	91	85	26

2,22,L

0	85	102	0
2	80	93	226
4	34	46	209

2,23,L

1	82	86	232

2,29,L

0	0	5	0

3,0,L

1	366	359	270
3	167	171	90
5	180	191	270
6	72	68	0
7	104	97	270

3,1,L

0	558	610	90
1	254	284	202
2	178	177	51
3	133	143	167
4	272	242	44
5	205	189	155
7	99	131	230

3,2,L

0	66	56	270
1	192	161	32
2	337	314	328
3	302	311	122
4	44	66	201
5	237	231	30
6	153	151	315
7	136	160	274

3,3,L

0	426	458	90
1	305	345	262
2	87	88	37
4	30	50	325
5	183	184	93
6	132	131	136
7	103	96	224
9	0	84	353

3,4,L

1	251	262	263
2	284	215	65
3	222	162	163
4	242	235	199
6	194	196	57
7	165	96	289

3,5,L

0	135	139	90
1	264	285	280
2	136	118	336
3	150	131	105
4	98	100	311
5	212	202	177
6	92	80	131
7	124	112	271

3,6,L

0	115	125	270
1	152	147	185
2	167	162	292
3	180	181	97
5	152	150	191
6	115	115	209

3,7,L

0	118	131	90
1	216	219	263
2	170	174	296
3	138	138	11
4	151	165	330
6	139	134	153

3,8,L

0	653	668	270
1	246	250	23
2	336	323	197
3	147	167	273
4	67	75	347
5	162	163	64
6	46	99	193

3,9,L

0	197	182	90
1	120	126	53
2	90	90	114
3	155	143	13
6	106	105	94
8	49	81	158

3,10,L

0	360	354	270
1	115	126	247
2	87	82	339
3	125	127	173
5	26	86	200
7	83	69	169
8	78	105	213

3,11,L

0	207	201	270
1	69	70	198
2	162	134	323
3	101	81	346
4	111	115	276
5	13	14	212
8	62	62	250

3,12,L

1	131	116	191
2	126	139	251
3	63	71	300
4	221	222	48
5	145	150	156
7	0	65	34

3,13,L

0	87	82	90
1	143	147	161
2	49	54	25
3	140	151	51
4	127	125	162

3,14,L

0	22	18	90
1	95	85	195
3	253	274	208
4	157	159	345
5	41	34	175
6	37	76	180

3,15,L

0	104	110	90
2	141	133	28
3	195	192	350
4	104	116	103
5	117	117	38
6	62	60	42

3,16,L

0	99	94	90
1	133	137	276
2	86	105	32
3	187	187	163
4	67	54	149
5	94	94	24
6	76	67	20

3,17,L

1	57	60	233
4	113	102	165
5	72	77	44

3,18,L

0	56	62	90
1	92	102	282
2	98	102	341
4	91	88	197

3,19,L

1	63	80	228
2	75	95	293
4	37	36	220
7	54	46	153

3,20,L

1	67	85	273
2	55	54	158
5	38	60	80

3,21,L

0	114	124	270
2	99	97	200

3,22,L

2	89	81	105
6	58	41	188

3,23,L

2	40	53	159

3,24,L

1	62	59	240

3,28,L

3	34	21	185

4,0,L

0	420	437	0
1	44	43	270
3	257	235	90
4	174	175	0

4,1,L

0	82	102	180
1	461	472	250
2	412	401	129
3	243	225	3
4	213	213	242
5	158	169	291
7	91	89	172

4,2,L

0	44	53	0
1	199	229	317
2	160	155	343
3	162	175	133
4	97	99	336
6	59	60	57

4,3,L

0	348	363	180
1	203	195	312
2	142	134	212
3	169	149	297
4	85	81	104
5	140	140	297
6	155	161	335
8	61	72	103

4,4,L

1	190	198	122
2	152	128	130
4	134	121	179
5	194	192	127
6	134	132	65
7	96	97	120

4,5,L

0	113	127	180
1	221	207	40
2	159	150	98
3	100	89	270
5	282	289	137
6	80	96	46

4,6,L

2	338	346	176
3	92	67	263
4	233	235	247
5	192	183	142
6	126	117	128

4,7,L

0	102	111	180
1	385	359	7
2	77	83	58
3	68	69	153
4	221	244	312
5	105	96	222
6	128	123	69
7	74	72	25

4,8,L

1	115	106	30
2	70	79	284
3	117	117	276
4	91	79	232
5	83	71	348

4,9,L

0	57	43	180
1	102	83	8
3	168	183	151
4	59	61	107
5	107	115	198
7	66	67	16

4,10,L

0	79	105	180
1	100	93	193
2	192	183	257
4	87	97	243
7	95	87	260

4,11,L

0	60	64	0
1	185	193	52
2	138	125	178
3	53	38	273
4	110	107	322
5	71	94	88
7	95	93	346

4,12,L

1	106	101	55
2	202	202	228
3	70	72	95
4	116	117	131
5	80	72	265
6	58	71	142
7	44	64	317

4,13,L

2	126	135	136
3	139	120	224
4	88	99	273
5	72	82	16
7	30	50	314

4,14,L

1	38	53	56
2	142	151	294
3	86	90	96
4	164	160	53
5	63	58	280

4,15,L

1	104	90	171
2	117	136	152
3	33	51	285

4,16,L

0	147	156	0
1	57	60	132
2	67	84	259

4,16,L

4	110	114	83
5	75	100	254

4,17,L

0	42	32	0
1	68	77	237
2	61	67	199
3	106	95	247

4,18,L

1	63	70	35
2	75	76	155
4	51	62	109

4,19,L

1	79	78	191
3	149	127	255
6	43	44	182

4,20,L

5	40	68	236

4,21,L

0	55	67	0
1	23	56	184

4,22,L

0	109	103	0
1	49	48	233
2	75	78	105

5,0,L

1	265	291	90
2	117	109	0
3	66	59	270
6	71	74	0
7	117	97	90

5,1,L

0	73	55	270
1	401	380	183
2	135	137	113
3	209	206	18
5	155	171	152
6	113	122	247

5,2,L

0	92	122	270
1	295	292	183
2	191	193	209
3	148	159	260
5	136	137	179

5,3,L

0	71	89	90
1	259	278	196
2	113	116	223
3	94	103	47
4	86	76	192
6	83	77	5

5,4,L

0	73	104	90
1	53	47	277
2	214	222	278
3	61	55	157
4	118	117	281
5	79	67	83

5,5,L

0	285	296	90
1	95	107	160
2	85	90	320
3	80	80	72
4	205	197	169
5	136	145	94
6	118	109	38

5,6,L

0	162	166	90
1	165	171	233
2	166	155	297
4	203	199	207
8	43	48	268

5,7,L

0	143	148	90
1	153	156	195
2	51	48	275
4	137	146	223
5	135	126	165
6	170	186	61
7	79	87	227

5,8,L

0	119	143	90
1	66	64	241
2	124	114	277
3	77	78	41
4	137	134	266
5	149	145	178
6	95	98	284
7	43	61	234

5,9,L

0	156	146	90
1	136	116	298
2	98	95	264
5	105	106	303

5,10,L

0	107	101	90
1	132	123	309
2	112	114	135
3	70	73	80
4	172	172	336

5,11,L

0	75	77	90
1	68	43	359
2	49	59	127
4	121	122	124

5,12,L

1	119	104	344
2	119	109	227
3	135	143	119
4	137	137	302
5	42	58	309
6	7	39	249

5,13,L

1	97	77	300
3	106	101	331

5,14,L

1	99	94	50
2	75	76	227
3	77	82	150
4	92	95	321
5	22	57	65

5,15,L

0	105	102	270
2	126	101	213
3	86	84	76
6	40	60	216

5,16,L

0	97	83	270
6	79	66	171

5,17,L

0	49	68	270

5,18,L

0	61	30	90
1	83	80	213
3	0	38	160
4	47	60	108

5,19,L

0	38	42	90
2	56	54	349
4	53	59	159
5	7	17	176

5,20,L

1	71	66	145
3	66	56	245
4	64	55	186

5,22,L

2	73	43	352

5,23,L

3	30	17	13

5,24,L

4	81	73	44

5,28,L

1	45	38	271

6,0,L

1	110	91	90
2	118	135	180
5	82	89	90
6	126	125	180

6,1,L

0	10	59	0
1	58	75	96
2	197	180	64
3	170	170	134
4	58	63	32
6	103	54	64
8	60	51	74

6,2,L

0	152	163	180
1	177	165	118
2	84	80	120
3	44	38	264
4	83	97	181
5	73	86	334
6	0	9	231
7	59	58	193

6,3,L

0	193	167	0
1	98	109	210
2	118	116	117
3	110	122	141
4	53	47	138
5	124	115	62
6	38	47	6

6,4,L

0	201	189	0
1	234	222	223
2	81	72	90
3	122	132	300
5	106	107	270
6	72	85	269

6,5,L

0	305	323	0
1	76	68	342
2	99	88	137
4	153	144	273
6	98	102	5

6,6,L

0	146	151	0
1	141	131	4
2	49	47	57
4	50	51	78
6	53	67	268

6,7,L

0	83	68	0
1	74	66	331
2	112	127	139
4	104	116	214
5	112	125	169
6	67	70	230
8	0	28	137

6,8,L

0	151	153	180
1	75	59	287
2	129	131	49
3	24	46	39
4	114	125	221
5	67	95	184
6	46	54	276
7	33	49	167

6,9,L

0	56	72	0
1	53	72	85
2	33	52	53
3	122	134	299
4	133	141	279
5	75	90	92
6	0	27	253

6,10,L

0	76	90	0
1	102	97	298

6,10,L

2	136	124	146
3	171	176	46
4	60	63	311
5	117	123	231

6,11,L

0	160	155	0
2	168	186	55
3	60	89	311
4	76	84	279
6	77	73	75
7	32	26	193

6,12,L

0	69	67	180
1	190	213	347
2	73	70	211
3	198	194	110
6	55	49	329
7	44	36	271

6,13,L

0	86	84	180
1	119	100	295
3	41	74	299

6,14,L

0	126	124	180
1	40	35	302
5	42	48	169

6,15,L

1	68	72	331
2	0	57	343
3	63	50	282
6	40	33	88

6,16,L

2	141	145	172
6	31	46	80

6,18,L

0	102	113	0
6	28	42	14

6,19,L

2	79	85	253
6	0	15	320

6,22,L

0	35	30	0
2	0	15	306

6,24,L

0	28	26	0

6,25,L

0	81	46	0

7,0,L

2	54	62	0
3	85	112	90

7,1,L

0	94	86	270
1	70	73	187
2	64	56	147
3	66	81	199
4	86	94	93

7,2,L

0	177	192	270
3	129	130	20
4	134	125	22
6	73	67	228

7,3,L

0	118	128	270
1	66	73	131
3	54	73	234
5	106	102	154

7,4,L

0	243	245	270
5	71	78	343

7,5,L

0	203	194	270
1	109	126	253
2	44	55	224
3	44	49	313
4	46	42	288

7,6,L

0	178	172	270
1	71	58	193
2	23	46	293
3	125	128	0

7,7,L

0	167	160	90
1	110	115	323
2	170	174	306
3	151	161	344
6	52	50	159

7,8,L

0	53	59	90
1	113	114	185
2	98	92	191
3	111	117	314

7,9,L

1	176	193	139
2	155	162	336
3	126	127	311
4	66	80	222
6	29	25	45

7,10,L

2	132	129	245
3	90	84	7
4	136	125	259

7,11,L

1	116	119	224
2	119	125	26
3	109	131	16

7,12,L

0	109	125	90
1	84	97	217

7,12,L

2	79	75	211
3	34	40	49

7,13,L

0	168	168	90
1	84	94	209
2	85	101	261

7,14,L

0	87	79	90
4	43	38	71
5	68	61	65

7,15,L

0	63	99	90
5	52	40	331

7,16,L

1	95	97	286
4	0	30	261

7,17,L

1	73	62	342
2	84	92	140

7,18,L

1	66	69	299
2	39	47	229

7,19,L

3	64	38	181

7,22,L

3	26	30	41

7,24,L

2	0	8	200

8,0,L

1	98	112	270
3	47	50	270
4	135	160	0
5	95	93	270

8,1,L

0	90	108	180
4	82	79	229
6	61	78	103

8,2,L

0	111	105	180
1	120	119	271
2	73	83	1
3	109	120	180
4	63	67	340
5	46	46	294

8,3,L

1	87	91	204
3	52	36	264
4	27	42	261

8,4,L

0	135	135	180
1	123	131	169
3	101	113	124
6	0	11	131

8,5,L

2	52	33	278
3	104	99	265

8,6,L

0	168	164	0
1	126	120	223
2	50	61	179
3	91	76	138

8,7,L

1	138	138	90
2	95	90	359
4	63	66	338

8,8,L

0	88	88	0
1	142	115	344
2	86	73	167
3	53	67	195
4	94	88	234

8,9,L

1	106	124	89
2	59	59	45
3	68	68	253
4	50	30	316

8,10,L

2	60	74	105
4	71	82	204

8,11,L

1	84	69	81
2	131	102	93

8,12,L

0	82	80	0

8,13,L

0	77	85	0
1	67	44	48
2	99	101	65
3	114	98	91

8,15,L

1	72	74	305

8,17,L

1	80	73	266

8,19,L

1	52	42	268

9,0,L

3	63	58	90
4	66	61	180

9,1,L

1	37	45	249

9,1,L

2	51	79	278
4	95	91	265
5	0	23	164

9,2,L

1	78	77	87
2	60	70	208

9,3,L

0	111	95	90

9,4,L

0	166	171	270
2	118	97	172
3	83	75	193
4	65	56	344

9,5,L

0	17	17	270
1	70	88	37
2	66	57	71
6	24	27	249

9,6,L

1	128	127	286
3	0	29	164

9,7,L

0	90	68	270
2	86	71	56
3	70	76	140

9,8,L

1	62	59	311
3	58	55	329
5	0	54	101

9,9,L

2	82	90	18
3	67	74	45

9,10,L

2	70	71	96

9,11,L

0	54	51	270
1	64	74	128
3	93	104	354

9,12,L

2	0	31	343
3	76	77	19

9,13,L

2	59	50	204

9,14,L

1	0	10	281
3	69	61	357

9,15,L

1	51	53	172
5	53	38	226

9,16,L

3	22	45	21

9,17,L

2	18	45	240

9,18,L

3	0	40	318

10,0,L

1	76	54	270

10,1,L

0	63	63	0

10,4,L

0	83	87	0
1	73	71	247
4	62	37	270

10,5,L

0	59	77	180
3	87	78	69

10,6,L

0	83	94	0

10,7,L

2	72	61	254

10,8,L

0	68	75	0
3	57	67	64

10,11,L

1	54	30	336
4	71	72	277

10,14,L

0	72	63	180

10,18,L

2	23	31	137

10,19,L

2	39	26	325

11,2,L

2	21	35	211

11,3,L

3	43	31	257

11,5,L

1	28	39	90

11,9,L

0	0	25	90
2	42	26	202
4	48	10	251

11,10,L

4 44 44 202

11,13,L

2 0 41 206

11,15,L

0 0 1 90

12,0,L

2 44 14 180

12,5,L

0 24 4 180
2 32 30 342

12,6,L

3 0 27 86

12,9,L

0 35 24 0

13,2,L

0 44 2 90

Data for the Tetranortriterpenoid-Spiro-Lactone

Crystal Data

$C_{26}H_{32}O_5$, M = 424.58; orthorhombic,

a = 9.608(2)Å, b = 22.359(5)Å, c = 10.202(2)Å, V = 2191.63Å^3;

D_c = 1.29 g.cm^{-3}, Z = 4; F(000) = 912; space group $P2_12_12_1$ (D_2^4, No.19);

$Mo - K\alpha$ radiation, μ ($Mo - K\alpha$) = 0.83 cm^{-1}. λ = 0.7114Å.

0,0,L

2	2210	2378	180
4	237	212	0
8	146	201	180

0,1,L

1	83	90	90
2	1454	1565	90
4	414	426	270
7	106	120	90

0,2,L

1	576	589	0
2	435	453	0
3	608	604	0
4	138	119	180
5	398	406	180
6	458	525	0
7	448	467	0
8	199	224	180
9	244	283	180

0,3,L

1	454	463	270
2	592	654	90
3	611	618	90
4	109	112	270
5	118	152	90
6	298	314	90
8	76	143	90
9	102	60	270
10	110	127	270

0,4,L

0	773	764	0
1	718	735	0
2	306	323	0
3	322	331	0
4	660	696	180
6	206	242	0
7	113	90	180

0,5,L

2	853	885	90
3	437	391	270
4	472	417	270
5	185	205	90
6	51	47	270
7	122	129	90
9	145	147	90

0,6,L

0	69	17	0
1	678	631	180
9	127	123	0
11	105	164	180

0,7,L

1	92	74	270
2	309	250	270
3	82	108	90
4	183	179	270
5	242	272	90
6	105	70	270
8	144	173	90
10	107	132	270

0,8,L

0	542	550	0
1	370	353	0
2	652	653	180
3	388	404	0
6	173	205	0
8	215	249	180

0,9,L

1	407	425	90
2	603	622	90
3	110	88	270
4	446	420	270
5	119	86	270
8	90	84	270

0,10,L

0	454	430	180
2	129	140	0
3	438	436	180
4	87	104	180
6	357	341	180
7	220	204	0
8	286	272	0

0,11,L

1	152	133	270
4	296	289	90
6	53	79	270
7	111	89	90

0,12,L

0	545	519	180
1	96	91	180
2	339	314	0
3	164	163	0
4	254	240	180
5	164	131	0
7	305	366	180
9	98	126	0

0,13,L

1	101	93	270
2	95	85	90
3	104	83	270
5	107	118	90
6	142	139	270
9	110	127	270

0,14,L

0	426	374	0
1	227	225	180
2	128	125	180
5	220	220	0
6	206	196	180
7	132	139	180
9	69	81	0

0,15,L

2	202	189	270
3	116	114	270
4	194	173	90

0,16,L

1	68	75	0
2	157	131	180
3	193	154	0

0,17,L

1	112	121	270
2	100	75	90
5	143	139	90

0,18,L

2	54	60	0
3	174	172	0
5	96	75	180

0,19,L

1	107	117	270
2	211	207	270
4	71	50	90

0,21,L

4	108	99	270

0,22,L

3	68	62	0

0,23,L

3	135	124	90

0,24,L

0	140	126	180
1	221	169	0
5	85	96	180

0,26,L

0	98	109	180

0,27,L

2	99	87	270
3	82	68	90

1,0,L

1	771	802	90
2	504	516	180
3	571	612	90
4	291	313	0
5	445	407	270
6	152	145	180
7	311	273	90
9	124	93	270

1,1,L

1	876	937	291
2	521	527	166
3	455	440	294
4	383	414	257
5	148	140	77
6	221	257	59
7	145	132	303

1,2,L

0	1137	1165	270
1	682	746	82
2	902	914	107
3	695	688	323
4	297	273	284
5	302	323	149
8	103	147	87
9	145	138	177

1,3,L

0	1107	1150	90
1	547	573	53
2	776	795	285
3	392	382	79
4	442	408	47
5	184	173	334
6	323	319	167

1,4,L

0	381	406	90
1	55	61	10
2	458	446	262
4	881	923	58
5	217	208	176
6	203	182	315
7	176	174	282
8	105	124	119
9	177	178	51
11	72	85	235

1,5,L

0	411	390	90
1	495	519	267
2	304	317	251
3	322	301	92
4	158	158	241
5	187	193	92
6	253	283	45
7	113	120	289
8	120	139	199

1,6,L

0	755	742	90
1	657	629	238
2	271	269	154
3	367	348	341
4	543	551	353
5	153	151	168
6	231	211	168
7	174	187	108

1,7,L

0	336	353	270
1	417	404	169
2	661	624	262
3	304	313	282
5	91	87	338
6	248	268	87
7	88	66	99
8	113	96	99

1,8,L

0	73	87	270
1	384	353	264
2	279	276	169
3	350	349	120
4	325	332	30
5	183	189	341
8	149	174	136

1,9,L

0	164	174	90
1	191	189	289
2	350	362	162
4	280	283	286
5	221	260	201
6	100	115	110
7	212	210	271
8	51	39	52
9	123	139	71

1,10,L

1	610	567	255
2	404	391	72
3	141	156	348
4	437	422	279
5	250	275	132
6	280	294	32
7	215	265	304
8	116	112	185

1,11,L

1	340	330	222
2	159	166	229
3	178	168	343
5	167	189	271
7	182	177	141
10	58	57	294

1,12,L

0	390	384	90
1	301	265	210
2	309	322	243
3	92	72	198
5	169	175	84
6	148	175	106
7	278	315	319
8	115	131	277

1,13,L

0	118	97	90
1	51	46	275
2	91	100	187
3	128	84	72
4	138	144	325
5	232	251	186
7	90	97	284

1,14,L

0	396	373	90
1	87	56	51
2	306	284	244
4	113	122	247
5	80	75	151
6	100	126	92

1,15,L

0	78	74	90
1	198	194	184
3	231	225	351
5	196	214	250
10	59	45	5

1,16,L

0	180	180	270
1	179	190	316
3	235	243	195
4	107	93	211
5	151	164	0
6	95	98	110

1,17,L

0	125	146	270
1	149	127	112
3	150	133	353
4	160	168	26
5	72	57	188

1,18,L

0	300	258	90
4	169	159	197
5	85	101	141
7	96	105	326

1,19,L

1	83	100	113
2	164	205	134
4	149	145	333

1,20,L

0	59	56	90

1,24,L

0	97	72	270
5	61	31	23

1,28,L

3	103	100	214

2,0,L

1	543	557	90
2	676	673	180
3	126	92	90
4	141	136	0
5	142	122	270
6	150	139	0
7	83	69	90
8	139	179	0
13	62	89	270

2,1,L

0	260	279	180
1	563	592	125
2	398	372	305
3	346	332	269
4	425	405	170
5	151	125	72
6	193	170	330
7	171	159	278
8	146	138	160
10	156	171	13

2,2,L

0	368	347	0
1	222	226	227
2	490	470	107
3	310	319	69
4	115	110	288
5	388	387	174
6	262	272	39
7	180	202	309
8	158	136	261
9	142	188	136
11	57	65	353

2,3,L

0	125	116	0
1	560	552	8
2	344	323	241
3	160	181	105
4	237	220	264
5	245	274	146
6	163	158	224
8	121	123	42

2,4,L

0	384	382	180
1	370	367	266
2	539	536	290
3	333	322	135
4	375	353	100
5	183	203	226
6	139	149	272
7	93	115	41
13	80	83	57

2,5,L

0	381	347	180
1	740	737	68
2	205	209	34
3	262	253	128
4	257	243	323
5	198	210	272
6	249	266	148
7	87	119	58
8	139	104	244
9	134	134	243

2,6,L

0	377	370	180
1	94	79	61
2	556	581	257
3	140	125	226
4	460	459	77
5	165	163	83
6	215	233	291
8	117	130	226

2,7,L

0	425	366	180
1	226	251	149
2	187	196	344
3	571	537	37
4	126	142	288
5	132	147	247
6	167	182	162
7	89	123	93
8	184	194	37
10	81	82	209

2,8,L

1	403	354	350
2	136	136	302
3	537	546	199
4	154	152	185
5	170	149	104
6	138	140	117
9	132	165	230

2,9,L

0	384	375	180
1	153	148	100
2	135	134	139

2,9,L

4	234	241	48
5	137	187	280
6	161	177	282
7	142	166	104

2,10,L

0	336	338	180
1	139	129	225
2	177	195	299
3	126	125	122
4	101	101	303
5	224	216	285
6	145	157	103
7	110	117	53
9	56	92	159

2,11,L

0	291	263	180
1	220	228	2
2	216	219	340
3	224	248	172
4	199	235	255
7	130	163	336

2,12,L

0	191	212	180
2	225	225	322
4	238	216	133
5	155	171	310
6	244	250	251

2,13,L

0	113	108	180
1	204	197	351
2	149	129	38
4	95	99	59
5	71	98	272
6	176	180	196
7	103	115	41
8	108	137	324

2,14,L

0	135	136	0
1	146	144	189
2	345	368	188
3	127	148	166
4	192	201	24
5	176	167	23
7	140	156	239

2,15,L

0	245	224	180
2	198	185	311
4	81	90	235
6	115	106	79

2,16,L

0	143	138	0
2	139	132	153
3	119	138	53
5	130	142	223

2,17,L

0	201	204	0
2	162	169	221
4	150	123	38
5	122	119	176
6	112	96	244

2,18,L

1	201	184	240
3	278	288	128
8	76	81	252

2,19,L

1	360	359	31
5	63	63	195

2,20,L

2	188	176	263
3	113	107	69

2,21,L

0	187	168	180
2	84	66	59
4	84	88	12

2,22,L

0	99	110	0
1	171	177	168

2,23,L

1	104	136	142
2	79	85	95

3,0,L

1	514	495	90
2	373	386	180
4	277	259	0
5	231	234	270
6	189	199	180
9	84	50	270

3,1,L

0	430	425	90
1	335	331	60
3	261	270	33
5	152	144	170
6	158	183	59
7	128	154	352
9	82	96	258

3,2,L

0	255	262	90
1	70	75	192
3	211	216	218
4	340	346	137
6	180	158	307
9	91	139	64
10	124	122	218
11	79	90	288

3,3,L

0	390	375	90
1	374	381	124
2	171	180	70
3	331	321	255
4	118	113	292
5	163	140	333
6	93	82	316
8	123	120	150
9	83	66	346

3,4,L

1	260	231	126
2	246	232	141
3	215	219	78
4	103	113	198
5	149	161	206
8	170	208	131
9	81	84	5
10	108	119	333

3,5,L

0	189	233	270
1	252	215	13
2	351	348	183
3	304	290	203
4	168	180	133
5	128	129	135
6	125	134	118
7	98	138	310

3,5,L

8	113	131	289

3,6,L

1	317	299	238
2	102	109	62
3	137	152	62
4	81	64	109
5	145	164	258
8	92	125	115

3,7,L

0	547	499	90
1	252	236	284
2	319	286	15
3	110	122	138
4	217	195	196
5	72	84	287
6	202	191	308
7	89	84	77
8	151	168	185
9	65	84	199
10	98	91	309

3,8,L

0	246	257	270
1	179	167	100
2	575	569	146
3	72	72	239
4	287	268	354
5	172	177	325
6	121	148	147
7	151	149	170
8	55	51	234

3,9,L

0	44	27	90
1	137	140	52
2	111	84	318
3	250	250	221
4	135	134	196
5	164	156	117
6	178	184	39
7	80	107	55
8	126	144	280

3,10,L

0	76	73	270
1	158	131	290
2	227	194	90
3	222	210	92
4	172	167	220
5	88	86	305
6	127	128	249
8	123	123	62

3,11,L

0	158	177	90
1	155	157	121
2	145	142	342
3	98	97	140
4	119	157	151
5	90	108	128
6	240	234	273
7	93	119	14

3,12,L

0	434	385	270
1	146	140	36
2	170	161	180
3	144	118	325
4	102	123	32
7	139	169	229

3,13,L

0	96	107	90
1	130	159	301
2	149	139	340
3	100	91	187
4	158	146	245
5	200	177	72
6	93	115	120
7	95	127	184

3,14,L

0	165	160	90
1	181	192	314
2	97	124	265
5	136	122	324
7	138	147	182
8	70	67	312
10	85	85	63

3,15,L

0	108	120	270
1	161	170	142
3	238	226	57
6	119	110	22

3,16,L

0	91	109	270
1	275	245	70
2	89	122	48
3	149	138	255

3,17,L

2	149	145	290
6	90	101	106
9	115	107	344
10	84	81	27

3,18,L

1	93	100	117
2	93	97	351
3	115	124	347
6	81	66	252

3,19,L

0	174	147	270
1	79	83	127
2	122	105	174
3	122	127	329

3,20,L

1	226	232	260
3	83	79	61

3,21,L

0	227	197	90
1	76	115	316
2	96	82	244

3,22,L

0	121	104	90
8	116	116	269

3,24,L

4	97	77	163

3,25,L

3	91	92	136

3,26,L

0	91	82	270
5	135	96	179

4,0,L

0	234	210	0
2	463	463	0
4	128	112	180
6	124	147	180
7	117	140	90

4,1,L

0	474	460	0
1	179	180	144
2	200	187	169
3	246	275	211
4	173	179	62
5	150	141	308
6	167	176	142
7	96	96	159
9	134	148	109

4,2,L

0	404	418	0
1	489	457	154
2	236	233	180
4	271	281	342
5	177	196	286
7	139	139	55

4,3,L

0	586	529	0
2	403	421	159
3	347	362	252
4	71	57	150
5	258	267	78
6	104	107	9
7	111	128	13
8	119	129	165
9	112	154	216

4,4,L

0	546	521	0
1	401	387	14
2	229	222	52
3	221	228	45
4	218	226	195
5	88	111	318
8	118	129	206
9	96	100	230
10	93	105	5

4,5,L

0	275	256	180
1	463	452	340
2	256	226	94
3	250	256	107
4	168	152	207
5	179	177	265
7	103	116	88

4,6,L

0	155	159	180
1	163	174	244
3	82	107	146
5	95	90	209
7	266	278	11
8	81	77	330
9	103	133	201

4,7,L

0	75	62	0
2	300	276	187
3	172	159	217

4,8,L

0	424	407	180
2	306	272	344
3	302	317	356
4	235	242	221
5	78	80	320
7	185	201	171
8	112	114	23

4,9,L

1	122	122	247
2	74	97	47
3	148	131	37
5	145	145	148
6	163	147	273
7	104	120	349

4,10,L

0	84	65	0
2	97	84	183
3	160	151	160
5	91	51	268
7	53	94	277

4,11,L

1	147	172	23
2	100	111	230
3	196	184	249
4	92	101	305
5	145	155	95
7	105	121	327

4,12,L

0	168	167	180
1	90	88	32
2	148	152	130
3	124	107	289
4	163	154	345
6	188	187	111
7	85	83	236

4,13,L

0	128	126	180
1	120	116	249
2	118	79	10
3	225	211	100
4	89	117	46
5	201	206	270

4,14,L

0	49	30	180
1	122	133	313
2	152	166	7
4	166	139	158
6	112	95	179
8	85	90	327

4,15,L

0	185	155	0
2	150	162	305
4	180	179	99

4,16,L

0	124	126	180
1	329	313	188
3	229	226	11
4	144	154	338

4,17,L

2	122	126	276
3	161	180	307
4	184	171	80
5	123	137	71

4,18,L

0	106	98	0
1	131	145	353
2	107	130	300
4	163	170	120

4,19,L

3	126	114	300
5	105	97	117

4,20,L

1	84	55	180
3	102	91	326
4	78	84	341
5	82	79	64

4,23,L

2	81	68	270

4,25,L

5	117	90	98

4,26,L

1	101	66	336
4	100	78	76

4,27,L

2	82	74	41

5,0,L

1	335	306	90
2	89	78	180
5	92	104	90
6	219	228	0
10	101	115	180

5,1,L

0	761	757	90
1	160	133	66
2	272	266	225
3	108	107	175
5	189	188	339
6	120	165	85

5,2,L

0	117	114	90
1	505	434	94
2	259	263	191
3	353	344	265
4	178	164	319
5	121	137	189
7	204	241	88

5,3,L

0	357	375	270
1	309	281	50
2	153	148	83
3	205	198	157
4	111	160	264
5	209	247	346
6	228	244	77
7	118	126	137
9	119	128	219

5,4,L

0	84	109	270
1	200	170	91
3	73	75	126
4	119	114	46

5,5,L

0	93	87	90
1	209	172	8
3	195	181	227
6	111	105	301
7	69	56	250
8	181	209	61

5,6,L

0	161	150	90
1	148	144	277
2	127	137	178
3	199	182	99
4	212	206	14
5	167	156	240
6	114	127	301
7	91	123	126

5,7,L

2	236	215	281
4	115	94	29
5	73	68	330
6	147	140	110

5,8,L

0	154	138	270
1	144	152	175
2	262	237	344
3	98	81	248
5	173	165	86
6	190	201	67
7	116	107	311
8	93	79	225

5,9,L

0	124	95	270
2	112	107	237
4	108	100	39
5	106	84	195
6	164	163	233
7	65	85	103

5,10,L

0	232	228	90
1	176	143	142
2	198	197	223
3	122	111	270
4	153	154	5

5,11,L

0	212	193	270
1	206	227	268
2	84	76	123
3	153	137	233
4	142	130	289
5	139	164	356

5,12,L

0	134	145	270
1	170	172	258
2	143	148	72
4	129	123	224

5,13,L

0	104	114	270
1	144	145	236
3	95	109	34
5	72	75	168
7	139	136	267

5,14,L

0	158	187	90
1	124	116	253
3	164	140	75

5,15,L

0	310	320	90
1	113	113	241
2	227	230	228
3	154	154	325
5	149	159	144
7	92	107	349

5,16,L

0	125	121	90
2	134	148	247
3	84	82	345
4	98	87	215
6	67	74	100

5,17,L

3	92	78	17
4	106	113	339

5,18,L

1	184	150	62
7	54	42	242

5,19,L

0	104	109	90
4	85	115	17

5,20,L

1	103	63	263

5,21,L

0	72	69	270
2	107	106	45

5,23,L

2	81	49	238

5,25,L

0	106	95	270

6,0,L

2	223	244	180
3	219	196	90
4	195	204	0

6,1,L

0	167	170	0
1	153	140	111
2	264	255	211
4	184	197	323
5	99	123	9
7	178	210	224
9	64	50	347

6,2,L

0	99	82	180
1	146	134	122
2	260	276	246
3	103	92	337
4	281	301	96
6	180	188	314

6,3,L

0	208	190	180
1	214	196	161
2	112	99	347
3	109	113	51
4	120	118	242
5	102	79	284
8	89	76	132

6,4,L

0	147	148	180
1	114	84	84
3	375	370	239
4	128	111	103
5	324	332	110
6	95	104	275
7	166	177	313

6,5,L

1	242	203	164
3	185	174	18
5	108	118	250
8	90	90	272

6,6,L

1	53	79	319
4	159	160	269
6	165	181	116
8	119	136	283

6,7,L

0	242	186	180
1	132	113	309
2	184	149	272
3	163	170	68
4	109	115	24
6	66	93	236

6,8,L

0	198	163	180
1	98	93	274
2	267	274	310
4	159	156	74

6,9,L

0	126	110	180
1	192	195	29
3	61	61	222
4	129	144	100
8	88	102	287

6,10,L

0	283	221	180
2	135	132	284
4	143	167	72
6	141	120	264

6,11,L

0	288	241	180
2	124	115	296
4	126	156	12
6	135	129	177

6,12,L

0	147	135	180
1	107	56	285
2	167	173	302
6	107	97	141
7	87	86	238

6,13,L

0	378	351	180
2	283	303	334
4	146	114	131
6	67	72	306

6,14,L

1	200	167	187
3	93	94	117
4	112	90	343
5	137	129	311
9	76	81	30

6,15,L

1	173	171	69
2	120	108	225
3	150	133	234
4	126	151	0

6,16,L

1	133	100	206
2	135	124	256
3	138	114	75
4	88	87	114

6,17,L

4	89	88	37
5	84	84	111

6,18,L

3	54	36	145

6,22,L

3	81	56	47

7,0,L

2	187	188	0
4	179	199	180
5	86	91	270

7,1,L

1	97	98	170
2	102	108	234
4	117	126	141
5	121	128	253
6	81	79	63
7	88	123	5

7,2,L

1	151	122	145
2	77	72	129
3	222	226	354
5	218	205	215
6	116	107	318

7,3,L

0	116	102	90
1	163	157	295
2	147	168	104
3	279	272	220
4	148	151	305
6	135	157	165

7,4,L

1	233	213	129
2	116	112	203
4	224	221	43
6	185	209	231
7	88	83	201

7,5,L

2	245	238	347
3	121	100	142
4	378	369	166
6	117	146	345

7,6,L

0	258	270	270
2	249	238	118
6	108	135	278

7,7,L

1	66	80	249
2	152	136	17
3	115	103	328
4	182	186	219
6	69	83	307

7,8,L

0	215	162	270
1	131	125	250
2	106	67	87
3	264	269	48
4	129	147	157
5	158	155	202
6	71	89	310

7,9,L

1	89	78	309
2	165	151	323
4	134	128	117
5	88	90	183
6	109	90	244

7,10,L

0	270	264	270
2	171	165	113
5	118	87	158

7,11,L

1	163	146	246
2	130	151	77
3	176	176	83
4	120	118	280

7,12,L

2	102	94	279
4	119	80	50

7,13,L

0	194	138	270
1	59	39	341

7,14,L

0	74	58	270
1	133	129	52
2	139	102	38
4	140	116	180
6	62	88	286

7,16,L

2	138	133	20
3	145	131	7
4	71	65	204

7,18,L

0	76	79	90
1	133	102	92

7,19,L

1	84	78	52

7,20,L

4	97	89	131

8,0,L

0	302	302	0
2	137	170	180
3	202	214	90
5	101	99	270

8,1,L

0	196	192	0
2	148	137	176

8,2,L

0	264	258	180
1	129	90	72
2	137	126	339
3	145	129	252
5	117	116	130

8,3,L

1	198	197	219
2	139	148	215
3	95	72	99
4	132	125	15

8,4,L

2	164	180	301
3	131	129	14
6	121	106	150

8,5,L

1	62	98	341
3	183	179	161

8,6,L

1	211	195	71
3	182	175	253

8,7,L

1	266	239	207
4	120	136	113

8,8,L

1	236	217	9

8,10,L

0	82	75	180
1	100	82	77
2	148	138	34
3	241	208	254
5	126	107	116

8,11,L

0	193	153	0
1	161	174	191
2	84	72	266
5	115	73	298

8,12,L

0	135	131	180
1	86	74	356
2	157	146	57

8,13,L

0	100	68	0
1	93	142	11

8,14,L

0	172	142	0
2	150	134	143
4	102	93	324
8	85	59	59

8,15,L

0	68	40	180

8,17,L

0	125	89	0
2	105	81	115

8,19,L

0	92	62	0

9,0,L

2	246	209	0
4	94	58	180

9,1,L

0	125	78	270
1	156	167	284
4	86	83	44
7	85	113	155

9,2,L

1	111	106	211
2	113	104	62
3	133	119	319
4	123	123	210
5	125	130	101

9,3,L

1	126	134	123
2	156	159	12
3	125	122	300
4	64	78	208
5	76	85	76

9,4,L

2	108	86	279

9,6,L

2	82	111	279

9,7,L

0	124	77	270
2	96	86	14

9,8,L

0	110	108	270

9,9,L

7	82	74	266

9,10,L

2	85	79	93

9,11,L

2	112	98	297
7	62	40	93

9,12,L

5	132	119	10

9,13,L

2	76	41	115
5	73	71	160

9,14,L

3	81	87	159
5	89	87	358

10,0,L

2	111	88	180

10,1,L

8	72	57	213

10,6,L

6	65	52	34

10,8,L

0	113	90	0

10,11,L

0	104	86	180

10,16,L

0	87	69	180

10,17,L

1	113	88	175

11,1,L

0	72	63	90
3	72	103	158
4	67	74	208

11,7,L

0	92	68	90

11,9,L

4	73	95	174

11,11,L

3	120	119	32

11,12,L

0	66	40	270

12,0,L

2	110	103	0

12,8,L 1 87 60 28