STRUCTURAL STUDIES OF YLIDES AND OTHER ORGANIC MOLECULES BY X-RAY ANALYSIS

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Fergus Dunbar Duncanson, B.Sc.

Chemistry Department

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ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

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CONTENTS

SUMMARY

This thesis is divided into three parts. Part I discusses some theoretical and practical aspects of crystal structure analysis by X-ray diffraction, in particular direct methods of phase determination which were extensively used in this research. Part II deals with structural studies of stabilised ylides and some related compounds.

Previous structure analyses of ylides have shown that detailed molecular geometries may be correlated with the expected stabilising bonding systems within the molecules and that the conformation, especially, may be indicative of delocalisation into an adjacent π-electron containing group. In an attempt to establish the extent of competition between the two stabilising moieties (the 'onium species and the π-electron-containing substituent) and to study further the relationship of conformation to the pattern of stabilisation when d-orbitals are available for bonding, the crystal structures of five ylidic compounds have been determined : two first-row ylides, trimethylammonium-N-(p-toluenesulphonyl)imine and a pyridyl analogue pyridinium-N-(p-chlorobenzenesulphonyl)imine, two second-row ylides, a Wittig reagent 1-methoxycarbonyl-2-tert.butyloxycarbonylethyl-triphenylphosphorane and a sulphonium imine N-benzoyliminodimethyl-sulphur(IV), and an aromatic analogue of the latter compound, N-(p-nitrobenzoyl)-2-iminophenyldimethylsulphur(IV). A discussion of these structures and the trends they display in comparison with other relevant molecules is presented in the concluding section of Part II .

In Part II are also described the structures of a diphenyl-phosphinamide and its N-methyl derivative. While both compounds

are themselves ylides, they are the subject of additional interest on account of the marked acid lability of such compounds in comparison with carboxylic amides, which has led to their use as a protecting function for amines. The analyses have shown that the nitrogen atoms are pyramidal, although tending towards trigonal, suggesting that N-protonation may be the initial step in acid hydrolysis.

In discussions of second-row ylides, in particular of sulphonium and sulphonyl-stabilised imines, the S-N bond in sulphamic acid is frequently referred to as a formal S-N single bond. In order to determine this bond length with a precision comparable to that of recent X-ray analyses, a new refinement of the structure using new three-dimensional intensity data has been carried out and is described here.

In addition to the above series of related compounds, the structures of two separate unrelated compounds have been determined and are presented in Part III . The analysis of the p-bromobenzenesulphonate derivative of prieurianin, a tetranortriterpenoid natural product, has confirmed the ε-lactone skeletal structure concurrently deduced from ^{13}C n.m.r. spectra, and has yielded details of stereochemistry not otherwise obtainable. The analysis of 5,6-dihydrothiazolo[2,3-c]-[1,2,4]thiadiazol-3-one has identified the path of the condensation of chloroformylsulphur chloride with 2-aminothiazoline and similar compounds, as spectroscopic methods were unable to differentiate between the two plausible isomeric products.

PART I

SOME THEORETICAL AND PRACTICAL ASPECTS OF CRYSTAL STRUCTURE ANALYSIS

1. Introduction

The discovery of the diffraction of X-rays by crystals in 1912 confirmed both the wave nature of X-radiation and the periodic nature of crystals. Rapid developments in understanding the geometry of diffraction and the relationship of the diffraction pattern to the internal crystal structure led to the emergence of the method of crystal structure analysis. In recent decades particularly, the development of high-speed electronic computers and of more accurate intensity counting systems has allowed the almost routine application of this method to increasingly large and complex crystal structures, with geometric results of high precision. In recent years especially, the development of highly sophisticated direct methods of phase determination has advanced these methods to the stage where, for example, forty to eighty-atom structures (per asymmetric unit) and low symmetry space group structures can be reliably attempted, and where direct phasing of large biological molecules can be realistically considered.

The succeeding sections of this part (I) present a brief description of the techniques used in the structure analyses of the compounds which are the subject of this thesis.

2. The Structure Factor

The structure factor is a complete description of the wave scattered by the contents of one unit cell in a particular direction which is characterised by the indices h, k and l , and is described in terms of the radiation that would be scattered by a single electron at the unit cell origin. The structure factor, F_{hkl} , therefore has contributions from all elements of unit-cell volume, and is given by

$$F_{hkl} = V \int_0^1 \int_0^1 \int_0^1 \rho(xyz).\exp\left[2\pi i(hx + ky + lz)\right].dxdydz$$

where $\rho(xyz)$ is the electron density at the point (x,y,z) in a unit cell of volume V . Since, in practice, it is more convenient to consider the unit cell contents as a set of discrete atoms rather than as a continuous electron-density function, the structure factor may be considered as the resultant of contributions from individual atoms, and defined by the expression

$$F_{hkl} = \sum_{j=1}^{N} f_j \exp\left[2\pi i(hx_j + ky_j + lz_j)\right]$$

where f_j is the scattering factor and x_j, y_j and z_j are the fractional coordinates of the jth atom, and the summation is performed over all N atoms of the unit cell.

The structure factor is thus a complex quantity and may be written

$$F_{hkl} = A + iB$$

where $$A = \sum_{j=1}^{N} f_j(hkl) \cos 2\pi(hx_j + ky_j + lz_j)$$

and $$B = \sum_{j=1}^{N} f_j(hkl) \sin 2\pi(hx_j + ky_j + lz_j) \quad .$$

This form of the structure factor expression is particularly useful from a computational standpoint. The structure factor is physically characterised by an amplitude, $|F|$, and a phase, α, relative to the unit-cell origin, defined by

$$|F| = (A^2 + B^2)^{\frac{1}{2}}$$

and $$\alpha = \tan^{-1}(B/A) \quad .$$

The atom scattering factor, f, is the Fourier transform of the atomic electron density and describes the amplitude of wave scattered by the atom in terms of the amplitude of wave that would be scattered by a single electron. Owing to the finite size of atoms and consequent interference of waves scattered by different parts of the atom, f attenuates as $\sin\theta$ increases (where θ is the scattering angle).

When the wavelength of radiation used is close to an absorption edge of the scattering element, the inner electrons with high binding energy scatter radiation with an anomalous phase change. This anomalous dispersion may be taken into account by the addition of real and imaginary dispersion corrections[1] to the scattering factor :

$$f_{corr.} = f + \Delta f' + i\Delta f'' \quad .$$

With non-centrosymmetric space groups, the effect is often sufficient to produce a marked breakdown of Friedel's Law, and may be used to distinguish enantiomorphic structures (see section 1 , Part III).

Vibrational motion of an atom modifies the scattering function by effectively smearing the atom over a larger volume. Harmonic motion may be allowed for by the function

$$f = f_o \exp\left[-8\pi^2 U(\sin\theta/\lambda)^2\right]$$

where f_o is the scattering factor of an atom at rest, and U is the mean-square displacement of the atom, perpendicular to the reflecting plane. Isotropic motion is represented by a uniform coefficient, U_{iso}, for all reflections, but expansion of $(\sin\theta/\lambda)$ in terms of the reciprocal-cell dimensions with a separate vibrational coefficient for each term allows correction for anisotropic harmonic motion. In general, the latter is a much better description of reality. This yields the function

$$f = f_o \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)\right] .$$

The six coefficients, U_{ij} $(i,j = 1,2,3$ are with reference to the reciprocal axes a*, b* and c*), are the six components of a symmetric tensor describing the ellipsoid of mean-square vibration. Since vibrational motion increases with temperature, the coefficients U_{iso} and U_{ij} are widely termed "thermal parameters" or "temperature factors".

3. Geometric and Intensity Data Measurement

In the initial examination of the compounds described in this thesis, unit-cell dimensions were determined from oscillation and Weissenberg photographs taken with Cu-Kα radiation and from precession photographs taken with Mo-Kα radiation. Systematically absent reflections were noted and on this basis an identification of the possible space group(s) was made. On transferring the crystal to a Hilger and Watts Y290 four-circle diffractometer, the unit-cell parameters were refined by least-squares methods using the diffractometer setting angles for twelve well-defined reflections and their Friedel partners, in the course of the orientation matrix calculation. Intensity measurements were then made, using graphite-monochromated or Zr-filtered Mo-Kα radiation, by the $\theta, 2\theta$ scan technique, with scan increments of 0.02° for θ . Typical scan parameters were 40 scan steps of one second duration, with background counts at both extreme positions and a total background count time equal to the total scan count time. In most cases, weak reflections were not counted, those reflections with $I \leqslant 2\sigma_I$ (where σ_I was obtained from counting statistics) being automatically identified and omitted from the counting procedure.

4. Data Reduction

The quantity measured by diffractometer scanning, after subtraction of appropriate background radiation, approximates to the integrated intensity, I_{hkl} , the theoretical measure of the total intensity of a reflection, integrated over a range of angular deviations from the ideal Bragg angle[2], which is dependent on crystal volume but not on crystal shape. The structure amplitude, $|F_{hkl}|$, may be obtained from this quantity by the relationship

$$|F_{o}hkl| = \left[\frac{I_{hkl}}{K.L.p}\right]^{\frac{1}{2}} .$$

The polarisation factor, p , corrects for the partial polarisation occurring on reflection and is given by

$$p = \tfrac{1}{2}(1 + \cos^2 2\theta)$$

for an unpolarised incident beam, and by

$$p = (1 + \cos^2 2\theta_m \cos^2 2\theta)/(1 + \cos^2 2\theta_m)$$

for an incident beam partially polarised by a coplanar crystal monochromator with Bragg angle θ_m . For the graphite monochromator utilised in part of this work, $\cos^2 2\theta_m$ has the value 0.965 .

The Lorentz factor, L , allows for the varying angular velocities with which different reciprocal lattice points traverse the sphere of reflection, and therefore for the different times spent in the reflecting condition. For diffractometers with normal-beam geometry, this factor is $1/\sin 2\theta$, but other recording methods have more complex functions.

The quantity K is a constant for a particular experimental set-up

and may be calculated from general diffraction theory[3] if the crystal volume and incident intensity are measured. However, this constant is usually disregarded and relative structure amplitudes, F_{rel}, on an arbitrary scale are obtained. These may be brought to an approximate absolute scale at a later stage by correlating $K\sum F_{rel}$ with $\sum F_c$ once a part-structure has been determined.

Alternatively, the scale factor, K, may be estimated by means of the Wilson Plot method[4]. It can be shown that

$$\ln \frac{\langle |F_{rel}|^2 \rangle}{\sum_{j=1}^{N} f_{oj}^2} = \ln(1/K^2) - 2B(\sin\theta/\lambda)^2$$

if an overall thermal parameter is assumed. Accordingly, the scale factor, K, and overall thermal parameter, B, may be obtained from the gradient and intercept of a graph of the left side of the above equation against $(\sin\theta/\lambda)^2$. The K-curve method[5] is a further method of estimating the scale factor and overall thermal parameter.

Other factors which affect intensity of diffraction are absorption and extinction. When part of the X-ray beam is absorbed by the crystal, the reduced intensity is given by

$$I = I_o \exp(-\mu t)$$

where I_o is the intensity of the incident beam, t is the path length and μ is the linear absorption coefficient of the crystal, a function of its elemental composition and of the wavelength of the X-rays employed. Corrections for high absorption can be made if the crystal can be indexed and measured accurately, or more simply if spherical or cylindrical crystals can be formed. With small crystals, however,

and a low linear absorption coefficient (e.g. less than 20 cm^{-1}) absorption can be neglected.

Primary extinction arises from destructive interference of a multiply diffracted beam with the incident and reflected beams (arising from the $\pi/2$ phase change at each reflection) and is a function of the scattering amplitude of the crystal planes concerned. Secondary extinction is essentially shielding. Where a sizeable proportion of the incident beam is reflected, the continuing incident beam is attenuated by that proportion, leading to a reduced reflected intensity from lower layers. Secondary extinction is therefore a function of the scattering power of individual mosaic blocks. Several forms of correction for secondary extinction have been proposed, with the isotropic form used in the XRAY72 CRYLSQ program being based on the work of Zachariasen[3,6], as described in section 6.2 , Part II . More advanced forms of anisotropic and anharmonic corrections have been proposed[7,8]. Since, in general, extinction is a function of the physical perfection of a crystal, it is rarely a problem with organic compounds and can usually be ignored.

In the present work, calculation of integrated intensities, correction for Lorentz and polarisation factors, elimination of unobserved reflections and calculation of relative structure amplitudes were carried out using programs on the Glasgow University KDF9 computer. In all cases absorption was considered negligible and no corrections were made. Data sets were initially placed on an approximate absolute scale by application of the Wilson Plot method, and subsequently by adjustment of the scale factor in least-squares refinement of the structure.

5. The Fourier Synthesis

W. H. Bragg first suggested in 1915 [9] that the triperiodic electron density of a crystal structure could be represented by a three-dimensional Fourier series. The general expression for a Fourier synthesis may therefore be written as

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

or in the more useful form

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

A trigonometrically expanded version of this equation is generally used for computational purposes.

The above equation illustrates the fundamental problem of crystal structure analysis, namely the Phase Problem. In order to calculate the electron-density distribution, the structure amplitudes and their phases are required. Since the amplitudes only can be obtained from intensity measurements, some other means of establishing the phases must be employed. Two methods have been utilised in the present work : i) the Patterson function, and ii) Direct Methods.

6. The Patterson Function and the Heavy Atom Method

Patterson in 1934/1935 [10] defined the function

$$P_{(uvw)} = V \int_0^1 \int_0^1 \int_0^1 \rho(xyz)\, \rho(x+u, y+v, z+w)\, dxdydz$$

which is the self-convolution of the electron-density distribution. This function has appreciable magnitude only where $\rho(xyz)$ and $\rho(x+u, y+v, z+w)$ are both large, and the plot of $P_{(uvw)}$ therefore gives a superposition of all $N(N-1)$ interatomic vectors for a unit cell of N atoms.

Substitution of the Fourier expression for electron density gives

$$P_{(uvw)} = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}|^2 \exp\left[2\pi i(hu + kv + lw)\right] .$$

The function may therefore be obtained by a Fourier series summation using the phaseless quantities $|F_{hkl}|^2$ as coefficients. Use of structure amplitudes derived for hypothetical point atoms by the approximation

$$F_{point} = \frac{\sum_{j=1}^{N} Z_j}{\exp\left[-B(\sin\theta/\lambda)^2\right] \sum_{j=1}^{N} f_{oj}} \cdot F_{real}$$

produces a sharpened Patterson function, which frequently allows clearer resolution of the interatomic vectors. Nevertheless, it is rarely possible to resolve the structure from a set of vectors, apart from very small structures, unless the structure contains a heavier atom which produces a set of $N - 1$ stronger vector peaks.

The Patterson function has a unique symmetry for each crystal

class. The symmetry of the electron-density distribution (the crystal space group) is not, however totally lost, since translational symmetry operations and those operations with constant coordinates give rise to concentrations, known as Harker lines and planes, containing vectors between symmetry-related atoms. When the structure contains a heavy atom which dominates the scattering, the Harker concentrations generally allow identification of the position of this atom. This is the usual starting point of the heavy atom method of phase determination. Phases calculated on the basis of the heavy atom alone are often a good approximation to the true phases. The errors in these approximate phases have been shown to be related to the ratio[11],

$$r = \sum Z^2_{heavy} / \sum Z^2_{light} \quad .$$

When $r \approx 1$, the phasing is generally reliable and resolution of the structure is likely to be straightforward. With lower values of r , the reliability of the phasing is less, and greater difficulty may be experienced in resolving the structure.

7. Direct Methods

The term "direct" is generally applied to those methods which attempt to derive phase information from observed structure amplitudes by mathematical means not requiring the intermediacy of a model or known part-structure.

The initial work in direct methods was the derivation of inequalities involving large intensities, by Harker and Kasper[12] and by Karle and Hauptmann[13], and their application to sign determination in centrosymmetric structures. The use of this method is limited to very small structures, as intensities are reduced with larger structures. Present-day methods utilise probability relationships.

For the purpose of evaluating phase relationships, use is generally made of normalised structure factors , E_h , which are point structure factors expressed as a fraction of the mean intensity (or r.m.s. of the set of structure factors). These are obtained using the expression[15]

$$E_h = |F_{\underline{h}}|^2 / \varepsilon \sum_{i=1}^{N} f_i^2 \qquad (1)$$

where ε is a coefficient introduced to correct for space group extinctions, and $\underline{h}$ is a set of indices h,k and l .

Probability relationships are based on the property that certain linear combinations of phases are structure invariant i.e. possess a value which is determined by the crystal structure and is totally independent of choice of origin. It can be shown that any linear combination of phases, $\sum_{\underline{h}} A_{\underline{h}} \Phi_{\underline{h}}$, is a structure invariant if

$$\sum_{\underline{h}} A_{\underline{h}} \underline{h} = 0 \quad , \quad \text{for integral } A_{\underline{h}} \quad . \qquad (2)$$

The most widely used example of this is the triple phase relationship where

$$\Phi_{\underline{h}_1} + \Phi_{\underline{h}_2} + \Phi_{\underline{h}_3}$$

is invariant if

$$\underline{h}_1 + \underline{h}_2 + \underline{h}_3 = 0 \quad .$$

It can be shown that triplet invariants have values distributed about zero, with cosines up to unity. As the product of the E's , $|E_{\underline{h}_1} . E_{\underline{h}_2} . E_{\underline{h}_3}|$, increases, the expectation value of the cosine tends to unity, and therefore the relationship

$$\Phi_{\underline{h}} \approx \left\langle \Phi_{\underline{k}} + \Phi_{\underline{h}-\underline{k}} \right\rangle_{\underline{k}} \qquad (3)$$

holds for a set of any number of high |E| reflections, $\underline{k}$ [14].

In practice, the tangent formula , related to the equation (3) ,

$$\tan \Phi_{\underline{h}} = \frac{\sum_{\underline{k}} |E_{\underline{k}} . E_{\underline{h}-\underline{k}}| \sin(\Phi_{\underline{k}} + \Phi_{\underline{h}-\underline{k}})}{\sum_{\underline{k}} |E_{\underline{k}} . E_{\underline{h}-\underline{k}}| \cos(\Phi_{\underline{k}} + \Phi_{\underline{h}-\underline{k}})} \quad , \qquad (4)$$

is more widely used as a phase-determining formula. The variance of a phase, $\Phi_{\underline{h}}$, determined using the relation (4) has been shown by Karle and Karle [14] to be dependent on the product $|E_h . E_k . E_{h-k}|$.

The analogous equation to (3) for the centrosymmetric case can be written as a product of signs, $S(E_{\underline{h}})$, as

$$S(E_{\underline{h}}) \approx S\left(\sum_{\underline{k}} E_{\underline{k}} . E_{\underline{h}-\underline{k}}\right) \quad . \qquad (5)$$

The probability that a sign thus determined would be positive was derived by Cochran and Woolfson in 1955 [16] as

$$P \approx \tfrac{1}{2} + \tfrac{1}{2}\tanh\left(S_3 S_2^{-3/2} |E_{\underline{n}}| \sum_{\underline{k}} |E_{\underline{k}} . E_{\underline{n}-\underline{k}}| \right)$$

where $S_n = \sum_{i=1}^{N} Z_i^n$, with Z_i the atomic number of the ith atom in a cell containing N atoms.

Relationships (3) and (5) form the basis of the Symbolic Addition method, first described by Karle and Karle in 1963 [17]. In this method a basic starting set of phases is used to calculate new phases in an inverted pyramid fashion. The basic set comprises up to three phases (according to space group) with values assigned in order to define an origin, with, in non-centrosymmetric cases, an enantiomorph defining reflection and a number of unknown phases with symbols assigned, sufficient to allow determination of all phases for the set of reflections with large $|E|$ values (typically $|E| \geqslant 1.4$). On completion of the phase expansion, the symbols may be given several possible values (0 or π for centrosymmetrically restricted phases, and generally $\pm\pi/4$, $\pm 3\pi/4$ for unrestricted phases) resulting in a series of alternative phase sets, one of which is likely to be close to the true set.

The tangent formula is employed in a similar fashion, but has the advantage that a reiteration procedure can be used to refine the newly calculated phases in terms of the remainder, until a self-consistent set is obtained. For non-centrosymmetric structures a combination of the two methods is generally used. The several alternative phase sets obtained may be evaluated by computing a Fourier summation with the appropriately phased normalised structure amplitudes (E-map). The point atom electron-density maps obtained should reveal the crystal structure for a correct set of phases. When tangent formula reiteration is carried out, the Karle residual,

R_K , may be an additional guide. This is defined as[14]

$$R_K = \frac{\sum_{\underline{k}} \left| |E_{\underline{k}}|_o - |E_{\underline{k}}|_c \right|}{\sum_{\underline{k}} |E_{\underline{k}}|_o} .$$

Of great importance for a successful phase determination is the careful choice of phases for the starting set in order to achieve a rapid and reliable initial expansion. This is ensured by selecting phases with largest possible $|E|$s (to ensure high probability in the associated triplets) and maximum number of triplets interacting with other reflections of the starting set.

The restrictions on the selection of origin-defining reflections were detailed by Karle and Hauptmann in 1959 [18] and were discussed by Main[19], who interpreted the requirement that the determinant of indices (reduced modulo(ω), where ω is the seminvariant modulus) should evaluate as unity, as defining a primitive reciprocal cell.

In the non-centrosymmetric case, change of enantiomorph leads to a reversal of the signs of values of all structure invariants. Accordingly, in defining a phase set, the two possible enantiomorphs may be distinguished by specifying one phase which with two other known phases will define a structure invariant with a positive or negative non-zero value. The identification of a suitable invariant with a value appreciably different from zero (i.e. violating the normal triplet relationship) may sometimes be a considerable problem.

The above operations have been automated in the multisolution tangent formula program of Germain, Main and Woolfson, MULTAN [20]. In this program a starting set of origin and enantiomorph-defining phases and a user-specified number of variable phases is chosen on

the basis of greatest reliability (calculated by the program) , and tangent formula expansion and reiteration procedures are applied to the series of starting sets obtained by assignment of trial values to the variable phases. Figures of merit are calculated for all phase sets and the most probably correct set is automatically used to compute an E-map. The remaining phase sets may then be examined in turn, if necessary.

The program MULTAN has allowed the widespread use of direct methods for small structures. With larger structures, as probabilities of triplet relationships being correct are reduced, difficulties increase and the method may be confounded by unreliable triplets involving the starting set of phases. Some of the more advanced methods presently under development are intended to alleviate this problem. These include calculation of the cosine of a triplet invariant (rather than assumption that the cosine is unity), extension of the starting set of phases e.g. the Magic-Integer method[21], and assignment of a greater number of trial values to variable phases[22]. Perhaps the most promising development in direct methods is the use of quartet relationships i.e. invariants of the form

$$\Phi_{\underline{h}} + \Phi_{\underline{k}} + \Phi_{\underline{l}} + \Phi_{\underline{m}}$$

where $$\underline{h} + \underline{k} + \underline{l} + \underline{m} = 0 \quad .$$

Quartets have, at present, an intrinsically greater reliability than triplets and, while present usage is primarily by the symbolic addition method[23], it is conceivable that a system akin to MULTAN may be developed to make use of them.

It is appropriate at this point to describe briefly a program

used extensively in the work described in this thesis, the PHASE link of the XRAY 72 system[24,25] (referred to as the 'multi-symbolic' method in the relevant experimental sections). This is a method of phase determination for centrosymmetric structures, based on the symbolic addition method. It operates by solving for a subset of high |E| value reflections, termed "generators", using triplet and quartet relationships, the latter generated from pairs of triplets by elimination of a common weaker reflection. All phases are initially assigned symbols, and, from the lowest |E| generators upwards, the symbols are systematically expressed as products of the phases of highest |E| . On defining the origin (by the program or the user), the set of phases is then determined. This is carried out for a set of generators numbering, typically, three times the number of atoms in the asymmetric unit, and a pedigree of relationships is recorded to allow identification and subsequent exclusion of any unreliable relations. Finally, a full set of phases down to a suitable |E| limit is generated by phase addition. This method has been found to work with ease and reliability for space groups possessing more than one translational symmetry element.

8. Least-Squares Refinement

Least-squares refinement is a powerful method of optimising the parameters of a model to obtain the best fit with the observed data. The technique operates in structure refinement by adjusting the positional and thermal parameters of the structure and the scale parameter for the observed intensities to minimise some function of the differences between the observed and the calculated structure amplitudes. The function most commonly used is

$$M = \sum_{hkl} W \left(|F_o| - |F_c|\right)^2 = \sum_{hkl} W\Delta^2 \qquad (1)$$

where the summation is taken over the set of crystallographically independent observed reflections with an appropriate weight, W, for each reflection.

For a set of n parameters, $p_1, p_2, \ldots p_n$, which determine $|F_c|$, the condition that the function M is a minimum is

$$\frac{\delta M}{\delta p_j} = \sum_{hkl} W\Delta . \frac{\delta |F_c|}{\delta p_j} = 0 \qquad (2) .$$

This set of n equations is termed the normal equations, and can be applied when $|F_c|$ is a linear function of the parameters p_j.

Approximation of Δ as a first-order Taylor series in terms of the set of trial parameters, p_j, close to the true values, gives

$$\Delta(\underset{\sim}{p} + \underset{\sim}{\varepsilon}) = \Delta(\underset{\sim}{p}) - \sum_{i=1}^{n} \varepsilon_i \frac{\delta |F_c|}{\delta p_i} \qquad (3)$$

where ε_i is a small change in parameter p_i, and $\underset{\sim}{p}$ and $\underset{\sim}{\varepsilon}$ represent the whole set of parameters and changes. Substitution of (3) into (2)

yields

$$\sum_{i=1}^{n}\left[\sum_{hkl} w\,\frac{\delta|F_c|}{\delta p_i}\cdot\frac{\delta|F_c|}{\delta p_j}\right]\varepsilon_i \;=\; \sum_{hkl} w\Delta\,\frac{\delta|F_c|}{\delta p_j} \qquad (4)\,.$$

This is the set of normal equations for p_j $(j = 1,2,\ldots n)$. Solution of these equations for $\underset{\sim}{\varepsilon}$ gives the shifts to be applied to the initial parameters.

The normal equations may be conveniently expressed in matrix form

$$\sum_i a_{ij}\varepsilon_i = b_j \quad ,$$

and may be solved by matrix algebra, since

$$\varepsilon_i = \sum_i (a^{-1})_{ij} b_j \quad .$$

where $(a^{-1})_{ij}$ is the inverse of the matrix a_{ij}. The full matrix for n equations has $\frac{1}{2}n(n+1)$ unique elements. In order to limit the computer store and time requirements to the available maximum, it is often necessary to neglect some of the small off-diagonal elements when handling large structures. This may be done using the blocked-matrix approximation, in which the matrix is factored into blocks about the diagonal and off-diagonal blocks are neglected. In the present work, this approximation has been applied using the smallest number of blocks necessary, and with the atoms grouped so that parameters expected to show significant correlation were grouped in one block.

Owing to the neglect of high-order terms in the Taylor series expansion, the shifts are not exact, and the calculation is an iterative one, requiring several cycles to converge to a minimum.

Convergence is judged to be attained when the calculated shifts are small in relation to the estimated standard deviations (e.s.d.s) of the parameters. The e.s.d. , $\varsigma(p_i)$, of a parameter, p_i , is given by

$$\varsigma(p_i) = \left[(a^{-1})_{ii} \frac{\sum W\Delta^2}{m - n} \right]^{\frac{1}{2}}$$

where m is the number of observations and n the number of parameters.

The least-squares method, unlike Fourier methods, has the advantage that series termination effects do not occur and, moreover, observations can be weighted according to their precision. Properly, W should have a value given by

$$W_{(hkl)} = 1/\varsigma^2_{(hkl)}$$

where $\varsigma_{(hkl)}$ is the e.s.d. of the amplitude $|F_{o\ hkl}|$. Since an exact e.s.d. is not accessible, an empirical weighting scheme is generally employed to maintain the function $W\Delta^2$ approximately constant when averaged over batches of reflections.

The quality of fit obtained in refinement of a structure is generally assessed in terms of a residual, R , defined by

$$R = \frac{\sum |(|F_o| - |F_c|)|}{\sum |F_o|} ,$$

and a weighted residual, R' , defined by

$$R' = \frac{\sum W(|F_o| - |F_c|)^2}{\sum W|F_o|^2} .$$

Both of the above quantities have been quoted in the relevant experimental sections of this thesis.

9. E.s.d.s and the Significance Test

One of the principal applications of e.s.d.s is in the judgement of whether the difference between two measurements is significant. Thus for a difference, Δ , between two measurements, x and y , with e.s.d.s , ς_x and ς_y , the e.s.d., ς_Δ , is

$$\varsigma_\Delta = \left[(\varsigma_x^2) + (\varsigma_y^2)\right]^{\frac{1}{2}} \quad .$$

The significance levels suggested by Cruickshank[26] are generally used, based on the probability, P , that the two measurements could differ by Δ , by chance. These levels, which assume a Gaussian error distribution, are :

if $\Delta \leqslant 1.645\varsigma_\Delta$, then $P \geqslant 5\%$, i.e. insignificant difference ;

if $2.327\varsigma_\Delta > \Delta > 1.645\varsigma_\Delta$, then $5\% > P > 1\%$, i.e. difference possibly significant ;

if $3.090\varsigma_\Delta > \Delta \geqslant 2.327\varsigma_\Delta$, then $1\% \geqslant P > 0.1\%$, i.e. <u>significant difference</u> .

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PART II

STRUCTURAL STUDIES OF YLIDES

INTRODUCTION

The term "ylide" was derived by Wittig in 1944 [1] to describe a class of phosphonium- carbon compounds. In present day usage the name encompasses all possible analogous compounds of the formal type $(\overset{+}{X} - \overset{-}{Y})$ with a range of different atom types.

Compounds of this type have been known since the 1920's, but the development of the Wittig reaction in the early 1950's and its subsequent widespread application in organic synthesis gave a powerful stimulus to the investigation of phosphonium and other ylides. A monograph by Johnson, published in 1966 [2], has provided an extensive yet detailed coverage of this work and of the preparation, reactions and applications of ylides in general. A review by Hudson of more recent work appeared in 1971 [3].

Ylides have been described as stabilised anions [3]. While some stabilisation is undoubtedly conferred by the vicinal zwitterion system, the small number of such stable ylides known suggests that this stabilisation is relatively small. The majority of ylides possess an electron-withdrawing group bonded to the $\overset{-}{Y}$ atom, which increases the stability by reducing the localised negative charge. The most widely used stabilising groups are those containing a π-electron system adjacent to the negative atom, where there exists the possibility of charge delocalisation by conjugation with the π-orbitals. The stability of any ylide is therefore determined by the relative properties of the three component parts :- the $\overset{+}{X}$ or 'onium species, the $\overset{-}{Y}$ or anionic species, and the stabilising group.

An early observation in preparative work on ylides[2] was that ylides of second-row and higher-row 'onium species (X = P,S; As,Sb) possessed much greater stability than their first-row analogues (X = O,N). This difference in stability is clearly illustrated by the relative acidities of the conjugate acids of the ammonium and phosphonium methylides[3] :-

$$(CH_3)_4\overset{+}{N} \underset{H^+}{\rightleftharpoons} (CH_3)_3\overset{+}{N}-\overset{-}{C}H_2 \qquad pK_a = 9.75$$

$$(CH_3)_4\overset{+}{P} \underset{H^+}{\rightleftharpoons} (CH_3)_3\overset{+}{P}-\overset{-}{C}H_2 \qquad pK_a = 3.37$$

The pK_a of the conjugate acid reflects the stability of the methylide, the lower value of 3.37 in the phosphonium case indicating the greater stabilisation conferred by the phosphorus atom in comparison to the ammonium case.

This enhanced stabilisation has been attributed[2,3] to a π-interaction of vacant 3d-orbitals on the phosphorus atom with the non-bonding electrons of the anionic atom, often described as "back-donation of the lone-pair electrons to the phosphorus 3d-orbitals", and resulting in valence-shell expansion. Such valence-shell expansion is not possible for first-row elements[4] as the energy gap to the next available orbitals is sufficiently large to prevent any appreciable bonding interaction. In ammonium ylides therefore, delocalisation of the negative charge to the 'onium atom cannot occur and the only sources of possible stabilisation are an inductive effect through the σ-bond and coulombic interaction. Further work on the acidities of conjugate acids of ylides has shown that these effects are small[2].

The anionic properties of an ylide might be expected to vary with the electronegativity of the negative atom, the number of lone pairs

present, and the type of hybridisation adopted. The electronegativity is a measure of the atom's ability to carry a negative charge, and the agreement between Pauling's values[5] (C 2.5 ; N 3.0 ; O 3.5) and the observed trend in ylide stability suggests this may be an important factor.

From the observed trigonal geometry in carbanion ylides[6,7,8] sp^2-hybridisation may be inferred in which the lone pair occupies the p-orbital perpendicular to the σ-bond plane. Such an arrangement is clearly ideally suited to both $p\pi$-$p\pi$ and $d\pi$-$p\pi$ overlap with the 'onium species or the stabilising group. No such clear inference can be drawn from the geometry of nitrogen ylides $(\overset{+}{X} - \overset{-}{N})$ where valence angles at the nitrogen atom are observed to range from 110° to 146°. In these cases, the two anionic lone pairs might be expected to occupy equivalent orbitals, possibly of an sp^3-hybrid nature, in the absence of π-bonding interactions. However, the presence of overlap interactions with orbitals on adjacent atoms may perturb the lone-pair electrons into non-equivalent orbitals, as in the distorted trigonal hybridisation generally observed where one lone pair may occupy a p-orbital and the other an sp^2-type hybrid orbital with a p-character determined by the valence angle. The exact nature of such perturbation will depend on the nature of the π-interactions with 'onium and stabilising groups.

The most important feature of a stabilising group is therefore the type of π-electron system available to allow charge delocalisation. Two general types are known :- i) single $p\pi$-$p\pi$ orbitals formed from first-row elements, as in carbonyl, alkene, and nitro groups, and

ii) more complex orbitals based on

d-orbitals of a central atom, as found in sulphonyl, sulphoxy, and phosphinyl groups. A further feature of importance may be the presence of halogen substituents which tend to enhance the elctron-withdrawing ability of a stabilising group in the usual way.

Ylides have, in recent years, been the subject of considerable structural study, largely by X-ray analysis, by Bart[6], Wheatley[9] and others, with a systematic study of sulphonium imines ($\overset{+}{S} - \overset{-}{N}$) by Kalman and coworkers[10-15] and of first and second-row imines by Hair[16-18]. The aim of these studies, in general, is the measurement of bond lengths, angles, and conformational parameters with the highest attainable accuracy , and from these the assessment of the different types of bonding interaction present and the extent to which they occur. In a review of the various structural studies of ylides, in a Ph.D. thesis (1972) [19], Hair concluded that i) the stabilisation requirements of ylides decreased as the electronegativity of the anionic atom increased (along the series C,N,O),

ii)the observed bond lengths provided clear evidence of delocalisation to the stabilising group in ammonium ylides, and to both the 'onium and stabilising groups in second-row ylides, and

iii) there appeared to be competition between the 'onium species and the stabilising group to delocalise the negative charge in $\overset{+}{P} - \overset{-}{C}$ and $\overset{+}{S} - \overset{-}{N}$ ylides.

He also showed that in ylides with a stabilising group possessing a single π-electron system, a planar conformation with respect to the trigonal anionic atom was invariably adopted, appropriate to maximum overlap of the π-orbital with the p-orbital lone pair, but that in second-row imines (carrying two lone pairs) with a sulphonyl stabilising

group, a non-planar conformation resulted, consistently 31° to 38° from syn-planarity. The latter conformation occurred solely when interaction of two lone pairs with the multiple π-system of the sulphonyl group was possible, and was interpreted as arising from the involvement of the second lone pair in delocalisation. Classification of ylides into two conformational types on the above basis was furthermore suggested.

However, the small number of measurements on which the above hypothesis was formed and the possible intermediacy of the conformation of a sulphonyl-stabilised Wittig reagent[9] have prompted a more detailed and more extensive investigation into the relationship between conformation and $d\pi$-$p\pi$ bonding in ylides. The aim of the work presented in this part, Part II, of this thesis is

i) a more detailed understanding of bonding in sulphonyl-stabilised ylides, and a test of the validity of Hair's conformational classification, and

ii) more extensive study of bonding interactions involving d-orbitals in second-row ylides and related compounds.

Accordingly, the crystal structures of six ylides and two related compounds have been determined and are described in this part. The structures of two sulphonyl-stabilised imines, an ammonium and a pyridinium compound, are discussed in the first two sections, while the third section deals with the structure analyses of a sulphonium imine and an aromatic analogue, the latter compound displaying an unusual solid-state feature. The fourth section is devoted to the structure analysis of a Wittig reagent. The structures of two phosphinamides are discussed in the fifth section, while a new refinement of the structure of sulphamic acid, a compound frequently referred to

in discussions of sulphonium imines, is presented in section 6 . Finally, a concluding section discusses the aspects of these analyses that are of overall relevance, in comparison with, where appropriate, structural studies of similar compounds, and in the context of present theories of π-bonding interactions in ylides. For the latter aspect, some description of these bonding theories is first required.

π-bonding in stabilised ylides containing second-row atoms

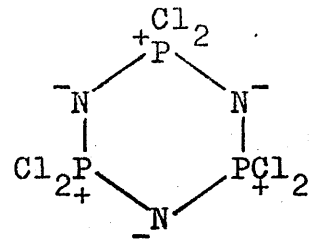
It has been suggested[19] that the two lone pairs on an imine nitrogen atom should be considered to occupy two equivalent orbitals, with such overlap that occurs involving each orbital equally with suitable d-orbitals or linear combinations thereof. This overlap can then be resolved into two mutually perpendicular components, most conveniently in the plane defined by the σ-bonds and in the perpendicular plane. This approach is theoretically valid but becomes somewhat detached from the geometric reality of orbital interactions and, although such a system may be usefully applied to a situation of overlap with d-orbitals, it appears confusing when overlap with a single π-orbital system, such as in a carbonyl group, is considered. In the latter situation the equivalent orbital theory seems irrelevant since the planar arrangement of a carbonyl imine[16] points to overlap with a simple p-orbital, the remaining lone pair being required to occupy an sp^2-type hybrid orbital. However, when bonded to a second-row atom, with d-orbitals necessarily present,

overlap of these with the lone pairs in both orbitals, p and sp^2, would occur giving a π-interaction in two orthogonal planes. While both approaches should give equivalent results, the latter concept with its more easily visualised geometric requirements for overlap is clearly more advantageous when considering possible interactions with d-orbitals in two groupings, and will accordingly be used here.

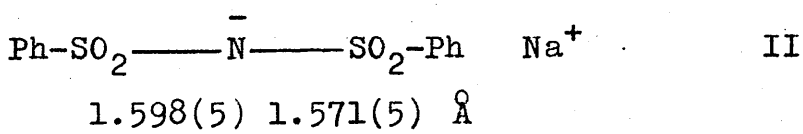
The above discussion highlights the similarity of the bonding in second-row ylides to that in the cyclic phosphonitrilic series of compounds. Indeed, as the bonding in these compounds has been the subject of extensive theoretical study[20-22], these compounds provide a useful model on which to discuss the bonding in ylides.

In the six-membered $(PNCl)_3$ system the σ-bond skeleton yields a structure that can be considered to have alternating charges around the ring, as in I . Craig and Paddock[20] showed that overlap occurred between the p-orbital lone pair of the nitrogen atom and the d_{xz} and d_{yz} orbitals of the phosphorus to form π-orbitals above and below the ring plane which were 3-centre orbitals localised on P-N-P units and therefore allylic in nature rather than benzenoid. Their calculations also showed considerable overlap of the sp^2-type hybrid lone pair with the $d_{x^2-y^2}$ and d_{xy} orbitals giving rise to localised 3-centre π-orbitals in the plane defined by the σ-bond skeleton, named π'-overlap to distinguish it from the previously mentioned type.

While, in the six-membered system, π-overlap appears to be greater than π' , on going to the analogous eight-membered rings in which puckered conformations are adopted the π'-overlap increases as a result of bond angle enlargement at nitrogen, with a consequent increase in the p-character of the hybrid lone-pair orbital. Craig



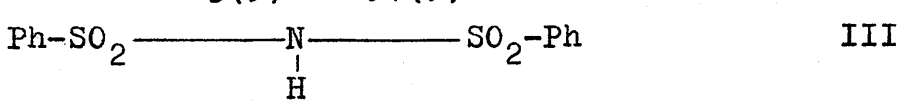
I



II

1.598(5) 1.571(5) Å

1.643(5) 1.657(5) Å



III

and Paddock suggested that this valence angle provided a "sensitive index" of the amount of π'-overlap and the amount of lone-pair donation to the phosphorus atoms. In addition, π and π'-overlap involve the d_{z^2} and $d_{x^2-y^2}$ orbitals principally but not exclusively, some overlap also occurring to a lesser extent with the remaining d_{xy}, d_{yz} and d_{xz} orbitals. However, on twisting the ring system, overlap with one orbital increases as that with another decreases[20]. The resulting lack of angular restriction in the total overlap allows the eight-membered and higher rings to adopt the observed variety of puckered non-planar conformations.

Phosphonium imines ($\overset{+}{P} - \overset{-}{N}$ ylides) can effectively be considered to be the monomeric units of such ring compounds, and sulphonium imines similarly for the analogous polythiazyl rings, $(SNR)_n$. The π-bonding in these ylides is therefore essentially the same as in the ring compounds but without the constraints of ring geometry. Paddock[22] showed that similar π and π'-overlap occurred involving principally the $d_{x^2-y^2}$ and d_{z^2} orbitals, the two more stable orbitals in an approximate tetrahedral valence field. Both types of interaction are illustrated in Figures 1 and 2 respectively. As with the ring compounds the presence and partial involvement of the remaining d-orbitals results in a total $d\pi-p\pi$ overlap which allows the system considerable torsional flexibility, much more than in corresponding $p\pi-p\pi$ overlap situations. This has been demonstrated by more recent theoretical and n.m.r. studies of sulphonium-imine and phosphonium-imine systems[23,24]. The corollary of this behaviour is that the conformations of compounds of this type, with $d\pi-p\pi$ bonding interactions, would be expected to be subject to the influence of other types of interaction, primarily

Figure 1

π-bonding involving $d_{x^2-y^2}$

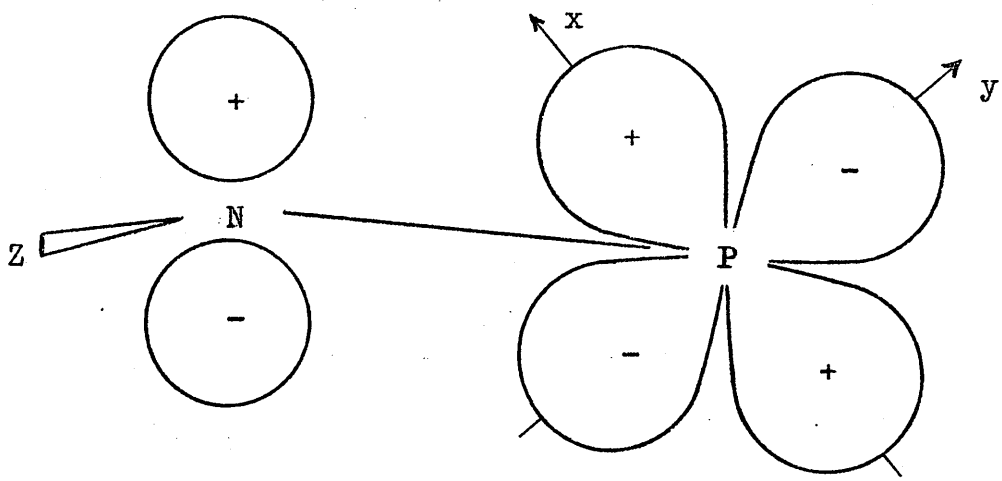
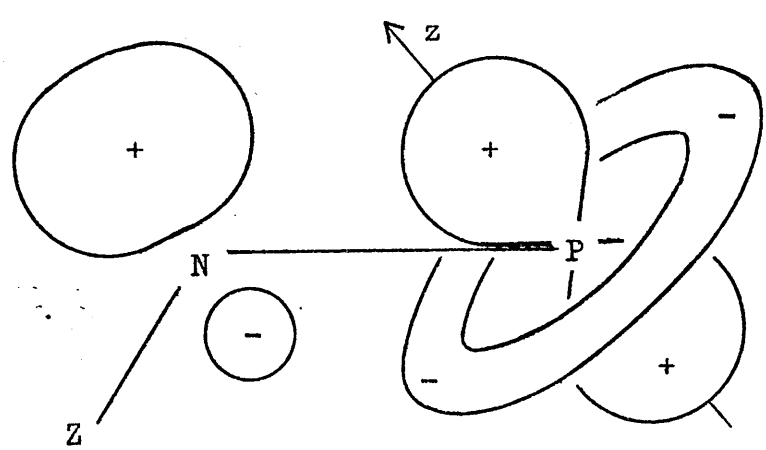


Figure 2

π'-bonding involving d_{z^2}



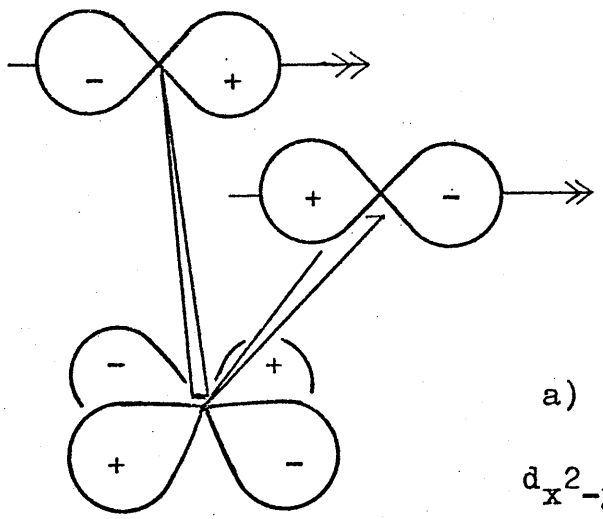
steric and crystal-packing effects. Paddock also pointed out that such bonding was merely a special case of the bonding in phosphates, sulphates and derived systems, which Cruickshank described in detail in 1961 [25].

In a tetrahedral system e.g. sulphate, SO_4^{2-}, Cruickshank showed that on forming the σ-bonded skeleton using sp-hybridised oxygen atoms, the remaining 16 valence electrons were accommodated in two strongly bonding molecular orbitals with the symmetry of the E representation (doubly degenerate) of the point group Td, three weakly bonding molecular orbitals of symmetry T_2, and three non-bonding orbitals of symmetry T_1. He concluded that the two strongly bonding orbitals, 5-centre orbitals based on the $d_{x^2-y^2}$ and d_{z^2} orbitals of the central atom, exerted a controlling influence on the geometry of the system with each d-orbital overlapping one p-orbital on each oxygen atom. On the basis of this double multi-centre π-orbital system he rationalised the geometries of a series of sulphur-oxygen, phosphorus-oxygen and other compounds and demonstrated the existence of an approximate linear relationship between the P - O and S - O bond lengths and their predicted valence-bond orders. He also suggested that on replacing oxygen by another ligand, the symmetry was lowered and consequently the E degeneracy split, but that the two molecular orbitals based on the $d_{x^2-y^2}$ and d_{z^2} orbitals would remain strongly bonding with a controlling influence on ligand geometry as long as the coordination remained approximately tetrahedral. This model necessitates a specific orientation of the p-orbitals, which for a system of exact tetrahedral geometry is a parallel arrangement for overlap with $d_{x^2-y^2}$

and a coplanar arrangement for overlap with d_{z^2}, as illustrated in Figure 3. The significance of these requirements in determining the possible preferred orientations of, for example, amine or aromatic substituents is manifest. Furthermore, an imine (–N–) substituent suitably oriented for p-overlap with either d_E orbital would necessarily have its sp^2-hybrid lone pair in an orientation suitable for overlap with the other d_E orbital, and some overlap would be expected to occur. Such overlap is similar to that described by Craig and Paddock and is, here, similarly termed π'-overlap, this name now encompassing all sp^2-lone-pair overlap with d-orbitals. The importance of such overlap in bonding is illustrated by the comparison of sodium dibenzenesulphonamidate, II, with its protonated form, the sulphonamide III. On protonation, removal of the sp^2-lone pair induces a lengthening of the two S–N bonds from 1.571(5) and 1.598(5) Å to 1.643(5) and 1.657(5) Å [26].

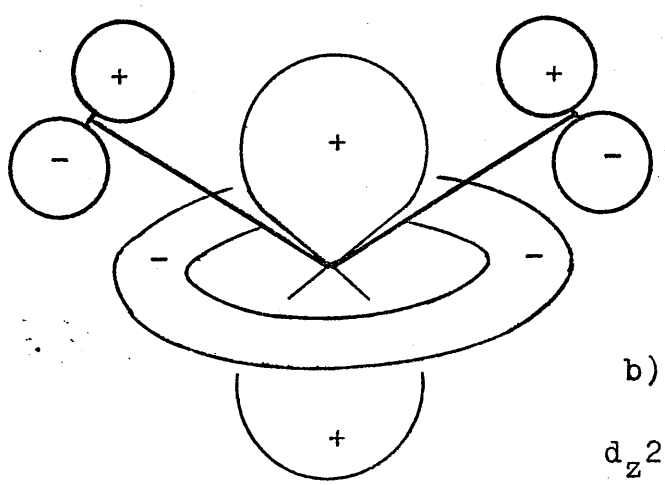
The bonding effectiveness of all the types of overlap discussed above is dependent on the size and energy of the individual d-orbitals involved. While this has been a topic of some controversy over the last two decades, S.C.F. calculations have now clarified the situation to some degree[27-31], showing that d-orbital sizes and energies vary with the oxidation state and formal charge on an atom and with the electronegativity of the substituents. In a neutral P or S atom, the d-orbitals are large and generally of too high an energy to allow appreciable interaction, but the presence of a formal positive charge, as on the 'onium atom of an ylide, or a high oxidation state, as in a sulphonyl or sulphoxy group, causes a contraction of the orbitals and a reduction in their energies which makes appreciable bonding interactions possible. This behaviour also explains the known stability of halogenated second-row compounds.

Figure 3



a)

$d_{x^2-y^2}$



b)

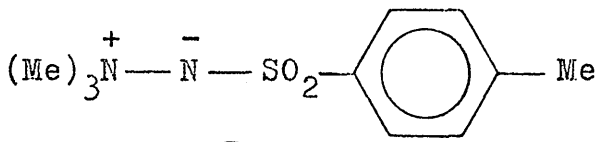
d_{z^2}

1. THE CRYSTAL AND MOLECULAR STRUCTURE OF A FIRST-ROW SULPHONYL-STABILISED YLIDE : TRIMETHYLAMMONIUM-N-(p-TOLUENESULPHONYL)IMINE.

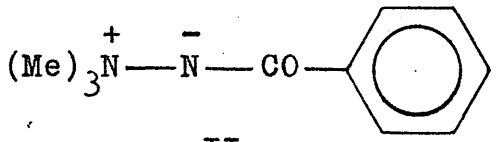
1.1 Introduction

It has been shown[16,19] that in the case of the ammonium imines, II and III , delocalisation of the negative charge takes place solely by conjugation with the stabilising group, the nitrogen-nitrogen bond remaining unaltered when a different stabilising group is present. The interaction between the imino atom and the stabilising group is therefore likely to be at a maximum in the ammonium ylide situation where π-donation to the 'onium atom is not possible.

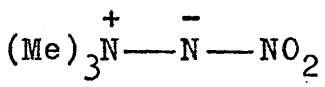
The crystal structure of the sulphonyl-stabilised first-row imine, I , has been determined in order to establish the geometry of the imine-sulphonyl interaction in the absence of the possibly competing interaction of a second-row 'onium species. The conformation adopted should accordingly result from the maximisation of the π and π'-overlap of the two lone pairs of the imine with the molecular orbitals of the sulphonyl group, based on the sulphur d-orbitals.



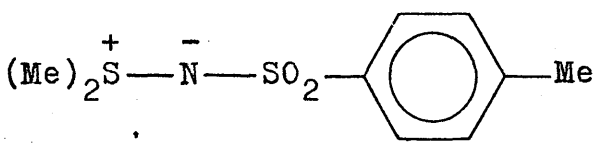
I



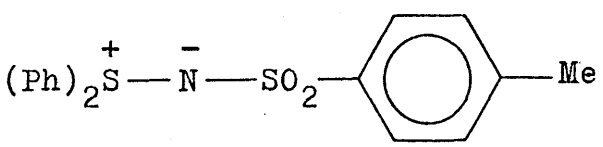
II



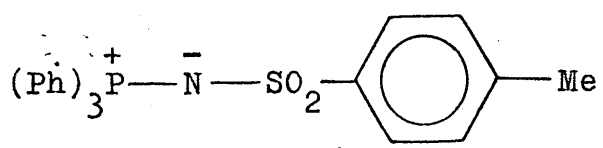
III



IV



V



VI

1.2 Experimental

Crystal Data

Trimethylammonium-N-(p-toluenesulphonyl)imine (hydrated)

$C_{10}H_{16}N_2O_2S.H_2O$, M = 246.3 .

Monoclinic, a = 6.128 b = 7.161 c = 28.142 Å , β = 93.66°,

U = 1232.4 $Å^3$,

D_m = 1.30 g cm^{-3}, Z = 4 , D_c = 1.33 g cm^{-3},

$F_{(000)}$ = 528 .

Space group : $P2_1/c$ (C_{2h}^5 , No.14), uniquely identified by systematic absences.

μ(Mo,Kα) = 2.57 cm^{-1}.

Data Collection

Radiation	: Mo,Kα
Filter	: Zr
Maximum scattering angle (2θ)	: 54°
Independent reflections (observed)	: 2116
Unobserved cutoff	: 2ς_I
Ratio of observations/parameters	: 9.69

Structure Determination

The phase problem was overcome by direct phasing methods using the multi-symbolic approach. Normalised structure factors were calculated and triplet relationships derived for those 160 reflections with $|E| > 1.78$. With a starting set of three origin-defining reflections, a solution for the 80 strongest reflections was obtained using relationships of probability $\geqslant 0.8$. A total of 157 reflections were then phased from this solution and an E-map, calculated with these reflections only, revealed the complete molecule although the N-methyl atoms and ring atoms 2,3,5 and 6 were poorly defined. A structure-factor and electron-density calculation based on the atoms which were unambiguously defined (S, 2N, 2O, 3C) gave clear positions for the remaining atoms. In addition a further cycle of structure-factor and electron-density calculation revealed the presence of an additional atom at a distance of approximately 3 Å from the molecule. The peak height of this extra atom, together with the location, suggested that it could plausibly be the oxygen atom of a molecule of water of crystallisation. This was confirmed in subsequent least-squares refinement.

In each structure-factor calculation an overall thermal parameter, $U = 0.05$ Å^2, was assumed, and the approximate absolute scale of the data was maintained by equating $\sum |F_o|$ with $\sum |F_c|$.

Structure Refinement

Refinement of positional, thermal and scale parameters converged after 16 cycles of least-squares minimisation with the residuals R and R' at 0.047 and 0.0035 respectively. Details of the refinement

are given in Table 1.1 . Convergence of refinement was judged to be complete when all parameter shifts were small in comparison to the estimated standard deviations.

15 hydrogen atoms were located from a difference synthesis calculated after cycle 4, while the remaining three hydrogen atoms were located from a similar calculation after cycle 5. Individual isotropic thermal parameters of $U_{iso} = 0.05$ Å^2 were initially assigned to these atoms, but were subsequently refined in later cycles. In the initial cycles of hydrogen-atom refinement, certain hydrogen atoms were observed to shift to positions of unreasonable geometry. A difference synthesis was calculated from which adjustments to several erroneous hydrogen atom positions were made. In further subsequent refinement the acceptable geometry of these positions was maintained. The difference synthesis showed no other errors in the structure.

After cycle 6 , four reflections with intensities high enough to cause serious innaccuracy in measurement due to counter saturation were removed from the refinement.

The weighting scheme applied at cycle 10 and thereafter was of the form

$$W = x.y$$

where $x = \sin\theta/B$ if $\sin\theta \leqslant B$, else $x = 1$

and $y = C/|F_o|$ if $|F_o| \geqslant C$, else $y = 1$.

Suitable values of B and C were determined by analysis of the variation of Δ^2 with $|F_o|$ and $\sin\theta$, the final values being $B = 0.40$, $C = 7.0$.

In all structure-factor calculations the atomic scattering factors used were taken from "International Tables for X-ray Crystallography", Vol.III [32].

Observed and final calculated structure factors are listed in Appendix 1 . Final fractional coordinates and thermal parameters are given in Table 1.2 , and bond lengths, valence angles and relevant intramolecular and intermolecular non-bonded distances are given in Table 1.3 . The estimated standard deviations quoted with the above quantities are obtained from the inverse of the least-squares matrix of normal equations and should be regarded as minimum values. Details of a least-squares plane through a section of the molecule are given in Table 1.4 . The atomic numbering scheme and the molecular packing viewed down the b-axis are shown in Figures 1.1 and 1.2 respectively.

Table 1.1

Course of refinement

Cycles	Parameters refined	Final R	Final R'
1 - 4	x,y,z,U_{iso} for S,O,N,and C, scale factor. Unit weights, full matrix.	0.148	0.0225
5 - 9	x,y,z,U_{ij} for S,O,N, and C, scale factor. Unit weights, H-atom contributions included but not refined, full matrix.	0.065	0.0052
10 - 13*	x,y,z,U_{ij} for S,O,N, and C, x,y,z for H, scale factor. Weighting scheme applied, full matrix.	0.048	0.0036
14 - 16	x,y,z,U_{ij} for S,O,N, and C, x,y,z,U_{iso} for H, scale factor. Weighting scheme applied, blocked matrix.	0.047	0.0035

* Adjustments to several erroneous H-atom positions were made prior to cycle 12 .

Table 1.2

a) Fractional Coordinates

	x/a	y/b	z/c
S	1.08153(9)	0.57462(8)	0.38918(2)
O(1)	1.11765(35)	0.76928(27)	0.40017(7)
O(2)	1.27582(26)	0.46148(30)	0.38586(6)
O(3)	0.59155(41)	0.81977(37)	0.44178(9)
N(1)	0.91982(30)	0.50826(27)	0.42790(6)
N(2)	0.88108(30)	0.30668(26)	0.43287(6)
C(1)	0.94753(34)	0.56867 (30)	0.33109(7)
C(2)	1.05574(38)	0.49886(36)	0.29335(8)
C(3)	0.95295(43)	0.49460(38)	0.24789(8)
C(4)	0.74175(41)	0.55911(32)	0.23965(9)
C(5)	0.63551(38)	0.62977(38)	0.27781(9)
C(6)	0.73597(38)	0.63457(37)	0.32341(8)
C(7)	0.63162(58)	0.55543(50)	0.19004(10)
C(8)	1.07594(51)	0.20478(49)	0.45446(13)
C(9)	0.79922(61)	0.21302(42)	0.38801(10)
C(10)	0.70394(52)	0.29907(45)	0.46741(10)

Table 1.2 (contd.)

b) H-atom fractional coordinates and isotropic thermal parameters ($Å^2$)

	x/a	y/b	z/c	U iso
H(2)	1.2007(48)	0.4576(44)	0.2984(11)	0.030(8)
H(3)	1.0282(55)	0.4433(49)	0.2212(12)	0.038(9)
H(5)	0.4868(52)	0.6845(46)	0.2732(11)	0.033(8)
H(6)	0.6582(39)	0.6761(34)	0.3475(9)	0.019(7)
H(71)	0.4958(70)	0.5674(63)	0.1948(16)	0.073(13)
H(72)	0.6463(75)	0.6811(73)	0.1748(18)	0.079(14)
H(73)	0.6808(71)	0.4516(69)	0.1699(17)	0.065(12)
H(81)	1.1936(68)	0.2069(59)	0.4314(15)	0.057(11)
H(82)	1.1208(77)	0.2641(70)	0.4803(18)	0.064(13)
H(83)	1.0433(58)	0.0832(59)	0.4590(13)	0.041(9)
H(91)	0.7652(46)	0.0916(46)	0.3947(10)	0.023(7)
H(92)	0.6792(66)	0.2857(56)	0.3737(14)	0.045(10)
H(93)	0.9168(57)	0.2136(47)	0.3666(13)	0.037(9)
H(101)	0.7537(65)	0.3641(63)	0.4980(15)	0.059(11)
H(102)	0.6666(62)	0.1679(55)	0.4735(14)	0.052(11)
H(103)	0.5689(82)	0.3564(71)	0.4503(18)	0.076(14)
H(01)	0.6666(91)	0.7375(81)	0.4364(20)	0.091(20)
H(02)	0.4756(66)	0.8050(58)	0.4286(15)	0.055(11)

Table 1.2 (cont.)

c) Anisotropic thermal parameters (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	0.0363	0.0398	0.0343	-0.0071	-0.0063	0.0051
O(1)	0.0750	0.0454	0.0521	-0.0238	-0.0090	0.0031
O(2)	0.0349	0.0737	0.0502	0.0040	-0.0054	0.0134
O(3)	0.0633	0.0643	0.0735	-0.0099	-0.0003	-0.0137
N(1)	0.0443	0.0366	0.0316	-0.0062	-0.0013	-0.0003
N(2)	0.0431	0.0376	0.0312	-0.0070	-0.0065	0.0047
C(1)	0.0376	0.0340	0.0338	-0.0009	-0.0019	0.0071
C(2)	0.0455	0.0427	0.0439	0.0088	0.0031	0.0044
C(3)	0.0621	0.0456	0.0385	0.0069	0.0075	0.0002
C(4)	0.0550	0.0367	0.0370	-0.0066	-0.0072	0.0067
C(5)	0.0388	0.0545	0.0460	0.0023	-0.0063	0.0108
C(6)	0.0402	0.0536	0.0381	0.0072	0.0034	0.0033
C(7)	0.0839	0.0606	0.0445	-0.0122	-0.0187	0.0061
C(8)	0.0586	0.0521	0.0760	-0.0002	-0.0202	0.0220
C(9)	0.0853	0.0454	0.0399	-0.0223	-0.0114	-0.0038
C(10)	0.0642	0.0635	0.0497	-0.0144	0.0129	0.0060

Mean estimated standard deviations (Å^2)

S	0.0003	0.0004	0.0003	0.0002	0.0002	0.0002
O	0.0011	0.0012	0.0011	0.0009	0.0009	0.0009
N	0.0010	0.0010	0.0009	0.0009	0.0007	0.0007
C	0.0014	0.0014	0.0013	0.0012	0.0011	0.0011

Table 1.3

Interatomic distances and angles

a) Bonded distances (Å)

S - O(1)	1.442(2)	C(1) - C(2)	1.381(3)
S - O(2)	1.448(2)	C(1) - C(6)	1.384(3)
S - N(1)	1.592(2)	C(2) - C(3)	1.390(3)
S - C(1)	1.782(2)	C(3) - C(4)	1.380(3)
N(1) - N(2)	1.471(3)	C(4) - C(5)	1.387(3)
N(2) - C(8)	1.495(4)	C(4) - C(7)	1.512(4)
N(2) - C(9)	1.488(3)	C(5) - C(6)	1.388(3)
N(2) - C(10)	1.504(3)	Mean O - H	0.78(5)
Mean C - H (aryl)	0.95(3)	Mean C - H (methyl)	0.97(4)

b) Interbond angles (°)

O(1)-S -O(2)	116.1(1)	C(8)-N(2)-C(9)	110.0(2)
N(1)-S -O(1)	103.6(1)	C(8)-N(2)-C(10)	108.1(2)
N(1)-S -O(2)	115.3(1)	C(9)-N(2)-C(10)	108.3(2)
N(1)-S -C(1)	110.5(1)	C(2)-C(1)-C(6)	119.6(2)
C(1)-S -O(1)	106.0(1)	C(1)-C(2)-C(3)	120.3(2)
C(1)-S -O(2)	105.1(1)	C(2)-C(3)-C(4)	120.8(2)
S -N(1)-N(2)	118.0(1)	C(3)-C(4)-C(5)	118.3(2)
S -C(1)-C(2)	119.9(2)	C(4)-C(5)-C(6)	121.5(2)
S -C(1)-C(6)	120.5(2)	C(3)-C(4)-C(7)	120.5(2)
N(1)-N(2)-C(8)	112.8(2)	C(5)-C(4)-C(7)	121.2(2)
N(1)-N(2)-C(9)	114.2(2)	C(5)-C(6)-C(1)	119.5(2)
N(1)-N(2)-C(10)	103.0(2)		

Table 1.3 (cont.)

c) Intramolecular non-bonded distances (Å)

S ...N(2)	2.63	O(2)...N(2)	3.04
S ...C(8)	3.22	O(2)...C(2)	2.87
S ...C(9)	3.11	O(1)...C(6)	3.23
O(1)...O(2)	2.45	O(2)...C(8)	2.98
O(1)...N(1)	2.39	O(2)...C(9)	3.42
O(2)...N(1)	2.57		

d) Intermolecular distances (Å)

$O(3)...S^{I}$	3.80	$C(9)...O(3)^{II}$	3.48
$O(3)...O(2)^{I}$	3.52	$C(10)..O(3)^{II}$	3.57
$C(6)...O(2)^{I}$	3.63	$N(2)...O(3)^{II}$	3.93
$C(9)...O(2)^{I}$	3.66	$C(10)..O(3)^{III}$	3.34
$C(10)..O(2)^{I}$	3.57	$C(5)...C(4)^{IV}$	3.86
$C(10)..C(8)^{I}$	3.90	$C(7)...C(5)^{V}$	3.60
$C(5)...C(2)^{I}$	3.73	$C(7)...C(6)^{V}$	3.77
$C(8)...O(1)^{II}$	3.49	$C(9)...C(7)^{V}$	3.51
$C(9)...O(1)^{II}$	3.73		

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

I	-1+x,	y,	z ;	II	x,	-1+y,	z ;
III	1-x,	1-y,	1-z ;	IV	1-x,	1/2+y,	1/2-z ;
V	1-x,	-1/2+y,	1/2-z .				

Table 1.3 (cont.)

e) Selected torsion angles (°)

O(1)-S	-N(1)-N(2)	-168.6	O(2)-S	-C(1)-C(6)	168.3
O(2)-S	-N(1)-N(2)	-40.7	N(1)-S	-C(1)-C(2)	-137.1
C(1)-S	-N(1)-N(2)	78.3	N(1)-S	-C(1)-C(6)	43.3
O(1)-S	-C(1)-C(2)	111.3	S	-N(1)-N(2)-C(8)	70.3
O(1)-S	-C(1)-C(6)	-68.3	S	-N(1)-N(2)-C(9)	-56.3
O(2)-S	-C(1)-C(2)	-12.1	S	-N(1)-N(2)-C(10)	-173.1

Mean e.s.d. 0.2°

Table 1.4

Least-squares plane

a) Equation of plane $0.3660X + 0.9131Y - 0.1796Z - 3.9585 = 0$

b) Deviation of atoms from the plane (Å)

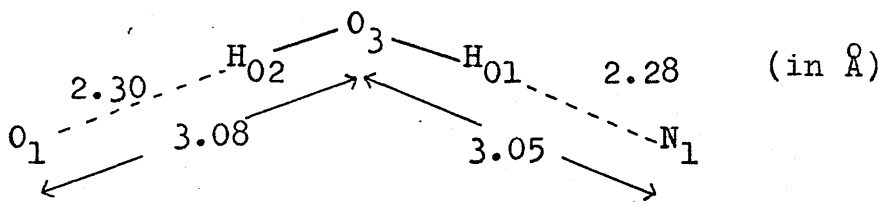
S	0.005*	C(1)	-0.003*	C(2)	-0.001*
C(3)	-0.001*	C(4)	-0.005*	C(5)	0.001*
C(6)	-0.003*	C(7)	0.006*		

* denotes atom used to define the plane.

X, Y and Z are orthogonal coordinates in Å.

Table 1.5

Dimensions of the bridging hydrogen bond



O(1)...H(02)—O(3)	171(5)°
N(1)...H(01)—O(3)	172(4)°
H(01)—O(3)—H(02)	109(5)°

Figure 1.1

Atomic numbering scheme

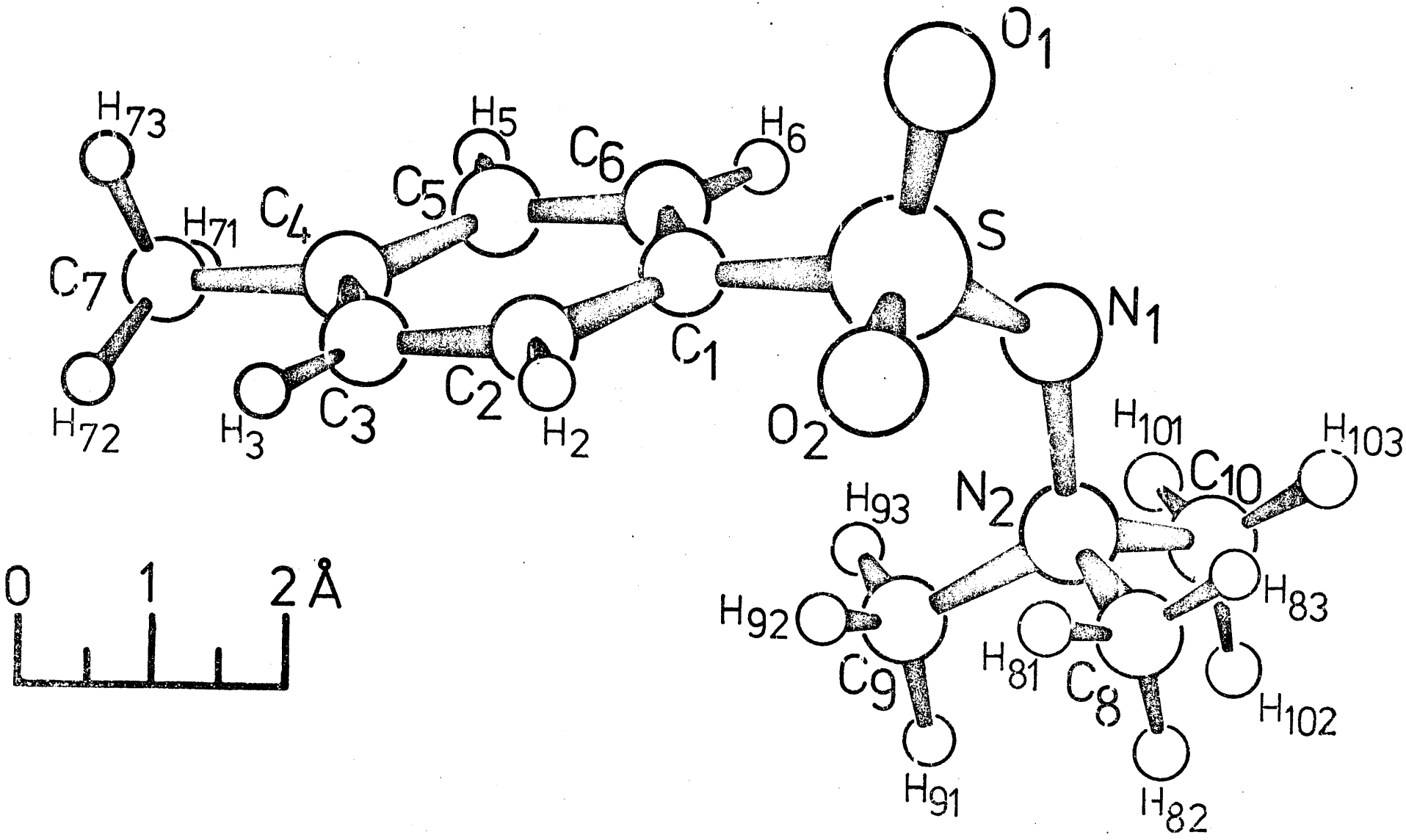
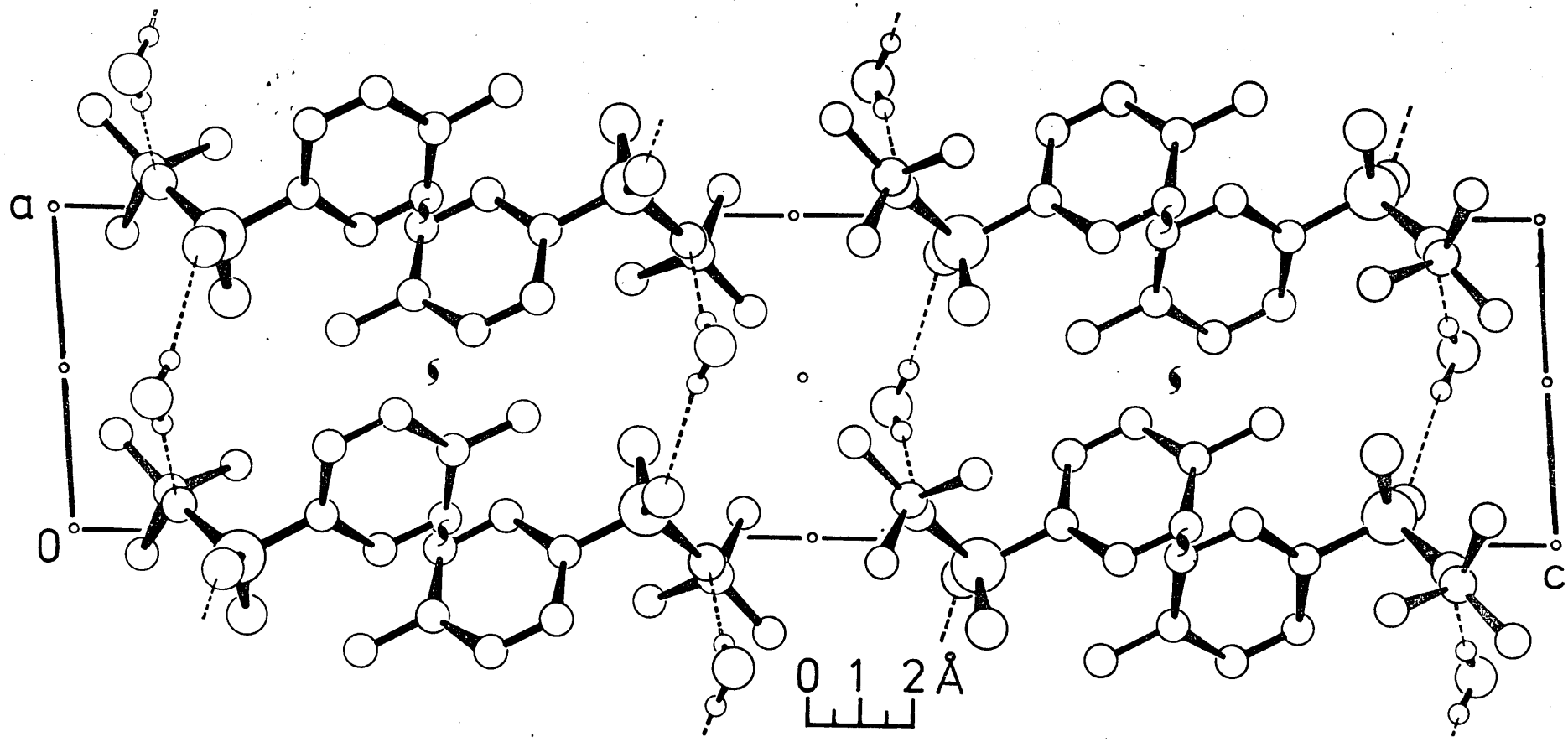

O1
H73
H5
C6
H6
C5
H71
C4
S
C7
N1
C1
H72
H3
C3
C2
H2
O2
H101
H103
C10
N2
H93
H92
H83
C9
H81
C8
H102
H91
H82
0 1 2 Å

Figure 1.2

Molecular packing arrangement

viewed down the b-axis


a
0
c
0 1 2 Å

1.3 Discussion

The structure analysis of the ylide, I , has revealed a hydrogen-bonded crystal structure in which the packing is characterised by the formation via a bridging water molecule of a chain-structure extending in the a-direction of the crystal, and resulting in the short a-axis and unusually long c-axis. While this bridging interaction from O(1) to N(1) might be expected to modify the conformation of the molecule, the similarity of the conformation to that of other sulphonyl-stabilised ylides[17,18] suggests that hydrogen bonding is a much lesser influence than the bonding interactions in the ylide.

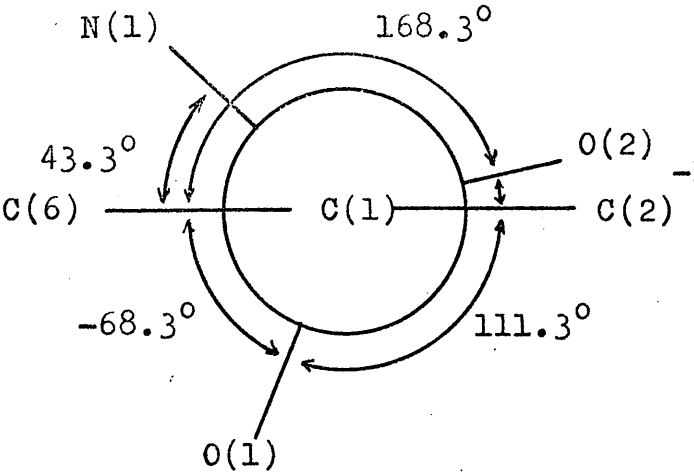
These results allow comparisons of geometry to be made with, particularly, the second-row sulphonyl-stabilised ylides, compounds IV to VI , and with other ammonium imines, compounds II and III .

The latter comparison shows that the $\overset{+}{N} - \overset{-}{N}$ length in I , 1.472(2) Å , is identical to that length in II and III , 1.471(5) and 1.470(8) Å respectively, confirming the invariance of this bond with change of stabilising group. The increase of this length over other single bond values (hydrazine, 1.451(5) and $N_2H_6^{2+}$, 1.41(2) Å [33]) appears to contradict the suggestion that opposed charges across a bond tend to cause bond shortening[34,35], but may alternatively indicate considerable reduction of the negative charge by delocalisation to the stabilising group. The latter feature is certainly indicated by the N-S bond length, 1.592(2) Å , whose shortness in comparison to the S-N single bond in sulphamic acid, 1.772(1) Å (see section 6), indicates considerable multiple bond order, appropriate to, in Cruickshank's theory[25], a π-bond order of 0.25 to 0.30 . The accompanying perceptible lengthening of the S-O bond lengths to 1.445(2) Å (mean value), appropriate to a

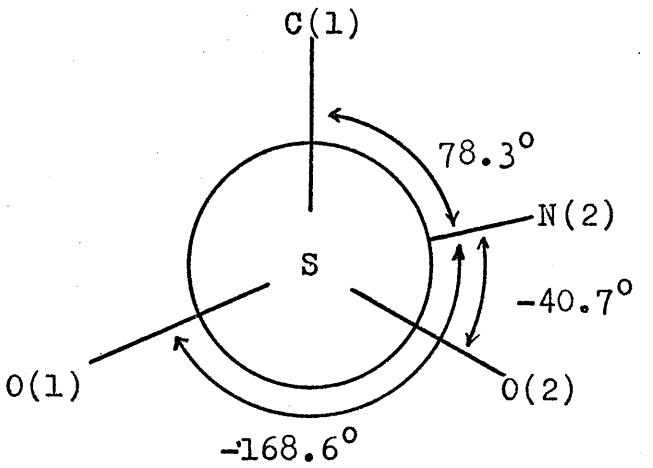
π-bond order of about o.6 , may be significant in comparison with, for example, 1.412(3) Å in dimesityl sulphone[36] where such delocalisation is not possible. However, S-O bond lengths in sulphonyl compounds are known to be much influenced by crystal environment and by the electronegativity of the substituents[37].

The conformation of the molecule is most simply illustrated by the three Newman projections in Figure 1.3 , which not only reveal the asymmetric orientation of the aromatic ring in relation to the sulphonyl group, deviating by 12.1° from coplanarity with one oxygen, O(2), with a contact diatance O(2)...C(2) of 2.87 Å , but also reveal the similar asymmetry in the orientation of the imino atom with respect to the sulphonyl group, at a torsion angle of 168.6° from the other oxygen atom, O(1), i.e. 11.4° from trans-planarity. This is an exactly similar conformation to that adopted by compounds IV,V and VI in the crystal state, for which the torsion angles from the toluene ring to one oxygen atom are 11.2 , 14.3 and 11.8° respectively, and the torsion angles from the imine moeity to the other oxygen atom are 167.2 , 163.9 and 167.7° , corresponding to 12.8 , 16.1 and 12.3° from coplanarity. This uniformity suggests that $d\pi$-$p\pi$ bonding in the $X^{+} - Y^{-}$ bond plays no part in determining the imine-sulphonyl conformation since in the absence or presence of such bonding, e.g. with first or second-row 'onium atoms, no significant difference occurs. Other features of the sulphonyl group remain similarly unaltered, the length of the S-N bond in I , 1.592(2) Å , being experimentally identical to the corresponding bond lengths in the second-row ylides, IV, V and VI , 1.591(8) , 1.598(8) and 1.586(4) Å respectively. The mean S-O bond lengths, 1.445(2) , 1.432(8) , 1.433(8) and 1.442(3) Å in compounds I, IV, V and VI respectively, are similarly uniform, the differences being less than

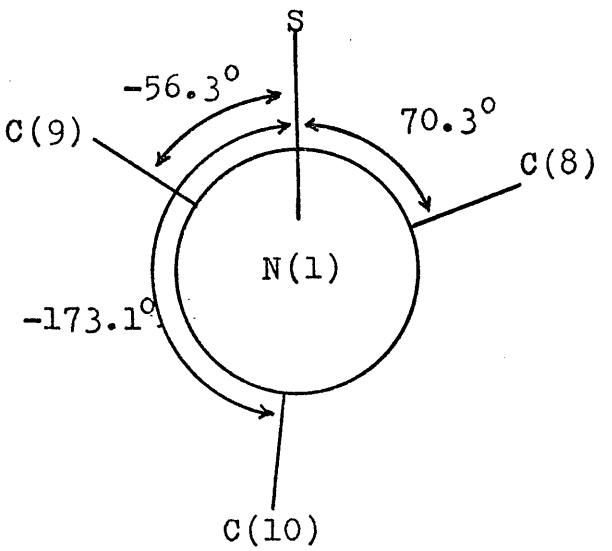
Figure 1.3



C(1) - S Projection



S - N(1) Projection



N(1) - N(2) Projection

the experimental uncertainty.

A feature of these compounds which does show some appreciable variation is the valence angle at the imine atom, with a range of values close to, but less than, the trigonal angle. However, as angle bending is a relatively low-energy process, these variations may equally arise from non-bonded interatomic forces as from π-bonding interactions. Indeed the pattern of variation suggests this, since in the sulphonium compounds, IV and V , the observed values of 113.4(5)° are commensurate with the possibly lower steric requirements of the tervalent sulphonium group, whereas the larger values of 116.4(2) , 114.2(3) and 115.0(5)° are observed for the tetravalent phosphonium and ammonium imines, VI , II and III respectively. The angle in compound I , 118.0(1)°, may therefore agree well with the expected outcome of pairing the bulky sulphonyl and trimethylammonium groups.

The staggered conformation of the trimethylammonium group with respect to the N(2)-S bond also tends to support the above hypothesis, with a torsion angle S-N(1)-N(2)-C(10) of 173.1°. So also does the asymmetry of this group, evident in the enlarged ammonium valence angles, N(1)-N(2)-C(8) and N(1)-N(2)-C(9), respectively 112.8(2) and 114.2(2)°, compared with the reduced valence angle, N(1)-N(2)-C(10) 103.0(2)°, involving the trans-methyl group. This is clearly a distortion arising from minimising the sulphonyl-methyl interactions, resulting in the contact distances O(2)...C(8) 2.98 Å , O(2)...C(9) 3.42 Å and O(2)...H(81) 2.30 Å . This asymmetry is a feature which is also present in compounds II, III and VI , where it arises from similar causes.

Examination of the toluene portion of the molecule reveals no

deviation from essentially normal benzenoid dimensions (mean C_{ar}-C_{ar} 1.385(3) Å , mean C_{ar}-C_{ar}-C_{ar} 120.1(2)°) and confirms the observation[19] that the aromatic system is unaffected by π-interaction with the sulphonyl group. In general, aromatic resonance energies are such that only severe perturbations give rise to significant distortion of six-membered rings.

The bond length to the p-methyl group, C(4)-C(7) 1.512(4) Å , is normal for a $C(sp^2)$-$C(sp^3)$ bond[33] and agrees with corresponding bonds in similar compounds. In the same way the S-C(1) bond length, 1.782(2) Å , is comparable with other S(VI)-$C(sp^2)$ bonds[19,33] and may indicate that there is little π-interaction across this bond.

Bond lengths in the trimethylammonium group (mean $C-\overset{+}{N}$ distance 1.496(3) Å) are similar to those in compounds II and III , and comparable with accepted $C(sp^3)$-$\overset{+}{N}(sp^3)$ distances[33].

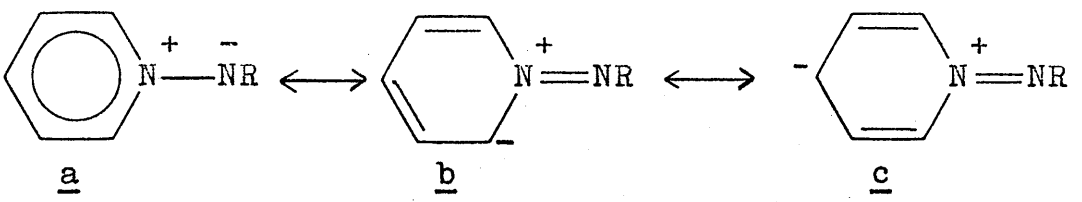
Apart from contact distances involving the water molecule bridge, there are no abnormally short intermolecular distances, confirming that the mode of crystal packing is dominated by the hydrogen bonding. Dimensions of the bridging system, shown in Table 1.5 , are those of long hydrogen bonds, the O....O and O....N distances of 3.08 and 3.05 Å exceeding the distances predicted for such interactions on the basis of hydrogen-bond donor and acceptor radii[38] by about 0.2 Å . Nevertheless, the nature and geometry of the interaction and especially the bond angles at hydrogen of 171(5)° and 172(4)° leave no doubt that it is, in conventional terms, hydrogen bonding. One observable consequence of this crystal interaction is the generally low overall thermal motion, with terminal atoms possessing the usual higher thermal parameters.

2. THE CRYSTAL AND MOLECULAR STRUCTURE OF A SULPHONYL-STABILISED PYRIDINIUM YLIDE : PYRIDINIUM-N-(p-CHLOROBENZENESULPHONYL)IMINE.

2.1 Introduction

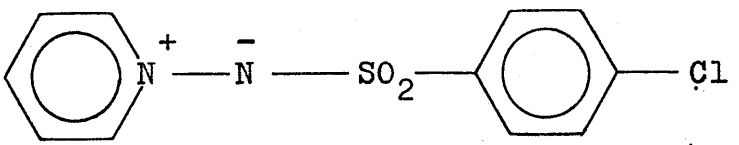
Preparative chemistry of pyridinium ylides[2] has shown that these compounds have greater stability than corresponding ammonium compounds. This increased stability has been postulated as arising from a resonance interaction of the anionic species with the pyridinium ring, as in VII a,b,c . Pyridinium ylides may therefore show properties intermediate to those of analogous ammonium and phosphonium ylides. However, the nature and possible extent of the interaction of a stable aromatic pπ-orbital with the lone pairs of an imine nitrogen is likely to be rather different from that of the interaction with vacant d-orbitals on a second-row atom.

In order to investigate these possible differences, the crystal structure of the sulphonyl-stabilised pyridinium ylide, VIII , has been determined. In addition this allows examination of the sulphonyl-imine system in the presence of a fourth type of 'onium group.

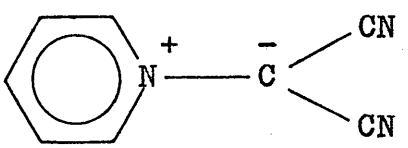


a b c

VII



VIII



IX

2.2 Experimental

Crystal Data

Pyridinium-N-(p-chlorobenzenesulphonyl)imine

$C_{11}H_9N_2O_2SCl$, M = 268.7 .

Monoclinic, a = 11.613 b = 7.372 c = 15.462 Å , β = 111.85°,

U = 1228.5 $Å^3$,

D_m = 1.41 g cm^{-3}, Z = 4 , D_c = 1.45 g cm^{-3},

$F_{(000)}$ = 552 .

Space group : P2/c (C_{2h}^4 , No.13) .

μ(Mo,Kα) = 4.67 cm^{-1}.

Data Collection

Radiation	:	Mo,Kα
Filter	:	graphite monochromator
Maximum scattering angle (2θ)	:	60°
Independent reflections (observed)	:	1643
Unobserved cutoff	:	$2\sigma_I$
Ratio of observations/parameters	:	8.62

Structure Determination

Systematic absences in the $h0\ell$ net indicated two possible space groups, Pc and its centrosymmetric analogue, P2/c . Statistical analysis of the data set suggested a non-centrosymmetric distribution, although the presence of four molecules in the unit cell made P2/c more likely.

A sharpened Patterson function was calculated, but no solution could be obtained compatible with either space group. The presence of two heavy atoms per molecule and the clear overlap of vectors in a broad peak at (0,0.5,0.5) on the Harker line (0,v,0.5) both contributed to the difficulty.

On the grounds that direct methods are simpler and faster in the centrosymmetric case, direct phasing was attempted for the space group P2/c . Despite the usual hallmarks of a reliable phase determination, the resulting E-map showed approximate mirror symmetry about $y = 0.25$, 0.75 and contained no recognisable fragments. Accordingly, the space group Pc was then assumed, with two molecules per asymmetric unit, and phasing by multisolution tangent formula methods was attempted. The resulting E-map, as before, showed partial mirror symmetry, and revealed no recogniseable fragments. Inspection of the data set revealed that this partial symmetry was a property of the intensity data. The four parity groups representing all reflections for which $k + \ell$ is odd, (eeo, eoe, oeo, ooe), were systematically weak and were present in smaller numbers than the other four groups, with only three members present in a list of the hundred highest $|E|$ values. Thus two largely non-interacting phase subsets existed, since the triplet

relationships rarely included members of both subsets. This systematic weakness of reflections with $k + \ell$ odd must result from an approximate A-face-centred electron-density distribution in the crystal structure, which is, in addition, suggested by the large vector at (0,0.5,0.5) in the Patterson function. As all direct phasing procedures use a subset of high |E| reflections, this partial symmetry is built into an initial phase set, and its E-map, more markedly than it is actually present in the crystal structure.

This difficulty was overcome by renormalising the data in individual parity groups, scaling each group such that $\langle |E|^2 \rangle = 1$. The scale factors obtained are listed in Table 2.1 . Phase determination was then carried out, again assuming space group Pc., by the automatic multisolution tangent method (MULTAN) using 350 reflections with $|E| > 1.20$. A starting set containing three general phases as variables yielded 64 possible phase sets, and the solution was contained in the 61st set in order of "merit". The E-map calculated with this phase set revealed both molecules of the asymmetric unit with all atoms clearly defined. The atomic positions thus obtained were immediately refined by least-squares methods.

Structure Refinement

The course of least-squares refinement is detailed in Table 2.2 . After convergence of refinement of positional and isotropic thermal parameters, all hydrogen atoms were located by means of a difference synthesis and were included in the calculations with isotropic thermal parameters, $U_{iso} = 0.05$ Å^2 , but were not initially refined. At cycle 7

and thereafter, anomalous terms in the scattering factors for S and Cl were included in the calculation of structure factors, and at cycle 8 corrections were made to reflections of large intensity to counteract errors due to counter saturation. After several cycles of anisotropic refinement had been completed, certain shortcomings in the refined model were observed, clearly as non-transient features : the pyridinium ring geometry was irregular, with one particular C-C bond in molecule A being very long (1.54 Å) while the equivalent bond in molecule B was short (1.21 Å), and the S-O lengths were significantly unequal in both molecules. These irregularities, coupled with the observation that the two molecules were related by an approximate centre of inversion, suggested that the space group might after all be P2/c with one molecule per asymmetric unit. Summation of the $\underline{x}$ coordinates of the equivalent atoms in molecules A and B, and similarly for the $\underline{z}$ coordinates gave $\sum_{A,B} x = 0.510 \pm 0.010$ and $\sum_{A,B} z = 0.808 \pm 0.011$, indicating an approximate centre of inversion at (0.255, 0.0, 0.404). Coordinates compatible with P2/c symmetry were thus obtained, and the correctness of space group P2/c was confirmed by subsequent refinement during which all irregularities in the geometry vanished. Moreover, with doubling the ratio of observations/parameters, refinement of the hydrogen atoms became possible. Convergence of weighted refinement occurred with R and R' at 0.037 and 0.0021 respectively.

From cycle 14., a weighting scheme of the form

$$W = (A + B|F_o| + C|F_o|^2)^{-1}$$

was applied using coefficients obtained from a quadratic function fitted to the curve of Δ^2 as a function of $|F_o|$. Final values obtained were $A = 0.5189$, $B = -0.0258$ and $C = 0.00128$.

In all structure-factor calculations, the atom scattering factors used were those derived by Cromer and Mann (1968) [39], for S, O, N, C and Cl, and by Stewart, Davidson and Simpson (1965) [40] for H.

Observed and final calculated structure factors are given in Appendix 2 . Fractional coordinates and thermal parameters are listed in Table 2.3 . Interatomic distances and angles, including intermolecular contacts are given in Table 2.4 . The estimated standard deviations quoted in the above tables are derived from the inverse of the least-squares normal-equation matrix. Details of two least-squares planes through several portions of the molecule are given in Table 2.5 .

The atomic numbering scheme and the molecular packing viewed along the b-axis are shown in Figures 2.1 and 2.2 respectively.

Table 2.1

Scale factors obtained by individual parity group normalisation

Parity group	Scale factor	No. of reflections (incl. equivalent reflections)
eee	1.167	998
oee	1.271	936
eoo	1.345	900
ooo	1.309	948
eoe	0.540	728
eeo	0.605	548
oeo	0.679	520
ooe	0.648	644
all	1.012	6212

Table 2.2

Course of refinement

Cycles	Parameters refined	Final R	Final R'
1 - 4	x,y,z,U_{iso} for S, O, N, C and Cl, scale factor. Unit weights, full matrix.	0.107	0.0102
5 - 10	x,y,z,U_{ij} for S, O, N, C and Cl, scale factor. H-atom contributions included but not refined. Unit weights, blocked matrix. Correction for anomalous dispersion included. Correction made to data for counter saturation.	0.045	0.0017
11 - 13*	x,y,z,U_{ij} for S, O, N, C and Cl, x,y,z,U_{iso} for H, scale factor. Unit weights, full matrix.	0.038	0.0014
14 - 16	x,y,z,U_{ij} for S, O, N, C and Cl, x,y,z,U_{iso} for H, scale factor. Weighting scheme applied, full matrix.	0.037	0.0021

* The space group was changed from Pc to P2/c prior to cycle 11 .

Table 2.3

a) Fractional Coordinates

	x/a	y/b	z/c
S	0.34435(6)	0.23542(9)	1.02985(4)
Cl	-0.09345(9)	0.76769(18)	0.83024(9)
O(1)	0.4008(2)	0.2894(3)	1.1262(1)
O(2)	0.2917(2)	0.0554(3)	0.0113(1)
N(1)	0.4484(2)	0.2724(3)	0.9888(1)
N(2)	0.4059(2)	0.2354(3)	0.8919(1)
C(1)	0.2191(2)	0.3842(4)	0.9725(2)
C(2)	0.1011(3)	0.3185(5)	0.9252(3)
C(3)	0.0052(3)	0.4359(6)	0.8814(3)
C(4)	0.0284(3)	0.6181(5)	0.8843(2)
C(5)	0.1450(3)	0.6871(5)	0.9301(2)
C(6)	0.2413(3)	0.5689(4)	0.9735(2)
C(7)	0.3868(3)	0.3788(4)	0.8341(2)
C(8)	0.3495(3)	0.3514(5)	0.7397(2)
C(9)	0.3337(3)	0.1783(5)	0.7050(2)
C(10)	0.3569(3)	0.0336(4)	0.7656(2)
C(11)	0.3929(2)	0.0640(4)	0.8591(2)

Table 2.3 (cont.)

b) H-atom fractional coordinates and isotropic thermal parameters ($\AA^2$)

	x/a	y/b	z/c	U iso
H(2)	0.087(3)	0.190(5)	-0.076(2)	0.075(10)
H(3)	-0.072(4)	0.390(6)	-0.151(3)	0.120(15)
H(5)	0.160(3)	0.810(5)	-0.067(2)	0.067(10)
H(6)	0.321(3)	0.614(4)	0.002(2)	0.066(9)
H(7)	0.403(2)	0.493(4)	-0.136(2)	0.040(7)
H(8)	0.341(3)	0.453(4)	-0.296(2)	0.067(10)
H(9)	0.311(3)	0.154(4)	-0.360(2)	0.067(9)
H(10)	0.349(3)	-0.082(4)	-0.252(2)	0.060(9)
H(11)	0.412(3)	-0.023(4)	-0.096(2)	0.056(8)

Table 2.3 (cont.)

c) Anisotropic thermal parameters (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	0.0526	0.0393	0.0401	-0.0014	0.0160	-0.0001
Cl	0.0675	0.1219	0.1249	0.0420	0.0218	0.0266
O(1)	0.0749	0.0609	0.0371	0.0036	0.0145	-0.0027
O(2)	0.0741	0.0399	0.0638	-0.0086	0.0309	0.0004
N(1)	0.0427	0.0433	0.0389	-0.0014	0.0081	-0.0028
N(2)	0.0377	0.0368	0.0413	0.0010	0.0129	0.0022
C(1)	0.0440	0.0464	0.0421	-0.0015	0.0166	-0.0048
C(2)	0.0519	0.0586	0.0872	-0.0132	0.0172	-0.0024
C(3)	0.0438	0.0879	0.1126	-0.0054	0.0130	0.0013
C(4)	0.0499	0.0820	0.0678	0.0158	0.0187	0.0062
C(5)	0.0632	0.0471	0.0671	0.0044	0.0184	0.0032
C(6)	0.0482	0.0445	0.0546	-0.0029	0.0103	-0.0076
C(7)	0.0503	0.0409	0.0581	0.0028	0.0256	0.0072
C(8)	0.0602	0.0670	0.0532	0.0099	0.0274	0.0182
C(9)	0.0564	0.0810	0.0413	0.0053	0.0193	-0.0014
C(10)	0.0509	0.0525	0.0524	-0.0009	0.0171	-0.0093
C(11)	0.0460	0.0394	0.0491	0.0025	0.0177	0.0017

Mean estimated standard deviations (Å^2)

S	0.0004	0.0003	0.0003	0.0003	0.0003	0.0003
Cl	0.0006	0.0010	0.0009	0.0006	0.0006	0.0007
O	0.0013	0.0012	0.0011	0.0011	0.0010	0.0009
N	0.0010	0.0012	0.0011	0.0009	0.0009	0.0009
C	0.0017	0.0019	0.0019	0.0015	0.0014	0.0016

Table 2.4

Interatomic distances and angles

a) Bonded distances (Å)

S - O(1)	1.443(2)	C(10)- C(11)	1.366(4)
S - O(2)	1.445(2)	C(1) - C(2)	1.379(5)
S - N(1)	1.584(2)	C(2) - C(3)	1.374(6)
S - C(1)	1.773(3)	C(3) - C(4)	1.367(6)
N(1) - N(2)	1.419(3)	C(4) - C(5)	1.371(5)
N(2) - C(7)	1.348(4)	C(5) - C(6)	1.379(5)
N(2) - C(11)	1.349(3)	C(1) - C(6)	1.385(4)
C(7) - C(8)	1.373(4)	C(4) - Cl	1.743(4)
C(8) - C(9)	1.370(5)		
C(9) - C(10)	1.378(5)	Mean C - H	0.93(3)

b) Interbond angles (°)

O(1)-S -O(2)	117.0(1)	C(5)-C(6)-C(1)	120.2(2)
N(1)-S -O(1)	104.2(1)	C(6)-C(1)-C(2)	119.7(2)
N(1)-S -O(2)	114.1(1)	C(3)-C(4)-Cl	119.4(2)
N(1)-S -C(1)	107.4(1)	C(5)-C(4)-Cl	118.8(2)
C(1)-S -O(1)	108.6(1)	N(1)-N(2)-C(7)	117.2(2)
C(1)-S -O(2)	105.1(1)	N(1)-N(2)-C(11)	121.5(2)
S -N(1)-N(2)	111.9(1)	N(2)-C(7)-C(8)	119.9(2)
S -C(1)-C(2)	121.1(2)	C(7)-C(8)-C(9)	119.7(2)
S -C(1)-C(6)	119.2(1)	C(8)-C(9)-C(10)	119.4(2)
C(1)-C(2)-C(3)	120.2(3)	C(9)-C(10)-C(11)	119.8(2)
C(2)-C(3)-C(4)	119.3(3)	C(10)-C(11)-N(2)	119.9(2)
C(3)-C(4)-C(5)	121.7(2)	C(7)-N(2)-C(11)	121.2(2)
C(4)-C(5)-C(6)	118.8(2)		

Table 2.4 (cont.)

c) Intramolecular non-bonded distances (Å)

S ....N(2)	2.49	O(2)...N(2)	2.96
S ....C(7)	3.41	O(2)...C(2)	2.87
S ....C(11)	3.16	O(1)...C(6)	3.16
O(1)...O(2)	2.46	O(2)...C(11)	3.00
O(1)...N(1)	2.39	C(1)...C(7)	3.39
O(2)...N(1)	2.54	C(6)...C(7)	3.49

d) Intermolecular distances (Å)

$C(5)...O(2)^{I}$	3.20	$Cl ....Cl^{IV}$	3.86
$C(6)...O(2)^{I}$	3.65	$Cl ....C(10)^{V}$	3.47
$O(2)...C(9)^{II}$	3.33	$C(7)...C(8)^{VI}$	3.65
$O(1)...C(10)^{II}$	3.37	$C(8)...C(8)^{VI}$	3.39
$O(1)...C(8)^{III}$	3.35	$C(8)...C(9)^{VI}$	3.68
$C(8)...C(3)^{IV}$	3.89	$C(9)...C(10)^{VI}$	3.61
$C(5)...Cl^{IV}$	3.89	$C(9)...C(11)^{VI}$	3.75
$C(4)...Cl^{IV}$	3.83	$C(10)..C(10)^{VI}$	3.53

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

I	x,	1+y,	z ;	II	x,	-y,	1/2+z ;
III	x,	1-y,	1/2+z ;	IV	-x,	y,	3/2-z ;
V	-x,	1+y,	3/2-z ;	VI	1-x,	y,	3/2-z .

Table 2.4 (cont.)

e) Selected torsion angles (^{o})

O(1)-S	-N(1)-N(2)	-176.8	O(2)-S	-C(1)-C(6)	-176.9
O(2)-S	-N(1)-N(2)	54.4	N(1)-S	-C(1)-C(2)	123.4
C(1)-S	-N(1)-N(2)	-61.7	N(1)-S	-C(1)-C(6)	-55.0
O(1)-S	-C(1)-C(2)	-124.5	S	-N(1)-N(2)-C(7)	109.0
O(1)-S	-C(1)-C(6)	57.1	S	-N(1)-N(2)-C(11)	-75.3
O(2)-S	-C(1)-C(2)	1.5			

Mean e.s.d. 0.2^{o}

Table 2.5

Least-squares planes

a) Equation of plane

i) $0.5394X - 0.0773Y - 0.8385Z - 13.558 = 0$

ii) $-0.9959X + 0.0150Y - 0.0893Z - 0.7119 = 0$

b) Deviation of atoms from the plane (Å)

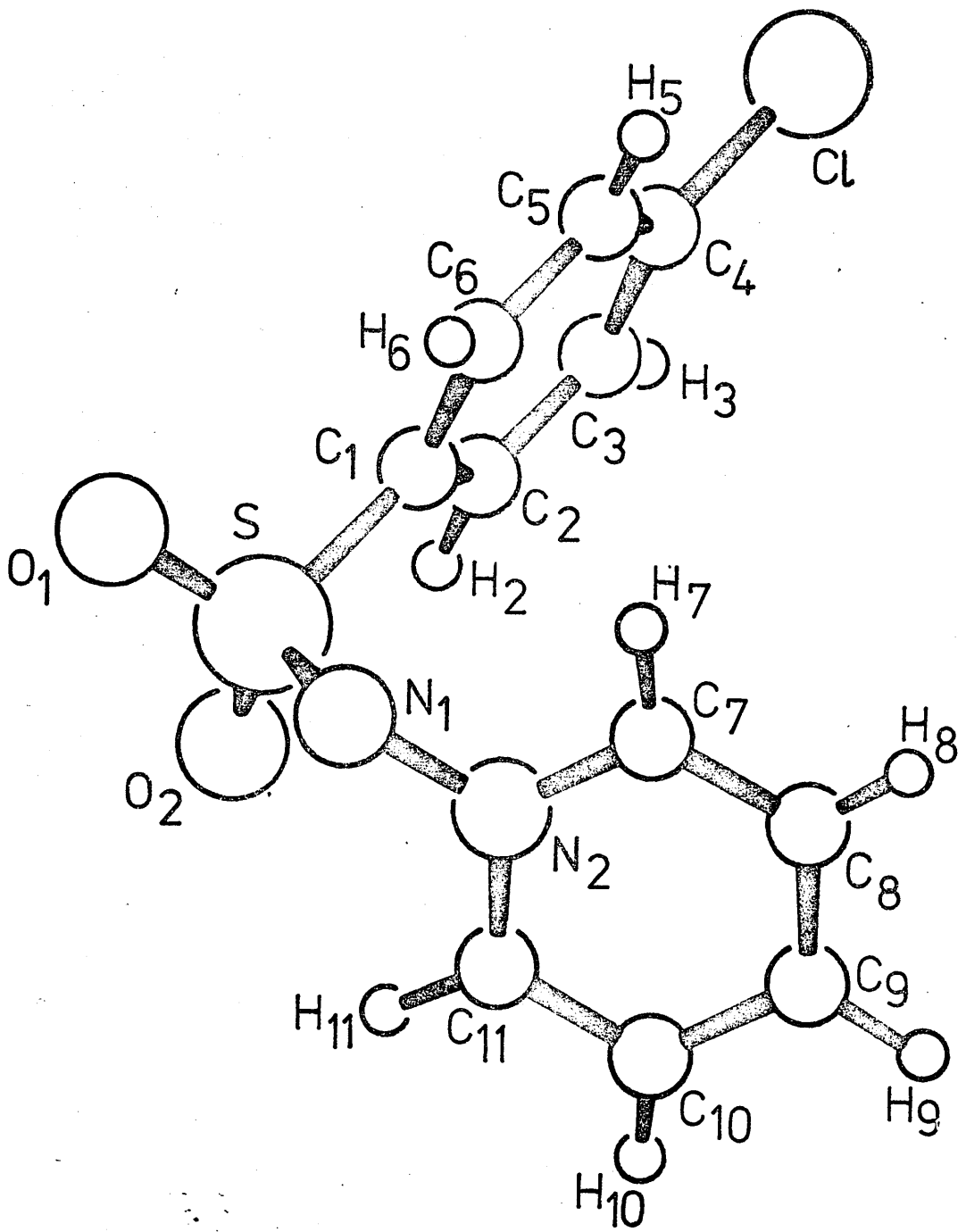
i)	S	-0.008	Cl	-0.032	O(2)	0.045
	C(1)	-0.010*	C(2)	0.004*	C(3)	0.001*
	C(4)	-0.002*	C(5)	-0.004*	C(6)	0.009*
ii)	N(1)	-0.046	N(2)	0.011*	C(7)	-0.009*
	C(8)	-0.001*	C(9)	0.008*	C(10)	-0.006*
	C(11)	-0.004*				

* denotes atom used to define plane.

X, Y and Z are orthogonal coordinates in Å .

Figure 2.1

Atomic numbering scheme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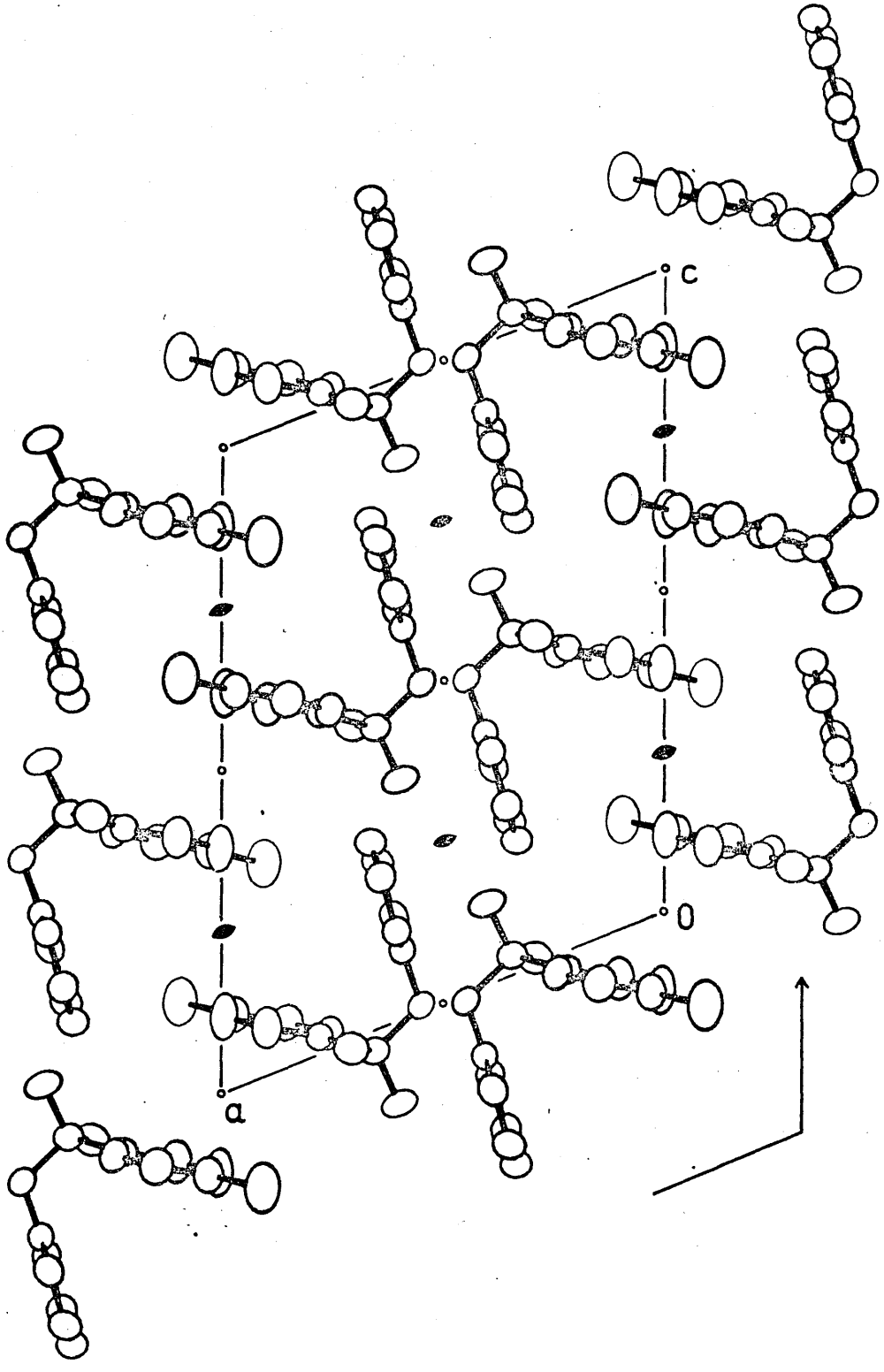
Cl
C5
C4
C6
H6
H3
C3
C1
C2
S
O1
H2
H7
N1
C7
H8
O2
N2
C8
C9
H11
C11
C10
H9
H10

Figure 2.2

Molecular packing arrangement viewed along the b-axis


c
a
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2.3 Discussion

Investigation of the crystal structure of the ylide, VIII, has revealed a conformation that has not previously been observed in sulphonyl-stabilised imines, in notable contrast to the conformations of compounds I, IV, V and VI .

However, many features of the geometry do bear comparison with these compounds. The S-N bond length, 1.584(2) Å , is comparable to the values of 1.592(2), 1.591(8), 1.598(8) and 1.586(4) Å observed in compounds I, IV, V and VI respectively, and indicates considerable multiple bond order by its shortness relative to the single bond length, 1.772(1) Å , in sulphamic acid (see section 6). The S-O bond lengths (mean value 1.444(2) Å) are identical to those in compound I (mean value 1.445(2) Å), and similarly correspond to an approximate π-bond order of 0.6 . These features therefore indicate considerable charge delocalisation from the negative atom into the sulphonyl group, to an extent similar to that in the other sulphonyl-stabilised imines discussed.

The N-N bond, on the other hand, shows no such indication, the bond length of 1.419(3) Å being approximately that expected for a $N(sp^2)$-$N(sp^3)$ single bond, and only slightly shortened from the corresponding length, 1.472(2) Å , in the ammonium imine, I . This length suggests that there is virtually no double bond character in this bond, and therefore little or no delocalisation from the imine nitrogen to the pyridine ring. This conclusion is supported by the essentially normal dimensions of the pyridinium ring, where the N-C bond lengths (mean 1.349(4) Å) are similar to those in the free

pyridine molecule (1.340(5) Å), and the C-C bonds are slightly shorter (mean values 1.372(5) Å compared to 1.395(5) Å for free pyridine[41]). Further support is given by the orientation of the pyridinium ring with respect to the imine-sulphonyl portion, where the C(7)-N(2)-N(1)-S torsion angle, 75.3°, reveals that the pπ-orbital on N(2) is approximately 75° away from coplanarity with the p-orbital lone pair on N(1), and correspondingly 15° away from coplanarity with the sp^2-orbital lone pair on N(1). This is clearly not an orientation conducive to effective orbital overlap, and is possibly more suggestive of repulsion between the imine lone pairs and the six-electron aromatic π-orbital, where minimisation of repulsive interactions would probably favour just such an orientation. This possibility may be supported by the low valence angle at the negative atom, 111.9(1)°, as a reduction in the interactions with the sp^2-type lone pair would accompany diminution of this angle. The observed angle is appreciably less than that in compound I, 118.0(1)°, but may equally be explained on the basis of reduced non-bonded interactions between the sulphonyl group and the pyridine ring compared to similar interactions with the trimethylammonium group of I (see section 1.3).

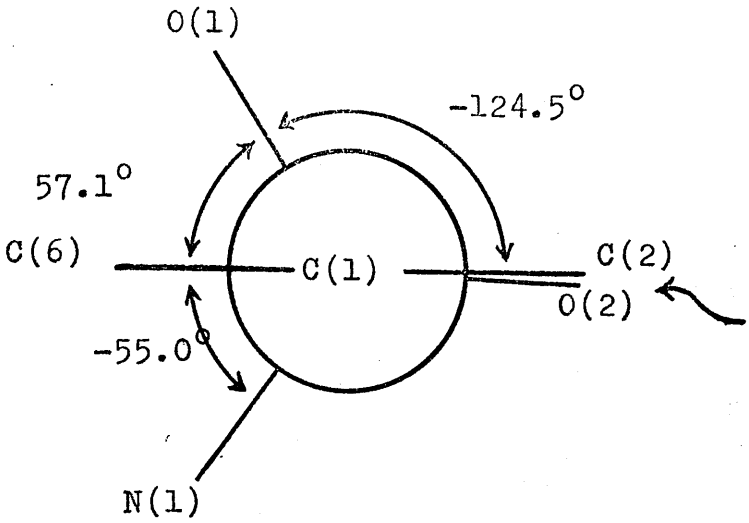
The orientation of the pyridine ring in this compound is in marked contrast to that in pyridinium dicyanomethylide, compound IX , where exact coplanarity with the trigonal methylide species is observed[6]. However, in the latter case the N-C bond length, 1.42(1) Å , is not appreciably short for a $N(sp^2)$-$C(sp^2)$ bond, being comparable to that in acetanilide, 1.42(1) Å , and suggests that despite the favourable overlap geometry, relatively little delocalisation occurs.

The unusual conformation of the sulphonyl group relative to the

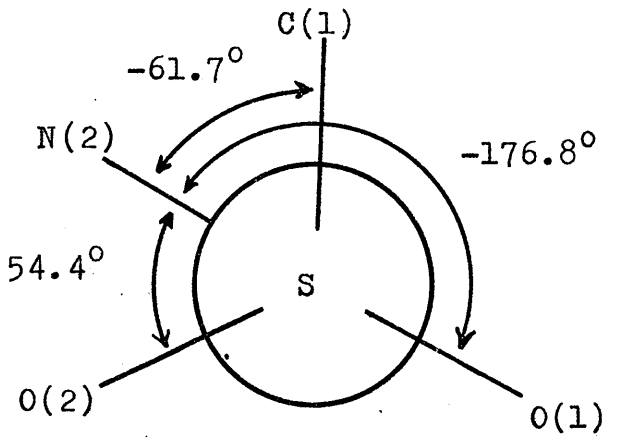
imine moiety is illustrated by the three Newman projections in Figure 2.3 . These clearly reveal the effective coplanarity of the benzene ring with one oxygen atom of the sulphonyl group, and the near planarity of the other oxygen, O(1), with the imine group, with a torsion angle N(2)-N(1)-S-O(1) of -176.8° being observed i.e. 3.2° from trans-planarity. This conformation thus provides ideal geometry for overlap of the lone-pair orbitals of the imine and the π-orbital of the benzene ring with the $d_{x^2-y^2}$ orbital of the sulphur atom, and might be expected to allow the maximum possible delocalisation into the sulphonyl group. However, as previously discussed, the geometry of the sulphonyl group indicates a comparable degree of delocalisation to that in compounds I, IV, V and VI . What is perhaps surprising is not that this compound adopts the unique conformation described, but that none of the other sulphonyl-imines discussed do so, preferring instead conformations with the relevant torsion angles consistently 10 to 20° from planarity. Examination of the two major features which distinguish compound VIII from the other sulphonyl-imines may yield some clue to the causes of this behaviour.

The presence of the p-chloro substituent, replacing the p-methyl group on the aryl portion of the molecule, is unlikely to have a major effect on the delocalisation. The observed ring geometry confirms this, with the mean C_{ar}-C_{ar} distance, 1.376(5) Å , showing no significant difference from the corresponding value in I , 1.385(3) Å . Further support is given by the experimentally identical S-C(1) bond lengths in I and VIII , 1.782(2) and 1.773(3) Å respectively. Furthermore, comparisons with a methylsulphonyl-imine[10] have suggested that the aromatic substituent plays a negligible part in influencing both

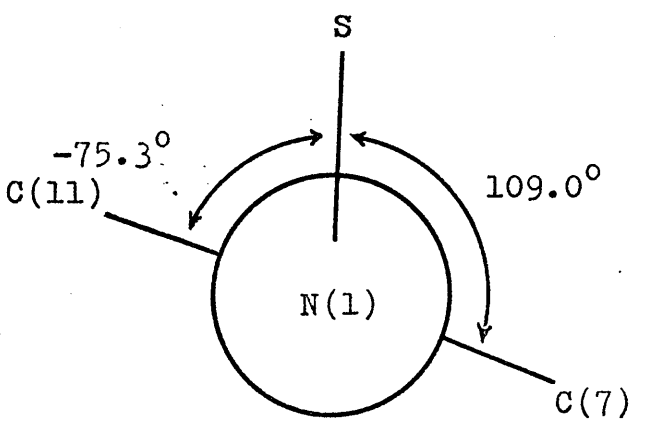
Figure 2.3



C(1) - S Projection



S - N(1) Projection



N(1) - N(2) Projection

charge delocalisation to the sulphonyl group and the conformation of the sulphonyl-imine portion.

The second distinguishing feature, the presence of the planar pyridinium group as the 'onium species, is in contrast to the other compounds considered which possess bulky 'onium groups with a threefold spatial distribution (including the sulphonium group where the lone pair has marked steric requirements). The intramolecular steric interaction of the 'onium group may therefore be a contributing influence in determining the conformation adopted. Steric interaction of the pyridinium and benzene rings in VIII may possibly influence the orientation of the pyridinium ring, the C(6)...C(7) and C(6)...H(7) contact distances of 3.49 and 3.01 Å being of moderate length, corresponding to only slight interaction. In the case of the more bulky trimethylammonium group in I, the C(6)...C(9) steric interactions decrease as the conformation moves from the possible coplanar arrangement of groups to the observed non-coplanar conformation (inspection of a molecular model clearly illustrates this). The C(6)...C(9) and C(6)...H(92) distances in the observed structure of I are 3.53 and 2.90 Å respectively, the latter indicating a possibly greater residual steric interaction than in VIII . While the conformation of I (and other sulphonyl-imines of non-coplanar conformation) may therefore arise as a compromise between steric and bonding interactions, the former type of interaction is difficult to quantify and rationalisations based on this are, at best, tentative.

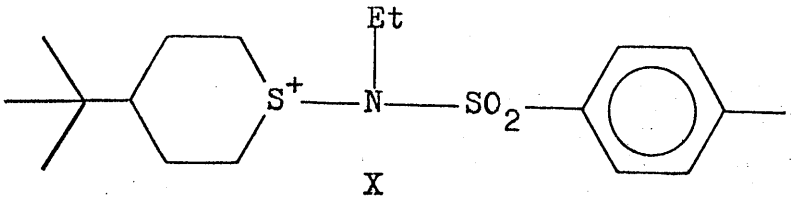
A further possible influence on the conformation of VIII may arise from the crystal packing, in which the adopted arrangement, with all rings stacked approximately parallel to the b-axis, is clearly

efficient and results in a crystal structure of relatively high density (1.45 g cm^{-3}). Dipole-dipole interactions appear to be the dominant force in this arrangement, resulting in pairing of molecules about a two-fold axis, with close contact of the chlorobenzene rings (Cl...Cl separation 3.86 Å), and of the chlorine atom and pyridinium rings (Cl...C(10) separation 3.47 Å). Close contact between pyridinium rings through a second two-fold axis is also observed, with a C(8)...C(8) distance of 3.39 Å .

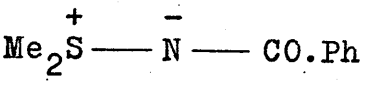
3. THE CRYSTAL AND MOLECULAR STRUCTURES OF A SULPHONIUM IMINE AND AN AROMATIC ZWITTERIONIC ANALOGUE : N-BENZOYLIMINODIMETHYLSULPHUR(IV) AND N-(p-NITROBENZOYL)-2-IMINOPHENYLDIMETHYLSULPHUR(IV).

3.1 Introduction

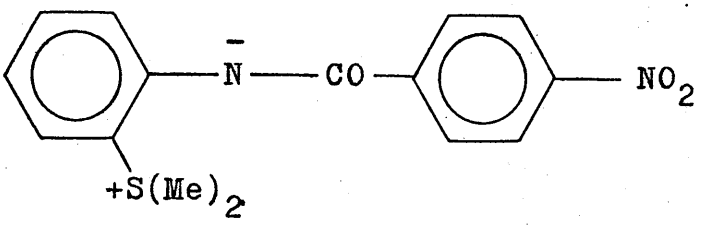
The involvement of $d\pi$-$p\pi$ interactions between lone-pair electrons of the anionic atom and vacant d-orbitals of the 'onium atom in the stabilisation of sulphonium imines ($\overset{+}{S}-\overset{-}{N}$ compounds) has been demonstrated by the structural studies of several of this class of compounds with sulphonyl stabilising groups and with halogen-containing carbonyl stabilising groups[10-14,17]. In addition, comparative examination of the sulphonyl-stabilised compounds and the N-alkylated imine, X ,[42] has established the importance of the π'-interaction of the imino atom with the sulphonyl system, but has suggested that in sulphonyl-stabilised compounds the similar π'-interaction with the sulphonium group is almost negligible[17]. However, in the analogous carbonyl-stabilised imines, in which π'-overlap with the stabilising group cannot occur, the presence of π and possibly π'-interactions with the sulphonium group may have some effect on the stabilisation by the carbonyl group, - effectively the competing influence of the 'onium group on multiple bonding from the imine nitrogen to the carbonyl group. Accordingly, in order to investigate this effect, the crystal structures of the benzoyl-stabilised sulphonium imine, XI , and of its aromatic analogue, XII , have been determined. The latter compound is of particular interest since instead of a direct



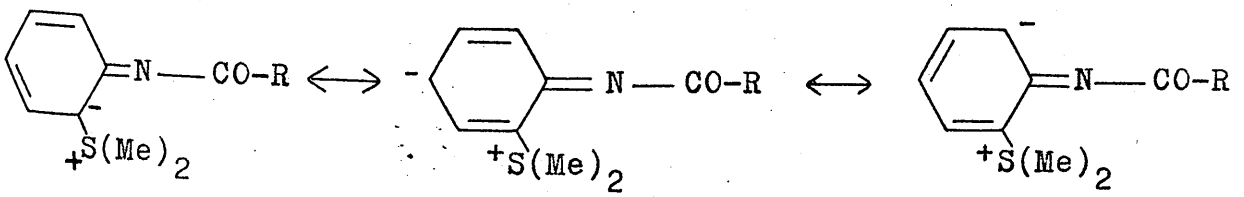
X



XI



XII



a b c

interaction between the S^{+} and N^{-} atoms, a delocalising interaction with the aromatic ring, represented by the resonance structures XII a,b and c, is possible with a further possible interaction between the sulphonium species and the aromatic ring, in which the ylidic resonance structure, a, would be expected to play a major rôle. These interactions may allow formation of an extended conjugated system, in possible concurrence with the bright orange colour of the compound.

3.2 Experimental Compound XI

Crystal Data (XI)

N-benzoyliminodimethylsulphur(IV)

$C_9H_{11}NOS$, M = 181.3 .

Monoclinic, a = 9.595 b = 8.632 c = 11.617 Å , β = 92.60°,

U = 961.1 $Å^3$,

D_m = 1.21 g cm^{-3}, Z = 4 , D_c = 1.27 g cm^{-3},

$F_{(000)}$ = 384 .

Space group : $P2_1/c$ (C_{2h}^5 , No.14) .

μ(Mo,Kα) = 2.88 cm^{-1}.

Data Collection

Radiation	:	Mo,Kα
Filter	:	Zr
Maximum scattering angle (2θ)	:	60°
Independent reflections (observed)	:	1481
Unobserved cutoff	:	$2\varsigma_I$
Ratio of observations/parameters	:	9.66

Structure Determination

The structure was determined using direct phasing by the multi-symbolic approach. Normalised structure factors were derived and triplet relationships generated for the 144 reflections with $|E| \geqslant 1.50$. A solution for the 60 strongest reflections was obtained with a set of three origin-defining phases chosen by the program, using relationships of probability $\geqslant 0.85$. All 144 reflections were then phased from this solution and an E-map calculated with these reflections revealed the complete molecule, although the two methyl groups were not resolved. A structure-factor and electron-density calculation resolved these atoms and gave improved atom positions for least-squares refinement.

Structure Refinement

Refinement of positional, thermal and scale parameters converged after 17 cycles of full-matrix least-squares minimisation with residuals R and R' of 0.034 and 0.0012 respectively. The course of refinement is detailed in Table 3.1 .

All hydrogen atoms were located by means of a difference synthesis calculated after cycle 3, and were included in the calculations with initial isotropic thermal parameters of 0.03 Å^2 , prior to refinement in later cycles. Two strong reflections whose intensities were inaccurately measured owing to counter dead-time losses were removed at cycle 7 , and a weighting scheme was applied. Final parameters in a weighting function of the form

$$W = (A + B|F_o| + C|F_o|^2)^{-1}$$

were A = 0.2627 , B = -0.0423 and C = 0.0027 . Anomalous terms in the scattering factor for S were included after cycle 14 .

A difference synthesis calculated on completion of refinement revealed no errors in the structure.

The atomic scattering factors used in final structure-factor calculations were those derived by Cromer and Mann (1968) [39] for S, O, N and C, and by Stewart, Davidson and Simpson (1965) [40] for H.

Observed and final calculated structure factors are listed in Appendix 3 . Fractional coordinates and thermal parameters are given in Table 3.3 , and interatomic distances, angles and intermolecular contacts are given in Table 3.5 , with the estimated standard deviations derived from the inverse of the least-squares normal-equation matrix. Details of two least-squares planes through sections of the molecule are given in Table 3.7 . The atomic numbering scheme and the molecular packing viewed down the a-axis are shown in Figures 3.1 and 3.2 respectively.

3.3 Experimental Compound XII

Preparation of crystals

A sample of the purified compound was recrystallised from a range of solvents. Suitable crystals (single, pyramidal in form and bright orange in colour) were obtained from ethylene chloride solution.

Crystal Data (XII)

N-(p-nitrobenzoyl)-2-iminophenyldimethylsulphur(IV)

$C_{15}H_{14}N_2O_3S$, M = 302.4 .

Orthorhombic, a = 25.971 b = 8.822 c = 13.310 Å,

U = 3046.7 $Å^3$,

D_m = 1.31 g cm^{-3}, Z = 8 , D_c = 1.316 g cm^{-3},

$F_{(000)}$ = 1264 .

Space group : Pbca (D_{2h}^{15} , No.61) , uniquely identified by systematic absences.

μ(Mo,Kα) = 2.23 cm^{-1}.

Data Collection

Radiation	:	Mo,Kα
Filter	:	graphite monochromator
Maximum scattering angle (2θ)	:	60°
Independent reflections (observed)	:	2209
Unobserved cutoff	:	$3\sigma_I$
Ratio of observations/parameters	:	8.93

Structure Determination

The structure was determined by direct methods using the multi-symbolic technique. Normalised structure factors were calculated and triplet relationships derived for those 256 reflections with $|E| \geqslant 1.40$. With a starting set of three origin-defining reflections, a solution for the 60 strongest reflections was obtained using relationships of probability $\geqslant 0.8$. A total of 231 phases were then determined from this solution and the resulting E-map gave positions for all atoms except the nitro group and the ring atom to which it is bonded. A structure-factor and electron-density calculation revealed the remaining four atoms, although both oxygen atom peaks were of unusually low electron density. However, this calculation gave atom positions suitable for least-squares refinement.

Structure Refinement

Refinement by least-squares minimisation was concluded after 22 cycles, with residuals R and R' of 0.040 and 0.0035 respectively, when convergence was indicated by all parameter shifts being small in comparison to their estimated standard deviations. The course of refinement is outlined in Table 3.2 , but requires some amplification.

A difference synthesis calculated at the convergence of isotropic refinement revealed clear positions for only the four hydrogen atoms on the S-phenyl ring, and showed marked anisotropy in the nitro group and neighbouring ring atoms. After several cycles of anisotropic refinement, the thermal parameters for these atoms had risen to a level far in excess of normal thermal vibration, especially in the

b-axial direction (U_{22} for atom O(2) rose to 0.65(2) $Å^2$). While such motion is mechanically plausible as overall motion of the nitrophenyl group (as can clearly be seen in Figure 3.3), various measures were taken to try to ascertain its true nature and to confirm that the effect did not arise from some aberration in the data set.

The affected atoms appeared in a difference map as elongated single peaks with no trace of the peak splitting that is generally indicative of positional disorder. Inspection of a reflection list revealed a considerable number of large discrepancies, Δ (= $|F_o| - |F_c|$), both positive and negative, associated with strong and with weak reflections, most of which occurred at low $\sin\theta/\lambda$ values, indicating generally that some aspect of the refined model was not a good fit to reality.

Anomalous terms in the scattering function for S were included from cycle 10 onwards, and corrections to strong reflections inaccurately measured as a result of counter saturation were made prior to cycle 12 , leading to a reduction in some negative Δ's without changing the overall distribution.

Absorption was not considered to be a serious source of error since the linear absorption coefficient is low and the crystal dimensions were small and not grossly unequal, with a maximum width approximately five times greater than the thickness. The involvement of weak reflections with large Δ's suggests that extinction is not an important factor although it may be present to some degree.

Accordingly, further investigation was carried out by refinement using subsections of the data set. In cycle 13 , ten reflections with $|\Delta| > 10.0$ were excluded from the least-squares calculation. In

cycle 14, 187 reflections with $\sin\theta/\lambda \leqslant 0.25$ were excluded, and in cycle 15, 970 reflections with $\sin\theta/\lambda \leqslant 0.45$ were excluded. In cycles 13 and 14, the residual, R , decreased but there were no major shifts in the parameters, while in cycle 15, a drop in the residual was accompanied by a slight reduction of some high thermal parameters without appreciably altering the pattern of vibration of the molecule. The anomalous thermal motion of the nitrobenzoyl group is thus conclusively shown to be a property of the whole data set.

All remaining hydrogen atoms were observed in a difference map at this stage, and were subsequently included and refined. No major errors in the structure were observed, but some residual electron density was present close to the nitro group oxygen atoms. A weighting scheme was applied at cycle 19 , with coefficients A = 2.701 , B = -0.241 and C = 0.0105 in a function of the form

$$W = (A + B|F_o| + C|F_o|^2)^{-1}$$

The atomic scattering factors used throughout were those derived by Cromer and Mann (1968) [39] for S, O, N and C, and by Stewart, Davidson and Simpson (1965) [40] for H.

Observed and calculated structure factors are listed in Appendix 4 . Fractional coordinates and thermal parameters are listed in Table 3.4 , and interatomic distances, angles and intermolecular contacts are given in Table 3.6 , with their estimated standard deviations, derived from the inverse of the least-squares normal-equation matrix. Details of some least-squares planes through sections of the molecule are given in Table 3.8 . A thermal ellipsoid diagram with the atomic numbering scheme is shown in Figure 3.3 , and the molecular packing viewed down the b-axis is shown in Figure 3.4 .

Table 3.1

Course of refinement (XI)

Cycles	Parameters refined	Final R	Final R'
1 - 3	x,y,z,U_{iso} for S, O, N and C, scale factor. Unit weights.	0.106	0.0112
4	x,y,z,U_{iso} for S, O, N and C, scale factor. H-atom contributions included but not refined. Unit weights.	0.089	0.0069
5 - 6	x,y,z,U_{ij} for S, O, N and C, scale factor. H-atom contributions included but not refined. Unit weights.	0.045	0.0026
7 - 8	x,y,z,U_{ij} for S, O, N and C, scale factor. H-atom contributions included but not refined. Weighting scheme applied.	0.043	0.0022
9 - 11	x,y,z,U_{ij} for S, O, N and C, x,y,z for H, scale factor. Weighting scheme applied.	0.035	0.0018
12 - 14	x,y,z,U_{ij} for S, O, N and C, x,y,z,U_{iso} for H, scale factor. Weighting scheme applied.	0.034	0.0017
15 - 17	x,y,z,U_{ij} for S, O, N and C, x,y,z,U_{iso} for H, scale factor. Anomalous dispersion correction included, weighting scheme modified.	0.034	0.0012

Table 3.2

Course of refinement (XII)

Cycles	Parameters refined	Final R	Final R'
1 - 5	x,y,z,U_{iso} for S, O, N and C, scale factor. Unit weights, full matrix.	0.130	0.0196
6 - 11	x,y,z,U_{ij} for S, O, N and C, scale factor. Contributions for 4 H-atoms included but not refined. Unit weights, full matrix.	0.070	0.0077
12	As previous, but with corrections to strong reflections for counter-saturation errors.	0.063	0.0055
13	As previous, but with all reflections with $\|\Delta\| > 10.0$ excluded (10 reflections). No major shifts in parameters.	0.062	0.0056
14	As previous, but with all reflections with $\sin\theta/\lambda \leq 0.25$ ($2\theta \approx 20^{\circ}$) excluded (187 reflections). No major shifts in parameters.	0.054	0.0035
15	As previous, but with all reflections with $\sin\theta/\lambda \leq 0.45$ ($2\theta \approx 37^{\circ}$) excluded (970 reflections). Some shifts in thermal parameters, but no major changes.	0.043	0.0025
16 - 18	x,y,z,U_{ij} for S, O, N and C, x,y,z,U_{iso} for H (14 H-atoms), scale factor, Unit weights, blocked matrix.	0.040	0.0014
19 - 22	x,y,z,U_{ij} for S, O, N and C; x,y,z,U_{iso} for H, scale factor. Weighting scheme applied, blocked matrix.	0.040	0.0035

Table 3.3

a) Fractional Coordinates for XI

	x/a	y/b	z/c
S	0.94523(6)	0.79026(7)	0.14911(5)
N	0.8318(2)	0.9268(2)	0.1081(2)
O	0.8397(2)	0.9923(2)	0.3008(1)
C(1)	0.6922(2)	1.1375(3)	0.1702(2)
C(2)	0.6210(3)	1.1445(3)	0.0638(2)
C(3)	0.5195(3)	1.2562(4)	0.0432(3)
C(4)	0.4890(3)	1.3626(4)	0.1266(3)
C(5)	0.5607(3)	1.3577(3)	0.2313(3)
C(6)	0.6613(3)	1.2456(3)	0.2537(2)
C(7)	0.7961(2)	1.0117(3)	0.1992(2)
C(8)	0.8391(4)	0.6319(4)	0.1890(4)
C(9)	0.9975(4)	0.7281(4)	0.0119(3)

Table 3.3 (cont.)

b) H-atom fractional coordinates and isotropic thermal parameters ($Å^2$) for XI

	x/a	y/b	z/c	U iso
H(2)	0.640(2)	1.066(3)	0.009(2)	0.063(7)
H(3)	0.469(3)	1.254(3)	-0.025(3)	0.080(9)
H(4)	0.422(3)	1.436(3)	0.114(2)	0.077(9)
H(5)	0.544(3)	1.437(3)	0.284(2)	0.069(8)
H(6)	0.714(3)	1.242(3)	0.332(2)	0.060(7)
H(81)	0.775(3)	0.613(4)	0.127(3)	0.091(11)
H(82)	0.798(4)	0.661(4)	0.270(3)	0.130(15)
H(83)	0.898(3)	0.547(4)	0.200(3)	0.095(11)
H(91)	0.910(3)	0.695(3)	-0.037(2)	0.085(10)
H(92)	1.062(3)	0.642(4)	0.027(2)	0.083(9)
H(93)	1.045(3)	0.816(4)	-0.016(3)	0.089(11)

Table 3.3 (cont.)

c) Anisotropic thermal parameters ($Å^2$) for XI

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	0.0495	0.0432	0.0519	0.0067	-0.0050	-0.0024
N	0.0570	0.0425	0.0486	0.0127	-0.0045	-0.0022
O	0.0572	0.0633	0.0456	0.0110	-0.0079	-0.0020
C(1)	0.0404	0.0375	0.0462	-0.0676	0.0064	0.0042
C(2)	0.0643	0.0543	0.0479	0.0147	0.0002	-0.0015
C(3)	0.0769	0.0808	0.0527	0.0295	-0.0071	0.0051
C(4)	0.0648	0.0626	0.0689	0.0266	0.0129	0.0107
C(5)	0.0672	0.0580	0.0646	0.0155	0.0142	-0.0074
C(6)	0.0545	0.0553	0.0490	0.0066	0.0029	-0.0047
C(7)	0.0392	0.0374	0.0495	-0.0050	0.0010	0.0015
C(8)	0.0680	0.0540	0.1068	0.0019	0.0020	0.0233
C(9)	0.0837	0.0547	0.0624	0.0167	0.0082	-0.0049

Mean estimated standard deviations ($Å^2$)

S	0.0003	0.0003	0.0003	0.0003	0.0002	0.0003
N	0.0012	0.0011	0.0011	0.0009	0.0009	0.0009
O	0.0010	0.0011	0.0009	0.0008	0.0007	0.0008
C	0.0016	0.0016	0.0017	0.0013	0.0013	0.0013

Table 3.4

a) Fractional Coordinates for XII

	x/a	y/b	z/c
S	-0.03927(2)	0.35228(6)	0.45909(4)
N(1)	0.01670(7)	0.12640(23)	0.37049(14)
N(2)	0.25542(15)	0.10654(87)	0.48720(44)
O(1)	0.05267(7)	0.05156(27)	0.21956(13)
O(2)	0.29145(12)	0.07771(122)	0.43575(41)
O(3)	0.25981(13)	0.13269(78)	0.57423(37)
C(1)	-0.06899(8)	0.21633(27)	0.38015(15)
C(2)	-0.03394(8)	0.11201(27)	0.33919(15)
C(3)	-0.05485(11)	-0.00220(33)	0.27799(18)
C(4)	-0.10712(11)	-0.00636(36)	0.25864(20)
C(5)	-0.14004(11)	0.10072(39)	0.29672(23)
C(6)	-0.12149(10)	0.21321(35)	0.35910(20)
C(7)	0.10753(9)	0.09538(30)	0.35806(18)
C(8)	0.11382(11)	0.12990(33)	0.45911(21)
C(9)	0.16264(13)	0.13595(46)	0.50121(28)
C(10)	0.20383(12)	0.10327(59)	0.44173(35)
C(11)	0.19908(13)	0.06907(84)	0.34125(38)
C(12)	0.15054(12)	0.06536(60)	0.30053(32)
C(13)	0.05496(9)	0.08832(29)	0.30976(17)
C(14)	-0.03174(13)	0.25035(37)	0.57472(21)
C(15)	-0.08967(11)	0.48056(37)	0.49308(23)

Table 3.4 (contd.)

b) H-atom fractional coordinates and isotropic thermal parameters ($Å^2$) for XII.

	x/a	y/b	z/c	U iso
H(3)	-0.035(1)	-0.078(4)	0.256(2)	0.060(8)
H(4)	-0.121(1)	-0.086(4)	0.219(2)	0.072(9)
H(5)	-0.177(1)	0.100(3)	0.286(2)	0.063(8)
H(6)	-0.143(1)	0.284(4)	0.393(2)	0.066(9)
H(8)	0.087(1)	0.150(3)	0.496(2)	0.053(8)
H(9)	0.164(1)	0.157(4)	0.568(3)	0.079(11)
H(11)	0.227(2)	0.045(6)	0.302(4)	0.138(17)
H(12)	0.145(1)	0.037(5)	0.226(3)	0.112(14)
H(141)	-0.012(1)	0.159(4)	0.559(2)	0.077(10)
H(142)	-0.063(1)	0.226(4)	0.597(2)	0.071(9)
H(143)	-0.013(1)	0.314(4)	0.620(3)	0.082(10)
H(151)	-0.117(1)	0.424(3)	0.520(2)	0.058(8)
H(152)	-0.075(1)	0.548(3)	0.543(2)	0.060(8)
H(153)	-0.098(1)	0.530(4)	0.431(3)	0.069(9)

Table 3.4 (cont.)

c) Anisotropic thermal parameters ($\AA^2$) for XII

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	0.0382 4	0.0442 4	0.0369 4	0.0000 2	0.0016 2	-0.0016 2
N(1)	0.0413 9	0.0493 12	0.0377 9	0.0058 9	-0.0009 7	-0.0048 8
N(2)	0.0488 19	0.3298 82	0.1556 42	-0.0167 33	-0.0268 26	-0.0048 50
O(1)	0.0572 11	0.0982 17	0.0434 10	0.0098 10	0.0022 8	-0.0201 10
O(2)	0.0445 17	0.6783 164	0.2037 47	0.0282 43	-0.0214 25	-0.0530 74
O(3)	0.0828 24	0.3867 87	0.1496 33	-0.0413 34	-0.0545 25	0.0033 47
C(1)	0.0398 11	0.0455 13	0.0365 11	-0.0041 10	-0.0007 9	-0.0008 10
C(2)	0.0453 11	0.0472 13	0.0298 10	-0.0655 10	-0.0010 8	0.0025 8
C(3)	0.0602 15	0.0511 14	0.0388 12	-0.0066 12	0.0008 11	-0.0020 11
C(4)	0.0653 17	0.0671 18	0.0458 13	-0.0212 15	-0.0068 12	-0.0049 13
C(5)	0.0441 13	0.0849 21	0.0612 16	-0.0175 14	-0.0087 12	-0.0025 15
C(6)	0.0404 12	0.0670 17	0.0565 14	-0.0002 13	-0.0027 11	-0.0028 14
C(7)	0.0425 12	0.0510 13	0.0524 13	0.0038 11	-0.0011 10	-0.0004 11
C(8)	0.0469 13	0.0692 18	0.0554 14	-0.0051 12	-0.0049 12	0.0061 14
C(9)	0.0605 18	0.1003 26	0.0697 20	-0.0173 17	-0.0192 15	0.0092 20
C(10)	0.0401 14	0.1478 39	0.1154 32	-0.0039 20	-0.0174 18	0.0078 30
C(11)	0.0425 17	0.2417 70	0.1068 33	0.0140 28	0.0029 19	-0.0395 38

Table 3.4.c (cont.)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(12)	0.0497	0.1617	0.0796	0.0154	0.0038	-0.0291
	16	41	23	21	16	26
C(13)	0.0463	0.0452	0.0414	0.0050	-0.0008	-0.0016
	11	13	12	10	10	10
C(14)	0.0679	0.0573	0.0372	0.0008	-0.0040	0.0025
	18	16	11	15	12	11
C(15)	0.0510	0.0611	0.0489	0.0100	0.0082	-0.0036
	14	17	14	13	12	14

Table 3.5

Interatomic distances and angles for XI

a) Bonded distances (Å)

S - N	1.659(2)	C(1) - C(2)	1.385(3)
S - C(8)	1.779(4)	C(2) - C(3)	1.384(4)
S - C(9)	1.776(3)	C(3) - C(4)	1.377(4)
N - C(7)	1.344(3)	C(4) - C(5)	1.371(4)
O - C(7)	1.246(3)	C(5) - C(6)	1.383(4)
C(7) - C(1)	1.502(3)	C(6) - C(1)	1.388(3)

b) Interbond angles (°)

S - N - C(7)	110.4(1)	C(7)-C(1)-C(2)	121.8(2)
N - S - C(8)	104.2(1)	C(7)-C(1)-C(6)	119.3(2)
N - S - C(9)	99.5(1)	C(1)-C(2)-C(3)	120.0(2)
C(8)-S - C(9)	101.0(2)	C(2)-C(3)-C(4)	120.9(2)
N - C(7)-O	125.9(1)	C(3)-C(4)-C(5)	119.4(2)
C(1)-C(7)-O	120.0(2)	C(4)-C(5)-C(6)	120.4(2)
N - C(7)-C(1)	114.1(1)	C(5)-C(6)-C(1)	120.5(2)
		C(6)-C(1)-C(2)	118.9(2)

c) Intramolecular non-bonded distances (Å)

S ....O	2.71	S ....C(7)	2.47
N ....O	2.31	N ....C(2)	2.79
O ....C(6)	2.81	O ....C(8)	3.37
C(7)...C(8)	3.31		

Table 3.5 (cont.)

d) Intermolecular distances (Å)

C(5)...C(8)^{I}	3.61	C(4)...C(1)^{II}	3.82
C(6)...C(8)^{I}	3.84	C(5)...C(7)^{II}	3.79
C(4)...O^{II}	3.49	C(5)...C(1)^{II}	3.64
C(4)...C(7)^{II}	3.71	O ....C(9)^{III}	3.40

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

I x, 1+y, z ; II -1-x, 1/2+y, 1/2-z ;
III x, -1/2-y, 1/2+z .

e) Torsion angles (^{o})

S - N - C(7)-O	-0.5
S - N - C(7)-C(1)	-179.4
N - C(7)-C(1)-C(2)	11.7
N - C(7)-C(1)-C(6)	-171.5
O - C(7)-C(1)-C(2)	-167.3
O - C(7)-C(1)-C(6)	9.5
C(7)-N - S - C(8)	87.4
C(7)-N - S - C(9)	-168.6

Mean e.s.d. 0.2^{o}

Table 3.6

Interatomic distances and angles for XII

a) Bonded distances (Å)

S	- C(1)	1.772(2)	C(5)	- C(6)	1.381(4)
S	- C(14)	1.793(3)	C(6)	- C(1)	1.392(3)
S	- C(15)	1.789(3)	C(7)	- C(8)	1.389(4)
N(1)	- C(2)	1.385(3)	C(8)	- C(9)	1.387(4)
N(1)	- C(13)	1.324(3)	C(9)	- C(10)	1.362(5)
O(1)	- C(13)	1.245(3)	C(10)	- C(11)	1.377(7)
C(13)	- C(7)	1.511(3)	C(11)	- C(12)	1.373(5)
C(1)	- C(2)	1.405(3)	C(12)	- C(7)	1.380(4)
C(2)	- C(3)	1.405(3)	C(10)	- N(2)	1.470(5)
C(3)	- C(4)	1.382(4)	N(2)	- O(2)	1.187(7)
C(4)	- C(5)	1.371(4)	N(2)	- O(3)	1.187(8)

Mean C - H (Methyl) 0.95(3) Mean C - H (Aryl) 0.94(4)

Table 3.6 (cont.)

b) Interbond angles (^{o})

C(1) -S -C(14)	102.5(1)	C(4) -C(5) -C(6)	120.0(2)
C(1) -S -C(15)	105.0(1)	C(5) -C(6) -C(1)	118.5(2)
C(14)-S -C(15)	100.4(1)	C(13)-C(7) -C(8)	121.8(2)
S -C(1) -C(2)	113.0(1)	C(13)-C(7) -C(12)	119.2(2)
S -C(1) -C(6)	124.0(1)	C(7) -C(8) -C(9)	120.5(2)
C(1) -C(2) -N(1)	116.0(1)	C(8) -C(9) -C(10)	118.4(3)
C(3) -C(2) -N(1)	127.4(2)	C(9) -C(10)-C(11)	122.7(3)
C(2) -N(1) -C(13)	120.4(1)	C(10)-C(11)-C(12)	118.1(3)
N(1) -C(13)-O(1)	128.2(1)	C(11)-C(12)-C(7)	121.3(3)
N(1) -C(13)-C(7)	114.1(2)	C(9) -C(10)-N(2)	118.2(3)
O(1) -C(13)-C(7)	117.7(2)	C(11)-C(10)-N(2)	119.1(3)
C(6) -C(1) -C(2)	122.9(2)	C(10)-N(2) -O(2)	118.5(4)
C(1) -C(2) -C(3)	116.4(2)	C(10)-N(2) -O(3)	119.6(3)
C(2) -C(3) -C(4)	120.5(2)	O(2) -N(2) -O(3)	121.9(4)
C(3) -C(4) -C(5)	121.7(2)	C(12)-C(7) -C(8)	119.0(2)

Table 3.6 (cont.)

c) Intramolecular non-bonded distances (Å)

S ....N(1)	2.73	O(1)...C(3)	2.93
N(1)...C(14)	3.19	O(1)...C(12)	2.76
N(1)...O(1)	2.31	O(2)...C(11)	2.71
N(1)...C(8)	2.78	O(3)...C(9)	2.70
O(1)...C(2)	2.81	O(2)...O(3)	2.08

d) Intermolecular distances (Å)

$N(1)...C(14)^{I}$	3.42	$C(14)..C(2)^{III}$	3.72
$C(9)...C(4)^{I}$	3.69	$C(14)..C(3)^{III}$	3.55
$C(9)...C(5)^{I}$	3.45	$C(15)..C(4)^{III}$	3.57
$C(14)..O(1)^{I}$	3.86	$S ....O(1)^{IV}$	2.98
$C(14)..C(13)^{I}$	3.41	$C(1)...O(1)^{IV}$	3.27
$C(14)..C(3)^{I}$	3.70	$C(6)...O(1)^{IV}$	3.63
$C(14)..C(7)^{I}$	3.74	$C(15)..O(1)^{IV}$	3.05
$S ....S^{II}$	3.48	$O(2)...C(5)^{V}$	3.58
$S ....C(15)^{II}$	3.71	$O(2)...C(15)^{VI}$	3.27
$C(15)..C(8)^{II}$	3.55	$O(3)...C(6)^{VI}$	3.48
$C(14)..O(1)^{III}$	3.40		

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

I	-x,	-y,	1-z ;	II	-x,	1-y,	1-z ;
III	x,	1/2-y,	1/2+z ;	IV	-x,	1/2+y,	1/2-z ;
V	1/2+x,	y,	1/2-z ;	VI	1/2+x,	1/2-y,	1-z .

Table 3.6 (cont.)

e) Torsion angles (^{o})

C(2)-N(1) -C(13)-O(1)	7.5	C(2) -C(1) -S -C(14)	-80.3
C(2)-N(1) -C(13)-C(7)	-174.2	C(2) -C(1) -S -C(15)	175.2
N(1)-C(13)-C(7) -C(8)	3.8	C(6) -C(1) -S -C(14)	100.6
N(1)-C(13)-C(7) -C(12)	-176.8	C(6) -C(1) -S -C(15)	-4.0
O(1)-C(13)-C(7) -C(8)	-177.6	C(9) -C(10)-N(2)-O(2)	179.8
O(1)-C(13)-C(7) -C(12)	1.8	C(9) -C(10)-N(2)-O(3)	2.3
N(1)-C(2) -C(1) -S	3.3	C(11)-C(10)-N(2)-O(2)	-0.9
N(1)-C(2) -C(1) -C(6)	-177.6	C(11)-C(10)-N(2)-O(3)	178.4
N(1)-C(2) -C(3) -C(4)	175.7	C(13)-N(1) -C(2)-C(1)	-149.5
		C(13)-N(1) -C(2)-C(3)	36.3

Mean e.s.d. 0.3^{o}

Table 3.7

Least-squares planes for XI

a) Equation of plane i) $0.7105X + 0.6161Y - 0.3400Z + 10.0379 = 0$

ii) $0.7593X + 0.6329Y - 0.1512Z + 10.8922 = 0$

b) Deviation of atoms from the plane (Å)

i)	S	-0.036	N	0.095	O	-0.336
	C(7)	-0.091	C(9)	0.583	C(8)	-1.774
	C(1)	-0.005*	C(2)	0.007*	C(3)	-0.002*
	C(4)	-0.004*	C(5)	0.006*	C(6)	-0.002*
ii)	S	-0.010	C(9)	0.327	C(1)	-0.002*
	C(7)	0.006*	O	-0.002*	N	-0.002*

c) Dihedral angle between planes i) and ii) : 11.2° .

* denotes atom used to define plane.

X, Y and Z are orthogonal coordinates in Å .

Table 3.8

Least-squares planes for XII

a) Equation of plane i) $-0.1430X - 0.5847Y + 0.7986Z + 3.1678 = 0$

ii) $0.0736X + 0.9699Y - 0.2322Z - 0.0846 = 0$

iii) $-0.0917X - 0.9578Y + 0.2723Z + 0.2374 = 0$

b) Deviation of atoms from the plane (Å)

i)	S	0.041	N(1)	0.056	C(13)	-0.535
	C(15)	-0.072	C(1)	0.013*	C(2)	-0.014*
	C(3)	0.002*	C(4)	0.012*	C(5)	-0.013*
	C(6)	0.001*				
ii)	N(1)	0.053	O(1)	-0.052	C(13)	-0.012
	N(2)	-0.022	O(2)	-0.040	O(3)	-0.058
	C(7)	-0.001*	C(8)	-0.006*	C(9)	0.010*
	C(10)	-0.008*	C(11)	0.001*	C(12)	0.003*
iii)	C(7)	-0.002*	C(13)	0.008*	N(1)	-0.003*
	O(1)	-0.003*				

c) Dihedral angles between planes : i) and ii) 139.7°,

ii) and iii) 2.6° , i) and iii) 37.8° .

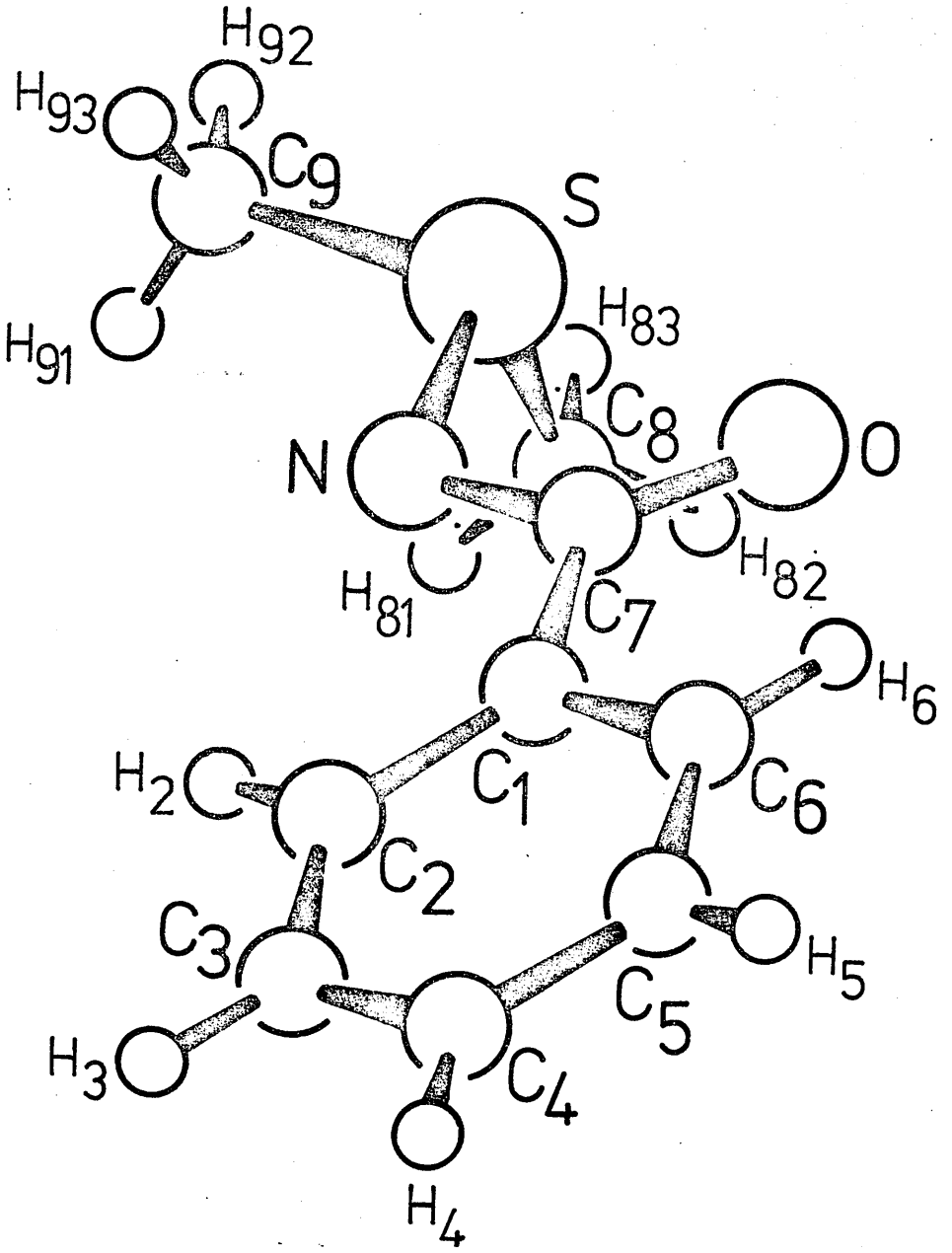
* denotes atom used to define plane.

X, Y and Z are orthogonal coordinates in Å .

Figure 3.1

Atomic numbering scheme

(XI)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H93
C9
S
H91
H83
C8
N
O
H81
H82
C7
H6
H2
C1
C6
C2
C3
H5
C5
H3
C4
H4

Figure 3.2

Molecular packing arrangement

viewed down the a-axis

(XII)

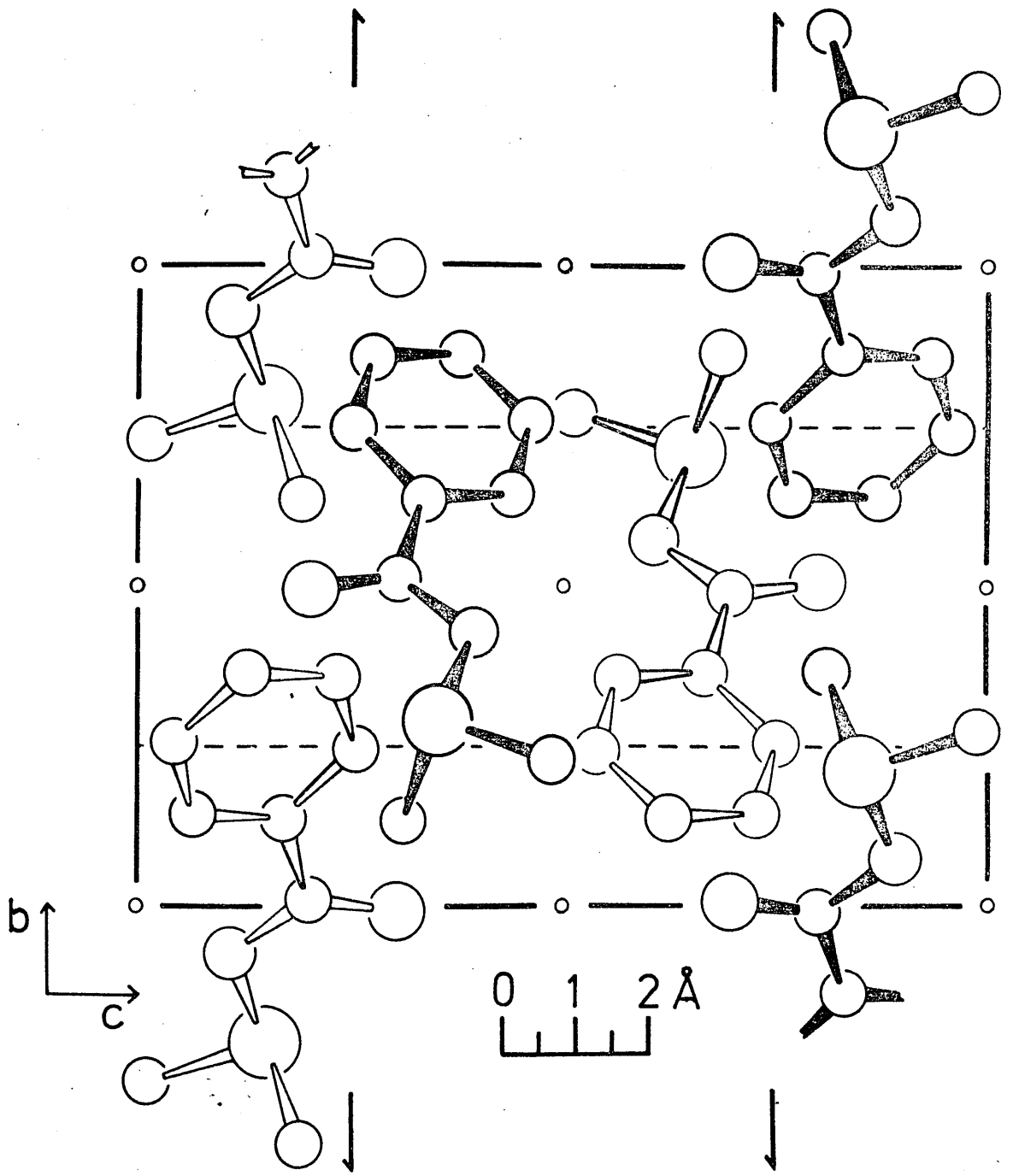

b
c
0 1 2 Å

Figure 3.3

Atomic numbering scheme

(XII)

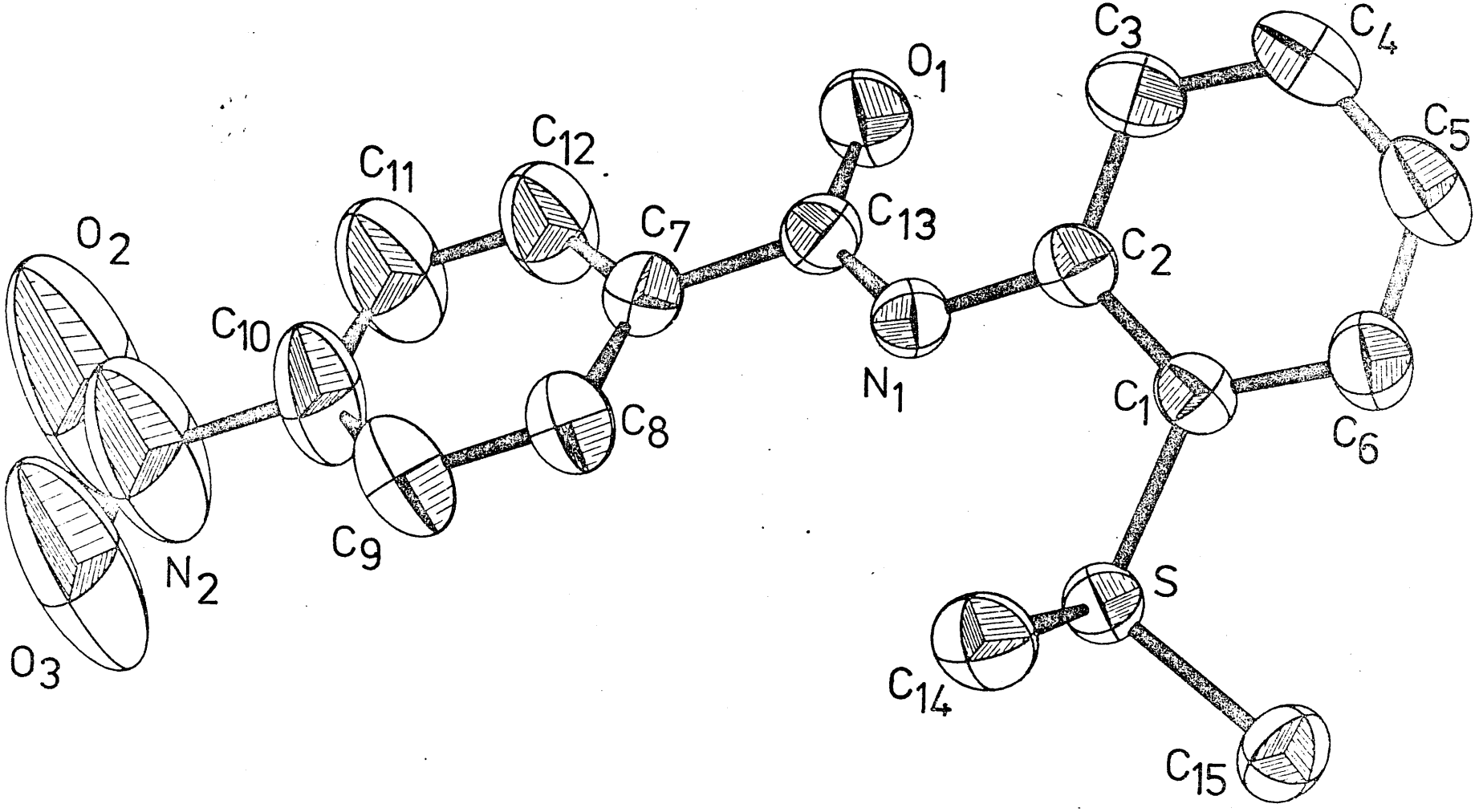
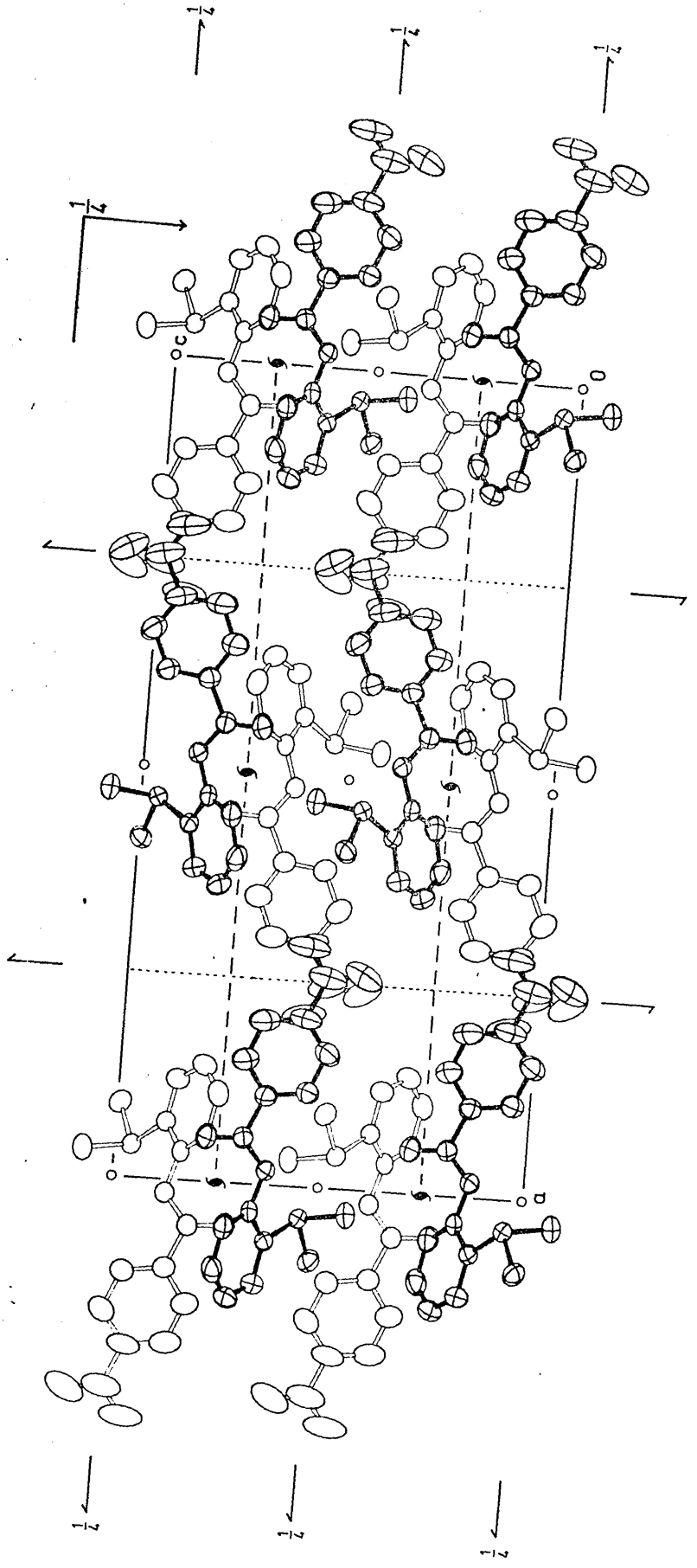

O1
C3
C4
C5
C12
C11
C7
C13
C2
O2
C10
N1
C1
C6
C8
C9
N2
S
O3
C14
C15

Figure 3.4

Molecular packing arrangement

viewed down the b-axis

(XII)

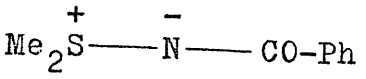


3.4 Discussion

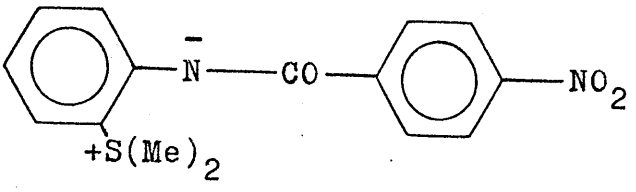
The structure analyses of compounds XI and XII have yielded results which give further insight into the stabilisation in sulphonium imines, and the interaction in a variety of environments of an imine nitrogen atom (carrying two lone pairs) with a stabilising carbonyl group. The analysis of XII has also revealed an unusual crystal-state phenomenon, which is indicated by the enlarged vibrational parameters of the nitrobenzoyl group in the refined model.

Comparison of details of the molecular geometry of these compounds with compounds XIII [13], II [16] and XV [43] is of great interest. Comparison with compound XIV [14] is also possible but is of less validity since e.s.d.s are not given with the quoted dimensions and, moreover, the high uncorrected absorption in the photographic data suggests that these results may be of low precision and accuracy. Consequently this comparison has not been made here. The structure of the ylide, XI , will be discussed first.

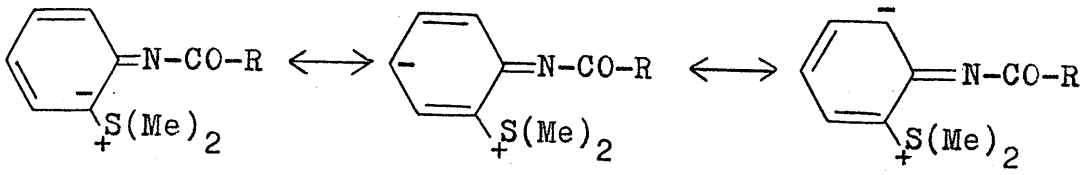
As in other sulphonium imines, clear evidence of charge delocalisation from the negative nitrogen atom to the sulphonium group in XI, by $d\pi$-$p\pi$ interaction is provided by the shortness of the S-N bond, 1.659(2) Å , relative to the single bond length in sulphamic acid, 1.772(1) Å (see section 6). This S-N length is experimentally identical to the value observed in the similar trichloroacetyl imine, XIII , 1.667(7) Å , but is probably significantly longer than the values in the sulphonyl-stabilised imines, IV [17] and V [11], 1.636(8) and 1.628(7) Å respectively. These differences provide further support for the suggestion[19] that the $\overset{+}{S} - \overset{-}{N}$ length may indicate the



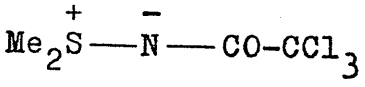
XI



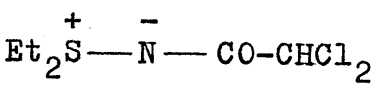
XII



a b c



XIII



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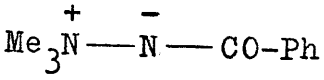
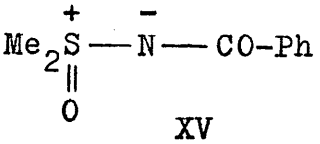
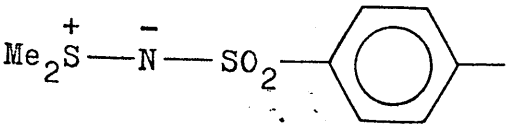


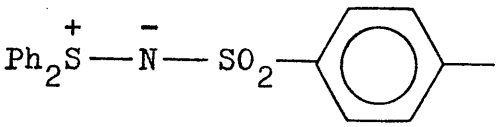
II



XV



IV



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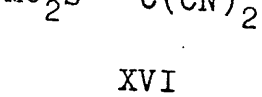
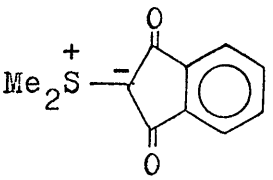


XVI



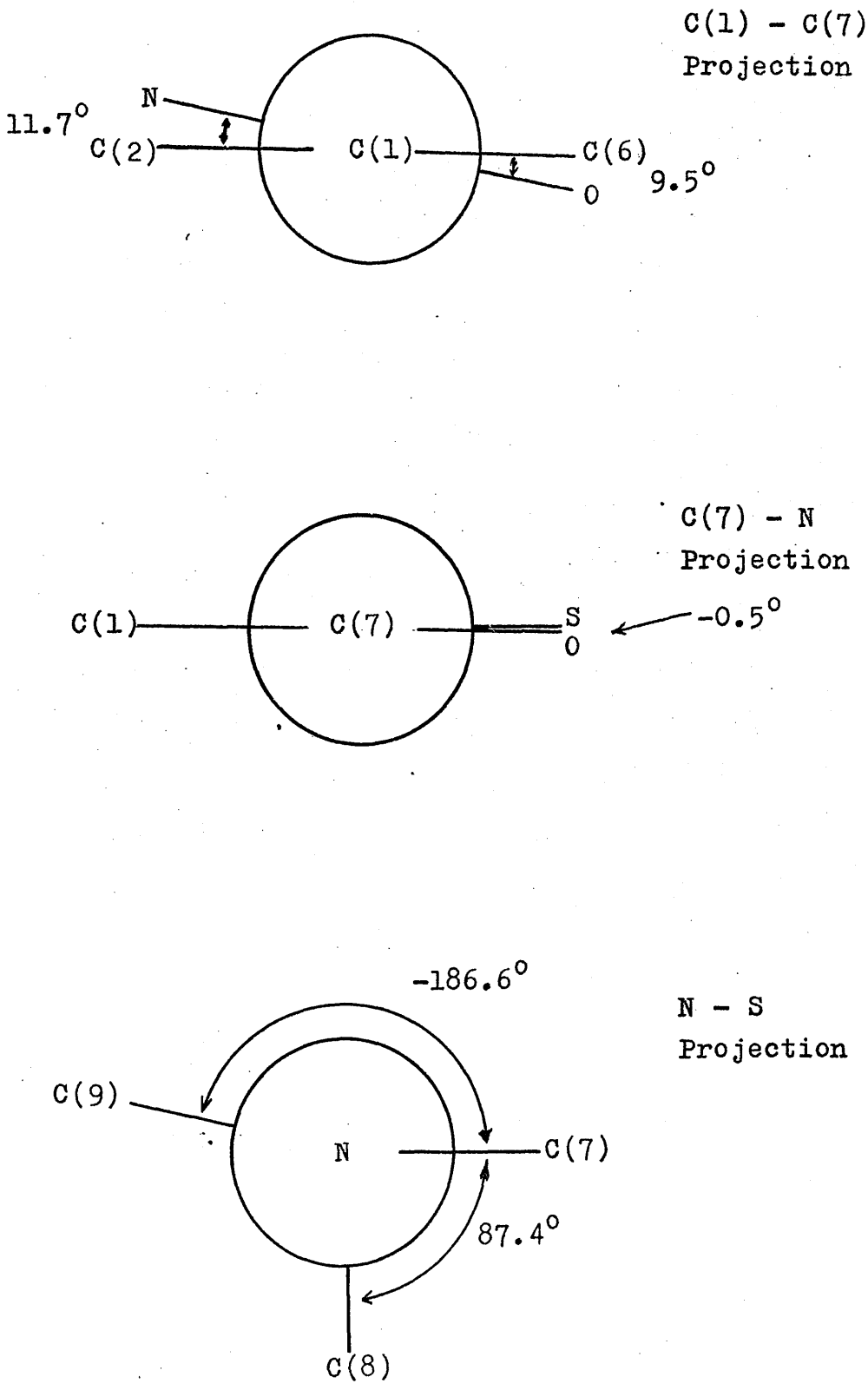
XVII

effectiveness of the stabilising group, since increasing the delocalisation to the stabilising group appears to detract from delocalisation across the ylide bond.

The carbonyl group in XI assumes an orientation effectively coplanar with the imine nitrogen, with a torsion angle S-N-C(7)-O of -0.5° , similar to the conformations observed in II, XIII and XV, and indicating π-overlap with the p-orbital lone pair on the nitrogen. The short N-C bond, 1.344(3) Å ,and the long carbonyl bond, 1.246(3) Å , indicate the considerable delocalisation resulting from this overlap. Appreciable involvement of the benzene ring is not indicated, since the C(7)-C(1) bond, 1.502(3) Å , is typical of $C(sp^2)$-$C(sp^2)$ single bond lengths, and no deviations from normal ring geometry occur (mean C_{ar}-C_{ar} = 1.381(4) Å and mean C_{ar}-C_{ar}-C_{ar} = 120.1(2)$^{\circ}$). Furthermore, the ring is twisted by 11.2° from the carbonyl plane, in common with the analogous molecule, II , where an 18° twist is found. This twisting may arise from the need to minimise the O....C(6) and N....C(2) close contacts (2.81 and 2.79 Å respectively in XI), and, although not sufficient to prevent overlap with the carbonyl group, will reduce any overlap occurring.

The asymmetric disposition of the pyramidal dimethylsulphonium group about the N-S bond is illustrated in Figure 3.5 by the Newman projection along that bond. This reveals the approximate staggered arrangement of the methyl groups relative to the imine moiety, and especially the trans-disposition of the sulphonium lone pair to the sp^2-type lone pair on the nitrogen. This type of asymmetric orientation is typical of sulphonium imines, where varying degrees of asymmetry are observed[10-14] with a range of about 35° in the

Figure 3.5


C(1) - C(7)
Projection
N
11.7°
C(2)
C(1)
C(6)
O
9.5°
C(7) - N
Projection
C(1)
C(7)
S
O
-0.5°
N - S
Projection
-186.6°
C(9)
N
C(7)
87.4°
C(8)

relevant torsion angles about the N-S bond. This variation has been explained by the theoretical study of rotation about the $\overset{+}{S} - \overset{-}{N}$ bond[23], which showed that when no other substituent on the $\overset{+}{S}$ atom provided a $d\pi$-interaction, rotational barriers were determined by steric interactions and, particularly, by lone pair - lone pair repulsion forces. The conformation observed is probably a compromise resulting from the balance of lone pair - lone pair repulsion with the steric interactions of the cis-oxygen with the sulphur lone pair and C(8) methyl group, (S....O 2.71 , C(8)...O 3.37 Å). That the crystal packing may also influence the conformation to a limited extent is suggested by the van der Waals contact distance of O....C(9), 3.49 Å . All other intermolecular distances are greater than the sum of the appropriate van der Waals' radii.

Another feature typical of sulphonium imines and present in this case is the small valence angle at the anionic nitrogen atom, 110.4(1)°, identical to that in XIII , 110.0(6)°, but less than the angles of 113.4(5)° in both IV and V . One consequence of this low angle is the increased s content of the trigonal lone-pair orbital, and a possible inference from this is that little π'-bonding to the sulphur occurs in this compound, as has been indicated in the sulphonyl-stabilised counterparts. It has been suggested[20] that a principal reason for this may be the destabilising effect of the sulphonium lone pair on those d-orbitals in the plane of the compound, with a resulting inhibition of the tendency to form π'-bonding.

The conformation adopted by compound XII is more or less extended, but with certain deviations from planarity that are significant with regard to the possible delocalisation throughout the molecule.

Primary among these is the torsion about the N(1)-C(2) bond, representing a twisting of the phenyl ring by 37.8° from the plane of the carbonyl-imine system. A twist of this magnitude is probably sufficient to reduce $p\pi$-orbital overlap to a small fraction of that possible in the ideal planar conformation, and therefore to prevent any appreciable delocalisation by resonance with the aromatic ring. In agreement with this is the N(1)-C(2) bond length of 1.385(3) Å which is relatively long for a $N(sp^2)$-$C(sp^2)$ bond, being significantly longer than the N-C distance in pyridine, 1.340(5) Å [41], although shorter than the $N(sp^2)$-$C(sp^2)$ bond in the pyridinium methylide, IX, 1.42(1) Å [7]. This implies, at most, a low double bond order in this bond. In further support is the long S-C(1) bond, 1.772(2) Å, comparable to the S-$C(sp^2)$ bonds in V, 1.769(8) and 1.799(8) Å [11], and effectively a single bond length in contrast to the S-C lengths in compounds XVI and XVII, 1.730(8) and 1.707(4) Å respectively[44,45], suggesting negligible interaction of the ring system with the sulphonium species, and no contribution from the ylidic resonance structure XIIa. Possibly conflicting with these conclusions is the perceptible lengthening of the C(1)-C(2) and C(2)-C(3) bonds to 1.405(3) Å although the differences from the other ring bonds are of the order of experimental uncertainty and may not be significant. However, the remaining ring bonds are unaffected and the overall ring geometry is nevertheless normal (mean C_{ar}-C_{ar} 1.384(4) Å and mean C_{ar}-C_{ar}-C_{ar} 120.0(2)°).

The major delocalisation of the negative charge on the nitrogen must consequently take place into the carbonyl group. In parallel with this conclusion is the evidence of the short N(1)-C(13) bond,

1.324(3) Å , indicative of high double bond character, and the long carbonyl bond length, 1.245(3) Å , suggestive of reduced double bonding relative to an unconjugated carbonyl group. In addition, the C(2)-N(1)-C(13)-O(1) grouping is close to planarity, although a significant deviation of 7.5° from exact planarity must lead to some diminution from the maximum possible interaction. This system therefore bears a marked similarity to that in II, the ammonium imine, where delocalisation to the carbonyl group alone occurs[16], in that the N-CO and C=O bond lengths, 1.313(6) and 1.243(5) Å , are identical to those of XII , and moreover a twist of 2.2° from planarity is observed. In the sulphonium imine XI , however, where some negative charge is delocalised to the sulphur, the N-CO bond lengthens significantly to 1.344(3) Å , although the carbonyl bond is unaffected, but on progressing to the sulphoxy-imine, XV [43], where the S-N distance of 1.565(4) Å indicates a powerful π-interaction to the 'onium group, the N-CO bond undergoes further significant lengthening to 1.367(4) Å with a concomitant shortening of the carbonyl bond to 1.222(4) Å . In addition, therefore, to the competitive influence of the stabilising group on the delocalisation to the 'onium group, suggested in previous studies[19] and supported by this work, the competitive influence of the 'onium group on the imine-carbonyl stabilising system is clearly demonstrated by the above discussion.

The effect of electronegative substitution on a stabilising group is illustrated by the trichloroacetyl-stabilised imine, XIII [13], in which both the N-CO and C=O bonds are shortened, to 1.320(10) and 1.227(10) Å respectively, suggesting that purely inductive electron-withdrawing effects may have only a minor influence on the efficiency

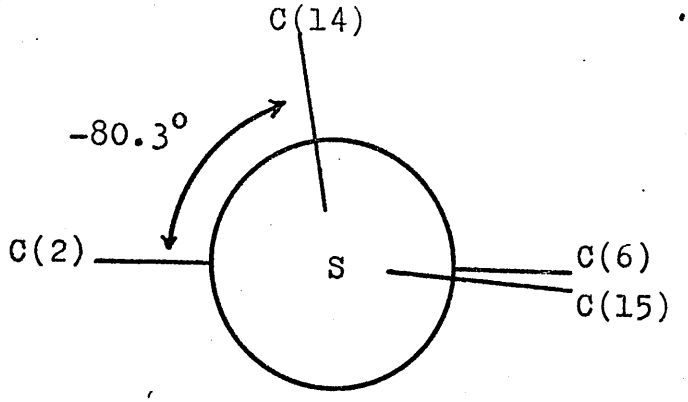
of a stabilising group. However, in view of the e.s.d.s quoted for the parameters of XIII , such small differences in dimensions are not statistically significant and may be misleading.

The major conformational features of XII are illustrated by the Newman projections in Figure 3.6 . The 36° torsion about the N(1)-C(2) bond may arise from the steric interactions O(1)...C(3) 2.93 Å , N(1)...S 2.73 Å and N(1)...C(8) 2.78 Å , which would increase as the torsion decreased, and may therefore force the molecule into its observed orientation. The orientation of the dimethylsulphonium group is also probably determined largely by these interactions, with a staggered arrangement of the sulphur lone pair and methyl group in relation to the nitrogen sp^2-type lone pair being adopted. A further possible consequence of these intramolecular contacts is the valence angle at the imine nitrogen, which, although almost exactly the trigonal angle, 120.4(1)°, is significantly larger than that in XI . Increasing this angle will tend to reduce the above steric interactions.

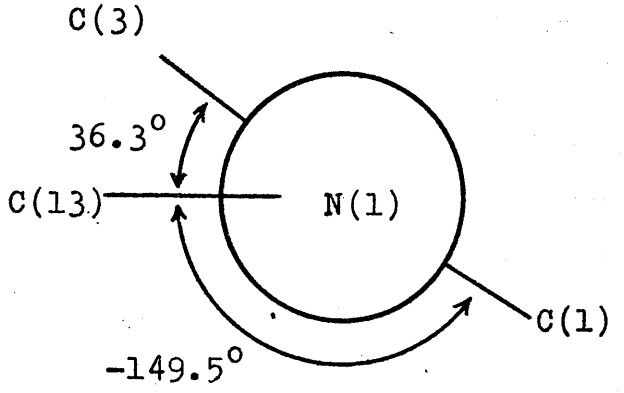
The S^+-Me bond lengths, 1.789(3) and 1.793(3) Å , are experimentally equal, and fall within the range 1.776(3) to 1.801(13) Å observed for similar S(IV)-C(sp^3) bonds in compounds IV, XI, XIII and XVII [13,17,45].

In compound XII the nitrobenzene ring adopts a conformation twisted by only 2.6° from coplanarity with the carbonyl plane despite the short contact O(1)...C(12) 2.76 Å . This contrasts with the conformations of the benzene rings in II and XI , where torsion angles of 18.5° and 11.2° are found. The geometry of the nitrobenzene ring is essentially normal, with mean C_{ar}-C_{ar} = 1.376(5) Å and mean C_{ar}-C_{ar} -C_{ar} = 120.2(3)°, but the shortness of the C(9)-C(10) bond, if significant, probably arises from errors resulting from the large vibrational motion at right

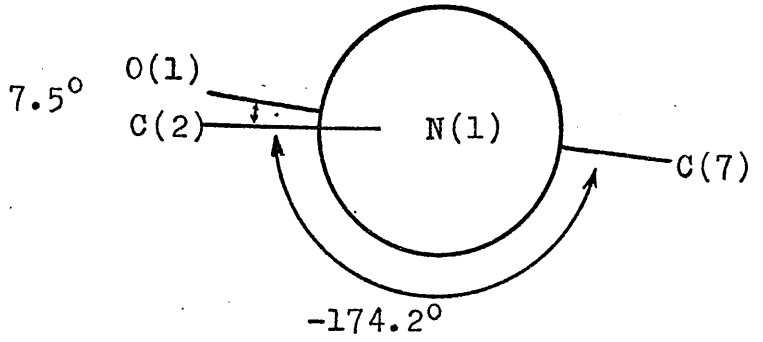
Figure 3.6



S - C(1)
Projection



N(1) - C(2)
Projection



N(1) - C(13)
Projection

angles to the ring plane. The C(10)-N(2) bond length, 1.470(5) Å, is in agreement with typical nitro - ring bonds in the literature, but the N(2)-O(2) and N(2)-O(3) bonds, 1.187(7) and 1.187(8) Å, are similarly shortened from typical values of 1.22 Å [33,46], almost certainly as a consequence of the large vibrational motion. Angular oscillation about the C-N axis is a well known feature of nitro-group behaviour, and, to counteract the bond shortening which results from the apparent centripetal shift in the oscillating atomic centres, corrections to atomic coordinates have often been made, e.g.[46]. In the present case, however, any axial oscillation of the nitro group is entirely swamped by the much greater overall vibrational motion of the whole nitrobenzene moiety. This motion is clearly illustrated by the thermal ellipsoid plot of the molecule in Figure 3.3 as being an overall "flapping" motion approximately normal to the ring plane, increasing in magnitude from C(7) and C(8) to the terminal oxygen atoms and at its greatest at O(2) with a U_{22} value of 0.678(16) $Å^2$, nearly twice that of O(3). Motion of this magnitude is some five times larger than normal high thermal motion, and accordingly must have some other cause. Inspection of the crystal packing viewed in projection down the b-axis, Figure 3.4, reveals an interesting overlap of the nitro groups of b-glide-related molecules, separated by a distance, b/2, of 4.41 Å. Enlarged views of this overlap, viewed parallel to and perpendicular to the b-axis, are shown in Figures 3.7 and 3.8 respectively, and clearly indicate that the "flapping" motion is of an angular oscillatory nature with an axis in the C(7) - C(8) region, approximately parallel to the a-translation. The nature of this motion suggests a tendency of the overlapped nitrobenzene groups

Figure 3.7

Enlarged view of the nitro-group overlap, parallel to the b-axis

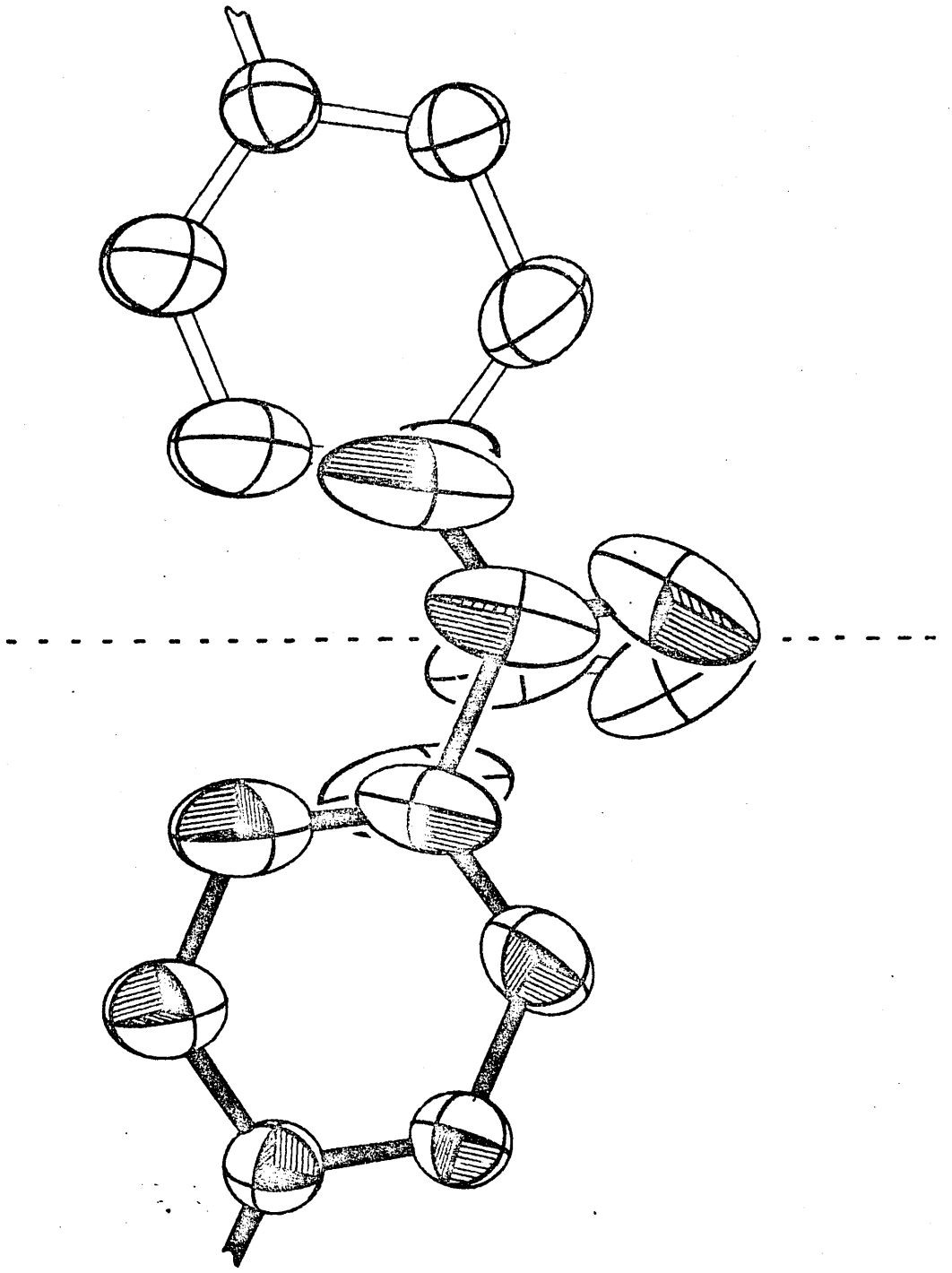
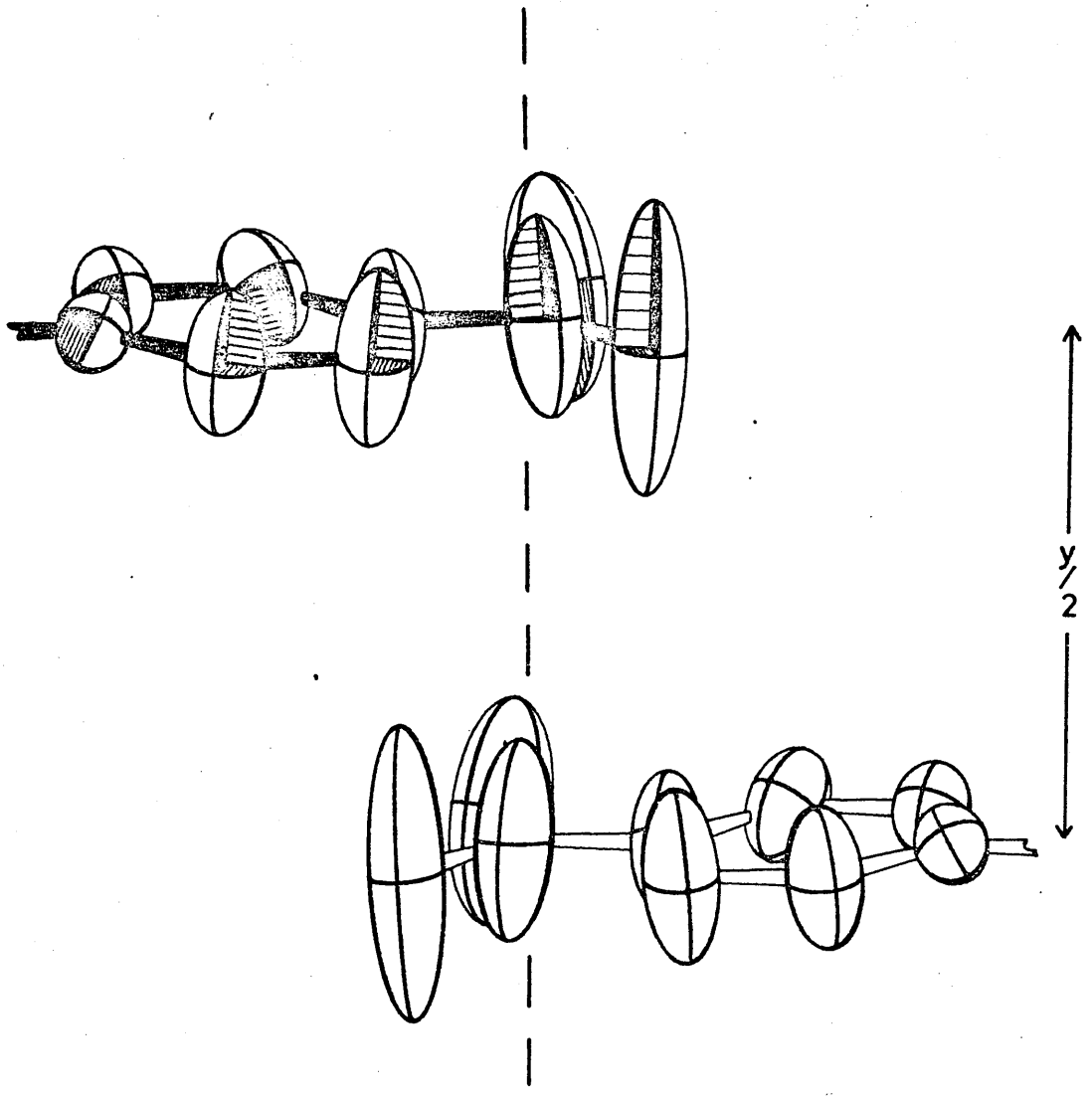


Figure 3.8

Enlarged view of the nitro-group overlap, perpendicular to the b-axis


y/2

to associate closely in pairs by the out of phase flexing of adjacent molecules, to give a stack of pairs of associated molecules extending through the crystal. Irrespective of the nature of the interaction responsible for this association, the necessary associative forces are likely to create an anharmonic potential well, distinctly different from the harmonic potential well of purely thermal vibration, with an accompanying anharmonic motion, to which the extended thermal vibration of the refined model may be only a crude approximation. Three general situations may occur :-

i) a W-shaped potential well may be created with a central barrier energy $\gg$ kT at room temperature, giving two preferred locations of the moving group. This is essentially orientational disorder, in which separate alternative positions will usually be resolved. No trace of this was detected in the present case.

ii) a flat-bottomed potential well may arise, with a large resulting oscillation about a poorly-defined equilibrium position.

iii) an intermediate situation with a W-shaped potential well, but with a low central barrier, less than or of the order of kT at ambient temperatures, which will allow rapid vibrational transition between preferred locations with a time-averaged motion sufficiently large to prevent resolution of separate positions.

The extended thermal (harmonic) motion of the refined model will accordingly be a closer approximation to situation ii) than to iii) . The relatively good fit of the model to the observed data (R = 0.040 and the absence of large discrepancies, Δ , at the conclusion of refinement) suggests that situation ii) may more closely resemble the actual structure of XII . It has been shown that a second analysis at

a lower temperature may allow these situations to be distinguished, by allowing "freezing out" of the motion in situation iii) [47]. This experiment has not, however, been carried out in the present case.

Consideration of the b-glide spacing (4.41 Å) and the r.m.s. amplitude of vibration, in the b-axial direction, of atoms N(2) , O(2) and C(10) indicates that the separation between an associated pair of molecules is 3.2 to 3.3 Å . The similarity of this interplanar spacing to that in crystal charge-transfer complexes has prompted the suggestion that this interaction may be of a charge-transfer (CT) nature. In support of this suggestion are certain other features, similar to those described in a review of CT complexes by Prout and Mayoh in 1972 [48]. Crystal CT complexes between nitroaromatic compounds and aromatic ring compounds are well known e.g. trinitrobenzene/pyrene[49], trinitrobenzene/naphthalene and trinitrobenzene/anthracene[48,50]. Stabilisation of the ground electronic state by the CT state imposes requirements of parallel plane orientation in the crystal, with a sufficiently small plane separation to allow orbital interaction[48], giving rise to spacing between complexed planes generally in the range 3.2 to 3.5 Å . A further similar feature is the intense colour of most complexes, since the CT transition usually lies in the visible range of the spectrum. There are, however, some dissimilar features. Firstly, the association of molecules is necessarily limited to pairs of molecules solely, whether in a random or ordered way, unlike the majority of CT complexes where stacks of alternate donor and acceptor molecules extend the interaction along the whole length of the crystal or, in some cases, through a specific number of stacked molecules. Furthermore, although compound XII has a bright orange colour, this

colour is not purely a feature of the crystal and exists in solution, where it is solvent invariant, in contrast to most CT complexes where the transition energy is solvent dependent. The orange colour may therefore arise instead from an electronic transition within the extended conjugation of the nitrobenzene group.

In view of these dissimilar features, some other type of interaction may be operative. Dipole - dipole interactions, in particular, are suggested by the exact eclipsing of the C(10)-N(2) and N(2)-O(3) bonds in the overlap, clearly illustrated in Figure 3.5 . Perhaps the best approach is simply to call it "polarisation bonding", in the non-specific usage of the term discussed by Wallwork in 1961 [50], which therefore embraces the types of interaction discussed above.

This interaction appears to be the dominant feature of the crystal packing, and is certainly responsible for the "herringbone pattern" arrangement of molecules, as shown in Figure 3.4 . In addition, the short intermolecular distances, S....S 3.48 , S...O(1) 2.98 , and C(15)...O(1) 3.05 Å , all appreciably less than the sum of relevant van der Waals' radii, suggest that other dipolar interactions may also be important.

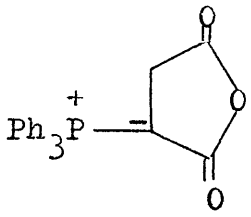
4. THE CRYSTAL AND MOLECULAR STRUCTURE OF A STABILISED WITTIG REAGENT : 1-METHOXYCARBONYL-2-TERT.BUTYLOXYCARBONYLETHYLTRIPHENYLPHOSPHORANE.

4.1 Introduction

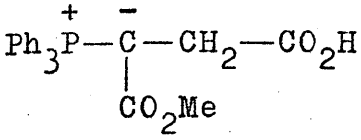
Methanolysis of the ylide, XVIII , yields a monomethyl ester product which can plausibly be assigned either of the isomeric structures XIXa or b . Infrared spectroscopic data were originally attributed to the carboxylate structure, b,[51] but ^{1}H n.m.r. evidence indicated the ylide structure, a . Synthesis of the t-butyl ester of XIX , the title compound XX , for which no isomer analogous to XIXb can be formed, supported the ylide form, a , since I.R. and ^{1}H n.m.r. spectra of XX are similar to, and reproduce the salient features of the spectra of XIX , thus indicating similarity of structure[8]. The ylide nature of both structures is further indicated by the strong shielding of the ylide-carbon in ^{13}C n.m.r. spectra, indicative of the presence of considerable localised negative charge.

Low temperature ^{1}H n.m.r. studies of XX have shown restricted rotation about the bond between the carbonyl-carbon and the anionic carbon, resulting in resolution of rotational isomers at around $-30^{\circ}C$. This is in keeping with the partial double bond known to result from delocalisation of part of the negative charge on the ylide-carbon to the carbonyl group[52].

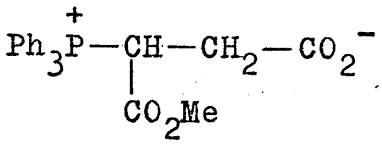
The crystal structure analysis of XIX [8] confirmed the Wittig reagent structure, a , but revealed a feature that renders this ylide structure anomalous in relation to most similar ylides previously



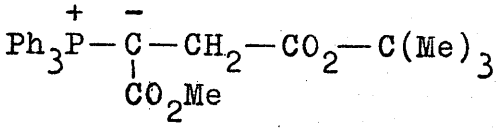
XVIII



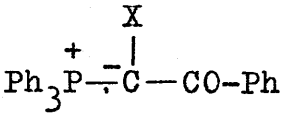
XIXa



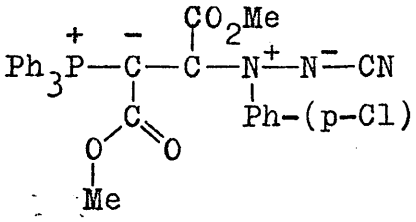
XIXb



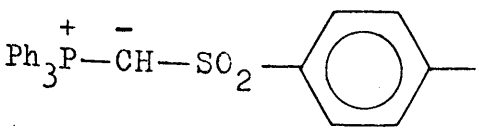
XX



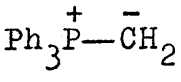
XXI (a) X = Cl
(b) X = I



XXII



XXIII



XXIV

studied. This is the non-planar $\overset{+}{P}-C-\overset{-}{C}=O$ portion of the molecule, with a torsion angle of $-165.9(4)^{\circ}$, 14.1° from trans-planarity, whereas practically all ylides of this type (generally, those ylides possessing a single π-orbital stabilising group) adopt the planar conformation that is necessary for efficient overlap. A further feature of the crystal structure may explain this anomaly, however. Intermolecular hydrogen-bonding was observed, involving the carboxylic acid function and the carbonyl-oxygen of the stabilising group, which may have caused this distortion from planarity. Accordingly, the crystal structure of the diester, XX , in which similar hydrogen-bonding is not possible, has been determined in order to verify the above postulate, and to allow comparison of the same ylide system in two crystal environments.

4.2 Experimental

Crystal Data

1-methoxycarbonyl-2-tert.butyloxycarbonylethyltriphenylphosphorane

$C_{27}H_{29}PO_4$, M = 448.5 .

Monoclinic, a = 15.731 b = 11.941 c = 13.194 Å , β = 97.22°,

U = 2458.8 $Å^3$,

D_m = 1.20 g cm^{-3}, Z = 4 , D_c = 1.21 g cm^{-3},

$F_{(000)}$ = 952 .

Space group : $P2_1/n$ (C_{2h}^5 , No.14), uniquely identified by systematic absences.

μ(Mo,Kα) = 1.47 cm^{-1}.

Data Collection

Radiation	:	Mo,Kα
Filter	:	Zr
Maximum scattering angle (2θ)	:	54°
Independent reflections (observed)	:	2883
Unobserved cutoff	:	$3\varsigma_I$
Ratio of observations/parameters	:	7.65

Structure Determination

The structure was resolved using initial phasing by the multi-symbolic method, with normalised structure factors and triplet relationships calculated for the 270 reflections with $|E| \geq 1.79$. A solution for the 80 strongest reflections was obtained, based on a starting set of three origin-defining reflections chosen by the program, using only relationships of probability ≥ 0.80 . A total of 270 reflections were then phased from this solution, and the resulting E-map clearly revealed the 20 non-hydrogen atoms of the triphenylphosphine group and the adjacent carbon atom. A structure-factor and electron-density calculation based on these atoms then revealed the complete structure.

Structure Refinement

Refinement of positional, thermal and scale parameters was concluded after 16 cycles of least-squares minimisation with residuals R and R' at 0.076 and 0.012 . Details of the refinement are given in Table 4.1 .

All but three of the hydrogen atoms were located in a difference synthesis calculated after cycle 3 , the remaining three being located from a similar calculation after one cycle of anisotropic refinement. These atoms were included in the calculations with arbitrary isotropic thermal parameters of 0.05 $Å^2$, although the positional parameters were refined in later cycles. Before cycle 8 , reflections with $I \leq 2\sigma_I$ were removed, and at cycle 11 this cutoff was raised to $3\sigma_I$ since the weakest reflections were found to

contribute unduly to the function $\Sigma\Delta^2$. One reflection of sufficient intensity to be measured with serious inaccuracy due to counter saturation was removed at cycle 9 . Certain hydrogen atoms whose initial determinations were of limited accuracy, shifted to positions of unrealistic geometry on initial refinement. Adjustments to these positions were made on the basis of a difference synthesis, and on further refinement a more acceptable geometry was maintained.

From cycle 10 onwards, a weighting scheme was applied using a function of the form

$$W = x.y$$

where $x = \sin\theta/B$ if $\sin\theta \leqslant B$, else $x = 1$,

and $y = C/|F_o|$ if $|F_o| \geqslant C$, else $y = 1$,

with final coefficients $B = 0.35$ and $C = 7.0$, determined by analysis of Δ^2 with $|F_o|$ and $\sin\theta$.

Limitations in computer time and storage necessitated the use of the blocked-matrix approximation, using six blocks with the atom order chosen so that a connected group of atoms (e.g. a phenyl group) was included in one block. Some correlation terms are however missed, and the estimated standard deviation of each parameter, derived from the inverse of the least-squares matrix, is best regarded as a minimum value.

A final difference synthesis revealed no errors in the structure. In all structure-factor calculations the atomic scattering factors used were those given in "International Tables for X-ray Crystallography", Vol.III [32] .

Observed and calculated structure factors are given in Appendix 5 . Fractional coordinates and thermal parameters are listed in Table 4.2

and interatomic distances, angles and intermolecular contacts are given in Table 4.3 . Details of some least-squares planes through various portions of the molecular framework are given in Table 4.4 , and the atomic numbering scheme is depicted in Figure 4.1 . Hydrogen atoms are not shown, but are numbered in relation to the carbon atoms to which they are attached. The molecular packing viewed down the c-axis is shown in Figure 4.2 .

Table 4.1

Course of refinement

Cycles	Parameters refined	Final R	Final R'
1 - 3	x,y,z,U_{iso} for P, O and C, scale factor. Unit weights, full matrix.	0.195	0.029
4	x,y,z,U_{iso} for P, O and C, scale factor. H-atoms included but not refined, unit weights, full matrix.	0.183	0.025
5 - 7	x,y,z,U_{ij} for P, O and C, scale factor. H-atoms included but not refined, unit weights, blocked matrix.	0.133	0.014
8 - 9	x,y,z,U_{ij} for P, O and C, scale factor. H-atoms included but not refined, unit weights, blocked matrix. Reflections with $I \leqslant 2\sigma_I$ removed.	0.101	0.010
10	x,y,z,U_{ij} for P, O and C, scale factor. H-atoms included but not refined, weighting scheme applied, blocked matrix.	0.104	0.018
11	As previous, but reflections with $I \leqslant 3\sigma_I$ removed.	0.093	0.016
12 - 13	x,y,z for H, scale factor. Non-hydrogen atoms not refined, weighting scheme applied, blocked matrix.	0.082	0.014
14 - 16	x,y,z,U_{ij} for P, O and C, x,y,z for H, scale factor. Weighting scheme applied, blocked matrix.	0.075	0.012

Table 4.2

a) Fractional Coordinates

	x/a	y/b	z/c
P	0.75754(9)	0.85297(10)	0.03112(8)
O(1)	0.6351(3)	1.1320(3)	-0.0196(3)
O(2)	0.6268(3)	0.9607(3)	-0.0927(3)
O(3)	0.8661(3)	1.1351(4)	0.0071(3)
O(4)	0.8311(3)	1.2492(3)	0.1307(3)
C(1)	0.7279(4)	0.9892(4)	0.0482(3)
C(2)	0.6609(4)	1.0356(4)	-0.0206(4)
C(3)	0.5591(7)	0.9971(8)	-0.1634(7)
C(4)	0.7734(4)	1.0669(4)	0.1258(4)
C(5)	0.8283(4)	1.1526(4)	0.0789(4)
C(6)	0.6786(4)	0.7479(4)	0.0549(4)
C(7)	0.5947(4)	0.7777(5)	0.0607(4)
C(8)	0.5359(4)	0.6977(6)	0.0790(5)
C(9)	0.5587(5)	0.5970(6)	0.0934(5)
C(10)	0.6422(5)	0.5562(5)	0.0869(6)
C(11)	0.7017(5)	0.6349(4)	0.0674(5)
C(12)	0.8514(3)	0.8243(4)	0.1231(3)
C(13)	0.9335(4)	0.8475(5)	0.1010(4)
C(14)	1.0023(5)	0.8321(6)	0.1755(5)
C(15)	0.9891(5)	0.7967(5)	0.2711(5)
C(16)	0.9088(5)	0.7752(5)	0.2946(4)
C(17)	0.8402(4)	0.7893(4)	0.2216(4)
C(18)	0.7855(4)	0.8260(4)	-0.0966(4)
C(19)	0.7610(5)	0.7282(6)	-0.1506(5)
C(20)	0.7806(5)	0.7167(8)	-0.2507(6)
C(21)	0.8219(5)	0.7985(7)	-0.2949(5)
C(22)	0.8451(5)	0.8951(7)	-0.2422(5)
C(23)	0.8253(5)	0.9092(5)	-0.1436(4)
C(24)	0.8847(4)	1.3442(5)	0.1046(4)
C(25)	0.9763(6)	1.3097(8)	0.1192(8)
C(26)	0.8536(7)	1.3832(7)	-0.0025(5)
C(27)	0.8664(5)	1.4311(5)	0.1829(5)

Table 4.2 (cont.)

b) Anisotropic thermal parameters ($Å^2$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	0.0620	0.0334	0.0345	0.0052	0.0062	0.0004
O(1)	0.1206	0.0691	0.0750	-0.0226	0.0551	-0.0253
O(2)	0.0809	0.0408	0.0499	-0.0043	0.0134	-0.0063
O(3)	0.1171	0.0396	0.0605	0.0232	0.0071	0.0081
O(4)	0.0883	0.0475	0.0494	0.0086	-0.0070	0.0016
C(1)	0.0727	0.0404	0.0443	-0.0041	0.0044	-0.0008
C(2)	0.0757	0.0533	0.0471	0.0070	0.0148	-0.0001
C(3)	0.0650	0.0800	0.0677	-0.0034	0.0223	0.0057
C(4)	0.0965	0.0628	0.0742	-0.0210	0.0071	0.0029
C(5)	0.1035	0.0423	0.0884	-0.0067	-0.0034	0.0063
C(6)	0.0827	0.0421	0.0836	0.0002	0.0066	0.0037
C(7)	0.0696	0.0367	0.0380	0.0018	0.0078	0.0016
C(8)	0.0722	0.0688	0.0484	0.0015	0.0203	0.0027
C(9)	0.0705	0.0857	0.0617	-0.0016	0.0138	0.0030
C(10)	0.0765	0.0661	0.0571	0.0018	-0.0024	0.0029
C(11)	0.0949	0.0583	0.0406	0.0034	0.0109	0.0090
C(12)	0.0775	0.0446	0.0478	-0.0001	0.0129	0.0071
C(13)	0.0655	0.0509	0.0397	0.0108	0.0072	-0.0030
C(14)	0.0961	0.0671	0.0624	-0.0075	0.0166	-0.0196
C(15)	0.0938	0.1036	0.0636	-0.0043	0.0109	-0.0429
C(16)	0.0864	0.1193	0.0426	0.0125	0.0106	-0.0175
C(17)	0.1112	0.0811	0.0503	0.0045	0.0311	-0.0021
C(18)	0.1090	0.0599	0.0441	0.0105	0.0211	-0.0024
C(19)	0.0891	0.0322	0.0377	0.0004	0.0090	0.0024
C(20)	0.0820	0.0418	0.0424	0.0027	0.0161	-0.0020
C(21)	0.0667	0.0454	0.0484	0.0017	0.0098	-0.0057
C(22)	0.0866	0.0473	0.0508	-0.0089	0.0064	-0.0024
C(23)	0.0822	0.0908	0.1140	0.0028	0.0185	-0.0256
C(24)	0.1312	0.0643	0.0577	-0.0159	-0.0019	0.0073

Table 4.2.b (cont.)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(25)	0.0871	0.0467	0.0635	-0.0050	-0.0034	-0.0075
C(26)	0.0802	0.0367	0.0427	-0.0010	0.0168	0.0050
C(27)	0.1300	0.0705	0.0854	0.0077	-0.0465	0.0022
	Mean estimated standard deviations ($Å^2$)					
P	0.0008	0.0006	0.0006	0.0006	0.0005	0.0005
O	0.0025	0.0020	0.0021	0.0020	0.0021	0.0017
C	0.0030	0.0027	0.0022	0.0023	0.0021	0.0020

Table 4.2 (cont.)

c) H-atom fractional coordinates

	x/a	y/b	z/c
H(31)	0.559(4)	1.077(7)	-0.179(5)
H(32)	0.526(5)	0.968(7)	-0.179(7)
H(33)	0.576(4)	0.945(6)	-0.241(5)
H(41)	0.732(5)	1.102(6)	0.169(6)
H(42)	0.820(5)	1.030(6)	0.181(6)
H(7)	0.577(4)	0.854(7)	0.057(5)
H(8)	0.482(5)	0.714(6)	0.090(5)
H(9)	0.520(4)	0.525(6)	0.113(5)
H(10)	0.661(4)	0.482(7)	0.088(5)
H(11)	0.757(5)	0.621(6)	0.064(6)
H(13)	0.938(4)	0.870(6)	0.038(6)
H(14)	1.052(5)	0.846(6)	0.154(5)
H(15)	1.040(5)	0.789(6)	0.319(6)
H(16)	0.892(5)	0.755(6)	0.352(6)
H(17)	0.791(5)	0.780(6)	0.236(6)
H(19)	0.726(4)	0.671(6)	-0.123(5)
H(20)	0.759(4)	0.646(6)	-0.283(5)
H(21)	0.850(4)	0.793(6)	-0.361(6)
H(22)	0.876(4)	0.947(6)	-0.272(5)
H(23)	0.842(4)	0.979(6)	-0.108(5)
H(251)	1.016(5)	1.370(6)	0.107(5)
H(252)	1.001(5)	1.281(7)	0.169(6)
H(253)	1.001(5)	1.271(6)	0.063(6)
H(261)	0.796(5)	1.399(7)	-0.016(6)
H(262)	0.866(4)	1.329(6)	-0.058(6)
H(263)	0.877(4)	1.457(7)	-0.009(5)
H(271)	0.899(4)	1.404(6)	0.255(6)
H(272)	0.897(4)	1.498(7)	0.175(5)
H(273)	0.813(5)	1.441(6)	0.174(6)

Table 4.3

Interatomic distances and angles

a) Bonded distances (Å)

P - C(1)	1.715(5)	C(3) - O(2)	1.394(11)
P - C(6)	1.817(5)	C(4) - C(5)	1.520(8)
P - C(12)	1.823(5)	C(5) - O(3)	1.198(7)
P - C(18)	1.823(5)	C(5) - O(4)	1.338(6)
C(1) - C(2)	1.415(7)	O(4) - C(24)	1.480(7)
C(1) - C(4)	1.495(7)	C(24) - C(25)	1.489(11)
C(2) - O(1)	1.221(6)	C(24) - C(26)	1.510(9)
C(2) - O(2)	1.366(6)	C(24) - C(27)	1.518(8)
Ring (1) :			
C(6) - C(7)	1.381(9)	C(9) - C(10)	1.377(12)
C(7) - C(8)	1.372(9)	C(10) - C(11)	1.373(10)
C(8) - C(9)	1.377(10)	C(11) - C(6)	1.403(7)
Mean C - C	1.381(10)	Mean C - H	0.94(8)
Ring (2) :			
C(12) - C(13)	1.387(8)	C(15) - C(16)	1.361(10)
C(13) - C(14)	1.380(9)	C(16) - C(17)	1.364(9)
C(14) - C(15)	1.371(9)	C(17) - C(12)	1.397(7)
Mean C - C	1.377(9)	Mean C - H	0.89(8)
Ring (3) :			
C(18) - C(19)	1.397(8)	C(21) - C(22)	1.373(11)
C(19) - C(20)	1.401(10)	C(22) - C(23)	1.386(9)
C(20) - C(21)	1.345(12)	C(23) - C(18)	1.364(9)
Mean C - C	1.378(10)	Mean C - H	0.98(7)

Table 4.3 (cont.)

b) Interbond angles (°)

C(1) -P - C(6)	115.5(3)	C(4) -C(5) -O(4)	110.8(4)
C(1) -P - C(12)	107.5(2)	O(3) -C(5) -O(4)	124.5(4)
C(1) -P - C(18)	112.9(2)	C(5) -O(4) -C(24)	121.7(4)
C(6) -P - C(12)	105.7(2)	O(4) -C(24)-C(25)	109.2(5)
C(6) -P - C(18)	106.5(2)	O(4) -C(24)-C(26)	109.1(4)
C(12)-P - C(18)	108.3(3)	O(4) -C(24)-C(27)	101.7(4)
P - C(1)-C(2)	118.7(2)	C(25)-C(24)-C(26)	113.7(6)
P - C(1)-C(4)	124.4(3)	C(25)-C(24)-C(27)	111.3(5)
C(2) -C(1)-C(4)	116.7(3)	C(26)-C(24)-C(27)	111.1(5)
C(1) -C(2)-O(1)	125.7(4)	P - C(6) -C(7)	120.8(3)
C(1) -C(2)-O(2)	112.7(3)	P - C(6) -C(11)	120.9(3)
O(1) -C(2)-O(2)	121.6(3)	P - C(12)-C(13)	121.3(2)
C(2) -O(2)-C(3)	117.5(5)	P - C(12)-C(17)	119.3(3)
C(1) -C(4)-C(5)	112.7(3)	P - C(18)-C(19)	122.4(3)
C(4) -C(5)-O(3)	124.7(4)	P - C(18)-C(23)	118.0(3)

Ring (1) :

C(6)-C(7)-C(8)	120.2(4)	C(9) -C(10)-C(11)	120.4(5)
C(7)-C(8)-C(9)	121.5(5)	C(10)-C(11)-C(6)	120.7(5)
C(8)-C(9)-C(10)	118.9(6)	C(11)-C(6) -C(7)	118.3(4)
	Mean C-C-C	120.0(5)	

Ring (2) :

C(12)-C(13)-C(14)	119.4(4)	C(15)-C(16)-C(17)	119.4(4)
C(13)-C(14)-C(15)	120.0(4)	C(16)-C(17)-C(12)	120.8(5)
C(14)-C(15)-C(16)	121.3(5)	C(17)-C(12)-C(13)	119.1(4)
	Mean C-C-C	120.0(4)	

Ring (3) :

C(18)-C(19)-C(20)	118.9(4)	C(21)-C(22)-C(23)	120.0(4)
C(19)-C(20)-C(21)	120.9(6)	C(22)-C(23)-C(18)	120.6(4)
C(20)-C(21)-C(22)	120.2(5)	C(23)-C(18)-C(19)	119.3(4)
	Mean C-C-C	120.0(5)	

Table 4.3 (cont.)

c) Intramolecular non-bonded distances (Å)

P ....O(2)	2.78	O(3)...C(1)	2.89
P ....O(3)	3.80	O(3)...C(24)	2.81
O(1)...O(3)	3.61	O(3)...C(25)	2.98
O(1)...O(4)	3.72	O(3)...C(26)	2.97
O(1)...C(3)	2.66	O(3)...C(2)	3.42
O(1)...C(4)	2.82	O(3)...C(23)	3.37
O(1)...C(5)	3.16	C(1)...C(7)	3.30
O(2)...C(6)	3.24	C(1)...C(23)	3.26
O(2)...C(18)	2.97	C(2)...C(5)	3.12
O(2)...C(23)	3.33	C(2)...C(18)	3.41
O(2)...C(7)	3.06	C(4)...C(12)	3.15

d) Intermolecular distances (Å)

$C(27)...C(10)^{I}$	3.89	$C(4)....C(10)^{IV}$	3.85
$C(27)...C(11)^{I}$	3.73	$C(16)...C(10)^{IV}$	3.83
$C(9)....C(9)^{II}$	3.56	$C(27)...C(7)^{IV}$	3.82
$C(15)...C(3)^{III}$	3.74	$O(1)....C(20)^{V}$	3.60
$O(1)....C(16)^{IV}$	3.57	$O(1)....C(21)^{V}$	3.29
$O(4)....C(17)^{IV}$	3.55		

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

I x, 1+y, z ; II 1-x, 1-y, -z ;

III 1/2+x, 3/2-y, 1/2+z ; IV 3/2-x, 1/2+y, 1/2-z ;

V 3/2-x, 1/2+y, -1/2-z .

Table 4.3 (cont.)

e) Torsion angles (^{o})

P - C(1)-C(2)-O(2)	1.3(6)
P - C(1)-C(2)-O(1)	-177.5(4)
C(4)-C(1)-C(2)-O(1)	-2.8(8)
C(4)-C(1)-C(2)-O(2)	-175.9(4)
C(1)-C(4)-C(5)-O(3)	-34.4(7)
C(1)-C(4)-C(5)-O(4)	147.8(4)
C(2)-C(1)-P - C(6)	-67.9(5)
C(2)-C(1)-P - C(12)	174.3(4)
C(2)-C(1)-P - C(18)	54.9(5)
C(4)-C(1)-P - C(6)	117.8(5)
C(4)-C(1)-P - C(12)	0.1(5)
C(4)-C(1)-P - C(18)	-119.3(4)
C(1)-P - C(6)-C(7)	14.9(5)
C(1)-P - C(6)-C(11)	-164.5(5)
C(1)-P - C(12)-C(13)	-87.0(5)
C(1)-P - C(12)-C(17)	86.3(5)
C(1)-P - C(18)-C(19)	-139.2(5)
C(1)-P - C(18)-C(23)	34.9(5)

Table 4.4

Least-squares planes

a) Equation of plane

i) $-0.1025X - 0.1555Y - 0.9825Z + 3.1702 = 0$

ii) $-0.1219X + 0.9502Y + 0.2867Z - 8.2173 = 0$

iii) $-0.8431X + 0.4097Y - 0.3484Z + 6.0582 = 0$

iv) $0.7232X + 0.2807Y - 0.6310 - 11.1726 = 0$

b) Deviation of atoms from the plane (Å)

i)	P	-0.030	C(6)	-0.003*	C(7)	-0.004*
	C(8)	0.008*	C(9)	-0.006*	C(10)	0.000*
	C(11)	0.005*				
ii)	P	0.132	C(12)	-0.009*	C(13)	0.009*
	C(14)	-0.003*	C(15)	-0.002*	C(16)	0.001*
	C(17)	0.004*				
iii)	P	0.085	C(18)	-0.014*	C(19)	0.005*
	C(20)	0.004*	C(21)	-0.004*	C(22)	-0.006*
	C(23)	0.014*				
iv)	O(2)	0.055	O(1)	0.031	P	0.010*
	C(1)	-0.032*	C(2)	0.011*	C(4)	0.011*

c) Dihedral angles between planes

i) and ii) : 114.6°

i) and iii) : 111.4°

ii) and iii) : 113.1°

* denotes atom used to define plane.

X, Y and Z are orthogonal coordinates in Å .

Figure 4.1

Atomic numbering scheme

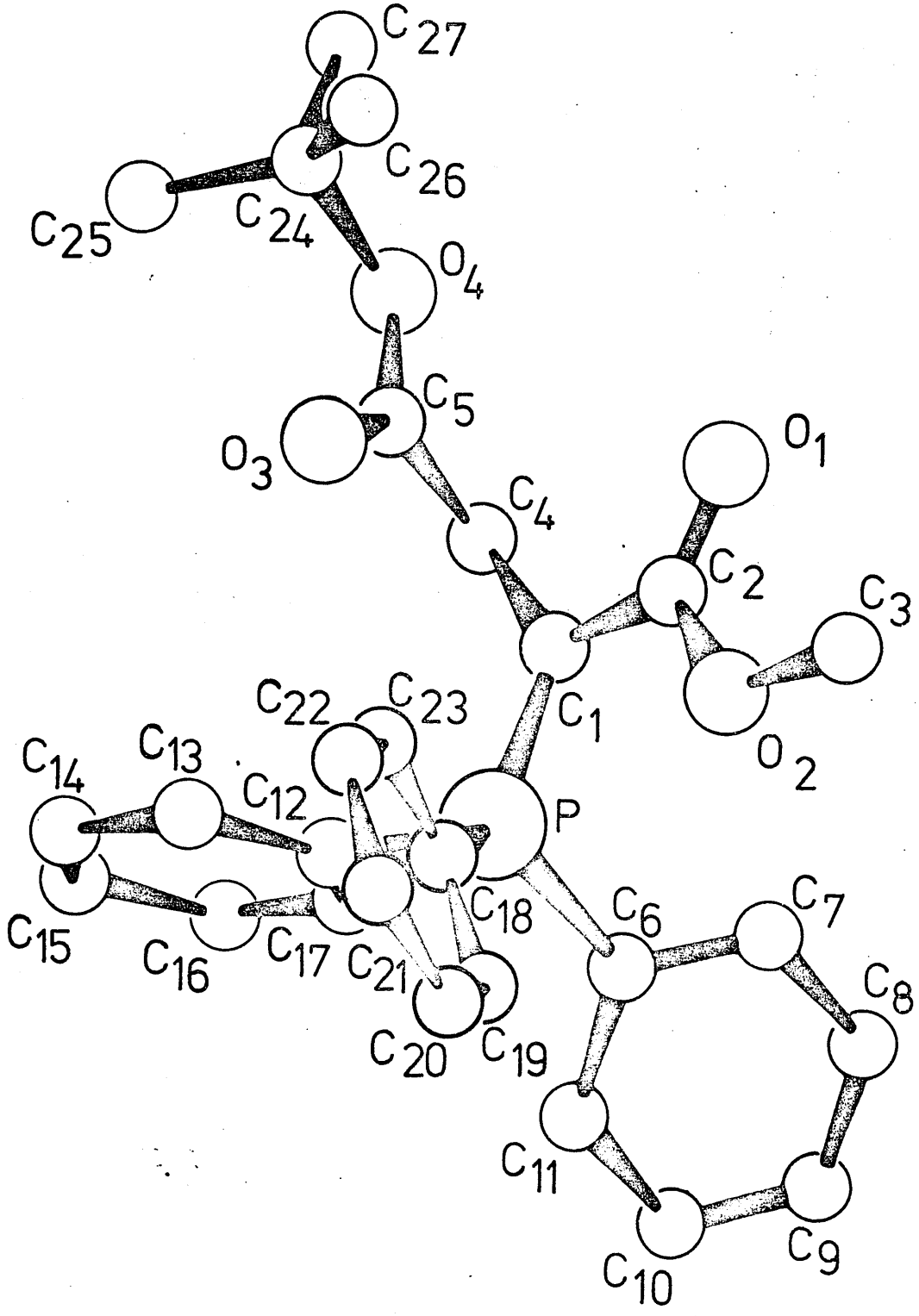
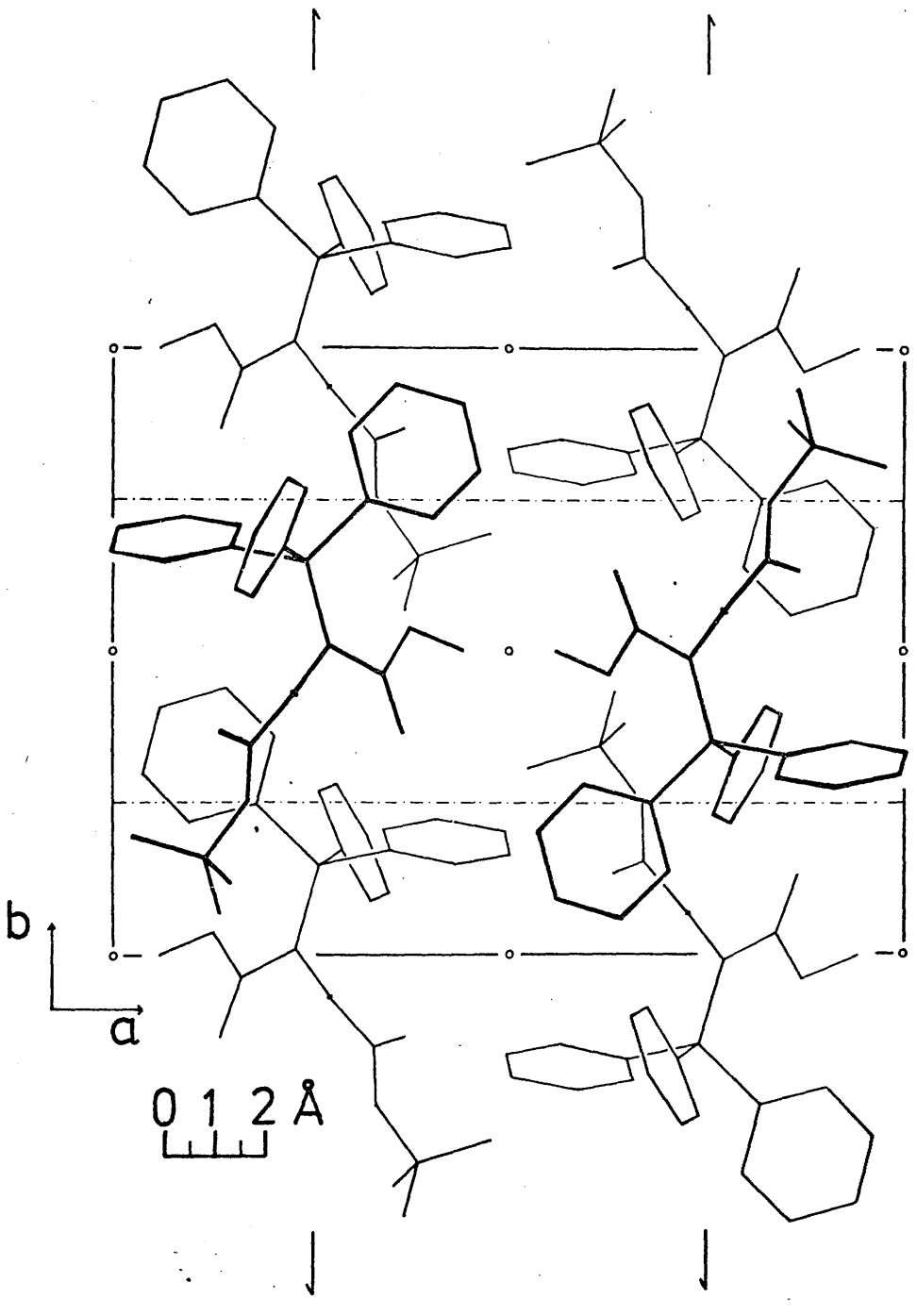

C27
C26
C25
C24
O4
C5
O3
C4
O1
C2
C3
O2
C1
C22
C23
C13
C14
C12
P
C15
C16
C17
C21
C18
C6
C7
C8
C20
C19
C11
C9
C10

Figure 4.2

Molecular packing arrangement viewed down the c-axis


b
a
0 1 2 Å

4.3 Discussion

The X-ray analysis of XX has confirmed the assigned structure and has revealed the approximate planarity of the $\overset{+}{P}-\overset{-}{C}-C=O$ moiety, as predicted on the basis of orbital overlap requirements. This provides evidence in strong support of the postulate that the 14° distortion from planarity in XIX arises from the intermolecular hydrogen-bonding previously described (section 4.1).

The molecule adopts a trans-conformation of the ylide and carbonyl bonds, with a torsion angle about C(1)-C(2) of -177.5(4)° i.e. 2.5° from planarity, broadly similar to the conformation of XIX , where however a torsion of 14.1° from trans-planarity is observed. This contrasts with the cis-conformation that is typical of many carbonyl-stabilised ylides, but the presence of a bulky alkyl substituent on the anionic atom is known to favour the trans-arrangement[52]. Both cis and trans forms are present in solution with restricted rotation allowing resolution of the rotamers at -30°C, but no trace of disorder in the crystal structure, from the possible presence of a proportion of the cis conformer, was detected.

Examination of some other compounds possessing a $\overset{+}{P}-\overset{-}{C}-C=O$ group of atoms reveals that the distortion from planarity in XIX is not unique. Thus in XXI(a) and (b) [53] and XXII [54], deviations from planarity of 4.8°, 12° and 8° are observed. The reduction in $^{31}P - {}^{13}C$ coupling constant from 130 Hz in compound XX to 90 Hz in XIX [8] correlates well with the observed distortion and provides clear evidence of the presence of considerable, if possibly diminished, π-overlap in XIX despite the 14° twist. Further evidence is provided by the $\overset{-}{C}-CO$

bond lengths, 1.415(7) Å in XX and 1.392(6) Å in XIX , which are not significantly different and indicate a partial multiple bond. The $P^{+}-C^{-}$ bonds are similarly equivalent, 1.715(5) and 1.732(4) Å in XX and XIX respectively, and are comparable with values observed in XXIa and b, and XXIII [9], 1.71(5) , 1.736(14) and 1.709(19) Å . Although not as short as the P-C bond in the phosphonium methylide, XXIV, 1.662(8) Å [6], in which delocalisation to the phosphonium group only can occur, these bonds are markedly shorter than a P-C single bond e.g. 1.841(5) Å in trimethyl phosphine[33], and indicate appreciable double bond character.

Further evidence of charge delocalisation to the carbomethoxy group is provided by the lengthening of the carbonyl bond relative to that in the t-butyl ester, 1.221(6) Å compared to 1.198(7) Å . A parallel trend is observed in the carbomethoxy and acid groups of XIX .

Most of the remaining features of compounds XIX and XX are experimentally identical. Thus the phosphorus atoms possess the usual distorted tetrahedral geometry, with the familiar "propeller" arrangement of the three phenyl rings. The phenyl rings have essentially normal geometry (mean $C_{ar}-C_{ar}$ 1.381(10) , 1.377(9) and 1.378(10) Å for rings 1, 2 and 3 respectively, and mean ring angles of 120.0° for each ring), and least-squares planes indicate the approximate planarity of each ring, with the phosphorus atom slightly out of the ring plane, as is generally observed in triphenylphosphorus compounds.

A feature common to both compounds and similar to that observed in the trimethylammonium compounds discussed in section 1.3 is the valence-angle asymmetry at the phosphorus atom, where the bond angle to one ring (ring 2, C(1)-P-C(12) , 107.5(2)°) is significantly reduced from the tetrahedral value, while the angles to the other two

rings are significantly increased (C(1)-P-C(6) 115.5(3)° and C(1)-P-C(18) 112.9(2)°). Inspection of the intramolecular contact distances reveals the much closer contact of rings 1 and 3 with the carbomethoxy and alkyl groups. The observed asymmetry is probably a manifestation of the resulting flexion of the molecule in order to reduce these close contacts.

The t-butyloxycarbonylmethyl side chain adopts an extended conformation with the t-butyl group staggered with respect to the carbonyl bond (O(3)...C(25) 2.98 , O(3)...C(26) 2.97 Å). All dimensions fall within the expected ranges.

Only one short intermolecular contact is observed, O(1)...C(21) 3.29 Å , but the mode of crystal packing illustrated in Figure 4.2 , with molecules stacked in a $\overset{+}{\underset{}{..P}}\overset{-}{\underset{}{-C.....P}}\overset{+}{\underset{}{-C.....P}}\overset{-}{\underset{}{-C...}}$ arrangement along the screw-axial directions, suggests that dipolar interactions may be an important packing force.

5. THE CRYSTAL AND MOLECULAR STRUCTURE OF TWO PHOSPHINAMIDES : N-(PHENYLETHYL)DIPHENYLPHOSPHINAMIDE AND N-(METHYL),N-(PHENYLETHYL)DIPHENYLPHOSPHINAMIDE (HYDRATED).

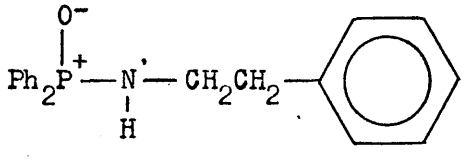
5.1 Introduction

Phosphinamides, $R^1R^2PO.NR^3R^4$, are ylides of the type $\overset{+}{P} - \overset{-}{O}$, within the broad definition given in the Introduction. On account of the high electronegativity of oxygen, such ylides are inherently completely stable (including the first-row counterparts, the amine oxides, $\overset{+}{N} - \overset{-}{O}$) and require no further stabilisation. The aspect of these compounds which is of principal interest is therefore the interaction of the formally positive phosphorus atom (where the d-orbitals should be appropriately lowered in energy) with other substituents, in this case the nitrogen atom of an amine function.

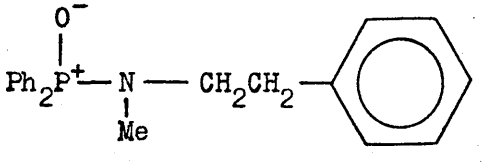
The broad similarity of the properties of phosphinamides to those of the carboxylic amides, with certain striking exceptions, has led to the use of the former class of compounds in organic synthetic work, where the diphenylphosphinyl group has proved effective as a protecting group for amines, being particularly valuable in peptide synthesis[63]. It has been shown[64] that phosphinamides and the corresponding carboxylic amides have comparable rates of basic hydrolysis but that phosphinamides undergo acid hydrolysis about 10^5 times faster. Chemical evidence has suggested[65] that acid hydrolysis occurs in the phosphinamides by protonation at nitrogen (in contrast to the O-protonation of carboxylic amides), with a consequent labilising effect on the P-N bond, possibly resulting from the removal of the $p\pi - d\pi$ interaction of the nitrogen

lone-pair electrons with the phosphorus, and subsequent nucleophilic attack by water at the (already positive) phosphorus atom. Thus as a protective function for amines, the diphenylphosphinyl group allows regeneration of the amine by cleavage under very mild conditions, with a weak acid byproduct, Ph_2POOH . A further advantage is the activation of an amide hydrogen by the diphenylphosphinyl group, which allows N-alkylation under gentle reaction conditions and is of particular value in the synthesis of N-methyl amino-acids.

In support of this work investigating the nature and reactivity of the P-N bond in phosphinamides, the crystal structures of the phosphinamide, XXV, and its N-methyl counterpart, XXVI , have been determined.



XXV



XXVI

5.2 Experimental Compound XXV

Crystal Data (XXV)

N-(phenylethyl)diphenylphosphinamide

$C_{20}H_{20}PNO$, M = 321.4 .

Monoclinic, a = 8.147 b = 19.036 11.563 Å , β = 90.10°,

U = 1793.1 $Å^3$

D_m = 1.20 g cm^{-3} , Z = 4 , D_c = 1.19 g cm^{-3} ,

$F_{(000)}$ = 680 .

Space group : Pc (C_s^2 , No.7) .

μ(Mo,Kα) = 1.59 cm^{-1}.

Data Collection

Radiation	:	Mo,Kα
Filter	:	graphite monochromator
Maximum scattering angle (2θ)	:	60°
Independent reflections (observed)	:	2315
Unobserved cutoff	:	$3\varsigma_I$
Ratio of observations/parameters	:	5.37

Structure Determination

Systematic absences in the $h0\ell$ zonal reflections indicated an ambiguity between two space groups, Pc and its centrosymmetric analogue P2/c . Statistical analysis of the normalised structure factors indicated a non-centrosymmetric distribution, and accordingly the space group Pc was assumed, with two molecules in the asymmetric unit. The correctness of this choice was confirmed by the determination and subsequent refinement of the structure.

Direct phasing by automatic multisolution tangent methods was attempted, but met with no initial success. A starting set of three origin and enantiomorph-defining reflections and three variable phases gave 64 possible phase sets, but examination of E-maps for the 40 phase sets with highest figures of merit yielded not even fragments of the structure although several showed two large peaks expected for the two heavy atoms in the asymmetric unit.

Concurrently, phasing by the heavy atom method was being attempted and was eventually to lead to determination of the structure. The coordinates of both phosphorus atoms were determined from a three-dimensional origin-removed sharpened Patterson function (the lack of solution for P2/c symmetry giving further support for the choice of space group Pc). A structure-factor and electron-density calculation based on the two heavy-atom positions yielded an electron-density map showing peaks clustered around the heavy atoms with partial mirror symmetry, but with no identifiable fragments of the structure. Tangent refinement of the 338 reflections with $|E| \geqslant 1.30$, yielded no improvement, and only after experimenting with different values of

a rejection coefficient to reject inaccurately phased reflections was an improved electron-density map obtained in which one phenyl ring and three atoms of a second ring bonded to the same phosphorus atom could be tentatively identified. Inclusion of these atoms in a cycle of Fourier synthesis revealed new atom positions completing the second phenyl ring and showed the two remaining atoms bonded to phosphorus, as well as the two phenyl rings bonded to the second phosphorus atom. A third cycle of Fourier synthesis indicated the complete structure, and gave atomic positions suitable for least-squares refinement.

Structure Refinement

Refinement of positional, thermal and scale parameters was completed after 21 cycles of least-squares minimisation, with R = 0.041 and R' = 0.0027 . The course of refinement is summarised in Table 5.1 , but requires some amplification.

In the initial cycles of refinement, the thermal parameters of the methylene carbon atoms of molecule B refined to very large anisotropic values suggestive of positional disorder, but inspection of the atoms in a difference synthesis calculated without the contributions from the affected atoms, while revealing elongated atoms, was unable to resolve separate disordered positions. Accordingly, refinement continued using single positions, but with, however, a clearly distorted geometry. Hydrogen atom positions were calculated for all aromatic positions and for the methylene groups of molecule A , and were included in calculations, with isotropic thermal parameters of 0.06 Å^2 , but were not refined. After a further six cycles of refinement, these positions

were recalculated to take account of shifts in the non-hydrogen atom positions. Prior to cycle 10 , corrections were made to all strong reflections to allow for inaccuracy in measurement due to counter saturation. The N-hydrogen atom in each molecule was located in a difference synthesis and included in the calculation at cycle 13 with $U_{iso} = 0.06$ Å^2 , and its positional parameters were refined in final cycles. A weighting scheme was applied from cycle 12 onwards, with final coefficients A = 0.6000 , B = -0.0116 and C = 0.0015 in a function of the form

$$W = (A + B|F_o| + C|F_o|^2)^{-1} \quad .$$

A further difference synthesis after cycle 13 , calculated with the contributions from the highly smeared methylene atoms excluded, now resolved two separate positions for atom C(14B) and refinement continued using both positions with initial occupancy factors of 0.5 , yielding an immediate improvement in the molecular geometry. Continuing high anisotropic thermal parameters in these and adjacent atom positions can be attributed to the effects of unresolvable disorder on the mean atom position.

A final difference synthesis showed no major irregularities in the structure, but revealed some slight residual electron density around the disordered methylene group, arising in part, presumably, from those hydrogen atoms not accounted for.

In all structure-factor calculations, the atomic scattering factors used were those derived by Cromer and Mann (1968)[39] for P, O, N and C, and by Stewart et al. (1965)[40] for H .

Observed and final calculated structure factors are given in Appendix 6 . Fractional coordinates and thermal parameters are listed

in Table 5.3 , and interatomic distances and angles, and intermolecular contacts are given in Table 5.5 . The estimated standard deviations quoted are derived from the inverse of the normal-equation least-squares matrix, and, owing to the use of the blocked-matrix approximation, are best regarded as minimum values. Details of some least-squares planes through various portions of the framework of both molecules are given in Table 5.6 , and the atomic numbering scheme is shown on a diagram of molecule A in Figure 5.1 , similar numbering being applied to molecule B , shown in Figure 5.2 which clearly illustrates the disorder and enlarged thermal ellipsoids. The molecular packing viewed along the a-axis is shown in Figure 5.3 .

5.3 Experimental Compound XXVI

Crystal Data (XXVI)

N-(methyl),N-(phenylethyl)diphenylphosphinamide (hydrated)

$C_{21}H_{22}PNO.H_2O$, M = 353.4 .

Monoclinic, a = 10.911 b = 7.942 c = 23.110 Å , $\beta = 104.35^{\circ}$,

$U = 1940.1$ Å^3 ,

$D_m = 1.17$ g cm^{-3} , Z = 4 , $D_c = 1.21$ g cm^{-3} ,

$F_{(000)} = 760$.

Space group : $P2_1/c$ (C_{2h}^5 , No.14), uniquely identified by systematic absences.

μ(Mo,Kα) = 1.60 cm^{-1} .

Data Collection

Radiation	:	Mo,Kα
Filter	:	graphite monochromator
Maximum scattering angle (2θ)	:	60°
Independent reflections (observed)	:	3098
Unobserved cutoff	:	$3\sigma_I$
Ratio of observations/parameters	:	9.83

Structure Determination

In the initial photographic examination of this compound, Weissenberg photographs, only, were taken and systematic absences were determined by inspection of the diffractometer data collection to be $h0\ell$ absent for $\ell = 2n+1$, indicative of space group Pc or P2/c. On the basis of an apparently non-centrosymmetric distribution of normalised structure factors and the similarity to compound XXV, known to have the space group Pc, the space group Pc was assumed, with two molecules in the asymmetric unit. The structure was determined by the automatic multi-solution method (MULTAN) using the 250 reflections with $|E| > 1.56$, with a starting set containing three variable phases which yielded 64 possible phase sets. The E-map calculated using the phase set with the highest combined figure of merit revealed both molecules with clear positions for all but four carbon atoms. A structure-factor and electron-density calculation with these 44 atoms gave positions for the remaining four atoms and indicated the presence of two additional isolated atoms, with peak height and location, some 3 Å from each phosphinyl group, suggestive of the oxygen atoms of two molecules of water of crystallisation. Subsequent refinement confirmed the correctness of this suggestion.

Structure Refinement

Refinement of positional, thermal and scale parameters by least-squares methods was completed after 16 cycles of minimisation, with residuals R and R' of 0.039 and 0.0027 respectively. Details of the

refinement are given in Table 5.2 .

By the convergence of isotropic refinement in cycle 4 , two features had become evident. Firstly, the two molecules in the asymmetric unit were related by approximate inversion symmetry. While this may be indicative of higher crystallographic symmetry, as was observed with compound VIII (see section 2.2), this need not be so, as may be seen from compound XXV where the two molecules within the asymmetric unit are related by an approximate a-glide perpendicular to the c-axis (see Discussion, section 5.4). Secondly, the two molecules were crystallographically interdependent, this dependency being inherent in the intensity data, such that displacement of one parameter of one molecule leads to a counteracting displacement, on refinement, in the equivalent parameter of the second molecule. This feature provides clear evidence of the reality of higher crystallographic symmetry.

Summation of the x coordinates of the equivalent atoms from both molecules, and similarly for y and z ,gave $\sum_{A,B} x = 0.944 \pm 0.015$, $\sum_{A,B} y = 0.500 \pm 0.035$ and $\sum_{A,B} z = 0.307 \pm 0.014$. This indicates a centre of inversion at (0.472 , 0.250 , 0.153), located at y = 0.25 , midway between the c-glide planes. However, this is not compatible with P2/c where the centres of symmetry are coincident with the glide planes, but only with $P2_1/c$ where the inversion centres and glide planes are separated by y = 0.25 . Re-examination of the intensity data revealed that halving of the 0k0 reflections was indeed present, having been previously overlooked, and this confirmed the correct space group as $P2_1/c$, with one molecule per asymmetric unit. New coordinates

compatible with the new symmetry were derived and refinement was resumed.

All hydrogen atoms, excluding those of the water molecule, were located in a difference synthesis and were included in the calculations with initially assigned isotropic thermal parameters of 0.05 $Å^2$, but were refined in later cycles. Prior to cycle 9 , corrections were made to all strong reflections to counteract errors in intensity measurements resulting from counter saturation.

A weighting scheme of the form

$$W = (A + B|F_o| + C|F_o|^2)^{-1}$$

was applied for the final four cycles, with coefficients A = 0.4766 , B = -0.0162 and C = 0.0019 determined by polynomial fit to the function Δ^2 .

A final difference synthesis revealed no errors in the structure. In all structure-factor calculations, atomic scattering factors derived by Cromer and Mann (1968)[39] for P, O, N and C and by Stewart et al.(1965)[40] for H were used.

Observed and final calculated structure factors are listed in Appendix 7 . Fractional coordinates and thermal parameters are given in Table 5.4 , and molecular dimensions and intermolecular contacts are listed in Table 5.5 , for comparison with the dimensions of the secondary phosphinamide, XXV . Estimated standard deviations, derived from the inverse of the least-squares normal-equation matrix, are best regarded as minimum values, as computer-storage limitations dictated the use of the blocked-matrix approximation. Details of some least-squares planes through various portions of the molecule are given

in Table 5.6 .

The atomic numbering scheme is shown in Figure 5.4 , and the molecular packing viewed down the b-axis is shown in Figure 5.5 .

Table 5.1

Course of refinement for XXV

Cycles	Parameters refined	Final R	Final R'
1 - 3	x,y,z,U_{iso} for P, O, N and C, scale factor. Unit weights, full matrix.	0.096	0.0121
4 - 5	x,y,z,U_{ij} for P, O, N and C, scale factor. Unit weights, blocked matrix.	0.076	0.0081
6 - 11	x,y,z,U_{ij} for P, O, N and C, scale factor. Calculated H-atoms included but not refined, unit weights, blocked matrix.	0.052	0.0026
12	x,y,z,U_{ij} for P, O, N and C, scale factor; H-atoms recalculated, (included but not refined), weighting scheme applied, blocked matrix.	0.049	0.0040
13	As previous, with two amido-H-atom positions included.	0.045	0.0032
14 - 15	x,y,z,U_{ij} for P, O, N and C, except C(14B) and C(14B') for which x,y,z and population parameter were refined, scale factor. Weighting scheme applied, blocked matrix.	0.043	0.0030
16 - 19	x,y,z,U_{ij} for P, O, N and C, scale factor. Weighting scheme applied, blocked matrix.	0.041	0.0027
20 - 21	x,y,z,U_{ij} for P, O, N and C, x,y,z for amido-H-atom only, scale factor. Weighting scheme applied, blocked matrix.	0.041	0.0027

Table 5.2

Course of refinement for XXVI

Cycles	Parameters refined	Final R	Final R'
1 - 4*	x,y,z,U_{iso} for P, O, N and C, scale factor. Unit weights, full matrix.	0.097	0.0108
5 - 10	x,y,z,U_{ij} for P, O, N and C, scale factor. H-atoms included but not refined. Unit weights, blocked matrix.	0.048	0.0025
11 - 12	x,y,z,U_{ij} for P, O, N and C, x,y,z,U_{iso} for H, scale factor. Unit weights, blocked matrix.	0.040	0.0016
13 - 16	x,y,z,U_{ij} for P, O, N and C, x,y,z,U_{iso} for H, scale factor. Weighting scheme applied, blocked matrix.	0.039	0.0027

* The four initial cycles were carried out using Pc symmetry with two molecules per asymmetric unit. Thereafter, the correct space group, $P2_1/c$, was used, with one molecule per asymmetric unit.

Table 5.3

a) Fractional coordinates for XXV

	x/a	y/b	z/c
P(A)	1.00000(-)	0.31502(6)	1.00000(-)
O(A)	1.0861(5)	0.2927(2)	1.1068(3)
N(A)	0.8396(5)	0.2696(2)	0.9570(4)
C(1A)	1.1380(6)	0.3122(2)	0.8784(4)
C(2A)	1.3058(7)	0.30647(3)	0.8968(5)
C(3A)	1.4133(8)	0.3084(3)	0.8036(6)
C(4A)	1.3548(8)	0.3167(3)	0.6940(5)
C(5A)	1.1889(8)	0.3209(3)	0.6730(5)
C(6A)	1.0806(7)	0.3185(3)	0.7647(5)
C(7A)	0.9216(6)	0.4032(3)	1.0133(4)
C(8A)	0.9753(8)	0.4428(3)	1.1065(5)
C(9A)	0.9238(10)	0.5110(4)	1.1212(7)
C(10A)	0.8198(10)	0.5405(3)	1.0428(8)
C(11A)	0.7641(9)	0.5023(4)	0.9506(7)
C(12A)	0.8151(8)	0.4339(3)	0.9355(5)
C(13A)	0.8603(8)	0.1935(3)	0.9439(5)
C(14A)	0.7171(9)	0.1620(3)	0.8793(5)
C(15A)	0.7320(8)	0.0833(3)	0.8688(5)
C(16A)	0.6666(9)	0.0394(3)	0.9528(6)
C(17A)	0.6745(11)	-0.0324(4)	0.9424(7)
C(18A)	0.7527(11)	-0.0614(3)	0.8521(8)
C(19A)	0.8193(10)	-0.0197(4)	0.7694(7)
C(20A)	0.8076(10)	0.0531(4)	0. 7764(6)

Table 5.3.a(contd.)

	x/a	y/b	z/c
P(B)	0.49624(20)	0.28125(7)	0.22652(13)
O(B)	0.5836(5)	0.2816(2)	0.1146(3)
N(B)	0.3348(6)	0.2300(2)	0.2418(4)
C(1B)	0.6336(6)	0.2561(3)	0.3426(4)
C(2B)	0.8008(7)	0.2644(3)	0.3273(5)
C(3B)	0.9069(8)	0.2476(4)	0.4168(6)
C(4B)	0.8481(8)	0.2236(4)	0.5205(6)
C(5B)	0.6826(9)	0.2157(3)	0.5365(5)
C(6B)	0.5748(7)	0.2319(3)	0.4472(5)
C(7B)	0.4182(6)	0.3675(3)	0.2612(4)
C(8B)	0.4643(8)	0.4228(3)	0.1920(5)
C(9B)	0.4095(10)	0.4906(3)	0.2168(8)
C(10B)	0.3124(10)	0.5015(3)	0.3116(7)
C(11B)	0.2635(9)	0.4462(4)	0.3799(6)
C(12B)	0.3187(8)	0.3795(3)	0.3552(5)
C(13B)	0.3524(12)	0.1538(3)	0.2209(10)
C(14B)	0.2917(30)	0.1237(8)	0.1334(15)
C(14B')	0.2192(20)	0.1164(7)	0.2179(17)
C(15B)	0.2490(11)	0.0409(4)	0.1514(10)
C(16B)	0.1681(11)	0.0141(5)	0.0578(7)
C(17B)	0.1601(12)	-0.0558(6)	0.0383(8)
C(18B)	0.2362(11)	-0.1013(5)	0.1103(11)
C(19B)	0.3212(11)	-0.0774(4)	0.2002(9)
C(20B)	0.3263(12)	-0.0061(4)	0.2240(10)

Table 5.3 (contd.)

b) H-atom fractional coordinates and isotropic thermal parameters ($Å^2$)

	x/a	y/b	z/c	U iso
H(1A)	0.763(5)	0.279(2)	1.000(4)	0.049(12)
H(2A)	1.3476	0.3002	0.9147	0.06
H(3A)	1.5927	0.3042	0.8179	0.06
H(4A)	1.4312	0.3211	0.6299	0.06
H(5A)	1.1483	0.3246	0.5948	0.06
H(6A)	0.9629	0.3216	0.7513	0.06
H(8A)	1.0530	0.4216	1.1609	0.06
H(9A)	0.9589	0.5382	1.1889	0.06
H(10A)	0.7834	0.5895	1.0511	0.06
H(11A)	0.6860	0.5227	0.8968	0.06
H(12A)	0.7784	0.4075	0.8679	0.06
H(131A)	0.9633	0.1823	0.9023	0.06
H(132A)	0.8716	0.1699	1.0203	0.06
H(141A)	0.6175	0.1728	0.9209	0.06
H(142A)	0.7123	0.1822	0.8034	0.06
H(16A)	0.6131	0.0600	1.0208	0.06
H(17A)	0.6263	-0.0623	1.0024	0.06
H(18A)	0.7610	-0.1118	0.8437	0.06
H(19A)	0.8768	-0.0412	0.7038	0.06
H(20A)	0.8527	0.0828	0.7138	0.06

Table 5.3.b (contd.)

	x/a	y/b	z/c	U iso
H(1B)	0.243(5)	0.246(2)	0.216(3)	0.045(12)
H(2B)	0.8446	0.2818	0.2534	0.06
H(3B)	1.0252	0.2531	0.4067	0.06
H(4B)	0.9245	0.2126	0.5828	0.06
H(5B)	0.6414	0.1977	0.6111	0.06
H(6B)	0.4566	0.2270	0.4590	0.06
H(8B)	0.5368	0.4135	0.1260	0.06
H(9B)	0.4391	0.5299	0.1676	0.06
H(10B)	0.2746	0.5483	0.3327	0.06
H(11B)	0.1897	0.4540	0.4445	0.06
H(12B)	0.2875	0.3409	0.4059	0.06
H(16B)	0.1110	0.0473	0.0062	0.06
H(17B)	0.1010	-0.0728	-0.0290	0.06
H(18B)	0.2296	-0.1521	0.0986	0.06
H(19B)	0.3795	-0.1108	0.2521	0.06
H(20B)	0.3852	0.0119	0.2925	0.06

Table 5.3 (cont.)

c) Anisotropic thermal parameters ($Å^2$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(A)	0.0457	0.0401	0.0404	0.0005	-0.0009	0.0024
O(A)	0.0626	0.0667	0.0483	0.0082	-0.0064	0.0122
N(A)	0.0498	0.0405	0.0580	-0.0010	0.0033	-0.0035
C(1A)	0.0466	0.0329	0.0467	-0.0005	0.0019	-0.0020
C(2A)	0.0473	0.0522	0.0621	0.0035	-0.0001	0.0069
C(3A)	0.0552	0.0584	0.0799	0.0093	0.0081	0.0006
C(4A)	0.0676	0.0631	0.0615	-0.0009	0.0247	-0.0064
C(5A)	0.0756	0.0701	0.0479	-0.0057	0.0007	-0.0052
C(6A)	0.0494	0.0555	0.0524	-0.0042	-0.0034	-0.0063
C(7A)	0.0505	0.0410	0.0508	-0.0036	-0.0011	-0.0069
C(8A)	0.0675	0.0608	0.0608	0.0031	-0.0060	-0.0112
C(9A)	0.0927	0.0636	0.0956	-0.0016	-0.0003	-0.0283
C(10A)	0.0931	0.0431	0.1190	0.0055	0.0250	-0.0154
C(11A)	0.0922	0.0611	0.1035	0.0187	-0.0109	0.0077
C(12A)	0.0825	0.0513	0.0606	0.0075	-0.0062	-0.0018
C(13A)	0.0610	0.0419	0.0759	-0.0027	0.0017	0.0028
C(14A)	0.0889	0.0512	0.0667	0.0005	-0.0170	-0.0032
C(15A)	0.0668	0.0434	0.0684	-0.0049	-0.0194	-0.0029
C(16A)	0.0937	0.0622	0.0707	-0.0042	0.0030	0.0003
C(17A)	0.1091	0.0583	0.0920	-0.0168	-0.0029	0.0181
C(18A)	0.1027	0.0433	0.1080	-0.0121	-0.0195	-0.0028
C(19A)	0.0992	0.0694	0.0938	0.0112	-0.0021	-0.0159
C(20A)	0.0967	0.0619	0.0793	-0.0052	0.0056	0.0055

Table 5.3.c (cont.)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(B)	0.0581	0.0457	0.0405	0.0083	-0.0011	-0.0008
O(B)	0.0677	0.0890	0.0430	0.0178	0.0066	0.0011
N(B)	0.0519	0.0457	0.0724	0.0066	-0.0145	0.0011
C(1B)	0.0557	0.0407	0.0447	0.0064	-0.0073	-0.0026
C(2B)	0.0541	0.0657	0.0579	-0.0019	-0.0023	0.0060
C(3B)	0.0568	0.0812	0.0760	-0.0055	-0.0119	0.0001
C(4B)	0.0697	0.0705	0.0704	0.0046	-0.0248	-0.0021
C(5B)	0.0862	0.0628	0.0488	0.0098	-0.0073	0.0041
C(6B)	0.0539	0.0573	0.0478	0.0081	-0.0001	-0.0007
C(7B)	0.0482	0.0459	0.0468	0.0033	-0.0067	-0.0014
C(8B)	0.0816	0.0513	0.0675	0.0047	0.0115	0.0097
C(9B)	0.0987	0.0461	0.1165	-0.0030	-0.0010	0.0136
C(10B)	0.0905	0.0397	0.1104	0.0163	-0.0152	-0.0141
C(11B)	0.0791	0.0675	0.0819	0.0156	0.0060	-0.0234
C(12B)	0.0775	0.0559	0.0609	0.0096	0.0142	0.0002
C(13B)	0.1103	0.0415	0.2019	0.0028	-0.0738	-0.0215
C(14B)	0.1830	0.0546	0.0952	0.0130	-0.0645	-0.0194
C(14B')	0.0871	0.0480	0.1203	-0.0066	0.0358	-0.0063
C(15B)	0.1002	0.0549	0.1806	0.0078	-0.0559	-0.0255
C(16B)	0.0985	0.0987	0.1079	0.0015	-0.0315	-0.0026
C(17B)	0.0973	0.1178	0.1080	-0.0072	-0.0136	-0.0530
C(18B)	0.0781	0.0767	0.1854	-0.0083	-0.0024	-0.0590
C(19B)	0.0943	0.0655	0.1626	0.0145	-0.0251	0.0073
C(20B)	0.1315	0.0678	0.1775	0.0181	-0.0853	-0.0373

Mean estimated standard deviations ($Å^2$)

P	0.0007	0.0006	0.0006	0.0006	0.0005	0.0006
O	0.0025	0.0027	0.0020	0.0021	0.0018	0.0018
N	0.0025	0.0022	0.0027	0.0020	0.0021	0.0020
C(A)	0.0043	0.0034	0.0041	0.0033	0.0034	0.0030
C(B)	0.0059	0.0044	0.0062	0.0041	0.0049	0.0042

Table 5.4

a) Fractional coordinates for XXVI

	x/a	y/b	z/c
P	0.08168(4)	1.18587(7)	0.12142(2)
O(1)	0.04441(13)	1.27389(20)	0.06277(6)
O(2)	0.15193(17)	0.49276(32)	-0.00659(10)
N	0.11214(14)	0.98289(22)	0.12130(7)
C(1)	0.22367(16)	1.27531(24)	0.16857(8)
C(2)	0.29278(20)	1.39134(31)	0.14443(10)
C(3)	0.40053(23)	1.46505(36)	0.18040(12)
C(4)	0.43884(21)	1.42618(33)	0.23986(11)
C(5)	0.37188(20)	1.31175(31)	0.26426(10)
C(6)	0.26440(19)	1.23639(29)	0.22905(9)
C(7)	-0.04158(16)	1.20678(25)	0.16067(8)
C(8)	-0.13140(20)	1.33276(30)	0.14335(10)
C(9)	-0.22429(22)	1.35742(34)	0.17403(11)
C(10)	-0.22709(22)	1.25988(35)	0.22242(12)
C(11)	-0.13865(23)	1.13507(34)	0.24036(12)
C(12)	-0.04648(20)	1.10667(30)	0.20951(10)
C(13)	0.23784(18)	0.92225(30)	0.11828(9)
C(14)	0.27101(22)	0.94591(41)	0.05817(10)
C(15)	0.40477(19)	0.89024(30)	0.06201(9)
C(16)	0.43180(20)	0.72622(32)	0.04913(10)
C(17)	0.55548(23)	0.67567(38)	0.05374(12)
C(18)	0.65316(22)	0.78794(38)	0.07098(11)
C(19)	0.62837(23)	0.94996(40)	0.08442(12)
C(20)	0.50493(23)	1.00097(36)	0.08007(11)
C(21)	0.00731(23)	0.87074(34)	0.09201(15)

Table 5.4 (contd.)

b) H-atom fractional coordinates and isotropic thermal parameters ($Å^2$)

	x/a	y/b	z/c	U iso
H(2)	0.265(2)	1.420(3)	0.102(1)	0.064(7)
H(3)	0.454(3)	1.535(4)	0.161(1)	0.097(10)
H(4)	0.519(2)	1.481(3)	0.266(1)	0.075(8)
H(5)	0.398(2)	1.286(3)	0.306(1)	0.066(7)
H(6)	0.221(2)	1.150(3)	0.246(1)	0.061(7)
H(8)	-0.129(2)	1.399(3)	0.110(1)	0.053(6)
H(9)	-0.290(2)	1.440(3)	0.160(1)	0.072(7)
H(10)	-0.298(2)	1.280(3)	0.244(1)	0.073(8)
H(11)	-0.142(2)	1.073(3)	0.274(1)	0.066(7)
H(12)	0.012(2)	1.018(3)	0.222(1)	0.059(7)
H(131)	0.303(2)	0.984(3)	0.150(1)	0.044(5)
H(132)	0.241(2)	0.805(3)	0.129(1)	0.059(7)
H(141)	0.213(3)	0.881(4)	0.029(1)	0.092(10)
H(142)	0.258(3)	1.060(4)	0.047(1)	0.087(10)
H(16)	0.367(2)	0.653(3)	0.037(1)	0.058(6)
H(17)	0.572(3)	0.565(4)	0.045(1)	0.087(9)
H(18)	0.737(3)	0.749(4)	0.073(1)	0.088(9)
H(19)	0.696(3)	1.027(4)	0.096(1)	0.087(9)
H(20)	0.485(2)	1.113(4)	0.087(1)	0.071(8)
H(211)	-0.071(3)	0.914(4)	0.094(1)	0.082(9)
H(212)	-0.001(3)	0.858(5)	0.047(2)	0.112(12)
H(213)	0.023(3)	0.759(5)	0.110(1)	0.106(11)

Table 5.4 (cont.)

c) Anisotropic thermal parameters ($Å^2$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	0.0332	0.0418	0.0383	0.0002	0.0092	0.0041
O(1)	0.0484	0.0634	0.0440	0.0023	0.0093	0.0129
O(2)	0.0635	0.1177	0.0960	0.0021	0.0179	0.0442
N	0.0352	0.0426	0.0519	-0.0020	0.0126	-0.0044
C(1)	0.0365	0.0389	0.0433	0.0003	0.0105	-0.0005
C(2)	0.0502	0.0632	0.0492	-0.0128	0.0092	0.0062
C(3)	0.0541	0.0727	0.0712	-0.0222	0.0099	0.0066
C(4)	0.0468	0.0592	0.0663	-0.0040	-0.0019	-0.0056
C(5)	0.0540	0.0554	0.0488	0.0078	0.0000	-0.0005
C(6)	0.0502	0.0457	0.0458	0.0009	0.0094	0.0057
C(7)	0.0365	0.0422	0.0460	-0.0009	0.0128	0.0007
C(8)	0.0510	0.0511	0.0523	0.0084	0.0150	0.0045
C(9)	0.0529	0.0586	0.0716	0.0134	0.0194	-0.0057
C(10)	0.0557	0.0657	0.0761	-0.0030	0.0347	-0.0126
C(11)	0.0637	0.0601	0.0638	-0.0091	0.0323	0.0039
C(12)	0.0466	0.0491	0.0617	0.0009	0.0212	0.0103
C(13)	0.0421	0.0470	0.0441	0.0060	0.0123	0.0004
C(14)	0.0487	0.0780	0.0468	0.0112	0.0158	0.0029
C(15)	0.0464	0.0623	0.0403	0.0029	0.0165	0.0014
C(16)	0.0489	0.0599	0.0633	-0.0057	0.0177	-0.0063
C(17)	0.0575	0.0648	0.0731	0.0084	0.0198	-0.0105
C(18)	0.0441	0.0833	0.0677	0.0013	0.0199	-0.0077
C(19)	0.0516	0.0798	0.0691	-0.0153	0.0195	-0.0065
C(20)	0.0631	0.0580	0.0578	0.0013	0.0211	-0.0036
C(21)	0.0466	0.0573	0.0876	-0.0117	0.0142	-0.0178
		Mean estimated standard deviations ($Å^2$)				
P	0.0002	0.0003	0.0002	0.0002	0.0002	0.0002
N	0.0007	0.0009	0.0006	0.0006	0.0006	0.0007
O	0.0010	0.0014	0.0011	0.0009	0.0008	0.0010
C	0.0011	0.0015	0.0013	0.0011	0.0010	0.0011

Table 5.5

Interatomic distances and angles

a) Bonded distances (Å)

	XXV A	XXV B	XXVI
P - O	1.481(4)	1.478(4)	1.489(1)
P - N	1.643(4)	1.647(5)	1.646(2)
P - C(1)	1.803(5)	1.810(5)	1.804(2)
P - C(7)	1.802(5)	1.806(5)	1.807(2)
N - C(13)	1.467(7)	1.477(8)	1.472(3)
N - H(1)	0.82(4)	0.86(4)	-
N - C(21)	-	-	1.475(3)
C(13)- C(14)	1.509(9)	1.281(20)*	1.532(3)
C(14)- C(15)	1.508(8)	1.639(18)*	1.506(3)
C(15)- C(16)	1.389(9)	1.365(13)	1.384(3)
C(16)- C(17)	1.374(10)	1.351(15)	1.387(4)
C(17)- C(18)	1.343(12)	1.352(15)	1.371(4)
C(18)- C(19)	1.357(11)	1.329(15)	1.366(4)
C(19)- C(20)	1.391(10)	1.386(12)	1.386(4)
C(20)- C(15)	1.362(9)	1.378(13)	1.384(3)
C(1) - C(2)	1.388(7)	1.383(8)	1.392(3)
C(2) - C(3)	1.390(9)	1.385(9)	1.390(4)
C(3) - C(4)	1.362(9)	1.370(9)	1.369(4)
C(4) - C(5)	1.375(9)	1.369(10)	1.377(3)
C(5) - C(6)	1.381(8)	1.390(9)	1.381(3)
C(6) - C(1)	1.400(7)	1.381(7)	1.393(3)
C(7) - C(8)	1.386(8)	1.374(8)	1.388(3)
C(8) - C(9)	1.375(9)	1.395(9)	1.387(3)
C(9) - C(10)	1.362(11)	1.369(12)	1.367(4)
C(10)- C(11)	1.367(11)	1.375(10)	1.374(4)
C(11)- C(12)	1.378(9)	1.377(9)	1.388(3)
C(12)- C(7)	1.379=8)	1.375(8)	1.392(3)

* denotes mean value

Table 5.5 (cont.)

b) Interbond angles (^{o})

	XXV A	XXV B	XXVI
O - P - N	118.5(2)	118.8(3)	117.90(9)
O - P - C(1)	110.3(2)	110.6(2)	111.40(9)
O - P - C(7)	111.3(2)	111.1(2)	110.20(9)
N - P - C(1)	104.1(2)	104.9(2)	104.06(9)
N - P - C(7)	103.5(2)	103.5(2)	105.46(9)
C(1)-P - C(7)	108.4(2)	107.1(2)	107.17(8)
P - N - C(13)	117.4(4)	119.1(5)	120.76(10)
P - N - H(1)	108.4(30)	116.2(28)	-
H(1)-N - C(13)	111.1(30)	112.2(28)	-
P - N - C(21)	-	-	117.26(11)
C(21)-N - C(13)	-	-	113.99(15)
N - C(13)-C(14)	110.8(5)	120.1(10)*	115.81(15)
C(13)-C(14)-C(15)	111.9(5)	113.2(13)*	110.72(15)
C(14)-C(15)-C(16)	120.7(6)	118.9(11)*	121.23(18)
C(15)-C(16)-C(17)	121.3(6)	120.1(9)	120.74(17)
C(16)-C(17)-C(18)	119.9(7)	120.5(9)	120.39(18)
C(17)-C(18)-C(19)	120.0(6)	120.0(9)	119.68(19)
C(18)-C(19)-C(20)	120.9(7)	120.5(9)	120.15(21)
C(19)-C(20)-C(15)	119.9(6)	121.6(8)	121.11(18)
C(20)-C(15)-C(16)	118.0(6)	117.4(8)	117.92(17)
C(14)-C(15)-C(20)	121.3(6)	120.1(10)*	120.83(19)

* denotes mean value

Table 5.5.b (cont.)

	XXV A	XXV B	XXVI
P - C(1)-C(2)	119.9(4)	118.9(4)	119.21(10)
P - C(1)-C(6)	121.5(4)	121.5(4)	122.11(9)
C(2)-C(1)-C(6)	118.6(5)	119.6(5)	118.64(15)
C(1)-C(2)-C(3)	120.0(5)	119.4(5)	120.08(16)
C(2)-C(3)-C(4)	120.3(6)	120.9(6)	120.54(17)
C(3)-C(4)-C(5)	120.9(6)	120.0(6)	119.92(18)
C(4)-C(5)-C(6)	119.4(5)	119.8(5)	120.29(16)
C(5)-C(6)-C(1)	120.7(5)	120.3(5)	120.53(15)
P - C(7)-C(8)	117.5(4)	118.0(4)	118.79(10)
P - C(7)-C(12)	124.2(4)	122.3(4)	122.52(9)
C(8)-C(7)-C(12)	118.3(5)	119.7(5)	118.62(15)
C(7)-C(8)-C(9)	120.9(6)	120.0(6)	120.49(15)
C(8)-C(9)-C(10)	119.8(7)	119.4(6)	120.36(18)
C(9)-C(10)-C(11)	120.3(7)	120.8(6)	119.95(17)
C(10)-C(11)-C(12)	120.1(7)	119.4(6)	120.43(17)
C(11)-C(12)-C(7)	120.5(6)	120.7(6)	120.13(16)

Table 5.5 (cont.)

c) Intramolecular non-bonded distances (Å)

	XXV A	XXV B	XXVI
O ....N	2.69	2.69	2.69
O ....H(1)	3.00	3.15	-
O ....C(13)	3.24	3.16	3.54
O ....C(2)	3.03	3.05	3.04
O ....C(8)	3.00	3.00	3.02
N ....C(6)	3.11	3.07	3.31
N ....C(12)	3.14	3.14	3.14
C(13)..C(16)	3.33	3.59	3.34
C(13)..C(20)	3.33	3.05	3.31
O ....C(21)	-	-	3.32
O ....C(14)	> 4.0	> 4.0	3.61
C(7)...C(21)	-	-	3.22
C(14)..C(21)	-	-	3.22
C(7)...H(1)	2.64	2.74	-
C(12)..H(1)	2.97	3.01	-
C(13)..C(1)	3.29	3.32	3.05

Table 5.5 (cont.)

d) Intermolecular contacts (Å) for XXV

O(A)....N(B)^{I}	2.82	C(5A)...C(4B)^{IV}	3.77
O(A)....H(1B)^{I}	2.00	C(19A)..C(15B)^{V}	3.78
C(2A)...O(B)^{I}	3.42	C(19A)..C(16B)^{V}	3.75
N(A)....O(B)^{II}	2.78	C(2A)...C(10B)^{VI}	3.78
H(1A)...O(B)^{II}	1.97	C(3A)...C(10B)^{VI}	3,71
P(A)....O(B)^{II}	3.70	C(4A)...C(10B)^{VI}	3.73
C(7A)...O(B)^{II}	3.78	C(4A)...C(9B)^{VI}	3.71
C(13A)..O(B)^{II}	3.44	C(17A)..C(5B)^{VII}	3.66
C(14A)..O(B)^{II}	3.71	C(18A)..C(4B)^{VII}	3.73
O(A)....C(2B)^{II}	3.49	C(18A)..C(5B)^{VII}	3.68
C(11A)..C(10B)^{III}	3.76	C(18A)..C(6B)^{VII}	3.72
C(12A)..C(10B)^{III}	3.74		

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

I	1+x,	y,	1+z ;	II	x,	y,	1+z ;
III	1+x,	y,	2+z ;	IV	x,	y,	z ;
V	1+x,	-y,	1/2+z ;	VI	1+x,	1-y,	1/2+z ;
VII	x,	-y,	1/2+z .				

Table 5.5 (cont.)

e) Intermolecular contacts (Å) for XXVI

O(2)...C(16)^{I}	3.53	C(19)...C(20)^{V}	3.74
O(1)...O(2)^{II}	2.81	C(20)...C(20)^{V}	3.74
O(2)...C(2)^{II}	3.54	O(2)....C(16)^{VI}	3.64
C(3)...C(16)^{II}	3.76	C(17)...C(17)^{VI}	3.73
O(1)...C(21)^{III}	3.67	C(11)...C(6)^{VII}	3.59
O(1)...O(2)^{III}	2.89	C(11)...C(5)^{VII}	3.59
O(2)...C(8)^{III}	3.41	C(10)...C(4)^{VII}	3.76
O(2)...O(2)^{IV}	3.41	C(5)....C(19)^{VIII}	3.66
O(2)...C(21)^{IV}	3.68	C(4)....C(5)^{VIII}	3.71
C(15)..C(19)^{V}	3.55	C(3)....C(5)^{VIII}	3.72
C(15)..C(20)^{V}	3.76		

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

I	x,	y,	z ;	II	x,	1+y,	z ;
III	-x,	-y,	-z ;	IV	-x,	-1-y,	-z ;
V	1-x,	-y,	-z ;	VI	1-x,	-1-y,	-z ;
VII	-x,	1/2+y,	1/2-z ;	VIII	1-x,	1/2+y,	1/2-z .

Table 5.5 (cont.)

f) Torsion angles (°)

	XXV A	XXV B	XXVI
O - P - C(1)-C(2)	-14.3	22.3	-9.9
O - P - C(7)-C(8)	12.0	-8.2	-18.4
O - P - N - C(13)	-52.9	56.8	83.9
O - P - N - C(21)	-	-	-63.2
N - P -C(1)- C(2)	-142.4	151.5	118.2
N - P -C(7)- C(8)	140.3	-136.8	-146.6
C(1)- P - N - C(13)	70.0	-67.5	-40.1
C(1)- P - N - C(21)	-	-	172.9
C(7)- P - N - C(13)	-176.7	-179.6	-152.7
C(7)- P - N - C(21)	-	-	60.2
P - N - C(13)-C(14)	-167.2	-139.6*	-71.3
C(21)-N - C(13)-C(14)	-	-	76.8
N - C(13)-C(14)-C(15)	-177.7	-177.0*	176.1
C(13)-C(14)-C(15)-C(16)	90.0	-154.9*	90.5
C(13)-C(14)-C(15)-C(20)	-91.0	24.7*	-87.8
O - P - N - H(1)	74(3)	-83(3)	-
Mean e.s.d. (excluding final angle involving H(1))	0.5	0.8	0.2

* denotes mean value

Table 5.6

a) Least-squares planes for XXV A

a) Equation of plane

i) $0.0556X + 0.9948Y + 0.0856Z + 7.2848 = 0$

ii) $0.7790X + 0.3191Y - 0.5397Z + 1.9575 = 0$

iii) $0.8649X + 0.0164Y + 0.5017Z + 10.2086 = 0$

b) Deviation of atoms from the plane (Å)

i)	P	0.123	0	-0.155	C(1)	0.011*
	C(2)	-0.003*	C(3)	-0.010*	C(4)	0.013*
	C(5)	-0.004*	C(6)	-0.008*		
ii)	P	0.047	0	-0.210	C(7)	0.002*
	C(8)	0.001*	C(9)	-0.004*	C(10)	0.006*
	C(11)	-0.003*	C(12)	-0.001*		
iii)	C(13)	1.373	C(14)	-0.019	C(15)	0.001*
	C(16)	0.012*	C(17)	-0.015*	C(18)	0.004*
	C(19)	0.009*	C(20)	-0.011*		

c) Dihedral angle between planes

i) and ii) : 71.7°

i) and iii) : 83.8°

ii) and iii) : 65.9°

* denotes atom used to define plane.

X, Y and Z are orthogonal coordinates in Å .

Table 5.6 (cont.)

b) Least-squares planes for XXV B

a) Equation of plane

i) $-0.0\,07X + 0.9402Y + 0.3352Z + 5.601 = 0$

ii) $0.8060X + 0.1458Y + 0.5737Z + 5.4928 = 0$

iii) $0.8299X + 0.0672Y - 0.5538Z + 0.7702 = 0$

b) Deviation of atoms from the plane (Å)

i)	P	0.066	0	-0.405	C(1)	-0.002*
	C(2)	0.004*	C(3)	-0.002*	C(4)	-0.001*
	C(5)	0.003*	C(6)	-0.001*		
ii)	P	0.045	0	-0.121	C(7)	0.002*
	C(8)	0.000*	C(9)	-0.007*	C(10)	0.012*
	C(11)	-0.010*	C(12)	0.003*		
iii)	C(13)	0.391	C(14)	0.504	C(14')	-0.538
	C(15)	-0.006*	C(16)	0.014*	C(17)	-0.005*
	C(18)	-0.011*	C(19)	0.018*	C(20)	-0.009*

c) Dihedral angle between planes

i) and ii) : 73.7°

i) and iii) : 99.9°

ii) and iii) : 68.8°

* denotes atom used to define plane.

X, Y and Z are orthogonal coordinates in Å .

Table 5.6 (cont.)

c) Least-squares planes for XXVI

a) Equation of plane

i) $0.6340X - 0.7431Y - 0.2142Z - 1.4976 = 0$

ii) $-0.4658X - 0.6470Y - 0.6037Z - 2.5921 = 0$

iii) $-0.1512X - 0.2588Y + 0.9540Z + 0.9407 = 0$

b) Deviation of atoms from the plane (Å)

i)	P	-0.057	0	-0.340	C(1)	0.000*
	C(2)	-0.003*	C(3)	0.004*	C(4)	-0.002*
	C(5)	-0.001*	C(6)	0.002*		
ii)	P	-0.095	0	0.278	C(7)	-0.002*
	C(8)	-0.005*	C(9)	0.007*	C(10)	-0.002*
	C(11)	-0.005*	C(12)	0.007*		
iii)	C(13)	1.456	C(14)	0.016	C(15)	-0.005*
	C(16)	0.001*	C(17)	0.004*	C(18)	-0.005*
	C(19)	0.001*	C(20)	0.004*		

c) Dihedral angle between planes

i) and ii) : 71.7°

i) and iii) : 96.2°

ii) and iii) : 109.8°

* denotes atom used to define plane.

X, Y and Z are orthogonal coordinates in Å .

Figure 5.1

Atomic numbering scheme

(XXV - molecule A)

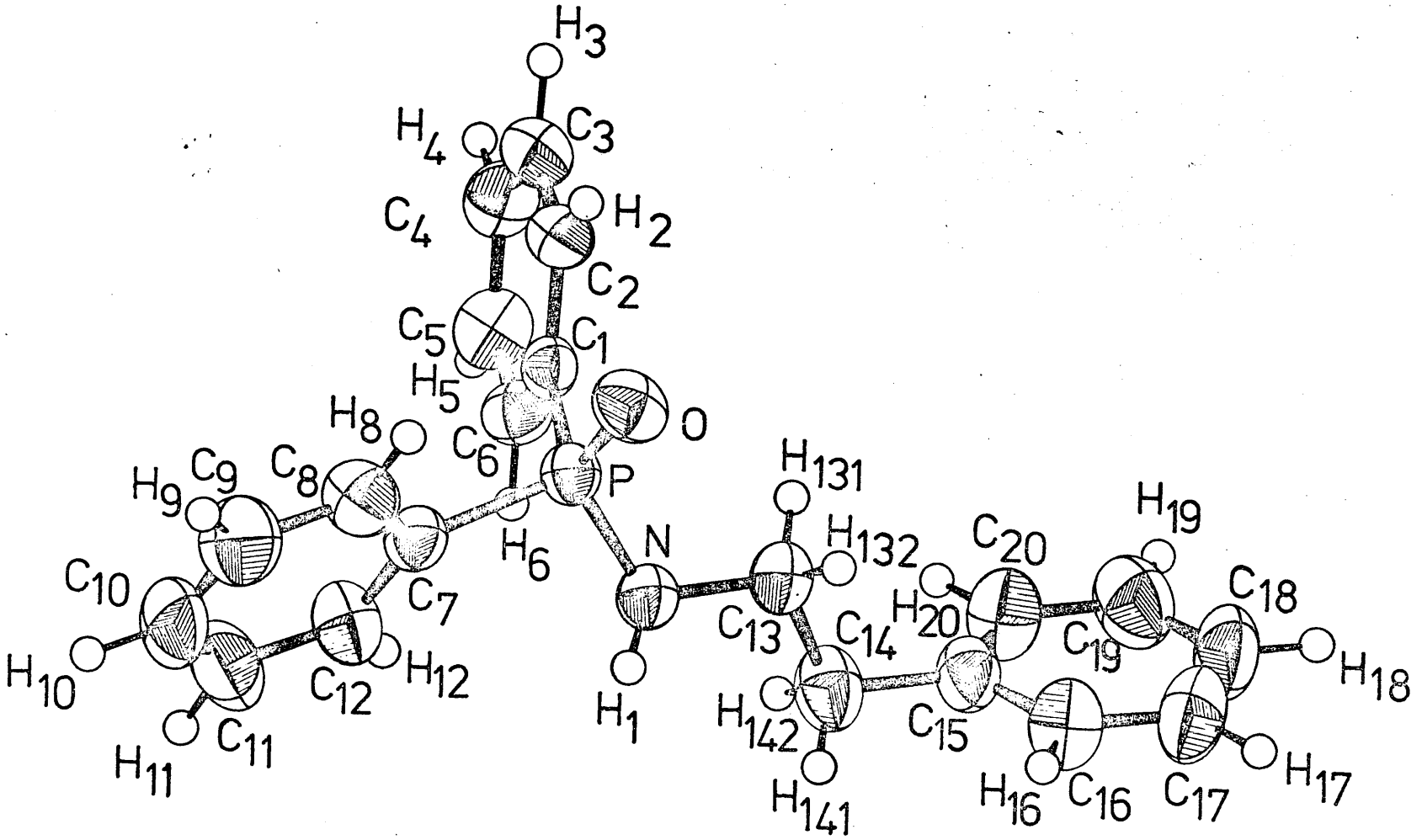

H3
H4
C3
C4
H2
C2
C5
C1
H5
O
H8
C6
P
C9
C8
H9
H131
H19
H132
C20
N
H6
C10
C7
H20
C18
C13
C14
C19
H10
C12
H12
H1
H18
H142
C15
H11
C11
H17
H141
H16
C16
C17

Figure 5.2

Thermal ellipsoid diagram of molecule B (XXV), showing positional disorder

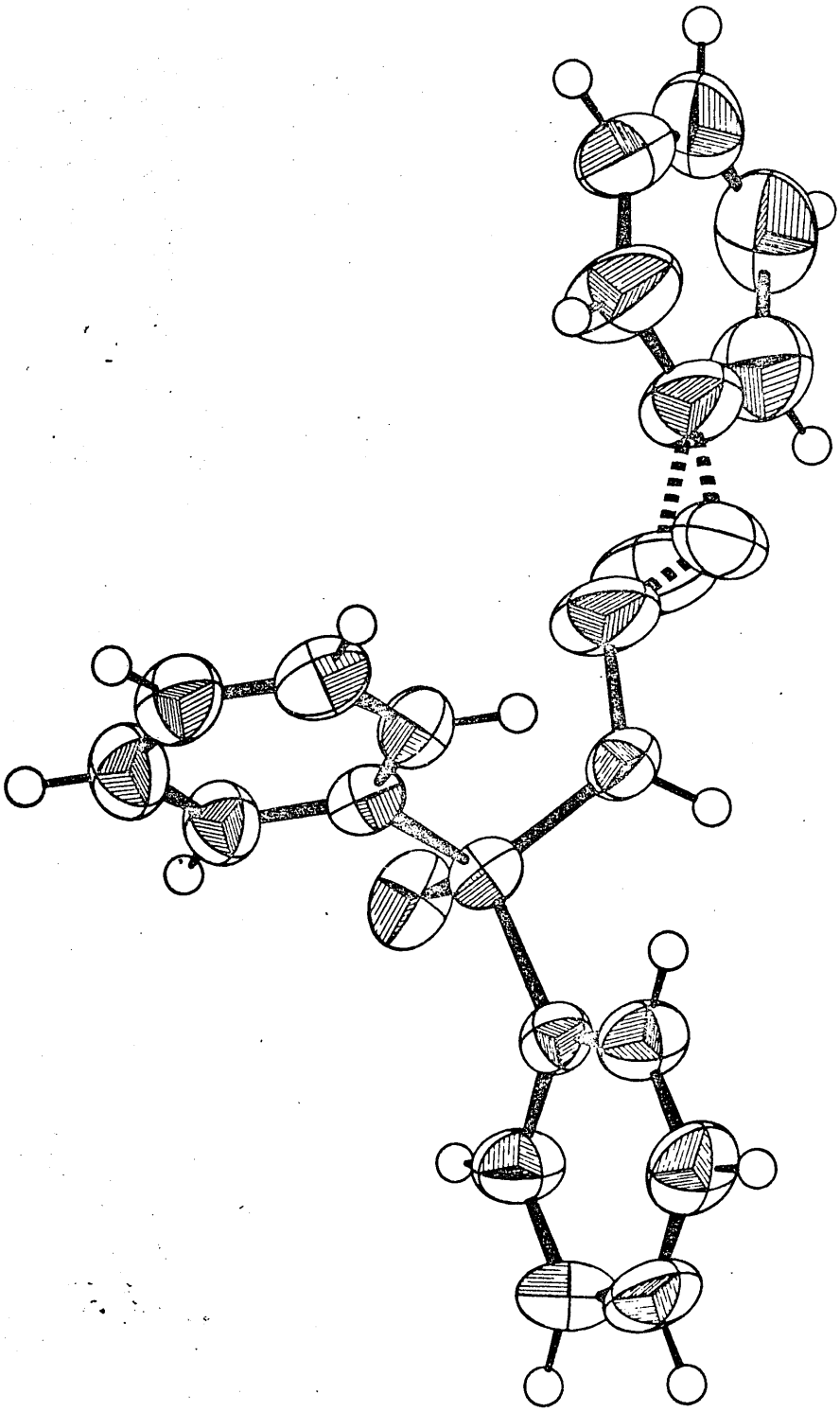


Figure 5.3

Molecular packing arrangement viewed along the a-axis

(XXV)

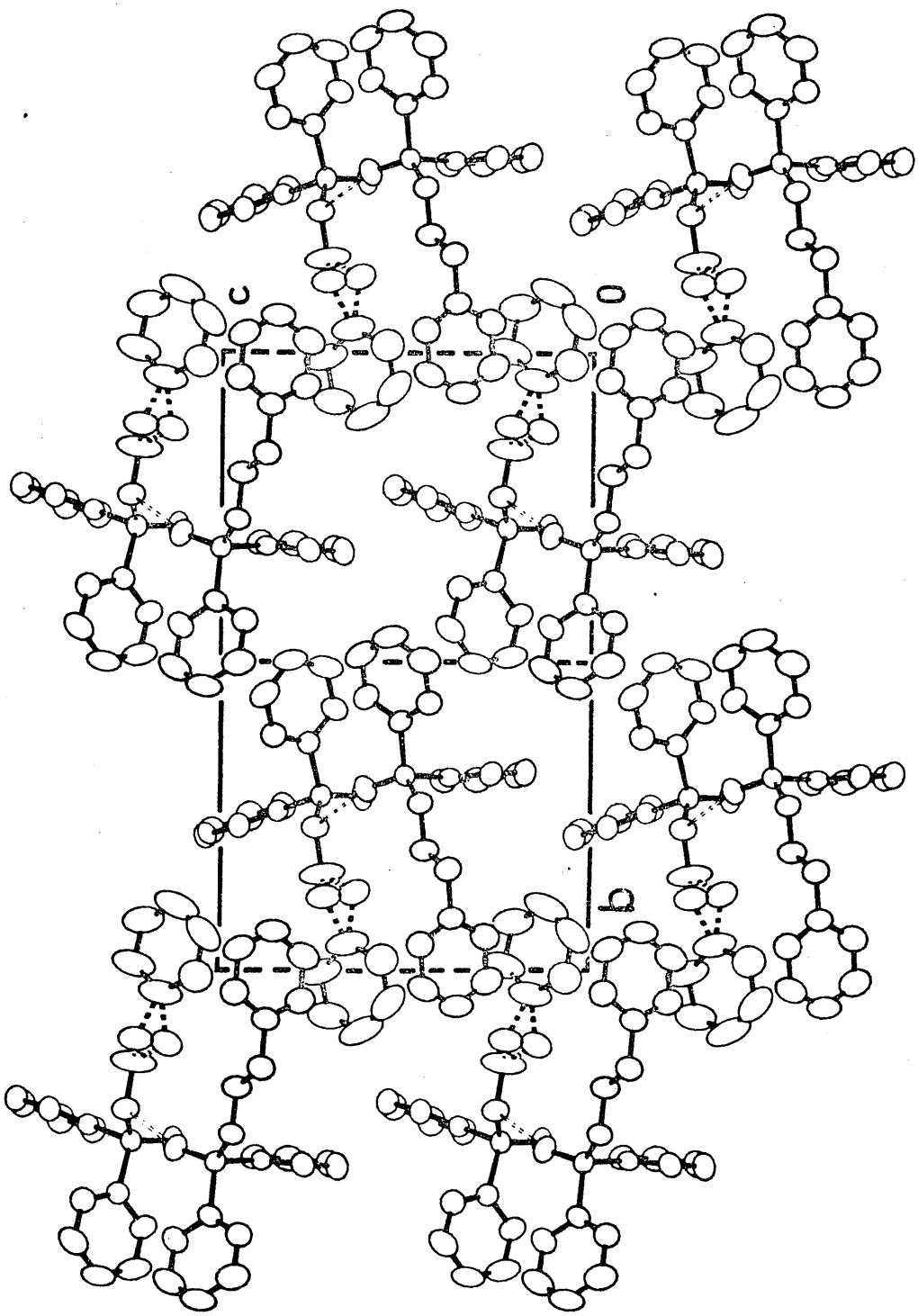

c
O
a

Figure 5.4

Atomic numbering scheme

(XXVI)

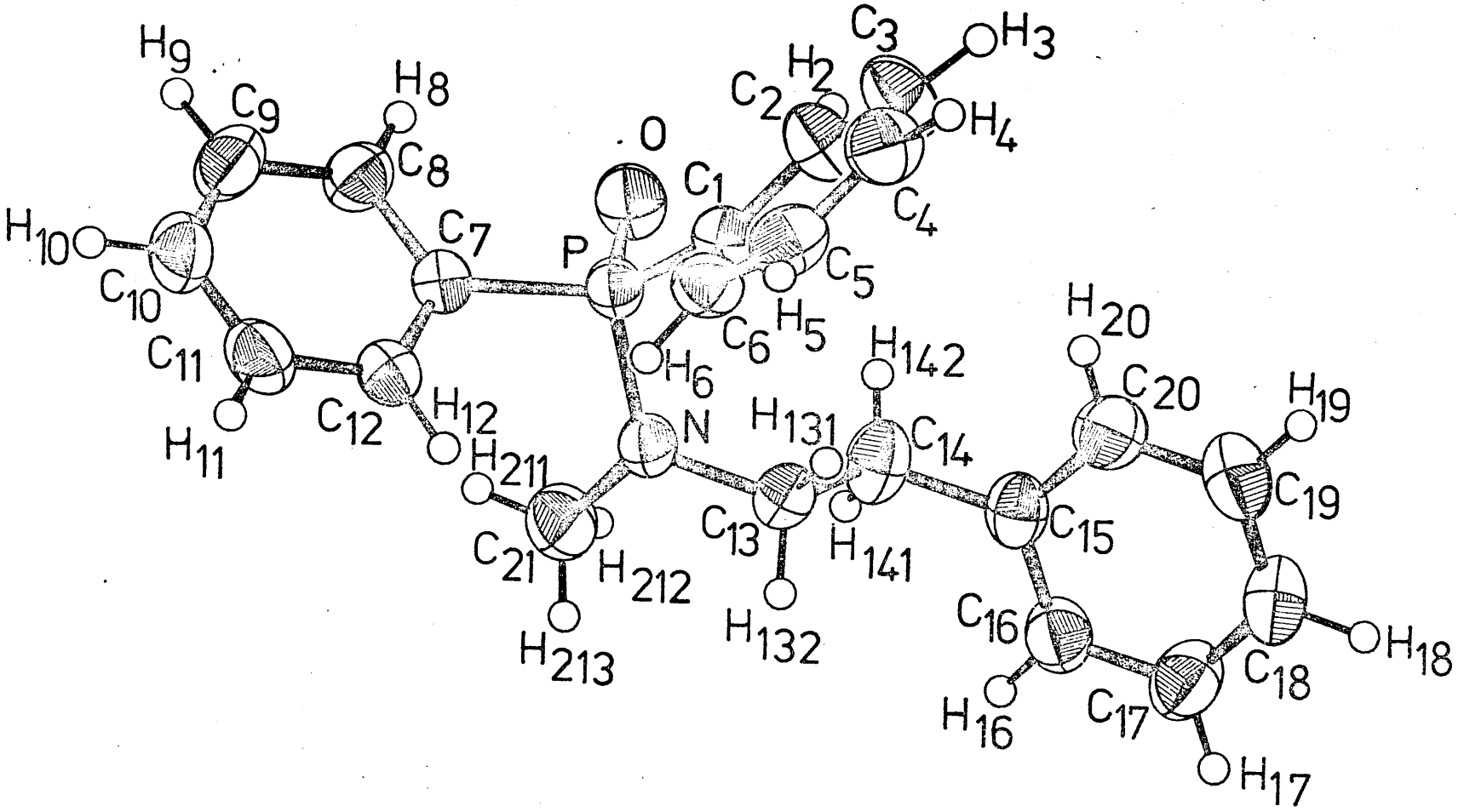
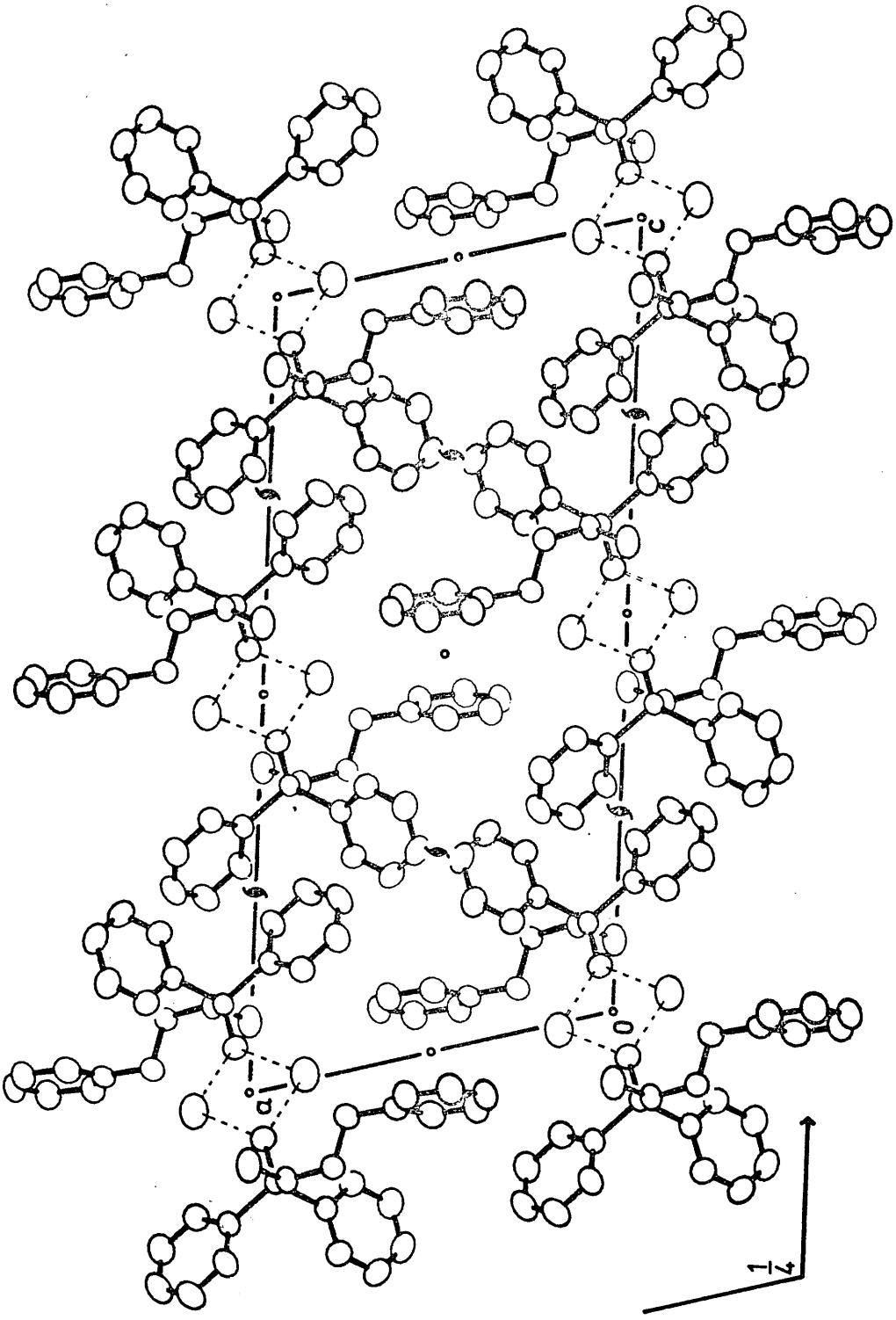

H9
C9
H8
C8
C7
H10
C10
C11
H11
C12
H12
H211
C21
H212
H213
O
P
C1
C2
H2
C3
H3
H4
C4
C5
H5
C6
H6
N
H131
H132
C13
H141
H142
C14
C15
H20
C20
H19
C19
C16
H16
C17
C18
H18
H17

Figure 5.5

Molecular packing arrangement viewed down the b-axis

(XXVI)

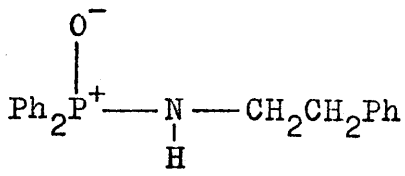

c
d
1-1/4

5.4 Discussion

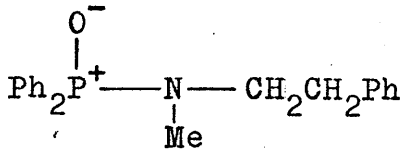
The structure analyses of the phosphinamides XXV and XXVI have revealed several structural features which correlate with their known hydrolytic properties and tend to corroborate the postulated mechanism of acid hydrolysis.

The most important feature, the length of the P-N bond, is particularly indicative. The shortness of these bonds, 1.643(4) , 1.647(5) and 1.646(2) Å in XXVA and B, and XXVI respectively, in relation to the length of a P-N single bond (1.76 Å from the Schomaker-Stevenson equation[61] and 1.77(2) Å in the phosphoramide ion[66]) indicates a substantial $d\pi$-$p\pi$ interaction of the nitrogen lone-pair electrons with the phosphorus d-orbitals, resulting in a considerable degree of π-bonding. Indeed, the closeness of this mean length, 1.645 Å to that at which maximum $d\pi$-$p\pi$ overlap was calculated would occur in the compound XXVII , 1.635 Å [67], suggests that overlap close to the maximum possible may be occurring in the phosphinamides. These observed bond lengths are not significantly different from those P-N multiple bond lengths in XXVII , 1.635(7) [67], and XXVIII , 1.64(2) Å [68], although in the latter compounds approximate 'double' and 'single' bonds alternate, the 'single' bond lengths being 1.769(7) and 1.78(2) Å respectively. The P-N bond length in the N,N-dimethyldiphenylphosphinamide, XXIX , is slightly longer at 1.67 Å , but may not be significantly so, as no e.s.d.s are quoted[69].

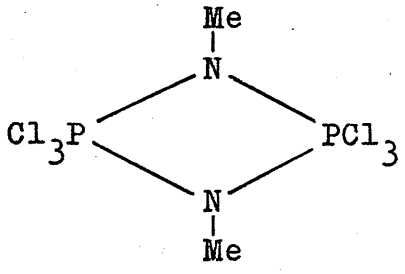
The substantial degree of multiple bonding implied by the above bond lengths would tend to reduce the positive charge at P , delocalising



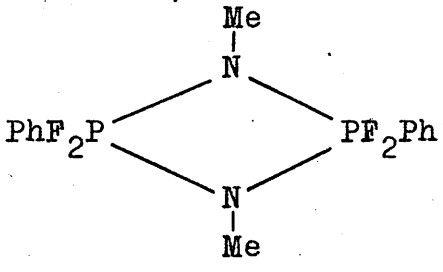
XXV



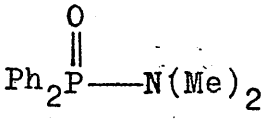
XXVI



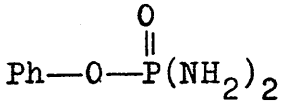
XXVII



XXVIII



XXIX



XXX

it to N , and therefore correlates with the relative inertness of the phosphinamides to nucleophilic attack (base hydrolysis), the reactivity being similar to that of carboxylic amides. It also correlates with the much greater reactivity in acid media, where N-protonation, by necessarily removing the $d\pi$-$p\pi$ interaction in toto from the P-N bond, would be expected to labilise this bond and render the phosphorus atom highly susceptible to nucleophilic attack.

Perhaps surprisingly, in view of the considerable P-N π-bonding, the nitrogen atom in phosphinamides is markedly pyramidal, although extended slightly from the geometry of tetrahedral hybridisation, with the sum of angles at nitrogen in compounds XXVA and B, and XXVI being $337(4)^{\circ}$, $347(4)^{\circ}$ and $352.0(2)^{\circ}$ respectively. In consequence, the lone-pair electrons must occupy a hybrid orbital approaching sp^3 in nature, with a degree of s character between zero and 0.25 , and with a greater amount of charge density localised in a major lobe. That such a lone-pair orbital is preferred to the pure p-orbital that would result from planar trigonal geometry, while still able to provide the strong π-overlap that the P-N bond length indicates, is an important indication of the efficiency of overlap possible between 3d-orbitals on phosphorus and an sp^n-type hybrid orbital, and hence provides evidence strongly supporting the belief that π'-overlap in phosphonitrilic ring compounds and $\overset{+}{P} - \overset{-}{N}$ ylides (overlap of 3d-orbitals with a trigonal sp^2-type lone-pair orbital, - see Introduction) may be as powerful an agent for stability as π-overlap, and in some circumstances possibly more powerful.

Clearly, in the present case, a planar nitrogen atom with a p-orbital lone pair would yield either no improvement in overlap or

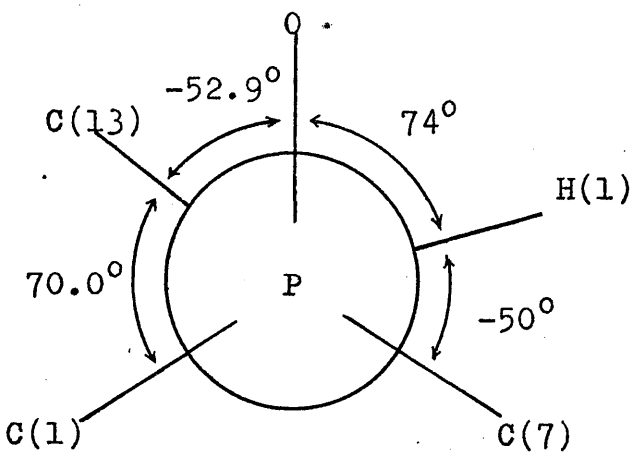
insufficient improvement to overcome other accompanying disadvantages.

Considering the features which may therefore favour a pyramidal nitrogen, it is clear from inspection of the Newman projections in Figure 5.6 , that the molecules XXVA and B, and XXVI assume a staggered conformation about the P-N bond, in which steric interactions will be minimised. Thus in XXVI , the contacts C(21)...O 3.32 , C(21)...C(7) 3.22 , C(13)...O 3.54 and C(13)...C(1) 3.05 Å are effectively as long as the configuration allows. In XXVA and B , similar contacts occur, H(1)...O 3.00 , 3.16 , H(1)...C(7) 2.64 , 2.74 , C(13)...O 3.24 , 3.16 and C(13)...C(1) 3.29 , 3.32 Å . Again, these interactions are close to the minimum possible within the restrictions of the molecular configuration. If a planar arrangement at nitrogen were adopted, the above staggered conformations would not be possible and a significant increase in these interactions would be expected. This would more strongly affect the N-methyl compound, and may be a major factor in favour of the non-planar geometry.

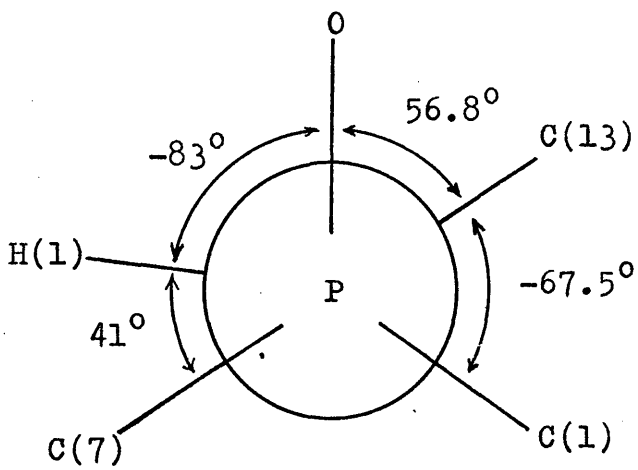
In XXV , the N-proton participates in intermolecular hydrogen bonding with the $\overset{+}{P} - \overset{-}{O}$ group of a neighbouring molecule, forming chains of alternating A and B molecules extending in the a-direction through the crystal. The geometry of this hydrogen bonding is shown in Figure 5.7 . The relatively short N(A)...O(B) and N(B)...O(A) distances, 2.78 and 2.82 Å , compared to other typical N-H....O bonds[38], implies bonding of considerable relative strength. This may play an important part in influencing the geometry at the nitrogen atoms, and the differing environments of molecules A and B may be responsible for the differences in valence angles at N(A) and N(B) , if significant.

Influence of this nature has been suggested by the analysis of

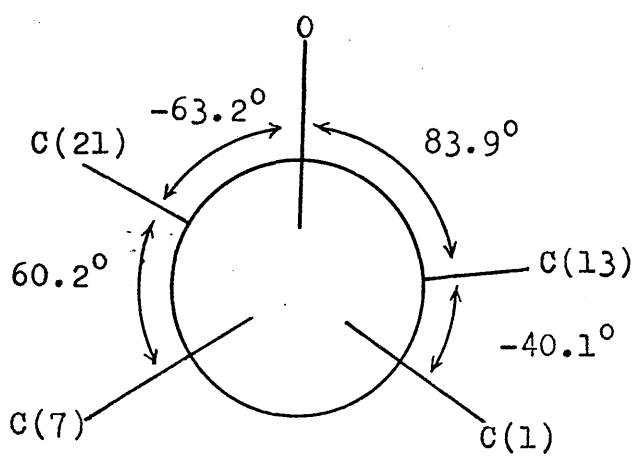
Figure 5.6



P - N Projection for XXV A



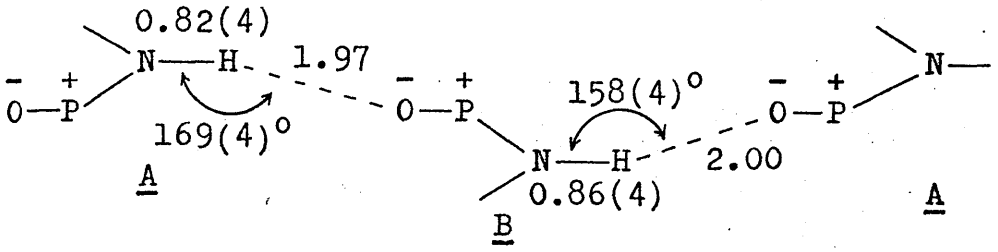
P - N Projection for XXV B



P - N Projection for XXVI

Figure 5.7

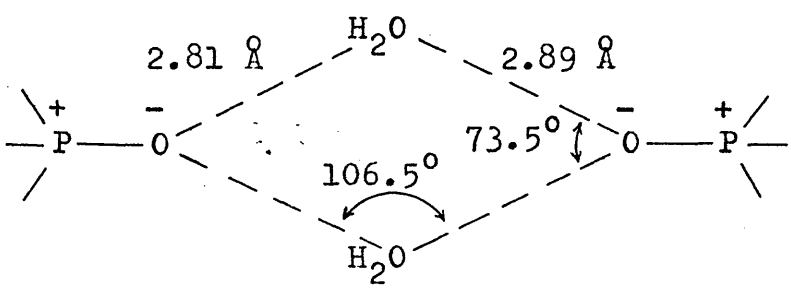
Dimensions of the hydrogen bonding in XXV



N(A)....O(B) 2.78 Å N(B)....O(A) 2.82 Å

Figure 5.8

Dimensions of the four-membered hydrogen-bonding arrangement in XXVI



the di-amide XXX [70], in which both nitrogen atoms are involved in hydrogen bonding, but one nitrogen is trigonal (planar) and is involved in two nearly coplanar hydrogen bonds whereas the second nitrogen atom is pyramidal (sum of angles = $343(4)^{\circ}$) and participates in two hydrogen bonds which are well away from coplanarity. One may infer that the energy gained from hydrogen bonding may be sufficient to outweigh any hybridisation and $d\pi$-$p\pi$ losses. In addition, the lowering of inversion barriers in nitrogen by participation of d-orbitals of a vicinal atom has been widely discussed[71,72].

The pyramidal nature of the nitrogen and the consequent sp^n-nature of the lone-pair electrons are in keeping with the proposed mechanism of acid hydrolysis, in that the sp^3-type lone pair will be easily accessible for protonation, which converts the amide function into a good leaving group. The remaining part of the mechanism is believed to vary from directly dissociative, A_1 , to associative, A_2 (involving formation of a five-membered intermediate), according to the detailed nature of the phosphinamide molecule involved[65]. Although formation of a five-membered intermediate at phosphorus is, with d-orbitals available, a relatively simple matter, in most examples A_1 character is believed to be predominant.

Most other features of molecules XXVA and B , and XXVI are experimentally identical and are essentially normal. Thus the P-O bond lengths, 1.481(4) , 1.478(4) and 1.489(1) Å respectively, are experimentally identical with 1.46(1) Å in triphenylphosphine oxide[73], and 1.485(2) and 1.497(5) Å in the p-chlorophenyl and p-bromophenyl-diphenylphosphine oxide analogues[74]. These bond lengths correspond to a valence-bond order of about 1.65 [25]. Mean P-C bond lengths,

1.805(5) and 1.806(2) Å for XXV and XXVI , are within the accepted range of values for P-C(sp^2) bonds from a formally positive phosphorus, 1.78 to 1.82 Å . The geometry of the phenyl rings is substantially normal in view of the sizeable errors in XXV . Mean C-C distances are :

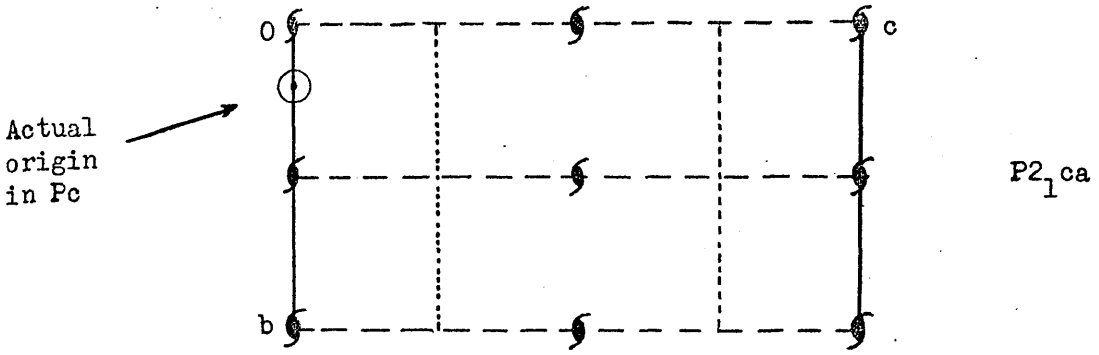
(in Å)	XXVA	XXVB	XXVI
Ring C(1) to C(6)	1.383(8)	1.380(9)	1.384(3)
Ring C(7) to C(12)	1.375(9)	1.379(9)	1.383(3)
Ring C(15) to C(20)	1.369(10)	1.360(14)	1.380(4)

Shortening of the C-C bonds furthest from the centre of inertia of a molecule (although possibly not significant in view of the large experimental errors) is probably due to the effects of thermal motion, either rotary oscillation of sections of the molecule or overall libration. No corrections for this have been made, since in molecule B the effects of positional disorder in the C(15) to C(20) ring have been accommodated by enlargement of the atom thermal parameters. The disorder in molecule B is primarily disordering of the methylene, C(14), occasioned largely by rotation about the N-C(13) bond. The very distorted geometry of the refined model (mean C(13B)-C(14B) 1.281(20) and mean C(14B)-C(15B) 1.639(18) Å), despite incorporation of two alternative C(14) positions, suggests that the disorder may be of a more general nature and that the positions C(14B) and C(14B') represent merely major centres of probability density. A requirement of this disordering of C(14) is the partial disordering of C(13) , C(15) and the remainder of the C(15)-ring. While not sufficient to allow resolution of separate maxima, this disorder is evident in the anisotropic enlargement of the thermal smearing functions. The

resulting high thermal parameters do not, therefore, properly represent actual thermal vibration. While crystal structures in which two molecules form the asymmetric unit, with one molecule disordered and the other not, are rare, they are not unknown and several other examples have been reported[75,76].

The hydrogen bonding previously mentioned is typical of crystal structures of amido and amino compounds. The N...O separations, 2.78 and 2.82 Å, are moderately short compared to the sum of Wallwork's donor and acceptor radii[38], 2.95 Å, but are comparable to values in aniline-chlorophenol complexes, e.g. 2.78, 3.13[77] and 2.60, 2.73 Å[78].

The most intriguing aspect of the crystal structure of XXV, on which the above features have some bearing, is the partial symmetry additional to the symmetry of the space group Pc. An approximate a-glide perpendicular to the c-axis, relating the pair of molecules in the asymmetric unit, is evident on examination of the packing diagram in Figure 5.3 and on inspection of the atomic coordinates. Combination of this a-glide with the space group c-glide generates an approximate two-fold screw-axis in the a-direction. Had this compound crystallised into a structure with the exact, rather than approximate, symmetry described, the resulting space group would have been the orthorhombic group $P2_1ca$ with one molecule in the asymmetric unit, analogous to (and transforming to, on renaming the axes) the space group $Pca2_1$, No. 29 in "International Tables for X-ray Crystallography", Vol. I. The arrangement of symmetry elements in $P2_1ca$ is illustrated overleaf :-



One may therefore visualise compound XXV, in crystallising, attempting to form a structure of high, orthorhombic symmetry with one molecule as the asymmetric unit, but owing to some agency (perhaps hydrogen bonding or a tendency to disorder) distorting the structure away from the full symmetry, crystallising instead with the much lower symmetry of the monoclinic space group Pc ; with $\beta = 90.09^{\circ}$, and with two molecules in the asymmetric unit. No close intermolecular contacts occur apart from those previously discussed in the context of hydrogen bonding.

In comparison, the crystal structure of XXVI is mundane, with the familiar space group $P2_1/c$ with one molecule per asymmetric unit. However, this has the marked advantage, inherent in the smaller asymmetric unit, of allowing a higher ratio of observations to variables and hence making possible the refinement of hydrogen atom parameters and achievement of a higher standard of refinement, with a consequent improvement in the precision of the whole analysis.

One feature of interest is exhibited by the crystal structure. Centrosymmetrically related molecules are linked in pairs by a four-membered planar hydrogen-bonded complex, utilising two bridging water

molecules bonding to the phosphinyl oxygen atoms. This arrangement is illustrated in the packing diagram in Figure 5.5 and in detail in Figure 5.8 . The O(1)...O(2) distances, 2.81 and 2.89 Å , are slightly longer than the sum of appropriate donor and acceptor radii, 2.70 Å [38], but fall within the range commonly observed for O-H...O hydrogen bonds. Four-membered planar arrangements of this type have been reported previously on several occasions, e.g.[77,79]. The absence of other short contacts suggests that van der Waals' forces may be responsible for the packing arrangement of these dimer units.

6. THE CRYSTAL AND MOLECULAR STRUCTURE OF SULPHAMIC ACID : NH_3-SO_3 .

6.1 Introduction

In structural investigations of ylides and other compounds, assessment of the amount of multiple bond character in any particular bond is based primarily on the extent of shortening of that bond from the appropriate single bond length. While some doubts have been expressed about the reliability of these inferences when non-bonded interactions are also present[55], this remains the single most important piece of evidence concerning bond order, although bond angles, conformations, n.m.r. data, dipole measurements etc. provide further information. The validity of this comparison depends accordingly on the availability of an accurate and precise measurement of a genuine single bond.

In studies of sulphonyl-stabilised imines and sulphonium imines, comparisons have been made with the single S-N bond length predicted using Pauling's covalent radii[5], 1.74 Å , and with the bond length in sulphamic acid, which, in the solid state, has the zwitterionic structure, $\overset{+}{N}H_3$-$S\overset{-}{O}_3$, with, on account of the quaternary nitrogen, a pure N-S σ-bond.

The crystal structure of sulphamic acid has been studied using diffraction techniques on three previous occasions. Kanda and King (1951) carried out a 2-D X-ray analysis based on Fourier refinement[56], while Osaki, Tadokoro and Nitta (1955) refined the structure using 3-D X-ray Fourier refinement[57]. Sass (1960) carried out a neutron

diffraction analysis, locating the hydrogen atoms for the first time and refining the structure by least-squares methods using three zonal data sets[58]. The S-N bond length from the latter analysis, 1.76(2) Å , has frequently been referred to in discussions of sulphonyl-stabilised imines and sulphonium imines in the context of bond shortening[11,17,18] (see sections 1.3 , 2.3 , 4.4). This value is discrepant, however, from Pauling's value by 0.02 Å , although the discrepancy is not significant in view of the e.s.d. quoted by Sass. However, in order to determine the S-N bond length in sulphamic acid with a precision and accuracy more comparable to that of present-day X-ray analysis, and therefore to enhance the validity of the above bond comparisons, a new refinement of the crystal structure by 3-D full-matrix least-squares methods has been carried out, using a new set of three-dimensional diffractometer data.

6.2 Experimental

Crystal Data

Sulphamic acid

NH_3SO_3 , M = 97.1 .

Orthorhombic, a = 8.115 b = 8.066 c = 9.248 Å ,

U = 605.3 $Å^3$,

D_m = 2.15 g cm^{-3} (ref. 56), Z = 8 , D_c = 2.13 g cm^{-3},

$F_{(000)}$ = 400 .

Space group : Pbca (D_{2h}^{15} , No.61).

μ(Mo,Kα) = 8.40 cm^{-1}.

Data Collection

Radiation	:	Mo,Kα
Filter	:	Zr
Maximum scattering angle (2θ)	:	60°
Independent reflections (observed) (averaged over two octants)	:	793
Unobserved cutoff	:	$2\sigma_I$
Ratio of observations/parameters	:	15.82

Structure Refinement

Atom coordinates from the neutron diffraction analysis[58] were taken as initial values for full-matrix least-squares refinement, which converged after 19 cycles with residuals R and R' of 0.027 and 0.0016 respectively. Details of the refinement are given in Table 6.1 . Initial refinement of the hydrogen atoms yielded positions of unacceptable molecular geometry, and accordingly the positions of these atoms from the neutron analysis were maintained unrefined thereafter. Corrections to all strong reflections affected by counter saturation errors were made prior to cycle 4 . The isotropic secondary extinction coefficient, g , was refined in the least-squares calculations from cycle 7 onwards, culminating in a value of 0.0103 at convergence.

The form of the extinction correction used in the CRYLSQ link of the X-RAY72 system of programs is based on the method of Larson (1967) [59] and of Zachariasen (1963) [60], and applies a correction to the calculated structure factor using the expression

$$F_{c(corr)} = F_c(1 + 2gQ)^{-\frac{1}{4}}$$

where Q is the scattering power of a small crystal block, given by

$$Q = \left[\frac{e^4}{m^2c^4}\right] \frac{\lambda^3}{V^2} \left[\frac{L\ (1 + \cos^4 2\theta)^2\ \bar{t}}{\sin 2\theta\ (1 + \cos^2 2\theta)}\right] F_c^{\,2}$$

where V is the unit cell volume, $\bar{t}$ is the mean path length and $\left[\frac{e^4}{m^2c^4}\right]$ is the classical radius of the electron.

A weighting scheme of the form

$$W = (A + B|F_o| + C|F_o|^2)^{-1}$$

was applied in the final six cycles, with coefficients A = 0.3117 , B = -0.0220 and C = 0.0011 , determined by polynomial fit to the function Δ^2.

In all structure-factor calculations, atomic scattering factors derived by Cromer and Mann (1968) [39] for S, O and N, and by Stewart et al. (1965) [40] for H were used.

Observed and final calculated structure factors are listed in Appendix 8 . Fractional coordinates and thermal parameters are listed in Table 6.2 and interatomic distances, angles and intermolecular contacts are given in Table 6.3 with their estimated standard deviations. The atomic numbering scheme and the molecular packing viewed down the c-axis are shown in Figures 6.1 and 6.2 respectively.

Table 6.1

Course of refinement

Cycles	Parameters refined	Final R	Final R'
1 - 2	x,y,z,U_{iso} for S, O, N and H, scale factor. Unit weights.	0.088	0.0137
3	x,y,z,U_{ij} for S, O and N, x,y,z,U_{iso} for H, scale factor. Unit weights.	0.070	0.0110
4 - 6	x,y,z,U_{ij} for S, O and N, scale factor. H-atoms included* but not refined. Unit weights.	0.052	0.0062
7 - 13	x,y,z,U_{ij} for S, O and N, scale factor, secondary extinction coefficient. H-atoms included* but not refined. Unit weights.	0.028	0.0012
14 - 15	x,y,z,U_{ij} for S, O and N, scale factor, secondary extinction coefficient. H-atoms included* but not refined. Weighting scheme applied.	0.028	0.0017
16 - 19	x,y,z,U_{ij} for S, O and N ; U_{iso} (only) for H, scale factor, secondary extinction coefficient. Weighting scheme applied.	0.027	0.0016

* H-atoms were included with the atom positions from the neutron diffraction analysis[58].

Table 6.2

a) Fractional coordinates and isotropic thermal parameters ($Å^2$)

	x/a	y/b	z/c	U_{iso}
S	0.16665(5)	0.09389(5)	0.17077(4)	-
N	0.04096(17)	0.24085(17)	0.08066(15)	-
O(1)	0.05922(18)	-0.04773(17)	0.17735(15)	-
O(2)	0.30448(17)	0.07669(17)	0.07448(15)	-
O(3)	0.20034(18)	0.17420(18)	0.30607(14)	-
H(1)	0.0947(29)	0.3556(35)	0.0651(32)	0.057(9)
H(2)	-0.0725(19)	0.2443(25)	0.1303(27)	0.088(12)
H(3)	0.0126(27)	0.1978(28)	-0.0202(24)	0.060(9)

b) Anisotropic thermal parameters ($Å^2$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	0.0175 2	0.0145 2	0.0144 2	0.0009 1	0.0005 1	0.0005 1
N	0.0198 6	0.0175 6	0.0173 6	0.0025 5	-0.0016 5	0.0016 5
O(1)	0.0315 7	0.0174 6	0.0278 7	-0.0066 5	-0.0008 5	0.0036 5
O(2)	0.0229 6	0.0272 6	0.0272 6	0.0070 5	0.0075 5	0.0020 5
O(3)	0.0281 7	0.0290 7	0.0155 6	0.0019 5	-0.0043 5	0.0038 5

Table 6.3

Interatomic distances and angles

a) Bonded distances (Å)

S - N	1.772(1)	N - H(1)	1.033(28)
S - O(1)	1.438(1)	N - H(2)	1.029(18)
S - O(2)	1.436(1)	N - H(3)	1.022(22)
S - O(3)	1.435(1)		

b) Interbond angles (°)

N - S - O(1)	101.67(7)	O(1) - S - O(2)	114.93(8)
N - S - O(2)	102.78(7)	O(1) - S - O(3)	115.91(8)
N - S - O(3)	102.57(6)	O(2) - S - O(3)	115.83(8)
S - N - H(1)	115.0(11)	H(1) - N - H(2)	114.6(18)
S - N - H(2)	108.9(9)	H(1) - N - H(3)	105.8(20)
S - N - H(3)	109.4(9)	H(2) - N - H(3)	102.4(18)

c) Intramolecular non-bonded distances (Å)

O(1)...H(2)	2.62	O(2)...H(3)	2.71
O(1)...H(3)	2.72	O(3)...H(1)	2.80
O(2)...H(1)	2.82	O(3)...H(2)	2.80

Table 6.3 (cont.)

d) Intermolecular distances (Å)

N ....O(1)^{I}	2.96	O(1)...O(3)^{IV}	3.08
H(3)...O(1)^{I}	1.98	O(3)...N^{V}	3.00
O(1)...O(1)^{I}	3.50	O(3)...H(2)^{V}	2.02
O(2)...O(2)^{II}	3.67	O(2)...N^{VI}	2.81
O(3)...N^{III}	2.93	O(2)...H(2)^{VI}	2.58
O(3)...O(2)^{III}	3.30	O(2)...H(3)^{VI}	2.53
O(3)...H(1)^{III}	2.55	O(2)...N^{VII}	2.99
O(3)...H(3)^{III}	2.44	O(2)...H(1)^{VII}	1.96
O(1)...N^{IV}	2.93	O(2)...O(3)^{VIII}	3.20
O(1)...H(2)^{IV}	2.44		

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

I	-x,	-y,	-z ;	II	1-x,	-y,	-z ;
III	x,	1/2-y,	-1/2+z ;	IV	-x,	-1/2+y,	1/2-z ;
V	1/2+x,	y,	1/2-z ;	VI	1/2+x,	1/2-y,	-z ;
VII	1/2-x,	-1/2+y,	z ;	VIII	1/2-x,	-y,	-1/2+z .

e) Torsion angles (°)

O(1)-S-N-H(1)	179.3(17)	O(2)-S-N-H(3)	57.3(13)
O(1)-S-N-H(2)	49.2(12)	O(3)-S-N-H(1)	59.1(17)
O(1)-S-N-H(3)	-61.9(13)	O(3)-S-N-H(2)	-71.0(12)
O(2)-S-N-H(1)	-61.5(17)	O(3)-S-N-H(3)	177.9(13)
O(2)-S-N-H(2)	168.5(12)		

Figure 6.1

Atomic numbering scheme

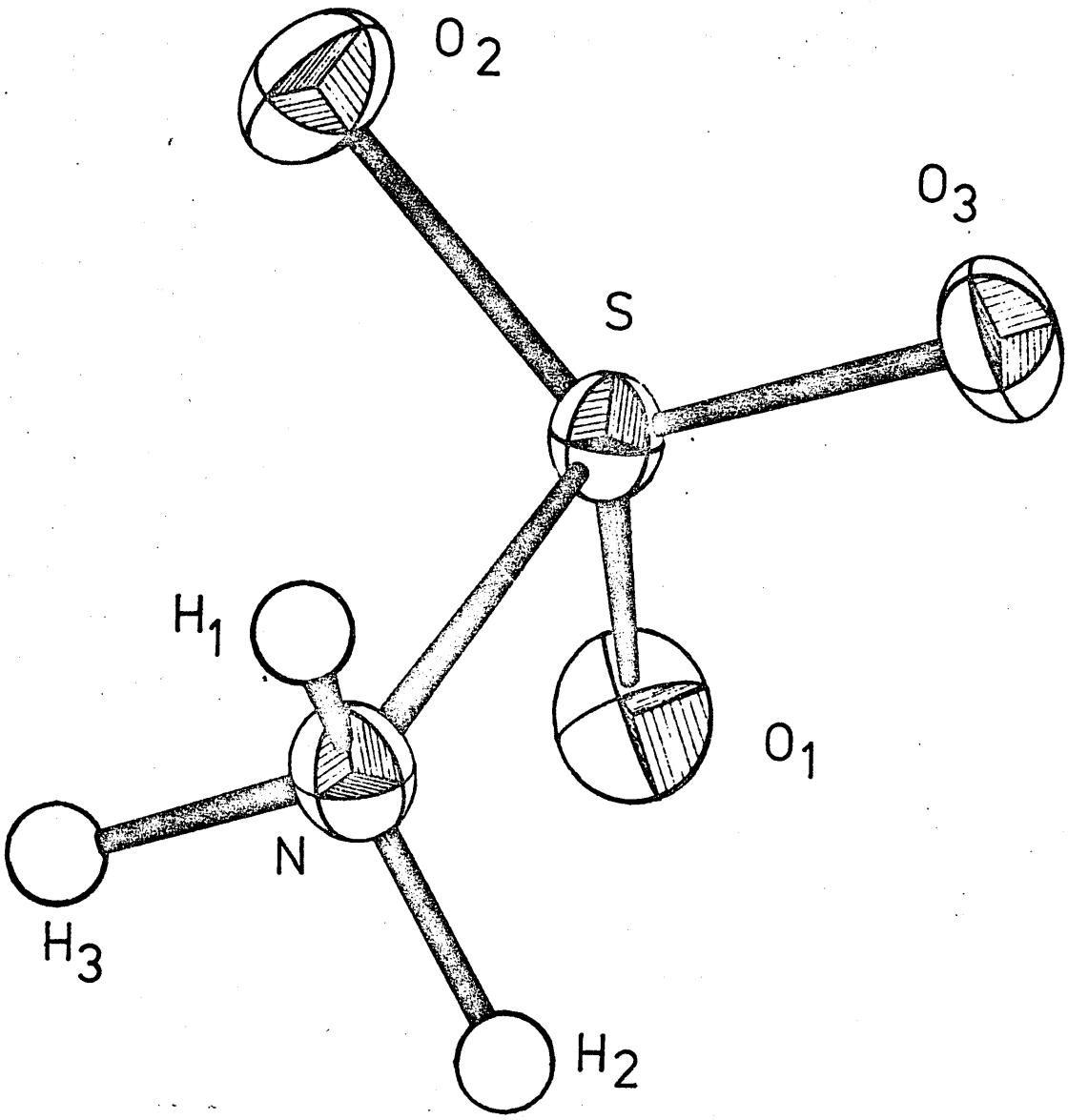
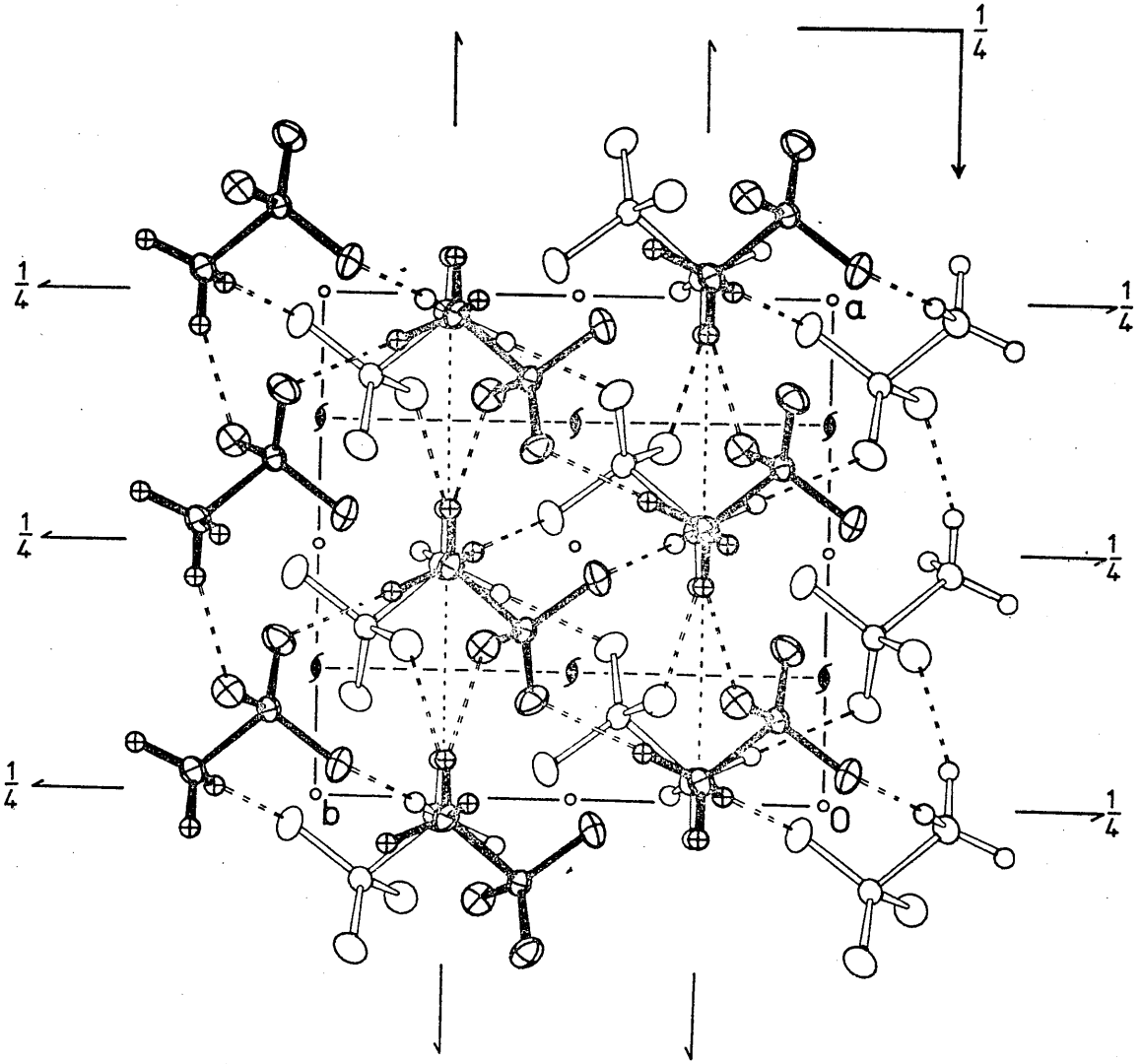

O2
O3
S
H1
O1
N
H3
H2

Figure 6.2

Crystal packing arrangement

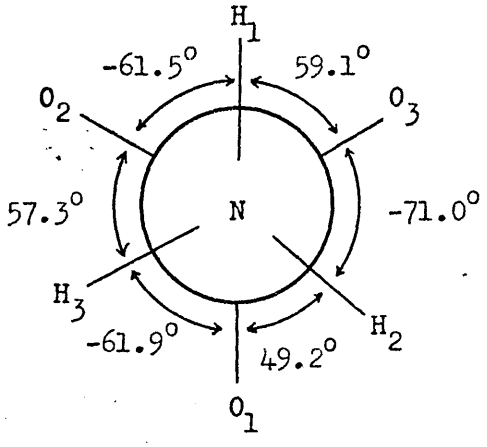
viewed down the c-axis


1/4
1/4
1/4
1/4
1/4
1/4
1/4
a
b
0

6.3 Discussion

The refinement of the crystal structure of sulphamic acid using three-dimensional X-ray diffractometer data has allowed the determination of the S-N bond length with an accuracy and precision comparable to that in contemporary X-ray analyses of the highest quality. The value obtained, 1.772(1) Å , is significantly longer than that obtained by Sass, 1.764(20) Å , although not so in terms of his quoted e.s.d., and is appreciably longer than the values predicted by Pauling[5], and by the Schomaker-Stevenson equation[61], 1.74 Å , suggesting that these values are slightly underestimated. In only one other reported structure is an S-N bond of comparable length found, namely 1.791(12) Å in the dinitrososulphate ion[62], SO_3-NO-NO , implying an essentially single bond. In the majority of compounds possessing an S-N bond, the bond length is appreciably shorter on account of the $d\pi$-$p\pi$ involvement of lone-pair electrons on the nitrogen atom. This is clearly illustrated by the reduction in bond length to 1.60(1) Å on loss of a proton from sulphamic acid to form the sulphamate ion[62].

The molecule exists in a staggered conformation, best illustrated by the Newman projection down the N-S bond.



Mean e.s.d.
1.4°

This shows the almost symmetric arrangement, with a slight distortion of the H(2) position on account of an asymmetric hydrogen bond to O(3) of a neighbour molecule. The mean S-O bond length, 1.437(1) Å , is in agreement with the valence-bond order of 1.66 ascribed by Cruickshank[25].

The crystal structure forms a compact network of hydrogen bonds, which results in the low vibrational parameters of the non-hydrogen atoms. Each molecule is bonded to six of its nearest neighbours, with a hydrogen bond from each hydrogen atom and to each oxygen atom with the following bond distances : O(1)...H(3) 1.98 , O(2)...H(1) 1.96 and O(3)...H(2) 2.02 Å . A further consequence of this close packing is the close contact of the hydrogen and oxygen atoms H(1)...O(3) 2.55 , H(2)...O(2) 2.58 , H(2)...O(1) 2.44 , H(3)...O(3) 2.44 and H(3)...O(2) 2.53 Å , at distances within the van der Waals' contact range.

The value of this redetermination of the S-N single bond length is much enhanced by the high precision resulting from the advanced level of refinement achieved. A major factor contributing to this has been the inclusion of the isotropic extinction coefficient, g , as a parameter for least-squares refinement, which reduced the residual R from about 0.05 to less than 0.03 in compensating for the "severe" extinction observed by Sass. Adjustment of this parameter, to a final sizeable value of 0.0103 , occurred with some adjustment of thermal parameters but very little change in positional parameters. The occurrence of "severe" extinction is a direct consequence of the crystal perfection arising from strong crystal packing forces (hydrogen bonding), which are further indicated by the compound's readiness to crystallise from aqueous solution.

OVERALL DISCUSSION

Three aspects of the previously discussed compounds which are of overall relevance in studies of ylides are considered here. Firstly, the postulated competition of 'onium and stabilising groups to stabilise the negative charge on the anionic atom is discussed. Secondly, the significance of the present work and other recent structure analyses in relation to conformational theories of ylide structures is considered, and finally, the large variation in valence angle at the N^- species in ylides and similar compounds is discussed.

The evidence presented by Hair in support of the competition postulate, the study of a series of $\overset{+}{P} - \overset{-}{C}$ and $\overset{+}{S} - \overset{-}{N}$ ylides, clearly showed the interdependence of the two partial-multiple bonds, $\overset{+}{X} - \overset{-}{Y}$ and $\overset{-}{Y} - ZO_n$, in second-row ylides, and thus supported his postulate. The more extensive evidence now available has, however, shed some doubt as to the extent of it's application. Thus in $\overset{+}{P} - \overset{-}{C}$ systems, Table 1 illustrates the decrease in $\overset{+}{P} - \overset{-}{C}$ interaction as the delocalising efficiency of the stabilising group increases. Similarly, for $\overset{+}{S} - \overset{-}{N}$ systems, Table 2 illustrates the decrease in π-bonding in the $\overset{+}{S} - \overset{-}{N}$ bond as the electron-withdrawing ability of the stabilising group increases. A clear trend is present despite the potential complication of the expected interaction of both of the nitrogen lone pairs with the sulphonyl group.

However, on examining similar $\overset{+}{P} - \overset{-}{N}$ compounds, of which fewer examples, unfortunately, are available, a rather different picture emerges, as shown in Table 3 . Competition between delocalising

Table 1

Delocalisation in $P^{+} - C^{-} - Z = Z'$ systems

Compound	Ref.	$P^{+} - C^{-}$ (Å)	$C^{-} - Z$ (Å)	τ(°)
$Ph_3P^{+}-CH_2^{-}$	6	1.661(8)	-	-
$Ph_3P^{+}-CH^{-}-CH=C(Me)_2$	80	1.677(3)	1.433(5)	~0
$Ph_3P^{+}-CH^{-}-SO_2$-tol.	9	1.709(19)	1.686(19)	8.3
$Ph_3P^{+}-CR^{-}-CO_2Me$				
R = $-CH_2-CO_2H$	8	1.732(4)	1.392(6)	14.7
R = $-CH_2-CO_2But^t$.	8	1.715(5)	1.415(7)	1.3
$Ph_3P^{+}-CCl^{-}-CO-Ph$	53	1.736(14)	1.361(20)	4.8

τ is the torsion angle $P^{+}-C^{-}-Z-Z'$

Table 2

Delocalisation in $S^{+} - N^{-} - Z = O$ systems

Compound	Ref.	$S^{+} - N^{-}$ (Å)	$N^{-} - Z$ (Å)	$\hat{N}$ (°)
$Ph_2S^{+}-N^{-}-SO_2$-tol.	11	1.628(7)	1.598(8)	113.4(5)
$Me_2S^{+}-N^{-}-SO_2$-tol.	17	1.636(8)	1.591(8)	113.4(5)
$Ph.nPr.S^{+}-N^{-}-SO_2$-tol.	12	1.620(7)	1.618(7)	115.7(4)
$Me_2S^{+}-N^{-}-SO_2-Me$	10	1.639(9)	1.581(10)	116.2(6)
$Me_2S^{+}-N^{-}-CO-Ph$	*	1.659(2)	1.344(3)	110.4(1)
$Me_2S^{+}-N^{-}-CO-CCl_3$	13	1.667(7)	1.320(10)	110.0(6)

(* section 3)

Table 3

Delocalisation in $\overset{+}{P} - \overset{-}{N} - Z$ systems

Compound	Ref.	$\overset{+}{P} - \overset{-}{N}$ (Å)	$\overset{-}{N} - Z$ (Å)	$\hat{N}$ (°)
$Ph_3\overset{+}{P}-\overset{-}{N}-\overset{+}{P}Ph_3$	81	1.56(2),1.59(2)	-	137(1) (mean)
$Ph_3\overset{+}{P}-\overset{-}{N}-Ph-Br$	82	1.567(6)	1.417(11)	124.2(5)
$Ph_3\overset{+}{P}-\overset{-}{N}-P(O)Ph_2$	83	1.557(2)	1.604(2)	146.0(1)
$Ph_3\overset{+}{P}-\overset{-}{N}-P(O)Cl_2$	83	1.582(2)	1.558(2)	139.6(1)
$Ph_3\overset{+}{P}-\overset{-}{N}-SO_2$-tol.	18	1.579(4)	1.586(4)	116.4(2)
$Ph_2F\overset{+}{P}-\overset{-}{N}-Me$	84	1.641(2)	1.469(4)	119.1(2)
$(PNMe_2)_4$		1.60		132
$(PNF_2)_4$		1.51		147.2
$(PN(NMe_2)_2)_6$		1.56		148

groups is clearly displayed by the diphenylphosphinyl and dichlorophosphinyl pair of compounds[83], with the chlorine substitution increasing the stabilising effectiveness of the phosphinyl group, presumably as a direct result of d-orbital contraction[22,27], and hence diminishing the $\overset{+}{P} - \overset{-}{N}$ interaction. However, no overall trend of increasing $\overset{+}{P} - \overset{-}{N}$ bond length with increasing stabilising group ability is observed, and some curious anomalies are present e.g. the $\overset{+}{P} - \overset{-}{N}$ bond length in $Ph_3\overset{+}{P}-\overset{-}{N}$-Ph-Br , 1.567(6) Å [82], compared to that in $Ph_2\overset{+}{F}P-\overset{-}{N}$-Me , 1.641(2) Å [84]. Both compounds would be expected to require more $\overset{+}{P} - \overset{-}{N}$ interaction than the corresponding sulphonyl-stabilised compound, for example, but do not appear to show this.

In general, the $\overset{+}{P} - \overset{-}{N}$ bond appears to be much less dependent on the nature of the stabilising group than the corresponding $\overset{+}{P} - \overset{-}{C}$ or $\overset{+}{S} - \overset{-}{N}$ bond. In a competitive sense this certainly appears to be the case, and it may be that stabilising interactions are more additive in these compounds than competitive. It is possible that this behaviour may be associated with the large variation in the valence angle at the nitrogen atom, and in particular the extension of this angle well above the trigonal angle in phosphorus compounds, enabling the formation of a more effective π'-interaction.

The interdependence of the π-interactions to the 'onium and stabilising groups in $\overset{+}{S} - \overset{-}{N}$ and $\overset{+}{P} - \overset{-}{C}$ compounds should be a mutual effect of one species upon the other, and accordingly, the influence of change of 'onium group on the bond between the negative atom and the stabilising group should be observable. In section 3.4 , this effect on the $\overset{-}{N}$–carbonyl interaction was demonstrated and discussed. The same effect on the $\overset{-}{N}$–sulphonyl interaction is also evident to some

extent in the comparative study of sulphonyl-stabilised imines, in Table 4 . In particular, with the compound $Me_2\overset{+}{S}(O)\text{-}\overset{-}{N}\text{-}SO_2Me$ [43], possessing a highly positive sulphoxy 'onium group, a very short $\overset{+}{S}\text{ - }\overset{-}{N}$ bond results, 1.554(2) Å , with an appropriately longer N-sulphonyl bond, 1.615(2) Å , compared to that in $Me_2\overset{+}{S}\text{-}\overset{-}{N}\text{-}SO_2Me$ [10], 1.581(10) Å . The di-ylide, $S(\overset{-}{N}\text{-}SO_2\text{-tol.})_2^{2+}$ [85], similarly has very long N-sulphonyl bonds, 1.685 Å (mean), coupled with very short $\overset{2+}{S}\text{ - }\overset{-}{N}$ bonds, 1.523 Å (mean), presumably resulting from the high positive charge on the 'onium species $\overset{2+}{S}$.

The latter compound also provides evidence of importance to theories concerning the conformations adopted by sulphonyl-stabilised ylides. To recap, Hair postulated i) that ylides stabilised by a single π-orbital-containing group adopted a planar conformation with that group. This has been broadly confirmed, but it has been shown that other factors can produce deviations from planarity (see sections 3.4 and 4.3),

and ii) that ylides stabilised by a multiple π-orbital system based on d-orbitals adopted a conformation coplanar with one oxygen atom if the negative atom possessed one lone pair, and a conformation deviating by 30 to 40° from cis-coplanarity with one oxygen atom if the negative atom possessed two lone pairs. These predictions were based on studies of five sulphonyl-stabilised ylides. The results of the present work, and other published and unpublished work have shown that this classification does not extend to ylides with other d-orbital-based stabilising groups, and is not general for sulphonyl-stabilised systems.

Table 4

Competition in $X^{+} - N^{-} - SO_2R$ systems

Compound	Ref.	$X^{+} - N^{-}$ (Å)	$N^{-} - S$ (Å)
$Me_3N^{+}-N^{-}-SO_2$-tol.	*1	1.471(3)	1.592(2)
Pyridinium^{+}-$\bar{N}$-SO_2-Ph-Cl	*2	1.419(3)	1.584(2)
$Me_2S^{+}-N^{-}-SO_2$-tol.	17	1.636(8)	1.591(8)
$Ph_2S^{+}-N^{-}-SO_2$-tol.	11	1.628(7)	1.598(8)
Ph.nPr.$S^{+}-N^{-}-SO_2$-tol.	12	1.620(7)	1.618(7)
$Me_2S^{+}-N^{-}-SO_2Me$	10	1.639(9)	1.581(10)
$Me_2S(O)^{+}N^{-}-SO_2Me$	43	1.554(2)	1.615(2)
$Ph_3P^{+}-N^{-}-SO_2$-tol.	18	1.579(4)	1.586(4)
$S(^{2+}-N^{-}-SO_2\text{-tol.})_2$	85	1.523**	1.685**

*n . . . section n

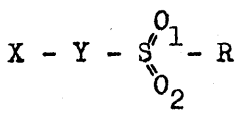
** . . . mean value

Consideration of theoretical aspects of the bonding interactions involved (see Introduction) has shown that a planar arrangement with one oxygen atom would give one of several weakly-defined maxima, with considerable flexibility possible. The significance of the frequently observed 30 to 40° torsion angle to the cis-oxygen in the sulphonyl-stabilised compounds may therefore lie in the accompanying 10 to 20° deviation from planarity with the trans-oxygen, particularly as this is generally accompanied by a near-planar arrangement of the toluene ring with the cis-oxygen, with a deviation from coplanarity in the range 10 to 15°. However, several examples which differ from this arrangement are now known, and the conformations of these and other relevant compounds are shown in Table 5 , summarised by the three torsion angles defined therein. The first seven compounds in the table adopt the near-trans-planar geometry, but the pyridinium compound has an almost exact trans-planar conformation. The possibility that differences in intramolecular non-bonded interactions may be responsible for these conformational differences has already been discussed (section 2.3). However, support is given by the di-ylide, $S(N\text{-}SO_2\text{-tol.})_2$[85], which exhibits entirely different conformations in the two sulphonyl-imine groupings, one having a near cis-planar arrangement, with $\tau_1 = 5.3°$, while the other adopts a staggered conformation, almost trans to the toluene ring. This may reflect the weak interaction involved, as implied by the long N-sulphonyl bonds. Nevertheless, in both groupings the toluene ring adopts a position not far from planarity with one oxygen atom ($\tau_3 = -8.7°$ and $-18.4°$).

A β-lactam-fused sulphonium imine, $S\text{-}N\text{-}SO_2\text{-tol.}$ [83], derived from penicillin, provides further evidence. In this compound the

Table 5

Conformations of sulphonyl-stabilised ylides and related compounds

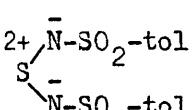
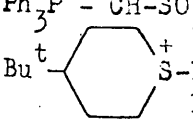


Torsion angles (°)

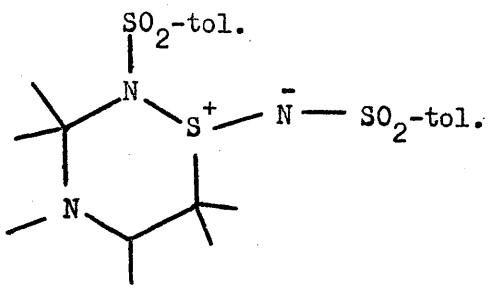
τ_1 X-Y-S-O_1

τ_2 X-Y-S-O_2

τ_3 O-S-Ring plane

Compound	Ref.	τ_1	τ_2	τ_3
$Me_3\overset{+}{N}-\overset{-}{N}-SO_2$-tol.	*1	40.7	168.6	12.1
$Ph_3\overset{+}{P}-\overset{-}{N}-SO_2$-tol.	18	37.6	167.7	11.8
$Me_2\overset{+}{S}-\overset{-}{N}-SO_2$-tol.	17	36.8	167.2	11.2
$Ph_2\overset{+}{S}-\overset{-}{N}-SO_2$-tol.	11	34.9	163.9	14.3
$Me_2\overset{+}{S}-\overset{-}{N}-SO_2Me$	10	31.7	160.5	-
$Me_2\overset{+}{S}(O)-\overset{-}{N}-SO_2Me$	43	32.1	161.2	-
Ph.nPr.$\overset{+}{S}-\overset{-}{N}-SO_2$-tol.	12	35.3	163.7	-15.4
Pyridinium$^{+}-\overset{-}{N}-SO_2$-Ph-Cl	*2	54.4	176.8	1.5
	85	78.5	52.2	-8.7
		5.3	135.4	-18.4
Penicillium$^{+}-\overset{-}{N}-SO_2$-tol.	83	-5.3	126.3	-30.4
$\overset{-}{N}(-SO_2-Ph)_2$	26	29.9	157.9	-6.5
		-37.0	-165.0	-12.0
$NH(-SO_2-Ph)_2$	26	8.8	162.3	3.1
		33.1	136.9	-7.8
$NH(-SO_2Me)_2$	86	36.7	164.6	-
$Ph_3P^{+}-\overset{-}{C}H-SO_2$-tol.	9	8.3	-122.8	21.3
	42	-50.9	180	0.6
Penicillium$^{+}-N-SO_2$-tol. (R)	83	-9.2	-137.3	1.1

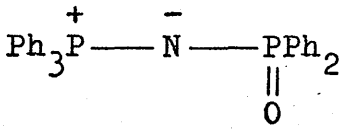
conformation of the whole grouping



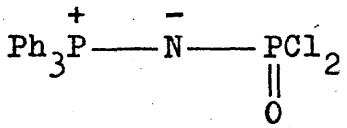
is restricted by the ring fusion, and the torsion angle $\overset{+}{S}\text{-}N\text{-}S\text{-}\overset{-}{O}_{cis}$ is -5.3° , close to cis-planarity. The toluene ring in this species is at 30.4° from coplanarity with the same oxygen, and 82.8° from coplanarity with the second oxygen atom. The reasons for these unusual conformations are believed to be the strong steric interactions brought about by the necessary close approach of the two p-toluene-sulphonyl sidechains[83].

The feature which is common to practically all cases is the planarity or near-planarity of pairs of ligands, and the consequent near coplanarity of the overlapping orbitals. It therefore appears likely that any of the various possible conformations which allow this arrangement may be suitable, and that the one adopted and any deviations from ideality may be determined by the steric interactions within the molecule. Similar behaviour is evident in the non-ylidic dibenzenesulphonamidate ion, $\bar{N}(\text{-}SO_2\text{-}Ph)_2$ [26].

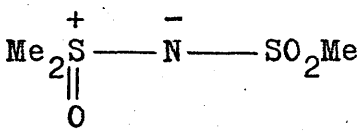
Theoretical considerations suggest that these principles should also apply to ylides with other groups containing d-orbitals e.g. phosphinyl groups, $R_2P(O)\text{-}$, and sulphoxy groups, $R_2\overset{+}{S}(O)\text{-}$. However, examination of the four compounds (1) - (4) containing these groups reveals a wide range of adopted conformations. Thus in (1) and (2)[83]



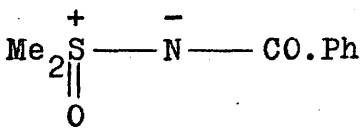
(1)



(2)



(3)



(4)

torsion angles, $\overset{+}{P}-N-\overset{-}{P}=O$, of -25.3° and 170.1° are observed, while in (3) and (4)[43] $\overset{-}{S}-N-\overset{+}{S}=O$ torsion angles of 55.3° and -64.2° are found. These values appear to suggest that the conformation adopted may depend purely on the groups involved and on the steric interactions to which they give rise.

The conformations of sulphonyl-stabilised carbanion ylides ($-\overset{-}{C}H-$), with one lone pair only to delocalise, and of isoelectronic compounds e.g. alkylated imines and sulphonamides, frequently show the same tendency to adopt a coplanar arrangement of pairs of ligands on a sulphur atom. However, as shown in the second part of Table 5 , this is not invariably the case and it is likely that the same factors determine the conformations of these compounds as with imines possessing two lone pairs on the negative atom.

The remaining feature of overall interest is the valence angle at nitrogen in the imino-compounds previously discussed. A range of values of 114.2 - 118.0° was observed in ammonium imines ($\overset{+}{N}-\overset{-}{N}$), 110.0 - 116.2° in sulphonium imines ($\overset{+}{S}-\overset{-}{N}$) and 116.4 - 146° in phosphonium imines ($\overset{+}{P}-\overset{-}{N}$). Since angle bending over a range of several degrees is a relatively low-energy process, the possibility that small variations could result from the changing steric interactions of different molecular environments has been discussed in sections 1.3 and 2.3 . However, the variation in this angle in $\overset{+}{P}-\overset{-}{N}$ compounds (Table 3) is strikingly greater than in $\overset{+}{S}-\overset{-}{N}$ compounds (Table 2), and enlargement of the angle beyond 130° , up to 146° , occurs purely in P - N - P compounds. It is interesting to note that this trend is paralleled in the phosphonitrilic and polythiazyl ring compounds, where valence angles at nitrogen fall within the ranges 120 - 148°

and 120 - 124° respectively[22,31]. In the eight-membered P-N-P rings where angle enlargement is feasible, angles of 132° to 134° are common, with enlargement up to 147.2° in the fluorinated compound $(PNF_2)_4$ [87]. On theoretical grounds of enhanced overlap, this has been interpreted as indicating a strong π'-interaction[20], and the experimental evidence of the very short P-N bond in the latter compound, 1.51 Å, is in agreement. Similar angle enlargement was observed in the isoelectronic oxygen-bridged phosphorus compounds e.g. 133.5° in the pyrophosphate ion, $P_2O_7^{4-}$ [25].

Several possible reasons for this difference in behaviour of phosphorus and sulphur compounds have been suggested. In sulphur(IV) oxidation state, the presence of a lone pair is believed to destabilise the d-orbitals coplanar with it[22,31] and hence to weaken considerably one component of $d\pi$-$p\pi$ bonding, generally the π' component with a consequent reduction in the tendency for angle enlargement. While this may well be a contributing factor to the low angles in sulphur compounds (less than trigonal), it is not sufficient by itself to explain the observed values since in similar sulphur(VI) compounds angles at nitrogen are still considerably less than those in the analogous phosphorus compounds. Thus in the dibenzenesulphonamidate ion, $\bar{N}(-SO_2-Ph)_2$ [26], the nitrogen angle is 127.5° and in the ylide $Me_2\overset{+}{S}(O)-\bar{N}-SO_2Me$ [43], the angle is 120.3°. Furthermore, in the six-membered ring compound, $(NSOCl)_3$ [88], a mean angle at nitrogen of 120.7° was observed, and the chair form of this ring implies no strong tendency to enlarge this value.

A possibly more likely explanation for this difference in geometry of phosphorus and sulphur compounds is therefore the greater electro-

negativity difference between phosphorus and nitrogen than between sulphur and nitrogen. Thus using Pauling's values[5], for P - N the electronegativity difference is 0.9 , while for S - N the difference is 0.5 . Since the effect of electronegative ligands is known to be a major influence in modifying d-orbital energies, reducing them to levels where appreciable interactions are possible[22,27], the 80% greater electronegativity difference with phosphorus may indicate a much greater contractile effect on the d-orbitals, with a consequent greater overlap capability.

On the other hand, this may be a rather oversimplified explanation since the applicability of a single value of electronegativity to the different oxidation states of sulphur can be disputed. Indeed, alternative values for S(II) , S(IV) and S(VI) have been proposed[37], although on an empirical basis derived from bond length measurements rather than thermodynamic data.

Nevertheless, it appears reasonable that electronegativity may be a major factor responsible for the differences between the bonding properties of phosphorus and sulphur in compounds with nitrogen, oxygen and carbon.

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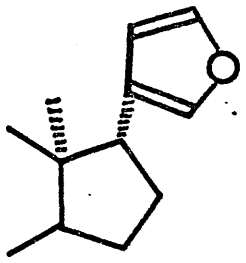
PART III

STRUCTURE ELUCIDATION OF TWO ORGANIC MOLECULES

1. THE CRYSTAL AND MOLECULAR STRUCTURE OF A COMPLEX TETRANORTRITERPENOID : PRIEURIANIN-2'-BROMOBENZENE-SULPHONATE.

1.1 Introduction

The X-ray structure analysis of the brosyl derivative of prieurianin was undertaken in order to elucidate its substantially unknown skeletal structure. Prieurianin, a highly complex tetranortriterpenoid, was first isolated by light petroleum extraction of the timber of Trichilia Prieuriana (Meliciae) in 1965[1]. The structure has remained obscure until recently owing to the unresolved nature of many of its ^{1}H n.m.r. peaks, preventing assignment of the signals and characterisation of many parts of the skeleton. The ^{13}C n.m.r. spectrum indicated the presence of 5 esters or lactones, 1 ketone, 1 formate, 1 furan ring, 1 exomethylene group, 2 hydroxy groups (one secondary, one tertiary), and a methyl ester group, but gave little information about the linkages. Mass spectra indicated the presence of a furan ring.[2] With this information and the possible part structures



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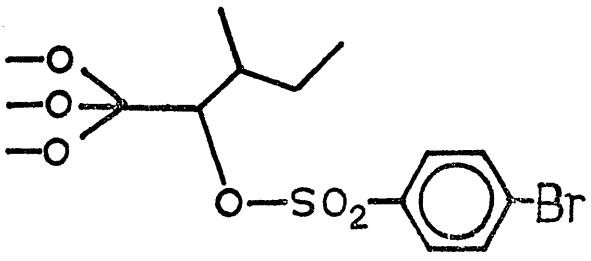


and five suggested cleaved-ring and bridged-ring skeletal structures (none of which subsequently proved correct), the X-ray analysis of the brosyl derivative was undertaken.

On account of the initial lack of success of this analysis, further spectroscopic examination was launched, including ^{13}C n.m.r. at elevated temperature using the more advanced techniques of proton-noise and continuous--wave decoupling, and ^{1}H n.m.r. at a range of elevated and sub-ambient temperatures. This work led to elucidation of the structure concurrently with that of the eventually successful X-ray analysis[3].

1.2 Experimental

Crystal Data

Prieurianin-p-bromobenzenesulphonate (solvated)

$C_{44}H_{53}O_{18}SBr.(CH_2Cl_2)_{\frac{3}{4}}$, M = 981.8 (excluding solvent)

M = 1044.8 (including solvent).

Orthorhombic, a = 11.339 b = 16.371 c = 27.737 Å ,

U = 4963.2 $Å^3$, D_m = 1.26 g cm^{-3}, Z = 4,

D_c = 1.31 g cm^{-3} (not inclusive of solvent),

$F_{(000)}$ = 2174 .

Space group : $P2_12_12_1$ (D_2^4 ; No. 19), uniquely identified by systematic absences.

μ(Mo,Kα) = 10.2 cm^{-1} , μ(Cu,Kα) = 29.8 cm^{-1} .

Data Collection

		1st Set*	2nd Set
Radiation	:	Cu,Kα	Mo,Kα
Filter	:	Ni	monochromator
Maximum scattering angle (2θ)	:	114°	50°
Independent reflections (observed)	:	3036	1926
Unobserved cutoff	:	$2\varsigma_I$	$3\varsigma_I$
Ratio of observations/parameters	:	-	6.96

* Shown later to be subject to machine errors

Structure Determination

The p-bromobenzenesulphonate derivative of prieurianin was prepared with a view to application of heavy atom methods of phasing, based on the dominance of scattering by the bromine atom. However, the low value of 0.35 for the ratio $Z^2_{(\text{heavy atom})}/\Sigma Z^2_{(\text{light atoms})}$ indicated that heavy atom phasing might have low reliability and, as expected, difficulty was experienced with this method. A sharpened origin-removed Patterson function was calculated which yielded the coordinates of the bromine atom but did not show the expected Br-S vectors despite a search of all peaks at a distance of approximately 6.4 Å from the origin, the distance typically observed in bromobenzenesulphonyl groups. A structure-factor and electron-density calculation based on the bromine atom yielded possible positions for the atoms of the benzene ring and the sulphur atom, although the latter peak was of low intensity. Inclusion of these atoms in a second cycle of Fourier synthesis gave little improvement in the resolution of the electron-density distribution but revealed two further atom positions. A third cycle gave no new atomic positions and showed several increasing faults in the model : the distortion of the ring, in both geometry and electron density, and its separation from the bromine and sulphur positions, and the shifting from cycle to cycle of the greater unresolved portion of the molecule. With the failure of Fourier methods to provide any further structural

information, phasing by non-centrosymmetric direct methods was undertaken.

Using a starting set of five reflections carefully chosen to give rapid initial phase expansion (Table 1.1) new phases were calculated and refined by reiteration using the tangent formula procedure with 432 reflections of $|E| \geqslant 1.35$. The four trial values of the variable phase lead to four possible phase sets whose correctness may be judged from the Karle residual, R_K , and from certain features of the calculation, namely the number of cycles of iteration required to obtain convergence, the level of oscillation of phases prior to convergence, and the number of phases not reliably determined. All these features indicated that the best phase set occurred with the variable phase at $+3\pi/4$, and $R_K = 0.301$, and an E-map was calculated with the 413 reflections whose phases had been determined. This map indicated the presence of the heavy atom in the same location as before, confirming the correctness of the Patterson solution, and also indicated the appearance of some realistic skeletal fragments although the resolution was poor and many positions could not be unambiguously determined.

Concurrently, a tangent-formula refinement of the heavy-atom phases was carried out, essentially a similar calculation to that outlined above, in which a starting set of 280 reflections with $|E| \geqslant 1.50$, from a previous

bromine-atom structure-factor calculation, was refined by reiteration, new phases being derived for a total of 381 reflections with $|E| \geq 1.40$. The E-map obtained with this phase set agreed closely with the direct phasing E-map in a number of features, but generally showed fewer peaks, with slightly improved resolution.

The structure determination proceeded by close comparison of these two E-maps. While no complete fragments could be identified, atom positions were selected which satisfied the following criteria :

(a) occurrence in both maps at closely agreeing positions with approximate separation no greater than 0.4 Å ,

(b) occurrence at comparable peak heights and with each peak height greater than the maximum "hole depth" in each E-map,

(c) occurrence in positions of apparently sensible molecular geometry.

This procedure yielded 31 new atom positions for inclusion as carbon atoms in a structure-factor and electron-density calculation. The resulting electron-density distribution indicated one of these atom positions to be erroneous, and revealed 14 new atoms in positions of realistic geometry, most of which were in agreement with smaller peaks in the initial E-maps.

The second cycle of Fourier synthesis was calculated with the inclusion of 44 atoms as carbon atoms, the

erroneous atom being omitted. This electron-density distribution revealed a further 11 new atoms, which were included in the third cycle with the omission of two suspect atoms from the previous cycle. The third electron-density distribution identified a further 7 new atoms, connecting isolated fragments into a recognisable skeleton with many side-chains, and identifying the sulphur atom. Only at this stage did the location of the benzene ring become apparent.

A fourth cycle of Fourier synthesis with the inclusion of 61 atoms (Br,S,59C) revealed the remaining 3 atoms completing the molecule, allowed assignment of 4 atoms as oxygen, and indicated the presence in the unit cell of another body, containing possibly several atoms, and assumed to be a molecule of solvent of crystallisation. A further four cycles of Fourier synthesis yielded improved coordinates for least-squares refinement and identified 5 more oxygen atoms. The remaining oxygen atoms were assigned on the basis of molecular geometry and behaviour of the isotropic thermal parameters on initial refinement of the structure.

Structure Refinement

Refinement of the structure by least-squares minimisation converged after 23 cycles with residuals R and R' at 0.096 and 0.015 respectively. In all cycles

the blocked matrix approximation was necessitated by the limited computer storage. Details of the course of refinement are given in Table 1.2 .

In order to maintain a sufficiently high ratio of observations to parameters, isotropic thermal parameters were refined for all atoms except the heavy atom for which anisotropic parameters were refined after cycle 5. Initial convergence of refinement at R = 0.178 confirmed the suspected high level of error in the intensity measurements, resulting from a diffractometer counter fault, which had been observed in other data sets collected sequentially with the present set. Accordingly, the intensity data were remeasured, with Mo,Kα radiation on this occasion, giving the advantage of reduced absorption effects but the penalty of a reduced number of observed reflections. The new data immediately improved the refinement and allowed the identification in a difference synthesis of the solvent body as a molecule of methylene chloride with partial occupancy of the site and some apparent disorder. This was included in the refinement with adjustment of an overall fractional population parameter, the final value being 0.74 .

Prior to cycle 16 , anomalous terms in the scattering factors for Br, Cl, and S were included, and five reflections of sufficiently high intensity to be seriously affected by counter saturation errors were

removed from the refinement. At cycle 18 the set of coordinates was inverted to give the correct absolute stereochemistry, known from the triterpenoid precursor, producing a marked improvement in refinement. In the final cycles, a weighting scheme of the form

$$W = \left[A + B|F_o| + C|F_o|^2\right]^{-1}$$

was applied with coefficients $A = 8.349$, $B = 0.4737$ and $C = 0.0013$ determined by polynomial fit to the function Δ^2.

A final difference electron density calculation showed no major errors in the structure, but revealed a number of small peaks in positions where hydrogen atoms would be stereochemically expected, and a number of small peaks associated with the solvent molecule, resulting from disorder or anisotropic thermal motion.

Atomic scattering factors derived by Cromer and Mann (1968)[4] were used in all structure-factor calculations.

Observed and calculated structure factors are listed in Appendix 9. Fractional coordinates and thermal parameters are given in Table 1.3 and molecular dimensions and intermolecular contact distances are listed in Table 1.4. Estimated standard deviations quoted with these quantities are derived from the inverse of the least-squares normal-equation matrix and are best considered as minimum values owing to the use of the blocked-matrix approximation. Details of some

least-squares planes through various portions of the molecular framework are given in Table 1.5 . The atomic numbering scheme is shown in Figure 1.1 and the molecular packing viewed down the a-axis is shown in Figure 1.2 .

Table 1.1

Starting set of reflections for direct phasing

h	k	l	|E|	No. of triplets	Function	Restriction (from symmetry)	Value
-3	3	0	3.78	129	O.D.	$\pm\pi/2$	$+\pi/2$
0	3	6	2.81	140	O.D.	$\pm\pi/2$	$+\pi/2$
0	17	5	2.38	67	O.D.	$\pm\pi/2$	$+\pi/2$
-4	0	5	2.05	110	E.D.	$\pm\pi/2$	$+\pi/2$
-4	5	2	2.39	194	variable	none	$\pm\pi/4, \pm 3\pi/4$

Correct solution has variable = $+3\pi/4$ (refined value = 141°), and residual, $R_K = 0.301$.

Table 1.2

Course of refinement

Cycles	Parameters refined	Final R	Final R'
1	x,y,z,U_{ov}, scale factor. Unit weights.	0.276	0.075
2 - 5	x,y,z,U_{iso}, scale factor. Unit weights.	0.195	0.039
6 - 7	x,y,z,U_{iso}(U_{ij} for Br), scale factor. Unit weights.	0.178	0.034
8 - 12	x,y,z,U_{iso}(U_{ij} for Br), scale factor. Unit weights. New data set, with Mo,K radiation.	0.125	0.022
13 - 17	x,y,z,U_{iso}(U_{ij} for Br), scale factor. Unit weights. Solvent molecule included and refined with overall population param.	0.108	0.013
18 - 19	x,y,z,U_{iso}(U_{ij} for Br), scale factor. Unit weights. Solvent molecule included. Coordinates inverted to give correct enantiomorph.	0.098	0.011
20 - 23	x,y,z,U_{iso}(U_{ij} for Br), scale factor. Weighting scheme applied. Solvent molecule included.	0.096	0.012

Table 1.3

Fractional coordinates and isotropic thermal parameters ($Å^2$)

	x/a	y/b	z/c	U_{iso}
Br	0.5559(3)	0.1624(2)	0.3891(1)	-
S	0.4787(5)	0.3368(4)	0.6000(2)	0.068(2)
O(1)	0.5106(16)	0.2830(10)	0.6401(6)	0.085(5)
O(2)	0.3717(16)	0.3785(11)	0.5995(11)	0.089(5)
O(3)	0.5839(12)	0.4018(8)	0.6000(5)	0.055(4)
O(4)	0.4963(13)	0.5328(9)	0.6484(5)	0.065(4)
O(5)	0.5397(11)	0.6163(7)	0.5830(4)	0.046(3)
O(6)	0.2536(17)	0.4778(11)	0.5156(7)	0.091(5)
O(7)	0.2092(14)	0.8982(10)	0.5671(6)	0.072(5)
O(8)	0.3132(11)	0.7879(8)	0.6501(4)	0.044(3)
O(9)	0.6827(12)	0.7017(8)	0.6478(5)	0.050(4)
O(10)	0.8343(16)	0.7377(11)	0.5948(7)	0.086(5)
O(11)	0.6494(14)	1.0265(9)	0.7501(5)	0.063(4)
O(12)	0.8017(20)	1.0014(13)	0.7993(8)	0.113(7)
O(13)	0.2468(14)	0.9190(9)	0.7085(6)	0.064(4)
O(14)	0.2408(15)	0.9680(9)	0.7861(6)	0.068(4)
O(15)	0.4082(14)	1.0817(9)	0.6736(6)	0.068(4)
O(16)	0.2825(21)	1.1574(14)	0.7158(9)	0.127(8)
O(17)	0.7816(13)	0.8833(8)	0.6844(5)	0.058(4)
O(18)	0.9292(19)	0.8087(12)	0.7189(7)	0.106(6)
C(1)	0.6984(17)	0.8411(12)	0.7190(7)	0.045(5)
C(2)	0.7101(21)	0.8803(14)	0.7716(8)	0.060(6)
C(3)	0.7193(27)	0.9714(18)	0.7740(10)	0.083(8)
C(4)	0.5706(19)	1.0092(12)	0.7082(8)	0.050(5)
C(5)	0.5013(17)	0.9277(12)	0.7084(7)	0.045(5)
C(6)	0.4295(17)	0.9230(12)	0.7584(7)	0.043(5)
C(7)	0.2944(19)	0.9350(13)	0.7464(8)	0.051(6)
C(8)	0.4634(17)	0.8649(11)	0.6050(7)	0.044(5)
C(9)	0.5738(16)	0.8364(11)	0.6372(6)	0.034(4)

Table 1.3 (cont.)

	x/a	y/b	z/c	U_{iso}
C(10)	0.5680(17)	0.8442(11)	0.6971(6)	0.037(5)
C(11)	0.5995(15)	0.7447(10)	0.6157(6)	0.033(4)
C(12)	0.4932(15)	0.6871(10)	0.6098(6)	0.031(4)
C(13)	0.4010(16)	0.7262(11)	0.5756(7)	0.035(5)
C(14)	0.3619(17)	0.8074(11)	0.6025(7)	0.043(5)
C(15)	0.2440(20)	0.8283(14)	0.5732(8)	0.058(6)
C(16)	0.1929(20)	0.7508(14)	0.5578(8)	0.057(6)
C(17)	0.2794(18)	0.6844(12)	0.5747(7)	0.051(5)
C(18)	0.4457(18)	0.7481(11)	0.5239(6)	0.040(5)
C(19)	0.5128(17)	0.7710(11)	0.7210(7)	0.042(5)
C(20)	0.2750(19)	0.6100(12)	0.5389(7)	0.049(5)
C(21)	0.2511(23)	0.5324(15)	0.5548(9)	0.067(7)
C(22)	0.2882(20)	0.6063(14)	0.4862(8)	0.060(6)
C(23)	0.2736(27)	0.5227(18)	0.4739(10)	0.090(9)
C(24)	0.8012(22)	0.6998(16)	0.6320(9)	0.072(7)
C(25)	0.1107(26)	0.9815(17)	0.7800(10)	0.086(9)
C(26)	0.9030(24)	0.8602(16)	0.6884(10)	0.080(8)
C(27)	0.9731(23)	0.9061(15)	0.6519(9)	0.077(7)
C(28)	0.6424(19)	1.0305(13)	0.6595(8)	0.053(6)
C(29)	0.4844(22)	1.0816(14)	0.7176(9)	0.070(7)
C(30)	0.4744(19)	0.9295(13)	0.5750(8)	0.054(6)
C(31)	0.3036(24)	1.1222(16)	0.6768(10)	0.076(8)
C(32)	0.2389(29)	1.1211(19)	0.6283(11)	0.107(10)
C(33)	0.5362(17)	0.5437(11)	0.6057(7)	0.045(5)
C(34)	0.5745(17)	0.4757(11)	0.5711(7)	0.044(5)
C(35)	0.7004(19)	0.4951(14)	0.5457(8)	0.060(6)
C(36)	0.7291(23)	0.4295(16)	0.5086(9)	0.081(7)
C(37)	0.7910(20)	0.4988(14)	0.5862(8)	0.062(6)
C(38)	0.9145(24)	0.5302(16)	0.5651(9)	0.083(8)

Table 1.3 (cont.)

	x/a	y/b	z/c	U_{isc}
C(39)	0.4977(19)	0.2858(13)	0.5421(8)	0.056(6)
C(40)	0.5743(25)	0.2214(17)	0.5405(10)	0.087(8)
C(41)	0.5920(27)	0.1848(19)	0.4918(11)	0.101(10)
C(42)	0.5304(23)	0.2117(16)	0.4515(9)	0.075(7)
C(43)	0.4429(25)	0.2748(17)	0.4540(10)	0.087(8)
C(44)	0.4255(22)	0.3138(15)	0.5018(9)	0.074(7)
C(45)	0.6460(50)	0.8002(33)	0.2313(19)	0.144(18)
Cl(1)	0.7305(12)	0.7514(8)	0.1936(4)	0.127(6)
Cl(2)	0.5597(21)	0.8675(12)	0.1936(7)	0.216(8)

Anisotropic thermal parameters ($\AA^2$) for Br

U_{11}	0.080(2)
U_{22}	0.088(2)
U_{33}	0.108(3)
U_{12}	-0.014(2)
U_{13}	0.026(2)
U_{23}	-0.044(2)

Table 1.4

Interatomic distances and angles

a) Bonded distances (Å)

C(1) - C(2)	1.55(3)	C(8) - C(14)	1.49(3)
C(1) - C(10)	1.59(3)	C(8) - C(30)	1.33(3)
C(1) - O(17)	1.49(2)	C(11) - C(12)	1.54(2)
C(2) - C(3)	1.50(4)	C(11) - O(9)	1.46(2)
C(3) - O(11)	1.36(3)	C(12) - C(13)	1.55(2)
C(3) - O(12)	1.25(4)	C(12) - O(5)	1.46(2)
C(4) - O(11)	1.46(3)	C(13) - C(14)	1.58(3)
C(4) - C(5)	1.55(3)	C(13) - C(17)	1.54(3)
C(4) - C(28)	1.57(3)	C(13) - C(18)	1.52(3)
C(4) - C(29)	1.56(3)	C(14) - C(15)	1.59(3)
C(5) - C(6)	1.57(3)	C(14) - O(8)	1.42(2)
C(5) - C(10)	1.59(3)	C(15) - C(16)	1.45(3)
C(6) - C(7)	1.58(3)	C(15) - O(7)	1.22(3)
C(7) - O(13)	1.18(3)	C(16) - C(17)	1.53(3)
C(7) - O(14)	1.34(3)	C(17) - C(20)	1.55(4)
O(14) - C(25)	1.50(3)	C(20) - C(21)	1.37(3)
C(10) - C(9)	1.61(2)	C(20) - C(22)	1.42(3)
C(10) - C(19)	1.49(3)	C(22) - C(23)	1.42(4)
C(9) - C(8)	1.59(3)	C(21) - O(6)	1.38(3)
C(9) - C(11)	1.63(2)	C(23) - O(6)	1.36(3)

Table 1.4.a (cont.)

O(9) - C(24)	1.41(3)	C(35) - C(36)	1.50(3)
O(10) - C(24)	1.23(3)	C(35) - C(37)	1.49(3)
O(17) - C(26)	1.43(3)	C(37) - C(38)	1.60(4)
O(18) - C(26)	1.21(3)	S - O(3)	1.60(1)
C(26) - C(27)	1.47(4)	S - O(2)	1.39(2)
C(29) - O(15)	1.46(3)	S - O(1)	1.43(2)
O(15) - C(31)	1.36(3)	S - C(39)	1.77(2)
O(16) - C(31)	1.22(4)	C(39) - C(40)	1.37(4)
C(31) - C(32)	1.49(4)	C(40) - C(41)	1.45(4)
O(5) - C(33)	1.33(2)	C(41) - C(42)	1.36(4)
O(4) - C(33)	1.24(2)	C(42) - C(43)	1.43(4)
C(33) - C(34)	1.51(3)	C(43) - C(44)	1.44(4)
C(34) - C(35)	1.61(3)	C(44) - C(39)	1.43(3)
C(34) - O(3)	1.44(2)	Br - C(42)	1.88(3)
C(45) - Cl(1)	1.60(6)	C(45) - Cl(2)	1.79(6)

Table 1.4 (cont.)

b) Interbond angles (°)

C(2) -C(1) -C(10)	113.6(16)	C(5) -C(10)-C(1)	113.5(15)
C(2) -C(1) -O(17)	108.4(16)	C(5) -C(10)-C(9)	106.1(14)
C(10)-C(1) -O(17)	110.3(13)	C(5) -C(10)-C(19)	114.1(15)
C(1) -C(2) -C(3)	117.2(19)	C(1) -C(10)-C(9)	109.0(14)
C(2) -C(3) -O(11)	126.9(20)	C(1) -C(10)-C(19)	101.9(14)
C(2) -C(3) -O(12)	117.7(25)	C(9) -C(10)-C(19)	112.3(14)
O(11)-C(3) -O(12)	115.4(25)	C(10)-C(9) -C(8)	118.9(14)
C(3) -O(11)-C(4)	126.1(18)	C(10)-C(9) -C(11)	115.5(13)
O(11)-C(4) -C(5)	118.3(16)	C(8) -C(9) -C(11)	102.7(13)
O(11)-C(4) -C(28)	106.0(16)	C(9) -C(8) -C(14)	116.6(15)
O(11)-C(4) -C(29)	96.5(15)	C(9) -C(8) -C(30)	119.1(17)
C(5) -C(4) -C(28)	117.2(16)	C(14)-C(8) -C(30)	123.1(18)
C(5) -C(4) -C(29)	109.7(17)	C(9) -C(11)-C(12)	117.4(14)
C(28)-C(4) -C(29)	106.9(16)	C(9) -C(11)-O(9)	110.6(13)
C(4) -C(5) -C(6)	108.0(16)	C(12)-C(11)-O(9)	105.8(13)
C(4) -C(5)-C(10)	119.9(16)	C(11)-C(12)-C(13)	109.9(13)
C(6) -C(5) -C(10)	111.6(15)	C(11)-C(12)-O(5)	104.7(13)
C(5) -C(6) -C(7)	108.9(15)	C(13)-C(12)-O(5)	106.5(13)
C(6) -C(7) -O(13)	126.4(19)	C(12)-C(13)-C(14)	105.8(14)
C(6) -C(7) -O(14)	109.3(17)	C(12)-C(13)-C(17)	115.9(15)
O(13)-C(7) -O(14)	124.3(20)	C(12)-C(13)-C(18)	114.6(15)
C(7) -O(14) C(25)	114.9(18)	C(14)-C(13)-C(17)	97.5(14)
C(14)-C(13)-C(18)	108.1(14)	C(26)-O(17)-C(1)	116.1(16)
C(17)-C(13)-C(18)	112.9(15)	O(17)-C(26)-C(27)	109.6(21)
C(13)-C(14)-C(8)	109.7(15)	O(17)-C(26)-O(18)	118.1(23)
C(13)-C(14)-C(15)	101.2(15)	O(18)-C(26)-C(27)	132.3(26)
C(13)-C(14)-O(8)	109.2(14)	C(4) -C(29)-O(15)	104.0(17)
C(8) -C(14)-C(15)	122.5(16)	C(29)-O(15)-C(31)	117.7(18)
C(8) -C(14)-O(8)	113.6(15)	O(15)-C(31)-C(32)	111.6(22)
C(15)-C(14)-O(8)	99.4(15)	O(15)-C(31)-O(16)	117.2(24)

Table 1.4.b (cont.)

C(14)-C(15)-C(16)	106.7(17)	O(16)-C(31)-C(32)	131.0(27)
C(14)-C(15)-O(7)	122.7(19)	C(12)-O(5) -C(33)	118.1(13)
C(16)-C(15)-O(7)	130.6(21)	O(5) -C(33)-C(34)	111.6(16)
C(15)-C(16)-C(17)	106.3(18)	O(5) -C(33)-O(4)	124.0(17)
C(16)-C(17)-C(13)	105.3(16)	O(4) -C(33)-C(34)	124.1(16)
C(16)-C(17)-C(20)	110.8(17)	C(33)-C(34)-C(35)	111.6(16)
C(13)-C(17)-C(20)	112.8(16)	C(33)-C(34)-O(3)	108.2(14)
C(17)-C(20)-C(21)	123.0(18)	C(35)-C(34)-O(3)	109.1(15)
C(17)-C(20)-C(22)	130.1(19)	C(34)-C(35)-C(36)	109.4(18)
C(21)-C(20)-C(22)	106.9(19)	C(34)-C(35)-C(37)	108.1(17)
C(20)-C(22)-C(23)	105.0(20)	C(36)-C(35)-C(37)	111.1(19)
C(22)-C(23)-O(6)	110.7(22)	C(35)-C(37)-C(38)	111.1(18)
C(20)-C(21)-O(6)	111.2(20)	C(34)-O(3) -S	120.3(12)
C(21)-O(6) -C(23)	106.0(20)	O(3) -S -O(2)	108.9(9)
C(24)-O(9) -C(11)	116.8(15)	O(3) -S -O(1)	102.8(9)
O(9) -C(24)-O(10)	121.5(22)	O(3) -S -C(39)	102.8(9)
C(39)-S -O(2)	109.1(11)	C(42)-C(43)-C(44)	117.0(23)
C(39)-S -O(1)	109.5(10)	C(43)-C(44)-C(39)	116.7(22)
O(1) -S -O(2)	122.0(10)	C(44)-C(39)-C(40)	125.9(22)
S -C(39)-C(40)	118.0(18)	C(41)-C(42)-Br	119.1(21)
S -C(39)-C(44)	116.0(17)	C(43)-C(42)-Br	117.2(18)
C(39)-C(40)-C(41)	115.9(24)	Cl(1)-C(45)-Cl(2)	106.3(29)
C(40)-C(41)-C(42)	120.5(27)		
C(41)-C(42)-C(43)	123.7(24)		

Table 1.4 (cont.)

c) Selected intramolecular non-bonded distances (Å)

C(1) ...O(9)	2.98	C(28)...O(17)	2.95
C(1) ...O(18)	2.67	C(29)...O(16)	2.61
C(2) ...O(18)	3.09	C(30)...O(7)	3.06
C(3) ...O(17)	2.88	C(31)...O(13)	3.49
C(5) ...O(13)	2.89	C(34)...O(2)	2.90
C(5) ...O(15)	2.89	C(35)...O(5)	2.87
C(6) ...C(19)	2.84	C(36)...O(3)	2.98
C(6) ...C(29)	2.88	C(37)...O(3)	2.86
C(6) ...O(11)	3.02	C(40)...O(1)	2.94
C(6) ...O(15)	3.35	C(40)...O(3)	3.36
C(9) ...C(28)	3.33	C(44)...O(2)	2.88
C(11)...O(10)	2.72	C(44)...O(3)	3.49
C(12)...O(4)	2.73	C(44)...O(6)	3.34
C(18)...C(30)	3.29	S . ....O(4)	3.46
C(18)...O(5)	2.88	O(2) ...O(4)	3.17
C(19)...O(8)	2.96	O(2) ...O(6)	3.07
C(19)...O(9)	2.97	O(3) ...O(4)	2.69
C(24)...C(26)	3.24	O(5) ...O(9)	2.76
C(24)...O(18)	3.27	O(7) ...O(8)	3.10
C(25)...O(13)	2.66	O(8) ...O(13)	2.76
C(26)...O(10)	3.30	O(9) ...O(17)	3.32
C(28)...C(30)	3.39	O(13)...O(15)	3.36
C(28)...O(15)	2.81		

Table 1.4 (cont.)

d) Selected intermolecular distances (Å)

O(1) ...O(15)^{I}	3.61	C(32)...O(4)^{III}	3.36
O(1) ...C(31)^{I}	3.66	C(36)...O(4)^{III}	3.18
C(27)...O(13)^{II}	3.46	Br .....O(2)^{IV}	3.65
C(27)...O(7)^{II}	3.51	C(6) ...O(6)^{IV}	3.24
O(12)...C(25)^{II}	3.56	C(8) ...O(7)^{V}	3.49
O(11)...O(4)^{III}	3.18	C(9) ...O(7)^{V}	3.48
O(14)...C(10)^{III}	3.47	O(10)...C(22)^{V}	3.42
O(16)...C(35)^{III}	3.42	O(1) ...Cl(1)^{VI}	3.31

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

I	x,	-1+y,	z ;	II	1+x,	y,	z ;
III	1-x,	1/2+y,	3/2-z ;	IV	1/2+x,	1/2-y,	1-z ;
V	1/2+x,	3/2-y,	1-z ;	VI	3/2-x,	1-y,	1/2+z .

Table 1.4 (cont.)

e) Selected Torsion Angles (°)

C(40)-C(39)-S -O(1)	-23	C(17)-C(16)-C(15)-C(14)	-3
C(40)-C(39)-S -O(2)	-159	C(16)-C(15)-C(14)-C(13)	31
C(40)-C(39)-S -O(3)	86	C(16)-C(15) C(14)-C(8)	153
C(39)-S -O(3) -C(34)	78	C(12)-C(13)-C(17)-C(20)	-83
S -O(3) -C(34)-C(35)	-140	C(13)-C(17)-C(20)-C(22)	-64
S -O(3) -C(34)-C(33)	98	C(8) -C(9) -C(10)-C(19)	87
O(3) -C(34)-C(35)-C(36)	65	C(1) -C(10)-C(5) -C(4)	36
O(3) -C(34)-C(35)-C(37)	-56	C(10)-C(5) -C(4) -O(11)	-74
C(34)-C(35)-C(37)-C(38)	-172	C(5) -C(4) -O(11)-C(3)	39
O(3) -C(34)-C(33)-O(5)	172	C(4) -O(11)-C(3) -C(2)	-16
C(34)-C(33)-O(5) -C(12)	174	O(11)-C(3) -C(2) -C(1)	48
C(33)-O(5) -C(12)-C(13)	-125	C(3) -C(2) -C(1) -C(10)	-81
C(12)-C(13)-C(14)-C(8)	65	C(2) -C(1) -C(10)-C(5)	40
C(13)-C(14)-C(8) -C(9)	-64	C(3) -C(2) -C(1) -O(17)	42
C(14)-C(8) -C(9) -C(11)	50	C(2) -C(1) -O(17)-C(26)	78
C(30)-C(8) -C(9) -C(11)	-118	C(1) O(17) -C(26)-C(27)	179
C(8) -C(9) -C(11)-C(12)	-47	C(19)-C(10)-C(5) -C(6)	25
C(9) -C(11)-C(12)-C(13)	57	C(10)-C(5) -C(6) -C(7)	-118
C(9) -C(11)-O(9) -C(24)	-99	C(5) -C(6) -C(7) -O(14)	-152
C(11)-O(9) -C(24)-O(10)	5	C(6) -C(7) -O(14)-C(25)	-179
C(11)-C(12)-C(13)-C(17)	-168	C(3) -O(11)-C(4) -C(29)	155
C(12)-C(13)-C(17)-C(16)	156	O(11)-C(4) -C(29)-O(15)	171
C(14)-C(13)-C(17)-C(16)	45	C(4) -C(29)-O(15)-C(31)	162
C(13)-C(17)-C(16)-C(15)	-27	C(29)-O(15)-C(31)-C(32)	177

Mean e.s.d. = 2°

Table 1.5

Least-squares planes

a) Equation of plane

i) $0.7168X + 0.6627Y - 0.2166Z + 3.9696 = 0$

ii) $0.9818X - 0.1460Y + 0.1218Z + 3.3468 = 0$

iii) $-0.3939X + 0.5269Y + 0.7531Z + 17.5039 = 0$

iv) $-0.5115X - 0.0468Y + 0.8579Z + 11.0785 = 0$

v) $0.6038X - 0.0180Y - 0.7969Z - 11.8424 = 0$

b) Deviation of atoms from the plane (Å)

i)	Br	0.06	S	0.10	O(1)	-0.46
	O(2)	-0.31	C(39)	0.04*	C(40)	-0.03*
	C(41)	-0.00*	C(42)	0.02*	C(43)	-0.02*
	C(44)	-0.01*				
ii)	C(17)	0.00	C(20)	0.01*	C(21)	-0.02*
	C(22)	0.00*	C(23)	-0.01*	O(6)	0.01*
iii)	C(8)	0.07*	C(9)	-0.02*	C(14)	-0.02*
	C(30)	-0.03*				
iv)	C(13)	-0.78	C(17)	-0.06	C(14)	0.001*
	C(15)	-0.005*	C(16)	0.001*	O(7)	0.002*
v)	C(1)	1.06	C(4)	0.36	C(5)	-0.09
	C(10)	0.63	C(2)	0.003*	C(3)	-0.011*
	O(11)	0.004*	O(12)	0.004*		

c) Dihedral angle between planes :

i) and ii) 54.5° , ii) and iv) 113.0° , iii) and iv) 34.7° .

* denotes atom used to define plane.

X, Y, and Z are orthogonal coordinates in Å .

Figure 1.1

Atomic numbering scheme

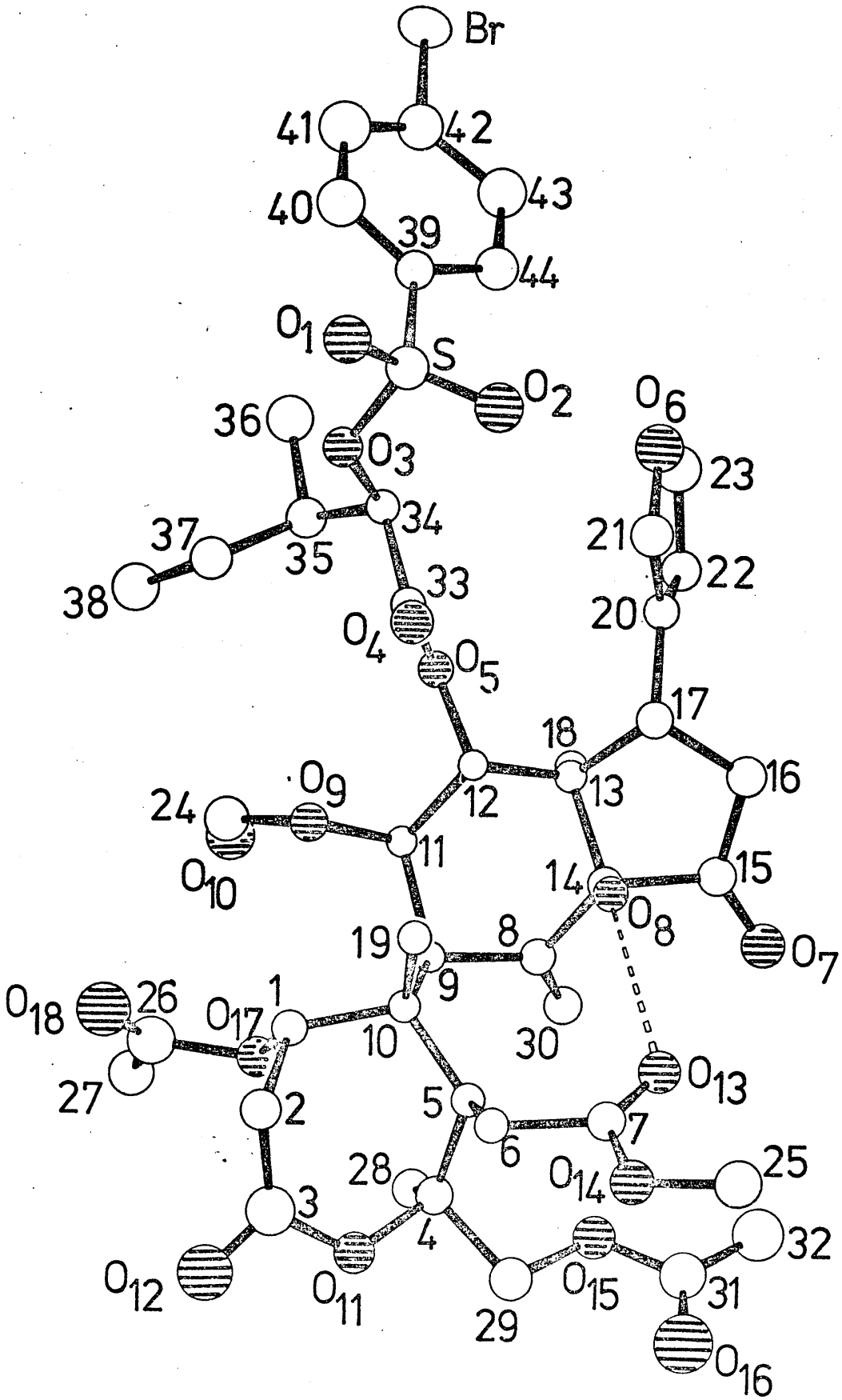
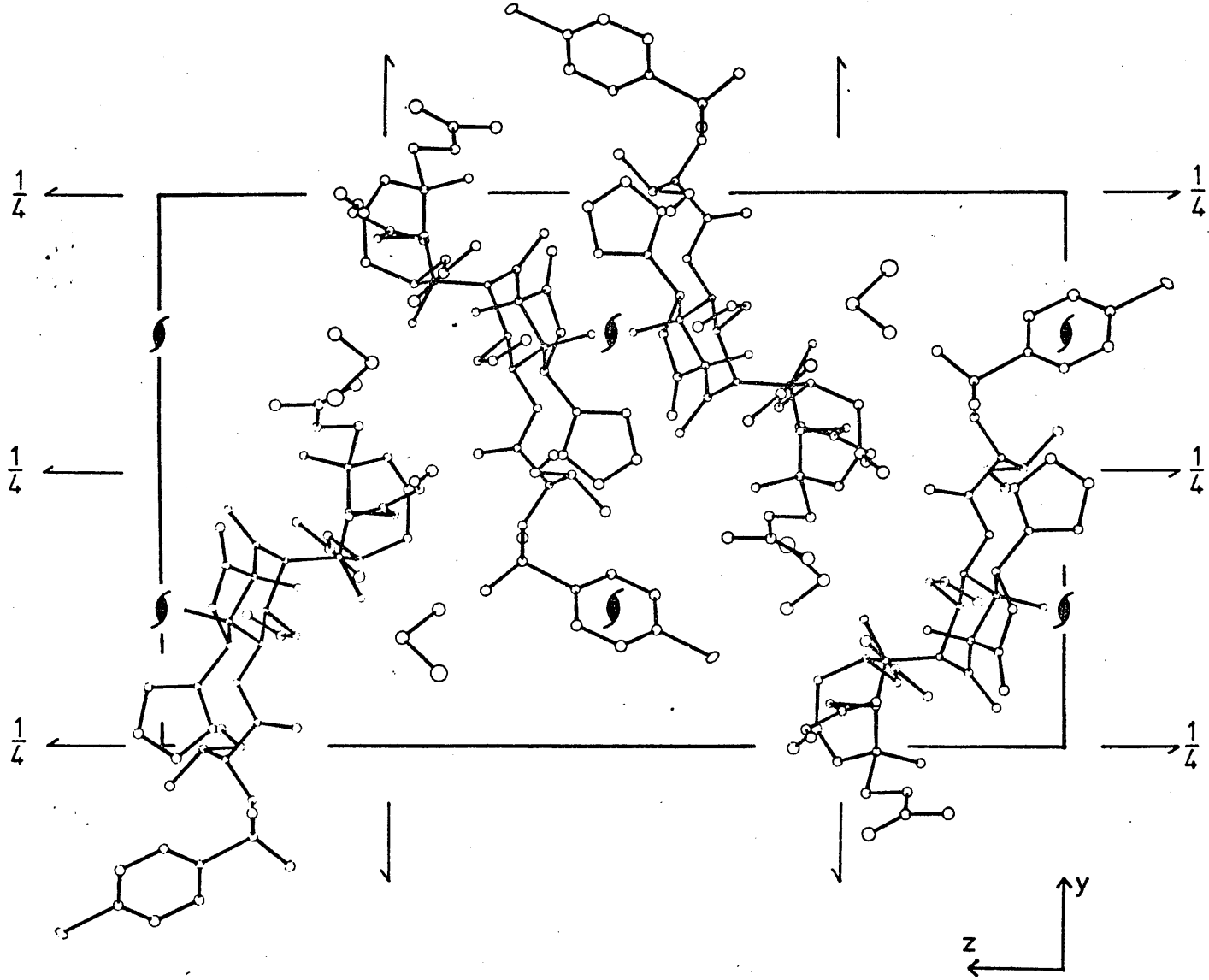

Br
41
42
40
43
39
44
O1
S
O2
36
O3
O6
23
34
21
22
37
35
38
33
20
O4
O5
17
18
O9
12
13
16
24
11
14
15
O10
O8
19
8
O7
O18
26
1
9
O17
10
30
27
O13
2
5
7
6
28
O14
25
3
4
32
O12
O11
O15
31
29
O16

Figure 1.2

Molecular packing arrangement

viewed down the a-axis


1/4
1/4
1/4
1/4
1/4
1/4
y
z

1.3 Discussion

The X-ray analysis of prieurianin has confirmed the structure determined concurrently by spectroscopic methods, indicating a cleaved B-ring structure with ring A expanded to a seven-membered lactone ring. The relative stereochemistry of the C(1), C(4) and C(14) atoms, which was not ascertained by the spectroscopic study, has been determined by this work, which has also confirmed the absolute stereochemistry.

The structural formula of prieurianin brosylate is shown in Figure 1.3 and illustrates the single bond linkage between the lactone section of the molecule and the C and D ring portion, allowing the possibility of free rotation of the lactone group about this bond relative to the remainder of the molecule. However, this rotation is likely to be somewhat hindered owing to the steric interactions between the two mobile portions and to the hydrogen bonding of the C(14) β-hydroxyl group. Evidence for hydrogen bonding was observed in the I.R. spectrum, and the crystal structure reveals this to be intramolecular bonding with the methyl ester carbonyl group with an O(8)...O(13) separation of 2.76 Å, comparable with commonly observed values [5]. However, the broadness of the n.m.r. spectra at ambient temperatures indicates a range of environmental conditions in the molecule, which vanishes at elevated

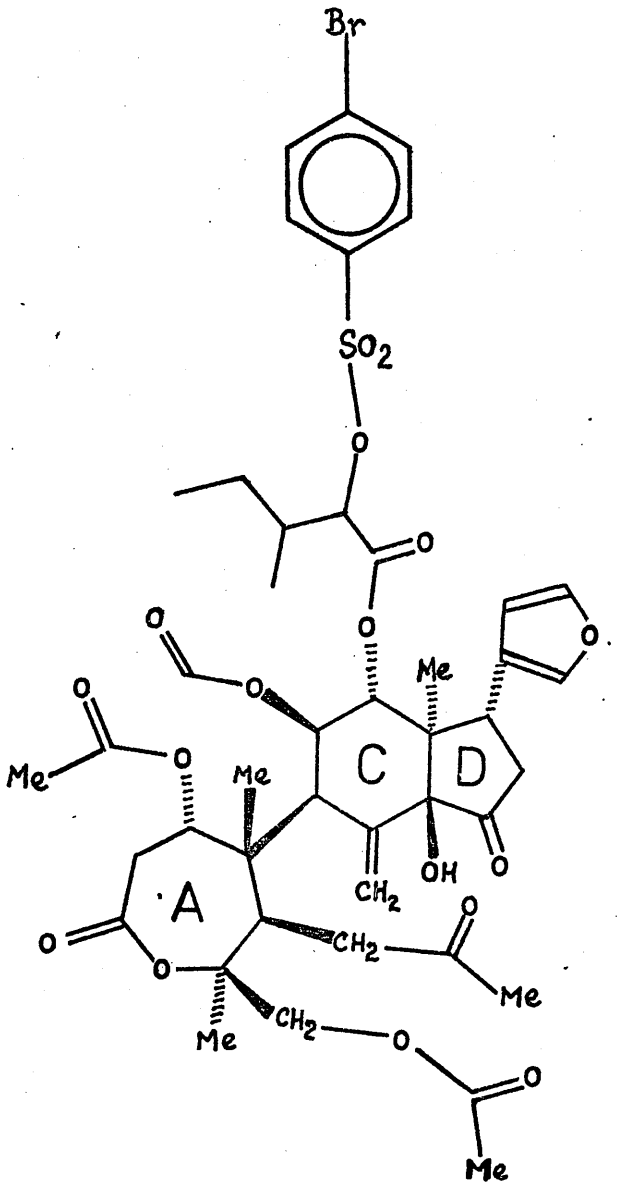


Figure 1.3

The structure of prieurianin brosylate

temperatures with a consequent sharpening of the spectra, presumably as the greater thermal motion produces a uniform time-averaged environment. Correspondingly at reduced temperature, the multiplicities of some peaks have been interpreted as showing the presence of several conformers differing in the rotation about C(9)-C(10) and/or the conformation of the lactone ring[3]. Inspection of the molecule reveals that a rotation of about 180° around the C(9)-C(10) bond would place the C(1) acetyl group in a position suitable for hydrogen-bonding with the C(14) hydroxyl function.

The conformation of the ε-lactone is illustrated in Figure 1.4 and may best be described as a "boat" conformation distorted by the presence of the planar lactone group and with C(2) and C(5) in apical positions. This places the substituents with C(6), C(28) and O(17) in axial locations with a resulting short transannular contact, C(28)...O(17), of 2.95 Å. It is possible that steric interactions between the many substituents cause this conformation to be adopted in preference to the "chair" conformation more usually favoured by seven-membered rings[6]. Thus the contacts C(6)...C(19), 2.84 Å, and O(6)...C(29), 2.88 Å, may have considerable influence on the ring geometry. Nevertheless, the relatively large thermal parameters of the C(2), C(3), O(11) and C(4) portion of the ring indicate appreciable flexibility. This is clearly seen in the thermal

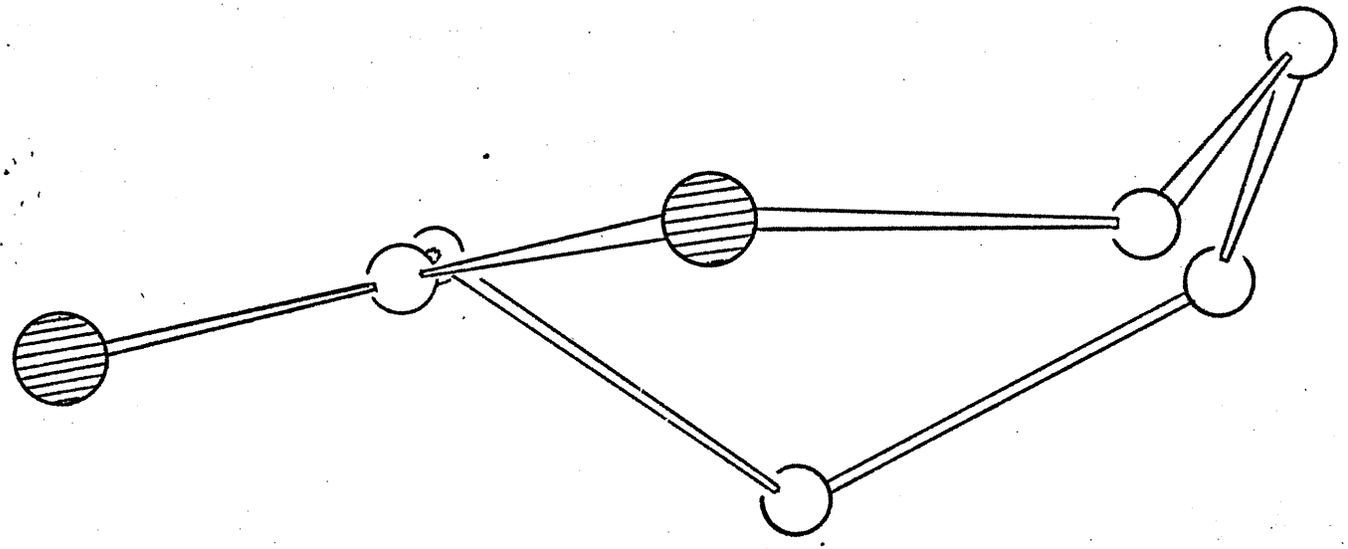


Figure 1.4

The conformation of the ε-lactone

ellipsoid diagram, Figure 1.1 .

The chair conformation of ring C and the puckered conformation of ring D are normal for triterpenoid systems, although the C(8)-C(30) double bond and C(15) ketone must impart some added restriction and strain. The mean of the interior angles in ring C (excluding that at C(8)) is 112.3°, while that in ring D (excluding the angle at C(15)) is 102.6°, indicating the strain built into the five-membered ring. The sum of interior angles in that ring, 517°, is typical for a trans-fused triterpenoid D-ring and illustrates the deviation from planarity, where a value of 540° is required.

Average bond lengths of all types are in good agreement with accepted values [7]. These are tabulated below for comparison.

Bond	Prieurianin (mean length, Å)	Accepted value (mean length, Å) ±0.005
$C(sp^3)$-$C(sp^3)$	1.56(3)	1.537
$C(sp^3)$-C(alkene)	1.54(3)	1.510
$C(sp^3)$-C(carbonyl)	1.51(3)	1.506
C(aryl)-C(aryl)	1.41(4)	1.394
$C(sp^3)$-O	1.46(2)	1.426
$C(sp^2)$-O	1.37(3)	1.358
C=O	1.22(3)	1.215

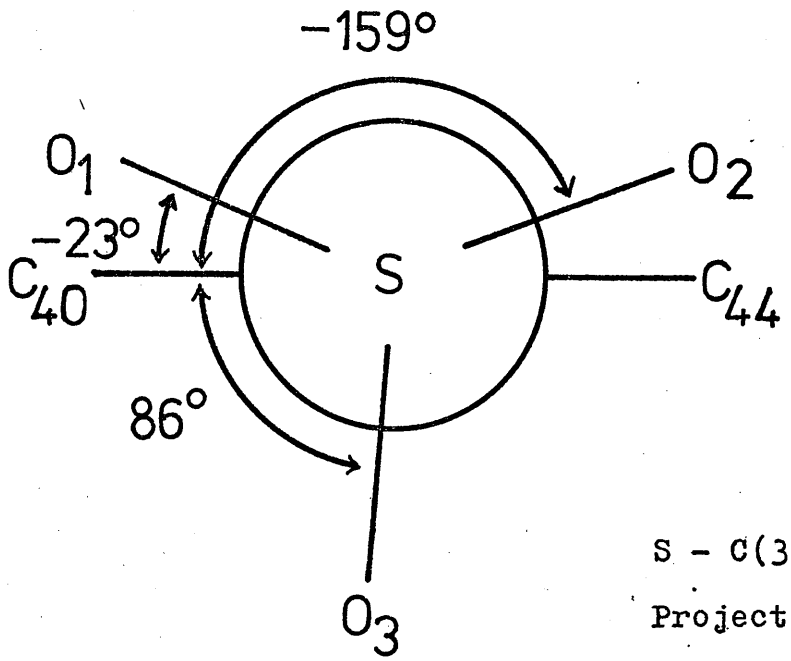
Little additional comment is required, save perhaps to draw attention to the wide range of $C(sp^3)$-$C(sp^3)$ bond lengths present, 1.49(3) to 1.63(2) Å . This may reflect

real differences in molecular strain and interactions, but may equally be a function of the low precision of the refinement. Refinement with anisotropic thermal parameters would considerably improve the level of refinement but cannot be justified with a small data set in relation to the large asymmetric unit.

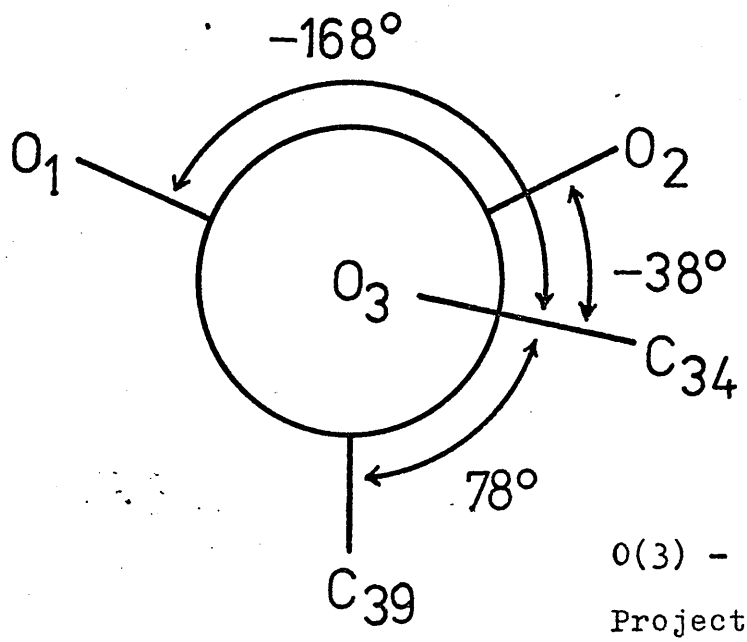
The C(8)-C(30) double bond, 1.33(3) Å , agrees with the standard value [7], 1.335(5) Å , as also does the C(42)-Br bond length, 1.88(3) Å , with the accepted value, 1.85(1) Å . The geometry of the benzene ring is normal, with a mean valence angle of 119.5(23)° and individual values which do not differ significantly from the trigonal angle. Least-squares plane calculations show the planarity of the benzene ring and of the furan ring, which similarly has normal geometry.

The conformation adopted by the sulphonate group is of some interest. The Newman projections in Figure 1.5 illustrate this clearly. The $-O-SO_2-$ group adopts a near-symmetric arrangement with the benzene ring, where the ring normal almost bisects the O(1)-S-O(2) angle, and a nearly coplanar arrangement of the C(34)-O(3)-S-O(1) grouping. This similarity with the conformations of sulphonyl-imines (see Part II) is merely what one would expect since the two species are isoelectronic. Accordingly, the conformations of sulphonates should be governed by the factors discussed in Part II, Introduction and Overall Discussion. The observed conformation here

Figure 1.5



S - C(39)
Projection



O(3) - S
Projection

is within the range of values observed in a series of benzenesulphonates by Exner and coworkers [8].

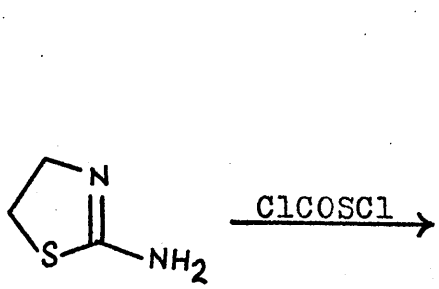
All other undiscussed sections of the molecule are essentially normal. The geometry of the methylene chloride solvent of crystallisation is particularly distorted, with "equivalent" C-Cl bonds of 1.60(6) and 1.79(6) Å, not significantly different in view of the large e.s.d.'s involved but not comparable with the 1.7724(5) Å measurement obtained from microwave spectroscopy [9]. This low accuracy probably stems from the positional disorder of the molecule.

The absence of short intermolecular contacts suggests that van der Waals' forces may determine the mode of packing adopted.

2. THE CRYSTAL AND MOLECULAR STRUCTURE OF 5,6-DIHYDROTHIAZOLO [2,3-c] [1,2,4] THIADIAZOL-3-ONE

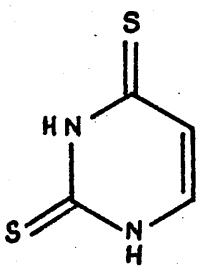
2.1 Introduction

The condensation of chloroformylsulphur chloride with 2-aminothiazoline and with similar compounds (2-aminothiazole, 2-aminopyrimidine and 4-amino-2,6--dimethylpyrimidine) has been shown to yield two possible isomeric products, I and II , when carried out in different solvents [10]. Attempts to distinguish between the two products using infra-red spectroscopic methods on the basis of an expected difference in stretching frequencies of the conjugated carbonyl function in II and the unconjugated carbonyl in I, and by comparison with spectra of model systems possessing a -N-C=N-C=O function, were not wholly successful, and reliable assignment of the structures I and II was not possible. Accordingly, the X-ray structure determination of the condensation product from ethanol-free chloroform solution was undertaken and has shown the structure to be the isomer I .

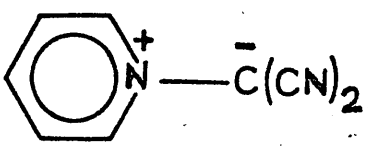


I

II



III



IV

2.2 Experimental

Crystal Data

5,6-dihydrothiazolo[2,3-c][1,2,4]-thiadiazol-3-one

$C_4H_4N_2OS_2$, M = 160.2 .

Monoclinic, a = 7.379 b = 14.587 c = 5.804 Å ,

$\beta = 102.3^{\circ}$, U = 610.3 $Å^3$,

$D_m = 1.45$ g cm^{-3}, Z = 4 , $D_c = 1.71$ g cm^{-3},

$F_{(000)} = 328$.

Space group : $P2_1/c$ (C_{2h}^5 , No.14), uniquely identified by systematic absences.

μ(Mo,Kα) = 7.50 cm^{-1}.

Data Collection

Radiation	:	Mo,Kα
Filter	:	monochromator
Maximum scattering angle (2θ)	:	50°
Independent reflections (observed)	:	962
Unobserved cutoff	:	$2\varsigma_I$
Ratio of observations/parameters	:	9.79

Structure determination

Structure determination was achieved by direct phasing using the multi-symbolic approach. Normalised structure factors were calculated and triplet relationships derived for the 132 reflections with $|E| \geq 1.50$. With a starting set of four phases, three origin-defining and one variable, a solution for the 60 strongest reflections was obtained using relationships of probability ≥ 0.9 . A total of 176 phases were then determined from this solution and were used to calculate an E-map which revealed the whole molecule. The atom positions obtained were immediately refined by least-squares calculations.

Structure Refinement

Convergence of full-matrix least-squares refinement of positional, thermal and scale parameters occurred after 16 cycles of calculation with residuals R and R' of 0.024 and 0.0008 respectively, as detailed in Table 2.1 .

All hydrogen atoms were observed in a difference map calculated after cycle 4 , and were included in calculations with initial isotropic thermal parameters of 0.05 $\AA^2$ and were later refined. Three strong reflections whose intensities were inaccurately measured because of counter saturation were removed from the calculation at cycle 9 . A weighting function of the form

$$W = x.y$$

where $x = \sin\theta/B$ if $\sin\theta \leqslant B$, else $x = 1$,

and $y = C/|F_o|$ if $|F_o| \geqslant C$, else $y = 1$,

was applied, with final parameters $B = 0.45$ and $C = 8.0$. A difference synthesis calculated near the conclusion of refinement showed no errors in the structure.

Atomic scattering factors used in all structure factor calculations were taken from "International Tables for X-ray Crystallography", Vol.III [11].

Observed and final calculated structure factors are listed in Appendix 10 . Fractional coordinates and thermal parameters are listed in Table 2.2 and interatomic distances, angles and intermolecular contacts are given in Table 2.3 . The estimated standard deviations quoted are derived from the inverse of the least-squares normal-equation matrix. Details of two least-squares planes through the thiadiazole ring are given in Table 2.4 , and the atomic numbering scheme and the molecular packing viewed down the a-axis are shown in Figures 2.1 and 2.2 respectively.

Table 2.1

Course of refinement

Cycles	Parameters refined	Final R	Final R'
1 - 4	x,y,z,U_{iso} for S,O,N, and C, scale factor. Unit weights.	0.109	0.0116
5	x,y,z,U_{iso} for S,O,N, and C, scale factor. H-atoms included but not refined, unit weights.	0.100	0.0098
6 - 8	x,y,z,U_{ij} for S,O,N, and C, scale factor. H-atoms included but not refined, unit weights.	0.041	0.0030
9 -13	x,y,z,U_{ij} for S,O,N, and C, x,y,z for H, scale factor. Unit weights.	0.026	0.0010
14 -16	x,y,z,U_{ij} for S,O,N, and C, x,y,z,U_{iso} for H, scale factor. Weighting scheme applied.	0.024	0.0008

Table 2.2

a) Fractional coordinates

	x/a	y/b	z/c
S(1)	0.32740(6)	0.16698(3)	-0.18077(7)
S(2)	0.90010(5)	0.16025(3)	0.03759(8)
N(1)	0.54608(19)	0.18892(10)	-0.21392(24)
N(2)	0.58803(17)	0.10794(8)	0.13266(22)
O	0.30219(17)	0.07305(10)	0.21274(24)
C(1)	0.39829(22)	0.10762(11)	0.09097(29)
C(2)	0.65824(21)	0.15454(10)	-0.03446(27)
C(3)	0.72043(23)	0.08310(13)	0.34847(29)
C(4)	0.90679(24)	0.07705(13)	0.27574(32)
H(1)	0.928(3)	0.016(2)	0.207(4)
H(2)	1.007(3)	0.091(2)	0.404(4)
H(3)	0.692(3)	0.027(2)	0.402(4)
H(4)	0.718(3)	0.131(2)	0.464(4)

Table 2.2 (cont.)

b) Thermal parameters ($Å^2$)

	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0297	0.0460	0.0366	-0.0003	0.0022	0.0052
S(2)	0.0271	0.0501	0.0424	-0.0030	0.0127	0.0092
N(1)	0.0356	0.0424	0.0322	-0.0007	0.0098	0.0055
N(2)	0.0265	0.0303	0.0296	0.0002	0.0105	0.0023
O	0.0324	0.0625	0.0559	-0.0034	0.0193	0.0158
C(1)	0.0303	0.0342	0.0383	-0.0006	0.0097	0.0000
C(2)	0.0308	0.0309	0.0291	-0.0016	0.0113	-0.0005
C(3)	0.0345	0.0416	0.0317	0.0038	0.0096	0.0066
C(4)	0.0305	0.0526	0.0408	0.0043	0.0081	0.0113
H(1)	0.021	-	-	-	-	-
H(2)	0.025	-	-	-	-	-
H(3)	0.017	-	-	-	-	-
H(4)	0.020	-	-	-	-	-

Mean estimated standard deviations($Å^2$)

S	0.0002	0.0003	0.0003	0.0002	0.0002	0.0002
N	0.0007	0.0007	0.0007	0.0005	0.0005	0.0005
O	0.0006	0.0008	0.0008	0.0006	0.0006	0.0006
C	0.0008	0.0009	0.0008	0.0006	0.0006	0.0006
H	0.005	-	-	-	-	-

Table 2.3

Interatomic distances and angles

a) Bonded distances (Å)

S(1) - N(1)	1.696(2)	N(1) - C(2)	1.286(2)
S(1) - C(1)	1.777(2)	C(2) - S(2)	1.746(2)
C(1) - O	1.213(2)	S(2) - C(4)	1.832(2)
C(1) - N(2)	1.369(2)	C(3) - C(4)	1.525(3)
N(2) - C(2)	1.373(2)	N(2) - C(3)	1.460(2)

Mean C - H 0.96(2)

b) Interbond angles (°)

N(1)-S(1)-C(1)	94.91(8)	N(2)-C(2)-S(2)	112.02(7)
S(1)-C(1)-N(2)	104.56(8)	C(2)-S(2)-C(4)	90.61(8)
S(1)-C(1)-O	128.44(8)	S(2)-C(4)-C(3)	106.84(10)
N(2)-C(1)-O	126.99(9)	C(4)-C(3)-N(2)	104.76(12)
C(1)-N(2)-C(2)	113.74(11)	C(3)-N(2)-C(2)	116.39(11)
N(2)-C(2)-N(1)	119.37(11)	C(1)-N(2)-C(3)	128.51(11)
C(2)-N(1)-S(1)	107.35(7)	N(1)-C(2)-S(2)	128.59(7)

Table 2.3 (cont.)

c) Intramolecular non-bonded distances (Å)

S(1)...O	2.703	O ....C(3)	3.022
N(2)...O	2.311	S(2)...N(2)	2.595
S(1)...N(2)	2.501	S(2)...C(3)	2.702
S(1)...C(2)	2.414	N(2)...C(4)	2.365
C(1)...N(1)	2.559	C(2)...C(4)	2.544
C(1)...C(2)	2.297	C(2)...C(3)	2.408
N(1)...N(2)	2.296		

d) Intermolecular distances (Å)

O ....$S(1)^{I}$	3.74	O ....$C(3)^{IV}$	3.45
C(3)...$N(1)^{I}$	3.44	S(1)...$S(1)^{V}$	3.78
S(1)...$S(2)^{II}$	3.64	S(1)...$N(1)^{V}$	3.54
O ....$S(2)^{II}$	3.19	N(1)...$N(1)^{V}$	3.41
O ....$C(4)^{II}$	3.02	N(2)...$N(1)^{V}$	3.12
S(1)...$C(3)^{III}$	3.77	C(1)...$S(1)^{V}$	3.62
N(2)...O^{III}	3.51	C(1)...$N(1)^{V}$	3.28
N(2)...$C(1)^{III}$	3.41	C(2)...$N(1)^{V}$	3.16
		C(3)...$N(1)^{V}$	3.56

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

I	x,	y,	1+z ;	II	-1+x,	y,	z ;
III	1-x,	-y,	-z ;	IV	1-x,	-y,	1-z ;
V	x,	1/2 -y,	1/2+z .				

Table 2.3 (cont.)

e) Torsion angles (^{o})

N(1)-S(1)-C(1)-O	179.8
S(1)-C(1)-N(2)-C(3)	168.4
O -C(1)-N(2)-C(3)	-12.6
C(1)-N(2)-C(3)-C(4)	168.3
C(2)-N(2)-C(3)-C(4)	-26.0
N(2)-C(3)-C(4)-S(2)	31.3
C(2)-S(2)-C(4)-C(3)	-24.6
N(1)-C(2)-S(2)-C(4)	-170.9
S(1)-N(1)-C(2)-S(2)	-176.5
Mean e.s.d.	0.16

Table 2.4

Least-squares planes

a) Equation of plane i) $0.1061X - 0.8589Y - 0.5011Z - 1.3041 = 0$

ii) $-0.0954X + 0.8610Y + 0.4995Z + 1.3346 = 0$

b) Deviation of atoms from the plane (Å)

i)	S(2)	-0.111	C(3)	-0.209	C(4)	0.229
	S(1)	0.006*	N(1)	0.001*	N(2)	0.018*
	C(1)	-0.003*	C(2)	-0.014*	O	-0.007*
ii)	S(2)	0.155	C(3)	0.230	C(4)	-0.192
	N(1)	0.023	C(2)	0.041	S(1)	-0.001*
	C(1)	0.005*	N(2)	-0.002*	O	-0.002*

c) Dihedral angle between planes i) and ii) : 0.63^{o}

* denotes atom used to define plane.

X,Y and Z are orthogonal coordinates in Å .

Figure 2.1

Atomic numbering scheme

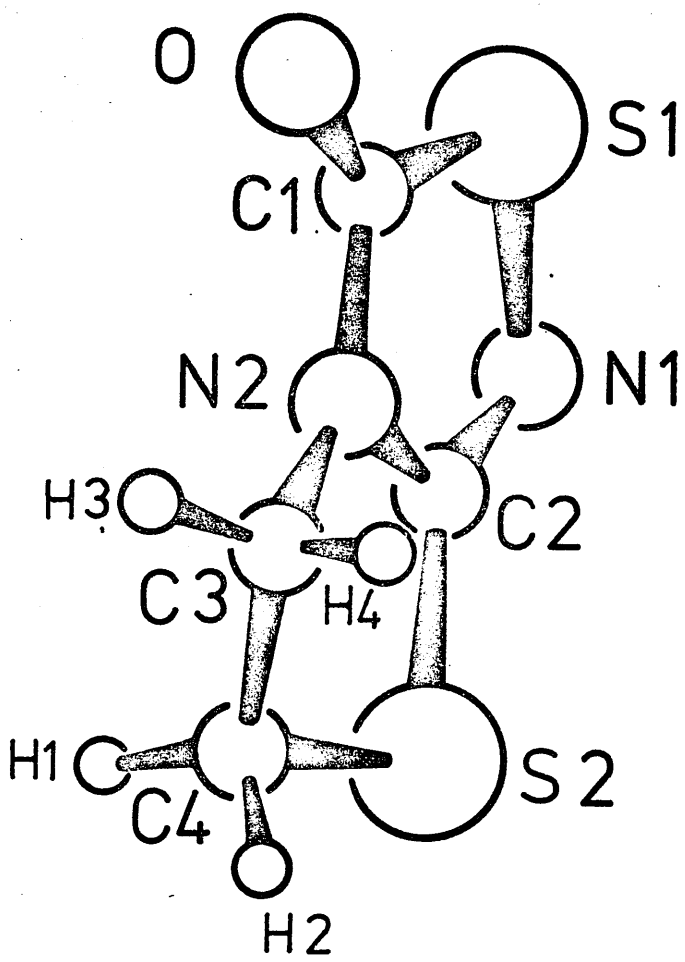
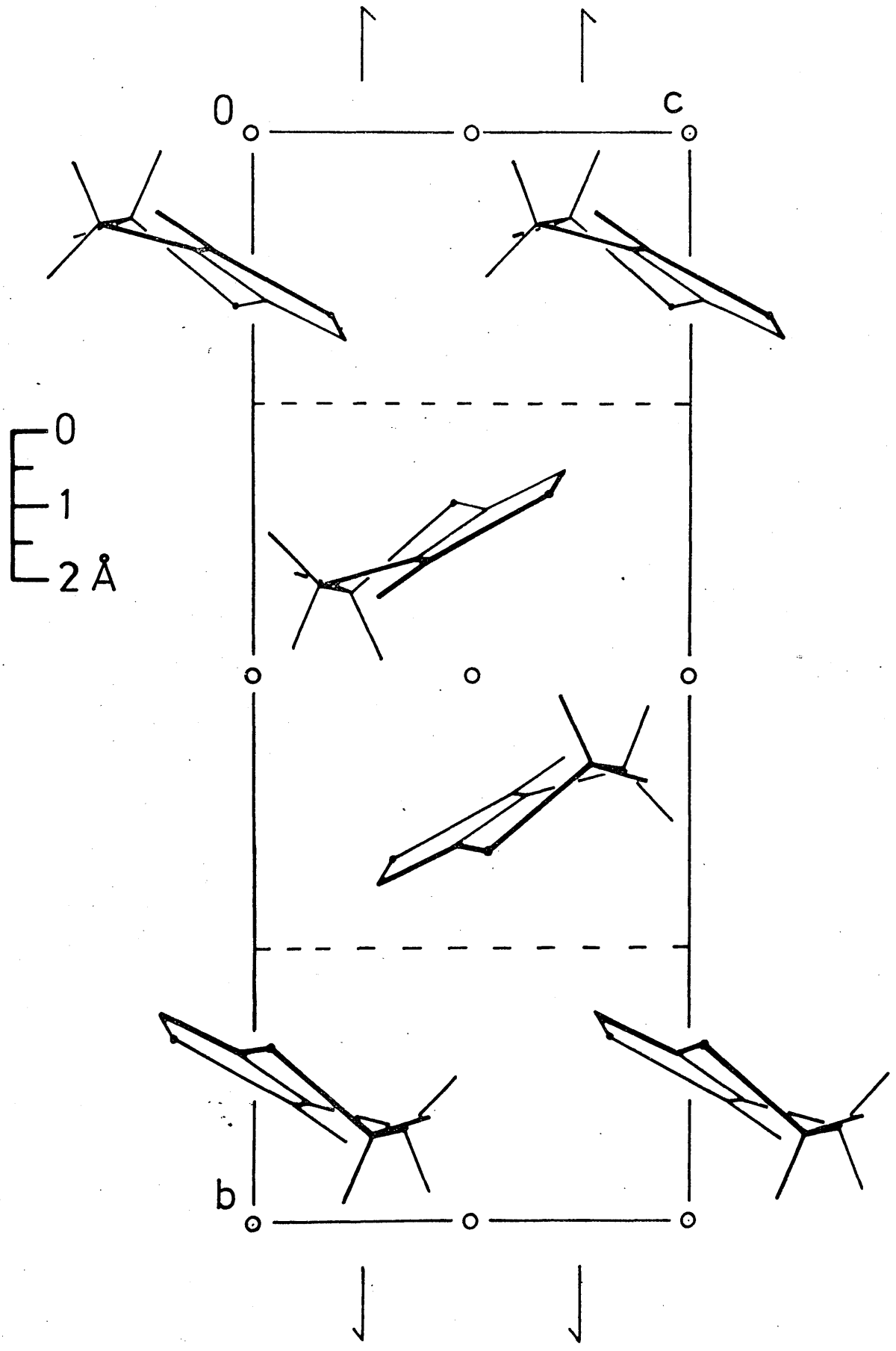

O
S1
C1
N2
N1
H3
C2
C3
H4
H1
S2
C4
H2

Figure 2.2

Molecular packing arrangement

viewed down the a-axis


0
c
0
1
2 Å
b

2.3 Discussion

The structure analysis of the condensation product of chloroformylsulphur chloride with 2-aminothiazoline in chloroform solution has confirmed the structure, I , suggested by spectroscopic evidence. Conclusive assignment of correct structures to the different reaction products has allowed some deductions to be made concerning the mechanism of the reaction. Thus the thiadiazol-2-one compound, II , is formed when the reaction is carried out in a proton--acceptor solvent, tetrahydrofuran, which is capable of solvating the exocyclic amino group, whereas the title compound, I , is formed by reaction in a proton-donor solvent, chloroform, which, if it were to solvate, would solvate the heterocyclic tertiary amine leaving the exocyclic group free to react. It is therefore likely that the initial kinetically-controlled reaction would be the attack of an amine function at the sulphur atom, the attacking site varying according to the nature of the solvent, with subsequent rapid cyclisation preventing thermodynamic control of the nature of the intermediate.

The molecular geometry is essentially just as would be expected, with no unusual features. The thiadiazole ring is planar (sum of interior angles = 539.9°) , while the thiazole ring adopts an "envelope" conformation (sum of angles = 530.6°, compared to 540° for a planar ring) with C(4) displaced from the approximate planar arrangement of the other four atoms, allowing staggering of the methylene hydrogen atoms and some reduction in angle strain.

The valence angles at S(1) and S(2) , 94.91(8) and 90.61(8)°, are less than the usual range of values found in aliphatic sulphur

compounds, 100-105° . This may be a direct result of the angular constraints in a five-membered ring when one atom bonds to its neighbours with lengths around 20% greater than the other bonds. Considering the sulphur atom as being hybridised, the observed valence angles imply participation of hybrid orbitals with very high p-character (almost pure p-orbital in the case of S(2)).

The S(2)-C(4) bond length, 1.832(2) Å , is a normal S-C(sp^3) single bond length, but the two S-C(sp^2) lengths, S(2)-C(2) 1.746(2) and S(1)-C(1) 1.777(2) Å , are possibly intermediate in character, being shorter than the S(2)-C(4) length but appreciably longer than typical double bonds e.g. 1.713(6) Å in thioacetamide [12], 1.713(12) Å in thiourea [13], 1.645(6) and 1.684(6) Å in compound III [14].

These bonds are therefore substantially single bonds with some degree of interaction with the vicinal π-orbitals, as is generally found with conjugated sulphur atoms. The S(1)-N(1) bond is similarly slightly shortened for a single bond, 1.696(2) Å , presumably on account of some interaction with the C(2)=N(2) π-bond. Such interactions are small on account of the high energy and diffuse nature of the d-orbitals in neutral S(II) atoms. Only with high oxidation state, positive charge or the presence of electronegative substituents are the size and energy of d-orbitals reduced sufficiently to allow appreciable interaction [15,16].

The normal carbon-nitrogen double bond length of the C(2)-N(1) bond, 1.286(2) Å , within the range 1.26 to 1.32 Å generally observed [17], provides further evidence that any interaction with the sulphur atom is of a very low order. The carbonyl bond length, 1.213(2) Å , is similarly unaffected and lies in the accepted range

of values. However, the two experimentally identical $N(sp^2)$-$C(sp^2)$ bonds, C(1)-N(2) 1.369(2) and C(2)-N(2) 1.373(2) Å, are slightly shortened from single bond values e.g. 1.42(1) Å in compound IV [18], although longer than the C-N bond length in pyridine, 1.340(5) Å [19], suggesting that there is some conjugation around the thiadiazole ring. The N(2)-C(3) bond length, 1.460(2) Å, is normal as is the C(3)-C(4) bond, 1.525(3) Å.

The relatively short intermolecular contact distances present in the structure (O....S(2) 3.19, O....C(4) 3.02, and C(2)...N(1) 3.16 Å), less than the sum of the appropriate van der Waals' radii, suggest that dipolar interactions may be a factor affecting the mode of crystal packing adopted.

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APPENDIX 1

Structure Factor List for compound I ,

Part II , p.36 .

Columns listed are ℓ, $|F_o|$ x10 , F_c x10 .

7,0,L

14	31	25
12	36	-39
10	128	-131
6	132	136
4	49	44
0	111	-117
-2	65	68
-4	49	46
-6	37	-44
-8	43	-43
-12	99	90
-16	52	-52
-18	73	-69

7,-1,L

13	31	-29
11	39	-38
9	101	-89
8	38	49
7	78	75
5	76	78
4	33	-33
1	69	-66
0	28	1
-2	65	56
-3	87	93
-4	36	-26
-6	44	-41
-9	31	-21
-10	62	59
-11	33	25
-13	41	35
-15	41	-32
-17	40	-45

7,-2,L

11	76	-75
10	34	-31
8	34	26
7	52	55
6	49	49
5	45	-31
3	96	-89
2	55	-46
1	62	-55
0	85	-81
-1	102	109
-2	31	38
-3	75	77
-4	31	28
-5	31	-27
-7	73	-64
-9	38	21
-11	64	57
-15	37	-28
-16	48	-49

7,-3,L

8	85	83
7	48	47
6	96	96
5	29	21
4	73	-62
3	38	-31
2	106	-96
1	73	-63
-2	124	116
-6	47	-57
-8	64	-50
-9	32	31
-10	75	72
-11	28	-17
-13	41	34

7,-4,L

1	33	-36
-1	62	56
-4	30	-35
-5	64	-58

6,0,L

20	53	-58
18	131	-130
14	90	88
10	122	-119
8	29	4
6	222	224
4	161	166
2	86	-90
0	306	-317
-4	132	132
-8	83	-82
-10	20	-23
-16	145	-143
-18	115	-107
-20	42	33
-22	93	92
-24	50	44

6,-1,L

20	64	-67
19	102	-99
17	68	-67
15	57	58
14	57	53
13	85	87
12	70	-74
11	81	-76
9	123	-128
8	38	-37
6	32	30
5	160	156
4	38	25
3	125	116
2	42	-50
1	183	-188
0	82	84
-1	90	-96
-2	107	106
-3	102	102
-4	34	43
-5	100	102
-6	68	-74
-7	51	-49
-8	74	-74
-9	49	-50
-10	38	-42
-11	96	-94
-12	61	62
-13	149	142
-15	32	-18
-16	75	-81
-17	76	-78
-19	35	-33
-21	85	82
-23	41	37

6,-2,L

19	41	-35
18	95	-101
17	44	47
15	80	81
14	41	43
12	31	35
11	109	-104
10	70	-66
8	141	-138
6	85	86
5	83	86
4	43	42
3	57	-55
1	78	-77
0	124	-127
-1	86	87
-2	43	48
-3	58	64
-4	118	121
-6	62	57
-7	76	-82
-8	33	-29
-10	80	-77
-11	33	25
-13	122	123
-14	54	52
-15	86	-89
-16	53	-48
-17	55	-50
-19	46	30
-22	35	43

6,-3,L

17	39	-32
16	67	66
15	46	47
14	68	62
13	28	-28
12	91	-93
11	55	49
10	30	-25
8	27	13
7	74	78
6	138	130
5	34	41
3	95	-91
2	181	-184
1	123	-121
0	33	-33
-1	40	-43
-2	69	67
-3	73	82
-4	57	58
-5	56	56
-6	26	-15
-7	36	28
-8	53	-51
-12	106	99
-13	75	67
-15	95	-95
-16	88	-84
-17	34	26
-20	55	56
-21	52	44

6,-4,L

14	44	-44
12	54	-52
11	48	-49
10	47	40
7	129	133
6	111	111
5	43	41
4	83	-83

6,-4,L

3	96	-97
2	53	-49
1	119	-127
-1	52	57
-2	33	29
-3	64	64
-6	41	-38
-7	82	-83
-9	36	-33
-11	58	62
-12	61	60
-13	50	52
-14	63	-64
-15	83	-75
-16	33	-32
-17	46	-38
-18	42	42

6,-5,L

7	67	72
6	88	88
5	40	-31
4	28	-25
2	36	-45
1	61	66
-2	43	34
-3	39	-37
-4	27	-9
-5	76	-64
-8	66	-67
-9	55	57
-10	36	37
-12	65	53
-13	35	-25

5,0,L

26	83	-85
24	69	-60
22	192	186
20	90	100
18	144	-141
16	105	-108
14	89	98
12	25	26
10	148	149
8	281	-280
6	96	90
4	280	292
0	322	-334
-2	202	-199
-4	125	133
-6	174	167
-8	102	88
-10	361	-357
-12	54	52
-14	205	207
-16	37	36
-18	40	-37
-20	35	-35
-22	52	54
-24	122	121
-26	63	-58
-28	123	-122

5,-1,L

25	119	-117
24	60	55
23	135	132
22	28	-17
21	177	176
20	33	-41
19	30	-25
17	204	-208
16	95	99
14	47	-51
13	54	51
12	104	-109
11	193	201
10	100	-102
9	175	-178
7	93	-96
6	202	200
5	134	136
4	81	78
3	205	201
1	174	-178
0	52	49
-1	272	-272
-2	76	72
-3	26	-14
-4	83	-80
-5	236	247
-6	153	-156
-7	125	122
-8	186	-192
-9	34	-33
-10	45	-44
-11	292	-289
-12	198	191
-13	230	227
-17	34	-26
-18	36	-26
-19	31	-89
-21	30	23
-22	45	44
-23	81	82
-25	52	58
-26	31	-41
-27	104	-106

5,-2,L

24	29	-25
23	56	58
22	166	153
21	89	-84
20	54	53
19	94	-94
18	148	-145
17	42	43
16	124	-127
15	144	141
14	53	50
12	132	130
11	50	52
10	62	59
9	161	-160
8	215	-210
7	95	91
5	100	92
4	125	128
3	107	-112
2	58	54
1	91	-86
0	104	-104
-1	33	27
-2	64	-55
-3	36	35
-4	149	152
-5	46	31
-6	150	150
-8	32	27
-9	160	-159
-10	208	-213
-11	117	122
-12	36	-45
-13	37	41
-14	49	58
-15	55	-55
-17	42	-43
-18	64	-64
-21	38	33
-22	31	36
-23	59	56
-24	42	50
-25	30	-23
-26	55	-57

5,-3,L

20	121	-111
19	48	-48
18	39	-47
17	33	-38
16	73	81
15	28	-18
14	94	89
13	37	34
11	108	107
10	110	-114
9	120	-123
8	41	-39
7	45	48
6	97	103
5	38	-41
3	58	65
2	163	-178
1	27	-24
0	51	-42
-2	72	71
-3	35	36
-4	108	114
-5	145	152
-6	77	74
-7	60	-57
-8	50	-50
-9	49	-52
-10	74	-77
-11	138	-145
-12	140	139
-14	44	-42
-15	35	29
-16	54	-49
-17	34	37
-23	31	-2
-25	33	-35
-26	76	-77

5,-4,L

21	75	-71
19	64	-63
18	29	12
16	40	27
15	52	51
14	65	-72
13	68	-64
11	92	-90
9	65	-57
8	101	97
7	149	151
6	90	90
5	97	96
4	83	-77
3	123	-124
2	62	-63
1	100	-100
0	44	-54

5,-4,L

-1	67	73
-3	102	104
-4	56	60
-5	49	54
-7	93	-93
-8	26	-17
-9	84	-87
-10	32	37
-11	98	99
-13	59	58
-14	34	-29
-15	30	-28
-17	69	-69
-19	53	45
-20	25	29
-21	40	37

5,-5,L

14	38	44
13	104	-99
10	50	-49
9	30	32
8	95	99
7	145	148
5	56	-60
3	107	-104
2	134	-136
1	38	-33
-2	53	52
-4	74	70
-6	43	-50
-7	41	-33
-8	46	-40
-9	104	98
-11	70	72
-12	55	61
-13	33	-35
-15	93	-93
-16	74	-72
-19	36	44
-20	55	50

5,-6,L

12	42	-43
8	94	93
7	33	-13
4	101	-104
0	57	54
-1	28	10
-3	40	-35
-6	79	-70
-8	54	51
-10	52	59
-14	87	-83

5,-7,L

1	44	42
0	45	48
-1	32	46
-4	34	-36

4,0,L

28	56	57
26	73	-70
22	189	189
20	137	142
18	184	-180
16	238	-254
14	318	-326
12	287	300
10	203	208
8	97	-86
6	29	-34
4	249	251
2	80	78
0	178	-189
-2	475	-454
-4	27	-18
-6	422	405
-8	402	398
-10	334	-327
-12	130	-137
-14	71	69
-16	198	217
-20	190	-182
-22	115	-116
-24	191	193
-26	43	-32
-28	37	-75
-30	78	-79
-32	58	56

4,-1,L

29	27	31
28	49	-48
25	125	-119
24	77	71
23	57	52
21	168	162
20	57	-55
19	37	37
18	78	84
17	160	-167
16	70	79
15	47	-49
14	26	-21
13	137	-134
11	472	478
10	232	-228
9	130	-130
8	114	109
7	174	-173
6	187	183
5	90	-78
4	32	-26
3	77	76
2	199	-195
0	57	-61
-1	23	-22
-3	193	-173
-4	119	120
-5	255	259
-7	329	335
-8	164	-174
-9	79	-87
-10	138	136
-11	286	-288
-12	118	116
-13	50	-46
-14	54	54
-15	96	97
-16	83	-88
-17	102	104
-18	79	-84
-19	47	-48
-21	95	-100
-22	97	94
-23	77	76
-25	58	63
-27	71	-72
-29	77	-70

4,-2,L

27	155	-151
26	96	-93
25	34	33
24	66	-65
23	128	125
22	48	35
21	30	-12
20	98	99
19	93	-93
17	46	39
16	39	-38
15	73	62
14	31	-35
13	205	211
12	179	178
11	204	-201
10	127	125
9	221	-223
8	109	-103
7	82	86
6	237	-240
5	229	219
4	58	-47
3	23	-14
2	84	87
1	114	-116
0	161	160
-1	62	-55
-2	65	-73
-4	92	81
-5	98	93
-6	30	-23
-7	162	-151
-8	119	115
-9	166	-166
-10	255	-261
-11	215	211
-12	92	-99
-13	131	129
-14	57	54
-15	72	76
-16	61	62
-17	93	-86
-18	64	60
-19	41	-48
-22	29	-30
-23	78	77
-24	74	77
-25	87	-86
-26	39	-41
-27	48	-37
-30	28	-11

4,-3,L

27	57	43
26	73	-73
24	153	154
22	93	90
20	162	-157
19	37	36
18	146	-158
17	148	-148
16	46	42
14	138	141
13	50	-48
12	188	183
11	151	149
10	287	-279
9	57	51
8	62	-55
6	178	178

4,-3,L

4	99	86
3	78	82
2	119	-121
1	50	46
0	84	-72
-1	107	-113
-2	27	3
-3	128	-125
-4	194	190
-6	66	66
-7	39	-43
-8	255	-249
-9	55	44
-10	27	-14
-11	187	-197
-12	51	52
-13	75	77
-14	77	78
-15	87	88
-16	74	-69
-17	77	84
-18	44	-32
-21	49	-53
-22	93	95
-26	75	-75
-29	34	-12

4,-4,L

25	120	114
23	106	103
22	47	-46
21	94	-90
19	160	-161
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-13	38	-23
-14	224	222
-15	203	191
-16	273	273

1,-2,L

-17	151	151
-18	35	-34
-19	120	-117
-20	136	-134
-21	204	-208
-22	256	-246
-23	226	230
-24	254	259
-27	25	-9
-28	57	55
-29	98	-102
-30	85	-83
-31	56	-59
-32	25	4
-33	86	81
-34	41	27
-35	53	58

1,-3,L

33	46	-45
32	30	25
30	135	136
29	27	28
28	59	54
26	56	-59
25	30	27
24	159	-158
22	62	63
21	84	-76
20	113	119
19	90	92
18	33	33
17	203	-196
16	198	-192
15	53	-53
14	241	-237
13	102	-96
12	219	206
11	225	216
10	53	54
9	154	145
7	21	-18
6	162	-146
5	29	20
4	77	78
3	104	-100
2	255	253
1	327	315
0	480	443
-2	644	-661
-3	364	-352
-4	70	-59
-5	164	167
-6	25	17
-7	159	-153
-9	198	193
-11	150	-143
-12	85	-75
-13	81	-81
-14	71	71
-15	62	-54
-16	226	223
-17	26	29
-18	122	-133
-19	47	-38
-20	253	-260
-23	65	64
-24	143	144
-25	49	55
-27	90	88
-28	59	-58
-30	51	-54
-31	26	-28

1,-4,L

31	152	142
29	47	57
27	90	-89
26	52	-42
25	118	-117
24	123	124
23	30	1
22	27	-23
21	29	27
20	30	-17
19	159	157
18	99	-97
17	170	-167
16	64	-62
15	72	75
14	151	156
13	242	239
12	107	106
9	354	-345
8	161	-157
7	338	-345
6	141	-129
5	182	-175
3	449	419
2	59	53
1	275	262
0	363	338
-1	69	-64
-2	183	-188
-4	301	299
-5	239	240
-6	283	-261
-7	212	216
-8	23	-21
-9	219	-212
-10	50	-48
-11	202	-209
-13	101	-104
-14	48	47
-15	166	166
-16	86	91
-17	58	69
-18	59	-56
-19	194	-196
-21	165	-171
-22	39	-44
-23	159	157
-24	35	-33
-25	64	73
-26	40	-42
-28	59	58
-29	61	-51
-32	45	42

1,-5,L

28	35	-31
26	35	-35
25	41	32
23	68	66
22	39	38
21	69	-68
20	115	116
19	83	-82
18	73	-70
17	88	-82
16	79	-80
15	226	228
13	197	190
12	123	124
11	32	-32
10	86	-85
9	180	-182
8	149	-156
7	183	-181
6	54	-49
5	51	52
4	160	155
3	66	-66
2	256	259
1	47	-50
0	59	-54
-1	64	-63
-2	336	-330
-3	275	279
-4	110	114
-5	241	226
-6	103	94
-7	213	-218
-8	128	126
-9	171	-181
-10	97	-93
-11	70	-74
-12	61	-60
-13	212	210
-14	74	74
-15	234	242
-16	192	199
-17	39	-41
-18	136	-134
-19	108	-101
-20	113	-119
-21	36	-37
-22	32	-35
-24	59	66
-25	77	-78
-26	68	69
-27	56	-58
-28	65	-64

1,-6,L

24	101	100
21	34	-39
20	37	-39
19	124	118
18	212	-208
17	109	-105
16	123	122
15	48	-44
14	174	175
13	39	-40
11	98	103
10	116	-111
9	127	135
8	39	-47
7	97	96
5	132	-127
4	111	105
3	43	39
2	222	-224
1	27	-1
0	109	-108
-1	95	-92
-2	66	65
-3	62	-63
-4	293	295
-5	116	-111
-6	35	-29
-7	70	66
-8	184	-179
-9	26	15
-10	90	-90
-12	85	86

1,-6,L

-14	155	162
-15	71	73
-17	41	33
-18	129	-134
-20	26	28
-22	56	52
-23	39	25
-24	26	8
-26	87	-80

1,-7,L

22	35	-42
19	117	-121
18	44	42
17	74	-72
16	33	35
15	121	118
13	45	51
12	29	10
11	98	-100
10	44	43
9	55	-46
8	44	47
6	25	-29
5	119	119
4	108	-114
3	31	27
2	52	-54
1	66	-72
0	53	54
-2	42	44
-3	155	156
-4	26	29
-6	49	-46
-7	142	-142
-9	80	-77
-11	36	36
-13	59	59
-14	55	-54
-17	141	-141
-19	49	42
-20	75	72
-21	70	61
-22	37	41

1,-8,L

16	44	55
15	42	41
14	64	60
11	64	-61
10	59	-60
9	40	-32
4	122	123
2	63	-56
0	36	-38
-1	57	61
-4	60	56
-6	31	-32
-7	32	-23
-8	70	-78
-11	45	44
-12	42	37
-14	50	54
-15	48	-44
-16	38	-39
-17	50	-46

1,-9,L

0	52	57
-1	48	-40
-2	54	44
-3	86	74
-4	82	-68

0,0,L

32	116	-113
28	281	279
26	107	112
24	142	-149
22	409	-419
18	511	516
16	326	313
14	690	-679
12	209	-220
10	269	259
8	151	-171
4	495	-532
2	48	33

0,-1,L

35	104	97
34	67	-63
33	94	-92
31	76	-100
29	105	97
28	27	-8
27	211	208
26	50	-50
24	162	160
23	82	-81
22	70	73
21	444	-452
20	146	146
19	256	256
18	90	-96
17	192	190
16	208	-208
15	66	-69
14	201	197
13	217	-217
12	54	47
11	175	167
10	236	-231
9	429	425
8	443	-441
7	32	-18
6	296	-292
5	485	-498
4	357	-366
3	557	-596
2	216	184
1	898	848

0,-2,L

35	84	-83
33	93	-89
32	95	-96
31	66	61
30	76	-74
29	137	138
28	71	68
26	92	93
25	80	-85
24	80	81
22	236	-235
19	126	124
17	229	-226
16	230	223
15	233	-223
14	143	-138
13	343	331
12	132	109
11	263	268
10	270	274
9	25	-24
8	300	303
7	184	-183
6	56	-42
5	355	-397
4	21	16
3	296	-281
2	876	-1001
1	698	750
0	323	284

0,-3,L

33	48	-53
31	76	-74
30	118	121
28	77	74
26	145	-139
25	56	56
24	89	-98
23	59	-61
22	131	-139
21	84	-87
20	261	269
19	221	223
18	44	49
17	34	38
16	240	-231
15	111	118
14	29	-18
13	189	-197
12	103	100
11	28	30
10	94	102
9	92	82
8	107	103
7	137	-137
6	96	-111
5	505	-489
4	83	76
2	386	373
1	397	381

0,-4,L

31	68	69
28	36	35
27	63	-63
25	152	-149
24	62	59
22	110	-115
21	137	136
20	90	83
19	103	102
18	140	-137
16	48	49
15	159	-168
13	116	118
11	37	-25
10	33	34
9	116	-115
8	23	21
7	62	-59
6	290	-274
5	171	167
4	36	-31
3	323	318
2	102	89
1	373	346
0	349	323

0,-5,L

30	39	39
29	48	45
26	34	-36
25	37	40
24	29	-30
21	58	-56
20	131	133
19	164	-164
18	74	-75
17	179	-176
16	58	-59
15	236	230
14	35	31
13	129	180
12	127	124
10	30	-26
9	150	-146
8	50	-50
7	127	-123
6	204	-217
5	166	174
4	152	152
3	144	130
2	91	81
1	110	-122

0,-6,L

27	73	66
26	74	-72
24	57	47
23	28	-28
21	26	32
20	37	-36
18	130	-131
16	64	63
15	87	-85
14	250	254
12	49	44
11	26	25
10	182	-186
9	37	37
8	229	-227
7	36	-33
6	20	-18
5	58	-62
4	234	234
0	64	-65

0,-7,L

23	49	51
22	37	-39
21	74	75
19	47	-48
17	69	-67
16	55	57
15	51	51
13	74	68
12	45	-49
10	39	-37
9	32	-37
8	61	63
7	123	-126
6	30	7
5	121	119
2	87	-88
1	24	-18

0,-8,L

17	54	53
16	54	-46
15	70	69
14	96	91
12	40	39
11	61	-64
9	34	-33
8	37	-31
7	66	67
6	27	13
5	33	30
4	83	82
3	44	-52
2	56	-52
1	31	-36
0	117	-113

0,-9,L

6	87	80
5	74	70

APPENDIX 2

Structure Factor List for compound VIII ,

Part II , p.45 .

Columns listed are ℓ, $|F_o|$ x10 , F_c x10 .

16,1,L

-7 74 -74

15,4,L

-8 63 60

15,1,L

-15 50 48

15,C,L

-8 88 90

14,4,L

-6 48 -39

14,3,L

-3 59 -54
-5 50 -48

14,2,L

-2 43 -46
-8 44 52
-10 77 82
-11 56 50
-16 54 52

14,1,L

-3 69 73

14,0,L

-6 97 -104
-10 85 -94
-14 48 -51
-16 39 -40

13,4,L

-4 65 -59
-5 68 69

13,3,L

-5 90 91
-7 69 66
-9 67 66
-11 55 56

13,2,L

-5 45 -54
-8 68 -63
-12 72 -67
-14 51 -49
-16 90 -90
-18 56 -52

13,1,L

-7 79 -79
-9 54 -50
-11 74 -72
-13 50 -43

13,0,L

-4 133 -135
-6 127 137
-8 45 34
-14 75 68

12,5,L

-8 49 38
-9 48 42

12,4,L

-2 72 73
-6 30 30
-14 77 -77
-16 41 -42

12,3,L

-1 73 66
-5 62 57
-6 58 -62
-9 109 -104
-10 59 -56
-17 62 -64

12,2,L

-2 65 -56
-5 51 -59
-6 99 -99
-16 79 77

12,1,L

-1 55 -56
-3 54 -53
-5 64 -64
-6 55 -60

-7 159 160
-8 50 -52
-9 169 159
-14 62 -62
-19 34 23

12,0,L

-2 71 70
-4 31 -26
-6 72 72
-8 106 109
-16 46 -40

11,7,L

-1 70 -68
-3 83 -76
-10 56 49

11,6,L

-3 64 63

11,5,L

-1 49 56
-2 105 -101
-3 95 95
-6 33 -26
-8 49 -57
-11 40 -37

11,4,L

-1 104 -108
-8 67 -59
-12 37 -41

11,3,L

-1 192 -192
-3 133 -133
-4 40 41
-5 81 -85
-7 73 -79
-15 97 102
-17 99 100

11,2,L

-1 116 117
-4 39 33
-8 115 117
-9 64 -66
-10 144 139
-12 51 47

-15 75 -75

11,1,L

-1 85 81
-3 132 131
-4 65 69
-7 123 131
-17 98 -89

11,0,L

-2 159 -165
-4 36 48
-8 103 -99
-10 135 -131
-18 44 43

10,7,L

-9 64 65

10,6,L

-2 98 101
-3 106 -113
-4 88 86
-8 33 -39
-9 59 -54

10,4,L

-2 119 -121
-3 61 60
-4 82 -80
-8 33 45
-9 139 133
-10 116 113
-11 74 76
-12 71 61
-13 87 85
-16 81 77

10,3,L

-2 84 89
-3 61 52
-4 69 -71
-5 203 201
-6 42 41
-9 60 65
-11 57 65
-12 79 -71
-13 40 52

10,2,L

-1	38	43
-2	214	214
-4	123	124
-5	82	84
-7	59	61
-9	50	-45
-10	69	-71
-12	105	-98
-15	41	41
-16	86	-80

10,1,L

-2	86	86
-3	327	-332
-4	78	82
-5	137	-135
-6	56	60
-7	72	-56
-9	78	-84
-10	82	91
-11	64	-61
-12	36	28

10,0,L

-2	180	-176
-4	434	-441
-6	139	137
-10	34	28
-14	61	58
-16	78	75
-18	48	48

9,7,L

-4	79	-76

9,6,L

-2	84	-85
-4	91	-92
-6	72	-72

9,5,L

-1	74	65
-4	104	105
-7	119	118
-9	65	75
-11	104	108
-18	46	-44

9,4,L

-1	41	41
-2	62	68
-4	159	157
-5	136	-137
-6	130	130
-7	30	-24
-9	54	-43
-12	97	99
-13	61	-57
-19	38	-42

9,3,L

-3	160	161
-6	56	-56
-9	63	-60
-10	68	-72
-11	154	-157
-13	142	-140
-17	33	-37

9,2,L

-1	46	-43
-2	85	-85
-3	49	49
-4	329	-330
-5	108	108
-6	294	-299
-9	74	61
-10	140	-145
-11	87	89
-12	83	-90
-14	50	-58
-16	91	85
-18	62	65

9,1,L

-1	121	123
-2	58	-57
-3	178	-177
-4	45	49
-5	167	-162
-6	92	-96
-7	150	149
-8	76	-76
-9	102	97
-11	50	57
-12	44	47
-13	123	120
-14	57	-57

9,0,L

-4	430	436
-6	111	112
-8	80	-71
-14	94	-84
-16	106	-102
-18	135	-140

8,8,L

-2	72	-65
-8	50	-44

8,7,L

-1	88	-81
-3	71	-66
-5	101	-102
-7	46	-47

8,6,L

-2	112	115
-3	34	28
-4	74	72
-8	64	59
-10	57	55
-12	75	70
-13	88	-88
-15	58	-61

8,5,L

-2	80	-79
-4	58	53
-5	162	160
-9	70	-58
-10	38	-35
-15	73	-81

8,4,L

-1	53	-42
-2	150	-152
-4	128	-129
-5	125	-124
-6	189	-194
-7	164	-163
-8	189	-184
-9	47	-43
-10	76	-77
-12	180	-179
-14	29	-38

8,3,L

-1	310	-315
-3	107	-110
-5	210	-216
-6	62	65
-7	120	-120
-9	90	91
-12	78	83
-17	64	57

8,2,L

-1	85	-91
-2	182	182
-3	103	-108
-4	53	54
-6	313	318
-8	228	228
-9	109	-111
-10	114	115
-11	69	-66
-12	144	145
-14	114	116
-15	90	-86

8,1,L

-1	251	256
-2	84	-91
-3	205	210
-5	271	271
-6	93	-88
-7	68	68
-8	82	-78
-9	210	-205
-10	55	-45
-11	78	83
-12	33	-41
-13	61	-56
-14	61	56
-15	91	-91
-17	65	-69

8,0,L

-2	425	-429
-6	133	-138
-8	122	-106
-10	147	-146
-12	85	-88
-14	68	-61

7,7,L

-3	105	101
-5	101	101
-10	70	-72

7,6,L

-2	81	77
-3	115	-115

7,6,L

-8	113	-118
-10	130	-133
-12	76	-80
-13	41	43
-14	63	-63

7,5,L

-1	160	-163
-3	305	-305
-4	93	-90
-5	196	-197
-7	87	-90
-8	65	67
-9	100	-104
-10	97	94
-11	76	-81
-12	74	70

7,4,L

-1	223	231
-2	77	-73
-3	89	92
-4	140	141
-6	58	-57
-7	63	64
-9	65	67
-10	167	167
-11	68	-69
-12	132	134
-14	31	28

7,3,L

-1	137	140
-2	89	83
-3	244	244
-5	250	247
-6	143	148
-7	285	287
-8	33	-35
-9	203	203
-10	58	-63
-11	77	82
-12	95	-89
-13	175	181
-14	82	87
-17	34	-45

7,2,L

-1	172	-166
-2	215	228
-4	138	-133
-5	30	29
-6	117	115
-7	45	-49
-8	99	93
-10	82	-77
-12	126	-128
-14	87	-84
-15	69	63

7,1,L

-1	104	104
-2	247	240
-3	699	-702
-4	140	142
-5	140	-142
-7	252	-254
-8	32	-28
-9	157	-158
-10	113	117
-11	126	-123
-13	100	-103
-14	66	-68
-15	45	30
-17	99	102

7,0,L

-2	220	213
-4	135	-137
-6	151	142
-8	199	198
-10	355	343
-12	117	114
-14	248	255
-16	168	181
-18	45	48

6,9,L

-2	65	60
-8	45	47

6,8,L

-5	40	-16
-6	38	42
-8	43	50

6,7,L

-4	103	-110
-6	52	-54
-9	88	-92
-11	84	-89
-13	68	-70
-15	38	-41

6,6,L

-2	38	-37
-3	98	104
-4	78	-72
-5	64	-67
-6	44	-45
-9	130	129
-11	111	116

6,5,L

-3	93	97
-5	239	237
-7	91	94
-8	75	80
-9	83	87
-11	216	219
-12	62	-68
-13	75	77
-15	49	51
-18	57	-51

6,4,L

-1	177	177
-2	269	273
-3	180	181
-4	340	343
-5	54	65
-6	114	118
-7	128	130
-8	105	102
-9	49	-43
-18	62	-63

6,3,L

-1	106	106
-2	138	-137
-4	120	114
-5	492	-483
-6	112	-107
-7	52	-53
-8	60	-66
-9	51	-52
-10	105	-106
-11	207	-207
-12	41	49
-13	217	-219
-14	55	-55

6,2,L

-3	130	128
-4	624	-616
-5	150	153
-6	191	-189
-7	39	-43
-8	51	-56
-9	100	100
-10	132	-126
-11	117	114
-12	98	99
-16	64	61
-21	39	-42

6,1,L

-1	262	-266
-2	91	82
-3	461	437
-4	239	228
-5	527	525
-6	40	35
-7	97	93
-9	211	205
-10	57	-50
-11	291	281
-12	54	54
-13	226	224
-15	116	117
-16	75	-71
-18	52	-47

6,0,L

-2	175	-169
-6	161	-151
-8	97	-86
-10	56	-55
-12	148	-156
-14	106	-104
-18	76	-66

5,9,L

-6	46	-45

5,8,L

-3	57	-52
-4	55	-52
-6	42	-47

5,7,L

-2	38	43
-4	89	94
-6	59	61
-7	53	45
-10	38	47

5,7,L

-13	69	69

5,6,L

-2	65	68
-4	234	236
-6	197	198
-8	102	108
-10	99	95
-12	108	108

5,5,L

-4	113	-115
-5	154	150
-6	137	-136
-8	82	-78
-9	55	-54
-10	49	-49
-11	172	-177
-13	78	-74
-15	103	-104
-18	45	31

5,4,L

-1	83	-90
-3	165	-165
-4	227	-219
-5	106	-110
-6	371	-364
-7	141	-139
-8	125	-126
-12	178	-176

5,3,L

-2	112	-108
-3	268	-267
-4	51	-53
-5	112	-116
-6	256	252
-9	73	-73
-10	47	-45
-11	101	96
-12	55	-58
-13	187	185
-15	48	49
-19	57	54

5,2,L

-1	56	-55
-2	128	-124
-3	53	58
-5	48	47
-6	435	428
-7	62	55
-8	73	-70
-9	54	-54
-10	163	164
-11	95	-87
-12	174	177
-13	83	81
-14	114	111
-19	48	-53

5,1,L

-1	232	-224
-2	63	-65
-3	161	173
-4	51	-51
-5	155	164
-6	172	-168
-7	179	-167
-8	111	-94
-9	184	-171
-10	91	88
-11	130	-129
-13	349	-355
-14	108	109
-15	173	-176
-17	48	-46
-19	64	-67

5,0,L

-2	156	-158
-6	654	-638
-8	123	127
-10	515	-502
-12	492	-496
-14	143	-145

4,9,L

-2	52	-52
-7	71	-67

4,8,L

-1	69	68
-5	86	85
-7	87	86

4,7,L

-2	45	-50
-5	134	140
-7	78	80
-8	27	-35
-10	93	-96

4,6,L

-2	88	-88
-3	91	-92
-4	139	-141
-5	204	-211
-6	30	12
-7	203	-208
-8	115	-111
-10	118	-116
-12	115	-122
-14	95	-96

4,5,L

-1	238	-237
-2	173	177
-3	116	-114
-4	123	-121
-5	214	-218
-7	152	-153
-8	93	95
-14	40	32
-15	84	83
-16	42	34
-17	49	47
-18	41	-29

4,4,L

-1	89	88
-3	105	-104
-4	129	126
-7	136	139
-8	57	59
-9	60	53
-10	71	69
-11	98	-104
-12	266	273
-14	137	141
-16	68	73

4,3,L

-1	445	447
-2	55	-56
-4	197	195
-5	102	103
-6	228	226
-7	297	292
-8	46	32
-9	46	46
-10	71	72
-11	55	-55
-12	80	-78
-15	61	-60
-19	59	-60

4,2,L

-1	311	-297
-2	113	113
-4	68	-60
-5	222	-220
-6	141	-137
-7	285	-286
-8	157	-157
-9	73	-68
-11	86	85
-12	241	-241
-13	76	-88
-14	217	-217
-15	89	89

4,1,L

-1	142	-151
-2	163	158
-3	395	-402
-4	46	45
-5	191	-189
-6	91	-87
-7	327	-317
-8	148	-136
-9	155	147
-10	59	58
-11	118	-110
-12	166	163
-13	29	-31
-15	78	75
-16	77	82

4,0,L

-4	227	222
-8	580	588
-10	451	441
-12	249	242
-14	236	233
-16	104	103

3,9,L

-2	61	62
-7	56	62
-9	43	25

3,8,L

-5	56	-60
-7	55	-58

3,8,L

-9	48	-42

3,7,L

-3	56	-59
-4	93	-95
-5	93	-99
-6	108	-113
-7	46	-36
-9	83	-82
-10	44	50

3,6,L

-2	216	-219
-3	277	286
-4	52	-44
-5	111	109
-6	136	-144
-7	147	144
-8	64	-59
-9	130	133
-10	65	66
-11	92	99

3,5,L

-1	196	-194
-2	67	70
-3	134	135
-4	121	128
-5	205	204
-6	152	156
-7	128	131
-8	89	93
-9	92	89
-11	144	149
-13	112	117

3,4,L

-1	54	54
-2	453	449
-3	150	141
-8	112	110
-9	91	-97
-10	148	-149
-11	131	137
-12	165	-169
-14	111	-114
-16	100	-105
-18	63	-65

3,3,L

-1	334	336
-2	357	-357
-3	99	-114
-5	99	-97
-6	174	-174
-8	120	112
-9	147	-147
-12	95	96
-13	155	-150
-14	75	-83
-15	46	-47

3,2,L

-1	120	123
-2	485	-512
-3	141	138
-4	360	346
-5	226	220
-7	101	94
-8	166	-166
-9	68	74
-12	277	284
-13	96	97
-14	169	173
-16	113	118
-20	78	75

3,1,L

-2	127	124
-4	335	331
-5	255	260
-7	33	39
-8	122	-121
-9	398	403
-10	226	-220
-11	259	259
-13	187	180
-15	74	76
-16	71	-67

3,0,L

-2	326	-320
-4	146	-133
-6	329	330
-8	770	764
-12	130	-139
-14	178	-187
-16	88	-96
-18	71	-71
-20	70	-74

2,9,L

-1	56	52
-4	29	-30
-6	61	-59
-8	63	-60

2,8,L

-2	45	46
-10	38	-37

2,7,L

-1	92	-94
-3	68	-73
-4	150	150
-6	175	177
-8	85	84
-10	77	76

2,6,L

-1	123	126
-3	44	44
-4	210	211
-5	71	70
-6	158	160
-8	122	123
-10	77	77
-12	49	43
-15	53	-53

2,5,L

-1	256	254
-3	107	108
-4	210	-210
-6	189	-190
-8	115	-110
-10	85	-90
-11	253	-256
-12	50	-45
-13	117	-116
-15	96	-97
-17	67	-64
-18	49	57

2,4,L

-1	136	129
-2	92	80
-3	157	-156
-4	130	-145
-5	77	70
-6	69	-69
-8	218	-218
-9	92	93
-10	71	-67
-13	56	56
-15	60	57

2,3,L

-1	374	-374
-2	181	-167
-3	529	-529
-4	313	-287
-5	343	327
-6	179	174
-8	51	45
-9	134	-130
-10	81	77
-11	159	162
-13	226	227
-14	40	36
-15	85	78

2,2,L

-1	60	64
-2	25	23
-3	331	331
-4	256	271
-8	60	-55
-9	28	-18
-10	200	196
-11	134	-132
-12	169	-172
-18	30	-33
-20	75	-69

2,1,L

-2	339	342
-3	310	318
-4	283	282
-5	607	-597
-6	113	-106
-7	267	246
-8	298	-285
-9	104	98
-10	33	-25
-11	222	-224
-12	119	-122
-13	240	-244
-14	36	-36
-15	132	-131
-16	64	-61

2,0,L

-8	84	73
-10	298	-299
-12	58	-58
-14	79	94

2,0,L

-18	69	72

1,9,L

-3	66	-57
-5	62	-63
-6	66	59

1,8,L

-2	35	-39
-4	41	37
-7	44	54
-8	56	60

1,7,L

-1	111	112
-4	71	-72
-5	146	155
-6	145	-147
-8	71	-69
-10	80	-78
-14	71	-69

1,6,L

-2	160	163
-3	101	-104
-4	50	-53
-5	280	-285
-6	90	-90
-7	179	-182

1,5,L

-1	283	-276
-3	96	-98
-4	74	-70
-5	256	-251
-6	153	156
-7	120	-130
-8	140	132
-9	140	-149

1,4,L

-1	215	-210
-2	193	-191
-3	60	-56
-4	34	27
-6	275	269
-7	68	-72
-8	118	124
-12	230	229
-14	83	84

1,3,L

-1	291	301
-2	33	-26
-3	66	73
-5	126	140
-6	349	-343
-7	51	48
-8	199	-203
-9	184	182
-10	89	96
-13	179	-186
-15	83	-88
-16	51	-48
-19	64	-62

1,2,L

-1	69	-75
-2	157	158
-3	128	-131
-4	365	363
-5	252	-249
-6	241	-247
-7	137	-133
-9	66	-68
-10	111	-113
-11	43	40
-12	225	-224
-13	120	-128
-14	117	-126

1,1,L

-1	280	-285
-2	47	53
-3	365	-370
-4	446	440
-5	553	-551
-6	465	445
-7	425	-410
-8	146	140
-9	159	-149
-11	93	-86
-12	206	209
-13	173	176
-15	109	116
-16	50	51
-19	76	83

1,0,L

-2	236	-226
-6	67	81
-8	309	-271
-10	157	158
-12	226	228
-16	69	60

0,9,L

-6	40	-42
-7	56	50

0,8,L

0	44	40
-4	42	40
-5	61	-67
-6	32	41
-7	96	-99

0,7,L

0	140	-141
-1	59	-58
-3	30	30
-5	72	-71
-7	58	-52
-9	44	-46

0,6,L

0	329	-327
-1	105	-107
-2	245	-247
-3	64	60
-4	75	-75
-5	61	57
-6	210	-210
-7	109	112
-8	99	-103
-11	54	58
-13	31	33
-14	76	81
-16	60	49

0,5,L

0	203	198
-1	102	104
-4	85	84
-5	192	192
-6	102	105
-7	356	355
-9	140	141
-11	92	90
-13	99	98
-14	103	-101
-16	77	-77

0,4,L

0	449	471
-2	255	253
-3	81	71
-4	88	93
-5	109	-107
-6	169	170
-7	140	-137
-8	53	62
-9	150	-151
-10	45	43
-11	49	55
-12	65	-62
-13	79	-71

0,3,L

0	517	494
-1	588	-581
-2	119	109
-3	48	-54
-4	82	78
-5	134	124
-6	149	-145
-7	328	-317
-8	144	148
-9	258	-253
-10	41	-38
-12	87	88
-14	32	30
-16	56	57

0,2,L

-1	63	59
-2	328	-338
-3	87	-87
-4	151	140
-5	193	175
-6	189	-188
-7	254	241
-8	119	125
-9	113	110
-10	36	-32
-11	55	-63
-12	85	90
-13	152	154
-14	113	115

0,1,L

-1	76	77
-2	281	-286
-3	459	444
-7	467	464
-8	41	40

0,1,L

-9	237	249
-11	95	92
-13	44	37
-14	60	73

0,0,L

-8	480	441
-12	95	-89
-14	141	-137
-16	68	-70
-18	76	-76
-20	55	-64

-1,10,L

0	41	44

-1,9,L

-1	100	93
-7	37	-39

-1,8,L

0	80	-72
-1	54	-53
-2	87	-87
-4	87	-84
-6	30	-37

-1,7,L

0	61	65
-1	153	-157
-3	73	-75
-4	89	86
-6	111	107
-7	41	42
-9	80	70

-1,6,L

0	144	143
-1	376	379
-2	232	225
-3	112	118
-4	117	115
-6	109	112
-11	66	-57
-13	38	-30
-15	68	-84

-1,5,L

0	44	39
-1	346	346
-4	146	-144
-8	90	92
-10	42	45
-11	85	-90

-1,4,L

0	294	-281
-1	130	118
-2	599	-584
-4	151	-155
-5	247	243
-6	134	-140
-7	108	105
-8	478	-477
-9	178	172
-10	156	-152
-15	76	73

-1,3,L

0	167	-159
-1	358	-366
-2	404	397
-5	80	76
-7	53	-54
-8	99	-97
-9	194	194
-12	49	-48
-13	88	88
-15	80	75

-1,2,L

-8	569	549
-9	39	43
-10	326	327
-12	94	-99
-16	32	-18

-1,1,L

-7	395	374
-8	334	-318
-9	184	-182
-10	70	-70
-11	123	-127
-12	74	-77
-13	65	-57
-14	53	-48
-15	113	-111
-16	51	-36
-17	56	-56

-1,0,L

-8	604	-593
-10	159	-160
-18	47	44

-2,10,L

-2	40	32

-2,8,L

-1	52	46
-3	74	76
-4	45	44
-8	80	77
-10	90	86

-2,7,L

0	45	47
-1	119	113
-2	134	143
-3	46	39
-6	98	-100
-10	40	-34

-2,6,L

0	37	28
-1	43	-41
-2	217	225
-3	34	-30
-6	67	-68
-8	119	-124
-10	123	-117
-12	65	-68

-2,5,L

0	62	-70
-1	393	-387
-2	262	-265
-3	355	-355
-4	92	-93
-5	164	-169
-6	79	81
-7	130	-133
-8	63	62
-9	241	-251
-10	83	84
-12	99	96

-2,4,L

0	95	89
-1	155	-151
-2	79	-81
-3	224	218
-4	192	197
-6	150	153
-7	148	-149
-8	205	207
-10	112	110
-15	89	-83
-16	45	38

-2,3,L

-1	216	207
-2	171	170
-3	603	596
-4	118	111
-5	73	78
-6	182	-175
-8	61	-57
-9	183	184
-12	76	-74
-13	92	-92

-2,2,L

-1	37	32
-6	359	-359
-7	56	67
-8	150	-155
-9	140	-138
-10	306	-302
-16	70	-65

-2,1,L

-7	366	-349
-9	259	-246
-10	132	-137
-11	37	42
-12	65	73
-13	47	54

-2,0,L

0	21	13
-8	101	97
-10	325	318
-12	123	127
-16	137	135
-18	60	60

-3,9,L

-4	61	60

-3,8,L

0	60	57
-2	53	54

-3,7,L

0	156	-157
-1	107	-104
-2	145	-143
-4	85	-87
-5	139	-141
-7	79	-72
-11	83	-79

-3,6,L

0	133	-136
-1	94	-95
-2	172	-169
-5	36	36
-6	74	75
-11	55	54
-12	55	39

-3,5,L

0	238	243
-1	203	199
-2	34	37
-5	209	204
-6	117	-118
-7	226	224
-8	106	-111
-9	134	134
-11	66	50

-3,4,L

0	125	124
-1	101	-96
-2	137	136
-3	81	-81
-4	350	350
-5	205	-198
-6	54	48
-7	41	-43
-8	74	-69
-10	34	37
-12	66	-62

-3,3,L

0	72	-75
-1	573	-558
-2	34	-40
-3	68	-66
-5	220	-227
-6	43	36
-7	220	-225
-8	183	179
-9	284	-283
-10	91	-96
-11	142	-137

-3,2,L

-1	31	-41
-6	113	-106
-8	182	188
-9	34	22
-11	98	-105
-12	97	86
-14	75	80
-16	70	72

-3,1,L

-4	444	420
-5	256	257
-6	155	147
-7	433	424
-8	55	56
-9	263	254
-10	144	139
-11	235	223
-13	72	73

-3,0,L

-6	107	-101
-10	72	-72
-12	176	-170
-14	74	-79

-4,9,L

-2	75	-72

-4,8,L

0	66	-59
-1	57	-54
-2	65	-55
-4	88	-77
-6	80	-72

-4,7,L

0	117	117
-1	56	55
-2	98	96
-7	84	85
-8	65	57
-9	85	79
-11	61	56

-4,6,L

0	44	43
-1	203	203
-2	91	92
-6	122	126
-7	43	-46
-8	87	88

-4,5,L

-2	69	-66
-3	61	65
-4	74	-76
-5	149	156
-6	96	-91
-7	96	-87
-12	44	-49
-13	63	-54

-4,4,L

0	369	-377
-1	30	20
-2	309	-302
-3	50	51
-4	84	-80
-6	116	-120
-7	95	-97
-8	109	-114
-9	87	86
-10	50	-49

-4,3,L

0	188	-178
-1	232	235
-2	308	309
-3	142	142
-5	64	-65
-6	81	80
-7	238	240
-9	321	336
-10	64	64
-11	85	84
-13	99	92
-15	69	76

-4,2,L

-3	137	130
-4	86	-77
-5	70	70
-6	325	325
-7	86	92
-8	84	84
-9	31	26
-10	87	82
-12	33	21

-4,1,L

-1	42	31
-5	109	115
-6	90	84
-7	318	-311
-8	104	-103
-9	335	-346
-11	79	-82

-4,0,L

-4	182	173
-6	343	-338
-8	215	-210
-12	134	-131
-14	45	-59

-5,9,L

-1	60	-63

-5,8,L

0	33	33
-1	86	83
-2	69	67
-3	93	95
-4	72	69

-5,7,L

-1	147	140
-3	65	56

-5,6,L

0	48	-51
-1	184	-181
-2	86	-86
-3	111	-110
-4	42	-40
-7	43	-41
-8	129	-127
-9	63	-64
-10	68	-67

-5,5,L

0	42	41
-1	298	-300

-5,5,L

-2	108	105
-3	164	-170
-4	161	161
-12	38	43

-5,4,L

0	151	-159
-1	211	219
-2	62	54
-3	327	328
-6	50	-49
-8	207	203
-10	93	94
-14	52	44
-15	34	-33

-5,3,L

0	113	115
-1	106	110
-2	152	-146
-3	144	143
-4	114	-114
-7	45	47
-9	120	-116
-11	47	-41

-5,2,L

0	272	269
-1	58	-61
-2	223	-233
-3	268	-255
-4	109	-113
-5	25	40
-6	77	-80
-7	96	96
-8	233	-233
-10	239	-242
-14	45	-46

-5,1,L

0	339	-332
-1	284	-307
-2	236	-226
-3	164	-167
-4	54	-44
-5	116	110
-6	135	-139
-7	229	-226
-8	72	-78
-10	108	-114
-11	75	79
-15	73	70

-5,0,L

0	80	77
-2	146	155
-4	98	-99
-6	106	108
-8	414	409
-10	229	241
-12	81	84

-6,9,L

-3	54	42

-6,8,L

0	36	34
-2	85	83
-3	82	-74
-5	49	-50

-6,7,L

-1	82	-82
-2	102	-106
-3	79	-75
-4	87	-87
-5	62	-56

-6,6,L

-2	161	-162
-3	89	91
-9	46	37

-6,5,L

0	47	51
-2	117	119
-4	77	77
-9	83	81

-6,4,L

-2	135	142
-3	68	-61
-4	74	82
-5	129	-127
-8	94	-105
-10	108	-108
-11	58	-58
-12	84	-77

-6,3,L

0	30	-38
-2	49	-60
-3	269	-270
-4	56	-60
-5	202	-201
-8	66	60
-9	141	-139
-11	78	-79
-12	55	59

-6,2,L

0	111	108
-1	60	-64
-2	146	-161
-3	53	-55
-4	133	-137
-6	68	66
-7	59	-60
-8	104	106
-9	118	112
-10	158	154
-12	64	68

-6,1,L

0	22	26
-1	125	-131
-3	292	296
-4	165	161
-5	186	191
-7	53	51
-8	73	-67
-9	55	58
-12	40	-52

-6,0,L

0	126	-121
-2	222	225
-4	159	159
-6	223	-223
-12	54	-59

-7,8,L

0	72	-66

-7,7,L

0	97	94
-2	65	61
-3	28	-36

-7,6,L

-2	83	77
-4	112	110
-7	56	-61

-7,5,L

0	205	-202
-2	80	-82
-3	73	71
-4	73	-74
-6	97	-100
-7	68	-67
-11	53	-48

-7,4,L

0	30	-39
-1	51	57
-3	59	57
-4	177	-172
-5	46	56
-8	58	58
-9	48	53

-7,3,L

0	95	94
-1	108	102
-2	112	108
-3	87	-90
-5	65	59
-6	93	86
-7	67	74
-9	96	97
-10	66	64
-11	95	83

-7,2,L

0	184	184
-1	51	-53
-3	70	-67
-4	197	203
-5	58	-59
-6	173	176
-7	34	-46
-8	93	-93

-7,1,L

-1	149	-144
-2	49	60
-3	304	313
-4	119	117
-5	118	123
-6	116	120
-7	106	-105

-7,1,L

-9	74	-72
-11	90	-81
-13	45	-50

-7,0,L

0	242	-234
-2	63	63
-4	364	-372
-6	200	-202

-8,7,L

-3	43	44

-8,6,L

-1	92	-97
-2	66	-66

-8,5,L

-2	114	116
-5	117	-116
-9	38	39

-8,4,L

-1	68	62
-2	58	57
-6	56	63
-7	79	78
-8	74	74

-8,3,L

0	93	97
-1	115	114
-2	161	-167
-3	61	62
-4	44	-47
-5	201	206
-7	55	68
-8	57	-61
-9	93	-90
-10	55	-55

-8,2,L

0	90	89
-1	68	73
-2	157	-150
-6	129	-125
-7	39	-41
-12	59	-53

-8,1,L

0	144	-140
-1	262	-264
-3	122	-126
-4	42	43
-5	96	-102
-7	28	4
-8	58	56
-9	93	91

-8,0,L

0	152	155
-2	235	233
-4	159	-161
-8	74	68

-9,8,L

0	36	41

-9,7,L

-1	88	-85
-3	63	-64

-9,6,L

0	61	-63
-1	37	29
-3	95	90

-9,5,L

-1	83	80
-2	59	61
-3	81	84

-9,4,L

0	120	119
-3	87	-90
-4	34	-31
-5	35	-40
-6	82	87

-9,3,L

-1	98	-100
-3	191	-195
-4	73	74
-5	107	-104
-7	82	-77

-9,2,L

0	191	-202
-1	58	62
-2	88	-96
-3	118	120
-6	52	-56
-7	50	-53
-9	59	58
-10	80	74

-9,1,L

0	118	-116
-1	49	-51
-2	108	-103
-3	189	188
-7	86	81

-9,0,L

0	250	256
-2	205	206
-4	88	94

-10,6,L

-2	86	76
-4	71	68

-10,5,L

-5	47	-45

-10,4,L

-2	110	-111
-4	139	-137
-5	60	58
-8	39	-27

-10,3,L

-1	117	-124
-4	35	44
-5	119	113

-10,2,L

0	35	37
-2	139	139
-3	34	43
-4	139	140
-6	74	75
-8	47	40

-10,1,L

-3	60	-53
-5	102	-97
-10	35	-33

-10,0,L

0	29	32
-2	67	-67
-4	211	-212

-11,4,L

0	77	70
-4	86	93
-6	82	80

-11,3,L

-3	82	82
-5	88	76

-11,2,L

0	37	-44
-2	38	-31
-4	101	-97
-6	145	-145

-11,1,L

-3	98	-100
-5	69	-62

-11,0,L

0	69	67
-2	53	52
-4	64	67
-6	55	55

-12,5,L

0	45	45
-1	59	54

-12,4,L

0	64	69

-12,3,L

0	90	-93
-1	99	-92
-5	49	-47

-12,2,L

0	88	-89

-12,1,L

-1 85 79
-3 75 69
-5 68 67
-7 58 60

-12,0,L

0 102 99
-2 63 -63

-13,3,L

-1 68 -64

-13,2,L

0 69 67
-2 80 72

-13,1,L

-3 87 -86

-4,0,L

-2 76 -84
0 1047-1103

-4,1,L

-3 70 -69
-2 190 -195
0 298 -303

-4,2,L

-2 539 547
-1 231 229
0 827 842

-3,0,L

-4 441 466
-2 128 -100
0 1177 1245

-3,1,L

-3 126 -115
-2 206 210
-1 452 454
0 228 228

-3,2,L

-4 500 -507
-3 155 -153
-2 133 124
0 88 75

-2,0,L

-6 325 338
-4 61 -51
-2 476 -505

-2,1,L

-6 102 103
-5 66 -65
-4 90 80
-3 779 -823
-2 231 -226
-1 507 -541
0 271 -268

-2,2,L

-5 103 -103
-4 489 -501
-3 371 -369
-2 345 -324
0 359 -346

-1,0,L

-6 340 -344
-4 168 -174
-2 133 -119
0 510 -569

-1,1,L

-6 124 -125
-5 132 -135
-4 144 -135
-3 118 -122
-2 317 -320
0 571 -605

-1,2,L

-6 214 220
-5 108 -116
-4 89 -88
-3 317 320
-2 873 903
-1 288 289
0 153 146

0,0,L

-6 532 536
-4 140 132
-2 759 787

0,1,L

-6 73 80
-5 106 -92
-4 274 280
0 332 -363

0,2,L

0 1110-1177

1,0,L

-4 1117-1137

2,0,L

-6 676 -706
-2 418 -412

2,1,L

-1 970 1026

3,1,L

-3 994 1040
-1 1119-1191

4,0,L

-6 656 650
-2 1042 1087

5,0,L

-4 843 -858

6,0,L

-4 774 804

-1,1,L

-1 1558 1639

APPENDIX 3

Structure Factor List for compound XI ,

Part II , p.56 .

Columns listed are ℓ, $|F_o|$ x10 , F_c x10 .

0,10,L

6	59	58
4	58	-58

0,9,L

8	33	-29
7	45	44
6	26	26
4	36	38
3	79	-82
2	151	-155

0,8,L

8	52	-57
7	50	-49
5	111	111
4	106	107
3	67	-69
2	77	-79
1	125	-126
0	129	129

0,7,L

11	48	48
8	46	38
7	97	-97
6	42	-40
5	42	46
4	35	31
3	229	232
1	93	-94

0,6,L

11	81	-80
10	41	41
8	108	-109
7	95	98
6	34	34
5	206	-206
3	126	125
2	150	-151
1	215	226
0	42	38

0,5,L

13	47	48
12	40	-34
11	62	-64
9	76	-76
8	22	22
7	145	152
6	103	-100
3	249	-255
2	247	243
1	47	51

0,4,L

13	32	36
12	18	-17
11	76	76
9	115	-118
7	50	-51
6	120	122
5	208	203
4	175	166
3	48	35
2	60	-58
1	124	-121
0	205	207

0,3,L

14	39	-38
13	48	-46
12	85	85
11	23	15
9	163	164
8	141	-144
7	91	-92
6	54	57
4	277	265
3	239	231
2	236	-236
1	121	-116

0,2,L

13	18	-23
12	79	-79
11	23	26
10	267	275
9	135	134
8	186	-191
7	235	-230
6	132	-138
5	176	-169
4	42	-28
3	107	104
2	323	-316
1	179	175
0	584	-603

0,1,L

14	49	48
12	38	-36
10	28	32
9	67	-62
8	148	142
7	81	79
6	260	-264
5	215	-207
4	351	-348
3	32	24
2	248	244
1	198	193

0,0,L

14	18	21
10	88	-91
6	279	275
4	69	-72
2	578	-600

-1,10,L

6	41	43
5	41	-44
4	30	-29
3	31	31
2	40	-37
1	17	-6
-4	44	-45

-1,9,L

0	100	-102
-1	72	73
-2	53	52
-3	106	-107
-6	45	-48

-1,8,L

10	78	78
9	33	-34
8	51	-51
6	31	-33
5	78	80
4	100	100
3	87	85
1	199	-199
0	116	-112
-1	46	43
-3	89	95
-5	123	-123
-6	51	52

-1,7,L

9	132	137
7	130	-132
6	59	-61
3	218	219
2	33	-34
1	113	-112
-1	107	-109
-3	126	129
-4	34	33
-5	53	59
-11	31	27

-1,6,L

11	37	-37
9	35	30
8	46	-53
7	44	38
6	52	-57
5	214	-212
4	90	89
3	91	-89
2	29	-27
1	346	339
-1	123	-128
-2	73	-78
-3	133	-134
-4	36	35
-5	170	170
-6	60	59
-7	74	73
-8	33	-29
-9	142	-142
-12	43	-38

-1,5,L

13	70	71
11	56	-57
9	78	-78
8	51	47
7	36	40
5	34	34
4	64	-64
3	83	-79
2	57	55
1	114	-117
0	100	96
-1	290	291
-2	90	85
-3	318	-318
-4	188	-184
-5	68	-75
-6	63	65
-7	199	206

-1,5,L

-8	108	-104
-9	125	-121
-10	18	-13
-11	41	-39

-1,4,L

12	22	18
11	110	112
10	42	-41
9	43	-42
7	111	-112
6	208	208
5	100	102
4	212	-204
3	22	18
2	62	55
1	110	-111
0	416	401
-1	199	197
-2	290	-282
-3	109	113
-4	42	-37
-5	306	-302
-6	44	43
-7	35	35
-8	61	60
-9	100	102
-11	60	-57
-13	50	-50

-1,3,L

14	55	-51
10	35	35
9	87	84
8	114	-121
7	126	-127
6	154	-139
5	81	-77
4	70	62
3	630	616
2	150	-150
1	311	-302
0	149	134
-1	116	120
-3	80	82
-5	72	64
-6	134	-131
-7	109	-112
-8	237	237
-9	113	-112
-10	56	55
-11	176	179
-12	48	-49
-13	48	-46

-1,2,L

12	86	-86
11	103	-103
10	67	63
9	95	98
8	49	-50
7	125	122
6	253	-249
5	315	-303
4	142	137
3	353	339
2	72	-69
1	202	-200
0	33	-22
-1	62	-63
-2	216	-208
-3	137	-142
-4	351	343
-5	46	-37
-6	330	-319
-8	192	-201
-9	76	80
-10	108	107
-11	30	32
-14	63	-62

-1,1,L

14	45	45
12	111	-117
11	95	-96
10	75	82
9	142	146
8	243	245
7	44	47
6	58	53
5	138	-135
4	378	-367
3	252	-246
1	482	-468
0	81	-78
-1	563	579
-3	39	-46
-4	201	-186
-5	292	-272
-6	181	183
-7	190	188
-8	173	-181
-9	43	-44
-12	51	52

-1,0,L

14	49	43
12	32	36
10	72	69
8	36	-32
6	505	506
4	205	-202
2	755	-794
0	275	273
-2	596	608
-4	374	-366
-6	370	360
-8	114	110
-14	72	70

-2,10,L

5	53	-51
4	32	-32
2	64	-61
1	64	66
-1	67	-66
-4	55	-55
-5	35	41

-2,9,L

8	59	-56
4	64	63
3	63	-63
2	71	-70
1	38	-40
-1	79	75
-3	62	-63
-4	58	61
-5	56	-57
-6	49	-51
-7	62	62

-2,8,L

9	41	-41
8	37	32
7	59	-56
6	67	-68
5	58	56
3	65	65
2	172	170
1	48	-46
0	59	-58
-3	115	122
-5	85	-84
-6	26	-31
-9	29	26

-2,7,L

9	86	81
7	47	-47
6	28	26
5	119	-120
4	55	-52
3	331	334
2	111	113
1	28	33
0	39	-40
-1	151	-155
-3	43	41
-5	92	92
-7	93	-90
-11	81	79

-2,6,L

11	70	-69
10	29	-30
9	47	48
8	45	55
7	102	103
6	78	-82
5	104	-100
4	69	-70
3	88	-91
2	90	90
1	75	77
0	71	-69
-2	122	-124
-3	168	-173
-4	48	-50
-5	72	72
-6	91	-89
-7	69	70
-8	92	95
-9	43	-40

-2,5,L

13	56	56
9	47	-43
8	75	79
5	65	66
4	126	-127
3	200	-205
2	63	56
1	129	-132
-1	334	343
-2	61	-57
-3	247	-250
-4	42	38
-5	189	-192
-7	243	248

-2,5,L

-8	101	104
-9	35	-32
-11	71	-71

-2,4,L

12	100	98
11	69	71
10	37	-41
9	22	27
8	59	-63
7	50	-57
6	186	189
5	121	119
4	85	-90
3	65	65
2	135	130
1	306	-300
0	108	95
-1	234	223
-2	320	310
-3	233	239
-4	63	-54
-5	211	-218
-6	108	109
-7	87	-87
-8	70	68
-9	158	161
-10	88	-85
-12	29	-30
-13	50	-47

-2,3,L

11	24	-30
10	62	62
9	203	204
8	110	-114
7	151	-154
6	134	131
5	46	-42
4	26	38
3	175	172
2	177	-170
1	232	-217
0	41	35
-1	252	231
-2	338	332
-3	66	61
-4	97	-95
-5	100	100
-6	239	-243
-9	105	-109
-10	140	142
-11	81	79
-12	47	-48
-13	22	-28

-2,2,L

14	23	-18
11	54	-51
8	77	75
7	123	118
6	244	-246
5	399	-380
4	219	-206
3	139	-122
1	787	804
0	803	-825
-1	198	-194
-2	254	-257
-3	16	-17
-4	347	339
-6	201	-205
-7	43	44
-8	82	-85
-9	119	-124
-10	25	26
-11	46	45
-12	84	80
-13	31	31
-14	40	-43

-2,1,L

14	50	49
11	84	-86
10	170	-169
8	193	198
7	57	59
6	70	-72
5	59	56
4	309	-301
3	195	187
2	231	-218
1	485	-472
0	979	1075
-1	140	135
-2	430	-439
-3	66	-56
-4	172	162
-6	150	154
-7	26	-20
-8	147	-144
-9	80	-83
-10	87	-85
-11	60	64
-12	83	82
-14	30	-29

-2,0,L

14	28	30
10	215	-217
8	113	121
6	472	473
4	107	111
2	237	228
0	454	467
-2	785	814
-4	220	-230
-6	216	-191
-8	257	251
-10	134	-126
-14	81	80

-3,10,L

3	40	-44
1	50	47
-2	50	54
-3	59	-62
-4	57	-62

-3,9,L

4	52	48
3	71	-68
1	23	-24
0	56	-56
-1	57	57
-3	49	-53
-5	75	-71

-3,8,L

8	56	61
7	80	-79
6	73	-72
5	81	83
4	31	-32
3	41	43
2	85	84
1	121	-118
0	49	-49
-3	87	83
-4	66	67
-5	31	-28
-7	42	-42
-9	55	56

-3,7,L

9	83	84
5	100	-101
4	90	-82
3	38	-43
2	26	32
1	229	232
0	55	56
-1	74	-75
-2	39	-44
-4	56	56
-5	132	138
-7	74	-73

-3,6,L

11	79	-78
10	33	-35
7	94	91
5	142	-139
4	174	-177
3	75	-79
2	180	187
1	208	207
0	73	-72
-2	118	114
-3	166	-177
-4	70	-70
-5	81	81
-6	28	-28
-7	62	63
-9	103	-101

-3,5,L

11	29	25
10	69	-75
9	89	-88
8	65	73
6	118	118
5	103	101
4	63	-68
3	153	-150
2	33	30
1	99	-105
0	130	124
-1	208	209
-2	105	-102
-3	68	-68
-4	48	54
-5	210	-214
-6	144	-149
-7	40	41
-8	66	-66
-9	79	80
-11	81	-76
-12	20	16

-3,4,L

12	45	44
11	45	41
10	34	-35
8	70	73
7	79	-76
6	97	103
5	126	131
3	112	110
2	131	-126
1	210	-210
0	49	49
-2	82	83
-3	248	257
-4	88	-89
-5	130	-136
-6	149	-150
-7	154	-157
-8	311	310
-9	73	74
-10	46	-49
-11	48	45
-13	49	-43

-3,3,L

13	50	-55
10	60	61
9	89	91
8	116	-118
6	64	-68
5	70	-66
4	103	98
3	404	400
2	276	-257
1	95	-80
0	248	-244
-1	361	-355
-2	375	366
-3	90	89
-4	139	139
-5	182	188
-6	88	-89
-7	112	-114
-8	38	34
-10	89	82
-11	64	66

-3,2,L

12	69	-73
11	41	-45
10	25	-26
8	69	69
7	142	143
6	114	-125
5	47	31
4	175	-168
3	430	-410
2	693	691
1	147	-136
0	697	-688
-1	184	170
-3	28	-31
-4	184	188
-5	122	123
-6	73	-72
-7	21	25
-8	140	-142
-9	18	-26
-10	34	-43
-12	38	37
-13	43	42

-3,1,L

14	43	41
13	31	30
10	29	24
9	106	-106
8	148	155
6	240	232
5	226	226
4	342	-334
3	470	-459
1	235	228
0	219	215
-1	57	59
-2	246	-258
-3	22	-26
-4	348	-342
-5	151	142
-6	306	297
-7	21	-19
-8	63	-62
-10	162	-164
-11	46	-43
-12	72	75

-3,0,L

12	240	245
10	196	-198
8	29	-25
6	186	185
4	87	86
2	60	-63
0	291	-276
-2	510	520
-4	69	48
-6	38	38
-8	261	265
-10	169	-172
-14	67	61

-4,10,L

3	37	-33
2	44	-41
1	49	43
-3	65	-65

-4,9,L

6	55	-56
5	62	62
4	73	71
3	87	-86
0	71	-68
-1	51	50
-2	63	64
-5	62	-64
-6	61	-66

-4,8,L

9	41	45
7	70	-69
5	27	21
3	115	111
2	81	79
1	39	-36
-3	61	58
-7	71	-69

-4,7,L

9	62	62
8	46	44
7	35	33
5	28	-25
3	33	29
1	75	77
0	64	63
-1	89	-84
-2	73	-77
-5	149	151
-7	70	-70

-4,6,L

11	55	-55
8	42	43
7	80	79
6	28	6
4	76	-75
3	253	-256
2	133	-129
1	52	50
0	29	-26
-1	111	120
-3	169	-172
-4	22	-21
-5	68	67
-6	50	-50
-7	97	99
-8	44	47
-9	71	-68

-4,5,L

11	38	46
9	109	-112
8	48	-52
7	34	31
6	106	109
5	118	117
4	171	-180
3	272	-276
0	57	52
-1	90	94
-3	55	60
-5	123	-124
-6	174	174
-7	41	-44
-8	65	-64
-9	126	125
-10	37	-38
-11	79	-77

-4,4,L

12	38	39
11	46	46
10	27	-32
8	53	-55
7	112	-108
6	64	68
5	140	134
4	121	123
3	126	125
2	55	50
1	243	-240
0	70	70
-2	287	282
-3	238	239
-5	66	72
-7	168	-170
-8	35	-38
-11	29	31
-12	35	-33

-4,3,L

10	22	17
9	26	22
7	46	47
6	92	-96
5	108	-101
4	365	370
3	113	-110
2	136	-133
1	619	616
0	315	-311
-1	397	-395
-2	41	56
-3	91	85
-4	202	205
-5	171	175
-6	238	-246
-7	184	-190
-10	60	58
-11	23	21

-4,2,L

11	54	-56
10	27	-29
8	101	102
7	82	84
6	293	-298
4	104	-102
2	143	137
1	146	147
0	287	-273
-1	130	-114
-2	405	-403
-3	144	-156
-4	121	117
-6	103	98
-7	57	53
-8	118	-116
-9	51	-55
-12	73	73
-13	53	47

-4,1,L

14	65	70
13	31	-26
11	106	108
10	133	-132
9	108	-106
8	65	74
7	83	-85
6	130	125
5	240	232
4	87	-89
3	112	-108
1	53	-49
0	110	113
-1	141	-132
-2	51	49
-3	174	-170
-4	182	-179
-5	153	151
-6	128	138
-7	23	-20
-9	96	97
-10	104	-97
-11	74	-78

-4,0,L

12	46	42
10	36	34
8	139	-136
6	334	330
4	212	203
2	33	-40
-2	426	425
-4	310	-314
-8	287	297
-10	83	-86
-12	88	-88

-5,10,L

1	20	17
0	30	31
-1	54	59

-5,9,L

6	58	-57
5	47	49
3	41	-37
2	32	30
1	63	-63
0	50	-49
-1	24	23
-5	51	-50

-5,8,L

7	53	-48
4	21	21
3	57	56
1	33	-32
-1	47	-46
-3	80	84
-4	61	62
-5	37	34
-7	102	-97

-5,7,L

9	47	43
7	42	44
5	76	-71
4	36	-38
1	143	144
-1	75	-69
-2	64	71
-3	24	23
-4	49	-54
-5	92	88
-6	54	55
-7	41	-40
-9	35	-35

-5,6,L

10	31	-29
9	56	-57
7	77	73
4	74	75
3	56	-55
2	67	-65
1	34	27
0	42	44
-1	78	86
-2	32	-28
-3	139	-138
-5	40	-41
-7	142	140
-8	78	-78
-9	41	-41

-5,5,L

11	48	50
9	91	-91
8	28	25
7	25	-26
6	39	44
5	205	200
4	202	205
3	137	-131
2	182	-183
1	134	-146
0	37	38
-1	59	50
-2	59	-57
-3	70	72
-4	79	-76
-5	104	-107
-7	61	-59
-8	46	46
-9	77	77
-10	55	-52
-11	43	-41

-5,4,L

11	41	46
10	75	78
9	47	48
8	67	-65
7	94	-90
6	92	88
5	45	43
4	84	85
3	237	240
2	273	-279
1	121	-119
0	44	37
-1	196	-202
-2	166	171
-3	122	124
-4	109	-118
-5	42	42
-6	113	116
-7	62	-62
-8	47	47
-9	30	26
-10	56	48
-11	39	35

-5,3,L

10	31	34
8	62	-67
7	59	58
6	152	-153
5	83	-82
4	15	16
3	50	-50
2	257	257
1	192	198
0	326	-321
-1	188	-197
-2	95	95
-3	101	-102
-4	188	188
-5	295	303
-6	68	69
-7	31	-38
-8	81	-80
-9	27	-31
-10	56	57
-11	22	17
-12	19	-22

-5,2,L

13	69	72
12	84	-82
11	37	-42
9	78	-80
8	66	71
6	142	-143
5	68	71
4	34	-35
3	208	-207
2	60	64
1	116	108
0	235	226
-1	82	84
-2	321	-323
-3	67	-73
-4	47	-45
-5	128	133
-6	175	168
-8	186	-181
-9	55	-61
-10	28	-33
-11	40	-39
-12	39	39

-5,1,L

12	75	78
10	105	-101
8	114	113
7	62	-60
6	99	106
5	37	33
4	176	-173
3	43	-35
1	199	198
0	249	244
-1	52	-47
-2	154	-157
-3	31	30
-4	195	-202
-5	144	-151
-6	109	113
-8	47	41
-9	90	94
-10	157	-151
-11	49	-53

-5,0,L

12	56	55
10	57	59
8	137	-138
6	90	-79
4	366	358
2	149	-154
0	66	68
-2	186	188
-4	128	-137
-6	41	-39
-8	89	91
-10	129	134
-12	101	-96

-6,9,L

1	94	-93
0	59	-56
-3	50	51
-4	47	45

-6,8,L

5	28	-29
3	79	73
0	64	65
-1	61	-66
-2	65	-69
-3	51	51
-5	30	27
-6	67	63

-6,7,L

7	62	61
5	79	-77
3	30	33
1	74	70
-1	65	-64
-3	51	-49
-4	24	-21
-5	137	136

-6,6,L

9	68	-68
8	49	-48
7	52	49
4	42	-43
3	129	-124
2	86	-86
1	43	40
-1	50	49
-2	26	-15
-3	22	-14
-4	22	-18
-5	69	-69
-6	80	81
-7	64	61
-8	60	-54

-6,5,L

11	34	34
9	54	-52
7	68	-71
6	58	-56
5	77	77
3	54	56
2	82	78
1	204	-207
-1	67	67
-2	52	59
-3	97	101
-4	74	-76
-5	133	-132
-6	48	50
-9	40	41
-10	38	-35

-6,4,L

9	47	47
7	92	-92
6	83	-88
5	46	-45
4	369	376
3	210	205
2	102	-103
1	51	52
0	29	28
-1	186	-191
-2	93	96
-3	126	126
-5	47	43
-6	71	-71
-7	99	-100
-11	26	20

-6,3,L

11	61	-64
10	40	42
9	68	66
7	57	54
6	90	-94
5	69	-63
4	81	82
3	46	44
2	99	97
1	132	134
0	138	-138
-2	139	-138
-3	84	-86
-4	83	80
-5	41	-44
-6	30	-30
-7	79	77
-8	21	-21
-9	64	-68
-10	57	53
-11	30	31

-6,2,L

12	68	-69
11	41	42
9	41	-43
8	57	55
7	42	42
6	84	-83
4	173	-173
3	61	-56
1	34	-33
0	83	90
-1	101	103
-2	206	-213
-3	253	-259
-4	129	-129
-6	227	226
-7	185	186
-8	127	-132
-11	33	-38
-12	44	39

-6,1,L

13	29	27
10	58	-54
8	55	-58
6	207	212
5	108	-112
4	72	-75
3	75	74
2	220	-221
1	109	-106
0	232	231
-1	92	92
-3	61	65
-4	170	-174
-5	75	-77
-6	82	88
-7	33	31
-8	136	135
-10	98	-97

-6,0,L

12	26	27
10	73	72
8	58	-59
6	70	70
4	142	147

-6,0,L

2	278	-283
0	310	305
-2	193	201
-6	108	-103
-8	39	41
-10	96	84
-12	81	-75

-7,9,L

1	63	-64
0	56	-55

-7,8,L

5	26	-24
3	82	79
-1	92	-94
-2	49	-43
-3	48	50

-7,7,L

7	68	67
5	44	-41
2	21	-11
1	72	71
0	43	45
-3	71	-71
-7	119	115

-7,6,L

9	72	-68
7	61	57
4	54	59
3	110	-109
1	36	33
-1	79	74
-2	64	-72
-3	80	-81
-5	36	-36
-6	22	15
-7	78	75

-7,5,L

7	82	-80
6	75	79
5	36	31
4	31	-33
3	114	124
2	44	-49
1	195	-194
-3	105	106
-4	57	-53
-5	108	-109
-9	25	30

-7,4,L

11	30	32
10	29	32
9	57	59
5	125	-124
4	64	-66
3	93	93
2	94	94
1	67	67
0	107	-108
-1	120	-125
-2	115	116
-3	20	22
-4	67	70
-5	69	68
-6	52	-49
-7	49	-49
-8	41	38
-10	50	52

-7,3,L

11	61	-63
10	19	23
9	43	43
8	24	23
7	41	40
6	164	-166
5	167	-167
3	71	74
2	134	137
1	49	45
0	23	23
-1	35	36
-2	79	-80
-3	43	-39
-4	122	122
-5	70	73
-7	68	67
-8	24	-30
-9	97	-94
-10	26	30

-7,2,L

10	72	-71
8	90	90
7	47	-45
5	68	61
4	158	-160
3	22	-24
2	37	37
0	161	161
-1	116	115
-2	143	-150
-3	27	30
-4	25	-22
-5	185	-187
-6	22	16
-7	48	50
-8	46	-53
-9	27	31
-10	73	-69
-11	45	-44

-7,1,L

12	29	28
8	33	-29
7	46	50
6	118	120
5	30	-28
4	29	-31
3	60	55
2	49	-55
1	153	-154
0	97	104
-1	84	82
-2	89	87
-3	75	78
-4	275	-275
-5	186	-187
-7	59	59
-8	82	79
-10	33	-26

-7,0,L

10	80	81
8	101	-104
6	30	31
4	203	206
2	184	-188
0	116	-115
-2	170	177
-4	30	28
-6	108	-107
-8	52	58
-10	112	110

-8,8,L

3	40	38
2	70	68
1	57	53
-1	56	-51

-8,7,L

5	47	-44
1	86	83
-3	60	-60
-4	27	-17

-8,6,L

7	18	-23
5	98	104
4	55	-61
3	94	-94
2	22	26
1	59	-58
-1	119	121
-3	24	-22
-5	104	-100
-6	44	-43
-7	49	47

-8,5,L

7	57	-53
4	36	41
3	76	71
2	39	-40
1	89	-81
0	65	71
-2	24	27
-3	66	65
-4	48	-45
-5	62	-62
-6	40	-38
-8	43	41

-8,4,L

9	69	68
6	49	47
5	34	-27
4	20	24
3	57	55
2	84	85
1	65	66
0	50	-47
-1	73	-71
-2	33	-36
-4	106	103
-5	55	52
-6	78	-76
-7	68	-65
-9	29	-24

-8,3,L

8	26	32
7	120	123
5	29	-31
4	109	-110
3	79	-79
2	85	84
1	48	47
0	31	-32
-1	51	51
-2	64	-65
-3	115	-115
-4	61	56
-7	92	89
-8	76	-75
-9	54	-54
-10	63	58

-8,2,L

10	66	-66
8	38	34
7	55	57
6	62	69
5	87	-84
4	199	-196
3	45	-48
1	26	-25
0	52	53
-1	73	73
-2	124	-124
-5	31	-30
-6	34	34
-7	19	18
-8	47	44
-9	48	40
-10	74	-68

-8,1,L

10	36	-33
8	38	-35
7	42	-38
6	77	78
3	57	60
2	193	-193
1	79	-84
0	125	124
-2	102	105
-3	113	113
-6	71	-66
-7	52	-51
-8	92	89

-8,0,L

8	34	-36
4	84	79
2	113	116
0	204	-208
-2	253	252
-4	120	118
-6	211	-210
-10	43	42

-9,7,L

3	95	-97
1	78	79
-1	46	46
-3	61	-60

-9,6,L

5	34	28
4	47	-51
1	79	-79
-1	98	96
-5	53	-53

-9,5,L

7	68	-67
5	28	28
3	35	31
1	52	-51
0	49	-53
-1	43	-39
-2	53	59
-3	67	63
-6	68	-63
-7	91	-86

-9,4,L

9	46	46
5	77	-74
4	17	15
1	39	35
-1	33	-27
-2	31	31
-4	53	54
-5	75	74
-6	66	-63
-7	41	-34
-8	26	27

-9,3,L

8	33	40
6	36	-34
5	49	51
4	22	-27
3	61	-58
2	35	32
1	75	73
0	44	43
-1	54	53
-2	66	-66
-3	74	-75
-4	48	50
-5	27	29
-6	51	48
-8	61	-60

-9,2,L

9	47	-52
8	21	-21
6	112	112
5	105	109
4	108	-109
3	79	-80
2	26	23
1	41	-42
0	42	42
-1	36	40
-2	26	-29
-4	82	-80
-5	61	-62

-9,1,L

8	38	-35
6	86	86
5	44	38
4	61	63
3	44	-41
2	138	-138
-1	48	-49
-2	76	78
-4	125	-122
-5	76	81
-6	44	-33
-7	59	-56
-8	58	56

-9,0,L

6	66	-66
4	94	86
2	40	43
0	170	-170
-4	243	246
-6	86	-86

-10,6,L

2	48	-53
1	73	-72
-1	29	25

-10,5,L

3	30	25
-1	46	-43
-3	45	40

-10,4,L

7	23	28
4	44	41
2	29	34
1	42	40
0	43	-49
-1	57	-54
-4	56	52
-5	77	74

-10,3,L

7	41	40
3	68	-72
1	30	27
-1	39	39
-2	34	-32
-3	41	-42

-10,2,L

5	34	30
2	86	-85
1	55	-57
0	77	77
-1	52	52
-4	71	-66
-6	60	56

-10,1,L

8	76	-76
7	64	-66
6	21	27
5	75	73
4	80	81
2	57	-55
0	57	-59
-2	168	170
-3	46	-46
-4	35	-33
-5	55	56
-6	61	-58

-10,0,L		
4	81	73
2	84	85
0	74	-79

-11,4,L		
1	53	50
-1	27	-22
-3	40	-41

-11,3,L		
2	57	60
1	39	36
-2	44	-39
-3	45	-42

-11,2,L		
2	64	-67
1	39	-41
0	50	47
-1	26	-28
-3	41	42
-4	101	-104

-11,1,L		
4	64	63
3	36	33
2	43	-38
0	55	-54
-2	31	29
-4	18	27

-11,0,L		
6	105	-108
4	58	59
2	54	51
0	59	-55
-4	55	53

APPENDIX A

Structure Factor List for compound [illegible],

Part II, p. [illegible].

Columns listed are [illegible], $|F_o|$ x10, F_c x10.

APPENDIX 4

Structure Factor List for compound XII ,

Part II , p.56 .

Columns listed are ℓ , $|F_o|$ x10 , F_c x10 .

0,12,L

-4	51	61

0,10,L

0	48	-25
-2	260	-260
-3	63	70
-4	108	-106
-5	84	-79
-8	96	93
-10	71	71

0,8,L

0	427	437
-1	312	-320
-2	139	145
-3	224	-238
-5	72	-70
-7	237	-239
-9	146	-151
-10	136	-129
-11	89	-79

0,6,L

0	51	44
-2	404	414
-3	111	90
-4	503	510
-5	244	252
-6	104	-91
-7	49	48
-8	135	142
-10	196	-191
-11	92	83
-12	103	-104
-14	145	-132
-16	67	-65

0,4,L

-2	798	-815
-3	93	-74
-5	370	380
-6	588	-569
-7	536	525
-8	365	360
-9	74	-73
-10	285	289
-11	61	76
-12	345	335
-13	66	-55
-14	190	184
-16	81	78
-17	74	-79

0,2,L

-6	134	126
-7	62	-84
-8	77	75
-9	145	-142
-10	167	169
-12	117	107
-13	121	-129
-14	82	92
-15	145	135
-17	130	128

0,0,L

-6	229	219
-8	79	-66
-10	391	-370
-12	455	-460

-1,11,L

-6	108	107

-1,10,L

-3	65	-62

-1,9,L

-1	225	-232
-3	115	120
-4	189	-199
-6	118	-123
-8	181	-172
-10	95	-100
-11	136	134

-1,8,L

-1	120	-116
-3	53	-56
-6	58	-44

-1,7,L

-1	345	345
-2	195	200
-3	175	174
-4	292	-292
-9	176	-187
-11	80	-76
-13	186	-191

-1.6,L

-1	270	273
-2	125	-148
-3	67	79
-6	110	-115
-7	54	51
-11	110	-110

-1.5,L

-1	317	296
-2	452	458
-3	141	-146
-4	495	492
-5	184	178
-6	530	536
-7	204	188
-8	223	230
-9	129	-132
-10	187	193
-11	126	120
-12	105	-113
-16	87	-87

-1.4,L

-1	239	-203
-2	198	-215
-3	256	269
-4	44	49
-6	53	71
-7	202	-186
-10	128	-129
-12	63	54

-1.3,L

-4	85	-78
-5	139	-129
-6	345	-330
-7	530	515
-8	381	-360
-9	291	303
-10	165	168
-11	249	247
-13	210	207
-15	205	202

-1.2,L

-4	66	62
-6	255	-235
-7	79	-72
-8	268	266
-9	191	176
-13	51	46
-14	74	-94

-1,1,L

-6	96	-114
-7	265	-244
-8	783	-762
-10	424	-430
-11	82	-74
-13	111	-106
-14	207	201
-15	88	-95
-16	135	137
-18	98	99

-1,0,L

-6	79	77
-8	310	320
-10	241	-226
-12	76	53
-16	67	49

-2,12,L

-4	55	49

-2,11,L

-5	89	103

-2,10,L

0	93	-92
-2	177	-183
-5	63	-72
-10	75	77

-2,9,L

0	95	-96
-1	123	129
-2	83	-71
-10	47	23

-2,8,L

0	285	285
-1	160	-153
-2	83	82
-3	180	-180
-5	111	-107
-7	201	-198

-2,8,L

-9	108	-103
-10	105	-106
-11	60	-57

-2,7,L

0	71	-67
-1	57	53
-2	168	-169
-3	339	-347
-5	62	-64
-8	51	-52
-9	156	-153
-11	67	-71

-2,6,L

0	198	206
-2	254	255
-3	73	86
-4	313	303
-5	382	388
-7	131	122
-10	162	-159
-11	93	91
-12	155	-157
-14	95	-88
-15	67	-57
-16	67	-66

-2,5,L

0	97	98
-1	493	468
-2	303	-306
-3	103	98
-4	135	140
-6	77	-80
-7	80	-97
-8	218	-209
-9	173	173
-10	112	-117
-12	129	-126
-13	86	-89
-16	77	-71

-2,4,L

0	126	-116
-1	162	144
-2	159	-136
-3	66	-70
-4	291	281
-5	275	261
-6	380	-376
-7	288	289
-8	126	116
-10	329	324
-12	254	249
-14	204	196
-16	67	56
-17	69	-72

-2,3,L

-1	87	79
-2	265	-267
-3	66	76
-5	708	687
-7	169	169
-8	119	121
-9	201	212
-12	83	-79
-14	78	82
-15	95	-96
-17	76	-72

-2,2,L

-3	359	-354
-7	640	-602
-8	169	175
-9	205	-212
-10	122	138
-11	55	-54
-14	78	74
-15	109	109
-17	114	114

-2,1,L

-5	72	62
-6	213	193
-7	586	-552
-9	79	-68
-10	146	135
-11	143	-137
-12	116	112
-13	81	80
-14	74	61

-2,0,L

-4	67	-55
-8	130	110
-10	336	-336
-12	387	-399
-14	95	-99
-16	88	-86

-3,11,L

-1	62	-61
-6	71	75

-3,10,L

-3	99	-98
-6	83	84

-3,9,L

-1	113	-101
-2	83	-90
-8	122	-115
-10	89	-90

-3,8,L

-1	257	-263
-3	165	-161
-6	106	-106
-11	89	93

-3,7,L

-1	227	235
-3	358	365
-4	184	-174
-5	91	93
-6	120	-132
-9	135	-129
-13	126	-128
-15	78	-79

-3,6,L

-1	345	354
-2	239	-218
-4	113	-116
-5	80	-79
-6	279	-276
-8	77	-79
-10	88	-95
-11	230	-235
-13	140	-142

-3,5,L

-1	91	-77
-2	551	527
-3	227	-200
-4	202	203
-5	151	-147
-6	260	260
-7	207	202
-8	193	189
-9	59	-70
-10	132	131

-3,4,L

-1	82	91
-2	270	-234
-3	380	341
-4	432	428
-5	223	215
-6	278	263
-7	300	-294
-8	253	243
-9	108	-112
-10	218	-226
-11	130	-131
-15	124	-111

-3,3,L

-2	235	-233
-4	453	-442
-5	367	-357
-6	302	292
-7	115	119
-8	250	-251
-9	150	161
-10	78	85
-11	172	166
-13	161	157
-15	89	84

-3,2,L

-2	55	53
-3	444	-450
-4	44	57
-5	226	-219
-6	605	-579
-7	200	-178
-8	413	404
-9	225	215
-11	208	216
-12	141	152
-13	263	263
-14	198	-201

-3,1,L

-2	159	174
-3	188	200
-4	330	-324
-7	272	-263
-8	413	-422

-3,1,L

-10	189	-198
-11	172	-177
-12	81	-91
-13	119	-109
-14	77	67
-16	144	142
-17	58	-46
-18	57	53

-3,0,L

-4	179	159
-6	701	-704
-8	102	-124
-10	546	-550
-12	125	132
-14	91	-81
-16	166	170

-4,11,L

-5	101	105

-4,10,L

0	155	-160

-4,9,L

0	231	-231
-1	113	120
-2	159	-158
-3	48	33
-4	90	-100
-5	83	78
-8	107	107
-9	68	69

-4,8,L

0	95	99
-3	86	-83
-4	139	-140
-5	168	-171
-7	131	-137

-4,7,L

-3	407	-424
-5	180	-168
-6	107	-106
-7	172	-165
-9	215	-214
-11	69	-72
-12	83	81

-4,6,L

0	107	110
-1	65	-65
-4	72	-60
-5	381	389
-6	78	79
-7	175	178
-8	45	-51
-10	72	-77
-11	51	54
-12	188	-185

-4,5,L

0	433	458
-1	409	402
-2	148	151
-3	97	-120
-4	455	452
-7	109	-108
-8	169	-168
-10	198	-194
-11	153	149
-12	195	-186
-13	94	-103
-14	128	-123
-15	52	-58
-16	108	-108

-4,4,L

0	595	-586
-2	123	-135
-3	219	222
-4	120	101
-5	147	157
-6	76	-81
-7	137	135
-8	179	-169
-9	148	150
-10	246	215
-14	117	119

-4,3,L

-1	359	357
-3	149	158
-4	240	-210
-5	580	569
-6	341	-334
-7	363	371
-9	226	234
-10	206	208
-11	67	75
-12	100	-105
-13	61	-76
-14	77	85
-15	87	-93
-16	77	78
-17	93	-84

-4,2,L

-1	374	-356
-2	67	-67
-3	305	-302
-4	466	-460
-5	660	-660
-6	209	204
-7	418	-410
-8	75	80
-9	85	-94
-11	103	-106
-12	82	-65
-13	101	91
-15	57	60
-17	91	72

-4,1,L

-4	79	59
-5	481	-485
-6	58	-46
-7	346	-354
-8	62	61
-9	56	-67
-10	250	250
-11	246	-255
-12	99	92
-13	83	86
-14	123	125

-4,0,L

-4	466	-464
-6	429	-418
-8	430	-433
-10	223	-224
-12	101	-98
-14	101	-102
-16	64	-78

-5,12,L

-1	81	73

-5,10,L

-4	91	88
-6	152	156
-8	96	91

-5,9,L

-2	98	-94
-3	62	-63

-5,8,L

-1	234	-245
-3	188	-181
-6	106	-117
-8	120	-126
-9	101	98
-11	140	139
-13	75	81

-5,7,L

-3	220	210
-5	98	102
-6	50	-59
-7	194	-192
-9	100	-96
-15	84	-87

-5,6,L

-1	249	255
-2	237	-233
-4	205	-213
-6	390	-408
-7	199	-200
-8	78	-79
-10	60	-57
-11	183	-179
-13	174	-181

-5,5,L

-1	77	53
-2	279	278
-3	249	-260
-4	101	102
-5	122	-124
-8	100	102

-5,4,L

-1	226	229
-2	260	251
-3	79	88
-4	753	728
-5	140	138

-5,4,L

-6	247	261
-7	105	-98
-8	479	494
-9	122	-130
-10	86	-99
-11	250	-254
-12	63	-58
-15	88	-98
-16	89	-79
-17	66	-58

-5,3,L

-1	578	-581
-2	571	-551
-3	382	-391
-4	86	-81
-5	113	-124
-6	147	140
-7	115	-114
-9	84	87
-12	59	58
-13	102	107

-5,2,L

-2	305	-287
-3	491	-474
-4	411	382
-6	166	-154
-7	252	253
-8	337	343
-9	284	280
-11	242	238
-12	206	205
-13	354	347
-14	153	-148
-16	66	-80

-5,1,L

-1	52	-47
-2	343	346
-3	91	95
-4	87	83
-5	153	-149
-6	182	-183
-7	354	-348
-8	123	-119
-9	87	-100
-11	210	-214
-13	103	-104
-15	82	-79

-5,0,L

-2	597	-591
-4	300	-315
-6	849	-851
-8	249	-233
-10	459	-456
-12	130	125
-16	244	254
-18	171	167

-6,11,L

-2	101	95

-6,10,L

0	93	-93

-6,9,L

0	249	-252
-1	78	72
-2	168	-170
-3	79	74
-4	123	-122
-7	97	99
-8	152	159
-12	64	73

-6,8,L

0	45	54
-4	102	-103
-5	84	-84
-7	45	-48

-6,7,L

-3	267	-287
-4	77	-80
-5	238	-244
-7	112	-104
-9	216	-219
-14	67	69
-15	106	106

-6,6,L

0	54	-58
-1	145	-146
-2	51	46
-3	64	-59
-4	177	-171
-5	163	154
-6	87	72
-7	139	134
-12	59	-63
-13	49	54

-6,5,L

0	729	713
-1	80	73
-2	334	323
-4	450	451
-5	165	151
-6	156	158
-7	66	47
-8	160	-165
-9	217	-228
-10	250	-252
-11	196	217
-12	252	-241
-13	48	-62
-14	168	-160
-16	123	-126

-6,4,L

0	675	-658
-1	95	85
-2	92	88
-3	99	97
-4	185	-164
-6	75	-74
-8	307	-312

-6,3,L

0	109	197
-1	148	141
-2	483	-480
-3	584	566
-4	104	98
-5	439	434
-6	263	-254
-7	486	496
-8	87	-91
-9	174	184
-10	372	376
-11	178	182
-13	132	-127
-14	110	98
-15	68	-69
-16	111	103

-6,2,L

0	595	-620
-1	330	318
-2	165	-168
-4	696	-668
-5	176	-163
-6	52	51
-7	127	-131
-8	89	-94
-9	104	-97
-12	111	-115
-14	71	-77

-6,1,L

-1	705	-733
-3	182	177
-4	318	-311
-5	480	-470
-6	231	233
-7	220	-215
-8	310	301
-9	87	-85
-10	347	357
-11	123	-125
-12	135	132
-13	74	71
-14	187	188
-15	141	131
-16	93	101

-6,0,L

-2	464	-483
-4	486	-497
-6	185	197
-8	246	-242

-7,12,L

-1	112	104

-7,10,L

-4	124	122
-6	163	160
-10	77	70

-7,8,L

-1	223	-226
-3	117	-118
-6	134	-128
-8	135	-133
-9	148	150
-11	137	138
-13	82	77

-7,7,L

-1	201	-201
-3	47	-57
-7	119	-117
-13	55	71

-7,6,L

-1	208	225
-2	155	-158
-3	297	291
-4	312	-309
-5	119	114
-6	387	-386
-7	107	-105
-8	80	-76
-9	72	77
-11	111	-104
-13	99	-106
-14	63	70

-7,5,L

-1	42	72
-2	70	61
-3	214	-199
-5	49	-61
-6	224	-221
-7	50	-72
-9	174	162
-11	109	-114

-7,4,L

-1	515	485
-2	505	505
-3	143	134
-4	544	537
-5	135	130
-6	404	398
-7	110	111
-8	536	531
-11	240	-237
-15	64	-64
-16	91	-75

-7,3,L

-1	114	129
-2	216	-187
-3	89	-85
-4	223	225
-8	253	246
-9	69	-69
-10	205	-201
-11	137	-147

-7,2,L

-1	337	-337
-2	331	-321
-3	334	-319
-4	196	191
-5	72	-73
-6	157	151
-7	111	108
-8	250	265
-9	155	152
-11	198	207
-12	183	187
-13	315	325
-16	80	-81

-7,1,L

-3	343	-353
-4	390	397
-5	331	-314
-7	50	65
-8	92	97
-9	148	-145
-10	72	-71
-12	65	68
-16	60	-60

-7,0,L

-2	223	213
-4	66	-93
-6	880	-909
-8	588	-606
-10	430	-443
-12	54	57
-16	228	228
-18	226	226

-8,11,L

0	81	81
-2	123	112
-3	71	71

-8,9,L

0	148	-143
-1	72	67
-2	119	-126
-3	45	45
-4	78	-85
-6	72	69
-7	142	140
-8	139	138
-12	72	65

-8,8,L

-3	80	79
-4	56	-51
-5	93	86
-7	96	88

-8,7,L

0	169	166
-1	71	-64
-3	195	-193
-5	214	-211
-6	57	50
-7	134	-129
-9	188	-187
-12	86	89

-8,6,L

0	96	-90
-1	169	-168
-2	122	-121
-3	112	-123
-4	75	-72
-5	107	-106
-9	121	-114
-10	79	72
-11	94	-92

-8,5,L

0	479	472
-1	261	-233
-2	232	237
-4	367	367
-5	82	83
-6	133	131
-8	176	-175
-9	74	-75
-10	174	-164
-11	145	138
-12	239	-234
-14	166	-167
-16	99	-99

-8,4,L

0	308	-253
-1	276	-263
-2	85	82
-3	96	92
-4	146	141
-5	117	-114
-6	82	77
-7	186	-183
-8	214	-206
-10	101	-93
-12	83	74
-14	95	-98

-8,3,L

0	58	-39
-1	106	-101
-3	597	579
-4	235	205
-5	239	241
-6	208	-202
-7	300	292
-9	245	260
-10	325	314
-11	199	190
-12	85	87
-13	87	-88
-14	127	120
-15	80	-80
-16	91	92

-8,2,L

0	434	-413
-1	128	-115
-2	339	333
-3	300	297
-4	113	-101
-6	79	-75
-7	191	176
-8	75	78
-9	391	397
-13	97	-97
-14	128	-134

-8,1,L

0	617	-664
-1	227	-216
-2	422	-444
-3	93	81
-4	85	-83
-5	581	-580
-6	61	66
-8	418	427
-9	115	-117
-10	387	387
-11	160	-153
-12	109	110
-13	66	58
-14	127	134

-8,1,L

-15	150	158
-16	129	132

-8,0,L

0	167	-177
-2	336	350
-4	407	-401
-6	99	92
-8	279	281
-10	134	-115
-12	82	108
-18	91	-94

-9,12,L

-1	81	90

-9,11,L

-1	56	53

-9,10,L

-4	102	112
-6	101	91

-9,9,L

-4	85	83
-5	66	71
-7	80	-69
-8	80	73

-9,8,L

-1	176	-175
-3	47	-47
-5	84	-75
-6	84	-100
-8	81	-71
-9	140	150
-11	111	102
-13	53	57

-9,7,L

-1	191	-203
-2	84	73
-3	137	-135
-4	135	138
-6	68	-64
-8	68	74
-9	126	123
-11	62	68
-13	172	166

-9,6,L

-1	226	221
-2	80	-77
-3	236	233
-4	300	-300
-6	187	-189
-11	131	-138
-13	68	-60

-9,5,L

-1	173	156
-2	89	-94
-4	108	-107
-5	159	-169
-6	244	-259
-8	73	-74
-9	65	67
-10	82	-84
-11	148	-142

-9,4,L

-1	447	438
-2	431	420
-3	46	66
-4	320	345
-5	72	64
-6	454	473
-8	221	216
-11	97	-100
-13	70	-69

-9,3,L

-1	501	475
-2	152	-137
-3	210	209
-4	81	-47
-6	221	215
-8	118	104
-9	225	-235
-10	186	-198
-11	255	-246
-12	114	108
-13	145	-159

-9,2,L

-1	651	-648
-2	268	-261
-3	705	-704
-5	124	124
-6	157	143
-8	180	174
-10	111	107
-11	275	265
-12	69	74
-13	289	275

-9,1,L

-2	167	-158
-3	133	138
-4	105	106
-5	200	267
-6	300	298
-8	66	74
-9	101	99
-11	396	405
-12	155	162
-14	77	-69
-15	76	81
-16	98	-110

-9,0,L

-2	846	-894
-4	320	-335
-6	638	-676
-8	437	-465
-12	67	69
-16	141	134
-18	182	185

-10,11,L

-2	81	75

-10,10,L

0	107	106
-2	138	133

-10,9,L

0	58	-75
-2	102	-108
-7	100	100

-10,8,L

-1	72	68
-3	91	95
-5	131	131
-7	194	192
-11	70	69

-10,7,L

-1	108	-111
-3	130	-128
-5	148	-150
-7	190	-195
-9	98	-95
-12	92	97

-10,6,L

-1	153	-162
-2	250	-267
-3	168	-173
-5	247	-248
-7	100	-92
-9	181	-171
-10	192	186
-11	76	-77
-12	125	127

-10,5,L

0	151	162
-2	245	247
-3	166	154
-4	214	224
-6	111	106
-9	127	140
-12	80	-85
-14	110	-106

-10,4,L

0	370	332
-1	395	-375
-2	293	284
-3	189	188
-4	430	415
-5	310	-318
-6	229	210
-7	249	-263
-8	102	-114
-11	133	-135
-14	135	-134

-10,3,L

0	156	-148
-1	189	182
-3	468	453
-4	237	-255
-5	429	420
-6	138	-136
-7	158	164

-10,3,L

-8	95	87
-9	260	261
-10	62	-70
-11	115	115
-13	46	-38
-14	115	113
-15	119	-121

-10,2,L

0	261	245
-2	899	860
-3	1308	1323
-4	184	-178
-5	436	445
-7	200	228
-8	155	152
-9	466	478
-10	172	-187
-11	86	-69
-12	109	98
-13	61	-63
-14	78	-77
-15	104	-97
-17	68	-69

-10,1,L

0	857	-870
-1	76	83
-2	490	-499
-3	592	-585
-4	386	-372
-5	208	-190
-6	108	-89
-7	67	-66
-8	340	339
-9	161	-170
-10	152	158
-11	72	-79
-13	126	120
-15	85	81
-16	80	90

-10,0,L

-2	406	379
-4	866	-843
-6	56	17
-8	464	470
-10	217	-232
-12	313	298
-14	77	73
-16	131	129

-11,11,L

-1	83	82

-11,9,L

-1	109	110
-4	140	140
-5	89	97
-8	101	110
-11	51	-48

-11,8,L

-2	70	70
-5	94	-102
-9	89	82

-11,7,L

-1	250	-255
-3	132	-139
-4	175	170
-9	171	168
-11	116	110
-13	146	147

-11,6,L

-1	149	148
-2	108	-118
-4	192	-194
-9	105	-112
-11	133	-126
-13	69	-75

-11,5,L

-1	140	157
-2	237	-240
-3	154	161
-4	336	-345
-5	56	-45
-6	382	-392
-7	113	114
-8	188	-186
-9	93	94
-10	126	-123
-11	74	-81
-16	72	73

-11,4,L

-2	116	-113
-3	54	54
-6	201	191
-7	55	-54
-10	72	-64
-13	131	-143

-11,3,L

-1	723	737
-2	188	177
-3	602	614
-4	65	71
-5	184	199
-6	331	320
-9	113	-112
-10	163	-163
-11	180	-175
-13	173	-173
-14	54	-42

-11,2,L

-1	504	-493
-3	58	64
-4	139	-128
-5	347	299
-7	69	48
-8	112	130
-9	123	116
-10	93	98
-11	378	389
-12	91	-96
-13	177	177

-11,1,L

-1	437	-450
-2	387	386
-3	454	-448
-4	166	175
-5	268	251
-6	447	439
-7	56	73
-8	309	316
-9	141	150
-10	62	71
-11	316	325
-12	48	28
-13	118	110
-14	87	-83
-15	97	94
-16	105	-106

-11,0,L

-4	615	584
-6	237	-240
-8	298	-281
-10	82	100
-12	133	-140

-12,11,L

0	67	57

-12,10,L

0	93	95
-2	165	165
-4	55	68

-12,9,L

-1	54	-59
-2	67	-64
-11	69	-57

-12,8,L

0	126	-126
-1	109	108
-2	55	-58
-3	130	139
-5	112	107
-7	204	216
-8	83	88
-9	84	81
-10	98	105

-12,7,L

0	111	-114
-1	84	-81
-5	83	-82
-7	124	-125
-8	99	-91
-11	70	-66

-12,6,L

0	56	-42
-1	61	-72
-2	157	-147
-3	78	-81
-4	133	-137
-5	179	-185
-6	83	86
-7	98	-97
-9	125	-129
-10	152	156
-12	162	171
-14	119	115

-12,5,L

0	181	-192
-2	90	84
-3	84	78
-7	58	-56
-9	143	141
-10	67	-56
-11	76	-67
-14	75	-66

-12,4,L

0	376	393
-1	257	-261
-2	371	396
-3	107	-112
-4	134	134
-5	240	-247
-6	160	168
-7	231	-233
-8	236	-233
-9	72	-75
-10	237	-225
-11	77	-71
-12	173	-177
-14	184	-185
-16	50	-58

-12,3,L

0	117	120
-1	295	295
-2	260	265
-3	61	56
-4	210	-209
-5	108	119
-6	45	-57
-8	62	49
-9	192	180
-10	168	-172
-11	64	67
-15	85	-89

-12,2,L

0	102	-85
-1	451	-420
-2	549	565
-3	53	83
-5	379	385
-6	173	166
-7	170	176
-9	286	281
-10	84	-71
-11	178	176
-15	135	-138
-17	60	-62

-12,1,L

0	334	300
-1	132	127
-2	137	124
-3	642	-609
-4	354	-330
-5	182	163
-7	112	-115
-8	226	226
-9	243	-257
-11	123	-116
-12	125	-130
-13	87	97

-12,0,L

-2	247	238
-6	224	219
-8	595	603
-10	556	593
-12	299	326
-14	127	129
-16	194	196

-13,11,L

-1	91	87

-13,9,L

-1	129	124
-4	139	145
-5	80	74
-6	140	139
-8	115	112

-13,8,L

-5	92	-89

-13,7,L

-1	225	-232
-3	150	-156
-4	125	120
-9	163	161
-11	129	117
-13	84	84

-13,6,L

-4	73	-58
-5	57	-44

-13,5,L

-1	91	-73
-2	318	-323
-3	80	92
-4	403	-404
-5	97	100
-6	458	-447
-7	67	-65
-8	229	-220
-9	110	112
-10	129	-133

-13,4,L

-1	59	69
-3	91	-89
-5	126	-142
-6	107	113
-7	73	64
-8	130	-131
-9	89	-97
-10	97	-100
-13	62	-61

-13,3,L

-1	464	472
-2	363	360
-3	477	464
-4	290	304
-5	181	173
-6	49	58
-8	295	287
-11	166	-164
-13	157	-161
-16	57	-59

-13,2,L

-1	338	-349
-2	264	-258
-3	68	48
-4	246	-244
-6	155	153
-7	235	-223
-8	175	-190
-9	340	-337
-10	99	94
-11	115	107

-13,1,L

-1	96	83
-2	318	302
-3	219	-228
-4	226	233
-5	132	-124
-6	345	356
-7	249	245
-8	615	640
-10	168	167
-11	79	75
-13	211	221
-16	103	-105

-13,0,L

-2	157	137
-4	424	-406
-6	164	-160
-8	136	-139
-10	423	416
-12	167	-168

-14,11,L

-4	50	-43

-14,10,L

0	126	121
-2	139	138
-4	61	67

-14,9,L

0	57	60
-1	59	-74

-14,8,L

0	194	-200
-2	78	-79
-3	110	111
-5	116	114
-7	164	166
-9	129	126

-14,7,L

-1	70	-72
-3	122	129
-8	107	-110
-9	73	64

-14,6,L

0	219	-232

-14,6,L

-2	100	-113
-4	228	-224
-5	218	-221
-6	50	54
-7	133	-133
-10	73	76
-12	155	153
-14	125	122

-14,5,L

0	339	-336
-1	183	-186
-2	105	-102
-4	113	-116
-7	144	-127

-14,4,L

0	474	458
-2	468	464
-3	292	-287
-5	72	-59
-6	248	242
-7	111	-108
-9	175	-182
-10	221	-225
-12	191	-189
-14	132	-133

-14,3,L

0	330	-339
-1	58	52
-2	146	147
-5	324	-326
-6	88	-94
-7	245	-245
-8	110	95

-14,2,L

0	169	156
-1	265	262
-2	300	289
-3	268	260
-4	103	83
-5	583	591
-7	199	199
-8	308	-321
-11	186	185
-13	91	-78
-15	132	-133

-14,1,L

0	162	143
-1	54	65
-2	88	101
-3	68	-84
-4	171	-174
-5	117	106
-6	119	116
-7	249	258
-8	269	275
-10	63	-58
-12	97	-96

-14,0,L

0	844	-874
-2	656	-676
-4	370	-380
-6	106	-106
-8	46	36
-10	523	513
-14	135	123
-16	142	138

-15,10,L

-2	53	-52

-15,9,L

-3	58	52
-6	94	106
-8	93	88
-9	95	-82

-15,8,L

-3	98	93

-15,7,L

-1	126	-124
-3	183	-187
-4	90	102
-5	77	-77
-6	107	108
-7	82	83
-11	113	110

-15,6,L

-1	172	-176
-2	146	142
-3	65	-72
-5	154	-151
-6	115	122
-9	68	63

-15,5,L

-1	106	-116
-2	317	-314
-3	113	117
-4	283	-273
-5	52	49
-6	234	-237
-7	206	-204
-8	194	-195

-15,4,L

-1	68	-79
-3	154	-157
-4	270	-279
-5	78	-80
-6	127	117
-7	171	173
-8	124	-132

-15,3,L

-1	296	296
-2	314	314
-3	181	181
-4	195	202
-5	50	-63
-6	101	-100
-7	162	-176
-8	132	139
-9	152	-155
-10	48	55
-11	228	-228
-12	81	-70
-13	206	-208

-15,2,L

-1	306	303
-2	42	-44
-3	349	348
-4	165	-157
-5	156	152
-6	178	181
-7	97	-103
-8	289	-287
-9	250	-255
-10	102	97
-11	47	-51
-13	161	-160

-15,1,L

-1	404	-421
-3	223	-225
-4	240	258
-5	134	-135
-6	311	321
-7	168	176
-8	316	330
-9	98	92
-10	71	81
-11	104	95
-13	172	173
-16	84	-91

-15,0,L

-2	594	591
-4	148	154
-6	187	199
-8	153	-146
-10	209	219
-12	225	-225

-16,10,L

0	129	134
-2	58	64

-16,9,L

0	131	138

-16,8,L

0	146	-146
-2	65	-70
-5	153	151
-9	91	78

-16,7,L

-1	124	-122
-3	158	164
-5	186	187
-7	199	195
-9	66	60

-16,6,L

0	187	-183
-1	124	124
-2	171	-161
-3	80	-67
-4	147	-132
-5	227	-219

-16,6,L

-6	98	-97
-7	150	-155

-16,5,L

0	353	-364
-1	175	-177
-2	78	-85
-3	170	159
-5	74	-79
-7	71	-71
-10	103	107
-12	153	153

-16,4,L

0	279	302
-3	247	-250
-6	89	93
-7	94	-90
-9	133	-132
-10	161	-171
-12	137	-134
-14	62	-56

-16,3,L

-1	181	-184
-2	279	299
-3	109	-106
-4	143	-142
-5	403	-410
-6	53	-69
-7	218	-232
-9	143	-149
-10	119	-118
-14	69	-74
-15	65	73

-16,2,L

-1	106	112
-2	64	-63
-3	128	141
-4	201	209
-5	371	378
-6	151	-147
-7	248	256
-8	190	-193
-9	209	207
-11	156	160
-15	90	-88

-16,1,L

0	220	210
-1	48	66
-2	334	333
-3	230	246
-5	259	271
-7	276	290
-8	92	-97
-9	54	-44
-10	239	-238
-11	108	112
-13	69	-61

-16,0,L

0	239	-247
-2	571	-594
-4	292	-297
-6	114	-114
-8	173	186
-10	173	178

-17,9,L

-8	55	50
-9	79	-67

-17,8,L

-1	112	107
-2	94	95
-3	213	202
-5	80	68
-7	53	-45

-17,7,L

-1	111	-108
-2	45	35
-3	183	-180
-5	121	-125
-7	100	104
-11	63	71

-17,6,L

-1	89	-90
-2	206	201
-3	212	-221
-4	86	80
-5	148	-140
-6	160	164
-7	108	117
-9	94	95
-10	106	101

-17,5,L

-1	161	-146
-2	139	-143
-3	98	109
-4	142	-137
-5	65	-57
-8	113	-108
-9	92	-86
-13	85	-76

-17,4,L

-1	220	-210
-2	238	-237
-3	154	-147
-4	285	-288
-8	248	-244
-10	84	-75
-11	101	108
-13	81	73
-14	89	89

-17,3,L

-1	128	129
-2	285	284
-4	60	-53
-5	72	-79
-6	74	81
-9	132	-133
-11	131	-130
-12	80	-76
-13	156	-154

-17,2,L

-1	367	393
-2	121	121
-3	329	324
-4	98	-92
-5	234	238
-6	115	-107
-7	113	-106
-8	136	-140
-9	133	-134
-10	87	78
-11	162	-160
-13	151	-162

-17,1,L

-1	176	-170
-2	104	-98
-3	313	-318
-4	100	-97
-6	205	213
-7	68	-68
-8	108	95
-10	73	66
-13	63	62
-16	74	-63

-17,0,L

-2	98	115
-4	263	261
-6	422	424
-8	292	300
-10	187	199
-12	65	-73
-16	108	-114

-18,10,L

0	76	79

-18,9,L

0	185	187
-2	117	125
-5	58	-59
-7	75	-74

-18,8,L

-4	60	62
-5	79	88

-18,7,L

-1	99	-97
-2	110	101
-3	71	76
-4	57	56
-5	245	258
-7	205	193

-18,6,L

-1	65	63
-2	84	-93
-3	66	-69
-5	79	-79
-6	127	-132

-18,5,L

0	489	-478
-1	86	93
-2	102	-100

-18,5,L

-3	111	107
-5	166	-158
-10	182	184
-12	208	210
-14	88	94

-18,4,L

0	120	112
-2	236	-242
-3	108	-100
-4	58	58
-6	90	-94
-7	50	-57
-10	99	-94

-18,3,L

0	131	135
-1	57	-52
-2	141	144
-3	223	-223
-4	158	-157
-5	278	-289
-6	93	94
-7	174	-172
-8	107	111
-9	182	-183
-10	99	-105
-12	110	-106

-18,2,L

0	234	233
-1	61	63
-2	214	-218
-3	87	96
-4	137	129
-5	157	160
-6	250	-265
-9	80	72
-11	72	72

-18,1,L

0	98	90
-1	104	111
-2	281	278
-4	185	189
-5	193	190
-7	268	268
-8	184	-182
-9	81	84
-10	171	-177
-11	109	113
-12	99	-106
-14	119	-110

-18,0,L

0	84	-85
-2	428	-435
-4	178	179
-6	118	-105
-8	122	121

-19,10,L

-2	48	-40
-4	87	-90

-19,8,L

-1	149	147
-2	106	113
-3	120	124
-5	110	115
-8	97	94
-9	79	-80
-10	60	52

-19,7,L

-5	63	-57
-7	46	32

-19,6,L

-1	55	58
-2	98	102
-3	240	-247
-4	226	232
-6	154	148
-7	153	156
-8	123	128
-9	118	119
-10	76	70

-19,5,L

-1	83	80
-5	71	-61
-10	70	66

-19,4,L

-1	210	-214
-2	441	-450
-4	135	-136
-6	149	-154
-8	204	-208
-9	82	74
-10	146	-142
-11	110	114
-13	101	103
-14	85	76

-19,3,L

-1	69	65
-3	159	155
-8	114	-116
-14	53	62

-19,2,L

-1	379	394
-2	61	66
-3	371	376
-6	194	-200
-7	106	-121
-9	126	-122
-11	147	-151
-13	133	-126
-15	95	-93

-19,1,L

-1	183	-200
-2	51	62
-3	68	-73
-5	125	-121
-6	58	-69
-10	77	80

-19,0,L

-2	180	173
-4	306	321
-6	400	405
-8	333	341
-10	154	148

-20,9,L

0	153	145
-2	164	158
-4	62	52
-7	80	-85

-20,8,L

-4	59	44

-20,7,L

0	127	-138
-1	62	74
-2	84	86
-4	96	100
-5	228	220
-7	148	148

-20,6,L

0	46	45

-20,5,L

0	373	-368
-1	333	329
-2	267	-263
-4	92	-86
-5	83	-83
-6	57	-54
-9	70	70
-10	168	178
-12	159	163

-20,4,L

0	135	-122
-1	271	263
-2	149	-147
-4	75	85
-7	56	53
-8	81	95
-13	63	-61

-20,3,L

0	609	634
-1	77	91
-3	255	-256
-5	217	-220
-6	165	176
-7	194	-192
-9	82	-81
-10	66	-61
-12	127	-122

-20,2,L

0	498	509
-1	138	144
-2	224	-226
-3	157	-159
-7	69	80
-8	68	65
-9	157	-152
-14	50	52

-20,1,L

0	710	725
-1	89	-91
-2	353	357
-3	139	145
-4	226	222
-5	370	383
-6	79	79
-7	47	53
-8	165	-177
-9	94	96
-10	155	-160
-12	125	-118

-20,0,L

0	597	627
-2	110	-125
-4	360	372
-8	164	-165

-21,9,L

-4	67	-64

-21,8,L

-1	158	161
-2	66	62
-5	50	66
-9	62	-69

-21,7,L

-1	100	96
-3	109	110
-5	81	73
-8	73	-69
-9	66	-65

-21,6,L

-3	130	-139
-4	253	246
-6	101	97
-7	92	82
-8	94	92
-9	55	66

-21,5,L

-3	97	-99
-6	90	83

-21,4,L

-1	215	-216
-2	383	-390
-4	122	-119
-5	72	-64
-6	235	-233
-8	151	-152
-9	100	105
-10	97	-106
-13	80	84

-21,3,L

-1	312	-306
-2	108	-120
-4	83	73
-9	72	84
-11	121	126
-12	50	-53
-13	69	78
-14	58	51

-21,2,L

-1	139	-132
-2	107	110
-3	402	415
-6	106	-107
-7	149	-156
-10	125	-132
-11	139	-117
-13	127	-122
-15	90	-88

-21,1,L

-1	277	281
-3	234	235
-4	133	-123
-6	286	-287
-7	106	100
-10	103	105
-11	90	-87

-21,0,L

-2	586	611
-4	170	169
-6	241	251
-8	467	497
-10	81	69
-14	112	-116

-22,9,L

0	76	66
-2	74	78
-3	96	-80

-22,8,L

-5	115	-112
-7	100	-93

-22,7,L

-1	141	144
-4	111	113
-5	126	124
-7	96	97
-9	52	58

-22,6,L

0	129	135
-2	138	145
-3	80	79
-5	102	110
-7	111	109

-22,5,L

0	46	-46
-1	164	168
-2	226	-217
-3	80	-75
-10	122	118
-12	77	87

-22,4,L

-1	82	83
-6	100	90
-8	100	93
-10	76	69

-22,3,L

0	260	257
-1	64	62
-2	158	-156
-3	115	-128
-5	219	-225
-6	101	109
-7	225	-222
-11	84	-82

-22,2,L

0	110	110
-1	173	-183
-3	408	-402
-5	161	-162
-7	181	-189
-8	85	82
-9	230	-236
-10	106	109
-14	53	53

-22,1,L

0	475	478
-1	242	-240
-4	71	-78
-5	286	300
-6	69	80
-9	90	88
-10	159	-163
-12	116	-110

-22,0,L

0	293	-321
-2	74	-78
-4	358	354
-8	184	-189
-12	81	-76

-23,8,L

-1	93	100

-23,7,L

-1	160	152
-3	128	127
-5	82	74
-9	53	-50

-23,6,L

-1	133	-139
-3	107	-113
-4	135	136
-6	74	82

-23,5,L

-2	78	84
-3	63	57
-4	114	111
-6	145	148
-8	102	101
-9	73	77
-10	61	47

-23,4,L

-2	107	-102
-3	97	-102
-6	83	-82
-11	47	-21

-23,3,L

-1	222	-224
-2	97	99
-3	102	-106
-4	117	-112
-9	117	115
-11	152	151
-13	147	153

-23,2,L

-1	298	297
-2	145	-142
-3	339	348
-5	129	134
-6	56	-56
-7	154	-163
-10	136	-146

-23,1,L

-1	336	340
-2	88	86
-4	154	-166
-5	119	126
-6	223	-225
-7	56	45
-8	125	-121
-11	136	-136

-23,0,L

-2	57	97
-4	65	-63
-6	206	-222
-8	264	261
-10	57	43
-12	74	61
-14	64	-58

-24,8,L

-3	71	-81
-5	91	-92
-7	82	-86

-24,6,L

0	153	153
-1	84	81
-2	126	124
-3	78	76
-5	61	61
-6	48	57
-9	80	80

-24,5,L

-2	59	-60

-24,4,L

0	161	-168
-2	182	-189
-3	115	124
-4	172	-179
-5	148	156
-6	50	62
-8	70	75
-9	69	60
-10	107	109

-24,3,L

0	59	-70
-2	73	-63
-4	58	49
-5	204	-216
-7	102	-102

-24,2,L

0	136	-146
-1	166	-179
-2	95	93
-3	111	-115
-5	114	-114
-7	149	-153
-9	118	-120
-10	79	78
-11	123	-116

-24,1,L

0	211	220
-3	91	88
-4	102	-114
-5	85	97
-7	74	81

-24,0,L

0	308	317
-2	580	597
-4	195	205
-8	109	-110
-10	126	-132

-25,7,L

-1	141	137

-25,5,L

-1	46	-23
-3	74	75
-4	188	186
-6	203	207
-8	133	129

-25,4,L

-3	97	-96
-11	56	-43

-25,3,L

-1	198	-196
-3	124	-116
-4	141	-151
-6	100	-107
-11	126	121

-25,2,L

-2	51	-44
-4	88	98
-10	116	-112
-11	95	-89

-25,1,L

-1	163	169
-2	142	-136
-4	193	-204
-6	185	-192
-7	97	-88
-8	195	-198
-11	87	-81
-13	100	-95

-25,0,L

-4	94	100
-8	73	80

-26,8,L

-3	101	-93

-26,7,L

0	71	-70

-26,6,L

0	123	117
-2	102	89
-5	59	53

-26,5,L

-6	59	-62
-7	71	72

-26,4,L

0	167	-155
-2	178	-174
-4	160	-168
-7	95	91
-8	88	82
-10	123	126

-26,3,L

-2	95	-93
-3	61	59
-6	83	76
-8	54	-50

-26,2,L

0	202	-210
-1	99	-100
-3	151	-145
-4	84	-81
-5	227	-230
-7	143	-142
-9	65	-72

-26,1,L

0	71	70
-1	127	-137

-26,0,L

0	155	152
-2	237	240
-6	64	71
-8	116	-119
-10	239	-239
-12	94	-83

-27,7,L

-1	102	112

-27,6,L

-5	56	38

-27,5,L

-4	148	146
-6	168	170
-8	132	130

-27,4,L

-3	77	71
-4	84	82

-27,3,L

-1	191	-197
-3	148	-158
-5	72	-72
-6	111	-105
-11	81	72

-27,2,L

-1	120	-120
-5	88	-84
-10	56	-28

-27,1,L

-1	58	52
-2	101	-95
-3	68	60
-4	110	-114
-6	171	-159
-8	135	-137
-10	93	-96

-27,0,L

-4	172	-179
-6	86	-75
-8	75	-71

-28,6,L

-3	74	85

-28,5,L

0	109	101

-28,4,L

0	137	-144
-3	74	80
-6	83	-68
-9	58	65
-10	79	76

-28,3,L

-2	53	-61
-3	106	101
-7	91	79

-28,2,L

0	130	-135
-2	58	-56
-4	51	-51
-5	126	-129

-28,1,L

-1	80	-83
-5	91	-86

-28,0,L

0	147	154
-2	178	178
-6	64	-63
-10	134	-126
-12	59	-57

-29,5,L

-3	51	-56
-4	71	76
-6	116	104
-8	86	76

-29,4,L

-4	48	44
-6	110	113

-29,3,L

-1	150	-151
-2	67	-63
-3	124	-116

-29,2,L

-1	143	-140
-3	102	-96
-4	47	51
-8	49	5

-29,1,L

-1	87	95
-3	66	76
-4	78	-66
-6	88	-90

-29,0,L

-2	70	-75
-4	82	-87
-6	109	-109
-8	63	-70

-30,6,L

-3	72	70

-30,5,L

0	147	138
-2	119	123

-30,4,L

0	65	-50
-3	56	47
-4	82	-81

-30,3,L

0	113	-102
-3	138	131
-5	140	136
-7	110	111
-8	74	69
-9	111	111

-30,2,L

0	89	-83
-4	51	-47
-5	105	-90
-7	49	-50

-30,1,L

0	183	-178
-2	109	-106
-3	128	-124
-4	119	-113
-5	48	-48
-8	81	69
-9	71	-72

-30,0,L

-2	128	116
-10	76	-81

-31,6,L

-1	75	77
-3	69	77

-31,4,L

-1	59	63
-6	139	134

-31,2,L

-1	180	-172
-3	125	-118
-9	100	99

-31,0,L

-4	89	-90
-6	191	-179

-32,5,L

0	99	95
-2	112	117

-32,4,L

0	109	97
-2	67	46

-32,3,L

0	77	-69
-5	123	114

-32,2,L

0	107	-87
-1	71	-67

-32,1,L

0	147	-140
-3	110	-101
-5	72	-71

-32,0,L

0	103	-105

-33,4,L

-3	50	46
-4	95	80

-33,2,L

-3	117	-118
-5	72	-72

-33,0,L

-2	206	-194
-4	169	-168
-8	172	-163

-34,3,L

0	91	-92
-5	88	88

-34,2,L

-5	102	96

-34,1,L

0	250	-226
-2	105	-108
-5	109	-92

-34,0,L

-2	68	-43

-35,2,L

-3	101	-99

-35,1,L

-1	106	-97
-4	74	66

-36,2,L

0	108	88

-36,1,L

0	94	-80

-36,0,L

0	73	-74
-2	123	-126

0,4,L

0	1065	-1084
-1	767	766

0,2,L

0	1416	1375
-2	1497	-1514
-3	316	-337
-5	1263	-1247

0,0,L

-2	1097	1158
-4	961	969

-1,3,L

-1	316	301
-2	1010	-987
-3	503	-489

-1,2,L

-1	2134	-2122
-2	750	710
-3	923	-899
-5	170	-180

-1,1,L

-1	214	-204
-3	1838	1884
-4	124	132

-1,0,L

-2	333	355
-4	242	232

-2,3,L

0	1425	1406
-4	396	-375

-2,2,L

0	341	-342
-1	558	521
-2	1044	-998
-4	660	633
-5	1226	-1154

-2,1,L

0	359	-363
-1	285	-282
-2	142	-150
-3	757	-730
-4	601	591

-2,0,L

-2	1000	-995

-3,3,L

-1	731	-741
-3	895	-859

-3,1,L

-1	729	737
-5	717	678

-3,0,L

-2	815	-854

-4,3,L

0	574	543

-2	577	-574

-4,2,L

0	534	-526

-4,1,L

0	1243	-1273
-2	1122	-1125
-3	444	-445

-4,0,L

0	539	522
-2	1376	1429

-5,2,L

-1	992	-990

-6,1,L

0	1064	-1078
-2	1431	-1451

-6,0,L

0	1022	-1035

-7,1,L

-1	924	-916

-10,0,L

0	1195	-1160

-11,0,L

-2	1152	1124

-12,0,L

0	1541	-1541

APPENDIX 5

Structure Factor List for compound XX ,

Part II , p.75 .

Columns listed are ℓ , $|F_o|$ x10 , F_c x10 .

20,1,L

-2 47 -19

19,3,L

1 45 -12

19,2,L

-1 49 -10
-4 54 46
-6 60 43

19,1,L

1 61 53

19,0,L

1 55 -22

18,6,L

-2 42 -43

18,5,L

-6 47 -36

18,4,L

3 53 50
-6 52 61

18,3,L

-1 44 18
-3 70 66
-5 69 78
-6 47 -2
-7 64 63

18,2,L

3 48 -50
-9 50 40

18,1,L

4 101 -70
2 61 -52
-3 50 -44
-5 64 -35

18,0,L

-2 103 -97
-4 131 -97

17,8,L

-2 57 -43
-3 49 -4

17,7,L

1 59 8
-3 46 -48

17,5,L

-3 56 47
-8 46 -13

17,4,L

3 48 -59
1 46 -70

17,3,L

-6 42 -14

17,2,L

-5 48 19
-6 66 -47
-9 46 34

17,1,L

6 51 28
5 80 36
4 53 37
-3 75 -50
-5 62 -41
-7 61 -58
-9 51 12

17,0,L

5 47 36
3 47 19
1 85 68
-1 65 65
-5 60 -44
-9 104 -80

16,9,L

0 45 15

16,6,L

5 48 -41
-4 44 53
-6 54 68

16,5,L

6 61 -61
4 56 -73
-7 45 -7
-10 52 42

16,4,L

3 49 -64
0 81 -85
-2 58 -80
-3 50 47
-4 85 -104
-6 93 -72
-7 55 28

16,3,L

-2 50 19
-3 81 -99
-5 95 -94
-7 83 -66

16,2,L

7 65 42
5 72 58
4 65 -45
3 70 68
1 41 29
-6 103 -83

16,1,L

7 59 -18
6 93 67
5 48 4
4 90 63
0 43 -6
-4 56 54
-5 43 26
-6 62 51
-7 48 31
-8 61 -35
-10 48 -39

16,0,L

-2 79 82
-6 153 125

-8 51 -35
-10 77 54

15,9,L

1 63 40
-5 60 66

15,8,L

0 78 71
-4 52 62

15,7,L

6 48 -33
5 53 43
4 69 -75
2 46 -68

15,6,L

6 46 21
-6 49 -50
-7 72 65
-8 65 -64
-9 48 32

15,5,L

8 48 24
-3 100 -130
-5 104 -117
-7 71 -72
-9 100 -79
-10 50 -43

15,4,L

3 86 118
1 77 105
-2 62 -75
-3 54 69
-4 77 -101
-6 54 -55
-7 102 -78
-9 52 -67
-11 70 -66

15,3,L

9 45 3
7 42 -7
6 90 68
4 98 103
2 70 94
0 46 25

15,3,L

-1	47	58
-3	62	71
-6	81	-69
-7	74	62
-8	75	-63
-10	61	-52
-12	58	-61

15,2,L

8	67	-46
5	78	54
3	93	80
2	96	98
-3	51	-59
-4	53	65
-6	133	126
-7	44	49
-8	47	53
-10	66	46
-12	54	-16

15,1,L

9	46	-39
6	95	-67
5	59	21
4	46	-24
3	100	95
1	67	101
-4	48	21
-5	157	114
-6	68	61
-7	135	106
-10	43	38
-12	65	47

15,0,L

9	86	-46
7	89	-58
5	67	-44
3	70	-68
-1	87	-68
-3	77	69
-5	201	143
-11	110	91

14,10,L

-4	54	68
-5	47	-33

14,9,L

4	64	-45
1	43	4
-3	68	85

14,7,L

-1	45	9
-3	83	-111

14,6,L

5	80	86
-4	43	-78
-6	57	-52
-8	50	-14
-9	70	-63
-11	47	-49

14,5,L

9	47	9
8	63	48
2	41	41
1	65	100
0	40	34
-2	63	78
-8	44	-43
-9	46	-10
-10	121	-104
-12	50	-65

14,4,L

7	78	70
6	44	-51
4	48	-20
3	42	14
-4	111	127
-6	89	65
-9	45	-33
-10	59	-60

14,3,L

9	61	-57
5	59	26
4	72	67
3	80	85
0	46	-64
-2	81	-107
-3	101	122
-4	42	-47
-5	121	115
-6	50	-31
-8	61	48
-9	48	-46
-10	81	69
-11	58	-62
-12	50	3

14,2,L

9	66	-41
8	66	-46
7	69	-60
5	120	-101
4	46	-28
3	110	-108
0	59	96
-2	95	110
-8	51	-55
-11	105	82
-12	55	-42

14,1,L

9	58	47
6	135	-102
4	160	-128
3	98	-77
2	68	43
0	90	-109
-5	45	-30
-6	173	138
-7	43	-35
-8	46	5

14,0,L

10	142	90
8	82	73
2	98	-73
-2	132	-113
-4	98	-80
-8	49	32
-12	51	42

13,11,L

0	48	-13
-1	49	15
-5	57	74

13,9,L

2	61	-59
0	72	-88
-3	79	-103
-4	51	84
-5	72	-83
-6	51	38

13,8,L

4	54	-57
3	61	69
0	47	51
-4	63	-75
-5	52	33
-6	99	-103
-7	55	-39

13,7,L

8	50	51
6	57	63
5	68	-59
4	48	57
2	48	70
1	63	102
-8	77	-64

13,6,L

8	47	-24
4	47	-25
2	59	65
0	48	37
-2	108	159
-3	54	-50
-4	85	101
-5	46	-10
-7	42	-35
-8	75	67

13,5,L

7	61	44
6	44	-16
5	48	56
2	51	-40
0	44	-3
-5	110	129
-7	108	114
-8	47	11
-9	128	108
-12	48	17

13,4,L

8	56	-55
7	75	-64
5	90	-98
4	108	129
3	51	-78
2	43	-48
0	54	84
-1	128	-165
-3	79	-93
-4	98	117

13,4,L

-6	63	55
-7	106	98
-8	67	51
-9	67	57
-10	85	61
-11	69	57
-13	68	86

13,3,L

10	60	-27
8	77	-71
7	45	-28
6	134	-120
5	108	-102
4	137	-138
3	50	50
0	88	-140
-4	63	74
-5	66	-69
-6	110	97
-7	185	-158
-8	51	39
-9	105	-85
-12	90	72

13,2,L

10	53	68
8	55	49
5	112	-101
4	134	-118
3	79	-71
2	75	-72
1	128	-201
0	80	-129
-2	71	-78
-3	75	73
-4	119	-124
-5	79	65
-6	130	-127
-7	49	30
-8	151	-132
-9	99	80
-12	49	16

13,1,L

11	83	69
9	75	70
6	42	27
5	59	-49
3	127	-106
2	65	73
1	54	43
0	58	99
-1	95	-133
-2	115	-99
-3	276	-269
-4	153	-139
-5	259	-224
-6	131	-106
-7	132	-110
-9	126	126
-14	62	-54

13,0,L

9	84	58
7	55	44
5	143	120
3	55	67
1	290	243
-1	61	68
-3	170	-150
-5	220	-205
-7	53	-44
-9	48	-41
-11	48	-37

12,12,L

-3	47	-26

12,11,L

-1	44	-47
-2	45	-15
-5	52	-68

12,10,L

6	49	13
5	48	51
2	50	-59
1	46	24
-2	112	-123
-4	68	-73
-6	64	-72

12,9,L

7	49	-38
6	54	56
5	50	-36
4	48	92
3	50	19
0	64	85
-1	63	-76
-3	71	-76
-5	62	-78
-8	59	-74

12,8,L

7	77	102
4	71	-91
3	56	70
0	47	63
-9	90	-99
-11	56	-55

12,7,L

7	44	-62
2	76	117
1	66	95
-1	46	68
-2	92	-95
-3	45	36
-6	44	37

12,6,L

8	67	-45
7	119	-114
6	46	57
4	47	78
2	44	26
-1	80	-109
-4	80	106
-5	42	23
-9	64	68
-10	54	37
-11	57	47

12,5,L

10	99	-101
8	69	-73
4	66	62
3	64	84
2	85	-110
0	117	-167
-1	53	59
-8	62	62
-9	44	3
-10	73	65
-12	88	106

12,4,L

10	60	63
9	51	-48
8	77	65
7	46	-56
5	57	-48
1	75	-126
-4	61	-78
-7	88	81
-8	82	-74
-11	56	57
-12	62	-56
-13	48	46

12,3,L

11	64	69
10	46	35
9	100	95
7	65	65
5	97	80
4	54	71
3	43	35
1	89	-114
0	64	-103
-1	161	-243
-2	76	-100
-3	101	-117
-4	130	139
-5	45	36
-7	41	29
-8	64	-56
-9	53	-18
-11	52	-50
-12	74	-66
-14	48	-48

12,2,L

9	68	65
8	50	14
7	51	36
6	101	80
5	169	153
4	152	111
3	171	164
2	57	46
1	160	200
0	135	-203
-3	69	-86
-4	83	-77
-5	79	-70
-6	164	-143
-7	176	-166
-8	73	67
-11	82	-79
-12	123	103
-13	88	-89

12,1,L

12	58	38
11	68	-52
9	77	-67

12,1,L

8	79	56
6	61	40
5	72	75
3	99	-66
2	176	147
0	171	232
-1	157	194
-2	70	93
-3	160	144
-4	130	-110
-6	258	-226
-8	50	-52
-10	138	-124
-11	71	51
-12	112	-109
-14	61	-73

12,0,L

12	89	-77
10	146	-128
8	71	-83
4	110	92
2	121	-96
0	147	199
-4	156	161
-6	249	205
-8	93	68
-12	108	-96

11,12,L

3	56	-48
-4	75	-75
-5	61	41

11,11,L

2	53	62
1	55	-57
-1	66	-65
-3	83	-82
-4	44	11
-5	57	-64

11,10,L

3	101	113
1	93	102
-6	60	-47
-9	68	-79

11,9,L

7	41	4
4	53	60
2	85	76
0	70	74
-1	64	82
-2	63	-63
-3	153	168
-4	50	-68
-5	105	96
-6	43	24
-8	77	65
-11	47	7

11,8,L

3	68	-89
1	48	-8
-2	56	45
-3	61	-74
-4	53	61
-6	48	50
-7	72	70
-8	42	-22
-9	87	83

11,7,L

10	49	-26
9	45	21
6	96	-94
4	202	-227
-2	136	155
-3	81	-84
-4	72	69
-5	50	-39
-12	90	91

11,6,L

9	124	-105
7	96	-89
6	48	-27
4	46	-40
3	48	-50
2	131	-172
0	124	-179
-2	96	-113
-4	53	-59
-5	101	93
-8	67	-70

11,5,L

10	46	-45
8	88	65
3	67	-87
2	138	-171
1	93	-118
0	59	72
-1	165	-198
-2	41	42
-3	71	-82
-4	50	50
-6	53	-54
-7	129	-105
-8	83	-81
-9	85	-88
-10	55	35
-12	73	-56
-13	94	94

11,4,L

10	62	58
9	99	68
8	64	42
7	170	155
5	46	41
3	113	134
2	66	-88
1	52	67
0	85	-123
-1	66	76
-2	44	-75
-4	146	-157
-5	67	-49
-7	41	-34
-8	41	2
-10	84	-91
-11	72	-73
-12	88	80
-13	104	-94
-14	75	57

11,3,L

10	59	49
7	47	46
6	52	48
4	90	95
3	80	96
2	357	428
1	48	70
-1	42	36
-2	81	-102
-3	73	-74
-4	180	-198
-5	62	-49
-6	89	-93
-10	144	-123
-12	128	-109
-14	64	-84

11,2,L

12	54	-52
10	83	-64
9	57	48
7	53	-44
6	56	39
4	69	62
1	158	198
0	117	142
-1	75	101
-2	184	203
-3	43	50
-4	289	268
-6	96	76
-7	183	-153
-9	138	-125
-10	78	-81
-11	113	-108
-12	84	-83

11,1,L

11	76	-69
10	44	-29
4	110	-100
3	165	-139
2	204	-180
1	171	165
0	48	51
-1	58	74
-2	56	58
-3	180	172
-4	121	106
-5	146	138
-6	64	52
-7	128	115
-8	138	-125
-9	134	116
-11	64	-69
-12	69	63
-13	137	-133
-15	82	-101

11,0,L

9	78	-69
5	288	-243
3	234	-230
1	102	-99
-3	98	89
-5	101	-93
-9	59	-71
-11	186	178
-13	101	89

10,13 L

1	64	-78

10,12,L

5	55	77
4	47	-5
1	53	66
-1	50	33
-4	46	50
-6	48	-2
-7	52	-79

10,11,L

4	72	81
2	75	79
1	52	56
0	77	69
-1	106	109
-3	151	135
-5	116	109
-8	54	-52

10,10,L

8	44	3
6	45	-30
3	45	-28
2	51	66
1	46	23
0	95	94
-2	138	127
-4	114	117
-6	167	176

10,9,L

9	52	5
6	104	-119
3	74	90
1	85	99
0	83	-100
-1	52	50
-3	72	76
-4	71	67
-6	54	56
-7	109	110
-8	135	133
-10	100	130

10,8,L

9	76	-76
7	60	-69
5	103	-112
3	97	-97
2	50	-73
1	75	-99
-3	93	114
-4	133	-136
-5	177	175
-6	221	-216
-7	46	41
-9	94	94
-11	94	100

10,7,L

10	61	-51
9	82	83
7	84	75
5	48	42
4	110	-122
3	168	-189
1	237	-318
0	141	173
-1	142	-188
-2	149	184
-3	78	-77
-4	45	24
-5	39	-9
-7	169	-164
-10	72	68
-11	75	-59

10,6,L

10	91	93
7	69	64
6	89	-97
5	109	118
4	123	-133
3	167	178
2	203	-236
1	121	148
0	78	-88
-1	56	58
-2	40	-65
-3	52	-47
-4	69	-75
-5	112	-103
-7	52	-61
-8	70	-64
-11	73	-58

10,5,L

11	43	-15
10	141	123
9	134	-109
7	45	-46
8	88	70
6	46	43
5	48	-31
4	153	152
2	163	207
0	72	89
-2	44	-53
-3	150	161
-4	54	-71
-7	43	37
-8	179	-165
-10	124	-107
-11	59	66
-12	79	-80

10,4,L

12	51	-61
11	56	62
10	118	-95
9	89	82
8	99	-97
7	62	-39
5	89	-91
4	194	221
3	111	111
1	220	255
0	127	172
-1	185	228
-2	205	235
-3	115	-119
-4	212	205
-5	177	-177
-6	74	64
-7	44	38
-8	230	209
-9	64	-56
-10	173	156
-11	75	-69

10,3,L

13	51	-37
11	69	-76
10	53	-51
9	59	-61
7	238	-215
5	68	-62
4	262	-250
3	215	238
2	65	-61
1	150	192
0	197	253
-1	138	174
-2	87	100
-5	249	243
-7	280	259
-8	236	231
-9	292	274
-11	68	-72
-13	83	-74

10,2,L

11	120	-115
9	115	-86
7	104	-88
6	77	-70
5	133	-119
4	121	-99
3	209	-209
2	175	184
1	84	-108
0	78	-126
-1	138	-153
-2	107	-137
-3	72	79
-4	58	59
-5	86	81
-6	267	231
-7	274	271
-8	239	222
-9	209	205
-11	116	121
-13	71	71

10,1,L

12	79	-65
11	94	88
10	58	-39
9	61	55
7	83	-70
6	61	-51
5	80	-60
4	183	-166
3	67	-59
2	219	-210
1	158	-164
-1	157	-198
-3	140	-148
-4	39	62
-5	130	-116
-6	132	122
-7	57	-58
-9	165	-160
-10	370	340
-11	52	57
-12	119	121
-13	53	56
-14	80	83

10,0,L

12	70	74
10	70	57
6	128	-111
2	264	-248

10,0,L

0	346	-400
-2	365	-316
-4	193	-173
-6	181	-143
-8	379	-360
-10	99	-87
-14	80	76

9,13,L

-2	50	-57

9,12,L

-1	42	-11
-2	108	90
-3	57	-59
-4	122	98
-7	64	-73

9,11,L

6	45	-89
4	53	-42
3	58	45
2	43	-39
1	44	33
-3	115	100
-4	51	-54
-5	111	92
-7	135	117

9,10,L

9	50	-44
7	78	-65
5	117	-112
3	77	-89
0	57	37
-1	90	-81
-2	45	-52
-3	80	-83
-4	43	-45
-5	54	-59
-6	129	117
-7	61	55
-9	90	87
-11	94	103

9,9,L

9	63	60
4	91	-106
3	78	83
0	64	-74
-1	45	-56
-5	43	-48
-7	48	-40
-8	51	31
-10	117	115

9,8,L

10	52	54
7	47	34
6	95	89
5	52	55
4	91	84
1	163	-172
0	154	-162
-1	53	58
-2	185	-193
-3	116	123
-4	56	-66
-6	119	-132
-7	57	-65
-8	92	96
-9	83	-80

9,7,L

7	92	89
6	168	187
5	84	76
4	147	181
3	142	-142
2	66	79
1	179	-205
0	99	104
-1	57	-71
-2	81	-93
-3	39	-9
-4	69	-60
-6	94	-90
-7	115	-117
-8	122	-118
-9	61	74
-10	105	-90
-12	52	-27
-13	52	-33

9,6,L

11	55	51
10	56	-61
9	108	110
7	119	127
6	103	-86
5	137	163
1	82	105
0	62	76
-1	44	-37
-2	157	169
-3	166	-177
-4	48	60
-6	66	63
-8	161	-165
-9	72	-68
-11	54	-55
-12	92	-94
-13	50	5

9,5,L

12	63	61
10	55	28
9	119	-116
7	88	-98
4	97	-106
3	197	239
2	86	-97
0	38	-63
-1	41	-59
-3	66	-59
-4	62	67
-5	139	138
-6	50	39
-7	166	156
-9	112	-98
-11	193	-193
-12	64	55
-13	92	-109

9,4,L

12	57	-60
9	123	-117
7	78	-76
6	57	42
3	102	-114
2	88	107
1	111	-131
-3	126	152
-4	55	63
-5	38	19
-7	185	168
-8	201	225
-9	57	61
-10	128	-115
-11	142	133
-12	82	-77
-13	80	76
-15	49	34

9,3,L

13	50	62
10	58	-63
9	49	39
6	107	-98
5	196	199
4	195	-197
3	113	-104
2	157	-197
0	73	101
-3	82	-77
-4	37	-11
-5	48	49
-7	123	102
-8	258	244
-9	68	66
-10	174	159
-11	117	120
-12	97	94
-13	45	-52
-14	67	71

9,2,L

12	51	61
11	99	-86
9	45	34
8	113	104
7	156	147
6	55	61
4	60	-46
3	98	-98
0	102	-138
-2	38	-44
-3	103	-102
-4	52	-52
-5	71	71
-7	55	-36
-8	152	-140
-9	163	162
-10	137	136
-12	88	91
-13	81	79
-14	53	53
-15	64	57

9,1,L

11	60	50
10	56	52
8	174	159
7	142	133
6	270	241
5	41	-16
4	139	128
3	99	78
2	80	-49
1	105	100
0	136	-150
-2	96	107

9,1,L

-3	150	99
-4	143	113
-5	86	-68
-6	181	172
-7	130	-116
-8	142	-127
-10	105	-96
-11	110	96
-13	102	100

9,0,L

11	190	161
7	149	142
5	76	99
3	46	64
1	199	174
-3	50	38
-5	112	105
-9	207	-191
-11	42	-32
-13	139	-128

8,13,L

4	45	-68
3	66	79
-1	52	45
-3	83	78
-4	44	36
-5	65	58

8,12,L

3	107	-103
1	68	-65
0	87	-71
-2	58	-61
-3	44	-16
-5	75	72
-7	67	74

8,11,L

4	72	-78
2	49	-38
1	56	-58
0	82	-85
-1	118	-120
-3	116	-117
-5	75	-74
-6	71	69
-8	72	67
-10	81	80

8,10,L

7	62	72
3	51	-44
2	60	-67
1	58	-54
0	111	-128
-2	75	-87
-3	47	-52
-4	72	-76
-5	96	-98
-6	145	-142
-7	45	32
-9	65	-36
-10	51	-51

8,9,L

8	112	108
6	127	114
0	78	84
-2	85	-81
-3	40	24
-5	75	-76
-6	67	-88
-7	154	-151
-10	121	-118
-12	86	-90

8,8,L

9	72	77
6	44	43
5	71	73
4	178	191
2	164	158
1	95	107
0	54	-41
-1	161	155
-2	67	79
-3	93	-103
-4	165	149
-5	120	-140
-6	143	132
-7	220	-218
-9	66	-63
-11	68	-58
-12	50	48

8,7,L

11	50	-66
10	50	-22
5	89	98
3	138	161
1	211	244
0	63	-65
-1	87	104
-3	177	188
-4	63	-64
-5	382	381
-6	239	-235
-7	145	144
-8	149	-147
-9	98	-92
-11	85	-101
-12	99	93

8,6,L

12	78	-92
7	41	22
5	108	-101
4	157	168
3	211	-211
2	223	253
1	224	-259
0	192	224
-1	253	-253
-2	88	97
-3	214	204
-5	157	155
-6	98	118
-7	109	103
-8	106	102
-9	69	58
-10	78	-76
-11	106	97
-12	74	-72
-13	79	72

8,5,L

12	66	-59
10	54	-56
8	155	-141
6	223	-224
5	100	93
4	207	-220
3	96	100
2	276	-326
1	59	57
0	46	-40
-1	203	-219
-2	77	-64
-3	240	-245
-5	135	-147
-6	235	239
-7	41	-12
-8	197	194
-9	97	-92
-10	53	36
-14	70	55
-15	52	41

8,4,L

12	76	74
11	101	-88
10	125	117
9	70	-51
8	50	43
6	177	-175
5	85	-100
4	252	-279
3	198	-206
1	237	-333
0	218	-277
-1	69	73
-2	331	-402
-3	92	111
-4	263	-271
-5	130	114
-6	355	-335
-7	38	-28
-9	49	12
-10	123	-135
-12	110	108
-14	72	73

8,3,L

13	88	70
11	53	54
10	115	110
9	201	184
6	169	168
5	295	-290
4	109	110
3	235	-256
2	67	47
1	136	-178
0	212	-234
-1	156	-183
-2	158	146
-3	119	-122
-4	132	122
-5	566	-522
-6	178	-165
-7	351	-338
-8	284	-283
-10	44	38
-12	103	91
-13	58	52
-14	52	-6

8,2,L

14	60	47
11	108	101

8,2,L

9	68	54
7	128	121
6	53	-27
5	117	110
3	263	250
2	208	-206
1	200	225
0	60	65
-1	324	-348
-2	410	403
-3	45	-57
-4	247	-218
-5	153	-153
-6	412	-393
-7	305	-296
-8	217	-208
-9	178	-170
-10	123	133
-12	81	-96
-13	59	-60
-14	53	-32
-15	73	-71
-16	67	57

8,1,L

13	54	-39
12	93	94
10	115	107
9	53	-34
8	234	199
7	42	-30
6	85	75
5	123	112
4	60	-21
3	513	461
2	52	20
1	212	206
0	209	266
-1	218	245
-2	246	233
-3	85	94
-4	159	-168
-6	53	-38
-8	264	-263
-9	89	93
-13	85	-86
-15	61	-60
-16	61	-56

8,0,L

14	133	-124
8	89	68
6	218	194
4	224	201
2	620	543
0	402	463
-2	79	-8
-4	401	380
-6	191	205
-8	165	158
-14	79	-75
-16	75	-76

7,14,L

2	63	37
-3	81	78

7,13,L

3	54	32
1	51	-17
-1	44	-42
-2	76	59
-3	104	-100
-4	65	58
-6	65	65

7,12,L

2	68	-62
1	58	46
0	146	-136
-1	91	91
-2	105	-103
-3	42	-27
-4	137	-130
-6	64	-19
-8	49	-23

7,11,L

8	80	88
6	107	111
4	98	90
3	57	-40
2	47	48
0	107	112
-1	113	-101
-2	75	69
-3	49	-52
-4	48	-25
-5	101	-94
-8	94	-99
-10	57	-66

7,10,L

9	74	78
8	74	-70
7	71	62
5	89	76
2	43	-37
1	92	94
0	41	51
-1	152	139
-2	155	154
-3	59	44
-5	100	-101
-6	49	-47
-7	49	-62
-9	70	-69
-11	90	-111

7,9,L

11	97	-90
10	58	46
9	88	-85
8	60	53
7	80	65
4	51	-50
2	97	-103
1	117	104
0	130	128
-1	246	250
-2	73	63
-3	81	96
-4	56	51
-5	60	53
-6	160	-160
-7	57	44
-9	74	70
-10	125	-121
-12	46	-41

7,8,L

12	46	-41
10	65	-61
7	61	-57
6	91	-85
5	153	-148
4	69	70
3	49	6
2	199	195
1	88	92
0	339	328
-1	101	84
-2	103	108
-4	133	119
-5	54	53
-6	180	171
-7	48	-34
-8	133	127
-9	64	70
-13	83	89

7,7,L

12	61	-66
10	74	-73
8	163	-183
7	117	-115
6	120	-124
5	66	53
4	117	-120
3	140	136
1	300	278
0	128	-123
-2	119	-109
-3	126	110
-4	114	-104
-5	103	105
-6	404	395
-8	70	82
-9	66	-54
-10	168	168
-12	77	77
-14	50	39

7,6,L

12	101	98
11	80	-90
9	188	-188
8	62	-51
7	74	-77
6	63	54
5	108	-120
4	168	146
3	181	-173
2	370	338
1	59	-60
0	67	-61
-2	247	-225
-3	85	98
-4	180	-161
-5	62	58
-6	103	-92
-7	246	253
-9	82	81
-10	47	0
-11	70	71
-14	51	29

7,5,L

13	60	78
11	77	92
10	58	-20
9	144	148
8	75	-57

7,5,L

7	46	30
5	55	-52
4	86	-76
3	69	-72
1	67	-82
0	336	308
-2	39	-10
-3	285	-271
-4	213	193
-5	347	-329
-7	114	110
-8	59	58
-10	125	-131
-11	55	34
-12	72	-60
-13	51	38

7,4,L

10	56	50
9	146	130
8	56	46
5	79	82
4	73	59
3	127	122
2	226	-233
1	193	185
0	85	-84
-1	202	-180
-2	264	-246
-3	123	-139
-4	48	-48
-7	94	-83
-9	308	-311
-10	93	102
-11	173	-179
-13	125	-133

7,3,L

14	48	1
13	88	-71
10	92	81
9	89	-98
8	91	84
7	226	-211
6	86	98
5	84	-84
4	141	137
3	479	453
2	367	353
1	232	-209
0	93	86
-1	91	92
-2	344	295
-3	158	134
-4	341	-325
-5	348	350
-6	185	-184
-7	115	-137
-8	291	-299
-9	64	67
-11	46	30
-12	57	-68
-13	46	51
-14	102	-107

7,2,L

14	128	-125
13	53	47
11	83	77
10	72	-76
9	213	-203
8	244	-240
7	48	50
6	300	-284
5	224	209
4	161	-148
3	84	-84
2	603	561
1	447	-402
0	268	268
-1	79	75
-2	296	273
-3	303	242
-4	309	300
-6	105	108
-7	71	-72
-8	80	-78
-9	71	70
-10	93	105
-11	64	-73
-15	57	-66
-16	49	-51

7,1,L

11	142	-136
10	242	-242
9	75	-72
8	272	-267
6	91	-99
5	79	79
4	47	-32
3	47	-48
2	497	-469
1	352	336
0	190	-179
-2	161	-159
-3	150	143
-4	320	283
-6	141	119
-7	264	269
-8	250	248
-16	60	54

7,0,L

13	42	-31
11	181	-167
9	282	-277
7	388	-360
5	122	107
3	73	-73
1	142	127
-1	95	88
-3	518	-462
-5	413	393
-7	459	444
-9	142	153
-11	176	189
-13	90	107
-15	69	102

6,14,L

2	66	-49
0	141	-141
-1	47	43
-2	135	-138
-4	50	-44

6,13,L

5	52	-35
4	65	50
0	52	48
-1	137	-128
-2	52	28
-3	171	-158

6,12,L

5	156	136
4	71	-75
3	186	169
2	44	-25
1	60	61
-1	49	-49
-3	52	-34
-4	100	-92
-7	82	-72

6,11,L

9	53	-47
6	50	50
5	58	-58
4	41	25
2	71	64
1	52	54
0	74	64
-1	84	87
-3	88	82
-4	50	-32
-6	67	-65
-8	75	-68
-11	57	-58

6,10,L

8	57	40
5	52	38
4	78	78
1	131	-126
0	62	60
-1	83	64
-3	133	125
-4	166	152
-6	57	54
-8	81	73
-12	64	-65

6,9,L

11	69	-70
10	111	-117
8	100	-98
7	101	-86
6	52	7
2	158	-157
0	60	-58
-1	60	-52
-2	44	48
-3	93	-91
-4	140	147
-6	67	58
-7	102	108
-8	56	-60
-9	80	79
-10	48	27

6,8,L

11	80	-72
10	43	2
9	52	-46
6	78	-72
5	173	-178
4	168	-164
3	147	-145
2	54	63
1	38	-6
0	115	-102

6,8,L

-3	113	116
-5	144	144
-8	158	158
-10	45	33
-11	58	56

6,7,L

11	91	98
7	41	-67
5	159	-150
2	80	69
1	147	-143
0	91	-104
-1	94	-90
-2	209	-178
-3	159	-152
-4	115	116
-5	106	-100
-6	291	295
-9	95	83
-10	145	-137
-11	79	65
-12	49	-48
-13	74	65

6,6,L

12	70	71
11	41	8
10	44	48
9	96	96
8	66	80
7	48	38
5	236	233
4	157	-155
2	256	-234
1	114	112
0	158	-157
-1	104	-104
-2	67	-82
-3	53	-40
-4	43	21
-6	95	-102
-8	147	-152
-9	199	-194
-10	161	161
-11	178	-167
-12	86	67
-13	107	-118

6,5,L

11	44	-39
10	118	107
9	110	119
8	152	158
7	130	131
6	347	333
5	102	94
4	296	295
3	112	-108
2	167	165
1	134	-117
-1	65	58
-2	53	43
-3	106	105
-4	224	-218
-5	93	85
-6	218	-217
-7	44	31
-10	70	-79
-11	103	101
-12	139	-144
-13	57	-53
-14	101	-112

6,4,L

14	57	-62
12	119	-107
11	82	92
10	46	-17
9	61	-52
8	42	47
7	143	148
6	82	-85
5	159	155
4	86	-70
3	275	254
2	370	319
1	179	171
0	148	141
-1	243	214
-2	115	94
-3	207	-195
-4	45	51
-5	201	-190
-7	178	-169
-8	61	63
-11	58	-65
-12	179	-183
-13	47	-47
-14	88	-108

6,3,L

13	90	-84
10	63	-76
9	76	72
8	53	55
7	77	68
6	270	-254
5	231	-203
4	189	183
3	113	128
2	298	-268
1	132	141
0	125	-119
-1	230	210
-3	660	604
-5	461	450
-6	142	138
-7	88	-85
-8	60	46
-9	48	-42
-10	108	-109
-11	119	-124
-12	43	-24
-13	76	-79
-14	50	29
-15	106	-100

6,2,L

11	57	-65
10	41	36
6	41	-49
5	96	-103
4	83	91
3	383	-351
2	200	195
1	351	-336
0	257	-248
-1	79	-69
-2	204	187
-3	107	109
-4	206	197
-5	581	549
-6	219	210
-7	222	221
-9	135	145
-10	42	20
-11	51	-47
-12	111	117
-14	65	-55
-15	71	72

6,1,L

13	63	63
12	65	-61
10	142	-139
9	72	70
8	188	-177
7	75	65
6	44	32
5	142	-139
4	527	-499
3	319	-280
0	173	-158
-1	400	-385
-2	137	146
-3	57	62
-4	281	250
-5	97	96
-6	70	-71
-7	114	112
-8	53	59
-9	83	72
-11	110	104
-13	103	119
-14	98	110
-15	83	78
-16	49	33

6,0,L

14	90	85
10	122	126
8	254	241
6	72	-55
4	449	-391
2	734	-660
0	582	553
-2	112	139
-4	355	332
-8	129	109
-10	39	12
-12	167	161
-14	215	223
-16	90	99

5,14,L

4	56	-69
3	107	114
0	47	-23
-3	53	-56

5,13,L

6	64	57
5	43	15
4	54	19
2	87	79
-1	84	83
-2	43	-28
-3	112	116
-4	60	-59
-5	87	100
-7	75	74
-8	72	-67

5,12,L

6	81	-74
4	61	52
3	90	-93
2	154	143
0	162	157
-1	43	37
-2	168	161
-4	137	126
-6	90	84
-7	49	40
-8	67	67

5,11,L

5	54	35
4	136	-140
2	280	-273
1	64	64
0	68	-54
-1	59	42
-2	61	39
-3	62	-44
-4	108	118
-6	77	74
-8	101	102
-10	79	94

5,10,L

11	94	-88
9	129	-116
7	103	-105
6	69	-63
5	107	-94
1	43	25
0	143	-139
-1	93	-82
-2	224	-232
-4	83	-85
-5	100	101
-6	126	-126
-7	141	152
-9	131	119
-11	126	135
-12	45	56

5,9,L

11	110	122
10	73	-70
7	147	-150
6	49	-62
5	196	-190
4	69	62
3	177	-189
2	61	-65
1	401	-403
0	106	-106
-1	271	-279
-2	91	92
-3	124	-123
-4	79	80
-5	84	-82
-6	84	77
-7	215	-217
-8	43	-5
-9	122	-120
-11	52	48
-12	50	74

5,8,L

11	56	50
9	61	51
8	73	81
7	119	132
6	90	-76
5	288	277
4	315	-320
2	350	-361
1	113	-115
0	500	-497
-1	78	-79
-2	74	-79
-4	128	-120
-5	66	-62
-6	64	-63
-8	185	-183
-11	59	-59

5,7,L

12	102	103
10	182	201
9	132	129
8	43	59
7	120	128
6	270	268
5	208	-207
4	229	214
3	235	-228
2	93	86
1	119	119
0	63	62
-4	231	-252
-5	59	-42
-6	288	-290
-7	103	94
-8	63	-71
-10	150	-152
-11	66	63
-12	65	-60
-14	77	-82

5,6,L

14	51	-80
13	44	31
12	79	-86
11	116	129
10	49	-38
9	43	43
8	54	-46
7	193	201
5	305	293
4	106	-82
3	207	200
2	157	144
1	88	-81
0	399	404
-1	148	-133
-2	158	163
-3	54	-58
-4	235	217
-5	120	-124
-6	94	93
-7	343	-358
-8	119	105
-9	177	-190
-10	77	82
-15	63	-55

5,5,L

13	48	-32
12	66	58
11	59	-59
9	63	-68
8	48	-28
7	180	-174
6	106	-96
5	60	63
4	203	192
3	415	424
2	280	-257
1	418	402
0	61	50
-1	855	810
-2	240	237
-3	570	540
-4	245	-211
-5	40	-27
-6	97	-106
-8	153	-159
-9	252	267
-10	161	169
-11	130	144
-13	49	-43
-15	83	-90

5,4,L

9	204	-206
8	56	-46
7	165	-167
6	89	-72
5	161	-169
3	311	-283
2	160	-139
1	353	-328
0	319	300
-1	380	371
-2	639	596
-3	105	-85
-4	98	-100
-5	51	-52
-6	157	158
-7	151	143
-8	133	118
-9	375	377
-11	97	101
-12	45	0
-13	65	66
-14	110	-117
-15	57	58

5,3,L

15	46	34
14	58	-37
12	69	-65
10	90	-92
8	205	-208
7	149	149
5	428	-403
4	55	-65
3	599	-583
2	53	57
1	113	-111
0	597	-527
-1	475	-442
-2	551	-502
-3	568	-519
-4	136	-131
-5	479	-463
-6	287	266
-8	515	517
-9	56	-60
-10	154	164
-11	140	-152
-12	94	105
-14	77	76
-15	58	57

5,2,L

14	65	56
9	188	188
8	229	237
7	264	-268
6	146	147
5	122	-115
4	513	-469
3	329	289
2	989	-938
1	144	140
-1	481	-436
-2	836	-777
-3	232	-210
-4	487	-444
-5	120	-83
-6	605	-586
-7	146	133
-8	165	-176
-9	100	-99
-12	69	53
-13	75	88
-14	105	125
-16	97	100

5,1,L

13	101	99
12	120	131
11	74	-70
10	178	180
9	64	84
8	130	127
6	107	106
5	64	-55
4	158	146
3	760	-717
2	281	271
1	1356	-1353
0	657	647
-1	576	-589
-2	466	-423
-3	141	-140
-4	636	-606
-5	227	-221
-6	267	-269
-7	440	-426
-8	239	-244
-9	75	-77
-10	157	-166
-11	104	-125
-12	76	-79
-15	72	76
-16	45	3

5,0,L

15	47	41
13	105	105
11	216	227
9	204	204
7	315	317
5	492	449
1	249	252
-1	453	456
-3	971	-938
-5	943	-907
-7	86	-83
-9	208	-232
-11	231	-241
-13	135	-135
-15	57	-39

4,14,L

2	82	87
0	106	103
-2	102	93
-3	50	-35
-6	51	58

4,13,L

4	102	-79
1	158	155
-1	135	143
-2	50	-26
-3	63	60
-5	60	56
-8	49	43

4,12,L

6	107	102
5	101	-101
4	89	84
3	111	-111
2	118	116
0	80	88
-2	104	99
-4	94	85
-5	45	23
-7	131	132
-9	115	114

4,11,L

10	50	-82
8	58	-62
6	139	-146
5	59	69
3	115	123
2	59	-62
1	105	115
0	156	149
-1	61	-62
-3	111	-113
-4	69	-68
-5	98	-94
-6	48	62
-7	58	-54
-8	72	81
-9	57	-37
-11	87	92

4,10,L

10	129	111
9	55	43
8	127	118
7	117	-110
6	148	-149
4	196	-189
3	108	118
1	151	159
0	59	58
-2	76	-59
-4	96	-101
-5	98	98
-6	65	-71
-8	113	-105
-12	77	79

4,9,L

12	45	21
11	44	39
10	129	130
6	188	180
5	61	-62
4	308	299
3	65	67
2	189	196
1	120	-109
0	276	-278
-1	224	-225
-2	209	-218
-6	115	114
-10	125	-132
-13	46	32

4,8,L

12	73	-61
11	68	77
10	87	-88
8	102	-102
7	268	265
6	46	51
5	189	185
3	214	211
2	50	54
1	58	53
0	53	-34
-2	80	-76
-3	81	-94
-4	85	-76
-5	210	-211
-6	145	-143
-7	138	-130
-8	158	-154
-13	46	-41

4,7,L

11	163	-163
10	49	-61
8	106	100
7	97	-92
6	125	125
5	53	-47
4	61	60
2	108	103
1	153	169
0	233	233
-1	178	184
-2	133	132
-3	137	136
-4	137	-129
-5	76	76
-9	161	-157
-10	162	180
-11	129	-126
-12	89	-85
-13	64	-39

4,6,L

14	47	-49
11	71	-60
10	42	-64
8	228	-232
7	273	-277
6	91	-83
5	65	-73
4	129	124
2	294	273
1	42	32
0	378	368
-1	98	-87
-2	121	-137
-4	201	200
-5	100	112
-6	175	170
-7	150	147
-8	41	-17
-9	151	158

4,6,L

-10	135	-124
-11	134	149
-12	110	-110
-14	48	-65

4,5,L

12	75	74
11	80	59
10	56	-53
9	186	-176
8	260	-254
7	124	120
6	307	-315
5	91	95
4	60	-69
3	217	206
2	38	-41
1	196	-195
0	131	-96
-2	180	179
-3	154	143
-4	381	365
-5	100	103
-6	186	173
-7	108	-111
-8	188	203
-9	50	61
-10	140	143
-12	169	183
-14	84	87

4,4,L

15	44	23
14	64	51
12	138	127
11	41	19
10	77	-74
9	222	-235
8	316	314
7	238	-254
6	158	155
5	143	127
4	298	276
3	336	294
2	164	-152
1	58	-46
0	86	59
-1	168	190
-2	139	150
-3	388	-327
-5	66	-58
-7	387	387
-8	74	67
-9	195	205
-10	151	139
-11	103	108
-12	127	132
-13	68	84
-14	72	72
-16	93	106

4,3,L

15	87	80
14	62	24
13	94	82
12	63	-60
11	165	-162
10	89	-90
9	134	129
8	99	92
7	114	109
6	241	238
4	54	-55
2	305	283
1	250	219
-2	275	-280
-3	193	-178
-4	145	-130
-5	136	-129
-6	110	-110
-7	123	-132
-8	39	68
-9	44	-70
-10	73	-71
-13	178	197
-14	48	-61
-15	147	160
-16	50	30

4,2,L

13	63	76
12	230	-234
11	69	-73
9	155	150
8	73	-59
7	281	271
6	163	163
5	543	522
4	352	-322
2	503	463
1	295	313
0	579	-547
-1	72	-59
-2	280	-307
-3	259	247
-4	277	265
-6	41	-57
-7	95	-90
-8	47	43
-9	267	-265
-10	93	-82
-11	103	-122
-12	52	-70
-13	64	-81
-14	108	126

4,1,L

13	112	-109
12	135	140
11	93	-98
9	193	-192
8	192	188
6	115	112
4	246	245
3	262	-250
2	394	-366
1	359	346
0	340	298
-1	278	-268
-2	378	-355
-3	72	-57
-4	51	52
-5	325	338
-6	321	-323
-8	90	-80
-9	119	-109
-12	114	-127
-13	141	-152
-14	69	-67
-15	46	-24

4,0,L

14	92	-91
12	129	-143
10	442	-461
6	133	-139
4	95	76
2	430	-406
0	478	-488
-2	189	-165
-4	407	-368
-6	194	202
-8	315	-306
-10	170	-170
-12	95	-94
-14	163	-185
-16	46	0

3,15,L

1	53	67
-1	89	77

3,14,L

5	79	-87
3	72	-80
2	78	77

3,13,L

8	87	-89
6	65	-71
5	75	-73
4	55	-45
3	68	-63
2	138	-138
0	69	-62
-1	51	-57
-3	48	-37
-5	87	-80
-6	47	52
-7	54	-59
-8	54	71

3,12,L

9	53	-62
7	121	-111
6	50	-39
5	70	73
4	116	-100
3	86	93
2	53	-57
1	112	-105
-1	125	-125
-2	154	-153
-4	160	-159
-5	118	122
-6	116	-116
-8	60	-55

3,11,L

10	56	65
9	95	101
7	67	65
4	67	67
3	175	-173
2	47	44
1	153	-159
0	50	-47
-2	41	-41
-3	86	77
-4	51	32
-5	116	-113
-6	67	-66
-8	148	-158
-9	59	-44

3,11,L

-10	75	-93

3,10,L

10	47	36
9	75	83
8	124	128
7	165	160
6	131	128
5	105	108
2	50	47
-1	95	-102
-2	89	87
-3	126	-139
-4	50	47
-5	179	-188
-6	55	58
-9	116	-129
-10	81	-67
-11	67	-68
-12	90	-102

3,9,L

8	57	70
6	59	-40
5	174	178
4	96	91
3	457	450
2	184	183
1	360	367
0	52	26
-1	248	252
-2	134	130
-4	179	-176
-6	109	-107
-9	63	-65
-11	90	-90

3,8,L

13	52	-48
12	61	-73
11	74	-78
10	98	-107
9	73	-82
8	41	-24
7	245	-242
6	307	303
5	158	-152
4	201	201
3	135	-134
2	58	62
1	84	-82
0	230	246
-1	107	113
-2	161	164
-3	199	206
-4	384	395
-5	158	161
-7	47	-29
-9	44	-35
-10	140	-141
-11	45	-44
-12	108	-112
-14	65	-64

3,7,L

12	108	-110
10	86	-83
9	95	-118
8	210	-208
7	88	83
6	179	-190
4	236	-236
3	127	-119
1	183	-177
-1	90	79
-2	163	-156
-3	209	211
-4	190	198
-6	332	352
-7	143	-154
-8	329	355
-9	154	145
-10	101	115
-11	59	-54
-13	111	-105

3,6,L

12	72	79
9	112	-118
8	88	80
7	198	-195
6	219	-213
5	77	-90
4	49	-50
3	244	-240
2	228	-242
1	98	-90
0	483	-499
-1	110	119
-3	259	-229
-4	327	-319
-5	349	347
-6	52	-69
-7	551	569
-8	226	-241
-9	128	119
-10	98	119
-12	60	56
-14	60	78
-15	51	49

3,5,L

12	101	94
11	43	47
10	133	-123
9	140	141
7	47	43
6	213	-204
5	68	-77
4	171	175
3	386	-391
2	80	-85
1	565	-558
0	46	25
-1	813	-789
-2	103	100
-3	461	-434
-4	38	-45
-5	203	190
-6	59	-67
-7	122	-122
-8	46	54
-9	294	-316
-10	168	-177
-13	157	166
-15	114	130

3,4,L

12	57	-55
11	93	101
10	241	255
9	213	214
8	54	61
7	185	189
6	64	-70
5	239	257
4	367	-358
3	274	251
2	278	-305
1	483	465
0	51	17
-1	321	310
-3	554	540
-4	149	134
-5	222	-231
-6	237	-234
-7	358	-368
-8	76	-84
-9	160	-177
-10	307	-334
-12	92	89
-14	86	84

3,3,L

14	53	52
10	262	259
9	90	-85
8	210	220
7	106	113
6	77	86
5	365	352
4	136	-126
3	520	512
2	73	-63
1	322	312
0	457	452
-1	169	-152
-2	532	519
-3	661	631
-4	59	38
-5	295	298
-6	353	-358
-8	157	-177
-9	155	-157
-10	152	-168
-12	135	-164
-13	79	-92

3,2,L

16	58	-65
15	46	-29
13	73	80
12	55	-39
11	40	21
10	60	-65
9	248	256
8	115	121
7	81	76
6	243	227
5	319	-319
4	696	686
3	82	-61
2	917	939
1	604	-576
0	115	-110
-1	1221	1250
-2	424	415
-3	492	478
-4	298	281
-5	286	-297
-6	407	410
-7	217	-204
-8	202	-191
-9	190	190
-11	61	-63
-12	68	-76

3,2,L

-14	132	-159
-15	50	-51
-16	135	-151

3,1,L

15	82	-81
14	52	-74
13	58	-68
12	47	-49
11	103	-108
10	40	19
9	61	60
8	192	-195
7	259	264
5	598	579
4	167	150
3	317	305
2	481	-461
1	1359	1441
0	92	-82
-1	279	-276
-2	1207	1233
-3	104	98
-4	508	466
-5	370	374
-6	335	343
-7	142	159
-9	46	-54
-10	208	223
-12	113	130
-13	79	-97
-14	46	-40
-15	64	-73
-16	46	-34

3,0,L

13	129	-126
9	570	-593
7	796	-782
5	240	-232
3	510	462
1	350	338
-1	919	-927
-3	667	668
-5	370	337
-7	280	270
-9	83	98
-11	168	194
-13	70	-75

2,15,L

1	48	-21
-2	52	34

2,14,L

4	89	-92
2	90	-98
0	79	-77
-1	49	50
-2	55	-55
-3	63	68
-5	59	71
-6	74	-64

2,13,L

5	69	-63
4	61	68
3	141	-144
1	112	-109
-1	94	-86
-2	58	-54
-4	44	52
-6	60	-19

2,12,L

9	69	78
7	67	63
6	64	-65
5	56	47
1	48	7
0	43	-55
-2	58	-60
-4	77	80
-5	61	-58
-6	109	109
-7	119	-118
-9	100	-115
-10	61	58

2,11,L

11	59	-53
8	62	78
6	113	115
5	95	74
4	107	106
1	95	-83
0	172	-175
-1	96	104
-2	113	122
-3	141	147
-4	87	-86
-5	255	263
-6	56	-62
-7	90	83
-8	67	-72
-9	64	27

2,10,L

12	74	-81
10	73	-62
9	69	-67
7	55	-63
6	116	118
5	89	-100
3	209	-222
2	64	57
0	300	314
-1	164	152
-2	369	360
-3	108	-115
-4	106	115
-5	137	-149
-6	52	-50
-8	45	-5
-9	59	68
-11	64	49

2,9,L

10	96	-93
8	133	-133
7	181	183
6	290	-299
5	90	-86
4	354	-371
3	78	-87
2	148	-153
1	165	161
0	201	193
-1	156	141
-2	108	108
-3	255	249
-4	147	143
-6	122	119
-8	174	192
-10	54	50
-11	61	-57
-12	60	47

2,8,L

13	84	80
12	48	57
11	97	-94
10	109	116
9	219	-222
8	120	116
7	265	-279
5	141	-163
4	44	-58
3	49	-55
2	194	-190
1	61	-54
0	276	-275
-1	80	-68
-2	199	-193
-3	54	-44
-4	193	-207
-5	150	164
-6	68	65
-7	227	238
-9	194	209
-10	64	73
-11	133	146
-12	42	-13
-13	62	63

2,7,L

13	114	115
12	62	63
10	105	-100
9	154	149
8	184	-183
7	139	151
6	87	-91
5	150	-149
3	271	-277
2	185	-186
1	169	-174
0	70	-53
-1	177	-178
-2	89	-81
-3	503	-512
-4	76	-82
-5	180	-194
-6	165	-168
-7	230	-246
-9	43	51
-10	100	114
-11	93	92
-12	78	75
-13	66	72

2,6,L

14	61	78
12	63	68
11	140	138
9	91	93
7	61	74
6	99	100
4	120	-138
2	117	-133
1	166	172
-1	220	210
-2	764	-734

2,6,L

-4	512	-514
-5	75	-64
-6	102	99
-7	187	-208
-8	176	175
-9	73	-73
-11	151	-164
-12	47	60
-13	51	-23
-14	61	55

2,5,L

14	73	-66
13	44	-10
11	43	-41
10	152	171
9	47	-27
8	246	260
7	97	83
6	128	-122
5	80	-65
4	236	-220
3	538	-504
2	295	276
1	186	184
0	414	388
-1	535	-513
-2	106	-108
-3	100	109
-4	553	-555
-5	140	145
-6	142	-141
-7	297	309
-8	322	-326
-9	96	-104
-10	243	-269
-11	46	53
-12	117	-111
-14	63	-58

2,4,L

15	54	-55
13	52	-55
12	87	-78
9	367	397
7	51	55
6	163	-143
5	390	-357
4	144	-111
3	53	-50
2	297	301
1	205	-215
0	244	249
-1	101	89
-2	287	286
-4	651	637
-5	472	-465
-6	330	351
-7	37	-45
-9	129	-138
-12	47	49
-13	46	-25
-14	58	-73
-15	73	-62
-16	58	-66

2,3,L

16	50	-42
15	91	-98
11	66	-66
10	291	297
8	298	-301
7	113	-115
6	134	-129
5	150	-142
4	262	-248
3	158	177
2	88	-104
1	386	400
0	427	433
-1	368	380
-2	389	-394
-3	58	63
-4	401	387
-5	174	181
-7	100	105
-8	127	141
-9	196	214
-10	263	279
-11	45	-7
-12	99	114
-13	64	-73
-14	70	53
-15	88	-98

2,2,L

16	51	-30
15	56	29
11	127	-144
10	209	-214
9	374	-396
8	167	173
7	439	-439
6	393	404
5	258	-249
3	172	175
2	205	-196
1	341	-316
0	55	40
-1	1326	-1448
-2	234	-235
-3	40	-35
-4	105	-89
-5	521	494
-6	324	-307
-7	201	209
-9	125	138
-10	126	138
-11	126	138
-13	88	95
-15	78	92
-16	58	-39

2,1,L

16	67	66
15	110	127
13	165	173
11	223	231
10	292	-308
9	112	-114
8	239	-246
7	60	-61
6	755	-746
5	413	401
4	450	-475
3	532	541
1	544	-547
0	317	300
-1	924	-949
-2	755	755
-3	1139	-1185
-4	357	-359
-5	179	-180
-6	620	606
-9	53	-55
-10	241	262
-12	145	164

2,0,L

14	113	123
12	388	409
10	422	436
8	188	-158
6	288	-272
4	767	-767
2	52	-52
-4	101	-119
-6	98	77
-8	213	-231
-10	48	-28
-12	50	-49
-15	43	27

1,15,L

1	69	-64
-1	67	-78
-3	52	-42

1,14,L

5	112	118
4	53	-19
3	100	100
2	84	-89
1	60	65
0	121	-106
-1	69	-64
-2	62	-70
-3	64	-57
-5	115	-104

1,13,L

8	107	104
6	73	82
4	139	138
3	47	57
2	131	126
-4	144	-139
-6	72	-73
-8	54	-66

1,12,L

9	65	82
8	52	-49
6	65	65
4	123	122
3	52	68
2	47	51
1	149	146
-2	62	49
-3	142	-143
-4	131	122
-5	56	-71
-6	59	68
-8	61	-47

1,11,L

9	56	-67
8	52	-52
6	48	-43
5	86	88
3	197	193
1	133	136
0	59	58
-2	84	81

1,11,L

-3	199	198
-5	123	113
-7	78	73
-8	102	110

1,10,L

11	72	-62
10	49	-27
9	107	-108
8	47	25
7	73	-52
3	112	-113
2	99	-84
1	213	-208
0	59	64
-1	109	108
-2	131	120
-3	276	280
-5	101	102
-6	117	129
-7	66	66
-8	55	75
-9	105	108
-12	76	83

1,9,L

13	106	121
11	49	34
10	54	-42
9	78	81
8	42	-59
7	66	62
6	47	-43
5	98	-101
4	67	68
3	81	-74
2	89	-78
0	40	-36
-1	115	-110
-2	146	-155
-3	168	-161
-4	68	63
-5	51	34
-6	45	-45
-7	170	169
-8	88	92
-9	239	255
-10	118	123
-11	65	69
-13	98	90

1,8,L

14	110	120
12	60	65
11	53	51
10	60	54
9	113	103
8	88	-84
7	80	78
5	142	149
4	97	95
3	281	290
1	49	26
0	123	-114
-2	350	-349
-3	127	-127
-4	143	153
-5	246	-259
-6	83	73
-7	135	-137
-12	64	67
-13	51	54
-14	143	160

1,7,L

13	46	30
12	125	127
10	42	12
9	101	-92
8	132	129
7	75	-68
6	246	251
5	108	101
4	183	186
3	58	67
2	175	179
0	159	-152
-1	391	-387
-2	53	58
-3	62	-63
-4	266	-275
-5	116	107
-6	176	-183
-8	185	-210
-9	224	-216
-10	60	-68
-12	78	-79
-14	54	-59

1,6,L

11	50	65
10	140	-151
9	233	243
8	152	160
6	86	75
4	136	121
3	58	58
2	235	256
1	189	177
0	140	-119
-1	286	265
-2	144	-126
-3	40	-50
-5	406	-419
-6	174	167
-7	248	-252
-8	195	201
-9	104	-106
-10	115	-130
-11	81	66
-13	71	-80
-14	116	-125

1,5,L

13	151	-144
12	140	-155
11	125	-136
10	128	132
7	80	66
6	158	155
5	233	248
4	123	132
3	266	-245
2	41	14
1	79	-64
0	64	55
-1	226	223
-2	462	-452
-3	61	-32
-4	321	313
-5	49	-40
-6	105	-99
-7	236	235
-8	49	-64
-9	113	122
-10	72	67
-11	194	-203
-12	102	101
-13	194	-197
-14	63	72
-15	109	-118

1,4,L

15	44	-44
13	170	-183
12	185	-201
11	150	-154
9	42	-58
8	59	-57
6	92	105
5	149	-152
3	150	-147
2	80	74
1	632	-610
0	401	394
-1	648	-632
-2	396	393
-3	323	335
-4	171	-158
-5	70	71
-6	241	-218
-7	188	200
-8	152	152
-10	213	222
-12	160	-172
-13	135	150
-14	72	-78
-15	58	71
-16	61	-57

1,3,L

14	69	-65
13	51	-12
12	137	-137
10	222	-221
9	44	-55
8	62	-66
7	93	90
6	197	-210
5	286	265
3	654	657
2	73	-83
1	193	-201
0	1018	-1046
-1	552	566
-2	722	728
-3	95	-86
-4	60	61
-5	438	425
-6	212	223
-7	162	170
-8	225	256
-10	97	112
-11	137	149
-13	78	85
-14	61	72
-15	53	73
-16	76	72

1,2,L

14	105	121
12	212	224
11	149	-157
10	89	-103
9	164	-173
8	279	-281

1,2,L

7	213	-229
6	294	-302
5	218	221
3	91	-111
2	1029	1061
1	566	-571
0	673	-694
-1	314	-317
-2	560	-576
-3	633	649
-4	128	-132
-5	563	552
-6	320	299
-7	274	-262
-8	188	196
-9	40	-11
-10	140	140
-12	57	57
-14	149	160
-15	91	98
-16	126	137

1,1,L

15	150	136
14	55	-64
13	57	47
12	48	-36
11	221	229
10	173	183
9	195	190
8	238	257
7	301	277
6	99	-101
5	171	176
4	57	-57
3	1076	-1146
2	504	-505
1	636	-660
-1	281	-279
-2	202	211
-3	855	866
-4	227	-228
-5	623	604
-6	502	-492
-7	212	197
-8	211	-201
-9	243	260
-10	191	-203
-11	103	102
-13	55	39
-14	96	118
-15	141	141
-16	43	29

1,0,L

15	91	-97
13	169	-176
11	165	171
9	192	194
7	808	795
5	394	367
3	943	952
1	407	409
-1	570	-556
-5	453	-469
-7	271	278
-9	99	100
-11	140	-154
-13	74	83
-15	78	76

0,14,L

5	54	45
4	83	94
3	79	75
2	59	49
0	131	125

0,13,L

4	62	-63
3	83	88
2	55	-47
1	110	107

0,12,L

7	115	-115
5	83	-76
4	192	-205
1	82	-78

0,11,L

9	63	-54
8	52	-55
6	86	-87
5	106	-114
4	65	-53
3	247	-252
2	57	60
1	150	-154

0,10,L

9	70	73
5	122	132
3	44	49
2	387	-389
1	61	71
0	357	-356

0,9,L

12	47	49
10	160	154
9	104	-101
8	257	274
7	66	-77
6	293	313
4	164	178
1	155	-164

0,8,L

13	76	83
11	168	175
10	147	-144
9	254	265
7	181	186
6	199	203
4	322	327
3	232	226
2	395	408
1	63	-59
0	218	212

0,7,L

13	78	-81
11	51	30
10	133	139
8	213	215
5	313	319
4	243	-233
3	193	188
2	52	60
1	682	675

0,6,L

14	132	-131
13	83	-93
11	137	-149
10	102	110
8	56	-51
4	101	105
3	470	-457
2	520	515
1	250	240
0	290	289

0,5,L

13	44	-12
12	124	-129
11	102	101
10	211	-220
9	103	-102
8	330	-351
7	91	-100
5	162	-151
4	261	234
3	179	164
2	580	-572
1	152	137

0,4,L

16	44	55
14	108	118
12	81	-77
11	106	-100
10	159	-172
9	243	-261
8	219	-231
7	313	296
6	184	-181
4	429	-433
3	330	-319
2	926	-928
1	1059	-1072
0	264	-286

0,3,L

15	93	99
14	66	57
13	50	69
12	113	116
10	143	152
8	178	182
7	201	-191
5	244	-252
4	154	150
3	511	-530
1	326	-319

0,2,L

14	72	-67
13	86	95
12	125	134
11	279	299
10	54	50
9	346	364
8	62	-54
7	499	499
6	258	242
5	82	75
4	76	-73
3	299	-287

0,2,L

2	465	460
1	213	228

0,1,L

15	95	-95
12	90	90
11	131	-143
8	239	238
7	317	308
6	916	903
5	177	208
4	872	882
3	286	291

0,0,L

16	53	-70
14	72	-76
12	55	-64
10	76	82
8	279	244
6	306	-273
4	231	-224
2	1021	1068

APPENDIX 6

Structure Factor List for Compound XXV,

Part II, p.[illegible].

Columns listed are l, $|F_o|$ x10, $|F_c|$ x10, [illegible],

APPENDIX 6

Structure Factor List for compound XXV ,

Part II , p.84 .

Columns listed are ℓ , $|F_o|$ x10 , $|F_c|$ x10 , α .

0.26,L

1	71	63	72

0.24,L

5	59	64	327

0.23,L

5	51	45	111
4	64	87	165
3	44	52	78
2	44	57	335
0	59	46	180

0.22,L

7	44	51	301
4	88	96	356
1	68	72	213
0	111	114	0

0.21,L

7	45	51	240
6	78	79	187
2	82	84	137
0	70	74	180

0.20,L

7	63	66	118
4	75	82	141
3	73	78	89
1	70	75	22

0.19,L

8	48	42	52
7	76	77	293
6	82	84	17
4	43	43	30
1	82	84	202
0	72	73	0

0.18,L

10	53	58	118
8	52	52	151
5	73	73	225
3	96	95	235
2	94	95	140
1	78	85	229
0	68	63	0

0.17,L

11	45	45	69
7	83	85	133
6	84	81	156
3	117	123	109
2	95	95	117
1	121	122	37
0	138	138	180

0.16,L

8	47	45	66
6	103	106	331
5	70	68	321
4	54	47	156
3	146	154	103
2	150	151	279
1	63	68	354
0	132	126	0

0.15,L

11	52	46	250
7	68	68	292
6	91	91	43
5	139	139	192
4	73	74	65
3	240	254	308
1	156	158	197
0	156	157	180

0.14,L

12	59	58	208
11	70	63	66
10	75	70	111
8	80	84	259
7	106	106	83
6	160	154	167
5	143	151	213
3	50	54	248
2	209	214	149
1	64	60	18

0.13,L

10	94	96	309
8	132	140	30
7	219	229	145
6	174	178	72
5	123	123	130
4	120	128	74
3	191	196	102
2	72	78	320
1	206	210	4
0	181	194	0

0.12,L

11	92	87	239
10	50	56	295
9	119	124	278
8	52	55	156
7	156	162	297
6	107	114	21
5	96	100	297
4	64	64	243
3	81	86	347
2	124	131	248
1	268	267	171

0.11,L

12	55	48	223
10	84	79	155
9	54	50	126
8	158	158	260
7	58	63	349
6	193	197	166
5	79	75	158
4	187	188	162
3	96	94	324
2	155	157	177
1	113	123	114
0	293	279	180

0.10,L

13	49	40	58
11	77	81	92
10	99	95	16
8	85	90	345
7	161	159	109
6	49	48	14
5	53	58	114
4	91	91	1
3	152	144	183
2	179	187	93
1	158	169	14
0	225	237	0

0.9,L

12	54	55	42
11	49	55	334
10	80	77	292
9	116	120	271
8	162	166	96
7	81	86	268
6	60	54	45

0,9,L

5	38	40	198
4	71	73	353
2	219	225	34
1	729	707	223
0	220	215	180

0,8,L

11	73	73	242
10	157	161	156
9	91	97	98
8	120	120	225
7	85	92	283
6	127	130	214
4	84	72	64
2	287	280	185
1	796	801	126
0	387	422	180

0,7,L

12	51	43	267
11	47	49	115
10	129	131	30
9	75	72	78
8	163	162	301
7	82	82	68
6	86	91	172
5	56	55	1
4	160	156	238
3	56	43	198
2	259	243	121
1	673	675	36
0	349	318	0

0,6,L

11	72	80	38
10	135	135	311
9	213	220	271
8	122	131	63
7	108	107	162
6	73	83	300
5	72	81	316
4	145	141	354
2	143	141	150
1	531	535	267

0,5,L

12	58	64	102
11	59	56	271
10	150	153	193
9	63	69	42
8	235	241	136
7	210	212	310
6	81	81	147
5	234	217	357
4	185	172	14
3	217	214	245
2	413	395	334
1	680	698	210
0	902	887	180

0,4,L

13	46	38	66
12	58	45	221
11	49	50	306
10	150	151	107
9	263	260	97
8	177	173	239
7	124	117	66
6	218	222	219
5	68	73	172
4	225	236	337
3	385	390	134
2	162	150	327
1	559	562	52
0	1228	1297	0

0,3,L

12	64	62	7
11	83	84	128
10	92	90	335
9	195	201	265
8	171	167	354
7	168	171	160
6	74	77	351
5	156	153	20
4	280	303	8
3	83	96	152
2	248	252	176
1	257	277	355
0	822	876	0

0,2,L

13	41	25	275
12	56	52	141
11	70	73	309
10	122	131	243
9	171	169	295
8	205	207	142
7	111	128	191
6	42	43	315
5	124	119	275
4	147	155	144
3	395	393	301
2	203	215	104
1	458	514	293
0	345	369	180

0,1,L

11	53	50	326
10	111	103	201
9	371	378	94
8	82	76	153
7	246	242	353
6	80	85	168
5	51	59	51
4	148	145	18
3	332	338	4
2	64	69	195
1	615	583	132

0,0,L

12	69	75	101
10	118	122	76
8	278	265	322
6	140	137	141
4	365	386	306
2	210	222	238

-1,26,L

-2	49	47	77

-1,25,L

2	72	60	2
-1	48	40	267
-2	47	37	62
-3	51	53	321

-1,24,L

6	60	59	197
0	68	55	177
-1	64	55	3
-3	53	57	228

-1,23,L

5	62	54	81
-1	76	77	109
-2	55	57	222
-3	75	68	103
-4	49	51	39

-1,22,L

4	60	43	39
-1	70	79	211
-2	101	96	34
-5	59	63	231

-1,21,L

8	63	53	169
6	50	53	262
4	44	38	156
1	42	55	221
0	84	80	184
-1	44	50	347
-3	45	47	213
-4	96	96	202
-5	63	54	337

-1,20,L

9	55	59	94
5	125	126	110
2	43	43	160
0	41	45	349
-1	132	136	56
-2	60	55	260
-3	52	57	144
-4	52	52	100
-9	62	66	104

-1,19,L

6	42	28	41
5	72	72	335
3	42	49	96
2	65	70	329
0	62	68	342
-1	96	88	199
-4	132	131	6
-5	57	45	264
-9	44	37	276

-1,18,L

9	54	56	250
8	74	74	147
5	82	78	263
4	76	73	144
3	44	45	291
0	69	72	176
-1	81	83	334
-3	45	55	300
-4	77	75	213
-5	46	35	211

-1,17,L

9	65	62	50
7	42	43	15
5	94	100	144
4	86	92	163
3	39	39	62
2	61	64	236
0	63	68	189
-1	177	172	64
-2	43	50	248
-3	102	99	173
-4	44	50	262
-5	80	80	89
-9	84	81	71

-1,16,L

8	113	116	332
6	53	40	350
5	50	53	94
4	129	131	318
3	123	124	53
1	84	89	191
0	201	208	324
-1	143	143	95
-2	75	67	336
-3	102	102	274
-4	104	108	58
-5	50	52	45
-6	82	87	197

-1,15,L

9	131	127	252
8	43	50	128
7	62	59	184
6	41	35	156
5	170	181	304
3	84	79	109
2	142	138	277
1	116	123	325
0	136	139	58
-1	194	204	242
-2	40	31	170
-3	102	110	358
-4	151	157	2
-5	96	94	276
-8	52	56	164
-9	109	116	277
-13	63	52	271

-1,14,L

9	102	97	75
8	118	118	159
6	62	67	255
5	79	81	308
4	154	164	184
3	132	126	357
1	108	108	120
0	247	253	175
-1	137	130	33
-2	111	116	37
-3	173	176	351
-4	277	274	207
-5	85	77	69
-6	134	130	89
-7	94	86	176
-8	58	58	163
-10	59	61	157

-1,13,L

8	40	34	14
7	55	57	155
6	114	113	100
5	133	138	141
3	120	121	41
2	127	119	125
1	109	103	221
0	247	235	296
-1	204	201	68
-2	171	167	341
-3	130	122	142
-4	207	202	345
-5	240	238	63
-6	101	105	356
-7	82	84	148
-8	149	152	22
-9	68	68	77
-10	71	63	5
-13	47	51	85

-1,12,L

9	143	143	254
8	122	119	44
6	57	59	154
5	188	191	315
4	211	210	293
3	107	99	140
2	158	156	352
1	142	134	206
0	79	85	16
-1	206	204	207
-2	153	152	158
-3	204	207	267
-4	157	163	303
-5	182	184	293
-7	119	120	263
-8	84	86	62

-1,12,L

-9	88	93	256
-10	56	54	237
-12	44	30	75

-1,11,L

9	54	58	349
8	196	199	184
7	179	177	134
6	105	99	211
5	71	73	238
4	162	170	213
3	130	127	76
2	193	196	275
1	172	179	12
0	239	233	139
-1	148	144	29
-2	77	81	277
-4	188	189	189
-5	57	61	162
-6	143	140	115
-7	51	44	288
-8	203	208	177
-10	71	73	146
-11	64	72	107

-1,10,L

11	87	83	199
10	50	51	265
9	116	120	85
8	84	82	43
7	57	62	33
6	81	80	328
5	125	130	125
4	112	107	48
3	107	112	29
2	79	91	50
1	117	119	73
0	242	243	280
-1	438	430	39
-2	330	332	19
-3	88	91	123
-4	72	66	99
-5	80	84	54
-6	105	100	32
-7	73	72	216
-8	123	118	17
-9	145	145	65
-12	54	49	314

-1,9,L

10	60	56	102
9	93	90	249
8	126	133	305
7	121	126	256
6	135	138	126
4	74	67	196
3	237	232	254
2	315	299	149
1	264	249	340
0	430	422	311
-1	421	400	285
-3	141	141	239
-4	245	248	26
-5	94	99	341
-6	73	72	272
-7	78	85	234
-8	163	148	12
-9	136	142	234
-10	82	88	328
-11	80	82	267

-1,8,L

11	61	66	48
10	52	56	74
9	118	119	263
8	182	180	176
7	116	112	109
6	99	99	115
5	153	149	250
4	181	184	246
3	458	436	155
2	152	140	121
0	385	378	176
-1	212	203	174
-2	111	113	131
-3	164	160	143
-4	276	267	193
-5	70	58	210
-7	102	96	76
-8	133	138	206
-11	67	74	75
-12	72	70	148

-1,7,L

12	90	93	69
10	91	103	256
9	123	133	66
8	67	67	43
7	71	76	75
6	159	152	316
5	60	64	165
4	184	181	95
3	285	274	77
2	349	338	317
1	70	79	112
0	139	134	270
-1	305	293	56
-2	259	248	359
-3	115	103	273
-5	126	125	163
-6	130	130	113
-8	80	77	252
-9	160	168	68
-10	56	56	81

-1,6,L

12	59	54	348
11	102	102	262
9	76	79	162
8	124	122	356
7	176	185	284
6	147	135	319
5	97	106	170
4	165	170	0
3	341	337	309
2	267	264	131
1	236	244	97
0	548	544	288
-1	280	298	295
-2	207	203	353
-3	183	188	254
-4	56	56	89
-5	145	138	79
-6	126	132	272
-7	177	176	269
-8	145	157	39
-11	113	107	279

-1,5,L

13	49	45	260
12	87	89	228
11	47	51	43
10	164	162	96
9	122	121	253
8	194	192	206
7	127	123	19
6	129	135	140
5	142	137	3
4	86	92	12
3	211	211	166
2	353	355	172
1	304	312	335
0	485	465	97
-1	118	136	317
-2	180	178	169
-3	198	195	211
-4	48	59	150
-5	317	315	266

-1,5,L

-8	169	176	233
-9	159	161	243
-10	52	58	253
-12	64	54	128
-13	58	60	319

-1,4,L

15	61	61	71
12	41	43	132
11	87	87	83
10	160	153	266
9	149	150	29
8	59	58	73
7	149	151	126
6	174	174	336
5	236	238	150
4	107	131	136
3	261	262	204
2	296	313	46
1	609	605	274
0	630	595	98
-1	706	747	85
-2	216	227	69
-3	294	296	102
-4	297	302	202
-5	368	361	148
-6	227	218	154
-7	256	249	46
-8	155	163	253
-9	85	85	122
-11	108	108	87
-12	71	69	325

-1,3,L

12	84	83	24
10	88	88	288
9	152	160	143
8	191	206	23
7	133	133	282
6	326	320	8
5	253	246	247
4	292	295	60
3	190	194	339
2	423	428	306
1	671	675	155
0	531	580	280
-1	504	502	231
-2	315	304	292
-3	310	309	279
-4	280	265	16
-5	291	286	52
-6	41	37	251
-7	69	72	234
-8	66	66	285
-9	157	162	60
-10	115	119	33
-12	44	44	341
-16	52	32	335

-1,2,L

12	79	78	205
10	119	126	91
9	120	128	225
8	40	49	230
7	211	207	299
6	165	159	231
4	246	236	50
5	84	86	315
3	347	358	296
2	248	251	155
1	221	260	199
0	176	186	330
-1	668	633	295
-2	660	638	228
-5	149	158	9
-4	266	256	202
-3	284	275	207
-8	153	160	83
-7	170	166	261
-6	325	324	223
-11	90	95	255
-10	172	172	211
-9	107	106	268
-12	73	67	135

-1,1,L

11	82	84	110
10	54	54	346
9	155	153	28
8	100	93	152
7	197	208	113
6	167	169	111
5	447	442	47
4	89	100	284
3	535	537	121
2	602	616	312
1	658	624	32
0	212	261	129
-1	630	649	140
-2	1337	1374	192
-4	219	218	300
-3	414	426	61
-5	334	320	231
-6	80	75	257
-7	247	254	77
-8	89	94	150
-9	159	156	229
-10	123	117	173
-11	80	75	51

-1,0,L

12	51	50	46
10	176	177	281
8	180	180	35
6	420	412	340
4	418	399	105
-2	1029	988	74
-4	213	217	279
-6	241	229	113
-8	275	269	292
-10	184	186	358
-12	168	174	325

-2,25,L

4	61	56	29

-2,24,L

6	50	42	174

-2,23,L

7	50	51	81
-1	65	63	105
-2	46	41	31

-2,22,L

0	43	49	41
-3	90	86	250
-4	71	69	27

-2,21,L

6	54	57	155
5	65	62	260
-2	86	88	176
-6	62	50	256

-2,20,L

8	50	36	171
7	84	87	113
5	55	46	73
3	49	46	142
1	56	63	52
0	65	57	167
-1	79	78	118
-3	81	77	65

-2,20,L

-7	59	48	113

-2,19,L

6	90	89	341
4	65	84	11
-2	83	81	18
-3	104	102	235

-2,18,L

7	52	56	247
6	89	85	150
5	48	44	273
-1	76	85	290
-2	85	94	219
-3	52	46	237
-8	58	59	116

-2,17,L

9	54	57	339
8	86	82	178
7	91	92	98
5	80	84	44
4	63	69	195
2	45	54	261
-5	67	74	120

-2,16,L

8	56	50	15
7	67	55	129
6	142	148	327
5	67	71	56
4	77	83	12
3	48	53	197
2	152	158	7
1	54	54	93
0	62	66	97
-1	54	68	130
-2	119	116	350
-4	90	88	271
-8	92	86	294

-2,15,L

7	174	179	281
5	51	53	210
4	70	66	312
2	87	81	76
1	157	161	217
-1	172	172	336
-2	142	144	90

-3	184	186	240
-4	60	62	164
-6	61	59	191
-7	89	97	265
-11	71	68	288

-2,14,L

12	48	35	198
8	62	60	259
7	95	97	71
6	77	78	160
5	106	103	15
3	144	146	144
2	109	113	163
1	87	86	341
0	94	92	74
-1	129	136	44
-2	330	337	223
-3	125	121	18
-4	181	179	146
-5	58	51	156
-6	88	90	193
-8	78	75	124
-10	74	70	236
-12	45	38	131

-2,13,L

12	54	47	45
7	108	117	140
6	163	164	277
5	137	139	35
4	63	69	40
3	111	114	135
2	167	164	318
1	88	81	335
0	36	31	30
-1	94	90	160
-2	236	232	357
-3	170	173	55
-4	108	112	22
-5	190	181	150
-6	258	264	52
-9	48	45	255
-11	77	77	105

-2,12,L

11	75	77	280
9	75	73	90
8	57	63	77
7	111	113	293
6	109	111	347
5	77	82	282
4	91	86	9

3	134	131	294
1	155	152	200
0	107	103	113
-1	142	140	290
-2	230	229	0
-3	275	279	250
-4	97	93	165
-5	226	234	295
-6	56	56	19
-7	154	156	231
-8	118	111	257
-10	71	72	50

-2,11,L

12	49	57	223
8	63	71	226
7	90	89	305
6	137	146	190
5	85	86	137
4	59	56	326
3	144	136	92
2	211	216	119
1	156	152	58
0	49	43	114
-1	75	73	8
-2	312	319	181
-3	135	134	199
-4	162	159	141
-6	185	186	191
-8	51	48	193
-9	98	99	75
-10	148	143	233
-11	58	58	257

-2,10,L

11	65	59	94
8	102	107	325
7	229	226	130
6	130	124	63
5	215	219	20
4	165	164	25
3	139	133	123
2	118	115	7
1	122	122	3
0	203	203	13
-1	268	268	150
-2	105	115	167
-3	294	297	34
-4	68	68	42
-5	89	89	129
-6	106	112	42
-7	140	146	39
-8	66	66	338

-2,10,L

-9	57	61	126
-10	54	60	321
-11	87	98	103

-2,9,L

12	43	50	73
11	65	59	303
8	55	54	118
7	51	40	149
6	229	231	307
5	234	222	256
4	65	68	164
3	192	181	11
2	204	187	295
1	467	449	313
-1	155	152	197
-2	426	423	51
-3	129	127	290
-4	140	141	253
-5	153	152	306
-6	183	174	30
-7	96	94	246
-9	131	125	257
-10	122	129	66

-2,8,L

13	43	38	102
12	45	43	175
11	47	56	232
10	71	72	223
9	84	81	99
8	199	201	115
7	203	203	302
6	132	131	162
5	215	207	162
4	246	253	195
3	69	64	303
2	224	222	252
1	169	162	182
0	271	265	118
-1	156	146	323
-2	45	48	119
-3	294	284	226
-4	205	200	141
-5	98	98	131
-6	190	189	227
-7	142	145	179
-8	64	65	139
-9	68	69	76
-10	78	80	170

-2,7,L

11	64	63	122
10	72	69	54
8	196	197	276
6	139	135	102
5	173	171	69
4	237	243	43
3	233	234	72
2	320	308	89
1	255	246	60
0	388	380	342
-1	109	112	89
-2	260	254	186
-3	141	153	91
-4	91	92	91
-5	94	92	124
-6	69	71	343
-7	90	98	55
-8	96	95	11
-9	106	103	92
-10	99	100	290
-11	53	58	129

-2,6,L

14	56	44	347
13	71	62	288
9	178	177	253
8	135	137	352
7	144	140	147
6	155	156	6
5	189	183	297
4	133	137	85
3	63	60	1
2	243	232	271
1	424	422	285
0	79	56	355
-1	378	371	181
-2	176	172	334
-3	225	216	109
-4	235	227	301
-5	153	156	324
-6	100	100	23
-7	109	112	14
-8	57	55	323
-9	129	123	259
-13	53	51	318

-2,5,L

15	50	32	257
12	99	92	144
11	79	67	297
10	75	85	250
9	103	109	83

8	257	258	127
7	60	64	305
6	89	95	297
5	268	275	187
4	383	379	198
3	57	49	265
2	170	147	257
1	291	288	119
0	249	245	141
-1	205	203	293
-2	165	167	63
-3	331	331	272
-4	271	251	175
-5	204	196	341
-6	60	54	334
-7	56	57	284
-8	170	170	153
-10	103	109	121
-11	83	85	338

-2,4,L

13	96	92	99
11	89	100	113
10	65	72	71
9	54	64	55
8	131	134	287
7	104	108	335
6	113	98	156
5	178	184	113
4	144	148	180
3	72	77	257
2	98	90	192
1	390	374	75
0	55	62	94
-1	303	293	348
-2	428	421	241
-3	254	246	158
-4	436	419	145
-5	310	307	92
-6	153	153	230
-7	198	187	162
-8	141	136	41
-9	158	154	64
-12	79	82	155

-2,3,L

13	49	49	259
12	44	47	336
11	64	53	184
10	114	118	40
9	149	146	247
8	122	132	329
7	88	79	184
6	66	71	194

-2,3,L

5	166	169	327
4	349	329	39
3	215	200	291
2	481	484	320
0	546	531	307
-1	230	212	116
-2	223	228	233
-3	363	350	108
-4	293	284	0
-5	230	231	286
-6	106	100	20
-7	66	69	56
-8	200	205	7
-9	137	134	198
-10	58	65	307
-11	110	111	134
-13	52	52	305

-2,2,L

12	45	56	169
11	67	72	312
9	103	99	234
8	191	194	112
7	84	86	270
6	142	133	16
5	230	222	312
4	445	444	207
3	65	63	283
2	383	393	210
1	383	362	279
0	867	840	165
-1	479	470	240
-2	632	626	296
-3	361	359	60
-4	325	317	266
-5	193	195	277
-6	78	69	328
-7	108	102	281
-8	116	122	179
-9	169	172	265
-10	86	83	100
-11	52	53	12
-12	65	61	315
-14	73	70	162

-2,1,L

11	80	78	113
9	146	151	44
8	159	159	144
7	195	186	51
6	62	57	319
5	495	473	139
4	92	90	196
3	532	547	154
2	897	890	283
1	476	490	144
0	976	1001	212
-1	503	511	54
-2	339	345	358
-3	425	406	275
-4	137	135	171
-5	364	339	89
-6	50	54	220
-8	131	130	169
-9	253	257	53
-10	70	72	152
-11	75	81	359
-13	92	86	105

-2,0,L

14	63	59	33
10	179	183	48
8	216	218	310
6	139	129	236
4	697	673	31
2	167	169	28
0	972	974	133
-2	1195	1213	262
-4	555	548	71
-6	99	91	78
-8	222	216	20
-10	221	217	337
-12	78	73	50
-14	62	50	12

-3,25,L

-2	62	51	356

-3,24,L

2	68	64	265

-3,23,L

-5	45	43	75

-3,22,L

5	49	43	289
-1	57	51	253
-2	47	37	34

-3,21,L

4	44	48	161
0	66	73	167
-1	45	48	305
-3	71	70	242
-4	63	57	215

-3,20,L

0	53	57	40
-2	62	59	186
-5	55	59	87

-3,19,L

7	47	47	118
5	65	60	318
4	81	78	337
0	71	72	300
-1	52	60	236
-2	60	62	17
-3	67	71	4
-4	76	69	356

-3,18,L

5	87	83	259
4	99	95	163
0	66	66	162
-1	55	69	192
-3	51	45	313
-4	76	74	227

-3,17,L

9	88	78	102
6	55	58	223
5	84	80	80
0	75	80	169
-1	42	49	338
-2	54	51	158
-4	101	109	129
-5	52	44	72

-3,16,L

8	92	86	313
5	41	40	88
4	112	112	341
3	78	80	197
2	68	62	93
1	68	59	242
0	131	128	346
-1	43	44	176
-2	56	42	221
-3	60	57	7
-4	94	100	315
-6	83	86	340

-3,16,L

-7	49	51	328
-8	79	71	35
-10	63	62	323

-3,15,L

9	68	70	295
5	73	81	280
4	52	59	111
3	141	137	254
1	153	158	358
0	121	123	168
-1	216	218	238
-3	56	62	263
-5	113	118	256

-3,14,L

9	53	58	100
8	90	91	124
5	71	76	96
4	174	178	149
3	41	32	353
2	54	56	162
1	85	87	35
0	160	156	215
-1	211	204	44
-2	77	77	223
-3	114	118	133
-4	83	87	230
-5	52	50	141
-6	50	40	159
-8	55	53	247
-9	60	59	94

-3,13,L

8	116	119	305
5	89	91	116
4	185	187	345
0	254	251	344
-1	100	93	57
-2	92	94	149
-3	153	153	181
-4	209	218	65
-5	110	116	106
-6	76	77	290
-8	47	38	10
-9	79	83	79

-3,12,L

7	39	46	115
6	55	64	55
4	61	66	46
3	236	240	238
2	139	145	159
1	198	198	303
0	110	109	342
-1	299	299	238
-2	110	109	169
-3	253	258	335
-4	189	192	19
-5	212	211	253
-6	110	106	244
-7	87	92	354
-8	63	59	23
-9	60	71	231

-3,11,L

10	54	56	266
8	58	56	100
7	54	40	252
5	103	106	22
4	246	243	168
3	166	159	117
2	68	65	208
1	58	64	27
0	272	274	171
-1	176	171	203
-2	94	99	205
-3	85	81	311
-4	249	244	198
-5	123	126	177
-6	49	54	284
-7	118	119	71
-8	102	102	230
-10	76	76	108
-11	57	41	65

-3,10,L

13	53	60	100
9	108	107	109
8	85	85	102
7	76	84	36
6	98	97	5
5	51	47	90
4	127	130	65
3	140	146	34
2	51	55	6
1	70	77	170
0	67	63	306
-1	261	259	59
-2	137	138	8
-3	75	78	153
-4	125	120	352
-5	237	245	85
-6	125	124	17
-7	117	118	164
-8	46	58	300
-9	105	113	93
-13	67	63	84

-3,9,L

10	64	63	47
8	135	137	323
7	152	155	275
6	76	79	190
5	44	37	135
4	262	264	346
3	288	282	301
2	89	84	85
1	88	89	242
0	185	191	40
-1	160	159	310
-2	204	215	213
-3	63	67	24
-4	154	156	6
-5	67	69	238
-6	77	82	249
-7	99	102	273
-8	79	77	60
-10	65	66	270
-11	67	69	291

-3,8,L

10	105	101	181
9	61	62	270
8	72	71	175
7	150	142	142
6	67	72	120
5	115	114	327
4	181	179	191
3	119	115	190
2	198	194	211
1	149	143	298
0	177	171	100
-1	326	322	200
-2	267	263	172
-3	130	132	2
-4	116	116	249
-5	134	131	240
-6	87	91	176
-7	71	75	55
-8	84	83	172
-10	92	84	182
-11	70	63	86

-3,7,L

10	90	91	310

-3,7,L

9	96	95	35
8	151	148	86
7	124	124	81
6	115	117	291
5	146	149	66
4	141	126	140
3	230	226	102
2	279	268	359
1	163	155	103
0	240	227	175
-1	264	268	99
-2	146	137	351
-4	92	87	203
-5	129	125	60
-6	140	140	34
-7	71	74	78
-8	47	49	341
-9	73	75	62

-3,6,L

11	80	82	277
10	77	85	21
8	67	65	284
7	186	198	290
6	54	60	63
5	98	100	139
4	235	232	311
3	346	340	336
2	110	104	305
1	297	284	197
0	405	391	323
-1	220	220	282
-2	97	81	24
-3	147	141	180
-4	257	241	9
-5	47	45	36
-6	120	108	36
-7	105	96	241
-10	85	89	319

-3,5,L

14	51	59	134
13	49	38	280
12	86	78	212
10	102	109	157
9	65	72	263
8	100	97	274
7	76	85	138
6	190	181	152
5	152	147	243
4	85	81	143
3	142	145	219
2	112	114	135
1	159	157	306
0	202	204	92
-1	61	65	211
-2	430	432	175
-3	304	302	34
-4	133	137	106
-5	77	71	302
-6	158	164	210
-7	79	71	169
-8	116	121	114
-9	47	44	289
-10	97	106	203
-12	44	47	134
-13	44	51	304

-3,4,L

11	77	91	93
10	60	58	298
8	83	81	124
7	166	168	116
6	128	123	304
5	193	193	11
4	120	122	233
3	409	416	90
2	67	79	338
1	236	231	23
0	239	238	152
-1	356	347	133
-2	177	160	199
-3	211	218	21
-4	182	179	225
-5	116	112	164
-7	182	185	71
-9	60	57	311
-11	100	97	85

-3,3,L

15	48	42	260
12	68	74	33
11	106	109	266
7	110	107	322
5	138	126	187
4	289	283	329
3	155	149	186
2	392	410	0
1	239	237	145
0	208	221	256
-2	495	494	26
-3	95	95	119
-4	165	161	196
-5	93	87	272
-6	313	306	87
-7	91	101	230
-9	49	41	103
-10	74	70	5
-11	79	66	276
-14	56	49	28

-3,2,L

14	60	51	116
10	103	105	112
9	63	74	342
8	109	112	232
7	79	76	307
6	112	93	200
5	160	154	210
4	388	378	221
3	346	339	338
2	407	405	216
1	30	32	291
0	83	89	308
-1	77	68	306
-2	91	93	297
-3	343	349	248
-4	232	229	57
-5	134	137	312
-6	127	120	125
-7	101	106	269
-8	227	221	101
-10	38	47	206
-11	95	98	272
-12	91	78	153
-14	49	65	260

-3,1,L

11	123	123	78
10	54	58	176
9	52	49	172
8	117	125	235
7	220	223	114
6	40	49	239
4	175	184	319
3	367	362	158
2	243	244	205
1	206	206	346
0	40	43	87
-1	238	247	72
-2	201	209	342
-3	310	298	74
-4	491	496	110
-5	93	87	167
-6	174	165	216
-7	201	196	85
-8	70	69	196
-9	94	100	54
-10	53	62	220

-3,1,L

-11	161	162	104

-3,0,L

12	72	70	39
8	144	145	13
6	249	242	2
4	156	156	274
2	272	266	128
0	59	67	319
-2	544	552	61
-4	305	310	224
-6	99	95	23
-8	172	174	355
-10	172	185	17

-4,23,L

3	64	58	131

-4,21,L

2	56	52	178
1	58	49	322
-1	50	42	251
-2	71	65	199

-4,20,L

3	60	51	105
-3	59	67	68

-4,19,L

2	54	65	2
-1	61	55	3
-2	92	88	334

-4,18,L

7	71	83	283
6	79	73	173
3	56	60	258
2	96	96	192
0	67	77	326
-1	73	69	240
-2	45	46	127
-3	79	74	187
-5	58	56	251

-4,17,L

7	71	76	92
1	45	53	357
-1	74	77	98
-2	105	110	170
-3	89	83	34
-5	69	70	145

-4,16,L

9	43	35	185
6	107	104	322
2	78	79	351
-2	202	201	349
-4	59	56	331
-5	66	68	48
-6	69	72	30

-4,15,L

7	115	110	270
6	44	43	161
5	60	64	178
3	102	98	322
2	67	61	172
-1	74	78	267
-2	64	67	163
-3	136	130	237
-5	65	66	271
-11	67	66	256

-4,14,L

6	108	119	153
5	83	86	36
4	69	72	202
2	155	156	220
1	116	124	79
0	72	74	296
-1	117	124	172
-3	117	121	88
-4	58	67	75
-6	61	66	245
-8	60	62	101
-10	72	66	208

-4,13,L

7	77	69	81
6	127	127	351
4	58	54	198
2	206	209	351
1	77	76	60
0	69	76	240
-1	158	164	166
-2	120	124	45
-4	118	115	312
-5	38	38	198
-6	67	67	78
-7	98	95	79
-8	47	54	326
-9	42	38	202
-11	44	56	72

-4,12,L

8	74	75	91
7	112	110	285
6	45	45	243
5	104	104	220
4	71	77	223
3	220	222	298
2	79	84	3
1	144	147	271
0	40	49	128
-1	110	112	325
-2	187	179	26
-3	130	134	280
-4	156	153	267
-5	87	91	30
-6	73	69	54
-7	62	58	266
-11	74	77	268

-4,11,L

6	89	92	158
5	104	107	154
4	63	69	149
3	66	64	70
2	155	165	213
0	70	70	308
-1	111	117	315
-2	240	246	204
-3	103	109	175
-4	49	39	87
-5	108	109	102
-6	211	222	237
-8	69	72	71
-9	60	61	38
-12	49	55	148
-13	55	44	142

-4,10,L

11	75	65	117
7	117	111	78
6	61	65	80
5	175	177	53
4	90	99	12
3	117	116	165
1	97	111	100
-1	113	113	99
-2	69	84	24

-4,10,L

-3	228	236	83
-4	201	212	30
-5	92	99	190
-6	62	61	26
-7	63	59	71
-11	99	96	78

-4,9,L

6	128	134	342
5	169	171	301
4	147	147	205
3	137	132	236
2	123	126	14
1	66	68	353
-1	183	169	193
-2	216	218	345
-3	87	83	313
-4	160	158	282
-5	126	131	270
-6	137	138	82
-8	53	64	255
-9	54	56	303
-10	66	63	61

-4,8,L

13	51	36	92
12	59	52	175
10	51	42	165
8	139	141	159
7	120	117	272
6	155	152	232
5	153	148	182
3	195	193	321
2	116	113	151
1	53	58	234
0	159	155	180
-1	171	165	326
-3	153	147	217
-4	121	115	154
-5	102	103	96
-6	100	95	212
-8	48	52	170
-9	61	57	70
-12	46	46	158
-14	56	45	181

-4,7,L

11	88	92	85
10	65	61	64
9	57	55	104
8	87	85	305
7	93	101	77
6	187	190	116
5	182	182	46
4	175	176	355
3	204	198	134
1	104	91	151
0	163	160	324
-1	182	177	27
-2	202	197	217
-3	190	181	64
-4	217	218	42
-5	120	116	86
-7	48	59	76
-9	56	55	74
-12	53	47	90

-4,6,L

13	72	70	263
12	55	51	359
8	78	68	6
7	143	134	135
6	173	174	342
5	206	205	341
4	150	148	347
3	163	163	202
2	266	260	346
1	53	63	317
0	114	115	121
-1	251	253	174
-2	303	300	20
-3	216	219	335
-4	102	106	317
-5	229	236	268
-6	84	95	55
-8	58	60	274
-9	74	75	256
-12	60	55	337

-4,5,L

12	73	69	158
8	105	103	150
7	113	113	282
6	76	71	261
5	127	118	180
4	303	307	171
3	162	159	279
2	249	239	133
1	69	65	206
0	283	271	152
-1	157	156	10
-2	115	106	137
-3	42	42	276
-4	200	194	203
-5	63	56	194
-6	105	104	143
-7	50	41	264
-8	61	68	215
-10	92	93	89
-14	69	63	174

-4,4,L

9	69	71	59
7	58	57	85
6	125	130	144
5	199	204	123
4	194	196	322
3	335	340	54
2	179	170	152
1	94	91	88
0	267	246	231
-1	315	304	18
-2	106	109	157
-3	212	204	187
-4	86	79	333
-5	310	302	93
-6	56	52	330
-7	62	58	331
-9	130	127	51
-13	74	68	109

-4,3,L

13	67	65	274
12	75	72	340
8	103	107	291
6	142	134	50
5	247	245	313
4	246	242	13
3	104	101	186
2	202	195	49
1	298	276	235
0	66	72	265
-1	240	234	143
-2	48	47	100
-3	186	187	324
-4	292	293	38
-5	101	103	216
-6	89	80	359
-8	102	107	323
-9	94	102	220
-10	114	115	289
-12	66	66	46
-14	65	61	355

-4,2,L

14	75	55	228
12	82	81	139

-4,2,L

10	75	81	216
9	168	166	292
5	67	55	355
4	201	204	190
3	50	57	303
2	90	89	156
1	152	140	349
0	287	272	55
-1	193	191	218
-2	312	305	60
-3	134	134	314
-4	363	379	192
-5	292	295	285
-6	132	132	150
-7	94	92	25
-8	129	128	175
-9	88	84	267
-12	96	83	267
-13	61	52	284

-4,1,L

13	72	75	76
11	44	38	142
9	116	119	74
7	78	70	182
5	274	283	160
4	180	193	191
3	206	203	43
2	273	264	83
1	227	229	92
0	92	106	161
-1	247	237	356
-2	446	437	140
-3	111	108	201
-4	230	231	239
-5	359	359	92
-7	56	61	92
-8	84	84	282
-9	102	101	64
-13	86	85	104

-4,0,L

12	83	86	316
10	100	96	33
8	113	109	312
6	211	199	101
4	83	73	335
2	208	203	150
0	216	206	264
-2	161	155	57
-6	251	245	353
-8	198	205	12
-12	74	73	77
-14	69	58	338

-5,22,L

1	71	74	329

-5,21,L

4	55	58	162

-5,20,L

4	47	37	55
1	47	59	150

-5,19,L

4	61	64	341
0	81	84	341
-4	50	51	334
-5	55	49	270

-5,18,L

3	57	57	242
1	81	87	280
-1	54	55	223
-3	56	56	264
-4	74	65	159

-5,17,L

3	70	70	36
1	104	109	126
0	44	52	143
-1	86	85	359
-2	71	70	146
-3	59	53	142
-5	83	83	40

-5,16,L

8	51	55	317
4	129	126	339
0	125	122	14
-3	53	51	98
-4	106	103	358

-5,15,L

9	78	68	277
5	65	59	276
4	73	76	172
3	68	67	215
-1	70	72	238
-5	98	91	223

-5,14,L

10	51	56	231
6	62	56	262
5	58	59	115
4	94	94	190
3	71	75	77
2	66	73	300
1	88	99	171
0	116	112	160
-1	55	62	131
-4	80	76	168
-5	105	99	65
-6	104	101	152
-7	42	38	126

-5,13,L

9	52	45	87
4	187	198	355
3	75	80	37
2	96	96	11
1	122	124	162
0	152	154	76
-1	72	67	336
-2	89	86	279
-5	90	87	61
-6	89	87	1
-7	60	58	225
-8	42	42	171
-9	59	54	62

-5,12,L

8	58	54	255
5	114	124	301
3	124	125	304
0	113	109	64
-1	58	58	268
-3	81	93	61
-5	154	157	264
-8	68	59	79
-9	79	77	278
-10	56	41	253

-5,11,L

8	59	67	136
6	56	50	223
5	68	72	141
4	151	152	161
3	67	71	280
0	107	120	241

-5,11,L

-2	58	61	1
-4	116	127	237
-6	104	106	121
-7	105	106	79
-10	55	47	144

-5,10,L

10	53	44	327
9	49	52	139
5	75	70	141
4	59	62	303
3	100	106	100
2	128	124	6
1	83	85	133
0	94	96	141
-1	101	105	99
-3	99	102	157
-5	171	168	52
-6	69	75	38
-9	86	81	87

-5,9,L

10	44	42	42
8	98	102	311
7	57	53	281
6	105	108	235
4	117	125	349
3	158	158	311
1	61	62	218
0	153	152	350
-1	67	71	353
-2	83	87	303
-3	67	72	247
-4	64	68	100
-5	115	121	259
-6	87	83	253
-7	96	97	323

-5,8,L

10	64	68	197
9	81	73	280
8	55	62	218
5	114	119	340
4	53	54	183
3	70	67	159
2	113	113	179
1	130	128	356
-1	86	87	238
-2	124	125	144
-3	78	75	31
-4	118	113	148
-5	124	130	226
-6	167	172	203
-9	84	83	263

-5,7,L

9	58	61	116
8	69	76	137
7	73	82	39
6	122	114	316
5	99	91	78
4	153	152	141
3	139	145	108
2	48	50	7
1	113	113	86
0	77	71	261
-1	56	56	45
-2	204	206	18
-4	52	56	239
-5	174	173	53
-6	142	141	31
-7	88	88	120

-5,6,L

10	57	64	18
8	67	68	339
7	87	82	286
6	120	114	82
5	188	195	184
4	230	234	337
3	158	150	282
2	87	84	83
1	74	77	252
0	114	109	46
-1	131	130	10
-2	106	99	296
-3	177	176	218
-4	117	124	22
-5	49	48	321
-6	110	112	332
-7	75	79	305

-5,5,L

10	60	60	179
7	105	103	201
6	147	158	179
5	235	243	303
4	134	140	177
3	101	101	247
2	227	227	190
1	68	69	357
0	77	80	232
-2	130	130	188
-3	62	69	95
-4	87	79	115
-5	115	119	208
-6	200	203	195
-8	48	53	134
-12	64	63	142

-5,4,L

7	114	114	87
6	160	161	327
5	185	189	58
4	97	92	136
3	239	250	108
2	104	103	267
1	175	174	52
0	62	61	236
-1	51	35	285
-2	168	170	6
-3	149	143	80
-4	101	103	214
-5	96	98	65
-6	65	67	319
-7	100	103	93

-5,3,L

10	50	55	349
8	54	57	65
7	134	132	326
5	77	81	110
4	81	81	41
3	198	195	297
2	85	82	48
1	100	93	169
0	70	76	6
-1	97	92	302
-2	131	136	38
-3	257	256	217
-4	173	176	297
-5	135	149	328
-6	285	302	22
-7	129	127	247
-8	98	101	304
-10	63	66	51
-11	47	50	284
-12	43	39	330

-5,2,L

10	57	59	171
7	104	114	247
6	238	235	142
4	54	43	198
3	82	84	304
2	196	189	131

-5,2,L

1	165	160	250
0	77	72	43
-1	92	92	354
-2	138	136	163
-3	121	122	305
-4	173	165	26
-5	60	64	129
-6	242	244	195
-7	145	141	306

-5,1,L

9	61	73	205
7	132	125	139
6	105	109	170
5	164	171	321
4	105	111	131
3	164	164	120
2	96	97	234
1	82	83	45
0	55	48	191
-1	77	82	167
-2	156	161	207
-3	281	276	66
-4	71	72	268
-5	176	176	104
-6	104	108	343
-7	160	154	113
-11	77	79	93

-5,0,L

12	45	55	38
10	49	45	359
8	86	81	102
6	150	152	298
4	72	70	1
2	139	140	10
-2	190	189	327
-4	217	212	303
-6	321	322	29
-8	62	64	176
-10	77	73	84
-12	69	70	305

-6,20,L

0	49	45	173

-6,19,L

2	100	96	351

-6,18,L

3	78	73	200
-2	53	54	195

-6,17,L

6	50	45	152
3	71	80	114
2	79	81	160
1	74	66	53
-1	67	68	126
-3	79	80	39

-6,16,L

6	69	63	353
2	131	128	7
0	48	46	87
-2	58	57	2
-6	86	76	11

-6,15,L

5	46	44	176
3	78	71	275
1	89	80	242
-1	86	89	313
-3	70	67	234
-7	67	82	255

-6,14,L

8	43	28	238
6	56	40	150
4	70	67	359
2	114	118	180
1	58	60	142
-2	84	80	208
-3	57	51	105
-6	82	86	212

-6,13,L

10	47	46	345
3	101	100	130
2	111	109	61
-1	53	52	57
-3	81	78	50
-6	71	73	300
-7	66	64	93
-8	63	57	355

-6,12,L

5	53	51	333
4	57	62	120
3	68	67	261
1	57	60	280
-1	72	73	25
-2	58	59	237
-6	67	64	77
-7	98	100	294

-6,11,L

8	72	59	237
6	82	76	173
2	105	104	194
-1	53	50	288
-2	57	53	223
-4	73	76	93
-5	84	82	63
-8	76	80	159

-6,10,L

6	48	43	78
5	49	57	250
4	79	79	310
3	90	87	62
1	117	116	126
-1	112	107	155
-2	65	61	101
-3	41	36	32
-4	45	31	89
-6	80	85	294
-7	96	96	114
-11	46	55	97

-6,9,L

10	59	54	2
8	68	65	63
6	60	66	324
3	131	135	213
2	146	152	44
1	72	64	331
0	56	53	318
-1	45	45	327
-2	116	120	331
-4	100	94	241
-5	69	69	249
-6	54	53	336
-7	77	71	283

-6,8,L

7	67	73	264
5	79	84	125
4	142	143	132
3	99	102	15

-6,8,L

2	132	129	214
1	78	65	219
0	107	102	186
-1	67	65	342
-2	148	148	180
-3	101	99	195
-4	93	93	236
-5	93	96	39
-7	70	67	303
-8	47	42	177

-6,7,L

9	59	68	87
8	51	53	281
7	113	114	98
6	60	59	162
5	51	53	175
4	148	158	311
3	124	123	50
1	104	104	77
0	125	124	25
-1	70	64	147
-2	86	88	134
-3	101	104	53
-4	111	112	51
-5	96	97	35
-7	103	105	99
-8	76	76	84

-6,6,L

9	69	74	293
8	66	60	83
6	86	93	347
5	98	95	297
3	169	173	212
2	151	160	10
1	95	104	326
0	64	69	319
-1	124	121	241
-2	131	147	34
-3	90	87	336
-5	134	138	209
-6	65	82	310
-8	50	56	4

-6,5,L

7	112	109	315
6	100	105	225
4	161	164	139
3	103	110	331
2	87	97	185
0	43	49	241
-2	83	84	286
-3	176	177	199
-4	156	159	202
-6	104	110	130
-7	68	77	258
-10	56	55	174

-6,4,L

9	80	77	117
6	60	71	122
5	133	136	117
4	109	111	0
3	220	225	65
2	81	91	241
1	68	75	114
0	140	137	24
-1	56	56	121
-2	112	107	205
-3	123	133	108
-4	199	201	345
-5	156	160	44
-7	93	98	75
-9	51	55	95

-6,3,L

7	77	73	97
6	50	60	46
5	83	76	304
4	148	148	295
3	221	220	212
2	147	143	353
1	85	89	338
0	154	155	22
-1	116	115	224
-3	236	241	356
-4	128	132	51
-5	145	136	242
-6	139	146	314
-8	83	89	71
-11	52	49	70

-6,2,L

9	74	74	283
8	88	95	167
6	152	144	252
5	54	50	291
4	172	171	123
3	183	181	231
2	53	60	110
1	62	55	344
0	148	146	150
-1	89	86	304
-4	165	163	187
-5	48	56	247
-6	167	166	138
-7	68	72	229
-8	85	89	228
-13	46	31	269

-6,1,L

7	106	114	307
5	87	97	86
4	67	70	59
3	244	257	32
1	63	68	168
0	128	120	286
-1	151	150	77
-2	55	58	276
-3	291	291	159
-4	105	102	32
-5	52	54	57
-6	98	95	166
-9	91	87	106

-6,0,L

4	196	212	317
2	121	114	333
0	220	212	24
-4	337	332	6
-6	145	143	286
-8	75	79	108
-10	43	51	302

-7,18,L

1	62	63	298

-7,17,L

1	60	56	127
-1	86	79	80
-5	70	67	68

-7,16,L

4	47	50	8
0	80	73	348
-1	51	44	91

-7,15,L

5	60	64	309
1	86	87	312
-1	54	46	262

-7,14,L

8	45	40	28
0	50	43	206

-7,13,L

0	80	83	342
-1	66	69	71

-7,12,L

9	71	62	271
5	67	66	323
3	86	84	163
0	73	72	270

-7,11,L

0	42	52	153
-6	87	71	149

-7,10,L

5	78	78	113
2	83	80	280
-1	48	56	357
-2	49	53	59
-5	58	46	46

-7,9,L

6	41	27	101
1	63	70	235
0	97	98	21
-3	69	73	285
-4	83	83	350
-8	51	50	56

-7,8,L

8	55	51	187
6	59	66	182
2	119	114	156
1	64	62	5
0	93	100	206
-1	106	110	189
-2	91	85	226
-6	70	67	120

-7,7,L

6	68	69	323
5	87	88	117
4	72	68	180
3	76	78	23
2	123	120	356
1	56	58	120
0	81	79	140
-1	140	139	73
-3	105	103	93
-4	86	82	222
-5	70	63	106

-7,6,L

8	54	52	9
5	44	50	248
4	60	72	46
3	77	72	339
2	99	102	284
1	115	116	220
0	101	101	10
-1	124	122	309
-6	86	82	328
-7	91	88	233

-7,5,L

10	60	50	152
8	71	76	209
6	90	79	179
4	63	57	294
3	96	95	204
2	128	128	147
-1	100	102	217
-2	128	136	194
-3	67	71	315
-5	86	99	268

-7,4,L

7	77	72	115
5	75	71	146
2	107	108	22
1	85	86	79
-1	128	140	121
-2	94	90	2
-3	68	67	95
-5	69	72	125
-6	80	78	66

-7,3,L

6	123	116	341
5	60	56	231
4	78	75	87
2	149	142	340
1	127	131	225
-1	118	115	354
-2	73	64	345
-11	49	35	271

-7,2,L

7	59	59	277
6	70	64	148
2	191	194	172
1	58	56	310
-2	195	206	197
-4	80	79	205
-5	60	57	238
-6	139	139	236

-7,1,L

11	65	61	84
7	97	105	94
1	176	171	58
-1	148	136	152
-5	85	81	263
-6	54	52	167
-7	91	99	82

-7,0,L

10	49	56	299
6	122	140	327
4	82	79	141
2	179	186	342
-2	249	251	29
-8	99	90	314

-8,16,L

-2	85	78	13

-8,12,L

1	57	60	216
-3	47	59	266
-7	51	41	262

-8,11,L

-6	53	51	190

-8,10,L

1	65	61	3
-1	60	56	64
-3	57	61	61

-8,9,L

-1	52	54	237
-2	69	61	359
-3	59	65	302

-8,9,L

-5	46	46	207
-6	55	53	36

-8,8,L

5	51	43	132
3	62	53	321
1	85	83	228
-2	68	59	184
-4	48	39	142

-8,7,L

5	50	47	66
4	63	67	348
2	85	91	180
1	74	72	114
0	62	61	29
-1	76	71	65
-3	86	92	103
-7	76	64	105

-8,6,L

5	68	76	295
2	94	92	1
1	87	89	5
-2	65	67	359
-5	84	89	224

-8,5,L

8	56	53	163
4	84	85	174
1	75	80	214
0	90	96	187
-2	62	69	191
-3	60	54	286
-4	93	99	191
-6	60	59	90
-7	60	69	264

-8,4,L

5	80	76	114
2	50	66	178
1	63	65	135
-1	60	62	42
-3	110	102	142
-4	64	73	74
-5	71	71	68
-6	44	48	251
-9	48	42	88

-8,3,L

4	68	74	350
1	51	54	345
-1	61	57	269
-3	41	46	345
-5	54	48	250
-6	47	40	317
-7	62	59	90

-8,2,L

8	57	51	164
5	74	76	277
0	96	94	223
-3	68	66	268
-4	90	92	227
-6	58	62	88

-8,1,L

5	88	87	93
3	80	80	32
-1	66	72	86
-5	74	85	58

-8,0,L

4	105	96	346
0	54	57	66
-2	87	87	343
-6	96	89	298
-8	77	75	78

-9,16,L

0	46	47	36

-9,13,L

-4	47	48	19

-9,11,L

0	90	71	172
-4	56	59	206

-9,10,L

3	52	47	356
1	51	53	115

-9,9,L

-2	43	29	302

-9,7,L

1	54	56	94

-9,6,L

-1	66	46	1
-3	83	82	234

-9,5,L

6	48	48	170
2	68	72	183
-1	54	49	239
-2	56	56	180

-9,4,L

-3	72	71	73
-7	47	52	67

-9,3,L

2	61	66	338
1	44	31	280
-2	55	53	355

-9,2,L

2	54	47	183
-2	44	51	193

-9,1,L

3	64	63	129
1	46	37	110

-9,0,L

6	76	69	338
2	76	72	343

-10,7,L

5	49	34	89

-10,3,L

0	66	54	356

-10,1,L

-1	52	44	41

-10, 0, L

4	56	54	7

APPENDIX 7

Structure Factor List for compound XXVI ,

Part II , p.84 .

Columns listed are ℓ, $|F_o|$ x10 , F_c x10 .

15,0,L

-2	66	73
-6	56	-58

15,-1,L

-4	89	-89
-6	41	44
-8	62	62
-10	34	-33

15,-2,L

-6	94	95
-7	53	48
-8	72	-72
-10	89	-82
-11	42	-40

14,0,L

2	49	-52
0	70	69
-2	76	74
-4	53	-51
-6	153	-144
-8	52	49
-12	55	55
-14	38	-39

14,-1,L

4	70	-70
0	64	60
-2	44	-37
-5	57	-52
-6	95	96
-7	41	-41
-8	55	55
-10	88	-88
-11	80	77
-12	62	-60
-16	65	60
-18	47	-44

14,-2,L

4	43	48
2	62	61
-2	48	-55
-3	49	-45
-6	61	62
-8	73	-70
-14	71	71
-15	93	85
-16	59	-51
-18	53	-47

14,-3,L

-1	58	-58
-3	57	-56
-4	35	37
-5	62	68
-6	74	-74
-8	69	-60
-9	82	-83
-12	39	40
-13	72	68
-14	70	70
-17	59	-55

14,-4,L

-4	39	38
-5	45	40
-7	87	-82
-9	49	-50
-10	55	-59
-11	49	56

13,0,L

8	114	107
6	55	49
4	64	-66
2	104	-99
0	44	40
-2	70	65
-4	78	-77
-8	95	87
-10	132	128
-12	39	-35
-14	111	-108
-18	70	69
-20	58	-57

13,-1,L

7	46	51
5	60	-55
2	39	44
1	65	-61
-2	97	-96
-6	87	84
-7	50	-49
-9	71	67
-10	42	-35
-12	56	-62
-13	45	-50
-14	71	65
-16	42	36
-18	88	-79
-22	61	67
-23	37	-29

13,-2,L

8	62	-61
4	57	50
3	32	31
2	40	30
-2	44	32
-3	65	-66
-4	80	76
-7	59	64
-8	63	-64
-10	82	-80
-11	67	-67
-12	121	114
-13	43	41
-15	53	62
-20	82	72

13,-3,L

7	34	-36
6	52	46
5	67	70
2	59	-53
-1	112	-105
-5	72	75
-8	64	-69
-9	104	-101
-10	58	53
-11	51	43
-12	53	51
-13	68	76
-15	31	-28
-17	84	-82

13,-4,L

5	43	43
4	54	48
3	44	-39
-2	49	-50
-3	75	80
-7	86	-88
-10	63	59
-15	50	-53

13,-5,L

-6	35	-29
-9	48	47
-11	39	-28

12,0,L

12	48	-43
8	93	91
6	66	-69
4	56	-56
2	77	75
-2	74	74
-4	108	-108
-8	45	48
-10	202	203
-12	137	-142
-16	98	96
-20	132	-134
-24	66	64

12,-1,L

10	82	82
6	123	-115
5	52	-49
4	47	45
3	39	-38
2	37	-42
1	40	42
0	43	46
-1	63	58
-2	40	-44
-4	57	51
-5	87	-81
-6	35	38
-7	37	40
-8	80	77
-9	31	-32
-10	162	-158
-11	34	-28
-12	74	-73
-13	40	-36
-14	130	135
-16	51	45
-18	81	-81
-22	68	65

12,-2,L

12	68	65
9	58	53
8	71	-70
7	61	-60
6	44	43
5	56	-55
3	40	44
1	52	43
-1	39	-38

12,-2,L

-2	33	30
-4	118	114
-5	86	88
-7	45	43
-8	66	-67
-9	83	-81
-10	73	-85
-11	49	-50
-12	112	111
-13	45	40
-15	51	46
-18	46	43
-20	88	87
-21	33	30
-24	58	-60

12,-3,L

10	66	-67
5	101	103
2	39	-28
1	135	-133
0	31	25
-1	81	-80
-3	95	101
-4	47	-43
-5	77	84
-7	58	-54
-8	36	-39
-9	79	-72
-10	85	82
-11	56	55
-14	85	-81
-15	119	-110
-16	31	30
-17	58	-54
-19	69	62

12,-4,L

7	75	75
3	45	-51
1	60	-63
-1	78	74
-4	96	86
-5	50	-47
-7	50	-51
-9	72	73
-10	63	61
-11	117	108
-13	103	-97
-15	83	-81
-19	68	66

12,-5,L

3	39	-28
-1	53	50
-5	54	-48
-6	51	-53
-8	64	64
-9	49	54
-10	55	62
-16	79	-74

12,-6,L

1	38	38
-7	55	56
-8	37	34

11,0,L

14	40	-32
12	76	-72
10	90	95
8	90	85
6	153	-149
4	35	-47
2	85	85
-2	42	41
-6	96	-102
-8	192	189
-10	57	-54
-12	131	-137
-16	150	147
-18	51	-60
-22	77	69
-24	48	43

11,-1,L

14	64	-64
12	60	63
11	35	31
10	98	93
8	74	-80
6	75	-77
5	50	-52
4	96	93
1	58	61
0	83	-88
-1	50	44
-2	42	43
-3	60	-60
-6	208	212
-10	194	-192
-12	73	-72
-13	30	-30
-14	140	137
-16	59	-63
-18	88	-91
-20	69	73
-22	74	74

11,-2,L

15	72	-72

11,-1,L

-26	45	-44

11,-2,L

14	54	50
12	51	44
11	47	43
10	113	-118
8	98	-98
6	79	83
4	48	43
3	128	128
2	57	-66
-1	89	-85
-2	57	53
-3	62	-68
-5	169	172
-7	55	-56
-8	79	-83
-9	62	-62
-10	34	35
-11	32	-35
-12	113	111
-13	95	94
-15	76	74
-16	123	-132
-17	39	-38
-18	73	68
-19	107	-106
-20	56	61
-21	62	57

11,-3,L

12	42	-46
9	120	-117
8	60	60
5	120	125
4	46	-48
3	65	61
1	114	-112
-3	116	117
-4	59	-61
-7	134	-136
-10	50	56
-11	91	94
-12	44	39
-15	99	-95
-19	119	118
-20	87	-88
-21	39	49
-23	79	-75

11,-4,L

12	52	-50
4	40	42
3	118	-112
2	41	-44
-1	151	143
-3	57	55
-5	72	-75
-7	28	-31
-8	44	35
-9	68	71
-13	120	-117
-17	87	77
-21	74	-75

11,-5,L

4	53	-63
3	69	-69
1	110	102
-2	70	72
-3	51	-52
-9	87	88
-11	98	-96
-13	71	-71
-14	53	-55
-15	76	75
-17	83	86
-21	36	-34

11,-6,L

0	48	48
-1	72	-72
-7	36	26
-11	41	-44
-12	78	-82
-17	60	-52

11,-7,L

-4	64	66

10,0,L

14	99	-93

10,0,L

12	63	-49
10	148	148
8	64	59
6	51	-48
4	236	-239
2	103	103
0	87	-83
-2	93	-96
-4	119	-125
-6	130	127
-8	47	43
-10	74	-73
-16	49	47
-18	127	-127
-20	104	-106
-22	50	48

10,-1,L

14	45	-40
12	122	119
10	34	35
9	60	57
8	124	-125
5	33	-26
4	143	137
2	85	85
1	70	70
0	256	-262
-1	95	100
-3	139	138
-4	54	62
-5	127	-133
-6	160	155
-8	230	-242
-10	57	-50
-12	84	86
-13	49	50
-14	113	112
-15	104	105
-16	44	-45
-17	51	53
-18	91	-90
-19	46	-42
-20	89	94
-21	51	-49
-26	70	-74

10,-2,L

14	42	52
13	30	35
11	52	54
10	164	-163
9	79	-76
8	44	-36
7	71	-73
6	78	83
5	51	59
3	79	77
2	117	-113
1	122	-124
0	112	116
-1	56	-48
-2	127	135
-4	56	-58
-5	135	138
-6	204	-210
-7	99	90
-8	262	-266
-9	176	-183
-10	67	64
-12	68	68
-13	62	61
-15	67	66
-17	139	-145
-18	100	100
-21	116	111
-22	92	-91
-23	45	43
-24	76	-74
-25	75	-72
-28	67	63

10,-3,L

13	75	74
11	59	-61
10	38	-40
8	85	89
7	88	84
6	53	-54
5	125	119
4	31	28
3	95	-96
1	89	-89
-1	51	53
-2	54	-44
-3	118	118
-4	112	117
-7	97	-95
-9	87	84
-11	133	132
-12	89	-86
-13	83	82
-14	30	-23
-15	117	-116
-19	78	80
-23	119	-115
-25	47	54
-27	73	78

10,-4,L

11	73	-66
9	44	43
7	43	45
3	99	-100
2	113	-114
0	32	-34
-1	95	95
-5	90	-94
-7	49	44
-8	97	99
-9	33	28
-13	96	-99
-14	73	-70
-17	169	167
-19	46	46
-21	72	-75
-24	51	44

10,-5,L

13	59	-58
12	44	36
9	68	65
7	36	20
5	107	-108
3	76	66
1	125	118
0	70	68
-3	139	-135
-4	55	-47
-7	59	52
-9	39	40
-11	89	-88
-14	72	-71
-15	129	125

10,-6,L

8	44	55
7	95	-87
6	94	-89
3	131	120
0	70	71
-1	94	-93
-2	102	-99
-3	59	52
-12	88	-84
-13	77	72
-17	92	-84

10,-7,L

0	52	-52
-1	100	95
-6	54	-56

9,0,L

18	57	59
14	130	-123
12	48	-49
10	85	92
8	70	80
6	101	-102
4	94	-97
2	232	238
-2	355	-366
-4	37	-49
-6	128	125
-8	72	73
-10	144	-147
-14	107	-112
-18	78	-71
-20	60	-58
-22	82	80
-24	102	108
-26	67	-65

9,-1,L

16	58	-55
14	81	78
13	68	-69
12	124	123
11	39	32
10	48	-47
9	54	50
8	168	-164
7	73	72
6	90	-94
4	102	103
1	36	32
0	165	-168
-1	46	-44
-2	189	189
-3	49	-51
-4	427	426
-5	100	-98
-6	95	-104
-7	255	263
-8	302	-303
-9	153	166
-10	55	-47
-11	52	55
-12	96	95
-13	69	-71
-16	31	-29

9,-1,L

-18	31	-33
-19	58	-65
-20	85	84
-22	70	72
-23	69	69
-24	133	-125
-28	52	50

9,-2,L

17	42	-42
14	41	48
13	42	48
12	57	-46
10	111	-107
9	99	-98
8	101	110
6	73	78
5	148	157
3	97	96
2	209	-202
1	159	-161
0	85	-85
-1	36	40
-2	66	66
-4	48	-55
-6	197	-195
-7	113	-116
-8	211	217
-9	178	-175
-10	127	132
-11	129	135
-12	89	-97
-13	240	242
-14	180	-175
-16	38	39
-17	132	-142
-18	52	48
-20	35	32
-21	65	60
-22	126	-120
-23	82	-85
-24	46	-53
-25	78	-77
-26	90	86
-27	46	48
-29	61	60

9,-3,L

19	61	-63
15	68	66
12	71	-77
11	88	-87
9	47	-53
7	155	161
6	115	122
5	106	100
4	37	41
3	150	-150
2	36	36
1	69	-72
0	72	-73
-1	207	198
-2	44	49
-3	62	-61
-4	230	-238
-5	124	109
-6	41	-44
-9	97	97
-10	125	131
-12	87	95
-13	89	-94
-15	186	-193
-17	160	157
-18	60	-56
-19	201	194
-22	89	-88
-23	73	-73
-24	39	42
-27	45	37

9,-4,L

13	49	-42
10	30	-32
7	100	106
5	173	-170
3	49	-51
2	58	-50
1	126	124
0	39	-36
-1	81	79
-3	107	-110
-9	91	88
-11	63	62
-12	196	-199
-13	122	-123
-17	105	107
-18	59	59
-25	69	66

9,-5,L

13	40	-36
9	66	75
7	100	-101
5	53	-54
3	133	128
1	73	68
0	104	106
-1	111	-116
-3	71	-74
-4	74	-73
-5	127	121
-8	98	98
-15	154	151
-19	74	-77

9,-6,L

12	40	-37
10	55	55
5	101	108
3	42	52
2	111	109
1	74	-68
-1	57	-55
-2	79	-73
-6	105	108
-7	120	-117
-10	116	-117
-12	52	-53
-13	78	73

9,-7,L

4	91	86
0	94	-93
-12	73	72
-16	113	-108

9,-8,L

6	53	54
1	36	36
-14	50	-45

9,-9,L

-4	42	-43

8,0,L

16	84	-82
14	42	-35
12	250	252
10	287	293
8	50	56
6	389	-400
4	165	-169
0	115	112
-2	118	-124
-4	193	201
-6	288	294
-10	243	-244
-12	72	-57
-14	82	72
-16	38	-35
-18	126	-115
-20	132	-124
-24	74	77
-26	148	-139

8,-1,L

22	56	53
18	94	-91
17	38	33
16	43	-44
15	77	-73
14	65	62
13	45	44
11	66	63
9	72	69
7	163	-165
6	135	135
5	282	-292
4	131	141
2	189	-191
1	293	302
0	230	-236
-1	30	-24
-2	119	119
-3	60	59
-4	247	251
-5	49	46
-6	143	-145
-7	71	-64
-8	184	-181
-9	68	-62
-10	91	96
-11	174	-170
-12	92	94
-13	79	76
-15	83	80
-16	79	-78
-17	53	52
-18	44	46
-19	91	-98
-20	106	104
-21	87	84
-22	37	42
-23	70	64
-24	184	-181
-27	33	-51
-28	59	53
-29	46	-45

8,-2,L

21	35	36
16	101	97
13	56	54
12	124	-122
11	32	-35
10	44	47
8	121	-126
7	67	67
6	90	96
5	121	116
4	86	-85
3	76	-75
2	118	113
1	360	-361
0	199	209
-1	63	-62
-2	337	341
-3	363	375
-4	346	-351
-6	241	-244
-8	94	100
-10	44	-42
-11	151	157
-13	97	-104
-14	68	-58
-15	124	-119
-16	84	96
-17	129	-128
-18	50	52
-19	76	79
-20	33	-31
-21	63	61
-22	110	-98
-24	64	63
-26	77	78
-27	65	66
-28	57	-59
-30	66	-61

8,-3,L

21	61	-61
19	42	-48
15	74	79
14	75	-79
11	63	-62
10	28	-34
8	127	126
7	158	152
6	95	106
5	58	-58
4	186	-191
3	210	-207
2	100	-104
0	64	64
-1	194	197
-2	66	72
-3	95	-93
-4	199	-213
-5	178	-183
-6	284	282
-7	85	86
-9	203	206
-10	52	47
-11	66	64
-13	115	-123
-14	111	-108
-18	62	-66
-19	43	40
-20	72	-71
-21	111	-114
-24	120	120
-25	101	95
-26	40	43
-27	67	62
-29	42	-41

8,-4,L

17	58	56
14	34	29
13	55	-56
11	56	-51
9	211	214
8	118	122
7	29	35
6	79	-80
5	156	-158
3	93	-92
1	203	199
0	37	42
-2	116	-109
-3	83	-83
-5	112	-113
-6	112	117
-7	93	97
-8	129	-123
-10	159	161
-11	39	-41
-12	89	-87
-13	60	-59
-14	45	43
-15	94	95
-17	114	113
-19	64	-63
-20	91	-94
-21	103	-106
-25	80	85

8,-5,L

15	73	-64
11	33	32
8	43	50
7	156	-160
6	58	-61
4	35	-34
3	198	197
2	37	-47
0	100	104
-1	71	-65
-5	74	75
-6	93	-99
-7	67	-78
-8	134	132
-9	72	-78
-11	60	-64
-12	119	-118
-13	103	94
-15	139	129
-16	65	68
-18	40	43
-19	43	-55
-23	48	43

8,-6,L

9	62	-64
6	45	-38
5	87	86
4	75	81
3	41	-47
1	113	-114
-2	120	-118
-3	53	56
-7	43	-42
-10	136	-140
-12	121	123
-14	58	64
-15	111	-111
-18	113	-117
-21	37	28

8,-7,L

7	43	43
4	66	58
3	56	-57
0	77	-73
-4	80	77
-5	46	-55
-8	129	-140
-10	101	100
-12	71	73
-16	82	-81

8,-8,L

2	75	-74
0	66	59
-2	70	69
-6	84	-86

7,0,L

24	91	-94
20	228	226
16	117	-117
14	57	-60
12	122	119
10	62	-57
6	57	-64
4	246	258
2	394	394
0	66	-68
-2	212	-204
-4	408	409
-6	161	166
-10	427	-396
-14	276	271
-16	74	68
-18	189	-181
-20	152	156
-22	224	228
-24	127	-129
-26	156	-146
-30	67	74

7,-1,L

24	53	-51
22	66	67
20	51	-58
19	88	89
18	47	-46
16	125	126
15	80	-79
14	208	211
13	127	-129
12	86	-86
11	73	72
10	89	-85
9	56	-56
8	178	-185
7	168	-174
6	44	-40
4	39	-36
3	203	201
2	77	-76
1	42	-41
0	30	-19
-1	381	-384

7,-1,L

-2	492	508
-3	116	-111
-4	121	128
-5	103	97
-6	121	-129
-8	117	-127
-9	285	-286
-10	121	-105
-11	71	-70
-12	100	94
-13	158	155
-14	116	-122
-16	48	-51
-18	41	42
-19	62	-63
-20	232	234
-22	137	-138
-23	43	39
-24	56	-51
-25	68	-69
-26	31	27
-28	68	68
-29	46	45
-30	67	-65
-31	68	61

7,-2,L

20	36	-43
18	85	86
16	108	105
15	46	41
14	95	-97
13	52	51
9	137	-136
8	96	102
7	116	107
6	118	120
5	123	124
3	27	-33
1	170	-171
0	304	313
-1	47	45
-2	138	-130
-3	295	305
-4	139	-132
-5	248	-257
-6	38	32
-7	158	-156
-8	190	200
-11	178	184
-12	39	-35
-13	188	-195
-14	133	142
-16	129	137
-17	98	106
-18	98	99
-20	148	-147
-22	118	-118
-23	59	-52
-26	42	43

7,-3,L

19	41	-34
17	42	48
15	60	55
14	62	-62
13	90	-82
11	175	-174
9	78	80
8	161	173
7	53	50
6	75	-74
5	84	-76
4	117	-123
3	169	-172
2	103	101
0	119	120
-1	218	220
-2	199	-200
-3	96	-97
-5	284	-286
-7	202	207
-8	107	111
-9	62	54
-10	197	-200
-11	315	-330
-13	226	-229
-14	53	-59
-15	162	170
-16	151	153
-17	121	108
-18	46	49
-19	83	72
-21	60	-58
-23	32	-38
-28	70	-72
-29	45	-51

7,-4,L

21	54	-52
18	57	50
17	115	114
13	61	-65
11	107	112
10	78	77
9	84	79
8	72	67
7	96	-94
5	273	-283
4	40	-37
3	32	22
2	86	89
1	162	161
0	99	-102
-1	200	204
-3	298	-300
-4	190	197
-5	164	169
-6	251	261
-7	255	259
-9	88	-86
-10	55	62
-11	358	-360
-12	180	-176
-13	51	-45
-14	162	-161
-15	50	50
-16	74	75
-17	98	96
-19	37	-33
-20	74	82
-23	78	73
-24	35	36
-27	76	-78
-29	54	-50

7,-5,L

19	40	53
18	39	45
15	37	-47
11	38	47
7	61	-58
6	132	-141
5	40	36
3	68	77
2	90	96
1	118	-129
-1	191	-195
-3	117	-118
-5	204	214
-7	61	64
-8	174	177
-9	101	-101
-10	48	49
-12	192	-199
-14	31	26
-16	69	70
-17	112	-114
-21	42	49
-25	49	-51

7,-6,L

17	40	-41
16	37	-40
15	73	63
12	44	44
9	55	-52
8	42	-42
7	63	62
5	101	112
4	75	77
0	73	-74
-5	76	-75
-6	90	98
-9	84	82
-11	95	98
-13	52	-47
-14	95	100
-15	98	-100
-26	36	-45

7,-7,L

6	103	109
5	69	-65
2	75	-70
-1	84	84
-2	48	48
-6	85	-90
-10	117	117
-13	66	-66
-16	54	-64

7,-8,L

0	68	69
-6	86	-85
-8	136	138
-12	34	-45

7,-9,L

-3	51	-46
-5	47	-47
-6	57	56
-10	44	-50

6,0,L

24	57	-59
22	41	40
20	72	64
18	174	-176
16	208	-215
14	237	235
12	231	225

6,0,L

10	221	229
8	239	-247
6	50	47
4	44	53
2	286	287
0	619	-594
-2	59	83
-4	578	589
-6	40	-33
-8	110	107
-12	613	615
-14	87	80
-16	303	-306
-18	239	-241
-20	206	206
-22	125	126
-24	44	-43
-26	38	-40
-28	62	59
-30	53	50
-32	56	-55

6,-1,L

22	74	75
21	58	58
18	124	-124
17	98	-90
16	130	133
15	100	-96
13	60	68
11	136	144
10	218	-218
9	211	-206
8	117	109
7	126	-125
6	36	42
5	84	80
4	123	122
3	105	100
2	187	-189
1	43	-52
0	61	66
-1	254	-261
-2	422	443
-3	269	-266
-4	189	-180
-5	89	64
-6	360	-364
-7	352	-361
-8	242	-241
-9	91	-103
-10	48	52
-11	113	105
-12	177	166
-13	277	268
-14	32	27
-15	213	-217
-16	107	108
-17	166	-164
-18	137	134
-19	133	-131
-20	47	46
-21	90	88
-22	182	-183
-24	57	-59
-25	49	-49
-28	40	47
-29	54	52

6,-2,L

24	40	51
21	84	79
19	67	-66
18	59	59
16	42	39
14	74	-82
13	92	89
12	86	-92
11	168	-168
8	138	138
7	116	116
6	65	-61
5	85	82
4	183	170
3	137	-135
2	214	212
0	268	283
-1	36	27
-2	147	-139
-3	239	241
-4	186	-181
-5	121	-120
-6	134	135
-7	208	-214
-8	105	117
-9	36	41
-10	138	132
-11	120	122
-13	36	-39
-14	201	205
-15	82	-79
-16	39	-37
-17	81	93
-18	67	66
-19	106	-110
-20	130	-130
-21	32	28
-23	71	-75
-24	67	73
-27	47	50
-31	44	-43

6,-3,L

21	68	-71
20	46	45
19	57	-44
18	64	72
17	81	79
16	91	-84
14	79	-82
13	76	-72
12	54	-54
10	132	142
9	103	99
6	76	-76
5	199	-200
3	127	-134
2	122	122
0	153	-157
-1	28	27
-2	217	-211
-3	265	-270
-5	127	-130
-6	59	56
-7	157	163
-8	199	203
-9	157	153
-10	41	-45
-11	229	-230
-12	167	170
-13	211	-207
-14	60	62
-15	172	177
-18	155	-153
-19	103	-107
-20	118	-119
-21	77	-70
-22	101	99
-24	54	50
-25	37	41
-28	39	-33
-29	69	-68

6,-4,L

19	116	109
15	139	-136
11	106	100
10	110	113
8	66	-75
7	114	-104
5	83	-89
4	88	88
3	199	186
2	112	126
1	354	363
-1	146	-146
-2	102	102
-3	318	-333
-4	97	-102
-5	52	-56
-6	87	85
-7	258	261
-8	52	51
-9	250	-257
-10	102	-99
-11	142	-137
-12	132	129
-13	248	253
-14	61	65
-15	194	200
-16	133	132
-17	127	-125
-18	44	-45
-19	142	-143
-22	75	-79
-24	53	47
-27	85	-77

6,-5,L

20	31	25
19	71	67
14	95	-94
13	90	87
12	63	65
11	73	-76
9	105	-102
8	160	-158
7	155	-157
6	114	-111
3	143	155
2	222	221
1	160	169
0	103	105
-1	241	-244
-2	59	63
-4	212	-212
-5	121	123
-6	160	164
-7	219	-215
-8	227	-218
-9	359	-364
-11	202	216
-12	78	-81
-13	65	71
-14	135	146
-16	82	81

6,-5,L

-17	82	-80
-18	64	59
-22	46	42
-24	39	39
-26	71	-75

6,-6,L

20	62	56
19	48	-44
16	66	-70
15	77	71
13	39	39
12	101	105
11	39	-42
10	65	-67
8	44	-40
6	75	-74
5	52	-57
4	145	150
1	40	-39
-1	34	36
-3	146	136
-4	126	129
-5	50	-49
-7	157	-156
-8	88	-93
-9	199	200
-13	129	-130
-14	101	90
-22	63	64

6,-7,L

14	99	102
13	62	-55
12	62	-59
10	52	-49
7	37	-39
6	58	56
4	50	-43
3	36	-43
2	146	-153
0	117	119
-1	70	76
-5	49	-50
-6	118	-119
-8	71	76
-11	106	-109
-14	46	-49

6,-8,L

10	64	63
8	76	72
6	54	-55
4	106	-112
0	108	104
-1	57	52
-4	84	-80
-8	80	79

6,-9,L

5	52	-54
-6	73	68

5,0,L

26	75	-70
20	68	69
18	166	-169
14	30	-34
12	445	442
10	157	-160
8	340	-346
6	97	93
2	630	-634
0	24	31
-2	505	533
-4	996	1044
-6	29	-26
-8	827	-792
-10	163	179
-12	85	85
-14	168	-175
-16	263	-269
-18	423	429
-20	54	55
-22	153	147
-24	130	-138
-26	51	-57

5,-1,L

25	34	-32
21	76	77
18	57	-55
17	121	-117
16	132	127
15	88	90
14	114	117
13	131	145
12	47	-36
10	354	-353
8	244	242
7	41	44
6	148	155
5	102	-98
4	313	-303
3	57	-68
2	326	-321
1	175	-181
0	124	131
-1	73	-80
-2	412	410
-3	398	364
-4	232	212
-5	200	165
-6	384	-392
-7	124	-135
-8	108	110
-9	92	-102
-10	189	182
-11	104	-101
-12	142	-138
-13	144	134
-14	242	-248
-15	179	-184
-16	188	194
-17	198	-189
-18	107	101
-19	133	147
-20	64	-67
-21	45	54
-23	59	-63
-24	66	-75
-25	72	-73
-26	47	50

5,-2,L

23	88	84
19	141	-141
18	64	60
15	114	113
14	123	-124
13	172	-175
12	154	-161
10	138	133
9	159	153
8	78	75
7	311	306
5	68	-55
4	46	37
3	91	-90
2	144	139
1	516	-504
0	159	-134
-2	275	-258
-3	194	194
-4	142	-145
-5	132	118
-6	64	77
-7	29	27
-8	239	244
-10	84	84
-11	149	148
-12	48	37
-13	34	-39
-14	106	110
-15	262	-265
-16	148	143
-17	116	112
-18	167	-175
-19	80	82
-20	50	-49
-21	68	-69
-23	49	-44
-24	56	46
-25	60	63
-26	38	24
-27	40	42
-29	52	-54

5,-3,L

21	108	-109
19	71	65
17	118	121
16	106	-108
15	94	-96
14	111	-112
13	111	-105
12	125	132
11	74	74
9	170	171
8	76	76
7	101	-95
5	80	66
4	71	69
2	195	-188
1	66	84
0	134	-136
-1	242	-226
-2	46	-53
-3	31	-24
-4	243	236
-5	127	-126
-7	327	320
-8	120	113
-9	36	-28
-10	249	-237
-11	176	-171
-12	38	40
-13	216	-208
-14	85	81
-15	149	159
-18	143	-146
-19	107	-103
-20	83	88

5,-3,L

-21	75	-67
-22	66	69
-23	79	82
-25	58	56
-27	77	-72

5,-4,L

19	102	102
17	43	-47
15	110	-112
13	62	66
11	163	159
9	96	-89
7	136	-139
6	44	-42
5	37	-40
3	168	165
2	137	-148
1	117	115
0	64	-66
-1	176	-183
-2	60	-53
-4	154	142
-5	216	216
-6	413	416
-7	173	184
-8	53	44
-9	389	-395
-10	175	-186
-11	120	-118
-12	47	-51
-13	259	258
-14	42	-45
-15	99	95
-17	104	-110
-19	96	-93
-20	113	111
-21	64	63
-25	67	-67
-27	45	-46
-29	61	64

5,-5,L

21	98	94
18	47	51
17	94	-95
16	46	-47
15	57	-52
14	47	-46
13	122	123
12	44	50
11	34	-35
10	55	55
9	80	-76
8	43	-46
7	72	71
5	128	127
4	65	62
3	226	234
2	75	81
1	361	-356
0	90	-84
-1	218	-226
-2	278	-283
-4	91	92
-5	273	289
-6	121	125
-7	177	-180
-9	80	-75
-10	45	-46
-11	188	194
-12	114	113
-15	141	-139
-17	78	-74
-23	46	-45

5,-6,L

17	43	-44
16	115	-113
15	45	48
13	87	-83
12	37	43
11	90	-86
10	82	-86
9	70	75
8	55	-47
7	86	83
6	121	120
5	89	87
4	214	215
1	116	-117
0	179	-190
-2	87	-91
-4	81	80
-5	118	-124
-6	28	-29
-8	120	-133
-9	213	211
-10	95	87
-12	133	134
-13	146	-142
-15	48	47
-20	69	65
-21	67	-66
-24	70	-71

5,-7,L

16	55	45
12	115	-121
8	70	70
7	79	-78
6	81	83
4	68	-65
3	36	39
-1	48	54
-4	101	-104
-6	71	-68
-7	98	96
-10	128	129
-11	157	-157
-12	105	-105
-13	68	70
-21	44	41
-22	69	-67

5,-8,L

4	70	-73
3	44	-50
2	113	106
-3	71	-72
-6	81	78
-10	45	-48
-12	78	-81

5,-9,L

3	55	54
2	44	52
1	50	48
-2	99	-94
-3	55	-55
-6	53	46
-15	54	57

4,0,L

18	49	-50
16	195	-201
14	244	253
12	112	112
10	312	-326
8	354	-368
6	281	281
4	304	-292
2	464	-467
0	43	51
-2	142	162
-4	244	253
-6	450	-454
-8	554	-528
-10	336	342
-14	252	-263
-16	305	-309
-18	349	356
-28	49	55
-32	48	-56

4,-1,L

28	48	-46
23	43	41
21	59	62
20	84	-80
18	69	68
17	71	-72
16	140	141
15	152	154
14	236	246
12	402	-411
11	74	75
10	209	-210
9	86	-88
8	91	94
7	174	169
6	220	223
5	216	206
4	433	-421
3	280	278
2	348	336
1	138	132
0	519	534
-1	285	277
-2	172	173
-3	75	64
-4	58	-71
-5	152	140
-6	982	-988
-7	266	-264
-8	216	218
-9	129	126
-10	156	149
-11	179	179
-12	36	-33
-13	126	123
-14	162	-163
-15	153	-148
-16	351	354
-17	53	-43
-18	41	43
-19	98	109
-20	204	-203
-24	35	-38
-26	95	91
-27	69	80

4,-2,L

21	50	-47
19	112	-115
18	43	41
17	171	172
15	113	109
14	111	-114
13	180	-174
12	119	-123
11	195	-187
10	99	91
9	85	75
8	176	-175
7	89	88
6	261	-252
5	101	-110
4	125	-137
2	262	258
1	37	36
0	268	-239
-1	276	274
-2	41	-51
-3	233	233
-4	149	-147
-5	340	-340
-6	245	-223
-7	145	-129
-8	306	300
-9	281	274
-10	339	-341
-12	104	-106
-13	49	-48
-14	212	209
-15	140	-149
-16	122	125
-17	242	245
-18	287	-291
-21	85	-83
-23	72	-69
-24	41	33
-25	118	109

4,-3,L

27	40	35
25	52	43
23	66	-68
21	74	-71
18	57	-58
17	189	192
15	76	-80
14	84	-84
13	51	50
12	209	211
11	254	262
9	101	101
8	78	80
7	366	-363
6	99	103
5	30	21
4	115	-117
3	55	55
2	142	-122
1	90	104
0	312	-316
-1	296	295
-2	125	118
-3	61	43
-4	295	-289
-5	319	332
-6	487	507
-7	128	158
-8	55	-53
-9	196	-193
-11	284	-276
-12	55	51
-14	44	43
-15	153	165
-16	290	-299
-17	182	189
-19	130	-131
-20	58	62
-23	66	67
-27	110	-104

4,-4,L

23	83	-81
20	37	-43
19	51	52
17	48	-45
16	65	-66
15	152	-152
14	83	91
13	153	162
12	79	83
11	178	183
10	224	-233
9	246	-252
8	99	91
7	117	-116
6	228	-226
5	66	66
4	77	60
3	176	187
2	93	-103
1	92	-95
-1	136	-135
-2	197	-198
-4	276	272
-5	296	293
-6	49	-60
-7	72	-74
-8	271	-263
-9	64	-68
-10	98	-107
-13	135	134
-17	121	-120
-18	80	80
-19	32	-31
-20	48	43
-21	149	144
-23	41	36
-24	36	-47
-25	107	-111
-29	50	44

4,-5,L

21	98	94
17	93	-100
15	83	76
14	124	128
13	202	202
12	66	-71
11	115	-116
10	64	69
9	178	-176
8	176	-173
7	108	109
6	136	-133
5	287	301
4	148	145
3	32	-32
2	257	260
1	235	-231
0	92	-90
-1	77	87
-2	52	-52
-3	226	237
-4	99	92
-6	97	-92
-7	111	-98
-9	86	-80
-10	136	-130
-11	266	280
-12	48	45
-13	55	56
-15	122	-123
-16	73	-73
-17	72	-75
-19	89	85
-20	68	72
-21	52	59
-22	48	42
-23	75	-75
-27	45	52

4,-6,L

23	46	44
22	35	41
21	57	-52
19	91	-88
18	97	-98
14	72	73
12	45	46
11	58	-60
10	61	-51
9	93	94
8	141	-148
6	61	64
3	193	-191
2	90	-94
1	122	116
0	253	-261
-2	289	291
-3	87	-90
-4	84	81
-6	83	-91
-7	142	137
-8	218	-225
-9	153	149
-10	117	120
-11	62	63
-12	161	162
-13	165	-173
-14	94	-97
-15	36	-39
-16	119	-123
-20	82	74
-22	43	-39
-23	50	35

4,-7,L

13	54	52
11	61	63
10	53	57
8	92	88
2	124	-128
1	75	72
-4	136	-134
-7	48	-44
-8	157	163
-9	69	-68
-10	134	139
-12	140	-132
-13	60	64
-14	92	-91
-17	49	-63
-21	47	38
-22	44	-40

4,-7,L

-24	82	83

4,-8,L

10	69	65
6	92	-96
-2	103	-98
-4	74	-75
-6	83	83
-9	35	-42
-14	119	125
-18	36	-40
-20	75	-72
-22	71	66

4,-9,L

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-1	62	-58
-2	85	-80
-4	83	84
-6	53	58
-8	56	-55
-10	94	-98
-18	46	-40

4,-10,L

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-13	70	57

3,0,L

24	38	-32
22	75	69
20	47	-53
18	211	-217
16	59	48
14	455	453
12	149	-152
10	173	-179
8	337	-330
6	156	-158
4	446	-445
2	130	-133
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-2	203	202
-4	156	-155
-6	584	-596
-8	681	-661
-12	196	181
-14	288	-304
-16	230	-240
-18	289	292
-20	117	118
-22	187	-196
-24	86	-87

3,-1,L

24	57	57
22	58	-55
20	51	-53
16	286	292
14	207	-213
13	246	250
12	223	-233
11	103	-96
10	161	158
9	140	-123
8	380	379
7	81	80
6	258	-256
5	516	532
4	181	-196
3	237	-230
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-1	33	-29
-2	302	306
-3	626	648
-4	235	-231
-5	90	-90
-6	412	-405
-7	265	-248
-8	57	-56
-9	281	284
-10	150	144
-11	322	322
-12	283	-273
-13	73	-68
-14	101	99
-16	326	322
-17	45	48
-18	148	148
-19	149	149
-20	301	-302
-21	42	41
-22	64	-70
-24	52	52
-25	43	-42
-26	45	42
-28	63	-66
-32	49	48

3,-2,L

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21	55	-53
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15	55	54
14	333	-334
13	186	-185
12	91	-89
10	71	74
9	308	310
8	228	-219
7	514	502
6	122	108
5	836	-831
4	478	444
3	438	-411
2	66	-65
1	61	61
0	452	-440
-1	320	320
-2	451	-450
-3	100	101
-4	799	-778
-5	75	-75
-6	202	206
-7	300	301
-9	281	282
-10	199	-202
-11	343	-339
-12	149	-146
-13	162	-159
-14	222	219
-15	83	90
-16	199	-195
-17	92	100
-18	68	-64
-19	90	-87
-20	34	-41
-21	29	-37
-22	111	110
-23	85	84
-25	73	70
-26	71	-75
-29	86	-82

3,-3,L

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19	83	76
18	39	36
17	61	63
15	73	-75
14	171	-172
13	113	-111
12	228	224
11	124	128
10	81	81
9	136	136
7	46	36
6	50	60
5	52	-56
4	194	-187
3	725	716
2	96	-91
1	138	-110
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-1	265	-248
-3	80	-89
-4	300	297
-5	429	429
-6	222	205
-7	211	213
-8	126	-123
-9	91	85
-10	220	-223
-11	73	-73
-12	174	160
-13	157	155
-14	216	-209
-15	177	191
-16	164	-166
-17	62	-63
-18	44	49
-19	55	-48
-21	66	65
-22	88	91
-31	50	53

3,-4,L

25	78	-77
22	37	-31
21	59	54
19	111	108
18	41	40
17	98	-91
15	115	-113
14	76	78
13	101	102
12	45	44
11	109	111
10	297	-298
9	225	-223
8	45	-35
7	305	-299
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3	169	154
2	258	-245
1	64	-71
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3,-4,L

-3	311	298
-4	99	97
-5	251	-231
-6	91	-91
-7	51	-55
-8	140	-140
-9	222	-209
-11	122	118
-12	28	-22
-13	244	243
-14	232	-234
-15	73	70
-16	106	108
-17	159	-166
-19	92	97
-21	64	56
-24	31	-35
-25	71	-69

3,-5,L

23	86	80
21	58	61
20	49	43
19	65	-58
18	35	-36
17	32	-16
15	119	119
14	90	89
13	89	88
12	61	59
11	304	-309
9	141	-149
8	47	-46
7	358	362
6	105	-105
5	298	304
4	86	81
3	136	-126
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1	105	-101
-1	199	192
-2	82	-80
-3	77	81
-4	115	115
-5	110	-107
-6	110	-103
-7	66	-69
-8	109	-105
-9	120	127
-10	89	-83
-11	214	217
-12	55	55
-13	49	54
-14	77	80
-15	214	-221
-17	84	85
-18	90	-93
-19	124	125
-20	70	74
-23	149	-145
-24	57	-56
-25	77	69
-27	65	66
-28	33	38

3,-6,L

24	33	31
22	70	75
21	54	-44
20	62	-58
18	52	-46
13	29	-32
12	129	-132
10	108	-109
9	89	92
8	65	67
7	65	-66
6	233	230
5	206	-200
4	112	117
3	64	-63
2	278	-282
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-1	85	83
-2	114	120
-4	55	-49
-6	220	-230
-7	58	55
-10	148	146
-12	124	135
-13	109	-116
-14	187	-189
-15	38	36
-16	76	-81
-17	126	126
-18	108	110
-22	106	-105
-23	45	33
-24	49	-46
-26	44	42

3,-7,L

18	41	52
16	57	48
7	70	72
6	58	-57
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-4	90	-83
-5	101	100
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-13	102	-102
-15	48	40
-16	112	117
-20	64	-64
-21	58	53
-25	63	-60

3,-8,L

10	87	84
7	68	-66
6	82	-77
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3	74	74
-6	107	106
-7	52	-53
-10	92	-98
-12	73	-80
-13	101	100
-18	62	-59

3,-9,L

16	49	-53
13	43	-39
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8	121	-120
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-8	130	-126
-12	83	86
-16	71	-72

3,-10,L

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-9	68	-73

2,0,L

28	63	-71
26	84	-81
24	161	153
22	92	96
20	41	-43
18	239	-236
16	163	170
14	262	260
12	241	-224
10	127	-118
8	152	156
4	845	-858
2	234	220
0	239	216
-2	891	937
-4	515	503
-6	1224	-1260
-8	906	-895
-10	232	218
-12	31	21
-14	274	-280
-16	65	58
-18	184	188
-20	115	119
-22	309	-314
-26	101	107
-30	95	-84

2,-1,L

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29	33	-21
28	34	-34
27	42	-41
23	74	79
22	103	-100
21	43	45
19	54	-56
18	218	220
17	216	-220
16	285	280
15	72	71
14	312	-320
12	265	-262
10	148	149
9	36	-35
8	58	-51
7	331	325
6	241	-241
5	404	405
4	50	-63
3	691	-683
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1	368	-334
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-1	778	836
-2	731	742
-4	735	-707
-5	496	-478
-6	465	479
-7	225	-216
-8	56	-47
-9	328	331
-10	103	100

2,-1,L

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-14	181	177
-15	50	-46
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-18	38	34
-19	35	34
-20	236	-239
-21	147	-146
-24	183	188
-26	44	-45
-27	84	79
-28	62	-63
-29	45	39
-31	37	-26
-32	74	74

2,-2,L

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23	50	-49
22	73	77
19	99	97
18	90	96
17	46	55
16	219	-218
15	50	49
14	82	-80
13	301	-299
12	203	211
11	34	-23
10	94	101
9	62	69
7	488	462
6	63	47
5	674	-648
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3	42	38
2	560	-560
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-1	233	-225
-2	1000	-1021
-3	551	-530
-4	382	380
-5	239	230
-6	383	-371
-7	106	108
-8	43	39
-9	242	-224
-10	233	210
-11	254	-250
-12	286	276
-14	119	118
-15	258	260
-16	180	-171
-17	162	163
-18	314	-320
-19	92	-88
-20	185	-188
-21	55	-55
-22	82	82
-23	80	80
-25	56	-60
-28	54	59
-29	49	-49
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2,-3,L

27	57	54
25	32	-35
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23	52	-50
22	27	-27
18	32	28
16	177	-189
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12	76	72
11	91	93
10	226	217
9	172	167
8	302	-294
7	435	-412
6	303	298
5	206	-205
4	123	-116
3	590	583
2	77	70
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-2	202	199
-3	462	432
-4	425	407
-5	228	242
-6	307	-281
-7	91	-81
-8	61	56
-9	236	-226
-10	304	-285
-11	134	-139
-12	82	77
-13	281	283
-14	67	57
-15	132	131
-16	67	63
-17	69	-74
-19	42	-49
-21	128	125
-24	93	-95

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18	87	-89
15	55	-50
13	161	155
12	129	116
11	74	69
10	115	-111
9	347	-333
7	335	-315
6	158	160
5	412	406
4	283	-274
3	155	149
2	106	-103
1	317	-300
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-1	55	43
-2	463	437
-3	162	150
-4	170	-165
-5	186	177
-6	39	38
-7	265	-263
-8	162	-147
-9	155	-160
-10	150	-142
-11	57	58
-12	144	-140
-13	314	325
-15	216	-219
-16	115	122
-19	81	81
-21	60	57
-23	120	-130
-29	55	57

2,-5,L

25	61	66
23	57	63
22	70	69
21	52	-49
20	88	84
19	125	-126
15	65	69
13	52	49
11	112	-117
10	278	-284
6	70	76
5	61	-58
4	271	273
3	282	-287
2	106	110
1	230	-222
0	33	-33
-1	309	292
-2	88	-92
-5	55	-65
-8	133	-133
-9	214	212
-11	215	213
-12	53	51
-13	182	-190
-14	95	98
-15	173	-182
-16	66	-68
-17	185	191
-18	35	-36
-19	75	73
-20	73	77
-21	114	-122
-22	38	-41
-24	61	-56
-25	107	101
-28	48	47

2,-6,L

25	53	46
24	55	50
20	92	-92
16	84	81
15	34	-41
14	78	85
13	93	-96
12	47	-52
10	126	-127
9	151	158
8	192	191
7	36	47
4	193	-195
3	89	86
2	149	-151
0	189	193
-1	139	-141
-2	122	130
-3	206	-204
-4	98	-98
-5	65	63
-6	134	-135
-7	88	90
-9	122	121
-10	178	184
-12	65	-63
-13	120	-125

2,-6,L

-14	112	-116
-15	64	63
-16	81	-87
-17	62	63
-18	119	127
-19	53	-58
-22	45	-43
-23	73	73
-26	86	84
-27	36	-35

2,-7,L

22	49	-45
20	48	-38
18	55	53
12	111	-108
10	124	123
8	121	124
7	187	-185
6	62	-57
4	77	-88
2	89	87
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-1	79	78
-2	157	-154
-3	86	85
-5	163	-170
-8	141	142
-12	62	-60
-16	53	54

2,-8,L

10	111	109
9	77	-69
8	120	-117
6	80	-76
5	103	105
2	185	181
0	53	-54
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-5	48	-47
-9	34	-41
-14	67	70
-18	84	-85

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10	75	-74
4	115	112
2	87	-90
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-2	95	101
-4	61	53
-8	94	-99
-12	59	55
-14	36	20
-16	91	-87

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9	34	-29
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-3	84	88
-5	41	51
-7	76	-76
-11	75	76

1,0,L

28	58	-58
24	124	120
22	82	-84
20	216	-217
16	278	288
14	409	414
10	88	91
8	516	543
6	921	935
4	953	-996
2	845	-935
0	443	444
-2	474	449
-4	585	-621
-6	71	46
-8	1171	1166
-10	646	669
-12	387	-385
-14	395	-413
-16	109	-104
-18	279	291
-22	194	-195
-24	89	91
-26	55	49
-30	83	-79

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27	47	-45
26	92	95
23	44	42
22	45	-43
21	82	-80
20	41	45
19	159	-164
18	168	174
17	91	92
16	37	-47
15	90	87
14	279	-288
13	120	-124
12	278	-285
11	422	-419
10	38	53
9	30	25
8	213	199
7	83	73
6	109	91
5	224	227
4	212	199
3	1237	-1283
2	1116	1197
1	33	-20
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-3	88	-70
-4	476	-479
-5	35	-21
-6	533	-531
-7	230	233
-8	146	-133
-9	422	429
-10	93	-85
-11	33	-26
-12	507	496
-13	524	-520
-14	317	328
-15	297	-296
-16	212	207
-17	134	124
-18	156	-157
-19	196	191
-20	266	-276
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-25	75	69
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-30	72	64
-31	52	-47

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20	106	111
19	52	56
17	71	70
16	76	-75
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13	54	-41
11	141	152
10	90	93
9	256	259
8	189	176
7	226	-219
6	76	61
5	59	62
4	607	602
3	569	-574
2	30	-42
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-2	403	399
-3	420	405
-4	553	538
-6	191	186
-7	304	290
-8	73	66
-9	86	-87
-10	135	120
-11	64	57
-12	320	-305
-14	111	-100
-15	51	52
-16	74	-63
-17	95	-100
-19	195	-194
-20	92	99
-21	36	-41
-22	118	129
-23	163	165
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29	75	69
28	34	27
25	89	-85
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22	59	61
20	82	83
18	231	-240
16	57	-59
15	60	-60
14	74	70
13	49	54
12	109	107
11	104	100
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7	54	-61
6	166	160
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-11	113	-129
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-15	42	42
-16	265	-273
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-18	51	-56
-19	48	-52
-20	109	108
-21	140	138
-22	55	59
-23	47	-55
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-25	102	-110
-28	60	52
-29	47	50
-30	48	-43

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27	91	-82
23	142	144
21	80	79
19	64	-62
18	58	53
17	168	-162
16	235	237
13	90	91
12	48	-50
10	89	-77
9	341	-327
7	246	248
6	91	89
5	469	460
4	192	193
3	171	157
2	44	50
1	367	-355
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-2	262	264
-3	274	271
-4	240	-213
-5	284	-270
-6	187	189
-7	332	-336
-8	124	127
-10	178	-170
-11	437	436
-12	37	-39
-13	100	102
-14	53	54
-15	201	-196
-17	123	-129
-18	148	152
-19	174	172
-22	70	-67
-23	99	-104
-24	35	-30
-27	83	79

1,-5,L

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22	43	42
21	62	-60
19	58	58
18	143	-134
17	93	96
13	158	-159
12	176	175
11	263	-263
10	214	-212
9	163	-156
8	116	-113
7	420	415
6	169	168
5	47	-45
4	244	237
3	116	-121
2	180	-176
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-1	181	164
-2	41	-36
-3	153	-163
-4	98	-90
-5	281	-280
-7	93	82
-8	112	-109
-9	163	160
-10	156	155
-11	48	42
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-15	45	41
-16	109	-110
-17	190	186
-18	56	54
-21	108	-113
-24	43	-48
-25	46	48
-28	32	30

1,-6,L

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22	30	37
20	45	-45
16	40	34
15	35	37
13	138	142
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11	59	-62
10	38	-41
9	158	158
8	307	315
7	161	-160
6	110	112
5	217	-210
4	167	-168
3	70	71
2	47	45
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-2	86	-75
-3	42	-39
-4	126	-125
-5	101	102
-6	48	-49
-8	159	169
-9	124	126
-10	45	47
-11	162	-166
-13	64	-65
-14	129	-126
-15	47	44
-16	112	119
-17	35	-35
-19	65	-63
-21	72	73
-22	83	-78

1,-7,L

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14	58	-53
13	63	-61
11	99	102
10	138	139
9	52	56
7	171	-167
6	240	-237
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2	121	122
1	56	-56
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-3	72	69
-5	65	-73
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-11	71	-67
-12	55	-51
-13	62	62
-16	64	65
-24	58	56

1,-8,L

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14	55	-52
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9	71	-71
8	79	-76
7	72	70
6	84	-86
5	32	41
4	145	141
3	59	-52
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-2	73	-68
-3	75	-76
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-5	52	-55
-10	56	-51
-14	40	42
-16	32	-22
-22	54	56

1,-9,L

6	92	91
2	90	-92
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-2	129	126
-3	75	-76
-5	96	96
-6	58	-58
-10	68	61
-12	41	36
-17	54	-51

1,-10,L

1	62	-60
-3	82	82
-7	92	-90
-8	39	35

1,-11,L

3	61	-61

0,0,L

-4	604	-626
-6	997	-1029
-8	112	112
-10	596	-571
-12	36	26
-16	408	413
-18	301	310
-20	196	-198
-22	72	-69
-24	56	58
-28	97	-98

0,-1,L

-1	668	716
-2	779	-757
-3	202	-174
-5	1198	-1198
-6	428	450
-7	770	-745
-8	109	-101
-9	365	362
-10	318	-323
-11	191	-180
-12	165	153
-13	128	-134
-14	91	-74
-15	106	94
-16	89	98
-17	84	83
-18	148	-153
-19	41	-41
-20	92	-94
-21	164	-170
-22	129	129
-24	43	44
-25	106	104
-26	39	-30
-27	37	-40
-29	64	-63

0,-2,L

0	472	-474
-1	505	514
-2	438	429
-3	535	537
-4	23	-23
-5	115	-118
-6	165	167
-7	47	41
-8	156	153
-9	166	-173
-10	511	500
-11	411	-414
-12	185	193
-13	93	83
-15	100	98
-17	46	48
-18	180	-186
-19	57	-57
-20	80	90
-23	125	123
-25	50	-52
-27	84	-85
-28	58	51
-30	32	-33

0,-3,L

-1	49	37
-2	471	473
-3	43	35
-4	350	342
-5	226	-220
-6	104	-97
-7	140	-149
-8	79	-75
-9	522	-523
-12	80	-73
-13	65	61
-14	54	-54
-15	54	53
-16	75	-75
-17	193	-188
-18	139	144
-19	59	52
-20	164	169
-21	59	64
-22	61	-70
-23	28	25
-25	104	-103
-30	94	-85

0,-4,L

0	330	303
-1	334	330
-2	174	171
-3	463	426
-4	87	97
-5	128	-135
-7	276	-274
-8	103	-98
-9	193	189
-11	146	147
-12	58	59
-13	108	-104
-14	60	63
-15	294	-292
-16	33	38
-18	106	110
-19	118	123
-20	101	-101
-23	93	-92
-26	37	36
-27	98	102

0,-5,L

-2	187	178
-3	329	-324
-4	100	87
-5	263	-259
-6	277	-280
-7	242	226
-8	69	70
-9	236	228
-10	121	128
-11	118	-125
-12	91	88
-14	139	-138
-15	37	-43
-16	73	70
-17	53	59
-19	133	-131
-21	67	-69
-22	47	-45
-25	103	103
-28	45	39

0,-6,L

0	60	70
-1	41	42
-2	75	80
-3	170	-169
-4	213	-210
-5	170	173
-6	76	76
-8	183	188
-9	127	-117
-10	69	72
-11	97	-95
-12	39	-43
-13	28	27
-14	34	-40
-16	97	95
-18	30	-32
-24	46	48

0,-7,L

-2	75	-79
-3	73	66
-6	210	212
-7	118	-119
-8	48	-46
-9	33	-28
-12	100	-105
-14	118	115
-15	43	-39
-22	56	54

0,-8,L

0	50	-40
-4	128	123
-5	69	-64
-8	115	-110
-11	31	37
-12	96	88
-14	46	48
-16	74	-76
-19	35	-34

0,-9,L

-2	77	73
-6	117	-115
-7	48	-46
-10	52	46
-12	39	38
-13	50	46
-14	57	-52

0,-10,L

0	60	59
-3	89	86
-4	68	-60
-5	45	-51

0,-11,L

-1	43	46
-3	40	-44

APPENDIX 8

Structure Factor List for Sulphamic Acid,

Part II , p.104 .

Columns listed are ℓ , $|F_o|$ x10 , F_c x10 .

0,0,L

12	403	397
10	50	52
8	737	-753
6	509	507
4	570	-559

0,-2,L

12	117	119
11	201	-202
10	126	-125
9	251	-261
8	137	-125
7	444	445
6	385	371
5	256	-271
4	161	-150

0,-4,L

12	116	-116
11	224	-229
10	74	72
9	38	38
8	176	178
7	77	71
6	409	-417
5	46	-36
4	89	90
3	361	351

0,-6,L

11	71	69
10	117	118
8	262	263
7	238	-241
6	160	-154
5	276	282
4	323	328
3	125	121
1	277	-272
0	640	-666

0,-8,L

9	106	110
8	84	84
7	287	-291
6	117	-112
5	249	252
4	12	-11
3	88	-87
2	113	116
1	439	-442
0	166	-163

0,-10,L

6	216	216
5	80	80
4	60	-61
3	25	23
2	137	-136
1	183	-184
0	146	147

-1,0,L

12	22	-21
10	419	-419
8	287	285
6	22	-5
4	83	34

-1,-1,L

11	140	141
10	137	-138
9	240	-239
7	154	151
6	64	-56
5	384	373
4	232	204

-1,-2,L

12	60	60
11	150	-152
10	186	-188
9	337	341
8	95	90
7	102	-96
6	197	196
5	94	81
4	383	-377

-1,-3,L

12	39	38
11	26	25
8	235	232
7	29	-26
6	23	-24
5	164	160
4	387	-374

-1,-4,L

12	19	-18
11	175	-176
10	177	182
9	240	239
8	190	-192
7	102	106
5	217	-221
4	202	207
3	440	451

-1,-5,L

11	80	-81
10	27	-27
9	156	154
8	80	-81
7	115	-120
6	20	-22
5	223	-230
4	174	177
3	318	322
2	22	21
1	34	-33

-1,-6,L

10	317	322
9	103	-105
8	141	-137
7	48	50
6	180	-182
5	195	198
4	346	347
3	277	-280
2	579	-598
1	81	79

-1,-7,L

10	198	203
9	109	111
8	69	-70
7	37	-36
6	90	-92
5	106	-105
4	224	225
3	196	200
2	365	-370
1	117	-115

-1,-8,L

9	244	-248
8	25	-24
7	22	21
6	28	31
5	214	214
4	85	-84
3	403	-407
2	23	-18
1	278	277

-1,-9,L

7	28	-27
6	22	-19
4	236	239
3	28	-31
2	65	-66
1	67	63

-1,-10,L

6	21	21
5	29	-24
4	199	-198
3	43	-41
2	179	178
1	75	75

-1,-11,L

1	14	-14

-2,0,L

12	49	-50
8	227	223
6	226	-237
4	12	12

-2,-1,L

12	126	-122
11	130	-126
9	89	-87
8	219	218
7	508	499
6	269	-266
5	561	-564
4	108	105

-2,-2,L

12	123	-126
11	104	101
10	50	53
9	195	196
8	31	36
7	364	-368
6	277	276
5	219	213

-2,-2,L

4	183	165
3	32	-33

-2,-3,L

12	141	-140
10	109	109
9	68	72
8	94	92
7	86	-91
6	512	-512
5	38	41
4	101	102

-2,-4,L

11	181	185
10	24	24
9	54	56
8	227	-233
7	141	-138
6	91	91
5	99	97
4	177	-179
3	267	-257
2	95	-92

-2,-5,L

11	153	154
10	38	41
9	19	-21
8	59	-63
7	312	-312
6	43	49
5	370	381
4	19	20
3	106	110
2	106	-99
1	292	-294
0	192	180

-2,-6,L

10	103	-105
9	22	20
8	42	-43
7	27	-24
6	139	139
4	78	-75
3	45	47
1	59	-64
0	95	91

-2,-7,L

8	162	-163
7	180	-181
6	257	261
5	208	207
4	156	-162
3	65	67
2	163	-163
1	207	-209
0	371	377

-2,-8,L

8	67	-67
7	82	81
6	126	-128
5	96	-95
4	20	-19
3	22	25
2	70	68
1	81	79
0	139	141

-2,-9,L

7	52	52
6	284	288
5	53	-54
4	66	-64
3	48	46
2	211	-214
1	75	72
0	214	212

-2,-10,L

4	88	89
3	59	59
2	87	85
1	121	120
0	259	-258

-2,-11,L

1	156	156
0	42	-40

-3,0,L

12	82	82
10	109	-103
8	16	-15
6	151	153
4	381	-384
2	402	418

-3,-1,L

11	113	-109
10	79	77
9	257	251
8	321	-321
7	295	-294
6	92	92
5	278	-272
4	397	395
3	327	390
2	115	79
1	113	100

-3,-2,L

10	36	35
9	68	-68
8	144	141
6	52	-51
5	86	-78
4	326	-306
2	114	-106
1	169	165

-3,-3,L

12	110	-109
10	324	324
9	86	-88
8	312	-309
7	98	100
6	80	-80
5	48	-42
4	619	636
3	35	-28
2	546	-549
1	11	-7

-3,-4,L

11	78	81
10	74	-73
9	80	-82
8	47	-45
7	111	-119
6	25	19
5	132	135
4	94	95
3	260	-254
2	163	153
1	283	278

-3,-5,L

11	201	202
9	296	-299
8	141	-139
7	137	137
6	66	-64
5	407	408
4	405	408
3	567	-585
2	44	-49
1	237	231

-3,-6,L

9	54	-53
7	20	21
6	59	63
5	59	62
4	47	-49
3	96	-104
2	24	5
1	51	51

-3,-7,L

9	120	-119
8	204	206
7	137	141
6	81	82
5	203	206
4	413	-417
3	247	-249
2	231	233

-3,-8,L

8	55	-57
6	28	-30
4	187	193
3	28	-33
2	15	-7
1	19	20

-3,-9,L

7	36	-35
5	176	-177
4	200	-203
3	255	255
2	197	195
1	117	-115

-3,-10,L

5	70	71
3	43	-45

-3,-10,L

2	91	-91
1	38	-36

-4,0,L

12	106	-104
10	84	86
8	43	38
6	302	-312
4	105	111
2	215	216
0	14	-23

-4,-1,L

11	55	51
8	162	-163
7	260	-264
6	515	536
5	324	337
3	276	275
2	550	-578
1	165	-183
0	302	326

-4,-2,L

11	99	96
8	79	77
7	172	-169
6	57	-47
5	237	232
4	62	64
3	46	43
2	61	52
1	172	-181
0	250	-252

-4,-3,L

10	54	-54
9	133	-135
8	246	-245
7	240	243
6	486	496
5	153	-160
4	220	-230
3	137	-130
2	395	-404
1	445	442
0	561	573

-4,-4,L

11	43	40
9	60	57
8	106	-109
7	156	-151
6	99	99
5	157	163
4	114	-114
3	67	64
2	55	-56
1	238	-244
0	293	296

-4,-5,L

10	64	-67
8	45	43
7	264	266
6	264	269
5	330	-328
4	20	-10
3	76	-72
2	184	-188
1	262	254
0	85	-82

-4,-6,L

9	34	-37
8	85	-85
7	52	51
6	246	246
5	23	-28
4	48	-52
3	28	26
2	203	-199
1	101	96
0	173	187

-4,-7,L

9	58	61
7	100	101
6	223	-223
5	166	-169
4	60	63
3	125	-127
2	89	87
1	37	35

-4,-8,L

7	129	131
5	137	-137
3	30	-41
2	23	20
1	148	150

-4,-9,L

6	164	-165
5	141	141
4	83	82
2	125	124
1	156	-152
0	217	-213

-4,-10,L

4	65	65
3	22	18
2	52	51
0	167	-165

-5,0,L

10	134	133
8	251	-253
4	369	372
2	134	-143

-5,-1,L

11	31	27
10	50	-49
9	81	-82
8	115	118
7	186	191
6	102	-110
5	117	119
4	42	-43
3	114	-124
2	31	-33
1	135	-130

-5,-2,L

11	185	180
10	129	124
9	282	-280
8	18	13
7	105	108
5	280	278
4	111	-111
3	501	-518
2	170	-180
1	270	282

-5,-3,L

10	69	-70
9	43	45
8	199	203
7	57	-60
6	28	20
5	105	113
4	447	-454
3	88	-88
2	84	87
1	21	-21

-5,-4,L

10	246	-244
9	239	-237
8	93	91
7	68	66
6	75	69
5	209	204
4	187	-185
3	415	-421
2	411	421
1	261	263

-5,-5,L

10	36	-34
9	105	106
8	26	26
7	80	-81
6	49	51
5	252	-253
4	196	-200
3	310	302
2	91	85
1	29	-27

-5,-6,L

9	54	53
8	206	207
6	23	25
5	21	22
4	331	-331
3	27	20
2	206	202
1	57	-56

-5,-7,L

8	53	-52
7	71	-71
6	74	-73
5	93	-92
4	197	197
3	102	101
2	190	-180
1	26	29

-5,-8,L

7	92	-93
5	129	-127
4	108	106
3	232	231
1	100	-101

-5,-9,L

5	85	85
4	143	141
3	147	-146
2	32	-28
1	109	106

-5,-10,L

2	269	-267
1	72	-70

-6,0,L

10	44	-44
8	253	-247
6	321	321
4	195	-205
2	212	-211
0	512	548

-6,-1,L

11	54	54
10	90	-89
9	28	-23
8	87	85
7	102	107
6	37	32
5	141	-146
3	183	-185
2	56	58
1	130	134
0	196	-202

-6,-2,L

10	36	-39
9	135	-131
8	55	-52
7	362	360
6	69	69
5	321	-328
4	76	-75
2	23	-22
1	510	531
0	123	128

-6,-3,L

10	23	25
9	74	74
8	158	-153
7	27	-24
6	120	-124
5	41	-40
4	88	-95
3	15	8
2	92	87
1	96	-92
0	380	393

-6,-4,L

10	39	36
9	71	-67
8	181	180
7	232	234
6	257	-256
5	230	-228
4	131	135
3	29	24
2	189	184
1	342	346
0	389	-391

-6,-5,L

9	90	-92
8	83	-85
7	37	34
6	128	127
5	50	47
4	14	13
3	57	56
2	129	-126
1	129	133
0	151	151

-6,-6,L

8	150	148
7	72	-72
6	212	-214
5	76	71
4	148	147
2	134	133
1	81	-74
0	357	-352

-6,-7,L

6	40	-39
5	35	33
4	53	-55
3	35	36
2	50	47
0	69	67

-6,-8,L

6	39	37
5	179	179
3	23	-22
2	28	-28
1	257	-253

-6,-9,L

4	41	40
3	78	80
2	93	-90
1	50	-48
0	52	-57

-7,0,L

10	313	-309
8	120	121
6	56	46
4	143	-142
2	474	504

-7,-1,L

10	94	-93
9	112	-106
8	62	54
7	27	-29
6	100	96
5	44	39
4	209	-207
3	107	-108
2	193	200
1	146	149

-7,-2,L

10	75	-74
9	204	207
8	116	119
7	42	-46
6	52	58
5	70	-64
4	246	-251
3	246	251
2	138	140
1	223	-231

-7,-3,L

9	34	33
8	112	109
7	22	21
6	67	66
5	139	-141
4	134	-135
3	164	168
2	307	315
1	63	-62

-7,-4,L

9	140	142
8	156	-157
5	113	-115
4	220	216
3	232	235
2	123	-117
1	157	-162

-7,-5,L

8	52	54
7	44	-42
5	32	-31
4	31	-29
3	123	122
2	85	88
1	108	-111

-7,-6,L

7	47	47
6	76	-74
5	125	124
4	149	150
3	168	-164
2	367	-367
1	49	49

-7,-7,L

6	42	42
3	30	33
2	20	-18
1	66	-68

-7,-8,L

3	270	-266
2	36	33
1	200	194

-8,0,L

8	265	257
6	146	-148
4	136	138
2	147	146
0	521	-534

-8,-1,L

9	44	-43
8	105	101
7	210	206
6	64	-56
5	170	-169
4	116	122
3	30	34
1	260	262
0	240	-245

-8,-2,L

8	46	44
7	124	-123
6	81	-84
5	62	62
4	43	47
3	45	-48
2	45	44
1	214	-216
0	110	-115

-8,-3,L

8	140	139
6	292	-293
5	33	32
4	83	83
3	30	-30
2	191	190
0	276	-279

-8,-4,L

8	61	-59
6	105	106
4	35	-36
3	100	-99
2	74	-72
1	14	-12
0	123	119

-8,-5,L

7	218	-215
6	24	26
5	184	185
4	45	47
3	46	43
1	260	-259
0	177	-180

-8,-6,L

5	86	-88
4	93	-93
3	32	-30
1	98	96
0	210	207

-8,-7,L

4	88	-88
2	116	-115
1	137	-137
0	295	288

-8,-8,L

1	139	135
0	71	67

-9,0,L

4	87	-85

-9,-1,L

7	58	-58
6	55	-52
5	210	-205
4	119	114
3	330	332
2	204	-201
1	180	-181

-9,-2,L

7	27	-22
6	49	-46
5	89	-91
4	48	-48
3	72	72
2	121	-124
1	29	29

-9,-3,L

6	31	-27
5	30	28
4	251	253
3	45	-40
2	172	-172
1	19	15

-9,-4,L

6	12	0
4	81	79
2	59	59
1	91	90

-9,-5,L

5	142	142
4	66	-68
3	242	-243
2	40	-40
1	116	113

-9,-6,L

4	40	-38
2	49	49
1	20	-15

-10,0,L

6	129	-125
4	86	84
2	71	70
0	121	-120

-10,-1,L

6	154	151
5	166	166
4	31	-29
3	42	39
2	92	-91
1	198	-198
0	76	77

-10,-2,L

5	103	101
2	138	136
1	24	-24
0	38	-33

-10,-3,L

5	42	-40
4	76	-80
2	100	-100
0	227	223

-10,-4,L

3	85	86
2	62	-61
1	66	-65

-10,-5,L

2	20	-17
1	185	183

-11,0,L

2	185	-179

-11,-1,L

3	69	-65

-11,-2,L

2	63	-63
1	58	56

0,-2,L

3	164	146
2	305	-301
0	285	264

0,-4,L

2	340	325
0	324	-339

-1,-1,L

3	641	-603
2	364	354
1	275	266

-1,-2,L

3	235	253
2	580	561
1	483	-466

-1,-3,L

3	247	-225
2	281	-247
1	57	42

-1,-4,L

2	294	-302
1	472	-471

-2,0,L

2	314	338
0	406	-424

-2,-1,L

3	381	-358
2	311	298
0	581	-586

-2,-2,L

2	501	-466
0	277	-269

-2,-3,L

3	51	49
2	397	386
1	190	-183

0	46	-86

-2,-4,L

1	301	-296
0	670	633

-2,-2,L

1	755	-725

-2,-1,L

1	700	695

0,0,L

2	587	-548

APPENDIX 9

Structure Factor List for

Pneumadin hemoglobin, Fe(II) [illegible]

Reflections listed are [illegible]

APPENDIX 9

Structure Factor List for

Prieurianin brosylate, Part III , p.124 .

Columns listed are ℓ, $|F_o|$ x10 , $|F_c|$ x10 , α.

12,-1,L

6 160 117 13

12,-2,L

2 178 164 105

12,-3,L

7 145 183 354

11,0,L

5 244 206 272
1 228 261 93

11,-1,L

12 126 146 184
7 125 85 210

11,-2,L

5 217 161 149

11,-3,L

9 218 204 22
6 218 175 315

11,-4,L

7 136 131 173

11,-5,L

6 152 171 138

10,0,L

10 173 165 185
9 214 217 93
3 231 202 271
1 350 344 92

10,-1,L

10 210 187 178
7 124 130 202
6 303 275 11
3 219 198 72
1 179 179 309

10,-2,L

14 152 137 133
13 152 133 95
12 251 230 94
11 207 189 229
10 164 84 335
8 237 248 261
7 153 121 328
5 219 235 42
3 199 157 173
2 310 327 86

10,-3,L

6 245 224 6
5 141 134 256
3 219 230 220

10,-4,L

12 221 213 252
7 292 280 194
6 166 166 154
4 264 270 189
3 242 259 27
1 209 206 314

10,-5,L

15 190 160 331
13 156 157 279
10 170 138 84
4 127 135 220
2 254 229 304
0 156 80 172

10,-6,L

4 168 173 38
2 217 178 279
1 246 182 96
0 160 201 186

10,-7,L

3 201 222 42

10,-9,L

0 165 158 182

9,0,L

17 312 330 272
11 236 207 98
10 212 234 182
8 237 245 359
7 425 397 275
4 274 304 179
3 318 328 96
2 361 382 180
1 205 196 97

9,-1,L

14 202 206 88
13 126 150 348
12 323 270 239
10 382 343 109
8 182 107 200
7 192 179 156
5 198 178 305
4 162 91 99
2 353 355 209
1 287 310 160

9,-2,L

11 310 294 338
10 186 188 325
8 364 277 270
7 431 420 127
6 329 338 137
5 224 256 222
4 247 263 130
3 326 311 236
1 372 357 324

9,-3,L

16 122 100 290
13 279 266 211
12 277 223 220
10 134 162 32
8 323 314 15
7 284 327 109
5 361 402 174
3 198 235 210
2 292 219 216
1 347 382 8

9,-4,L

11 182 174 299
8 229 217 152
7 275 213 19
4 206 215 227
2 139 127 359

9,-5,L

10 138 139 86

9,-5,L

8	359	352	188
5	240	224	334
4	181	116	140
3	125	139	29
2	430	422	355
1	127	126	220
0	146	147	272

9,-6,L

6	190	155	277
4	213	170	244
3	182	220	59
2	381	327	163

9,-7,L

15	173	131	58
14	129	121	12
13	199	152	315
10	193	170	218
9	148	164	184
6	272	215	32
5	139	118	113
3	216	186	17
2	258	271	251
1	184	152	116
0	188	117	92

9,-8,L

14	147	182	93
6	123	156	87
3	149	162	194
1	205	200	311
0	133	121	282

9,-9,L

12	177	149	167
5	172	202	187

9,-10,L

7	142	154	71
3	178	166	334

9,-11,L

11	131	43	318

9,-12,L

2	162	156	154

8,-0,L

21	123	97	96
19	259	245	90
9	188	204	87
8	117	106	195
5	490	474	269
4	206	204	11
0	418	386	187

8,-1,L

18	157	135	10
17	255	271	284
15	239	237	143
13	353	385	33
12	238	237	174
11	209	200	262
9	250	287	300
8	231	240	306
7	213	229	48
6	179	178	320
5	245	260	122
4	212	201	140
3	351	287	202

8,-2,L

18	200	159	282
15	368	352	62
14	290	250	52
12	140	111	166
10	254	292	245
9	269	253	219
8	245	258	314
7	307	296	354
6	331	338	340
4	445	385	91
3	114	96	222
2	415	432	88
1	218	218	213
0	383	385	3

8,-3,L

20	176	153	226
17	211	199	43
14	265	232	352
10	271	280	213
9	318	348	30
8	157	191	143
6	228	245	91
5	188	136	281
3	303	278	60
2	178	162	197
0	249	236	181

8,-4,L

19	156	166	324
16	158	129	285
13	271	177	242
11	445	423	4
10	165	118	344
9	211	220	211
8	176	228	44
3	165	133	127
2	278	240	152
1	168	139	347
0	228	219	7

8,-5,L

18	142	158	121
12	230	173	43
11	165	132	114
10	221	173	292
8	208	149	155
6	217	196	289
5	151	208	328
4	180	200	118
1	213	205	128
0	219	150	357

8,-6,L

18	145	141	112
13	144	107	205
12	354	324	4
11	256	271	24
10	326	326	215
5	204	146	47
4	124	122	339
2	278	260	348
0	252	278	187

8,-7,L

11	185	147	235
8	193	222	62
5	320	313	89
4	335	326	75
3	245	194	316
1	235	244	274

8,-8,L

13	167	161	314
8	326	268	346
3	189	180	195

8,-8,L

1	225	246	187

8,-9,L

11	155	173	37
8	243	175	341
5	201	170	153
4	167	169	326
3	134	81	151

8,-10,L

11	173	181	356
6	163	163	231

8,-11,L

0	130	140	182

8,-13,L

5	131	132	70

8,-15,L

7	133	107	51

7,0,L

17	170	184	276
16	200	306	3
14	192	195	4
12	318	349	183
11	407	376	95
10	207	250	185
9	329	274	272
7	199	290	278
6	180	216	9
5	280	277	272
3	549	529	94
1	561	516	94

7,-1,L

18	217	225	325
17	143	145	45
13	224	183	9
12	340	287	143
11	147	156	257
10	155	212	253
9	323	315	117
7	396	397	122
6	394	366	4
5	369	324	347
4	271	232	176
3	523	534	326
2	658	577	137
1	462	447	285
0	196	129	279

7,-2,L

22	133	120	8
17	217	208	76
16	293	295	159
15	269	324	121
14	281	298	129
13	173	163	188
12	323	325	6
11	298	305	305
10	401	433	292
8	361	345	53
7	260	223	95
6	266	250	139
5	535	597	189
4	342	345	73
3	336	294	206
2	409	402	304
1	629	641	353
0	542	489	275

7,-3,L

21	133	101	285
19	182	135	2
18	252	275	54
17	197	190	72
15	207	237	207
14	298	337	280
13	263	274	167
10	202	270	125
9	307	296	348
8	245	237	68
7	224	211	7
6	317	378	306
5	373	410	190
3	224	190	191
2	445	462	43
1	293	323	358
0	216	204	101

7,-4,L

20	141	98	94
16	205	224	213
14	193	220	291
13	138	172	308
12	300	291	45
11	295	272	302
10	127	36	214
9	240	226	113
8	323	340	117
7	292	290	151
6	614	605	241
5	245	220	4
4	343	291	336
3	459	508	310
1	264	232	146
0	653	618	93

7,-5,L

13	232	225	45
10	196	240	299
9	273	291	145
8	277	292	166
7	199	191	290
6	444	455	109
4	251	206	356
3	499	448	60
2	372	426	8
1	397	380	170

7,-6,L

17	133	184	260
16	204	206	48
15	252	226	288
13	636	613	81
12	272	312	127
11	262	248	153
9	244	214	139
8	269	264	11
7	553	549	279
6	297	294	15
5	128	129	290
4	113	140	316
3	466	465	110
2	293	304	172
0	221	262	92

7,-7,L

19	206	201	223
14	160	137	262
11	253	267	232
9	465	460	187
8	197	178	308
7	352	396	36
6	238	188	63
5	200	174	49
4	241	246	78
3	341	358	308
2	168	144	154
1	337	324	225

7,-7,L

0	238	190	275

7,-8,L

19	193	174	340
18	133	116	271
17	236	236	71
14	213	242	81
13	292	271	165
11	224	269	273
10	293	319	274
9	415	395	359
8	275	234	256
6	229	232	124
4	302	294	47
3	223	249	225
0	195	219	82

7,-9,L

13	136	151	205
12	291	285	171
10	178	154	124
9	304	293	43
8	193	202	13
4	341	310	273
3	170	148	149
2	290	234	157
1	345	309	12
0	422	419	93

7,-10,L

17	205	197	132
7	267	230	170
6	126	148	238
5	113	105	22
2	250	238	2

7,-11,L

11	146	157	97
8	249	209	189
4	236	246	86
2	348	330	4
0	277	254	272

7,-12,L

8	180	132	34
6	185	222	340
4	231	238	220
2	211	199	183

7,-13,L

7	162	127	77
1	249	210	223
0	248	196	272

7,-15,L

4	161	128	290
0	195	201	93

6,0,L

20	254	249	358
19	224	165	274
16	379	393	179
15	220	193	267
13	189	197	100
12	189	164	2
10	668	694	182
9	168	179	285
8	469	404	358
7	248	244	86
5	715	774	94
4	677	658	178
1	98	151	286
0	1074	922	182

6,-1,L

22	177	166	184
20	139	179	113
19	219	281	276
15	299	253	51
14	354	375	149
13	325	314	191
12	221	231	217
11	194	170	254
10	134	157	139
9	336	318	254
8	618	675	339
7	285	232	298
6	211	225	41
4	688	628	134
3	248	269	133
2	357	310	358
1	749	633	211

6,-2,L

20	175	144	255
18	128	140	186
16	207	241	34
14	393	384	110
13	144	169	120
12	111	118	338
11	267	276	214
10	287	241	285
8	215	142	91
7	309	306	18
6	161	87	347
5	306	245	285
3	227	143	330
2	328	310	259
1	464	448	181
0	473	406	178

6,-3,L

19	154	148	54
16	137	150	57
14	203	204	220
11	228	179	356
9	168	159	251
7	172	190	224
6	372	313	74
5	525	481	154
4	112	121	2
3	281	262	17
2	432	413	68
1	172	149	320

6,-4,L

20	215	207	22
18	143	178	118
17	143	135	317
15	168	171	177
14	259	254	239
12	166	195	73
10	345	313	124
9	227	223	138
8	340	350	309
6	164	197	306
5	550	507	239
4	381	417	171
3	174	162	0
2	604	577	122
1	215	236	139
0	399	397	3

6,-5,L

18	356	333	132
15	169	202	335
14	171	220	13
13	423	401	336
10	267	285	238
9	367	417	167
8	159	111	212
7	349	345	137

6,-5,L

6	216	212	41
5	307	325	278
4	362	394	346
3	340	286	78
2	272	255	253
1	177	170	279

6,-6,L

15	172	151	188
14	416	415	174
13	419	394	103
11	158	192	100
9	274	292	226
7	275	248	319
6	181	118	62
5	168	153	291
4	170	121	213
3	402	386	51
2	156	104	201
1	178	160	249
0	125	145	189

6,-7,L

20	167	183	175
19	205	128	214
17	136	121	347
16	273	287	322
15	245	211	357
11	326	279	172
9	313	314	302
8	267	287	128
7	232	250	286
6	276	268	204
5	132	179	289
4	163	195	130
3	162	159	193

6,-8,L

17	117	143	124
15	168	148	250
13	275	271	289
9	261	277	147
7	364	370	122
6	190	146	107
5	158	176	59
4	303	323	44
3	183	209	230
2	260	251	285
1	332	394	172
0	249	234	180

6,-9,L

23	131	154	223
19	169	143	2
15	173	198	202
14	165	154	138
11	167	194	50
10	200	203	335
9	300	209	329
7	393	418	135
6	165	122	266
5	170	123	289
4	157	110	185
2	307	292	10
0	306	264	179

6,-10,L

18	145	118	116
13	247	195	180
12	153	143	165
4	177	192	189
2	136	199	107
0	197	167	6

6,-11,L

13	167	175	337
12	226	181	157
9	236	240	213
7	191	153	232
5	123	85	56
3	318	310	27
1	165	95	313

6,-12,L

17	155	144	282
5	193	185	248
4	229	230	312
1	172	181	181
0	286	277	182

6,-14,L

10	124	104	256
5	278	233	265

5,0,L

20	214	306	185
17	566	594	271
16	395	370	6
15	368	395	90
13	152	163	264
12	165	165	195
10	336	402	186
9	442	487	89
7	341	378	273
6	737	669	6
5	216	149	90
4	922	811	182
3	517	439	268
2	446	455	189
1	742	683	91

5,-1,L

17	183	244	111
15	183	199	61
14	239	222	73
12	463	470	120
11	356	363	298
10	111	143	265
9	393	330	337
8	210	166	324
7	943	908	126
6	733	646	282
5	397	415	90
4	560	523	169
3	226	183	246
2	522	481	239
1	785	734	214

5,-2,L

21	153	128	199
17	188	229	52
15	306	328	251
13	316	329	218
12	278	305	11
11	357	381	353
9	439	448	17
8	616	549	212
7	325	323	176
6	563	478	167
5	838	815	160
4	619	570	348
3	136	146	25
2	515	490	43
1	440	466	333
0	268	191	85

5,-3,L

28	141	140	138
21	131	151	29
20	245	240	100
18	173	184	109
14	368	381	263
13	355	337	246

5,-3,L

12	183	181	310
11	429	436	2
10	343	362	118
8	458	422	119
6	501	451	214
5	742	701	160
4	966	935	316
3	294	262	287
2	494	442	330
1	312	350	345
0	1481	1434	93

5,-4,L

20	232	195	24
19	125	159	198
18	131	157	170
17	267	307	177
16	339	349	233
14	242	267	182
13	298	319	344
11	380	373	254
10	320	280	12
9	596	558	104
8	432	462	171
7	237	291	141
6	316	240	261
5	486	481	314
4	241	308	286
1	545	570	209
0	543	564	91

5,-5,L

22	168	148	5
19	251	229	197
18	176	179	230
15	221	259	344
13	203	212	353
12	258	212	73
11	585	556	85
10	437	426	250
9	416	345	232
8	289	301	254
7	271	296	266
6	318	286	87
5	368	360	357
4	516	519	141
3	464	475	90
2	562	527	320
1	614	686	103
0	1242	1150	271

5,-6,L

22	153	184	204
17	290	289	298
16	314	368	4
15	214	204	300
13	387	436	134
12	326	278	184
9	162	212	254
8	190	253	39
7	300	281	319
6	596	578	353
5	156	204	14
4	323	371	210
3	741	682	59
2	656	577	178
1	500	453	106
0	621	539	269

5,-7,L

24	137	129	165
21	152	197	267
20	153	191	350
18	267	226	353
17	237	204	76
15	242	270	86
14	163	150	127
13	379	386	256
12	343	376	167
11	619	619	286
10	444	440	251
9	335	338	220
8	192	225	330
7	471	464	63
5	147	148	22
3	318	315	280
2	309	294	42
1	648	582	260
0	347	312	277

5,-8,L

21	199	226	282
19	151	142	5
15	360	369	198
14	268	325	125
13	138	138	200
11	300	290	338
10	444	401	238
9	618	627	24
8	207	195	204
7	255	285	32
6	300	284	70
5	528	554	192
4	161	112	217
3	376	391	232
2	359	356	354
1	508	523	318

5,-9,L

16	172	166	24
13	181	149	271
11	426	392	21
10	315	343	99
9	237	190	341
8	329	327	77
7	168	179	80
6	355	307	278
5	495	527	189
4	586	610	272
3	238	203	178
2	242	245	159
1	191	188	333
0	217	197	104

5,-10,L

19	119	73	192
14	256	264	330
13	214	211	297
12	289	299	36
10	131	127	78
9	247	247	113
8	346	296	216
7	240	202	106
6	293	265	167
5	248	215	348
4	280	267	359
3	178	211	355
2	312	322	24
1	235	262	220

5,-11,L

18	199	209	201
17	252	204	256
11	226	244	110
8	284	259	263
7	255	229	291
6	385	346	183
5	189	225	282
4	375	337	41
3	259	282	90
2	265	303	0
1	159	186	169

5,-12,L

12	264	249	157
8	276	275	357

5,-12,L

7	173	132	309
6	251	198	312
5	258	267	43
4	251	270	228
3	118	71	325
2	386	331	155
1	292	275	229
0	617	608	91

5,-13,L

13	204	160	339
10	176	160	248
9	155	176	296
7	206	255	139
6	157	159	80
4	256	236	99
1	162	162	322
0	146	159	277

5,-14,L

10	166	172	302
9	205	147	29
8	162	160	11
0	247	193	272

5,-15,L

0	177	148	97

5,-17,L

3	123	96	117
1	177	146	91

4,0,L

16	241	221	178
15	339	316	94
14	505	471	359
13	409	391	97
12	854	799	181
11	280	192	273
10	297	304	2
9	1010	1088	273
8	267	296	178
5	1180	1009	94
4	241	237	356
3	854	743	93
1	813	841	274
0	2963	2878	0

4,-1,L

22	230	228	210
21	172	168	72
19	231	188	176
18	351	374	22
17	236	171	2
16	219	218	105
13	488	496	235
12	432	381	196
11	257	225	312
10	139	71	298
9	331	359	38
8	491	439	282
7	1069	1002	13
6	727	579	157
5	239	314	215
4	253	184	299
3	921	907	213
2	339	314	259
1	933	764	173
0	753	744	5

4,-2,L

22	218	261	264
19	178	152	34
16	284	293	131
14	313	323	25
13	375	351	274
12	343	360	279
11	139	77	219
10	616	521	311
9	134	98	242
8	161	178	305
7	544	409	57
6	541	529	80
5	346	340	312
4	564	618	54
3	860	703	254
2	935	837	307
1	548	553	30
0	348	299	357

4,-3,L

19	254	249	347
18	182	197	350
17	293	288	140
16	229	285	242
15	281	311	182
14	195	220	307
13	254	282	129
12	230	247	69
11	789	746	344
10	150	149	59
9	431	437	121
8	308	291	318
7	460	400	147
6	910	754	211
5	612	539	43
4	830	758	145
3	964	905	60
1	1344	1184	293
0	246	166	179

4,-4,L

22	214	195	42
21	161	161	30
17	215	239	26
15	194	207	323
14	306	307	275
13	260	208	301
12	236	278	156
11	164	87	355
10	151	148	132
9	189	185	184
8	452	391	101
7	362	345	9
6	1123	999	308
5	173	156	354
4	294	317	50
3	758	741	162
2	559	539	87
1	451	402	55
0	318	262	181

4,-5,L

19	345	335	207
18	518	518	154
15	357	343	32
14	550	508	15
12	174	138	304
11	277	278	137
10	443	463	231
8	900	809	164
7	286	255	346
6	439	351	32
4	447	441	11
3	520	463	69
2	1283	1206	284
1	615	518	6
0	245	309	192

4,-6,L

23	207	176	151
21	292	307	120
16	127	142	242
15	240	275	297

4,-6,L

14	367	401	196
12	491	489	75
10	297	289	48
8	500	492	303
7	177	152	306
6	462	422	178
5	535	501	46
4	800	795	192
3	116	83	144
2	666	613	331
1	773	659	320

4,-7,L

17	153	121	322
16	185	184	265
15	250	222	236
13	272	268	211
12	237	247	176
10	288	256	10
9	353	333	114
8	475	471	81
7	485	450	341
6	256	254	258
4	221	187	154
3	290	281	175
2	195	156	224
1	121	136	103
0	247	193	14

4,-8,L

22	191	185	18
18	161	159	241
17	175	192	129
14	237	253	107
13	475	458	327
12	204	164	310
11	382	406	302
10	165	100	193
9	136	71	244
8	254	187	146
7	470	483	158
6	379	414	26
5	186	234	310
4	491	433	312
3	132	148	70
2	187	212	279
1	140	134	190
0	156	151	183

4,-9,L

20	175	157	119
19	195	212	350
16	184	139	266
15	144	153	126
12	287	293	83
11	351	317	39
10	183	144	10
9	252	216	68
8	270	315	240
7	346	312	285
6	381	408	279
5	297	299	141
2	409	410	71
1	226	258	35
0	126	138	5

4,-10,L

16	234	254	298
14	211	176	293
13	147	150	284
12	264	305	103
10	330	303	145
9	235	232	37
6	359	355	294
5	221	216	339
3	357	343	233
2	210	160	41

4,-11,L

17	131	137	194
14	195	171	3
12	197	171	282
11	289	270	310
9	165	112	245
8	201	208	129
6	164	214	83
5	232	242	85
4	124	130	281
1	296	273	259

4,-12,L

12	109	102	303
10	277	207	349
9	283	288	301
7	194	237	331
6	191	180	152
5	201	251	109
3	396	364	152

4,-13,L

15	158	101	337
13	166	203	218
12	237	294	248
11	132	122	86
9	280	243	92
8	170	191	275
6	129	149	111
5	171	183	329

4,-14,L

7	176	163	186
6	166	103	115
3	267	241	346
1	220	232	23

4,-15,L

6	204	202	199
4	133	96	224

3,0,L

27	149	137	271
24	171	131	175
23	112	158	93
20	135	125	191
17	149	164	92
16	404	387	6
15	424	402	93
14	294	267	177
13	165	116	270
12	1372	1399	182
11	696	647	87
9	973	1076	270
8	360	292	170
6	1696	1587	2
5	557	422	92
4	391	365	185
3	872	906	88
2	744	594	352
1	553	449	86

3,-1,L

21	238	262	243
20	293	351	305
18	350	358	1
17	220	220	16
16	248	225	182
15	305	257	53
14	354	359	218
13	279	253	162
12	742	676	44
11	407	388	247
10	398	372	270
9	620	653	75
8	710	649	208

3,-1,L

7	609	606	134
6	490	360	329
5	318	295	48
4	896	643	45
3	1452	1239	321
2	962	932	61
1	784	878	275
0	515	459	276

3,-2,L

22	198	207	352
19	321	294	21
18	202	212	74
15	501	472	129
13	759	750	219
12	305	379	336
11	617	565	11
9	881	780	336
8	1080	982	122
7	248	274	40
6	418	462	275
5	875	841	222
4	526	427	287
3	493	441	18
2	824	695	354
1	1505	1333	6

3,-3,L

24	213	230	245
22	133	148	324
19	151	134	53
17	186	192	138
16	306	359	44
15	252	248	223
14	203	171	355
13	165	132	100
12	242	324	283
11	183	214	74
10	663	634	130
9	156	119	348
8	312	324	78
7	357	348	245
5	396	328	280
4	562	525	236
3	836	721	301
2	1115	1168	24
1	337	209	90
0	2934	2570	92

3,-4,L

22	245	260	55
20	383	439	23
19	278	243	168
17	373	372	210
16	453	537	208
15	484	473	16
14	234	208	74
13	291	285	328
12	452	291	43
11	540	540	123
10	273	299	337
9	785	717	191
7	208	127	26
6	640	629	162
5	297	285	347
4	446	421	4
3	142	113	297
2	109	132	51
1	812	760	139
0	190	123	285

3,-5,L

25	185	176	316
21	143	103	183
19	249	241	207
18	176	226	196
17	231	214	30
16	114	169	65
14	335	383	38
13	418	409	89
11	238	192	163
9	508	465	150
8	280	262	280
7	637	601	289
6	187	222	31
5	236	254	56
4	474	448	16
3	1283	1186	75
1	846	777	182
0	1172	1167	271

3,-6,L

24	157	136	280
20	207	145	147
19	303	310	311
18	397	363	18
16	653	684	13
14	255	261	264
13	307	320	113
12	285	321	209
10	625	587	160
9	210	189	181
8	394	445	5
6	1116	1103	17
5	460	447	281
4	966	941	196
3	549	580	4
2	365	409	184
1	532	460	263
0	162	186	90

3,-7,L

24	212	213	168
23	184	173	216
21	164	197	337
20	165	146	308
18	111	33	335
15	236	269	141
14	524	560	129
13	349	322	197
11	210	293	256
10	545	575	311
8	461	503	354
7	649	693	33
6	578	551	155
5	447	453	174
4	816	881	118
3	483	507	275
2	520	362	109
1	328	320	306
0	285	239	281

3,-8,L

19	388	351	0
15	287	290	160
14	161	181	143
12	286	314	274
10	229	189	338
9	507	487	357
7	291	304	164
6	259	251	141
5	568	468	191
3	692	698	170
2	309	310	30
1	483	520	27

3,-9,L

25	136	146	172
22	203	189	354
20	162	85	130
19	235	237	60
18	208	225	167
17	121	135	56
16	115	87	137
15	394	381	128
14	330	397	326
10	564	529	92

3,-9,L

9	333	257	55
8	453	445	74
7	515	458	120
5	237	214	55
4	218	208	256
3	364	386	299
2	486	492	354
0	568	613	95

3,-10,L

18	197	224	219
17	199	162	135
14	246	254	49
13	183	180	186
12	253	234	57
11	138	164	139
10	157	162	47
9	335	326	195
8	437	428	211
7	232	259	207
6	144	150	284
5	337	315	33
4	216	181	305
3	349	344	225
2	351	346	44
0	177	162	276

3,-11,L

18	139	127	302
15	220	221	309
14	227	176	315
13	171	161	77
12	224	171	56
11	411	407	119
8	235	224	232
7	258	268	309
5	337	320	279
3	195	187	103
1	630	589	82

3,-12,L

16	205	187	346
15	268	234	47
12	246	261	232
9	209	199	225
5	289	286	25
4	229	277	229
2	243	197	199
0	183	110	89

3,-13,L

13	171	175	108
12	171	148	156
10	197	205	297
9	119	109	41
8	328	318	25
6	292	248	113
3	204	255	252
2	224	232	295
1	230	183	299
0	390	456	273

3,-14,L

6	221	221	66
4	326	370	180
2	210	173	181

3,-15,L

2	182	176	195

2,0,L

25	173	160	270
20	286	289	1
19	250	279	274
18	311	367	5
16	393	393	179
15	280	277	266
14	745	747	183
13	325	374	95
12	222	233	186
11	471	520	89
10	664	678	4
9	140	105	299
8	1068	998	3
7	648	636	271
6	973	947	182
5	1087	1027	93
4	2426	2469	182
3	406	383	266
2	494	649	1
1	168	206	77
0	549	398	12

2,-1,L

22	245	237	235
19	262	282	101
17	129	120	91
16	262	310	119
15	350	341	334
14	422	403	204
13	522	467	210
12	423	404	295
11	373	402	208
10	377	369	53
9	400	458	300
8	561	548	18
7	316	429	126
6	1527	1585	109
5	1408	1358	291
4	1001	993	242
3	580	565	137
2	1327	1141	324
1	1993	1961	105
0	559	634	5

2,-2,L

19	229	260	183
18	290	332	210
17	458	483	147
15	490	419	179
14	624	634	32
13	195	198	298
12	652	687	351
11	615	578	326
10	382	285	195
9	321	343	354
8	819	756	170
7	1195	1115	161
6	126	191	299
5	850	727	187
4	1353	1255	178
3	1665	1468	8
2	1272	1201	208
1	523	535	330
0	1864	1727	181

2,-3,L

28	124	57	92
21	276	268	328
20	361	375	55
18	118	114	280
17	320	319	145
16	449	453	318
15	153	161	247
14	177	172	182
13	642	589	297
12	659	671	94
11	467	540	71
10	523	545	131
9	313	329	77
8	1177	1195	293
7	1067	1017	250
5	1108	1010	106
4	725	734	65
3	272	293	173

2,-3,L

2	1678	1608	96
1	1716	1499	331

2,-4,L

20	390	438	172
17	169	224	306
16	179	178	21
14	380	405	338
13	272	312	79
12	376	305	155
11	858	863	182
10	990	1040	159
9	560	484	118
8	288	343	263
7	589	484	349
6	501	506	350
5	744	837	280
4	831	741	8
3	537	513	131
2	441	248	63
1	1614	1748	178
0	984	897	183

2,-5,L

27	178	161	254
25	198	172	30
24	211	193	63
21	211	202	128
19	218	188	268
18	420	443	163
17	231	223	359
16	304	360	107
15	196	159	90
14	298	352	6
13	418	386	23
12	428	468	357
11	673	675	252
10	585	531	216
9	881	914	249
8	495	479	249
6	777	841	104
5	214	197	58
4	483	527	344
3	557	513	135
2	259	197	242
1	957	962	299
0	596	542	355

2,-6,L

24	157	167	188
21	286	280	164
20	393	383	16
18	387	381	303
17	379	383	16
16	288	347	346
14	539	531	172
13	487	434	154
12	164	161	196
11	467	469	191
10	737	801	20
9	165	222	149
8	552	486	24
7	380	349	317
6	118	80	270
5	378	308	330
4	1027	1105	218
3	476	473	114
2	234	193	60
1	398	392	278
0	363	382	11

2,-7,L

22	216	235	151
19	195	161	229
18	193	197	353
16	259	270	21
15	169	198	357
14	267	307	241
12	162	149	291
11	336	361	143
10	174	127	146
9	410	457	32
8	329	399	100
7	108	166	140
6	541	479	143
5	690	729	268
4	327	317	216
3	469	425	200
2	230	239	270
1	500	534	34
0	718	631	3

2,-8,L

22	118	107	224
21	222	214	19
19	138	141	300
18	161	181	177
16	165	217	212
15	369	349	197
14	257	329	32
13	351	325	348
12	260	297	8
11	241	247	30
10	273	290	224
9	548	514	173
7	526	460	150
6	267	310	115
3	493	478	357
2	218	211	293
0	808	805	181

2,-9,L

19	150	170	40
18	210	259	251
16	449	462	273
13	205	177	310
12	378	393	49
11	273	293	62
10	448	545	112
8	498	593	255
7	456	456	198
6	320	324	307
5	431	494	304
3	424	492	72
2	369	365	79
1	366	422	274

2,-10,L

24	172	156	356
17	147	153	116
14	125	203	14
12	108	120	106
11	242	206	192
10	269	340	127
9	187	221	79
8	222	159	191
7	189	234	42
6	190	155	293
4	546	585	326
3	357	364	219
2	357	464	131
1	381	393	164
0	478	509	183

2,-11,L

15	345	361	92
12	218	174	240
10	219	253	238
9	512	528	267
8	283	331	122
7	203	217	69
6	117	164	6
5	521	528	101
1	124	118	178
0	165	188	351

2,-12,L

14	224	218	144
13	223	196	120
11	186	260	155
10	172	141	34
9	302	351	315
8	408	407	342
4	289	316	214
3	228	232	120
2	175	241	144
1	257	310	223

2,-13,L

15	145	185	1
11	250	213	74
9	251	281	124
7	248	265	282
5	322	298	260
1	177	170	105

2,-14,L

13	145	199	11
9	205	125	211
8	368	372	153
7	390	357	173
4	281	276	340
3	226	205	329
2	304	349	260
1	182	185	22

2,-15,L

8	205	183	281
6	188	214	231
4	174	182	122
3	185	145	301
2	361	335	83
0	192	148	3

2,-16,L

11	169	152	152
0	216	200	184

2,-17,L

1	258	209	277

1,0,L

24	183	136	2
20	276	308	182
19	407	432	273
18	131	151	179
16	248	263	4
15	720	710	94
13	339	480	88
12	257	353	357
11	283	352	281
10	174	147	353
9	91	120	90
8	368	282	4
7	800	948	265
6	138	141	14
5	321	169	101
4	1270	1370	181
3	928	1187	86

1,-1,L

28	228	200	31
24	267	318	157
23	247	251	298
21	380	384	154
20	295	303	357
19	173	212	311
18	147	184	20
17	226	281	61
15	194	212	347
14	497	579	128
13	425	396	224
12	337	356	24
11	884	782	253
10	624	533	347
9	370	378	308
8	562	545	224
7	945	886	117
6	896	935	247
5	1305	1399	59
4	767	887	287
3	378	366	144
2	1253	1103	0
1	351	628	223

1,-2,L

30	189	202	282
23	256	258	209
20	339	375	302
19	237	245	17
18	229	294	107
15	359	313	262
14	374	413	346
13	342	290	14
12	182	203	186
11	228	204	250
10	337	421	216
9	341	370	329
7	226	236	256
6	476	508	110
5	1369	1434	169
4	1470	1443	346
3	453	504	273
2	276	144	48
1	707	683	74

1,-3,L

25	192	135	92
23	268	241	310
22	140	184	99
20	175	202	208
19	208	164	253
18	281	310	141
17	373	350	210
16	274	300	1
14	271	267	218
13	598	501	332
12	217	158	263
11	328	393	341
10	693	667	98
9	256	326	132
8	287	366	235
7	1257	1314	222
6	766	671	252
5	945	993	37
4	477	406	55
3	95	105	199
2	482	459	155
1	358	318	283
0	531	321	96

1,-4,L

26	168	148	270
25	180	203	286
22	354	388	123
21	239	270	148
20	208	244	87
19	220	208	141
18	290	292	217
16	491	472	239
15	161	236	342
14	188	160	104
13	185	232	306
12	307	275	104
11	178	160	161
10	445	369	307
9	814	741	91
8	652	652	185
7	1001	1023	154
6	855	877	93
5	650	697	305
4	276	357	328
3	119	156	251

1,-4,L

2	1501	1374	340
1	1224	1191	162
0	224	254	75

1,-5,L

24	147	152	301
22	208	211	98
19	137	88	256
16	315	327	301
15	141	98	269
14	304	277	2
13	304	321	235
12	204	197	221
11	256	227	62
10	300	297	260
9	377	329	337
7	133	157	131
6	574	457	39
5	338	307	126
4	875	889	267
3	682	746	252
2	558	559	176
1	1694	1836	82
0	606	528	271

1,-6,L

23	233	221	101
22	246	252	214
21	221	229	31
19	352	393	270
18	183	178	127
15	151	172	122
14	242	240	247
13	167	126	230
12	760	752	197
11	427	445	271
10	174	173	105
9	132	164	189
8	574	507	42
7	941	936	19
6	537	500	10
5	402	420	328
4	229	229	228
3	529	558	178
2	512	447	247
1	919	881	311
0	197	207	88

1,-7,L

22	232	216	27
20	271	254	293
16	241	275	175
14	215	189	165
13	294	308	120
12	188	174	353
11	434	447	245
10	485	417	333
9	422	447	337
8	417	413	279
7	548	429	315
6	911	900	203
5	392	401	199
4	293	314	151
3	247	226	225
2	927	954	43
1	233	299	37
0	1374	1279	271

1,-8,L

23	155	139	254
21	124	116	265
19	193	215	114
18	187	175	100
17	246	236	9
15	269	249	179
14	237	276	263
12	400	398	331
11	575	559	20
10	332	380	173
9	224	270	70
8	765	771	115
7	454	462	339
6	234	232	326
5	214	269	161
4	307	273	280
3	323	366	25
2	385	409	318
1	191	176	257
0	363	422	98

1,-9,L

19	150	148	341
15	180	210	202
14	160	213	27
13	265	264	299
12	132	150	6
11	213	238	286
10	238	264	344
9	137	136	105
7	363	360	103
6	191	149	264
5	375	382	339
4	780	816	252
3	359	336	315
2	261	316	36
1	587	580	192

1,-10,L

18	344	317	273
17	145	151	255
13	244	273	27
12	335	356	100
9	179	188	282
8	196	185	302
7	236	235	322
6	252	218	208
4	317	353	47
3	218	273	98

1,-11,L

21	160	125	163
20	181	152	179
17	298	292	274
15	219	228	353
14	246	250	347
13	175	161	227
12	122	144	166
11	128	102	176
10	228	261	200
8	251	212	290
7	276	276	291
6	167	148	263
3	241	250	143
2	273	290	180
0	151	180	89

1,-12,L

14	135	155	69
13	185	176	351
9	184	145	287
7	244	224	72
5	211	249	76
3	286	355	271
2	300	324	262
0	352	382	88

1,-13,L

14	215	215	205
13	122	130	264
10	293	312	347
9	285	327	325
8	246	196	358
7	198	222	152
4	271	323	112
3	297	292	175
1	341	318	25

1,-14,L

11	133	123	343
4	288	306	356
3	190	188	284

1,-15,L

5	143	140	204
2	162	132	172
0	269	281	92

1,-16,L

7	122	134	311

0,0,L

28	414	381	1
24	276	260	183
22	222	200	187
20	467	527	1
18	337	291	8
16	574	534	179
14	179	156	337
12	541	574	183
10	1631	1784	2
8	181	166	158
6	1802	1916	181
4	655	729	188

0,-1,L

22	303	302	271
21	263	330	88
19	351	345	94
18	261	245	91
17	535	552	93
16	465	413	94
15	624	617	272
14	434	430	269
13	945	1076	273
12	196	178	281
11	217	323	93
10	644	634	272
9	981	886	95
8	1053	907	92
7	419	458	91
6	912	1095	92
5	551	680	84
2	755	968	273

0,-2,L

26	175	211	182
25	144	129	187
24	250	247	1
23	275	308	0
21	479	530	3
17	307	295	186
14	261	335	4
13	407	459	3
12	591	663	2
11	1389	1240	3
10	371	300	186
9	486	405	180
8	665	568	183
7	1488	1617	183
6	130	97	169
5	639	618	358
4	1868	2089	1
3	1081	1067	5
2	977	1221	180
0	859	849	184

0,-3,L

25	201	222	271
18	172	224	271
16	533	576	275
15	628	713	271
14	216	241	86
13	577	534	90
12	1016	965	94
11	240	243	92
10	150	201	104
9	1325	1221	90
7	237	218	89
5	473	669	271
4	1733	1966	91
3	859	1013	270

0,-4,L

24	133	143	4
18	253	195	187
17	547	567	2
15	506	492	4
14	692	687	3
13	294	216	184
12	432	462	179
11	431	357	189
10	1374	1472	182
9	241	126	182
8	296	214	189
7	502	471	9
6	271	311	6
5	1103	1163	1
4	1319	1304	2
3	1148	1183	183
2	688	585	359
1	465	533	186
0	277	284	348

0,-5,L

23	306	265	94
20	213	253	273
19	459	435	274
18	355	339	272
16	165	243	266
15	486	480	94
14	468	536	92
13	223	278	180
11	247	271	274
9	1055	942	274
8	253	234	267
6	127	162	259
5	1772	1870	92
4	208	203	88
3	169	209	181
2	2025	2085	271
1	1019	1086	274

0,-6,L

25	192	189	1
24	200	133	184
23	151	169	183
21	324	332	182
20	195	174	2
18	283	273	8
15	382	373	0
14	123	98	210
13	402	479	182
12	331	351	184
10	684	753	4
9	338	299	2
8	767	769	4
7	648	603	1
6	554	525	185
5	360	427	359
4	863	767	186
3	889	935	181
1	274	281	181
0	894	877	6

0,-7,L

21	273	276	273
20	193	233	274
19	150	130	96
18	308	317	93
17	197	156	180
16	255	264	96
14	339	350	271
11	273	255	90

0,-7,L

9	610	637	95
8	786	759	93
6	280	253	261
4	380	398	274
3	665	618	87
2	434	442	277
1	692	757	93

0,-8,L

22	152	156	4
16	135	101	189
15	178	128	194
14	265	301	179
13	282	308	4
11	825	834	3
10	240	316	3
9	464	435	181
8	828	921	182
7	428	507	187
4	258	187	7
3	784	741	5
1	163	193	13
0	465	398	357

0,-9,L

22	214	238	91
20	426	364	94
19	158	162	95
17	227	308	271
16	448	435	274
12	520	537	94
10	195	216	99
9	249	248	93
7	384	438	272
6	576	594	275
4	105	91	257
3	530	676	270
2	203	231	106

0,-10,L

23	230	215	3
22	190	153	3
21	197	197	183
19	197	157	353
18	167	134	188
14	425	375	5
12	131	109	2
10	489	494	184
8	148	141	187
7	554	507	4
6	329	343	4
4	250	197	10
3	476	525	184
2	236	176	357
1	462	523	183

0,-11,L

23	172	157	96
21	148	170	268
16	234	193	91
15	258	247	95
12	191	246	270
11	314	354	272
9	209	75	304
7	278	344	270
5	537	545	95
3	285	252	96
1	246	290	278

0,-12,L

21	179	116	185
19	244	216	2
18	134	104	12
14	148	120	193
10	611	582	3
7	220	195	4
6	336	307	183
1	297	274	181
0	326	384	7

0,-13,L

22	172	144	275
16	254	242	95
12	390	401	274
11	220	193	88
10	167	138	87
9	346	342	94
6	358	391	93
4	213	279	273
3	411	401	272

0,-14,L

11	228	224	6
7	275	254	187
4	175	154	2
3	401	337	5
2	239	252	179
1	258	295	4
0	204	246	181

0,-15,L

16	183	155	276
15	228	224	274
12	254	258	93
8	366	341	272
7	151	146	273
6	224	175	277
5	275	248	273
4	136	141	93
2	339	295	95
1	361	360	91

0,-16,L

16	193	129	2
5	164	197	2
0	215	180	186

0,-17,L

13	232	228	93
9	181	157	276
5	380	302	93

APPENDIX 10

Structure Factor List for thiadiazolone compound,

Part III , p.139 .

Columns listed are ℓ , $|F_o|$ x10 , F_c x10 .

8,6,L

0	36	-38
-1	41	40
-2	132	135

8,5,L

0	58	55
-2	113	112
-3	103	102

8,4,L

0	24	25
-1	52	-51
-2	121	-114
-3	179	178

8,3,L

1	68	69
0	30	-27
-1	78	-67
-2	29	-33
-3	182	-180

8,2,L

1	178	-172
0	22	21
-1	70	-70
-2	75	-73
-3	147	-147
-4	39	-39

8,1,L

1	58	-60
0	84	-82
-1	60	53
-2	69	-71
-3	76	79
-4	162	-157

8,0,L

0	102	-108
-2	288	280
-4	40	42

7,10,L

0	100	99
-1	66	63
-2	22	20

7,9,L

-1	119	117
-2	32	-31
-3	84	-84

7,8,L

1	113	-113
-1	171	-171
-2	28	28

7,7,L

1	36	36
0	152	-151
-1	160	-160
-2	72	-73
-3	96	96
-4	30	-29

7,6,L

1	31	32
0	153	-154
-2	38	-32
-4	215	210

7,5,L

2	59	59
1	34	30
0	177	176
-1	105	-106
-2	60	61
-3	99	91
-4	39	36

7,4,L

1	104	102
0	21	14
-1	202	202
-2	63	63
-4	36	-36

7,3,L

2	40	36
0	90	-91
-1	155	152
-2	113	114
-3	77	-78
-4	71	-70
-5	122	-117

7,2,L

1	211	-210
0	75	77
-1	82	-75
-2	25	24
-3	44	39
-4	118	-117
-5	169	-161

7,1,L

2	21	-19
1	59	-57
0	257	-252
-2	11	12
-3	37	-39
-4	65	-69
-5	82	79

7,0,L

2	20	-18
-2	110	-104
-4	92	95

6,12,L

0	32	34
-1	26	-27
-2	64	-64

6,11,L

-2	118	117

6,10,L

2	98	100
1	93	-89
0	82	-79
-1	115	115
-2	50	50
-3	80	81
-4	71	70

6,9,L

0	26	23
-1	56	-53
-2	70	-69
-3	148	150
-4	34	-29

6,8,L

1	25	24
0	76	-80
-1	148	-149
-2	72	69
-3	72	-67

6,7,L

3	58	-56
2	55	54
1	82	-84
0	37	-38
-2	109	-109
-3	72	-69
-4	45	-43
-5	60	60

6,6,L

3	31	-32
2	246	-243
1	33	-30
0	139	139
-1	93	90
-2	77	-81
-3	87	84
-4	94	-94

6,5,L

3	83	-83
2	124	-120
1	64	64
0	80	83
-1	36	26
-2	300	301
-3	86	-88
-4	73	72

6,4,L

3	34	-32
2	124	125
1	22	-22
0	80	81
-1	224	230
-2	81	81
-3	35	34
-4	90	-89
-5	129	127

6,3,L

3	225	222

6,3,L

1	86	84
-1	41	38
-2	133	-132
-3	86	89
-4	14	-18
-5	129	-128

6,2,L

3	19	-19
2	141	145
1	211	207
0	71	-76
-1	348	-357
-2	39	40
-3	297	-292
-4	42	40
-5	21	-18

6,1,L

3	157	-153
2	139	135
1	72	-71
0	119	-121
-1	60	-61
-2	336	-339
-4	88	-87
-5	104	105

6,0,L

2	177	-174
0	75	-73
-2	204	-206
-4	171	167

5,14,L

0	75	-74

5,13,L

1	108	-109
0	79	79
-1	136	-136
-3	43	-40

5,12,L

2	53	-54
1	40	-39
0	245	-245
-1	120	122
-2	73	73
-3	27	28

5,11,L

2	23	20
1	42	-43
0	31	-30
-1	67	63
-2	142	145
-4	145	145

5,10,L

3	22	24
2	81	81
1	64	-61
0	219	223
-1	55	52
-2	100	98
-3	129	125
-4	57	57

5,9,L

3	67	-67
2	69	68
1	347	357
0	89	-91
-1	146	145
-2	26	-21
-4	18	-16
-5	106	107

5,8,L

3	31	32
1	63	-59
0	247	246
-1	80	75
-2	179	-184
-3	332	-335
-4	51	48
-5	55	-55

5,7,L

2	40	-45
1	207	-208
0	100	101
-1	115	-115
-2	244	-246
-3	95	-97
-4	139	-140
-5	123	-123

5,6,L

4	102	100
2	230	-235
1	92	96
0	264	-277
-1	73	-75
-2	141	-143
-3	28	-29
-4	137	-137
-5	65	67

5,5,L

4	103	-105
3	107	106
2	142	141
1	347	-348
0	96	-96
-1	25	-23
-2	105	104
-3	55	58
-4	239	239
-5	27	-28
-6	26	24

5,4,L

2	57	60
1	143	148
0	169	170
-1	258	-263
-3	451	462
-4	247	253
-5	23	24
-6	56	53

5,3,L

4	31	-24
3	63	-64
2	107	-107
1	424	435
0	48	46
-1	60	62
-2	112	111
-3	216	222
-4	43	-27
-5	202	203
-6	53	-55

5,2,L

4	73	-72
3	143	-139
2	157	159
0	104	103
-1	35	29
-2	69	70
-3	174	-176
-4	89	91
-5	128	-129

5,1,L

4	117	118
2	270	-271
1	111	-109
0	242	239
-1	40	-44
-2	115	-116
-3	155	-157
-4	242	-242
-5	150	-152
-6	46	-46

5,0,L

4	37	32
2	90	-88
0	515	-536
-2	191	185
-4	451	-459
-6	49	-47

4,15,L

0	95	94
-1	166	165
-2	33	34

4,14,L

0	47	47
-1	74	74
-2	53	51
-3	69	69

4,13,L

2	99	98
1	26	-28
0	60	-58
-1	121	-122
-2	36	35
-3	86	-86

4,12,L

2	32	30
1	29	-28

4,12,L

0	123	-124
-1	113	-114
-2	136	-140
-3	50	-48
-4	47	-48

4,11,L

3	22	23
2	81	-81
1	68	66
0	20	-18
-1	156	-156
-2	204	-205
-3	54	54
-4	39	40

4,10,L

3	162	-162
1	65	64
0	126	129
-1	17	-23
-2	147	145
-3	188	-184
-4	80	79
-5	189	192

4,9,L

4	46	47
3	65	65
1	66	-67
0	115	122
-1	305	308
-2	52	51
-3	99	101
-4	56	60
-5	59	59

4,8,L

4	66	64
3	173	171
2	68	-67
1	54	53
0	23	-13
-1	181	177
-2	91	96
-3	100	97
-5	73	-70

4,7,L

4	81	78
3	54	-56
2	115	114
1	73	-68
0	117	-115
-1	275	-272
-2	318	321
-3	74	-73
-4	54	-54
-5	113	-116
-6	119	-123

4,6,L

4	190	-194
3	75	-71
2	147	148
1	90	-88
0	265	-270
-1	54	-54
-2	475	-480
-3	57	60
-4	127	128
-5	80	-82
-6	180	-180

4,5,L

5	67	-67
4	170	-166
3	84	-84
2	270	-276
1	225	226
0	29	28
-1	213	-220
-2	272	-273
-5	57	-58
-6	101	102

4,4,L

4	33	32
3	224	-225
2	59	57
1	72	-72
0	320	308
-1	139	-135
-2	179	175
-3	110	-110
-4	52	52
-5	112	115
-6	73	73

4,3,L

5	58	58
4	44	46
3	91	93
2	142	138
1	22	21
0	38	42
-1	689	727
-2	65	-66
-3	55	55
-4	27	-29
-5	83	85
-6	63	65

4,2,L

4	111	110
3	449	459
2	112	-111
1	40	36
0	140	143
-1	37	-27
-2	341	347
-3	361	363
-4	129	-128
-5	249	-248
-6	122	119

4,1,L

4	166	166
2	417	422
1	134	-124
0	164	-156
-1	441	-453
-2	316	319
-3	51	-53
-4	77	-79
-6	83	-82

4,0,L

4	111	-112
2	50	-47
0	482	-473
-2	365	-362
-4	54	-51
-6	130	-133

3,16,L

0	57	-60
-1	58	58

3,15,L

1	37	-37
0	29	31
-1	25	-24
-2	31	25

3,14,L

1	191	191
-3	59	61

3,13,L

3	40	-41
2	108	109
1	67	68
0	64	68
-1	30	-29
-2	74	-76
-3	48	-47
-4	79	78

3,12,L

3	81	-86
2	56	-58
1	80	-80
0	160	163
-1	35	-33
-2	185	-185
-3	73	-73
-4	91	-91

3,11,L

4	40	-41
3	44	-43
2	231	-235
0	175	-178
-2	24	20
-3	63	-64
-4	136	-137

3,10,L

4	78	-78
3	41	-44
2	41	45
1	202	-202
0	102	-98
-1	47	-43
-2	110	109
-3	31	30
-4	55	51
-5	50	-43

3,9,L

4	23	-19
3	69	68
2	151	150
1	72	-72
0	13	-14
-1	50	-50
-2	132	134
-3	275	277
-4	24	-23
-5	32	32

3,8,L

5	34	35
4	29	-27
3	150	151
2	78	80
1	431	442
0	87	-90
-1	73	-69
-2	103	103
-3	168	166
-4	111	112
-5	52	51
-6	59	-54

3,7,L

5	53	51
3	32	25
2	264	265
1	47	42
0	242	246
-1	82	81
-2	65	-65
-3	220	-223
-4	118	123
-5	11	13
-6	74	-72

3,6,L

5	26	-26
4	128	125
2	82	-83
1	120	-119
0	82	80
-1	23	15
-2	50	-58
-3	99	-105
-4	255	-260
-5	28	29
-6	20	-19

3,5,L

5	49	50
4	52	50
3	63	59
2	405	-418
1	133	-123
0	277	-277
-1	183	178
-2	18	-24
-3	261	-267
-4	147	-148
-5	18	-17
-6	73	73

3,4,L

4	21	-20
3	146	-146
2	16	-5
1	526	-547
0	284	-279
-1	158	151
-2	240	230
-3	125	-127
-4	66	72
-5	108	-112

3,3,L

5	145	-141
4	69	69
3	21	22
2	85	-83
1	70	-61
0	143	137
-1	219	-209
-2	107	-108
-3	425	440
-4	51	49
-6	13	14

3,2,L

5	52	56
4	74	-77
3	46	44
2	49	53
1	472	482
0	50	42
-1	379	378
-2	77	-64
-3	68	-53
-4	191	193
-5	100	101

3,1,L

5	127	125
4	43	44
3	131	-137
2	256	257
1	214	204
0	541	546
-1	82	-79
-2	217	-201
-3	128	-123
-4	202	204
-6	51	-50

3,0,L

4	43	38
2	18	-25
0	591	606
-2	476	-476
-4	217	-227
-6	85	85

2,16,L

1	18	20
0	27	29
-1	136	-133
-2	34	-34

2,15,L

2	35	-36
1	77	77
0	50	51
-1	95	-92
-3	50	51

2,14,L

2	53	51
1	41	41
0	45	-44
-1	176	175
-2	38	-37
-3	32	-34
-4	58	57

2,13,L

3	101	103
2	83	-82
0	136	137
-1	25	-25
-2	106	104
-4	36	-33

2,12,L

4	175	171
2	73	76
1	31	-32
0	122	-116
-1	34	-33
-2	113	114
-3	40	41
-4	126	-124

2,11,L

4	68	-66
3	14	-16
2	111	110
0	319	-322
-1	37	29
-4	36	-32
-5	91	-88

2,10,L

4	108	-113
3	100	104
2	94	-98
1	165	-159
0	108	110
-1	133	-137
-2	55	-57
-3	54	49
-4	112	112
-5	60	-62

2,9,L

5	82	-81
3	240	-244
2	41	36
1	100	99
-1	40	35
-2	71	72
-3	31	-32
-5	176	174

2,8,L

5	105	106
4	100	-94
3	53	-53
2	36	-38
1	55	60
0	108	105
-1	403	406
-2	34	-38

2,8,L

-3	81	-84
-4	33	-35
-5	125	122
-6	58	53

2,7,L

5	51	53
4	13	-18
3	274	280
1	190	-176
0	315	321
-1	201	200
-2	22	32
-3	150	-146
-4	45	-47
-5	94	-95
-6	149	149

2,6,L

4	283	291
3	62	-64
2	17	-14
1	129	122
0	48	40
-1	198	-189
-3	79	-79
-4	226	-223
-5	33	-33
-6	111	-109

2,5,L

5	53	48
4	38	-34
3	168	161
2	27	30
1	163	-159
0	323	-314
-1	13	11
-2	356	-353
-3	42	-38
-4	31	35
-5	28	29
-6	169	-166

2,4,L

5	130	-125
4	204	-209
3	79	78
2	89	-95
1	54	-44
0	65	60
-1	472	-472
-2	168	-159
-3	15	-17
-4	279	283
-5	49	-45
-6	110	110

2,3,L

5	185	-187
4	96	99
3	324	-343
2	236	-225
1	127	129
0	250	235
-1	232	-230
-2	15	-9
-3	175	161
-4	169	170
-5	311	314
-6	98	-95

2,2,L

5	83	83
4	174	-172
3	136	-133
2	84	80
1	354	345
0	152	-138
-1	449	458
-2	20	8
-3	172	165
-4	124	125
-5	116	116
-6	64	66

2,1,L

6	37	35
5	119	122
4	63	61
3	63	68
2	188	-185
1	206	202
0	548	591
-1	43	0
-2	278	274
-3	39	40
-4	116	113
-5	310	-313
-6	53	53

2,0,L

4	395	402
2	193	197
0	172	-167
-2	136	127
-4	354	-351
-6	233	-234

1,17,L

-1	45	-43

1,16,L

2	51	-49
0	41	-41

1,15,L

3	61	-61
1	114	-111
0	79	76
-1	104	104
-2	98	99
-3	68	-71

1,14,L

3	95	95
2	117	-113
1	17	-18
0	118	119
-1	93	92
-2	52	49
-3	209	210
-4	75	-74

1,13,L

4	22	20
3	25	27
2	36	33
1	180	176
0	32	-34
-1	32	33
-2	111	109
-3	28	28

1,12,L

2	172	177
1	46	-48
0	60	63
-1	88	-86
-2	31	26
-3	189	-188
-4	49	49

1,11,L

3	102	102
2	60	-60
1	55	49
-1	153	-149
-2	411	-409
-3	45	44
-4	143	-141

1,10,L

5	109	112
4	26	26
3	202	-197
2	167	-169
1	212	210
0	201	-196
-1	180	-179
-3	291	-291
-4	40	-39
-5	45	44

1,9,L

5	72	73
3	135	-137
2	58	53
1	332	-332
0	60	66
-1	32	-26
-2	127	128
-3	113	-109
-4	117	119
-5	88	85

1,8,L

5	69	-67
3	61	65
2	152	-157
1	36	-42
-1	393	388
-2	120	-121
-3	386	385
-4	90	92
-5	32	31
-6	50	52

1,7,L

5	57	57
4	115	114
3	23	25

1,7,L

2	95	-98
1	290	297
0	94	-90
-1	38	-34
-2	613	625
-3	131	130
-4	124	122
-6	26	-27

1,6,L

6	54	57
4	176	-176
2	652	667
1	291	-277
0	72	68
-1	105	102
-2	26	-31
-4	157	159
-5	72	-67
-6	119	-116

1,5,L

6	184	180
5	52	-50
4	119	-118
3	37	38
2	130	-126
1	311	307
0	84	-74
-1	129	116
-2	575	-583
-3	55	53
-4	168	-177
-5	137	-135
-6	101	-100

1,4,L

6	30	-24
5	55	55
4	68	-67
3	72	-78
2	224	-228
1	169	159
0	195	189
-1	696	-733
-2	76	-70
-3	288	-284
-4	203	-202
-5	51	-49
-6	33	31

1,3,L

6	42	40
5	94	95
4	107	-109
3	343	-347
2	332	322
1	409	-409
0	120	126
-1	353	346
-2	187	-174
-3	364	-366
-4	15	-14
-6	65	62

1,2,L

6	31	-31
5	213	-214
4	133	129
3	513	516
2	535	-548
1	213	-209
0	118	119
-1	341	333
-2	12	-11
-3	411	421
-4	80	-77
-5	74	75
-6	66	64

1,1,L

6	182	-181
5	89	-85
4	89	89
3	322	321
2	255	249
1	128	131
0	134	130
-1	389	-405
-2	603	632
-3	219	207
-4	96	99
-5	69	70
-6	126	122

1,0,L

4	118	112
2	472	474
0	426	-468
-2	362	362
-4	230	235
-6	82	-82

0,17,L

1	20	25

0,16,L

2	90	-87
1	65	-65
0	131	-133

0,15,L

3	28	29
2	51	53
1	161	-159

0,14,L

3	46	-44
2	17	18
1	12	8
0	78	-75

0,13,L

4	150	-144
3	127	124
2	37	40
1	101	99

0,12,L

4	59	57
3	106	-105
2	33	-35
1	28	28
0	413	416

0,11,L

4	134	132
3	86	-85
2	141	-139
1	63	59

0,10,L

5	102	101
4	146	-144
3	30	25
2	158	-154
1	69	-72
0	116	-116

0,9,L

5	191	-189
4	61	59
2	64	-66
1	272	-275

0,8,L

5	143	-143
4	82	-79
3	102	-101
2	257	262
1	424	414
0	356	-356

0,7,L

6	18	-17
5	98	95
4	217	-217
3	55	53
2	268	262
1	375	369

0,6,L

6	102	99
5	23	-20
4	158	154
3	100	100
2	258	249
1	153	144
0	390	391

0,5,L

6	25	-27
5	164	163
4	288	297
3	92	-95
2	74	-71
1	127	123

0,4,L

6	58	-58
5	150	150
4	12	-12
3	301	299
2	128	-129

0,3,L

5	214	-208
3	95	93
2	182	-174

0,2,L

6	55	-56
5	116	-121
4	77	-75
3	310	-311
2	161	-156
1	295	-297
0	238	-217

0,1,L

6	46	43
5	97	104
4	378	-383
3	68	-71
2	120	122
1	591	664

0,0,L

6	114	111
4	104	102
2	252	-241