STUDIES OF YLIDES AND OF
TWO SYNTHETIC INTERMEDIATES
BY X-RAY ANALYSIS

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SUMMARY

In this thesis the techniques of crystal structure analysis are applied to the study of bonding and molecular conformation. The contents are divided into three parts, and in PART I various theoretical aspects of the methods of structure determination are discussed, with special emphasis being placed on the Direct Methods of structure elucidation which are used extensively in this research.

PART II is concerned with the study, by X-ray analysis, of five Ylide-type compounds. In an attempt to rationalise the little-studied bonding systems and conformations exhibited by such molecules, the crystal structures of the three first-row ylides N-trimethylammonio-benzamidate, N-trimethylammonio-nitramidate and (+)-3-diazocamphor, and of the two second-row ylides N-(p-toluenesulphonyl)-iminodimethylsulphur(IV) and N-(p-toluenesulphonyl)-iminotriphenylphosphorane have been determined. The results of these analyses allow trends in the stability of this class of compound to be examined in relation to the bonding interactions involved, and in the case of second-row ylides, the possible involvement in the bonding of d-orbitals of the second-row element can be examined. The final section of PART II is devoted to comparisons with the structures of other relevant molecules, in an effort to further investigate bonding and conformational trends in this class of chemical compound. Moreover, an interesting correlation is suggested between the bonding interactions involved in ylides and the conformations adopted by these molecules.

Accounts of the structure analyses of two terpenoid

synthetic intermediates are contained in PART III. A knowledge of the relative stereochemistries of the diol systems in both 2β-carbomethoxy-5α,6α-dihydroxy-7,7-dimethyl-tricyclo$[6.2.1.0^{1,6}]$undecane and also the unsubstituted derivative of 2α-carbomethoxy-5β-chloroacetoxy-7,7-dimethyl-tricyclo$[6.2.1.0^{1,6}]$undecan-6β-ol is essential to a better understanding, in mechanistic terms, of the novel rearrangements of these compounds. The overall similarity of both systems, but yet differing relative stereochemistries, provide an opportunity to study in detail the changes which may result from alterations in the relative stereochemistries of substituents and ring fusions. Interesting features reproduced in both molecules are the long $C(sp^3)$-$C(sp^3)$ bonds (ca. 1.59 Å) connecting completely substituted, eclipsed sp^3 centres, probably the result of the strain inherent in these bonds.

Finally, the thesis contains several published papers by the author, two of which are not otherwise included in the contents. Both describe the crystal structure analysis of 5-methoxycarbonylmethylene-2-piperidino-Δ^2-thiazolin-4-one, the addition product of N-thiocarbamoylpiperidine and Dimethylacetylenedicarboxylate, a reaction which has caused considerable speculation.

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PART I

A BRIEF DISCUSSION OF SOME THEORETICAL PRINCIPLES OF CRYSTAL STRUCTURE ANALYSIS

1. INTRODUCTION TO X-RAY DIFFRACTION

The practical applications of the diffraction of X-rays by crystals were first developed by W.L. Bragg in 1913 [1], although Laue [2] had previously described the phenomenon of X-ray diffraction in terms of a set of mathematical equations,

$$\begin{aligned} (\underline{a}.2\sin\theta)/\lambda &= h \\ (\underline{b}.2\sin\theta)/\lambda &= k \\ (\underline{c}.2\sin\theta)/\lambda &= \ell \end{aligned} \qquad (1)$$

where $\underline{a}$, $\underline{b}$, $\underline{c}$ are the unit cell dimensions,
θ is the diffraction angle of the X-ray beam,
λ is the X-ray wavelength,
h, k, ℓ are integers.

Bragg recognised that the integers h, k, ℓ should correspond to the Miller indices of the crystal lattice planes causing diffraction of the X-ray beam, and in so doing he gave physical meaning to these equations. By treating the diffraction of an X-ray beam as "reflexion" from stacks of parallel, equally spaced planes characterised by Miller indices (hkℓ), he derived his now famous equation

$$n\lambda = 2d(hk\ell)\sin\theta \qquad (2)$$

where d(hkℓ) is the interplanar spacing for the set of planes (hkℓ).

An alternative interpretation of equations (1) and (2) introduces the concept of the reciprocal lattice which provides a convenient method in crystallography for discussing X-ray diffraction patterns.

Perhaps Bragg's main contribution was the realisation that these diffraction patterns, measured as diffraction intensities from distinct sets of lattice planes, could be used in the solution of crystal structures.

2. DATA REDUCTION TO THE STRUCTURE AMPLITUDE

The quantity $|F(hk\ell)|$ is the amplitude of the wave diffracted from the set of planes $(hk\ell)$ within a crystal. The knowledge of a comprehensive set of these structure amplitudes for a particular crystal is essential to the solution of its crystal structure. However, the only quantity which can be measured is the intensity of the diffracted beam, $I(hk\ell)$, for a particular reflexion $(hk\ell)$.

There are two main methods of collecting such a set of intensities. Firstly, photographic methods of which the multiple-film technique [3] is the most commonly used, and secondly, automatic data collection by computer-controlled diffractometers. The latter method has been described by Arndt and Willis [4].

The structure amplitude $|F(hk\ell)|$ can be related to the measured intensity $I(hk\ell)$ by the following expression :-

$$|F(hk\ell)| = \sqrt{(K.I(hk\ell)/L.p)} \qquad (3)$$

where

(i) L is the Lorentz factor correcting for the varying times different crystal planes spend in the reflecting position. This correction therefore depends both on the reflexion in question and also on the specific geometry of the method of data collection.

(ii) p is the polarisation factor which allows for a reduction in intensity of the reflected X-ray beam arising from polarisation effects. This correction is independent of the method of data collection but does depend on the reflexion being considered.

(iii) K is a scale factor which, once applied, will place the set of observed structure amplitudes on the correct absolute scale. However, since atomic positions are usually unknown at the data reduction stage and the scale factor cannot therefore be calculated, K is taken as 1.

The set of structure amplitudes, thus obtained, are known as relative structure amplitudes, $|F_{rel}|$, and are on an arbitrary scale. Subsequently, in the early stages of an analysis, these relative structure amplitudes can be placed on an approximate absolute scale by equating $\sum|F_{rel}|$ and $\sum|F_{calc}|$.

However certain methods of structure solution, known as direct methods (see section 5.3), require that the data be placed on an absolute scale. Two methods commonly in use are the "Wilson-plot" method described by Wilson (1942) [5] and the "K-curve" method of Karle and Hauptman [6]. The scale factor, from either of these methods, is used to calculate the normalised structure amplitudes which are required for direct methods of phase determination.

The normalised structure amplitude, $|E(hk\ell)|$, is given by

$$|E(hk\ell)|^2 = \frac{|F(hk\ell)|^2}{\varepsilon\sum_{j=1}^{N} f_j^{\,2}} \qquad (4)$$

where f_j is the atomic scattering factor for the j^{th} atom in a unit cell containing N atoms,

ε is a factor which corrects for space group extinctions, e.g. in space group $P2_1/c$ $\varepsilon_{h0\ell}$ and

$\varepsilon_{0k0} = 2.$

The term "normalised" appears since, in the calculation of $|E|$ values, a normalisation factor is applied such that $\langle |E|^2 \rangle = 1$.

Since the distribution of $|E|$ values is independent of the size and contents of a unit cell, but is dependent on the presence or absence of a centre of symmetry in the space group, the distribution of the normalised structure amplitudes provides a simple statistical test [7] for centric and acentric distributions of intensities.

3. THE STRUCTURE FACTOR

The structure factor, $F(hk\ell)$, can be described as the resultant wave scattered from the set of planes $(hk\ell)$ and is obtained by compounding, by vector addition, the waves scattered from individual atoms in that order. The expression arrived at for the structure factor is thus

$$F(hk\ell) = \sum_{j=1}^{N} f_j \exp\left[2\pi i(hx_j + ky_j + \ell z_j)\right] \tag{5}$$

where f_j is the scattering factor of the j^{th} atom,

(x_j, y_j, z_j) are the fractional coordinates of the j^{th} atom.

The factor $2\pi(hx_j + ky_j + \ell z_j)$ represents the phase of the wave scattered by the j^{th} atom. As a complex quantity, the structure factor can be expressed alternatively as

$$F(hk\ell) = A + iB \tag{6}$$

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

$$B = \sum_{j=1}^{N} f_j \sin 2\pi(hx_j + ky_j + \ell z_j)$$

Hence

$$A = |F(hk\ell)| \cos\alpha \quad \text{and} \quad B = |F(hk\ell)| \sin\alpha$$

where the phase α of $F(hk\ell)$ is given by

$$\alpha = \tan^{-1}(B/A) \tag{7}$$

If atoms were point scatterers of X-rays then the values of the atomic scattering factors, f_j, would simply be the atomic numbers of the atoms in question. However there are other effects which must be considered. Electrons in atoms occupy a finite volume and the phase differences, between waves scattered from different points in this volume, increase as the diffraction angle, θ, increases thus resulting in a weaker diffracted beam. In effect this means that the atomic scattering factor for a particular atom decreases as $(\sin\theta/\lambda)$ increases.

Another factor influencing the intensities of the scattered X-ray beams is the extent to which atoms vibrate about their lattice positions. This "thermal motion" has the effect of smearing the atomic electron density, thus decreasing the atomic scattering power. If f_o represents the atomic scattering factor for an atom at rest, then the scattering factor corrected for isotropic thermal motion is given by

$$f = f_o \exp\left[-B(\sin\theta/\lambda)^2\right] \tag{8}$$

where the Debye factor, B, can be related to the mean square displacement of the atom perpendicular to the reflecting plane, $\bar{\mu}^2$, by the expression

$$B = 8\pi^2\bar{\mu}^2 \tag{9}$$

However, in many cases this is a simplification of the real situation in which atoms may undergo anisotropic modes of vibration. In order to treat such cases properly, anisotropic vibration expressions of the following form must be used :-

$$\exp\left[-2\pi^2(U_{11}h^2\underline{a}^{*2} + U_{22}k^2\underline{b}^{*2} + U_{33}\ell^2\underline{c}^{*2} + 2U_{23}k\ell\underline{b}^*\underline{c}^* + 2U_{31}\ell h\underline{c}^*\underline{a}^* + 2U_{12}hk\underline{a}^*\underline{b}^*)\right] \qquad (10)$$

where $\underline{a}^*$, $\underline{b}^*$, $\underline{c}^*$ are the reciprocal cell translations, U_{ii} and U_{ij} (for $i,j = 1,2,3$) are the elements of the symmetric tensor $\underline{U}$.

A more fundamental approach to the structure factor is possible in which the structure is not reduced to a set of point atoms. The expression thus derived is the following :-

$$F(hk\ell) = V\int_{0}^{1}\int_{0}^{1}\int_{0}^{1}\rho(xyz)\exp\left[2\pi i(hx + ky + \ell z)\right]dxdydz \qquad (11)$$

where $\rho(xyz)$ is the electron density at the point (x, y, z) in a unit cell of volume V.

4. THE ELECTRON DENSITY DISTRIBUTION

Since the electron density distribution contained in a repeating array of unit cells must be periodic in 3-dimensions, it can be represented, as was first suggested by W.H. Bragg in 1915 [8], by a 3-dimensional Fourier series.

By employing the method of Fourier transforms in the reorganisation of the structure factor expression given in equation (11), it can be shown that the Fourier coefficients are directly related to the set of structure factors, $F(hk\ell)$. The electron density distribution thus derived can be represented by

$$\rho(xyz) = 1/V\sum\sum\sum_{h,k,\ell=-\infty}^{\infty} F(hk\ell)\exp\left[-2\pi i(hx + ky + \ell z)\right] \qquad (12)$$

However, consideration of the complex nature of the structure factor and introduction of the phase angle, α, leads to a more practical expression

$$\rho(xyz) = 1/V\sum\sum\sum_{-\infty}^{\infty}|F(hk\ell)|\cos\left[2\pi(hx + ky + \ell z) - \alpha(hk\ell)\right] \qquad (13)$$

The application of this equation can be simplified to a large extent by the presence of symmetry in the reciprocal lattice.

5. THE PHASE PROBLEM

The fundamental problem in crystal structure analysis, namely the Phase Problem, arises because the structure factors which are required as fourier coefficients cannot be observed experimentally. Although values of the structure amplitudes, $|F(hk\ell)|$, can be calculated from intensity measurements, knowledge of the phases of the scattered waves is lost in the recording process.

However, several methods have been developed whereby sufficient phase information can be derived from the observed structure amplitudes. In this section those methods which have been applied are briefly discussed.

5.1 The Patterson Method

Whereas a triple Fourier series using $F(hk\ell)$ as coefficients yields a map of atomic positions, Patterson (1934, 1935) ^{9} demonstrated that a function of the form

$$P(uvw) = 1/V\sum_{-\infty}^{\infty}\sum\sum|F(hk\ell)|^{2}\exp\left[2\pi i(hu + kv + \ell w)\right] \qquad (14)$$

employing $|F(hk\ell)|^{2}$ as coefficients would give an interatomic vector representation of the crystal structure. A peak in this function P(uvw) at the point in space $(u_1\ v_1\ w_1)$ corresponds to an interatomic distance in the crystal defined by a vector whose components are u_1, v_1 and w_1, the value of the function being proportional to the product of the scattering factors of the two atoms involved. For a unit cell containing N atoms there will be N(N-1)/2 distinct pairs of peaks generated in the cell of the vector map.

Hence for all but the simplest structures it will be almost impossible to deduce the atomic arrangement directly from the vector map as a result of factors such as peak overlap. However, the presence of an atom of high scattering power in the structure, i.e. a heavy atom, alleviates this problem since vector peaks involving such atoms will have considerably greater peak heights than those involving only lighter atoms.

An additional tool in the solution of the Patterson function was introduced by Harker in 1936 [10], when he pointed out that, in cases where certain symmetry elements are present in the crystal, many of the useful heavy-atom peaks are concentrated in particular lines and sections of the P(uvw) function.

5.2 The Heavy Atom Method

The application of this technique requires the presence of at least one heavy atom in the structure undergoing analysis. When the scattering power of such atoms approximately equals the total scattering power of the remaining atoms, it is usually possible to determine the heavy atom positions from a Patterson function. This results from the heavy atoms giving rise to interatomic vector peaks which should be easily distinguished from the other light-atom peaks (see section 5.1).

Since the heavy atoms dominate the scattering of the complete structure, the phases of the structure factors, calculated with contributions from the heavy atoms alone, will be a reasonable approximation to the true phases. An electron density distribution calculated with these phases and the observed structure amplitudes will thus approximate to the true electron density and therefore reveal further atomic positions. The phase determination then usually proceeds by a reiteration process.

The first direct application of the Heavy Atom Method was made in the structure determination of phthalocyanine by Robertson and Woodward in 1940 [11]. The main drawback in this method is the reduction in the accuracy of location of light atoms which results from the heavy atoms contributing the major part of each structure amplitude.

5.3 Direct Methods

The main feature of the so-called Direct Methods of structure solution is that a trial set of phases may be postulated directly from the intensity data without prior knowledge of the molecular structure. This precludes the requirement of a heavy atom as in the previous methods, and direct methods may therefore be applied to the solutions of structures for which heavy-atom derivatives either, cannot be prepared, or, are not desirable.

Early attempts by Härker and Kasper (1948) [12] and subsequently Karle and Hauptman (1950) [13] to relate phases to intensities led to a set of inequality relationships, applicable to sign determination, whose derivation depended solely on the positivity of electron density. However as the complexity of the crystal increases, it becomes necessary to bring in probability methods since inequalities, by themselves, impose restrictions only on phases whose intensities are very large.

The basis for these methods lies in the equation derived by Sayre (1952) [14] for the special case of centrosymmetric crystals

$$F_{\underline{h}} = \langle F_{\underline{k}} \cdot F_{\underline{h}-\underline{k}} \rangle_k \qquad (15)$$

where large structure magnitudes are involved. In these methods, which will be described in two parts, it is more convenient to use normalised structure factors (see section 2) which effectively concentrate the scattering material about the atomic positions.

(i) Centrosymmetric Direct Methods

In the case of centrosymmetric crystals, the most useful sign-determining formula has been that termed the $\sum_2$ relationship in a monograph by Hauptman and Karle (1953) [15],

$$S(E_{\underline{h}}) \approx S(\sum_k E_{\underline{k}} \cdot E_{\underline{h}-\underline{k}}) \qquad (16)$$

where S = "sign of", and the summation, which is carried out over high $|E|$ values, can involve simply one or many terms, depending on the stage of the analysis. The associated probability that the sign of $E_{\underline{h}}$ be positive was derived by Woolfson in 1954 [16],

$$P_+(\underline{h}) \approx 1/2 + 1/2 \tanh \sigma_3\sigma_2^{-3/2} |E_{\underline{h}}| \sum_k E_{\underline{k}} \cdot E_{\underline{h}-\underline{k}} \qquad (17)$$

where $\sigma_n = \sum_{j=1}^{N} Z_j^n$, with Z_j the atomic number of the j^{th} atom in a unit cell containing N atoms.

It is possible to utilise the latter two equations to obtain phase information by the Symbolic Addition method which was first described by Karle and Karle in 1963 [17]. In this method a basic set of phases is required in order to determine additional phases. This basic set will be composed of those linearly independent phases which must be specified in order to fix the origin in the crystal and also some additional phases denoted by symbols. The restrictions which must be placed on the assignment of the origin phases are dealt with by Hauptman and Karle [18]. However, the choice of the starting set should also involve high $|E_{\underline{h}}|$ values which enter into a sufficient number of $\sum_2$ relationships, in order that equations (16) and (17) can be used effectively.

An essential feature of this method is, therefore, the formation of a $\sum_2$ listing which will allow all possible combinations of $\underline{k}$ and $(\underline{h}-\underline{k})$ for a given $\underline{h}$ to be used in conjunction with the phase-determining equations.

(ii) Non-centrosymmetric Direct Methods

Analogous to equation (16), for non-centrosymmetric crystals with generalised phases, φ, there is the following triple phase relationship,

$$\varphi_{\underline{h}} \approx \langle \varphi_{\underline{k}} + \varphi_{\underline{h}-\underline{k}} \rangle_k \qquad (18)$$

where the k-range is over only those vectors associated with large $|E|$ values. This expression is applicable to any number of contributors, even only one set as in the initial stages of the Symbolic Addition method. The reliability of the contributors is assessed by a function which represents the variance of the phase angle determined from known values of other phase angles [19].

The method by which the basic set is chosen for non-centrosymmetric crystals is similar to that employed in the centrosymmetric case and has been fully described by Hauptman and Karle (1956, 1961) [20]. However one additional phase requires definition, namely the enantiomorph-fixing reflexion, and this necessarily arises since

$$\varphi_{\underline{h}}(D) = -\varphi_{\underline{h}}(L)$$

where D and L represent the two possible enantiomorphs which could be present in a non-centrosymmetric space group. Hence, in order to specify which set of phases and consequently which enantiomorph is being considered, one further correctly chosen reflexion is assigned a phase within the ranges 0 to π or $-\pi$ to 0.

Once the initial symbolic addition calculation of phases has been carried out, a stage will be reached at which phase indications are obtained from several known pairs of phases. When this situation occurs, the probable phase of this reflexion can be given by the following expression, named the tangent formula [21],

$$\tan \varphi_{\underline{h}} = \frac{\sum_{\underline{k}} |E_{\underline{k}} \cdot E_{\underline{h}-\underline{k}}| \sin(\varphi_{\underline{k}} + \varphi_{\underline{h}-\underline{k}})}{\sum_{\underline{k}} |E_{\underline{k}} \cdot E_{\underline{h}-\underline{k}}| \cos(\varphi_{\underline{k}} + \varphi_{\underline{h}-\underline{k}})} \qquad (19)$$

Refinement of a set of phases can be achieved by a recycling process, employing the tangent formula, which can be continued until negligible shifts in the derived phase angles are observed from one cycle to the next.

There are several methods of measuring the probability of correctness of a given set of phases calculated by the tangent formula reiteration method. One example is the "Karle R-index" defined by [19],

$$R = \frac{\sum_{\underline{k}} \left| |E_{\underline{k}}|_{obs} - |E_{\underline{k}}|_{calc} \right|}{\sum_{\underline{k}} |E_{\underline{k}}|_{obs}} \qquad (20)$$

where $|E_{\underline{k}}|^2_{calc}$ is computed from the sum of the squares of $|E_{\underline{k}}|\cos\varphi_{\underline{k}}$ and $|E_{\underline{k}}|\sin\varphi_{\underline{k}}$ and subsequently scaled by equating $\sum|E_{\underline{k}}|^2_{calc}$ and $\sum|E_{\underline{k}}|^2_{obs}$. This indicator is not absolute and will vary from structure to structure but, however, solution sets of highest R-value have much less probability of being correct.

Once the phases of the larger normalised structure factors have been determined by either method (i) or (ii), the atomic positions of the molecule under study can usually be found from a Fourier summation calculated with the appropriately phased normalised structure amplitudes as coefficients. Ideally a ratio of approximately 10 E-values per atom in the asymmetric unit should be used in the calculation of the "E-map" [22]. In cases where an incorrect solution has been obtained, the peaks in the E-map generally do not make good chemical sense, though sometimes partial structures can be found which are incorrectly orientated in the unit cell. Under such circumstances it is usually best to choose a different basic starting set.

Several completely automatic computer programs have been developed which will carry out the E-generation, Σ_2 listing, symbolic addition and solution procedures, but, in many cases, a combination of automatic methods and manual symbolic addition calculations, in which a good initial set of phases is obtained, has proved the most reliable method of direct structure solution.

6. ACCURACY AND LEAST SQUARES REFINEMENT

The accuracy of a structure analysis is usually estimated in terms of the R-factor or "residual index" defined as

$$R = \frac{\sum(k|F_{obs}| - |F_{calc}|)}{\sum(k|F_{obs}|)} \qquad (21)$$

where k is a scaling constant. The value of R is a measure of the discrepancy between the calculated model of the crystal structure, as measured by the calculated structure amplitudes, and the "true" crystal structure, represented by the observed structure amplitudes.

The method of Least Squares, as applied to crystal structure refinement, consists in systematically varying atomic parameters such that a suitable function of the discrepancies between the observed and calculated structure amplitudes is minimised. The function most commonly employed is

$$D = \sum_{hk\ell} w(|F_o| - |F_c|)^2 = \sum_{hk\ell} w\Delta F^2 \qquad (22)$$

where the summation is taken over all independent structure amplitudes and w is the weight associated with each term.

Ideally each w should equal the inverse square of the standard deviation of the corresponding observation, but, in practice it is usually necessary to apply a more flexible weighting scheme, such as that proposed by Cruickshank et al. (1961) [23]. In this scheme several parameters can be varied in order to give approximately the same average $w\Delta F^2$ for systematic groups of the data, batching of the data being carried out according to $|F_o|$, $\sin\theta/\lambda$ or any other factors which are considered to influence the standard deviations of the observations.

If the atomic parameters which determine $|F_c|$ are $p_1, p_2, \ldots\ldots p_n$, then the condition that the function, D, approaches a minimum is

$$\frac{\partial D}{\partial p_s} = \sum_{hk\ell} w(|F_o| - |F_c|).\frac{\partial |F_c|}{\partial p_s} = 0 \qquad (23)$$

for s = 1 to n.

When the set of parameters, p_s, used in this refinement procedure approximates reasonably to the true values, ΔF can be expanded as a first order Taylor Series involving the set of parameters, p, and parameter changes, Δp, i.e.

$$\Delta F(p + \Delta p) = \Delta F(p) - \Delta p_1.\frac{\partial |F_c|}{\partial p_1} - \ldots\ldots$$

$$\ldots\ldots - \Delta p_n.\frac{\partial |F_c|}{\partial p_n} \qquad (24)$$

Substituting equation (24) into equation (23) yields the set of n normal equations of least squares for s = 1 to n,

$$\sum_{r=1}^{n}\left[\sum_{hk\ell} w\frac{\partial |F_c|}{\partial p_r}.\frac{\partial |F_c|}{\partial p_s}\right]\Delta p_r = \sum_{hk\ell} w\Delta F.\frac{\partial |F_c|}{\partial p_s} \qquad (25)$$

These equations can be solved to give the set of parameter shifts to be applied to the initial parameters.

The solution process is best achieved by automatic computer, using matrix algebra on the matrix equivalent of the normal equations,

$$M\Delta p = N \qquad (26)$$

The solution set of parameter shifts is therefore

$$\Delta p = M^{-1} N \qquad (27)$$

Since the number of independent elements of the matrix M is equal to $n(n+1)/2$, as the complexity of the structure increases, it is sometimes necessary to make approximations to M owing to limited computer storage. One such approximation is called the Block Diagonal approximation, in which any elements of M representing cross terms between parameters of different atoms are neglected. In terms of equation (25), the only elements which are calculated are those for which the subscripts r and s refer to parameters of the same atom. The result is a matrix composed of submatrix blocks, centred on the diagonal and pertaining to individual atoms.

The refinement process can be assumed complete when the calculated shifts are considerably less than the estimated standard deviations for the corresponding parameters. Usually this requires several cycles before a minimum is reached owing to the neglect of high order terms in the Taylor Series.

It is customary to test the refined model, obtained by least squares methods, by calculating a Difference Fourier summation with $(|F_o| - |F_c|)$ as coefficients. This "Difference Map" will indicate any significant departure of the calculated model from the true crystal structure.

7. ESTIMATED STANDARD DEVIATIONS

The least squares method of refinement allows the calculation of new parameters but, to assess their precision, it is necessary to have knowledge of the corresponding estimated standard deviations.

The estimated standard deviation in a parameter p_i is given by

$$\sigma(p_i) = \sqrt{M_{ii}^{-1} \left(\sum_{hk\ell} w\Delta^2\right)/(m - n)} \qquad (28)$$

where M_{ii}^{-1} is the ith diagonal element of the inverse matrix M^{-1},

m is the number of observations,

n is the number of parameters,

w is a set of weights appropriate to the structure (see section 6).

Perhaps of greatest application are the estimated standard deviations of atomic positional parameters. Once derived, they can be employed in the calculation of bond-length and bond-angle standard deviations which will give a measure of the reliability of determined molecular dimensions.

One possible use of such bond-length standard deviations can be in the assessment of whether a particular bond length in a molecule differs significantly from a similar bond or a theoretical value. If two bonds l_1 and l_2, with estimated standard deviations $\sigma(l_1)$ and $\sigma(l_2)$ respectively, are found to differ experimentally by δl, the possible significance of this difference can be estimated using a set of numerical significance levels suggested by Cruickshank (1953)[24]. He defined P as the probability that the two bonds could differ by δl by chance and also the standard deviation of δl as

$$\sigma = \sqrt{\sigma(l_1)^2 + \sigma(l_2)^2} \qquad (29)$$

Hence it is possible to assess the significance level of differences in bond lengths as follows:-

If $\delta l \leq 1.645\ \sigma$, then $P \geq 5\,\%$, i.e. insignificant difference.

If $2.327\ \sigma > \delta l > 1.645\ \sigma$, then $5\,\% > P > 1\,\%$, i.e. possibly significant difference.

If $3.090\ \sigma > \delta l > 2.327\ \sigma$, then $1\,\% > P > 0.1\,\%$, i.e. significant difference.

PART II

STRUCTURAL INVESTIGATIONS OF YLIDES

INTRODUCTION

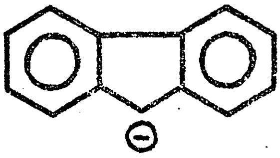
Ylides can be formulated in general terms as $(\overset{+}{X} - \overset{-}{Y})$, and as such can be described as vicinal zwitterions. Although the term "ylide", when devised by Wittig in 1944,[25] referred solely to carbanion types ($Y = C<$), it has come to represent the complete series of $(\overset{+}{X} - \overset{-}{Y})$ compounds.

The first phosphonium ylide ($X = Ph_3P$; $Y = CH\text{-}CO_2Et$) was prepared by Michaelis and Gimborn in 1894 [26] and since that time considerable research has been carried out on ylide-type compounds :- ylides and related imines ($Y = N-$) in the 1920's,[27,28] iminosulphuranes [29] and iminophosphoranes [30] ($X = S$ and P respectively; $Y = N-$), and phosphonium [31] and ammonium [32] ylides ($X = P$ and N respectively; $Y = C<$). The phosphonium group of compounds were later to prove of great synthetic value in the conversion of ketones to alkenes <u>via</u> the now famous Wittig reaction.[33] An extensive coverage of the reactions, preparations and physical properties of ylides in general was published in a monograph by Johnson in 1966 [34] and has been recently updated in a review on the chemistry of ylides by Hudson.[35]

That ylides are stable chemical compounds, whereas anions are reactive, must result from some unique stabilisation afforded the negative atom Y by the presence of the adjacent $\overset{+}{X}$ grouping, otherwise known as the 'onium residue. However although such stabilisation probably occurs, almost all stable compounds of this type have an electron-withdrawing group attached to the $\overset{-}{Y}$ portion of the molecule. This electron-withdrawing group will have a stabilising effect on the molecule by virtue of its ability to delocalise part of the negative charge formally residing on the $\overset{-}{Y}$ atom. Consequently, factors affecting the stability of ylides should be the effectiveness of the stabilising group, the electronegativity of the negative atom Y (as a measure of how successfully a net negative charge can be borne by that atom), and also the stabilising effect resulting from the involvement of the 'onium residue $\overset{+}{X}$.

It has generally been observed[34,35] that second-row ylides (X = S, P) are, by far, more stable than their first-row counterparts (X = O, N), and it therefore appears that this greater stability must be attributed to some involvement, other than just simple coulombic interaction, of the 'onium residue in the stabilisation of second-row ylides. The existence of this stabilising interaction in second-row ylides can be readily seen from an examination of the following series of compounds

Y =



; X = (I) $P(Ph)_3$
(II) $N(Me)_3$
(III) H

in which the pK_a values of the conjugate acids should give an indication of the relative stabilities of the parent compounds ($\overset{+}{X} - \overset{-}{Y}$). The conjugate acid of (III), fluorene, has a pK_a of 25[36] which is only marginally larger than that observed for the conjugate acid of the ammonium ylide (II),[25] thus inferring that the inductive effect of the trimethylammonium group does not greatly affect the stability of the fluorenyl anion. However, the pK_a value of 7.5 obtained for the conjugate acid of the phosphonium ylide (I)[37] displays a stabilising effect necessarily involving the phosphonium residue, which far exceeds a simple coulombic interaction. Moreover, such coulombic interaction would be expected to be smaller in (I) as a result of the longer P - C bond.[38] This enhanced stabilisation may possibly be attributed to an involvement of the vacant 3d-orbitals on the phosphorus atom in a π-type interaction, affording delocalisation of the negative charge on the carbanion. However, this expansion of the valence shell, which can occur for phosphorus, is not possible for the ammonium ylide since the energy jump to the next vacant orbitals on nitrogen will be sufficiently large that any involvement of such orbitals in effective bonding can be ignored. The resulting non-expansion of the octet of first-row elements has recently been discussed by Webster and Stewart.[39]

Since first-row elements can be excluded from valence-shell expansion on energy grounds, a prerequisite of 3d-orbital involvement in second-row ylides must therefore be not only that the orbitals are vacant , but also that they are of appropriate size and energy. Craig et al. suggested in 1954 that 3d-orbitals would be too diffuse to contribute to molecular binding unless modified sufficiently by the molecular environment.[40] They proposed that the presence of a formal positive charge on the second-row atom or the attachment of very electronegative ligands could serve to contract the 3d-orbitals in the bonding state to an extent that 3d-orbital involvement would become feasible. Cruickshank and Webster [41,42] subsequently showed by SCF calculations that a 3d-orbital should be nearer the nucleus in the free atom than it would be in the positively-charged ion, after contraction, as proposed by Craig. The arguments for and against the involvement of 3d-orbitals in bonding are summarised in a recent review by Mitchell,[43] and it would appear that proposals of d-orbital involvement are justified providing a favourable molecular environment exists.

From the very existence of penta- and hexa-valent phosphorus and sulphur atoms in such molecules as PF_5, PCl_6^- and SF_6 it can be postulated that valence-shell expansion is certainly involved in the construction of the σ-bond framework about P and S. However, since in second-row ylides it is possible to form the σ-bond framework without utilising the 3d-orbitals of the 'onium residue, the type of interaction involving the d-orbitals can be assumed to be π in nature. Although this exact definition of the participation cannot be proved beyond question, a certain justification for using the d-orbital model in π-bonding can be derived from the many experimental observations explained by its invocation. Examples of such observations may be taken from :-

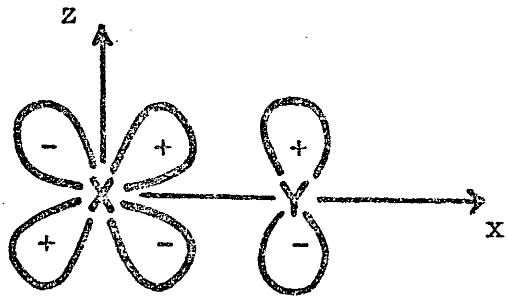
(i) Studies of the "Trans Effect" in Transition-metal complexes.[44]

(ii) Nuclear quadrupole resonance studies of inorganic sulphur and phosphorus compounds.[45]

(iii) Marked differences in the reactions of first- and second-row vinyl 'onium ions with base.[46]

(iv) Differences in the deuteration rates of ylides resulting from stabilisation of an ylidic intermediate in the second-row case only.[47]

The most popular representation of the π-bonding interaction involving $\underline{d}$-orbitals of the 'onium group in second-row ylides has been termed $\underline{d}_{\pi}$- $\underline{p}_{\pi}$ bonding,[34]



where the orbitals involved are (relative to the axes shown) $\underline{d}_{xz}$ on $\overset{+}{X}$ and $\underline{p}_z$ representing the lone-pair orbital on $\overset{-}{Y}$. Although this description is perfectly valid for ($Y = C<$) ylides in which it has demonstrated [48,49] that the carbanion is planar, the lone-pair electrons necessarily occupying a $\underline{p}$-type orbital, reservations must be held about the applicability of this model in ($Y = N—$) ylides, known as 'onium imines, where two lone-pairs are available on the nitrogen atom for bonding. It has previously been held in such instances [50-54] that the nitrogen atom assumes an $\underline{sp}^2$ hybridised configuration with the two lone-pairs occupying a pure $\underline{p}$-orbital and an $\underline{sp}^2$ hybrid orbital respectively, since the angle subtended at the nitrogen atom is consistent with the formation of both σ-bonds by approximate $\underline{sp}^2$ hybrid orbitals. Moreover, it would appear that this formulation merely provides a convenient method of obtaining a $\underline{d}_{\pi}$- $\underline{p}_{\pi}$ interaction analogous to that for ($Y = C<$) ylides, since no allowance has previously been made for the possible involvement of the second nitrogen lone-pair of electrons in $\underline{d}$-orbital overlap.

Possibly it would be more correct to envisage the two lone-pairs occupying equivalent orbitals, both of which can interact equally with suitable combinations of the d-orbitals of the 'onium group. The problem can then be simplified by resolving the d-orbital overlap into two mutually perpendicular components, one in the plane of the σ-bond framework and the other perpendicular to this plane. Nevertheless, the former representation, requiring the involvement of two different types of lone-pair, has enabled Paddock and Craig [55,56] to explain successfully the π-bonding which exists in cyclic phosphonitriles. In the latter authors' description of the π-bonding in such systems, they recognised the necessity for two distinct types of π-bonding, named π and π' (or σ' for planar molecules), which in the case of second-row (Y = N—) ylides will correspond to the suggested components of the d-orbital interaction perpendicular to the σ-framework and in the molecular plane respectively. The possibility of such π-overlap in two mutually perpendicular planes was also suggested in a review by Cruickshank [57] to account for reported bond distances and angles in P-O-P bridged systems.

Thus a possible description of the π-bonding arrangement in second-row 'onium imines is that two equivalent lone-pairs on the negatively charged nitrogen atom can interact with suitable combinations of d-orbitals on the 'onium residue to form bonding overlaps which may theoretically be resolved into two mutually perpendicular components, i.e. (i) named σ', in the plane of the σ-bond framework, and (ii) named π, perpendicular to the σ-bond plane.

In the case of first-row ylides no such interaction should be possible between the 'onium group and the lone-pairs of the negatively charged nitrogen atom and, consequently, the relative stability of this type of molecule must derive from delocalisation of the negative charge solely into the stabilising group. For ylides of second-row elements, however, d-orbital participation is possible as a second mode of stabilising the molecule, and it is therefore reasonable to regard the bonding situation in second-row ylides as the 'onium and stabilising groups competing to delocalise the lone-pairs of the nitrogen atom. Not only should the choice of stabilising function have a marked effect on the $\overset{+}{X} - \overset{-}{N}$ bond in the latter compounds, but it may also affect the conformations of these second-row systems.

In an attempt to rationalise the little-studied bonding systems and conformations exhibited by first- and second-row 'onium imines and in the latter compounds to examine the applicability of the suggested π-bonding system, the structures of two ammonium imines (X = N; Y = N—), an iminosulphurane (X = S; Y = N—), and an iminophosphorane (X = P; Y = N—) have been investigated. This study of ylides in general was continued by the examination of a diazoketone in order to assess the importance of the role played by the ketonic function in the stabilisation of this particular type of ylide.

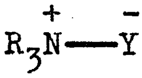
The first section of PART II will deal with both ammonium imines, while a separate section will be devoted to each of the three remaining ylide structures. To complete PART II a further section will discuss the preceding analyses and also, where appropriate, other relevant structures in an effort to examine possible trends in the bonding and conformations of ylides which may result from changes in stabilising group, negatively charged atom, and 'onium residue.

1. THE CRYSTAL AND MOLECULAR STRUCTURES OF N-TRIMETHYLAMMONIO-BENZAMIDATE AND N-TRIMETHYLAMMONIO-NITRAMIDATE : TWO STABILISED NITROGEN - NITROGEN YLIDES.

1.1 INTRODUCTION

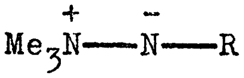
Ylides ($\overset{+}{X} - \overset{-}{Y}$) of first-row elements in general contain a quaternary ammonium group ($X = R_3N$—) vicinal to an electronegative atom Y as in (I),[34] although the transient formation of ylides of the type $Ph_2\overset{-}{C}-\overset{+}{O}HR$ has been recently demonstrated in the reaction of diphenyl-carbene with alcohols.[58] While the simplest compounds of the former type, the amine oxides (I; Y = O), are stable, in cases where Y is either a nitrogen or a carbon atom, the ylide will possess appreciable longevity only if further stabilisation is provided, usually by the presence of electron-withdrawing groups such as -CHO, -COMe, -COPh, $-CO_2Me$, $-NO_2$ or $-SO_2Ar$, bonded to the electronegative atom Y. In ylides of this type, although formal π-bonding between the 'onium nitrogen and vicinal electronegative atoms is not possible,[34] the $\overset{+}{N} - \overset{-}{Y}$ bond order being formally restricted to unity, there exists the possibility of the negative charge being delocalised through the electronegative moiety.

As part of an examination of the bonding, charge distributions and conformations of first-row ylides, the crystal structures of the N-trimethylammonio-amidates (IIa) [59] and (III),[60] which are representative of the class of ylides (I; Y = N—), have been determined.[61,62]



$R_3\overset{+}{N}-\overset{-}{Y}$

(I)



$Me_3\overset{+}{N}-\overset{-}{N}-R$

(II)

(a) R = -COPh

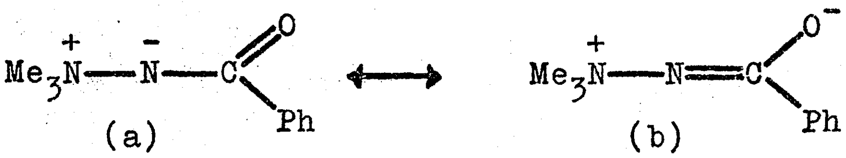
(b) R = -CHO

(c) R = -COMe

(d) R = $-CO_2Me$

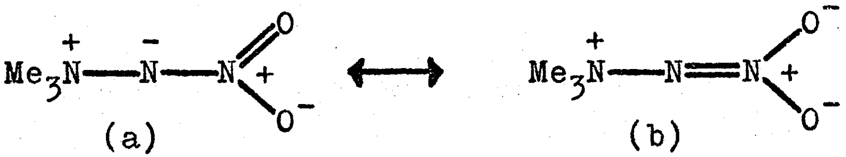
$Me_3\overset{+}{N}-\overset{-}{N}-NO_2$

(III)



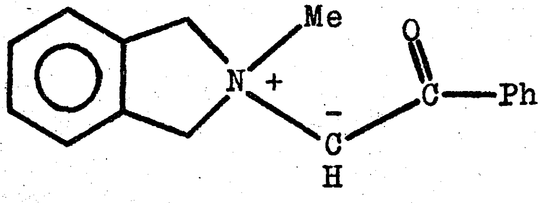
(a) (b)

(IV)



(a) (b)

(V)



(VI)

1.2 EXPERIMENTAL

Crystal Data

(IIa); N-trimethylammonio-benzamidate, $C_{10}H_{14}N_2O$, M = 178.2.

Monoclinic, a = 11.620(10), b = 7.928(6), c = 11.454(10) Å,

β = 113.75(3)°, U = 965.8 Å^3.

D_m = 1.21 g.cm.$^{-3}$ (by flotation in aqueous KI), Z = 4,

D_c = 1.23 g.cm.$^{-3}$, F(000) = 384.

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

Linear absorption coefficient for X-rays (λ = 0.7107 Å),

μ = 0.87 cm.$^{-1}$.

(III); N-trimethylammonio-nitramidate, $C_3H_9N_3O_2$, M = 119.1.

Orthorhombic, a = 12.245(6), b = 6.718(3), c = 7.099(5) Å,

U = 574.1 Å^3.

D_m = 1.36 g.cm.$^{-3}$ (by flotation in aqueous KI), Z = 4,

D_c = 1.38 g.cm.$^{-3}$, F(000) = 256.

Space group Pnma (D^{16}_{2h} , No.62).

Linear absorption coefficient for X-rays (λ = 0.7107 Å),

μ = 1.23 cm.$^{-1}$.

Crystallographic Measurements

Unit-cell parameters for both crystals were initially determined from oscillation and Weissenberg photographs taken with Cu-K_α (λ = 1.5418 Å) radiation, and from precession photographs taken with Mo-K_α (λ = 0.7107 Å) radiation. Subsequently refined values for these parameters were obtained, by least-squares techniques, from the Busing and Levy orientation-matrix program [63] prior to the diffractometer data collections. The space group to which (IIa) belongs is uniquely determined by systematic absences in the 0k0 and h0ℓ spectra, whereas the absences in the hk0 and 0kℓ spectra of (III) indicate the possible space groups Pnma and Pna2_1. However, the correctness of Pnma was indicated firstly by statistical tests, and was later vindicated by a trial refinement using the non-restrictive symmetry of space group Pna2_1. Consequently molecules of (III) in the solid state are restricted to possess crystallographic mirror symmetry, the mirror plane containing the atoms O'(1), O'(2), N'(1), N'(2), N'(3) and C'(1).

Table 1.1 contains details of the crystal morphologies and data collections for compounds (IIa) and (III). Both sets of intensity data were collected on a Hilger and Watts Y290 computer-controlled diffractometer using Mo-K_α radiation, structure amplitudes on an overall non-absolute scale being obtained by applying the appropriate Lorentz and polarisation corrections. Absorption effects were considered negligible in both cases and were therefore ignored.

Structure Determinations

Both structures were solved by the application of the symbolic addition method,[19] using programs developed by Stewart et al.[64] and modified by the Glasgow group. Both sets of data were initially placed on absolute scales using the "K-curve" method,[6] normalised structure amplitudes, $|E(hk\ell)|$, subsequently being derived (see PART I, Section 2). Statistical analyses of both data sets, shown in Table 1.2, indicate centric distributions appropriate to the centrosymmetric space groups $P2_1/c$ and Pnma of molecules (IIa) and (III) respectively.

$\sum_2$ relationships for use in the symbolic addition procedures were then generated for the 144 reflexions of (IIa) with $|E| > 1.50$ and the 80 reflexions of (III) with $|E| > 1.70$. The phasing process, applied to the origin-defining sets shown in Table 1.3, determined the signs of 140 reflexions (64+, 76-) for (IIa) and 80 reflexions (49+, 31-) for (III), all of which subsequently proved to be correct.

In both cases an E-map, calculated with the appropriate terms, revealed the entire structure. Inclusion of both sets of atomic positions in structure-factor calculations yielded R-values of 24 % and 36 % for (IIa) and (III) respectively. Improved coordinates, for subsequent refinement by least-squares methods, were obtained in each case by performing two rounds of structure-factor and electron-density calculations. After each structure-factor calculation, in which overall isotropic thermal parameters $U_{iso} = 0.05$ Å^2 were assumed, the two sets of data were placed on approximate absolute scales by equating $k\sum|F_o|$ and $\sum|F_c|$.

Structure Refinements

The refinement of positional, vibrational and overall-scale parameters by three-dimensional least-squares calculations converged, in the case of compound (IIa), after 15 cycles when R was 0.072 and R' ($= \sum w\Delta^2/\sum w|F_o|^2$) was 0.005, while compound (III) required 10 cycles, the final R and R' values being 0.078 and 0.007 for the statistically observed data ($I > 3\sigma_I$). Full details of both refinements are given in Table 1.4. During the refinement of compound (III) it was essential to restrict the y-coordinates of atoms lying on the crystallographic mirror plane to be equal to zero, and in the later stages, the cross-terms of the anisotropic vibrational tensor, $2U_{12}$ and $2U_{23}$, were necessarily assigned zero values.

Difference syntheses, calculated after the isotropic refinements, revealed all the hydrogen atoms of the two structures. In later cycles, the hydrogen atom parameters were refined, individual isotropic thermal parameters U_{iso} = 0.08 and 0.05 $\mathring{A}^2$ being assumed as starting values for (IIa) and (III) respectively. A weighting scheme of the form

$$\sqrt{w} = \left\{\left[1 - \exp(-p_1(\sin\theta/\lambda)^2)\right] / \left[1 + p_2|F_o| + p_3|F_o|^2\right]\right\}^{1/2}$$

was applied in all cycles of the refinement of (IIa). Initially the p-parameters were chosen to give unit weights to all reflexions, but in later cycles they were adjusted in accordance with an ($|F_o|$ and $\sin\theta/\lambda$) analysis of $w\Delta^2$, the final values being $p_1 = 500$, $p_2 = 0.01$ and $p_3 = 0.0001$. Throughout the refinement of (III), however, it was not found necessary to apply other than unit weights to the data, and therefore no weighting scheme was used.

Both refinements were judged to have converged when the parameter shifts calculated by a least-squares cycle were insignificant compared to the corresponding estimated standard deviations. Structure factors were then calculated using the respective final positional and thermal parameters, the subsequent calculation of electron-density distributions and difference syntheses revealing no errors in either structure. Observed and final calculated structure factors for both compounds are listed in Tables 1.5 and 1.6 respectively. In all structure-factor calculations, the atomic scattering factors used were taken from 'International Tables for X-Ray Crystallography,' Vol.III.[65]

Final fractional coordinates and thermal parameters for both compounds are given in Table 1.7, the values of U_{ii} and $2U_{ij}$ referring to the anisotropic temperature factor expression given in PART I, Section 3. It is noticeable that, for atoms of molecule (III) lying on the crystallographic mirror plane, the tensor elements U_{22}, perpendicular to the mirror plane, are not significantly greater than the other diagonal elements, U_{11} and U_{33}, as would be expected were the structure disordered, in which case that determined would be the statistical average of molecules not lying exactly on the crystallographic mirror plane.

All bond lengths, valency angles, and pertinent intra- and inter-molecular non-bonded distances are shown in Table 1.8. The appropriate estimated standard deviations, σ, derived from the inverses of the respective least-squares normal equation matrices are included in Tables 1.7 and 1.8. In the case of (IIa), the average σ for C-O, C-N, C-C and N-N bonds is 0.006 Å, while for C-H bonds and valency angles σ is 0.05 Å and 0.4° respectively. The corresponding values for (III) are 0.008 Å, 0.06 Å and 0.5°. These are probably best regarded as minimum values, especially for (IIa), where the block-diagonal approximation was used in the final stages of the refinement owing to computer-storage limitations.

Details of least-squares planes calculated for various portions of the molecular framework of (IIa) are given in Table 1.9. The atomic numbering schemes, used in every table, are shown in Figures 1.1 and 1.2 for (IIa) and (III) respectively, while Figure 1.3 shows a projected view of the molecular packing of (IIa) and Figure 1.4 gives a three-dimensional view of the contents of a unit cell of (III).

Table 1.1

Details of Crystal Morphologies and Data Collections

	Compound(IIa)	Compound(III)
Crystal shape	Flat hexagon	Flat plate
Crystal size (mm.)	0.6 × 0.5 × 0.2	0.4 × 0.2 × 0.05
Rotation axis	$\underline{b}$	$\underline{c}$
Scan technique	ω	2θ
Step size (°)	0.02	0.02
Number of steps	40	40
Step time (secs)	2	2
Total background count (secs)	40	40
Radiation filter	Sr/Zr balanced	Zr
2θ range (°)	$0 \rightarrow 44$	$0 \rightarrow 50$
Independent reflexions	977 ($I > 0$)	730 (378 with $I > 3\sigma_I^*$)

* σ_I, the standard deviation in the measured intensity, I, is derived from counting statistics

$$\text{i.e.} \quad \sigma_I = \sqrt{(P + B_1 + B_2)}$$

where P, B_1 and B_2 are the peak and two background counts respectively.

Table 1.2

Statistical Analyses of both Data Sets

	Theoretical		Experimental	
	Centric	Acentric	(IIa)	(III)
Average $\|E\|$	0.798	0.886	0.713	0.732
Average $\|E\|^2$	1.000	1.000	0.950	0.941
Average $\|E^2 - 1\|$	0.968	0.736	0.973	0.927
$\|E\| > 1$	31.73	36.79	28.21	28.52
$\|E\| > 2$	4.55	1.83	4.68	3.52
$\|E\| > 3$	0.27	0.01	0.38	0.15

Table 1.3

(a) Origin-defining Reflexions for (IIa)

h	k	ℓ	Sign	$\|E\|$
2	7	3	+1	3.49
1	6	4	+1	3.47
1	5	-6	+1	3.38

(b) Origin-defining Reflexions for (III)

h	k	ℓ	Sign	$\|E\|$
4	6	5	+1	2.85
6	7	5	+1	2.84
3	2	9	+1	2.36

Table 1.4

(a) Course of Refinement for (IIa)

Cycles	Parameters refined	Final R	Final R'
1 - 3	x, y, z, U_{iso} for O, N, C, Overall scale factor, Full matrix, unit weights.	0.164	0.0221
4 - 9	x, y, z, U_{ij} for O, N, C, Overall scale factor, Full matrix, weighting scheme adjusted, hydrogen atom contributions included but not refined.	0.083	0.0070
10 - 12	x, y, z, U_{iso} for H only, Overall scale factor, Full matrix, weighting scheme applied, contributions of other atoms included but not refined.	0.076	0.0057
13 - 15	x, y, z, U_{ij} for O, N, C, x, y, z, U_{iso} for H, Overall scale factor, Block diagonal, weighting scheme applied.	0.072	0.0053

Table 1.4 (contd.)

(b) Course of Refinement for (III)

Cycles	Parameters refined	Final R	Final R'
1 - 4	x, y, z, U_{iso} for O, N, C,* Overall scale factor, Full matrix, unit weights.	0.195	0.026
5 - 10	x, y, z, U_{ij} for O, N, C,* x, y, z, U_{iso} for H,* Overall scale factor, Full matrix, unit weights.	0.136	0.013
Structure - factor calculation on final parameters using only the statistically observed data ($I > 3\sigma_I$).		0.078	0.007

* The appropriate restrictions were applied for atoms lying on the crystallographic mirror plane at y = 0.2500.

Table 1.5

Observed structure amplitudes and final calculated structure factors

(IIa)

H	K	L	F OBS	F CALC
6	2	-2	7.6	-7.3
6	2	-3	9.4	9.4
6	1	0	14.0	-11.9
6	1	-1	4.7	-4.8
6	1	-4	20.5	19.3
6	0	0	7.9	-8.4
6	0	-2	44.7	42.0
6	0	-4	7.0	6.4
5	3	-1	1.5	-1.3
5	3	-2	0.8	0.7
5	3	-3	10.3	9.7
5	2	1	26.6	-25.3
5	2	0	15.9	15.0
5	2	-1	15.4	14.8
5	2	-2	3.2	-3.6
5	2	-3	5.2	-5.1
5	2	-4	7.6	8.3
5	2	-5	7.3	-6.5
5	1	1	18.7	-17.5
5	1	0	7.6	-7.2
5	1	-1	22.1	21.0
5	1	-2	2.0	-1.7
5	1	-3	8.0	-7.5
5	1	-4	15.6	15.5
5	1	-5	4.6	-4.3
5	0	2	0.7	0.5
5	0	0	24.4	-23.0
5	0	-2	4.2	-4.6
5	0	-4	11.6	-11.2
5	0	-6	6.1	-5.6
4	3	1	9.2	-9.3
4	3	0	1.0	0.9
4	3	-1	2.3	1.9
4	3	-2	15.5	14.8
4	3	-3	31.5	-30.9
4	3	-4	35.1	-35.6
4	2	2	3.2	-3.8
4	2	1	16.4	-16.6
4	2	0	1.9	-1.4
4	2	-1	1.9	-1.9
4	2	-2	8.4	8.5
4	2	-3	19.5	-19.9
4	2	-4	17.7	-16.3
4	2	-5	39.8	39.5
4	1	3	6.8	-6.9
4	1	2	5.4	-5.1
4	1	1	16.9	18.1
4	1	0	21.6	21.2
4	1	-1	9.0	-7.7
4	1	-2	1.0	1.0
4	1	-3	27.0	27.7
4	1	-4	33.5	-32.7
4	1	-5	21.5	21.7
4	1	-6	14.4	14.9
4	0	2	9.5	-9.4
4	0	0	23.1	-23.2
4	0	-2	12.9	-12.6
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3	4	0	23.4	23.3
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3	2	2	35.9	-38.1
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3	0	4	20.6	-20.5
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3	0	-2	39.3	-41.5
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2	4	-1	5.9	-6.3
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5	2	-7	11.0	11.2
5	2	-8	4.2	-6.0
5	2	-9	1.8	-1.4
5	2	-10	3.5	3.4
5	2	-11	7.3	-7.4
5	1	7	7.5	-7.6
5	1	6	2.6	3.0
5	1	5	2.3	0.6
5	1	4	6.6	6.6
5	1	3	1.3	-1.8
5	1	2	17.1	16.1
5	1	-6	0.9	0.4
5	1	-7	6.4	6.6
5	1	-8	7.7	-7.0
5	1	-9	5.4	-5.4
5	1	-10	4.4	3.9
5	0	8	3.9	-3.5
5	0	6	10.7	11.5
5	0	4	12.8	-13.2
5	0	-8	17.4	-16.9
5	0	-10	9.3	10.0
5	0	-12	8.8	-9.7
4	7	3	4.8	-7.8
4	7	2	2.8	2.8
4	7	1	1.5	-0.9
4	7	0	1.4	-1.3
4	7	-1	4.3	5.4
4	7	-2	4.1	3.4
4	7	-3	2.7	-3.9
4	7	-4	2.4	1.4
4	7	-5	3.9	4.2
4	6	5	2.6	0.7
4	6	4	1.7	-0.7
4	6	1	11.9	12.1
4	6	0	1.0	-0.7
4	6	-1	4.1	-4.4
4	6	-2	2.3	-4.5
4	6	-3	2.5	3.3
4	6	-4	0.7	-0.6
4	6	-6	2.3	-0.0
4	6	-7	1.9	0.8
4	6	-8	1.7	-1.0
4	5	6	3.6	3.8
4	5	5	2.1	2.9
4	5	4	5.9	-6.6
4	5	3	5.6	4.9
4	5	1	0.3	-1.8
4	5	0	4.9	-4.8
4	5	-2	2.5	2.3
4	5	-3	3.4	3.9
4	5	-4	2.7	2.5
4	5	-5	10.8	9.8
4	5	-6	7.6	7.4
4	5	-7	2.6	-3.7
4	4	6	4.2	-4.0
4	4	5	3.4	-4.2
4	4	3	2.5	2.9
4	4	2	3.5	2.6
4	4	1	1.3	0.6
4	4	0	6.6	6.1
4	4	-1	7.9	-7.5
4	4	-2	8.3	7.8
4	4	-3	18.9	19.6
4	4	-4	12.9	13.7
4	4	-5	18.7	-18.1
4	4	-6	9.9	-10.4
4	4	-7	14.9	-15.9
4	4	-8	10.2	10.2
4	4	-9	4.1	4.2
4	4	-10	7.9	-8.4
4	3	8	1.9	-3.3
4	3	7	2.9	1.1
4	3	6	0.6	0.5
4	3	3	4.5	3.6
4	3	2	0.6	0.2
4	3	-5	19.9	-21.0
4	3	-6	14.8	17.7
4	3	-7	5.2	5.2
4	3	-8	13.8	-13.5
4	3	-9	3.3	3.7
4	3	-10	7.6	-8.3
4	2	8	5.4	-5.0
4	2	7	5.5	6.5
4	2	6	10.7	-10.9
4	2	5	6.7	-7.0
4	2	4	8.9	9.3
4	2	3	2.8	2.0
4	2	-6	3.2	-3.0
4	2	-7	2.1	1.5
4	2	-8	6.0	-6.0
4	2	-9	12.9	13.1
4	2	-10	1.1	-0.8
4	2	-11	3.8	-3.1
4	1	8	10.4	-10.5
4	1	7	1.1	2.3
4	1	6	10.4	11.3
4	1	5	6.3	-6.0
4	1	4	20.8	22.7
4	1	-7	12.3	-12.1
4	1	-9	3.0	2.5
4	1	-10	10.7	10.7
4	1	-11	4.7	-4.2
4	0	8	0.5	-0.5
4	0	6	24.5	26.0
4	0	4	9.0	-9.3
4	0	-8	5.5	5.1
4	0	-12	5.2	-4.8
3	8	0	4.6	-5.2
3	8	-1	1.1	2.8
3	8	-2	3.9	3.1
3	7	3	2.6	2.7
3	7	2	1.9	-2.1
3	7	1	0.6	-0.9
3	7	0	3.0	4.0
3	7	-1	5.2	-5.9
3	7	-2	2.5	-2.9
3	7	-3	4.5	-5.3
3	7	-5	3.5	4.5
3	7	-6	2.3	-0.9
3	6	6	4.0	3.0
3	6	4	5.7	-5.5
3	6	3	3.9	3.7
3	6	2	8.0	8.0
3	6	1	7.8	-8.4
3	6	0	9.8	-10.1
3	6	-1	5.3	-5.6
3	6	-2	4.6	4.7
3	6	-3	1.3	-0.9
3	6	-4	4.3	-4.5
3	6	-5	0.7	-0.4
3	6	-6	3.8	3.7
3	6	-7	4.2	-4.4
3	6	-8	1.7	-1.1
3	5	7	1.9	1.1
3	5	6	3.3	-3.0
3	5	5	5.9	6.2
3	5	4	2.9	-2.7
3	5	2	2.5	-2.8
3	5	1	9.5	-9.5
3	5	0	8.7	-8.7
3	5	-2	13.5	13.2
3	5	-3	9.4	8.7
3	5	-4	1.5	1.7
3	5	-5	2.8	2.7
3	5	-6	1.8	1.0
3	5	-7	7.6	8.0
3	5	-8	3.4	3.6
3	5	-9	4.6	6.2
3	4	8	1.5	-0.4
3	4	7	4.3	4.7
3	4	6	3.8	-2.9
3	4	5	3.5	2.9
3	4	3	19.8	-19.4
3	4	2	4.7	5.1
3	4	1	5.7	6.1
3	4	-3	3.3	2.8
3	4	-4	4.5	5.0
3	4	-5	7.7	9.8
3	4	-6	3.3	-3.6
3	4	-7	7.6	7.9
3	4	-8	5.1	-5.3
3	4	-9	9.0	-9.7
3	4	-10	2.1	0.7
3	3	8	5.0	4.7
3	3	7	8.4	-8.2
3	3	6	3.5	-4.3
3	3	5	5.7	-5.5
3	3	4	17.3	20.7
3	3	3	3.9	-3.5
3	3	-6	23.7	-27.0
3	3	-7	2.5	2.7
3	3	-8	14.3	14.7
3	3	-9	18.4	-18.9
3	3	-10	1.7	-2.3
3	3	-11	6.0	6.9
3	2	9	8.5	-9.2
3	2	8	3.0	3.1
3	2	7	2.6	-2.7
3	2	6	1.8	-1.1
3	2	5	8.2	8.3
3	2	4	22.0	20.7
3	2	-7	13.5	-15.8
3	2	-8	5.2	5.9
3	2	-9	0.9	0.9
3	2	-10	2.4	-2.0
3	2	-11	10.0	10.8
3	1	7	5.6	5.4
3	1	6	2.0	2.1
3	1	5	0.6	1.4
3	1	-7	6.5	6.3
3	1	-8	4.1	4.4
3	1	-9	3.6	3.8
3	1	-10	5.0	-5.1
3	0	8	2.8	3.7
3	0	6	4.5	-4.1
3	0	-8	4.9	5.2
2	8	1	11.1	11.2
2	8	0	4.3	3.6
2	8	-1	5.3	-5.7
2	8	-2	3.8	-3.5
2	8	-3	4.8	6.1
2	7	3	16.8	18.5
2	7	2	0.9	0.4
2	7	1	6.7	-7.2
2	7	0	3.6	-2.8
2	7	-1	4.0	3.9
2	7	-3	1.2	2.2
2	7	-4	1.6	-1.9
2	7	-5	3.2	-3.4
2	6	6	2.2	-2.6
2	6	5	5.7	5.6
2	6	4	3.3	-0.2
2	6	3	3.3	-2.9
2	6	2	1.9	-2.3
2	6	1	9.0	-9.5
2	6	0	3.5	-4.3
2	6	-1	1.9	1.5
2	6	-4	4.5	4.4
2	6	-5	9.0	-9.3
2	6	-8	2.9	3.7
2	5	6	2.7	-2.2
2	5	4	3.4	3.5
2	5	3	11.9	-12.0
2	5	2	8.6	-9.0
2	5	1	2.9	3.0
2	5	0	15.2	21.2
2	5	-1	5.2	-5.2
2	5	-3	4.3	-4.6
2	5	-4	2.9	-2.3
2	5	-5	11.6	-11.7
2	5	-6	7.7	8.6
2	5	-7	6.7	6.6
2	5	-8	10.3	-10.4
2	4	8	4.7	-5.1
2	4	6	4.5	5.3
2	4	5	3.2	-3.6
2	4	3	10.1	11.4
2	4	2	3.1	3.5
2	4	-4	1.9	2.6
2	4	-5	0.9	-0.2
2	4	-6	2.7	-3.6
2	4	-7	18.8	18.9
2	4	-8	11.6	-12.0
2	4	-9	4.0	-3.7
2	4	-10	6.7	6.8
2	3	9	6.9	7.1
2	3	8	5.3	6.2
2	3	7	5.7	-5.3
2	3	6	5.4	5.4
2	3	5	5.1	4.7
2	3	4	1.2	-0.9
2	3	-6	11.2	-11.6
2	3	-8	9.3	9.6
2	3	-9	2.9	-3.0
2	3	-10	4.9	6.2
2	2	9	3.3	-3.5
2	2	8	4.6	4.1
2	2	7	5.6	-5.9
2	2	6	1.0	0.9
2	2	5	9.4	-9.7
2	2	-7	4.6	-5.1
2	2	-8	5.9	-5.6
2	2	-9	6.2	-5.8
2	2	-10	3.0	-3.3
2	1	10	2.8	-2.9
2	1	9	2.3	-4.7
2	1	8	6.4	6.4
2	1	7	5.0	5.3
2	1	6	2.8	-2.6
2	1	-7	12.5	-11.9
2	1	-8	7.1	-7.2
2	1	-9	9.1	8.7
2	1	-10	1.6	2.0
2	1	-11	3.6	-3.1
2	0	10	0.6	1.0
2	0	8	2.0	-2.3
2	0	6	10.2	-11.8
2	0	-8	4.9	4.9
2	0	-10	3.8	4.6
1	8	2	6.2	-6.0
1	8	1	2.2	-1.0
1	8	0	5.3	5.6
1	8	-1	5.7	-5.2
1	8	-2	2.7	-0.8
1	8	-3	4.9	5.7
1	7	5	3.1	-3.1
1	7	4	1.2	-1.5
1	7	3	5.9	5.9
1	7	2	10.5	11.3
1	7	1	5.5	-5.7
1	7	-1	5.4	5.7
1	7	-2	9.4	10.0
1	7	-3	3.5	2.8
1	7	-5	4.9	-5.2
1	7	-6	6.4	-7.2
1	6	7	2.1	2.4
1	6	6	4.9	-4.8
1	6	5	9.2	9.3
1	6	4	20.7	20.5
1	6	3	10.8	-10.6
1	6	2	4.4	-4.6
1	6	1	7.3	7.8
1	6	0	7.3	7.3
1	6	-1	8.5	8.0
1	6	-2	3.8	-3.5
1	6	-3	9.2	-10.0
1	6	-4	16.6	-16.6
1	6	-5	11.5	11.8
1	6	-6	2.1	0.7
1	6	-7	3.5	2.4
1	6	-8	4.4	4.8
1	5	8	1.6	-2.6
1	5	7	4.6	3.8
1	5	6	13.7	13.6
1	5	5	14.4	-14.0
1	5	4	6.6	6.4
1	5	1	12.8	14.3
1	5	0	16.0	-16.0
1	5	-1	9.7	-10.4
1	5	-2	3.0	4.0
1	5	-3	1.9	0.5
1	5	-4	12.7	-13.8
1	5	-5	9.4	10.2
1	5	-6	22.0	21.5
1	5	-7	12.8	-12.4
1	5	-8	4.6	-3.7
1	4	9	2.7	-3.2
1	4	7	6.3	-6.8
1	4	6	12.4	12.1
1	4	4	7.7	-9.0
1	4	-4	5.5	5.9
1	4	-5	3.8	3.9
1	4	-6	1.2	2.0
1	4	-7	18.6	-18.6
1	4	-8	3.7	-2.8
1	4	-9	8.3	8.6
1	4	-10	2.5	-1.1
1	3	9	1.7	-2.2
1	3	7	1.7	1.4
1	3	6	1.8	-1.6
1	3	5	8.3	9.3
1	3	-5	5.9	6.1
1	3	-6	7.4	8.7
1	3	-8	4.2	-4.2
1	3	-9	9.4	9.3
1	2	9	5.1	5.1
1	2	7	4.9	5.2
1	2	6	6.9	-7.6
1	2	-6	1.5	-1.9
1	2	-7	3.6	3.2
1	2	-8	3.9	3.8
1	2	-10	1.7	-2.3
1	2	-11	5.8	-5.0
1	1	10	3.5	2.9
1	1	9	3.1	4.1
1	1	7	10.7	-10.2
1	1	6	13.7	-13.2
1	1	-8	4.9	-3.7
1	1	-9	7.6	-7.5
1	1	-10	2.6	2.8
1	1	-11	0.7	1.7
1	0	8	5.7	-5.9
1	0	6	17.5	16.7
1	0	-8	8.7	8.9
1	0	-10	0.9	-0.7
0	8	3	0.6	1.3
0	8	2	2.6	1.3
0	8	1	6.0	-6.9
0	8	0	4.0	-3.3
0	7	6	2.5	3.1
0	7	5	0.8	0.6
0	7	4	5.6	-5.4
0	7	3	13.0	-13.5
0	7	2	1.1	1.3
0	7	1	2.7	2.0
0	6	7	0.5	-1.1
0	6	6	4.5	-4.1
0	6	5	12.2	-12.5
0	6	4	1.6	-0.9
0	6	3	5.8	8.8
0	6	2	11.6	11.3
0	6	1	8.7	-8.4
0	6	0	3.7	-5.0
0	5	8	2.6	-3.3
0	5	7	3.3	-3.6
0	5	6	10.4	10.2
0	5	5	11.1	10.9
0	5	4	2.3	-3.3
0	5	3	0.9	0.9
0	5	2	10.9	12.7
0	5	1	7.8	8.3
0	4	9	3.2	-3.6
0	4	8	4.8	4.8
0	4	7	3.9	4.1
0	4	6	4.6	4.4
0	4	5	2.7	3.2
0	4	4	5.6	-5.2
0	3	10	2.6	3.3
0	3	9	3.2	-4.6
0	3	7	6.6	6.5
0	3	6	3.4	3.3
0	3	5	17.1	-17.3
0	2	9	6.8	7.5
0	2	8	2.7	2.6
0	2	7	8.9	-8.9
0	2	6	3.5	-3.9
0	1	10	4.8	5.3
0	1	8	1.9	-2.3
0	1	7	8.1	9.7
0	1	6	17.9	-17.2
0	0	10	2.0	-1.7
0	0	8	14.8	-14.5

Table 1.6

Observed structure amplitudes and final calculated structure factors

(III)

H	K	L	F OBS	F CALC
17	1	1	2.2	3.7
17	0	1	2.2	1.4
16	3	0	3.7	-1.6
16	1	3	3.5	3.9
16	1	2	3.7	4.0
16	1	1	2.2	-2.6
16	1	0	1.8	-0.8
16	0	3	3.5	-4.8
16	0	2	5.1	3.7
16	0	1	2.4	3.0
16	0	0	2.6	1.1
15	3	3	1.4	-3.2
15	3	1	2.3	2.2
15	2	4	2.2	1.5
15	2	3	1.9	-2.3
15	2	2	2.5	-3.2
15	1	4	3.7	2.5
15	1	3	2.1	2.1
15	0	3	1.3	0.6
15	0	1	2.8	2.8
14	5	1	1.7	-1.6
14	5	0	3.0	-1.2
14	4	3	4.1	4.7
14	4	1	2.9	-0.3
14	4	0	3.2	-0.6
14	3	4	2.4	-3.4
14	3	3	1.7	-1.6
14	3	2	1.5	1.3
14	3	1	4.0	-2.8
14	2	4	2.6	1.0
14	2	3	6.9	-7.0
14	2	2	2.0	1.0
14	2	1	2.4	2.7
14	2	0	2.2	-1.7
14	1	5	1.7	-1.1
14	1	4	4.8	4.0
14	1	3	4.3	3.0
14	1	2	3.3	-0.9
14	1	0	2.6	-0.5
14	0	5	1.9	-1.4
14	0	3	6.4	7.0
14	0	2	2.5	2.7
14	0	1	2.5	-1.4
13	6	1	2.4	0.6
13	4	5	1.1	1.1
13	4	4	3.1	3.1
13	4	3	2.1	-1.1
13	4	2	2.5	-1.1
13	3	2	0.7	1.0
13	3	1	4.6	-5.0
13	2	5	1.1	0.7
13	2	3	1.7	-1.6
13	2	2	3.3	0.9
13	2	1	1.2	2.1
13	1	6	3.7	-1.8
13	1	5	2.7	1.2
13	1	4	3.1	-2.4
13	1	3	2.5	3.2
13	1	2	4.1	2.1
13	1	1	4.9	4.4
13	0	5	1.8	2.8
13	0	4	3.6	1.9
13	0	3	3.8	-3.3
13	0	2	1.2	1.3
13	0	1	2.0	0.7
12	6	1	2.7	2.9
12	5	3	2.9	-2.8
12	5	2	4.0	2.3
12	5	1	2.9	1.2
12	5	0	9.5	9.6
12	4	5	0.8	0.2
12	4	4	4.0	3.6
12	4	3	2.3	-0.6
12	4	2	2.3	1.5
12	4	1	2.1	-1.5
12	4	0	1.8	0.2
12	3	6	2.7	1.6
12	3	5	2.4	-3.8
12	3	4	3.0	-1.3
12	3	3	4.1	5.2
12	3	2	8.2	-7.8
12	3	1	5.2	-5.7
12	3	0	6.0	-6.7
12	2	4	4.8	-4.8
12	2	3	1.8	1.8
12	2	1	2.2	-0.2
12	2	0	4.7	-4.5
12	1	7	4.9	-3.7
12	1	6	0.8	1.2
12	1	5	4.9	5.0
12	1	3	5.2	-5.7
12	1	2	5.9	6.4
12	1	1	5.2	5.4
12	1	0	14.3	15.2
12	0	7	3.2	-2.0
12	0	5	2.4	2.7
12	0	4	4.4	5.2
12	0	1	4.6	-6.9
11	7	2	0.8	1.2
11	7	1	3.1	-3.0
11	6	4	2.9	1.3
11	6	3	5.2	-5.2
11	6	1	2.2	-2.2
11	5	5	1.7	-1.5
11	5	4	3.2	1.8
11	5	3	4.2	5.0
11	5	1	3.3	3.3
11	4	6	3.0	0.9
11	4	3	5.3	5.4
11	4	2	3.6	0.9
11	4	1	4.9	5.7
11	3	7	1.8	3.0
11	3	6	3.3	-3.1
11	3	5	2.0	-2.8
11	3	4	3.1	-1.2
11	3	2	2.0	-0.4
11	3	1	8.5	-9.4
11	2	7	2.1	1.3
11	2	5	2.3	-1.6
11	2	4	1.8	-2.0
11	2	3	8.5	-9.4
11	2	2	3.0	1.7
11	2	1	7.6	-7.9
11	1	7	3.1	-3.5
11	1	6	3.6	3.3
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11	1	3	5.9	6.3
11	1	2	1.6	-1.8
11	1	1	8.2	8.6
11	0	7	4.3	-1.6
11	0	6	4.0	2.1
11	0	5	2.9	0.8
11	0	4	4.7	-5.0
11	0	3	10.5	11.7
11	0	2	5.7	5.6
11	0	1	6.9	7.5
10	7	3	2.1	-1.2
10	7	2	3.9	-2.6
10	7	0	2.9	3.8
10	6	5	4.8	-3.0
10	6	4	0.8	0.0
10	6	3	1.5	1.3
10	6	2	2.5	-4.1
10	6	1	4.7	-5.5
10	6	0	7.7	-7.1
10	5	5	1.7	-1.4
10	5	4	3.1	0.3
10	5	0	1.5	-0.2
10	4	5	5.5	4.1
10	4	4	2.6	2.2
10	4	3	1.7	-1.4
10	4	2	8.8	9.6
10	4	1	8.3	8.7
10	4	0	7.4	7.4
10	3	6	1.8	0.7
10	3	5	2.5	-1.1
10	3	4	3.4	-1.7
10	3	3	2.8	-3.0
10	3	2	5.5	-5.3
10	3	1	6.3	5.6
10	3	0	6.2	6.7
10	2	7	1.5	-0.1
10	2	5	4.3	-4.6
10	2	4	0.6	-2.5
10	2	3	2.6	4.0
10	2	2	13.3	-14.6
10	2	1	15.5	-17.5
10	2	0	9.4	-9.0
10	1	8	2.7	-0.8
10	1	7	2.1	3.5
10	1	5	2.6	-1.5
10	1	4	2.0	2.5
10	1	3	2.5	2.8
10	1	2	3.7	2.5
10	1	0	1.5	-1.6
10	0	8	4.7	-5.5
10	0	7	3.9	-2.5
10	0	6	4.8	4.4
10	0	5	7.2	7.1
10	0	2	11.7	12.7
10	0	1	11.1	11.8
10	0	0	19.5	21.1
9	8	1	2.6	3.2
9	7	4	3.4	3.2
9	7	3	3.2	2.0
9	6	5	1.7	-0.5
9	6	4	1.7	-2.3
9	6	3	1.2	-1.7
9	6	1	2.9	-3.8
9	5	5	1.9	1.7
9	5	3	2.9	-0.9
9	5	2	3.2	-2.6
9	5	1	3.9	-3.1
9	4	7	2.1	0.1
9	4	6	4.0	2.5
9	4	5	2.2	2.4
9	4	3	0.9	-0.3
9	4	2	4.8	4.6
9	4	1	9.3	9.3
9	3	6	2.0	1.5
9	3	5	3.1	-2.3
9	3	4	9.0	9.4
9	3	3	0.6	1.0
9	3	2	6.1	-5.6
9	3	1	4.9	5.0
9	2	6	1.5	-2.8
9	2	5	7.4	-7.3
9	2	4	2.9	-3.2
9	2	3	4.0	3.5
9	2	2	3.7	-4.6
9	2	1	16.6	-17.0
9	1	7	3.8	2.5
9	1	6	4.6	-4.2
9	1	5	3.1	4.5
9	1	4	3.7	-3.6
9	1	3	2.8	-3.1
9	1	2	2.4	-1.9
9	1	1	3.3	-4.3
9	0	8	2.0	-1.2
9	0	6	2.9	3.2
9	0	5	1.4	0.9
9	0	4	4.0	3.6
9	0	3	8.6	7.7
9	0	2	3.9	4.5
9	0	1	12.8	12.1
8	8	2	2.5	1.2
8	8	1	4.0	-4.0
8	8	0	2.8	-1.5
8	7	4	1.1	-1.6
8	7	2	3.2	3.7
8	7	1	5.1	4.9
8	7	0	3.3	-2.1
8	6	5	0.8	2.9
8	6	1	3.2	2.8
8	6	0	2.8	-2.4
8	5	6	1.3	-0.0
8	5	5	8.1	-7.9
8	5	4	1.8	1.9
8	5	2	3.7	-4.5
8	5	1	2.7	-2.8
8	4	7	2.0	-0.4
8	4	6	0.7	2.3
8	4	5	1.2	-1.0
8	4	4	3.5	2.2
8	4	3	2.2	1.5
8	4	2	3.2	0.1
8	4	1	9.3	-9.8
8	4	0	6.0	6.2
8	3	8	3.1	-2.8
8	3	6	4.6	-4.5
8	3	5	7.7	8.1
8	3	4	3.1	-2.1
8	3	3	2.9	-2.0
8	3	2	10.8	11.5
8	3	1	13.8	15.5
8	3	0	13.6	-14.5
8	2	6	4.4	-3.7
8	2	5	2.8	1.3
8	2	4	4.7	-4.1
8	2	3	2.7	-2.4
8	2	2	5.0	-5.2
8	2	1	15.3	15.3
8	2	0	3.0	-3.3
8	1	8	6.3	5.7
8	1	7	3.5	1.2
8	1	6	1.1	1.1
8	1	5	11.6	-13.3
8	1	4	5.4	4.7
8	1	3	2.6	2.6
8	1	2	9.3	-9.1
8	1	1	13.1	-14.6
8	1	0	6.8	8.0
8	0	8	2.5	0.9
8	0	7	1.8	2.9
8	0	6	7.1	5.9
8	0	5	5.1	-5.5
8	0	4	2.8	3.5
8	0	3	0.5	2.4
8	0	2	2.1	-0.4
8	0	1	9.5	-10.2
8	0	0	17.1	20.4
7	8	2	2.1	-0.8
7	8	1	1.1	-0.7
7	7	5	3.4	1.3
7	6	6	4.1	2.9
7	6	5	3.0	-1.6
7	6	2	6.9	7.1
7	5	7	2.4	1.9
7	5	6	2.8	-1.4
7	5	5	3.0	2.6
7	5	3	4.2	-2.7
7	5	2	6.1	-5.6
7	5	1	3.7	4.2
7	4	8	1.4	-0.4
7	4	7	1.0	1.2
7	4	6	5.3	-5.0
7	4	4	6.6	-5.9
7	4	3	6.3	6.9
7	4	2	7.0	-7.6
7	4	1	1.6	-0.7
7	3	7	4.7	-3.6
7	3	6	3.7	2.1
7	3	5	4.2	4.6
7	3	4	3.3	-2.9
7	3	3	9.4	-9.6
7	3	2	7.3	7.9
7	2	7	2.2	-1.2
7	2	6	4.6	3.4
7	2	5	6.1	-5.0
7	2	4	12.3	13.1
7	2	3	5.3	-7.0
7	2	2	6.0	6.5
7	2	1	2.4	-1.9
7	1	8	2.0	1.1
7	1	7	6.1	5.0
7	1	6	2.5	-2.4
7	1	5	1.7	0.7
7	1	4	4.2	3.9
7	1	3	2.1	1.7
7	1	2	9.7	-12.0
7	1	1	7.5	8.0
7	0	9	4.7	3.6
7	0	8	2.8	-2.6
7	0	7	1.4	1.7
7	0	6	8.9	-8.5
7	0	5	4.5	4.5
7	0	4	2.2	-2.3
7	0	3	10.9	11.6
7	0	2	22.4	-23.5
6	8	4	1.1	2.9
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6	8	0	3.6	3.7
6	7	5	6.2	-5.6
6	7	2	1.7	-1.6
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6	6	4	6.8	-6.2
6	6	3	2.8	1.6
6	6	2	1.6	-0.4
6	5	6	1.8	-1.9
6	5	5	8.4	8.9
6	5	4	2.3	1.0
6	5	3	0.6	0.8
6	5	2	8.1	9.0
6	5	1	2.5	2.5
6	5	0	10.2	-10.5
6	4	8	4.5	2.6
6	4	7	2.9	0.4
6	4	5	9.3	-9.8
6	4	4	8.8	9.1
6	4	3	0.8	-2.9
6	4	2	2.2	-0.9
6	4	1	4.1	-5.1
6	4	0	10.4	11.7
6	3	8	1.5	2.2
6	3	7	3.1	-2.4
6	3	6	3.5	-4.4
6	3	5	10.4	-10.0
6	3	4	2.4	1.6
6	3	2	9.1	-9.2
6	3	1	15.3	-19.6
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6	2	7	2.4	2.1
6	2	5	11.5	12.5
6	2	4	14.2	-15.3
6	2	3	2.4	0.0
6	2	1	17.6	18.1
6	2	0	23.5	-24.6
6	1	9	3.6	2.2
6	1	7	2.4	-0.5
6	1	6	2.7	-0.0
6	1	5	16.0	17.2
6	1	4	1.5	0.4
6	1	3	0.8	-0.0
6	1	2	20.4	21.5
6	1	1	11.5	11.0
6	1	0	21.7	-21.6
6	0	8	7.2	5.6
6	0	7	5.1	4.7
6	0	6	5.0	-5.0
6	0	5	19.9	-21.0
6	0	4	18.3	19.3
6	0	3	2.0	-3.3
6	0	2	1.5	2.6
6	0	1	2.9	-1.2
6	0	0	15.4	15.5
5	8	3	1.3	2.1
5	8	2	1.5	1.1
5	8	1	1.5	0.4
5	7	6	2.9	-2.1
5	7	5	2.2	0.2
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5	7	2	4.4	-4.6
5	7	1	1.9	2.0
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5	6	6	2.1	1.1
5	6	5	3.6	-2.7
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5	6	3	0.9	1.9
5	6	2	1.4	-0.8
5	6	1	6.0	-5.7
5	5	6	6.7	7.4
5	5	5	1.8	1.8
5	5	4	4.0	1.3
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5	5	1	1.3	-1.7
5	4	8	3.8	3.3
5	4	7	2.8	3.1
5	4	6	2.5	-3.0
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5	4	4	3.7	2.5
5	4	3	4.2	5.3
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5	3	3	6.2	-6.4
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5	2	7	6.4	-6.5
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5	2	4	2.0	-0.6
5	2	3	15.3	-16.8
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5	2	1	11.7	-11.5
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4	8	1	2.9	3.3
4	8	0	2.1	0.7
4	7	6	1.4	-3.2
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4	7	3	1.0	-1.9
4	7	2	1.7	-1.5
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4	7	0	3.0	2.5
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4	3	7	7.0	-6.1
4	3	6	5.3	-5.8
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4	3	3	4.6	-4.6
4	3	2	11.5	-11.0
4	3	1	24.9	-26.3
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4	1	4	9.5	-10.0
4	1	3	6.5	7.1
4	1	2	3.8	2.9
4	1	1	17.9	18.4
4	0	9	2.6	2.6
4	0	8	5.2	5.1
4	0	7	3.0	-2.0
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4	0	5	20.7	21.6
4	0	4	7.1	-8.5
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4	0	2	45.3	44.6
4	0	0	39.8	-41.3
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2	1	9	3.1	-1.9
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2	1	6	11.1	-12.5
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2	1	4	25.4	24.3
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2	1	2	13.1	-12.7
2	1	1	27.5	-28.0
2	1	0	93.3	96.1
2	0	8	3.1	1.3
2	0	7	4.7	-3.4
2	0	6	5.0	7.4
2	0	5	6.6	6.1
2	0	4	9.4	10.7
2	0	3	5.0	7.6
2	0	2	24.8	26.2
2	0	1	23.2	-23.5
2	0	0	10.6	-10.9
1	9	2	2.8	0.1
1	9	1	0.8	2.1
1	8	2	2.5	0.2
1	8	1	3.9	5.2
1	7	6	2.2	0.5
1	7	5	2.3	-0.3
1	7	3	2.7	-3.3
1	7	1	3.2	-4.1
1	6	5	1.8	-0.2
1	6	4	4.3	5.6
1	6	3	7.8	-7.3
1	6	2	6.2	-5.4
1	6	1	7.2	-7.7
1	5	8	2.2	1.3
1	5	7	2.9	-4.4
1	5	6	2.9	-4.9
1	5	4	4.3	4.0
1	5	3	10.1	10.8
1	5	2	6.6	-7.0
1	5	1	5.0	5.1
1	4	9	1.8	-1.8
1	4	8	1.3	-1.6
1	4	5	4.0	1.6
1	4	4	6.0	-7.3
1	4	3	8.4	8.7
1	4	2	4.8	6.7
1	4	1	21.7	22.3
1	3	8	1.6	-3.5
1	3	7	3.2	7.4
1	3	5	3.7	-3.2
1	3	4	6.0	6.7
1	3	3	5.1	-5.2
1	3	2	6.2	-5.4
1	3	1	21.8	-21.5
1	2	8	0.7	1.8
1	2	7	1.4	3.1
1	2	5	8.8	-13.6
1	2	4	5.4	7.1
1	2	3	7.2	-8.2
1	2	2	3.0	-3.5
1	2	1	53.9	-54.7
1	1	9	2.7	-2.0
1	1	8	1.2	2.5
1	1	7	6.3	-9.4
1	1	6	6.0	-6.5
1	1	5	2.5	-3.1
1	1	4	4.1	4.7
1	1	3	23.3	24.6
1	1	2	14.6	-14.2
1	1	1	17.6	17.8
1	0	8	1.0	-1.1
1	0	7	1.4	-1.9
1	0	6	6.1	5.0
1	0	5	3.4	2.0
1	0	4	27.9	-27.2
1	0	3	37.7	36.8
1	0	2	38.0	39.0
1	0	1	40.5	41.5
0	9	1	2.2	1.3
0	8	4	5.1	3.7
0	8	2	1.9	2.4
0	8	0	7.4	5.8
0	7	5	2.2	0.7
0	7	3	0.7	-0.2
0	6	6	3.2	1.4
0	6	4	6.0	-6.5
0	6	2	1.7	1.3
0	6	0	30.6	-31.8
0	5	7	1.9	2.6
0	5	5	2.0	-2.9
0	5	3	2.4	-2.2
0	5	1	11.1	12.1
0	4	8	1.7	-0.4
0	4	6	3.9	-6.5
0	4	4	16.1	18.0
0	4	2	2.7	3.9
0	4	0	58.6	60.6
0	3	9	3.3	-3.6
0	3	7	1.5	3.0
0	3	3	4.6	-5.9
0	3	1	13.0	12.3
0	2	8	1.2	-2.6
0	2	4	24.1	-26.7
0	2	2	17.2	-19.5
0	2	0	94.9	-93.7
0	1	7	1.4	3.3
0	1	3	1.5	2.5
0	1	1	29.7	31.5
0	0	8	4.6	-3.1
0	0	6	2.7	-2.4
0	0	4	40.5	38.5
0	0	2	22.9	-23.3

Table 1.7

(a) Fractional Coordinates for (IIa)

	x/a	y/b	z/c
O(1)	0.57612(28)	0.56779(43)	0.18706(31)
N(1)	0.73327(33)	0.79510(43)	0.35623(33)
N(2)	0.78068(33)	0.64719(44)	0.31187(32)
C(1)	0.84956(52)	0.87933(73)	0.44653(54)
C(2)	0.66483(54)	0.91490(64)	0.25102(48)
C(3)	0.65195(51)	0.74764(65)	0.42487(46)
C(4)	0.69233(41)	0.55200(52)	0.23021(37)
C(5)	0.74644(39)	0.40627(50)	0.18261(37)
C(6)	0.87096(41)	0.35595(56)	0.24328(39)
C(7)	0.91848(43)	0.23305(57)	0.19039(43)
C(8)	0.84249(47)	0.15877(57)	0.07625(43)
C(9)	0.71855(45)	0.20743(57)	0.01660(40)
C(10)	0.66940(43)	0.32943(54)	0.06963(40)

Table 1.7 (contd.)

(b) H-atom Fractional Coordinates and Isotropic Thermal Parameters (Å^2) for (IIa)

	x/a	y/b	z/c	U_{iso}
H(11)	0.8255(43)	0.9797(64)	0.4847(43)	0.065(16)
H(12)	0.8960(51)	0.9145(74)	0.3925(51)	0.097(20)
H(13)	0.8779(40)	0.7870(56)	0.5186(40)	0.050(14)
H(21)	0.5922(48)	0.8530(70)	0.1896(48)	0.083(18)
H(22)	0.6395(44)	1.0099(65)	0.2857(45)	0.068(16)
H(23)	0.7314(48)	0.9535(70)	0.2145(48)	0.089(19)
H(31)	0.5748(46)	0.6847(67)	0.3574(46)	0.076(17)
H(32)	0.6313(35)	0.8616(50)	0.4586(35)	0.071(12)
H(33)	0.7121(45)	0.6691(66)	0.4939(45)	0.076(17)
H(6)	0.9204(35)	0.4092(50)	0.3271(35)	0.032(12)
H(7)	1.0121(46)	0.1981(62)	0.2363(46)	0.064(16)
H(8)	0.8714(41)	0.0694(59)	0.0321(41)	0.055(14)
H(9)	0.6635(38)	0.1495(54)	-0.0613(37)	0.039(12)
H(10)	0.5836(45)	0.3667(68)	0.0273(47)	0.077(18)

Table 1.7 (contd.)

(c) Anisotropic Temperature Factors (Å^2) for (IIa)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O(1)	0.0566	0.0805	0.0841	-0.0493	0.0419	-0.0027
N(1)	0.0653	0.0503	0.0600	-0.0169	0.0466	0.0032
N(2)	0.0641	0.0510	0.0610	-0.0223	0.0487	0.0072
C(1)	0.0858	0.0846	0.1030	-0.0930	0.0599	-0.0273
C(2)	0.1179	0.0600	0.0794	0.0228	0.0916	0.0479
C(3)	0.1072	0.0716	0.0730	-0.0047	0.1147	0.0069
C(4)	0.0721	0.0479	0.0476	0.0034	0.0454	-0.0070
C(5)	0.0649	0.0410	0.0511	0.0010	0.0546	0.0019
C(6)	0.0654	0.0559	0.0533	0.0002	0.0441	0.0087
C(7)	0.0688	0.0543	0.0699	-0.0018	0.0583	0.0051
C(8)	0.0890	0.0505	0.0673	-0.0072	0.0765	0.0024
C(9)	0.0846	0.0523	0.0551	-0.0071	0.0520	-0.0160
C(10)	0.0749	0.0496	0.0547	-0.0064	0.0534	-0.0088

Average estimated standard deviations (Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O	0.0019	0.0023	0.0022	0.0038	0.0033	0.0035
N	0.0024	0.0021	0.0022	0.0036	0.0037	0.0038
C	0.0034	0.0028	0.0029	0.0048	0.0052	0.0052

Table 1.7 (contd.)

(d) Fractional Coordinates and H-atom Isotropic Thermal Parameters (Å^2) for (III)

	x/a	y/b	z/c	U_{iso}
O'(1)	0.49169(45)	0.25000	0.50415(89)	-
O'(2)	0.37461(53)	0.25000	0.26996(78)	-
N'(1)	0.33316(43)	0.25000	0.75728(78)	-
N'(2)	0.30833(43)	0.25000	0.55464(74)	-
N'(3)	0.39474(53)	0.25000	0.44281(77)	-
C'(1)	0.22237(62)	0.25000	0.84537(119)	-
C'(2)	0.39067(50)	0.06268(97)	0.81910(82)	-
H'(11)	0.2353(94)	0.2500	0.9976(159)	0.058(30)
H'(12)	0.1785(47)	0.1328(89)	0.7959(85)	0.033(18)
H'(21)	0.4598(40)	0.0594(76)	0.7610(73)	0.011(13)
H'(22)	0.4001(47)	0.0481(88)	0.9732(81)	0.025(16)
H'(23)	0.3316(59)	-0.0573(110)	0.7748(107)	0.060(25)

Table 1.7 (contd.)

(e) Anisotropic Temperature Factors ($\overset{o}{A}^2$) for (III)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O'(1)	0.0336	0.0642	0.0540	0.0000	0.0190	0.0000
O'(2)	0.0647	0.0634	0.0352	0.0000	0.0036	0.0000
N'(1)	0.0280	0.0351	0.0289	0.0000	0.0134	0.0000
N'(2)	0.0291	0.0392	0.0275	0.0000	-0.0091	0.0000
N'(3)	0.0491	0.0350	0.0260	0.0000	0.0143	0.0000
C'(1)	0.0358	0.0469	0.0457	0.0000	0.0334	0.0000
C'(2)	0.0512	0.0520	0.0455	0.0303	0.0041	0.0384

Average estimated standard deviations ($\overset{o}{A}^2$)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O	0.0031	0.0037	0.0030	-	0.0050	-
N	0.0028	0.0029	0.0025	-	0.0044	-
C	0.0032	0.0036	0.0034	0.0053	0.0054	0.0056

Table 1.8

Interatomic Distances (Å) and Angles (°)
with estimated standard deviations in parentheses

(a) Bonded Distances (IIa)

O(1)-C(4)	1.243(5)	C(5)-C(10)	1.383(6)
N(1)-N(2)	1.471(5)	C(6)-C(7)	1.375(6)
N(1)-C(1)	1.489(7)	C(7)-C(8)	1.380(7)
N(1)-C(2)	1.488(6)	C(8)-C(9)	1.377(7)
N(1)-C(3)	1.500(6)	C(9)-C(10)	1.382(6)
N(2)-C(4)	1.313(6)	average C-H(Ph)	0.99(5)
C(4)-C(5)	1.518(6)	average C-H(Me)	1.02(5)
C(5)-C(6)	1.388(6)		

(b) Interbond Angles (IIa)

N(2)-N(1)-C(1)	103.7(3)	N(2)-C(4)-C(5)	112.0(4)
N(2)-N(1)-C(2)	112.5(3)	C(4)-C(5)-C(6)	122.6(4)
N(2)-N(1)-C(3)	112.6(3)	C(4)-C(5)-C(10)	117.8(4)
C(1)-N(1)-C(2)	108.4(4)	C(6)-C(5)-C(10)	119.5(4)
C(1)-N(1)-C(3)	109.6(4)	C(5)-C(6)-C(7)	120.4(4)
C(2)-N(1)-C(3)	109.9(4)	C(6)-C(7)-C(8)	120.2(4)
N(1)-N(2)-C(4)	114.2(3)	C(7)-C(8)-C(9)	119.5(4)
O(1)-C(4)-N(2)	129.6(4)	C(8)-C(9)-C(10)	120.9(4)
O(1)-C(4)-C(5)	118.3(4)	C(5)-C(10)-C(9)	119.5(4)

Table 1.8 (contd.)

(c) Intramolecular Non-bonded Distances (IIa)

O(1)...N(1)	2.74	N(2)...C(10)	3.58
O(1)...C(2)	2.93	C(1)...C(4)	3.54
O(1)...C(3)	2.88	C(2)...C(4)	2.92
O(1)...C(6)	3.63	C(3)...C(4)	2.90
O(1)...C(10)	2.78	C(4)...C(7)	3.80
O(1)...H(21)	2.27	C(4)...C(9)	3.76
O(1)...H(31)	2.17	C(5)...C(8)	2.77
N(1)...C(5)	3.71	C(6)...C(9)	2.75
N(2)...C(6)	2.78	C(7)...C(10)	2.77

(d) Intermolecular Distances (IIa)

O(1)...C(2^{I})	3.38	C(1)...C(10^{V})	3.75
O(1)...C(3^{I})	3.52	C(2)...C(9^{VI})	3.78
O(1)...C(3^{II})	3.75	C(3)...C(4^{V})	3.69
O(1)...C(9^{III})	3.73	C(3)...C(9^{IV})	3.75
O(1)...C(10^{III})	3.27	C(3)...C(10^{V})	3.71
N(2)...C(8^{IV})	3.72	C(4)...C(9^{IV})	3.78
C(1)...C(5^{V})	3.77		

Roman numerals as superscripts refer to the equivalent positions which should be applied to the coordinates of the second atom :

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

Table 1.8 (contd.)

(e) Bonded Distances (III)

O'(1)-N'(3)	1.265(8)	N'(1)-C'(2)	1.507(7)
O'(2)-N'(3)	1.252(8)	N'(2)-N'(3)	1.323(8)
N'(1)-N'(2)	1.470(8)	average C-H(Me)	1.05(6)
N'(1)-C'(1)	1.490(9)		

(f) Interbond Angles (III)

N'(2)-N'(1)-C'(1)	102.8(5)	N'(1)-N'(2)-N'(3)	115.0(5)
N'(2)-N'(1)-C'(2)	112.4(3)	O'(1)-N'(3)-O'(2)	121.5(6)
C'(1)-N'(1)-C'(2)	107.6(4)	O'(1)-N'(3)-N'(2)	123.0(6)
C'(2)-N'(1)-C'(2')	113.2(4)	O'(2)-N'(3)-N'(2)	115.5(6)

(g) Intramolecular Non-bonded Distances (III)

O'(1)...N'(1)	2.65	O'(2)...N'(1)	3.50
O'(1)...C'(2)	2.85	N'(3)...C'(1)	3.55
O'(1)...H'(21)	2.26	N'(3)...C'(2)	2.95

Table 1.8 (contd.)

(h) Intermolecular Distances (III)

$O'(1)\ldots O'(1^{I})$	3.37	$O'(2)\ldots C'(2^{III})$	3.44
$O'(1)\ldots N'(3^{I})$	3.65	$O'(2)\ldots C'(2^{I})$	3.62
$O'(1)\ldots C'(1^{II})$	3.02	$O'(2)\ldots C'(2^{IV})$	3.88
$O'(1)\ldots C'(2^{I})$	3.43	$N'(2)\ldots C'(1^{IV})$	3.69
$O'(2)\ldots N'(1^{III})$	3.67	$N'(2)\ldots C'(2^{IV})$	3.63
$O'(2)\ldots C'(1^{III})$	3.54	$N'(3)\ldots C'(1^{IV})$	3.72
$O'(2)\ldots C'(1^{IV})$	3.60	$N'(3)\ldots C'(2^{I})$	3.84

Roman numerals as superscripts refer to the equivalent positions which should be applied to the coordinates of the second atom :

I	$1-x$,	$1/2+y$,	$1-z$	III	x,	y,	$-1+z$
II	$1/2+x$,	$1/2-y$,	$3/2-z$	IV	$1/2-x$,	$-y$,	$-1/2+z$

Table 1.9

Least-squares Planes for (IIa)
given in the form $\ell X' + mY' + nZ' = d$,
where X', Y' and Z' are coordinates in Å

(a) Plane equations

Plane (1) : $0.2586\,X' + 0.7014\,Y' - 0.6642\,Z' = 5.2347$
Plane (2) : $0.0145\,X' + 0.5667\,Y' - 0.8238\,Z' = 3.0936$
Plane (3) : $0.0345\,X' + 0.5386\,Y' - 0.8418\,Z' = 3.1207$

(b) Deviation of atoms (Å) from planes (starred atoms not used to define plane)

Plane (1) : O(1)* -0.124, N(2)* 0.567, C(4)* 0.141,
C(5) 0.010, C(6) -0.002, C(7) -0.005, C(8) 0.005,
C(9) 0.003, C(10) -0.010

Plane (2) : O(1) 0.003, N(2) 0.003, C(4) -0.009,
C(5) 0.002

Plane (3) : N(1) 0.000, N(2) 0.000, C(4) 0.000

(c) Dihedral angles between planes (°)

(1) - (2) 18.5, (2) - (3) 2.2

Table 1.10

Examples of A - H ... B Interactions

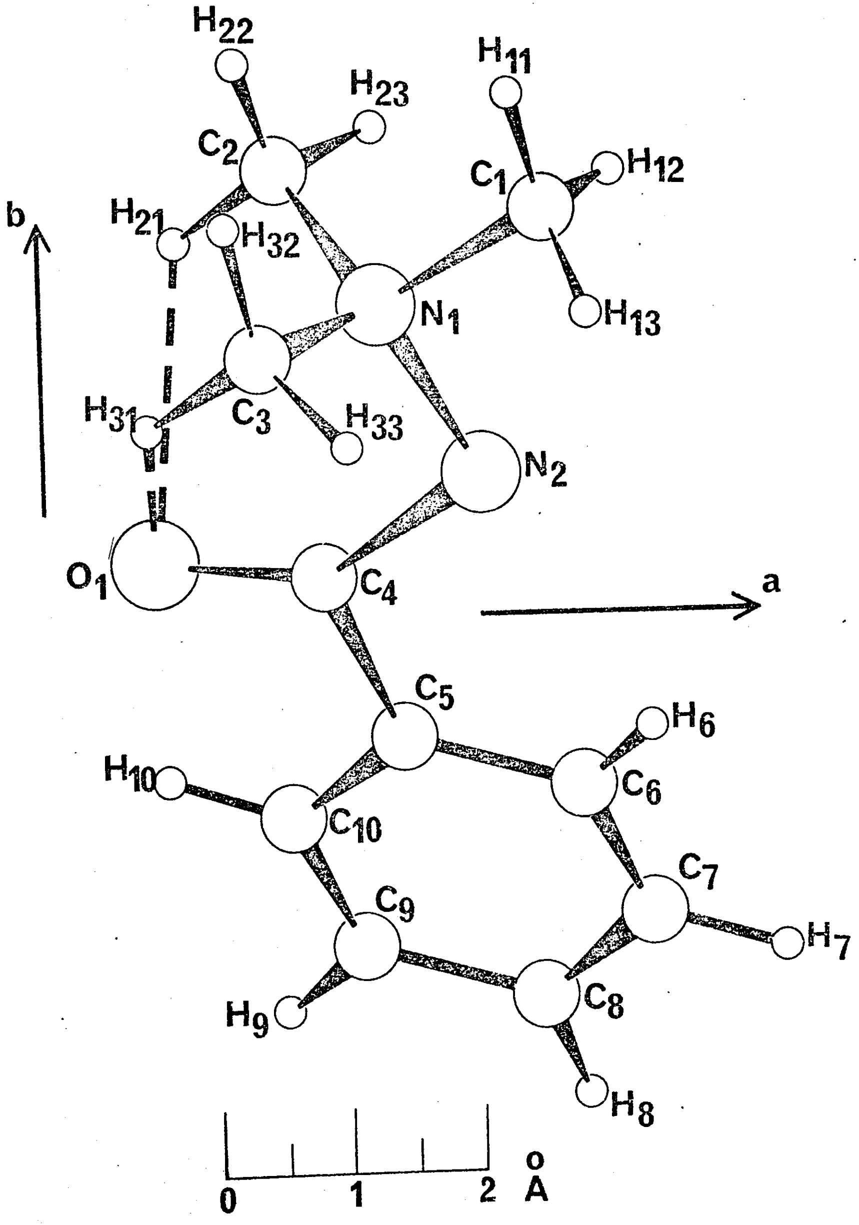
Compound	Ref.	A	B	A...B	H...B	∠ AHB
(IIa)	61,62	C	O	2.90*	2.22*	123°*
(III)	61,62	C	O	2.85*	2.26*	120°*
Nitroguanidine	78	N	O	2.57	-	-
dl-isoproterenol sulphate dihydrate	79	N	O	2.65	2.04	113°
α-1-(p-bromophenyl)-phenylmethylene-3-oxo-1,2-diazetidinium inner salt	70	C	N	2.91	2.15	128°
Aflatoxin B_1	80	C	O	3.19	2.40	144°
1-(4-chlorobenzyl)-1-nitroso-2-(4,5-dihydro-2-imidazolyl)hydrazine monohydrate	81	C	O	3.23	2.27	164°

* :- mean value .

Figure 1.1

Atomic numbering scheme

(IIa)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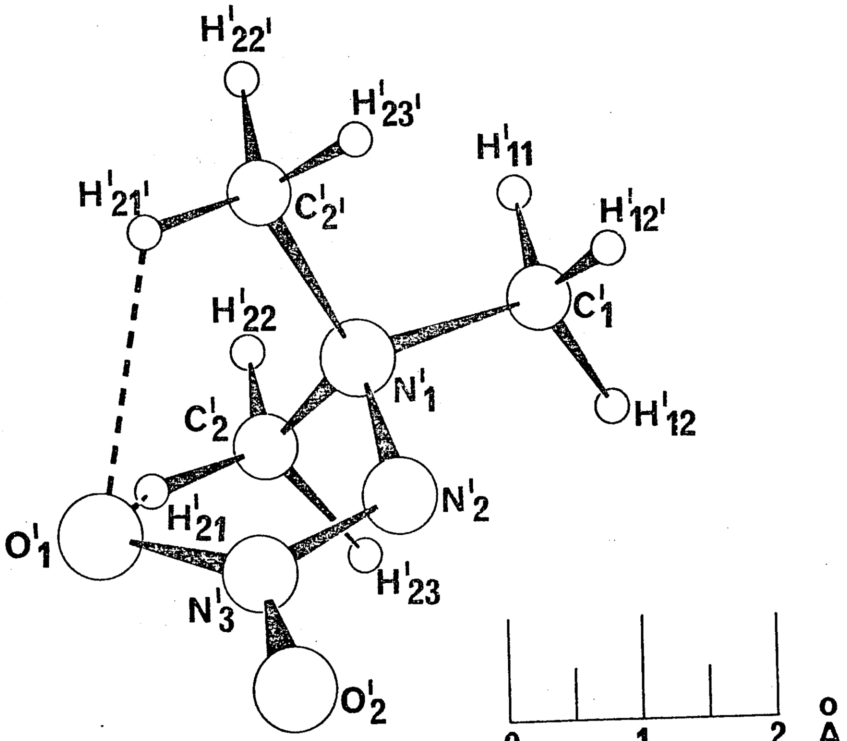
H_{23}
H_{11}
C_2
C_1
H_{12}
b
H_{21}
H_{32}
N_1
H_{13}
H_{31}
C_3
H_{33}
N_2
O_1
C_4
a
C_5
H_6
H_{10}
C_{10}
C_6
C_7
C_9
H_7
H_9
C_8
H_8
0
1
2
Å

Figure 1.2

Atomic numbering scheme

(III)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H'23'
H'11
H'21'
C'2'
H'12'
C'1
H'22
N'1
C'2
H'12
N'2
O'1
H'21
H'23
N'3
O'2
0
1
2
Å

Figure 1.3

Molecular packing arrangement
viewed along the b-axis

(IIa)

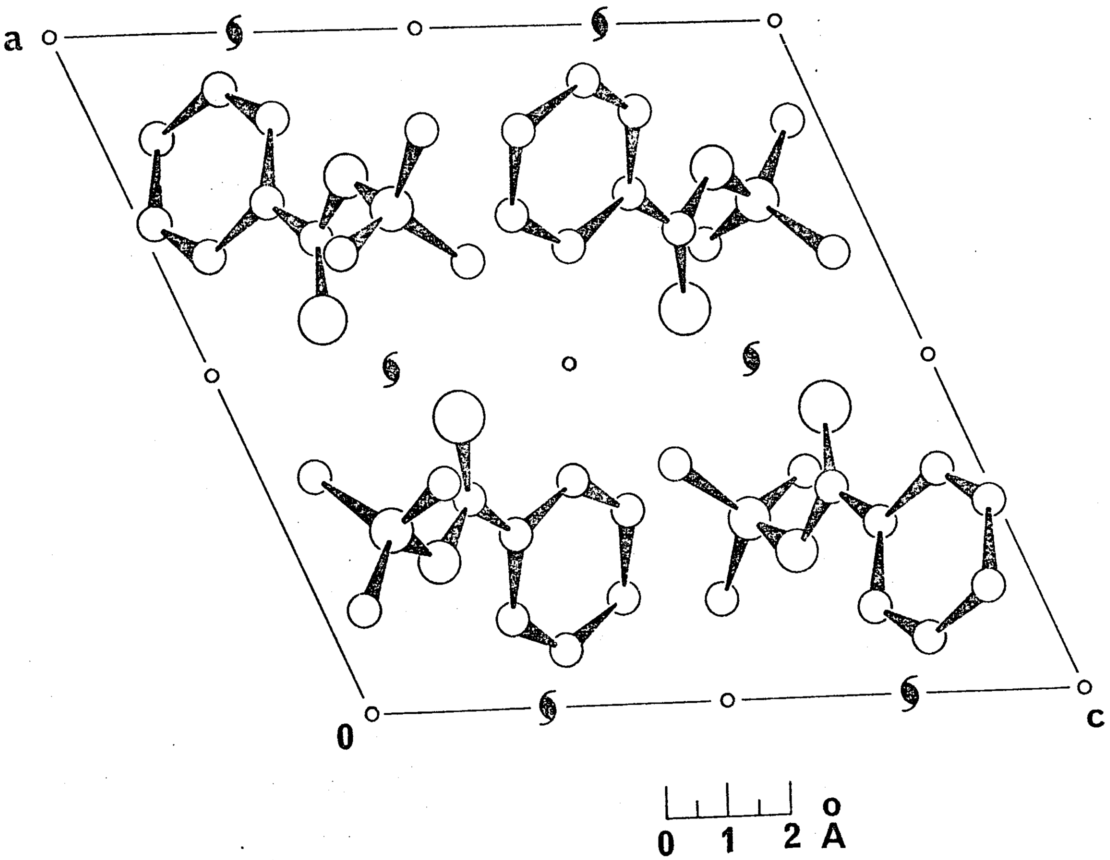
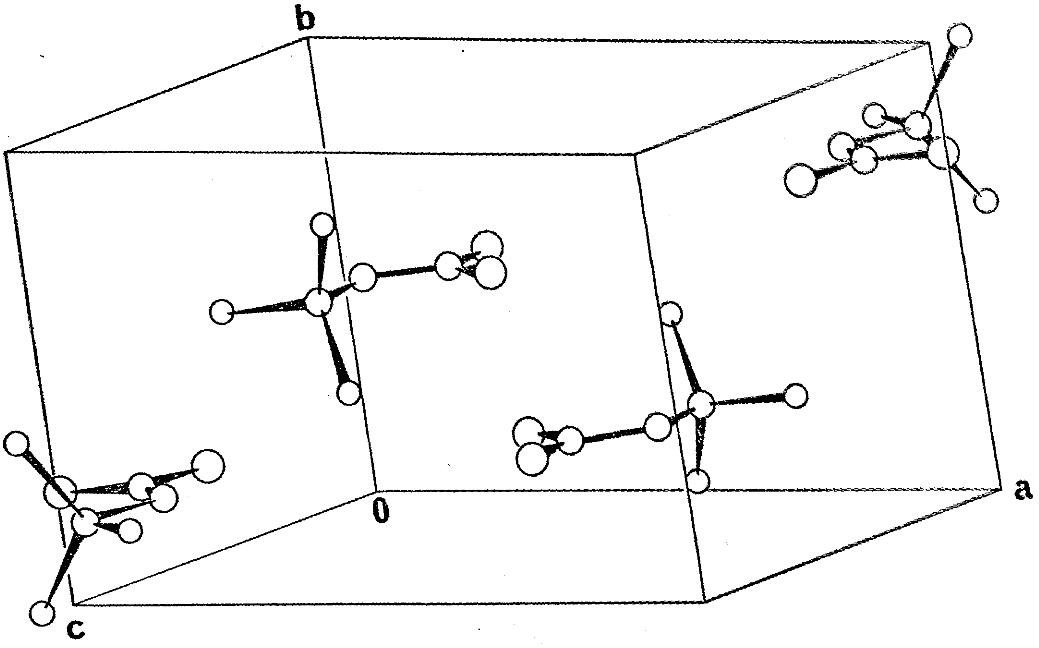

a
0
c
0 1 2 Å

Figure 1.4

3-dimensional view of the
contents of one unit cell

(III)


b
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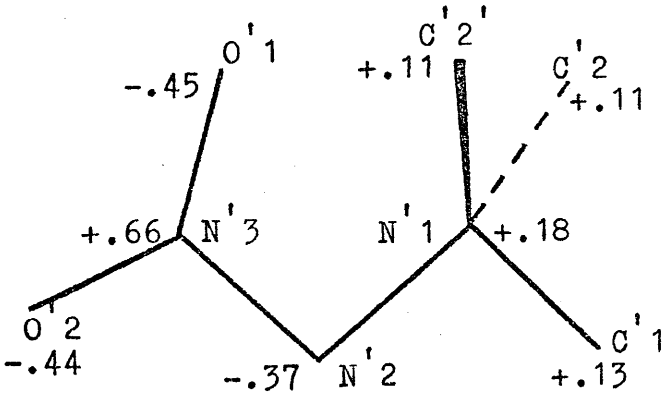
a
c

1.3 DISCUSSION

The structure analyses of the compounds (IIa) and (III) have revealed some interesting geometrical features of the class of ylides (I; Y = N—) which they represent. Moreover, the results obtained allow comparisons to be made with the bonding and charge distributions found in the series of first-row ylides (I; Y = O, N—, C<).

Examination of the relevant bond lengths in (IIa) and (III) shows that the N(1)-N(2) [1.471(5) Å] and N'(1)-N'(2) [1.470(8) Å] bonds are identical within experimental error, and are similar to the N-N single-bond value of 1.45 Å found in hydrazine.[66] Since it has been demonstrated that opposite formal charges across a bond have a shortening effect,[67] the absence of any such shortening in the N(1)-N(2) bond of either molecule suggests minor contributions from the resonance forms (IVa) and (Va), in which negative charges are placed on N(2) and N'(2) respectively, and is therefore consistent with significant delocalisation of the negative charge into the respective electronegative moieties. Furthermore the lengths of the N(2)-C(4) [1.313(6) Å] and N'(2)-N'(3) [1.323(8) Å] bonds indicate important contributions from the canonical forms (IVb) and (Vb), since these values are not much longer than the range 1.27 - 1.29 Å [68] and 1.25 Å [66] quoted for C=N and N=N bonds respectively, but are appreciably shorter than the corresponding values of 1.47 Å [69] and 1.45 Å [66] given for single bonds. In accord with this suggestion of significant charge delocalisation onto the carbonyl and nitro oxygen atoms respectively, both the carbonyl bond of (IIa) [1.243(5) Å] and the nitro bonds of (III) [mean 1.259(6) Å] are slightly longer than would be expected for similar bonds in environments where no charge delocalisation can take place, e.g. lengths of 1.22 Å are found for the N-O bonds of nitromethane.[66] Moreover, it has been previously observed that, where significant delocalisation into such groups is possible, only slight lengthening of the bonds to oxygen results.[70,71]

In order to further investigate the possible charge delocalisation in (IIa) and (III), theoretical INDO calculations [72] were carried out [73] on the determined coordinates for molecule (III), the mirror plane through atoms O'(1), O'(2), N'(3), N'(2), N'(1) and C'(1) facilitating the separation of σ and π (perpendicular to the molecular plane) contributions to the atomic charge densities which are shown below :-



π - populations

Atom	Formal	Found
O'1	1.00	1.670
O'2	1.00	1.632
N'2	2.00	1.763
N'3	2.00	0.924

Examination of the π-populations on O'(1), O'(2), N'(2) and N'(3) reveals delocalisation of the π-electrons onto O'(1) and O'(2) primarily from N'(3) but also significantly from N'(2) which bears the formal negative charge in (Va). Furthermore, the overall charge distribution shows a transference of charge from N'(2) and N'(3) to O'(1) and O'(2) consistent with the postulated delocalisation into the nitro stabilising group and also consistent with a significant presence of the resonance structure (Vb).

However, a recent analysis of the similar first-row ylide (VI),[74] in which the electronegative atom Y is carbon, reveals that in this case the carbonyl bond is considerably lengthened (1.27 Å), while the vicinal C-C bond (1.36 Å) approaches a double-bond value. By comparing the dimensions of (VI) with those of (IIa) and (III), it is possible to contrast the bonding properties of the class of first-row ylides (I; Y = O, N—, C<). Since the amine oxides (I; Y = O) are stable compounds, it may be inferred that the negative charge may reside on the oxygen atom without the need for further stabilisation. However, it becomes clear that, on moving to nitrogen ylides (I; Y = N—) and then to carbon ylides (I; Y = C<), extra stabilisation is required in the form of increasing charge delocalisation into the attached electronegative groupings. This order of increasing charge delocalisation required by each system is that which would be expected from simple electronegativity considerations.

The solid-state conformations of (IIa) and (III) are virtually identical, and are characterised by synplanar relationships within the N(1)-N(2)-C(4)-O(1) and N'(1)-N'(2)-N'(3)-O'(1) systems respectively, the torsion angle about the N(2)-C(4) bond being approximately 2°, and that about the N'(2)-N'(3) bond being restricted to 0°. Such synplanar relationships of 'onium and vicinal groups have been observed using n.m.r. techniques for certain other ylides.[75] In the present structures, these *cis*-relationships may be regarded as arising, at least in part, from electrostatic interactions between the quaternary nitrogen atoms and the appropriate oxygen atoms; in (IIa) the N(1)...O(1) separation is 2.74 Å, while in (III) the corresponding N'(1)...O'(1) non-bonded distance is 2.65 Å, both values being considerably shorter than the sum of the van der Waals' radii (~2.90 Å). Moreover, since no evidence of conformational mobility about the N(2)-C(4) bond in the *N*-ammonio-amidates (II a-d) has been found by variable temperature n.m.r. techniques,[62,76] it is possible that in cases (II a-d) the *N*-ammonio-amidates exist solely in a *cis*-conformation as revealed by the present X-ray studies.

A further feature of the conformations of both molecules is that the N(1) and N'(1) substituents and their respective methyl hydrogen atoms are all fully staggered, presumably to minimise torsional interactions. A consequence of this and of the *cis*-conformations is to place two methyl hydrogen atoms of each molecule [H(21) and H(31) in (IIa); H'(21) and H'(21') in (III)] in close proximity to the carbonyl oxygen of (IIa) and to the nitro oxygen atom O'(1) of (III), the H...O separations being 2.17(5) Å and 2.27(5) Å in (IIa), and identically 2.26(5) Å in (III). In molecule (IIa) the mean C-H...O angle is 123°, while the corresponding values in (III) are both 120°. Since it has been stated that significant interaction may exist between hydrogen and oxygen atoms when the H...O separation does not exceed 2.4Å,[77] a possible interpretation of the conformations and non-bonded separations of both (IIa) and (III) is that there exists a degree of hydrogen-oxygen interaction, although this can at best be very weak. While evidence for this C-H...O interaction has not been forthcoming from variable temperature n.m.r. techniques,[76] several examples of intramolecular hydrogen bonding have been reported in similar systems and are listed in Table 1.10.[70,78,79] Also included in Table 1.10 are two examples of C-H...O intermolecular hydrogen bonding in which the relevant parameters can reasonably be expected to define upper limits for such C-H...O interaction.[80,81]

In recent studies of biologically active choline derivatives, it has been postulated that intramolecular C-H...O interactions may play a significant role in the stabilisation of the molecular conformations observed in these systems by the formation of *quasi* six-membered rings.[82-84] Moreover, it has been suggested that there may be an important correlation between the resulting conformations of such molecules and their biological activity in cholinergic systems.[85,86] Since C-H...O interactions of a comparable nature are observed in (IIa) and (III), it is reasonable to suggest that the *quasi* hetero-bicyclo 2.2.2 octyl systems formed in both molecules [involving O(1), C(4), N(2), N(1), C(2), C(3), H(21) and H(31) in (IIa), and the corresponding atoms in (III)] provide analogies to the hydrogen-bonded conformations postulated, usually without knowledge of H-atom positions, for the biologically active systems.

Consideration of previously undiscussed regions of both molecules shows that the dimensions of the essentially tetrahedral trimethylammonium groups in both (IIa) [mean C-N = 1.492(6) Å; mean C-H = 1.02(5) Å] and (III) [mean C-N = 1.501(8) Å; mean C-H = 1.05(6) Å] are consistent with accepted values for similar bond types.[66] Moreover, the planar aromatic ring in (IIa) has essentially normal dimensions [mean C-C 1.381(6) Å; mean C-H 0.99(5) Å] [66] which suggests a negligible involvement between the respective π-systems of the aromatic ring and the enolate moiety. The possibility of any such interaction is further precluded both by the length of the connecting C(4)-C(5) bond [1.518(6) Å] which is comparable to that expected for C(sp^2) - C(sp^2) bonds,[66] and also by the observed rotation of the ring plane with respect to the plane containing the atoms O(1), N(2), C(4) and C(5), which represents a twisting of the two π-systems about the C(4)-C(5) bond by approximately 18°.

An interesting feature of (IIa) is the value of the valency angle O(1)-C(4)-N(2) [129.6(4)°], and it is likely that this reflects a degree of mutual repulsion between the O(1)-C(4) and C(4)-N(2) bonds, both of which have considerable double-bond character. The possiblity of an extra repulsion effect by the two methyl groups involved in the weak C-H...O interactions may be partially discounted since angles of comparable magnitude have been recently observed for the amide groupings in a carbamoyl chloride [87] and a similar sulphur(IV) ylide.[52]

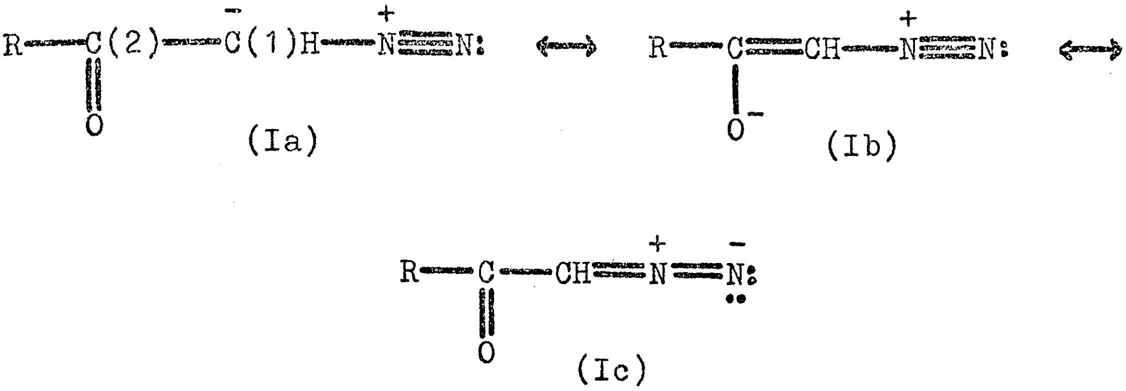
Apart from the C-H...O interactions, the only other short intramolecular contacts of interest occur in molecule (IIa), namely O(1)...C(7) and N(2)...C(3), both of which are 2.78 Å, and it appears probable that the twisting observed in this region of the molecule results from a reduction of such steric interactions. Since there are no short intermolecular contacts of significance in either structure, it may be assumed that the crystal packing has been determined in both cases by van der Waals' forces.

2. THE CRYSTAL AND MOLECULAR STRUCTURE OF (+)-3-DIAZOCAMPHOR.

2.1 INTRODUCTION

Diazoketones (I a-c) and diazoalkanes (II a-e) may both be regarded as fist-row ylides $(\overset{+}{X} - \overset{-}{Y})$ [34] where the 'onium residue is a diazonium function $(\overset{+}{X} = -\overset{+}{N}\equiv N)$ and the anion Y is a carbanion. The enhanced stability of the former compounds over the latter is considered to arise from contributions (Ib) in which the negative charge is delocalised into the carbonyl grouping, [88,89] and, moreover, evidence for the stabilisation of other first-row ylides *via* similar delocalisation into enolate groupings has already been found [61,62,74] (see PART II, Section 1.3). However, in contrast to the *cis* - conformations observed for the latter compounds, it has been shown, from variable temperature n.m.r. studies of diazoketones, diazoaldehydes and diazoesters, that both the *cis* and *trans* forms (with respect to the C(1)-C(2) bond in (I)) may exist in solution.[90]

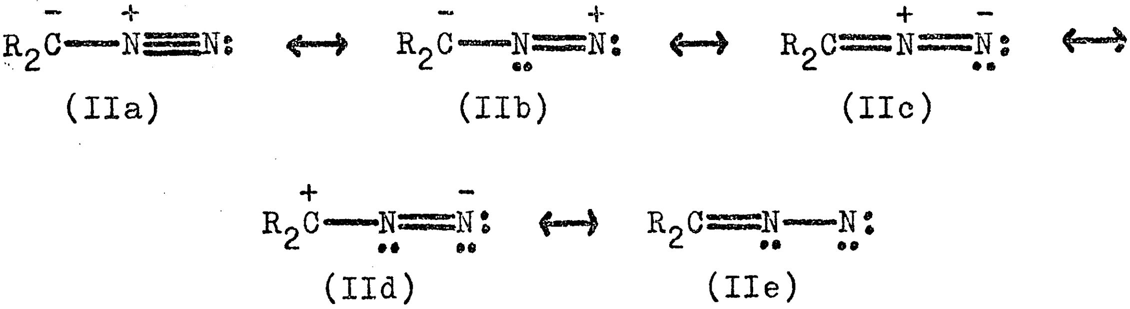
As part of a study of ylides of first-row elements,[61,62] the crystal structure of (+)-3-diazocamphor (III), an all-*cis* diazoketone which contains a non-aromatic carbocyclic residue, has been determined.[91] Of particular interest in this investigation has been the extent to which the resonance form (Ib) is involved in the stabilisation of diazoketones, since, in this particular form of ylide, there are two competing stabilising systems, namely the diazonium and enolate moieties, both of which could plausibly delocalise the negative charge formally residing on C(1) in (Ia).



$$R-\underset{\underset{O}{\|}}{C}(2)-\overset{-}{C}(1)H-\overset{+}{N}\equiv N: \longleftrightarrow R-\underset{\underset{O^-}{|}}{C}=CH-\overset{+}{N}\equiv N: \longleftrightarrow$$

$$R-\underset{\underset{O}{\|}}{C}-CH=\overset{+}{N}=\underset{\cdot\cdot}{\overset{-}{N}}:$$

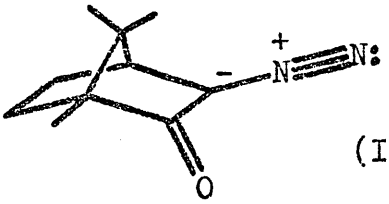
(Ia) (Ib) (Ic)



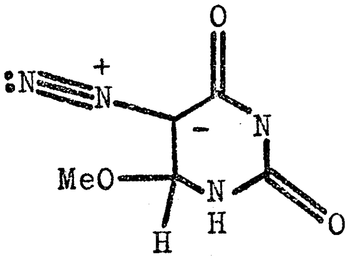
$$R_2\overset{-}{C}-\overset{+}{N}\equiv N: \longleftrightarrow R_2\overset{-}{C}-\underset{\cdot\cdot}{N}\equiv\overset{+}{N}: \longleftrightarrow R_2C=\overset{+}{N}=\underset{\cdot\cdot}{\overset{-}{N}}: \longleftrightarrow$$

$$R_2\overset{+}{C}-\underset{\cdot\cdot}{N}=\underset{\cdot\cdot}{\overset{-}{N}}: \longleftrightarrow R_2C=\underset{\cdot\cdot}{N}-\underset{\cdot\cdot}{N}:$$

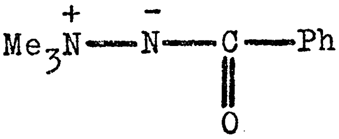
(IIa) (IIb) (IIc) (IId) (IIe)



(III)

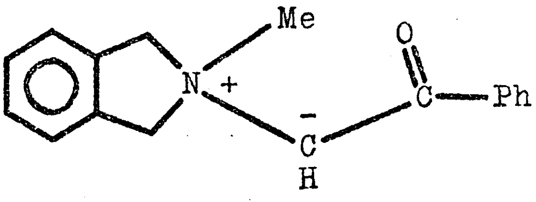


(IV)



$$Me_3\overset{+}{N}-\overset{-}{N}-\underset{\underset{O}{\|}}{C}-Ph$$

(V)



(VI)

$$Me_3\overset{+}{N}-\overset{-}{N}-NO_2$$

(X)

2.2 EXPERIMENTAL

Crystal Data

(III); (+)-3-diazocamphor, $C_{10}H_{14}N_2O$, M = 178.2.

Monoclinic, a = 7.119(2), b = 7.466(2), c = 9.279(2) Å,

β = 91.75(2)°, U = 492.9 Å^3.

D_m = 1.18 g.cm.$^{-3}$ (by flotation in aqueous KI), Z = 2,

D_c = 1.20 g.cm.$^{-3}$, F(000) = 192.

Space group $P2_1$ (C_2^2 , No.4).

Linear absorption coefficient for X-rays (λ = 0.7107 Å),

μ = 0.87 cm.$^{-1}$.

Crystallographic Measurements

The initial determination of the unit cell dimensions was made from oscillation and Weissenberg photographs taken with Cu-K_α (λ = 1.5418 Å) radiation, and from precession photographs taken with Mo-K_α (λ = 0.7107 Å) radiation. Refined values for these parameters were subsequently obtained, by least-squares techniques, from the Busing and Levy orientation-matrix program [63] prior to the diffractometer data collection. The choice of space group $P2_1$ was indicated both by systematic absences in the 0k0 spectra and also by the known optical activity of molecule (III).

Table 2.1 contains details of the crystal morphology and data collection for compound (III). Intensity measurements were made on a Hilger and Watts Y290 computer-controlled diffractometer, and during the data collection, it was necessary to seal the crystal in a quartz capillary tube in order to avoid extensive radiation damage. Structure amplitudes on an overall non-absolute scale were obtained by applying the appropriate Lorentz and polarisation corrections, but absorption effects were considered small and were ignored.

Structure Determination

The data contained in Table 2.2 suggest that compound (III) is isomorphous with certain other camphor derivatives, the structures of which have been previously determined.[92,93] It was therefore assumed, as an approximation, that the crystalline arrangement and molecular geometry of the $C_{10}O$ fragment of (+)-3-bromocamphor [93] would represent a reasonable model for the structure of molecule (III). Consequently, the quoted values for the coordinates of the carbon and oxygen atoms were used in a preliminary structure-factor and electron-density calculation which revealed the two nitrogen atoms of (III). Two further rounds of structure-factor and electron-density calculations yielded an improved set of coordinates for subsequent refinement by least-squares methods. After each of the previous calculations, in which an overall isotropic thermal parameter $U_{iso} = 0.05$ $\overset{o}{A}^2$ was assumed, the data were placed on an approximate absolute scale by equating $k\sum|F_o|$ and $\sum|F_c|$.

Structure Refinement

The refinement of positional, vibrational and overall-scale parameters by full-matrix least-squares calculations converged after 13 cycles when R and R' ($= \sum w\Delta^2/\sum w|F_o|^2$) were 0.087 and 0.012 respectively for the statistically observed data ($I > 3\sigma_I$). Full details of the refinement are given in Table 2.3. Throughout the refinement, the y-coordinate of atom O(1) was not allowed to vary in order to fix the origin on the 2-fold screw axis of space group $P2_1$.

A difference synthesis, calculated at the end of the isotropic refinement, revealed the positions of the five non-methyl hydrogen atoms which were refined in later cycles, an overall isotropic vibrational parameter $U_{iso} = 0.06\ \mathring{A}^2$ being assumed throughout. In the initial stages of the refinement, unit weights were assigned to all reflexions, but in later cycles it was found necessary, from an $|F_o|$ analysis of $w\Delta^2$, to apply a weighting scheme of the following form to the data :-

$$\sqrt{w} = 1 \text{ for } |F_o| \leq p; \quad \sqrt{w} = p/|F_o| \text{ for } |F_o| > p \text{ ,}$$

since it was essential to downweight observations of high $|F_o|$. The optimum value for the parameter p was 10.0.

The refinement was judged to be complete when the parameter shifts calculated by a least-squares cycle were insignificant compared to the corresponding estimated standard deviations. The subsequent calculation of an electron-density distribution and a difference synthesis revealed no gross errors in the structure, but, although the difference synthesis failed to resolve the methyl hydrogen atoms, it did however contain peaks of residual electron density ($0.4 \rightarrow 0.6$ e) roughly centred on the non-hydrogen atom positions. It is possible to interpret this as either a failure of the present model to account for a highly anisotropic motion of the molecule (see Table 2.5), or an effect of radiation damage to the crystal. Similar evidence of radiation damage has been observed for (+)-3-bromocamphor,[93] and for the diazo-compound, 2-bromodiazofluorene.[94] Observed and final calculated structure factors are listed in Table 2.4. In all structure-factor calculations, the atomic scattering factors used were taken from 'International Tables for X-Ray Crystallography,' Vol.III.[65]

The final fractional coordinates and anisotropic thermal parameters are given in Table 2.5, the non-methyl hydrogen atoms being numbered according to the numbering of the attached atoms. In Table 2.5, the values of U_{ii} and $2U_{ij}$ refer to the anisotropic temperature factor expression given in PART I, Section 3. All bond lengths, valency angles, and pertinent intra- and inter-molecular non-bonded distances are listed in Table 2.6. The appropriate estimated standard deviations, σ, derived from the inverse of the least-squares normal-equation matrix are included in Tables 2.5 and 2.6. The average σ for C-O, C-N, C-C, C-H and N-N bonds are 0.008, 0.008, 0.011, 0.10 and 0.008 Å respectively, while for valency angles σ is 0.6°. These are probably best regarded as minimum values.

A rigid-body analysis of the molecular vibration was attempted, but the results did not differ to any level of significance from the uncorrected model. Details of least-squares planes calculated for various portions of the molecular framework are shown in Table 2.7.

The atomic numbering scheme, used in every table, and the molecular packing viewed along the *a*-axis, are shown in Figures 2.1 and 2.2 respectively.

Table 2.1

Details of Crystal Morphology and Data Collection

	Compound(III)
Crystal shape	Flat plate
Crystal size (mm.)	0.6 × 0.2 × 0.1
Rotation axis	b
Scan technique	2θ
Step size (°)	0.02
Number of steps	40
Step time (secs)	2
Total background count (secs)	40
Radiation filter	Zr
2θ range (°)	0 → 60
Independent reflexions	1252 (661 with $I > 3\sigma_I$*)

* σ_I , the standard deviation in the measured intensity, I, is derived from counting statistics

$$\text{i.e.} \quad \sigma_I = \sqrt{(P + B_1 + B_2)}$$

where P, B_1 and B_2 are the peak and two background counts respectively.

Table 2.2

Crystallographic data for various camphor derivatives

Ref	Compound	a	b	c	β	U	Space group
92	3-cyano-	7.13 Å	7.44	9.40	94.5°	496 $Å^3$	$P2_1$
"	3-chloro-	7.25	7.51	9.04	93.25	491	$P2_1$
"	3-bromo-	7.38	7.57	9.12	94.0	508	$P2_1$
93	(+)3-bromo-	7.36	7.59	9.12	94.1	508	$P2_1$
-	(+)3-diazo-	7.119	7.466	9.279	91.75	493	$P2_1$

Table 2.3

Course of Refinement

Cycles	Parameters refined	Final R	Final R'
1 - 4	x, y, z, U_{iso} for O, N, C, Overall scale factor, Full matrix, unit weights.	0.213	0.038
5 - 9	x, y, z, U_{ij} for O, N, C, Overall scale factor, Full matrix, weighting scheme adjusted, non-methyl H-atom contributions included but not refined.	0.142	0.025
10 - 13	x, y, z, U_{ij} for O, N, C, x, y, z, for non-methyl H-atoms, Overall scale factor, Full matrix, weighting scheme applied.	0.135	0.023
Structure - factor calculation on final parameters using only the statistically observed data ($I > 3\sigma_I$).		0.087	0.012

Table 2.4

Observed and final calculated
structure amplitudes

H	K	L	F OBS	F CALC
10	0	0	0.9	0.9
9	4	0	1.7	0.7
9	3	0	2.4	1.6
9	2	0	2.8	2.2
9	1	0	2.5	0.9
9	0	0	2.7	2.3
8	6	0	1.8	1.3
8	5	2	1.7	0.9
8	5	1	2.2	1.7
8	5	0	1.4	0.4
8	4	5	1.1	0.6
8	4	4	0.8	0.9
8	4	2	2.6	2.6
8	4	0	3.0	2.8
8	3	6	2.6	1.5
8	3	5	1.7	0.7
8	3	4	1.4	0.6
8	3	3	1.6	1.8
8	3	2	0.8	1.7
8	3	0	1.3	0.9
8	2	7	1.7	1.5
8	2	6	2.0	1.9
8	2	5	1.5	0.6
8	2	3	1.9	0.4
8	2	2	3.2	2.6
8	2	1	2.4	1.3
8	2	0	2.0	2.4
8	1	5	1.2	1.2
8	1	3	0.6	1.2
8	1	0	0.7	0.4
8	0	7	1.7	0.2
8	0	6	1.9	1.8
8	0	2	3.0	3.0
8	0	1	0.3	0.5
8	0	0	0.3	1.4
7	7	3	1.6	1.5
7	7	1	1.4	0.8
7	7	0	1.7	0.8
7	6	3	0.5	1.4
7	6	2	1.5	1.5
7	6	1	1.0	0.7
7	6	0	1.6	0.9
7	5	6	2.5	0.3
7	5	5	0.7	0.9
7	5	2	2.3	1.7
7	5	0	2.8	2.5
7	4	6	2.7	0.6
7	4	4	2.4	1.6
7	4	3	1.5	1.5
7	4	2	2.4	1.8
7	4	1	2.1	1.6
7	4	0	2.6	2.3
7	3	8	1.2	1.7
7	3	7	3.2	2.8
7	3	6	1.1	1.6
7	3	5	2.8	1.9
7	3	3	2.2	2.7
7	3	2	1.5	2.2
7	3	1	2.7	2.4
7	3	0	2.3	2.4
7	2	8	1.7	1.4
7	2	7	1.0	2.0
7	2	6	2.3	0.7
7	2	5	1.2	0.7
7	2	4	2.3	0.9
7	2	2	3.6	3.6
7	2	1	5.7	5.5
7	2	0	0.5	1.5
7	1	8	2.1	0.7
7	1	7	3.5	2.7
7	1	6	2.0	2.7
7	1	5	1.8	1.1
7	1	2	2.4	2.3
7	1	1	3.5	3.8
7	1	0	2.2	1.9
7	0	9	2.2	0.4
7	0	7	2.6	2.8
7	0	5	1.0	0.9
7	0	4	1.7	2.2
7	0	2	3.4	2.9
7	0	1	6.4	5.7
7	0	0	1.5	1.2
6	9	2	1.6	1.1
6	8	1	1.7	1.3
6	8	0	1.2	0.8
6	7	5	0.7	1.3
6	7	4	2.1	2.0
6	7	3	1.3	1.2
6	7	2	2.4	1.2
6	7	1	1.5	0.8
6	7	0	0.9	1.0
6	6	7	2.4	0.3
6	6	6	0.5	0.5
6	6	5	2.7	1.1
6	6	4	1.9	1.5
6	6	3	0.4	1.0
6	6	1	2.1	2.3
6	6	0	1.8	2.5
6	5	8	0.7	0.1
6	5	7	1.4	0.4
6	5	5	0.9	1.4
6	5	4	2.0	1.5
6	5	2	2.0	2.2
6	5	1	1.9	1.2
6	5	0	5.7	5.6
6	4	8	3.0	1.5
6	4	7	1.5	1.3
6	4	6	2.1	0.9
6	4	5	2.9	2.4
6	4	3	2.6	2.7
6	4	2	3.6	3.3
6	4	1	4.1	4.4
6	4	0	2.9	3.4
6	3	9	1.1	0.5
6	3	7	0.4	1.6
6	3	5	2.9	2.7
6	3	4	5.6	5.2
6	3	3	4.2	3.7
6	3	1	5.9	5.6
6	3	0	3.9	3.7
6	2	9	2.1	2.0
6	2	7	1.5	1.6
6	2	6	1.3	0.8
6	2	5	3.2	2.7
6	2	4	2.0	0.7
6	2	3	3.8	3.5
6	2	2	9.1	8.5
6	2	1	2.5	3.3
6	2	0	4.7	4.6
6	1	10	2.3	1.4
6	1	9	2.4	2.5
6	1	8	1.0	0.6
6	1	7	4.1	3.8
6	1	5	2.4	2.2
6	1	4	3.8	3.6
6	1	3	8.5	8.0
6	1	2	3.5	2.9
6	1	1	9.9	10.4
6	1	0	8.0	7.1
6	0	10	2.2	1.2
6	0	7	2.6	2.5
6	0	5	2.9	2.3
6	0	4	0.4	1.2
6	0	3	3.4	2.9
6	0	2	10.5	10.7
6	0	1	5.0	3.8
6	0	0	6.2	5.6
5	8	5	2.3	1.0
5	8	4	1.3	0.9
5	8	3	1.3	1.4
5	8	2	3.2	1.5
5	8	1	1.5	1.4
5	8	0	1.9	1.4
5	7	5	1.9	1.0
5	7	4	2.0	1.4
5	7	3	0.9	0.7
5	7	2	1.5	1.7
5	7	1	1.2	0.8
5	7	0	1.7	1.7
5	6	5	0.9	0.5
5	6	4	0.3	0.7
5	6	3	1.5	0.6
5	6	2	2.9	2.2
5	6	1	1.3	1.7
5	6	0	1.8	2.0
5	5	9	2.5	1.7
5	5	8	0.8	2.1
5	5	6	1.6	0.6
5	5	5	1.1	1.2
5	5	4	1.9	1.3
5	5	3	2.4	2.8
5	5	2	1.7	1.6
5	5	1	6.1	5.9
5	5	0	2.5	2.0
5	4	9	1.9	0.5
5	4	8	0.8	1.3
5	4	7	1.6	1.2
5	4	6	2.2	1.2
5	4	5	0.7	0.8
5	4	4	2.5	1.8
5	4	3	1.9	2.2
5	4	2	2.0	2.2
5	4	1	3.8	3.5
5	4	0	3.9	4.1
5	3	10	1.0	1.7
5	3	9	3.6	3.3
5	3	8	3.2	2.3
5	3	7	1.3	1.5
5	3	5	4.2	3.7
5	3	4	4.7	4.8
5	3	3	1.0	1.0
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5	3	0	4.9	4.4
5	2	9	3.2	2.9
5	2	8	2.1	1.7
5	2	7	1.8	1.5
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5	2	4	2.8	2.7
5	2	3	7.4	7.3
5	2	2	2.5	2.7
5	2	1	3.1	3.3
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5	1	8	2.6	2.2
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5	1	0	6.0	6.0
5	0	11	2.1	1.9
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5	0	0	5.6	4.4
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4	9	0	1.0	1.1
4	8	6	2.0	1.3
4	8	4	1.0	1.5
4	8	3	0.9	0.7
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4	8	0	1.8	1.0
4	7	8	1.9	0.4
4	7	7	1.5	1.4
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4	7	5	1.9	1.0
4	7	4	1.8	1.3
4	7	3	1.3	1.3
4	7	1	2.3	2.1
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4	4	2	2.4	2.5
4	4	1	1.9	1.2
4	4	0	2.3	2.1
4	3	11	2.1	1.6
4	3	10	1.6	1.3
4	3	8	1.8	2.0
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4	3	1	7.8	7.6
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4	2	9	2.7	2.6
4	2	8	2.5	1.6
4	2	7	0.5	0.5
4	2	6	7.2	7.2
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4	2	4	4.4	5.2
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4	2	2	2.6	1.9
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4	1	7	5.4	5.2
4	1	6	6.4	6.3
4	1	5	7.3	7.3
4	1	4	2.7	2.1
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4	1	1	16.5	14.8
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4	0	11	2.1	1.3
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4	0	7	3.4	2.4
4	0	6	2.4	3.2
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4	0	4	1.4	0.5
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4	0	1	7.4	7.2
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3	9	3	1.4	0.7
3	9	1	0.6	0.9
3	9	0	0.7	0.3
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3	8	6	1.5	1.3
3	8	5	1.9	1.7
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3	8	2	1.7	0.9
3	8	1	2.0	1.4
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3	7	6	1.7	0.6
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3	7	1	1.5	0.9
3	7	0	1.9	1.2
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3	6	7	1.7	1.8
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3	6	3	3.1	2.7
3	6	1	4.3	3.6
3	6	0	2.7	2.5
3	5	7	2.2	2.0
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3	5	5	5.7	5.4
3	5	4	3.3	3.4
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3	5	2	3.9	3.5
3	5	1	2.6	3.7
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3	4	11	1.6	1.6
3	4	10	0.9	0.7
3	4	9	2.4	1.6
3	4	8	3.1	1.6
3	4	7	2.0	2.4
3	4	6	8.2	7.7
3	4	5	7.7	7.1
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3	4	2	3.9	3.7
3	4	1	7.1	7.2
3	4	0	5.0	4.9
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3	3	10	0.7	0.5
3	3	9	2.0	1.6
3	3	7	3.4	3.4
3	3	6	1.8	1.4
3	3	5	7.8	7.7
3	3	4	5.3	5.4
3	3	3	5.6	7.4
3	3	2	3.7	3.0
3	3	1	4.0	3.1
3	3	0	6.3	7.1
3	2	11	2.1	1.5
3	2	10	2.1	2.2
3	2	9	2.0	2.2
3	2	8	1.5	2.6
3	2	7	11.6	11.1
3	2	6	11.6	11.1
3	2	5	3.7	3.4
3	2	4	4.5	5.5
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3	2	2	2.1	2.9
3	2	1	23.2	21.1
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3	1	11	2.2	0.7
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3	1	9	1.5	1.1
3	1	7	4.3	3.8
3	1	6	4.1	3.4
3	1	5	4.9	4.1
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3	1	3	9.7	7.6
3	1	2	4.4	5.4
3	1	1	7.5	6.5
3	1	0	11.0	9.3
3	0	11	1.6	1.1
3	0	10	3.1	2.9
3	0	9	0.9	1.0
3	0	8	4.6	4.1
3	0	7	6.5	6.5
3	0	6	10.1	9.3
3	0	5	11.5	11.5
3	0	4	10.4	8.6
3	0	3	7.6	6.2
3	0	2	13.7	12.9
3	0	1	20.2	18.0
3	0	0	4.1	3.3
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2	10	1	2.2	0.6
2	10	0	0.2	1.3
2	9	5	1.9	1.1
2	9	3	1.7	1.2
2	9	2	1.1	1.0
2	9	1	1.1	1.3
2	8	4	0.9	1.4
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2	8	2	0.3	1.2
2	8	0	0.7	0.5
2	7	8	1.3	0.8
2	7	6	2.9	3.1
2	7	4	1.3	1.4
2	7	3	0.6	1.0
2	7	2	1.9	1.1
2	7	1	1.6	1.7
2	7	0	1.8	2.1
2	6	10	1.7	0.5
2	6	9	1.4	0.7
2	6	7	1.4	2.0
2	6	6	3.3	3.0
2	6	5	3.8	3.8
2	6	4	3.7	3.4
2	6	3	1.0	1.3
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2	6	1	3.7	3.6
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2	5	1	4.5	4.5
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2	4	7	3.5	3.3
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2	4	2	8.5	8.3
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2	4	0	5.0	4.7
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2	2	7	2.9	3.3
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-7	3	2	2.8	2.6
-7	3	1	1.8	1.4
-7	2	9	3.7	3.4
-7	2	8	2.8	2.2
-7	2	6	1.3	1.0
-7	2	5	2.5	2.1
-7	2	3	2.3	2.7
-7	2	2	1.4	0.7
-7	2	1	4.0	3.6
-7	1	8	1.6	0.9
-7	1	6	0.6	1.2
-7	1	5	2.0	2.1
-7	1	4	2.2	1.9
-7	1	3	2.5	1.9
-7	1	2	3.1	3.0
-7	1	1	2.8	2.6
-7	0	9	3.9	3.3
-7	0	8	2.3	1.5
-7	0	7	1.4	0.4
-7	0	6	0.9	1.8
-7	0	5	3.9	3.7
-7	0	4	2.9	3.2
-7	0	3	3.2	2.7
-7	0	1	4.9	4.2
-8	6	1	1.1	1.0
-8	5	5	1.8	1.0
-8	5	1	1.9	1.7
-8	4	6	1.4	1.8
-8	4	5	1.0	0.9
-8	4	4	1.0	0.9
-8	4	3	1.6	1.1
-8	4	2	1.5	1.5
-8	4	1	1.7	1.1
-8	3	7	1.8	1.2
-8	3	6	2.1	0.9
-8	3	5	2.0	1.6
-8	3	4	2.7	1.3
-8	3	3	1.8	1.2
-8	3	2	2.2	0.4
-8	3	1	2.5	2.0
-8	2	6	1.6	2.3
-8	2	5	0.5	1.0
-8	2	3	2.5	1.7
-8	2	2	2.8	2.7
-8	2	1	1.8	2.1
-8	1	8	2.4	1.4
-8	1	7	1.6	0.5
-8	1	6	1.5	0.4
-8	1	5	0.9	1.6
-8	1	4	1.4	1.2
-8	1	3	1.5	1.3
-8	1	2	0.6	0.3
-8	0	7	2.1	1.4
-8	0	6	1.7	1.6
-8	0	5	0.6	0.1
-8	0	3	0.2	0.6
-8	0	2	4.1	3.5
-8	0	1	4.0	3.4
-9	4	1	2.0	1.4
-9	3	4	0.9	0.4
-9	3	3	2.1	0.9
-9	3	1	0.9	0.9
-9	2	5	1.8	1.4
-9	2	4	0.9	2.0
-9	2	3	1.8	0.9
-9	1	5	2.5	2.7
-9	1	2	2.9	2.3
-9	0	6	3.4	1.8
-9	0	5	1.7	0.4
-9	0	4	1.3	1.7
-9	0	3	2.2	1.7
-9	0	2	1.8	1.1
-9	0	1	1.7	0.6
-10	0	1	1.5	0.5

Table 2.5

(a) Fractional Coordinates

	x/a	y/b	z/c
O(1)	0.3929(7)	0.2862	0.0723(6)
N(1)	0.7263(8)	0.3047(15)	-0.1045(6)
N(2)	0.7214(11)	0.3142(20)	-0.2255(7)
C(1)	0.6290(8)	0.3172(13)	0.2708(6)
C(2)	0.5551(9)	0.2939(13)	0.1165(7)
C(3)	0.7252(9)	0.2913(13)	0.0348(7)
C(4)	0.8912(9)	0.3132(14)	0.1392(7)
C(5)	0.8882(13)	0.5099(14)	0.1923(9)
C(6)	0.7040(13)	0.5129(12)	0.2770(9)
C(7)	0.8153(8)	0.2061(10)	0.2704(7)
C(8)	0.7816(15)	0.0044(15)	0.2427(10)
C(9)	0.9387(12)	0.2262(15)	0.4091(8)
C(10)	0.4834(11)	0.2645(19)	0.3844(9)
H(4)	1.010(13)	0.257(15)	0.094(9)
H(51)	0.996(13)	0.526(15)	0.254(10)
H(52)	0.842(13)	0.602(17)	0.113(10)
H(61)	0.631(14)	0.568(16)	0.212(10)
H(62)	0.736(13)	0.537(15)	0.378(10)

Table 2.5 (contd.)

(b) Anisotropic Temperature Factors (Å^{2})

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O(1)	0.0430	0.1475	0.0699	0.0251	-0.0217	0.0030
N(1)	0.0537	0.1065	0.0396	-0.0034	0.0043	0.0247
N(2)	0.0815	0.1766	0.0427	0.0065	0.0179	0.0342
C(1)	0.0401	0.0659	0.0391	-0.0038	0.0084	0.0072
C(2)	0.0417	0.0650	0.0472	0.0018	0.0048	-0.0090
C(3)	0.0498	0.0655	0.0406	0.0072	-0.0001	-0.0026
C(4)	0.0412	0.0750	0.0414	-0.0097	0.0068	-0.0149
C(5)	0.0787	0.0679	0.0564	0.0143	-0.0063	-0.0510
C(6)	0.0879	0.0390	0.0643	0.0015	-0.0020	0.0105
C(7)	0.0371	0.0357	0.0433	-0.0113	-0.0160	0.0128
C(8)	0.0988	0.0516	0.0836	-0.0153	-0.0221	0.0278
C(9)	0.0590	0.0879	0.0562	0.0337	-0.0329	-0.0081
C(10)	0.0531	0.1332	0.0559	0.0070	0.0350	0.0179

Average estimated standard deviations (Å^{2})

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O	0.0025	0.0068	0.0033	0.0097	0.0046	0.0093
N	0.0039	0.0083	0.0029	0.0103	0.0054	0.0123
C	0.0041	0.0052	0.0037	0.0083	0.0064	0.0087

Table 2.6

Interatomic Distances (Å) and Angles (°) with estimated standard deviations in parentheses

(a) Bonded Distances

O(1)-C(2)	1.215(8)	C(3)-C(4)	1.514(9)
N(1)-N(2)	1.125(8)	C(4)-C(5)	1.549(14)
N(1)-C(3)	1.296(8)	C(4)-C(7)	1.566(10)
C(1)-C(2)	1.520(9)	C(5)-C(6)	1.549(13)
C(1)-C(6)	1.556(13)	C(7)-C(8)	1.546(13)
C(1)-C(7)	1.565(10)	C(7)-C(9)	1.543(10)
C(1)-C(10)	1.551(10)	average C-H	0.98(10)
C(2)-C(3)	1.448(9)		

(b) Interbond Angles

N(2)-N(1)-C(3)	177.8(8)	C(2)-C(3)-C(4)	108.2(5)
C(2)-C(1)-C(6)	104.5(7)	C(3)-C(4)-C(5)	106.7(7)
C(2)-C(1)-C(7)	101.9(5)	C(3)-C(4)-C(7)	99.3(5)
C(2)-C(1)-C(10)	113.1(6)	C(5)-C(4)-C(7)	103.2(6)
C(6)-C(1)-C(7)	102.0(6)	C(4)-C(5)-C(6)	101.3(7)
C(6)-C(1)-C(10)	116.6(8)	C(1)-C(6)-C(5)	105.2(7)
C(7)-C(1)-C(10)	116.8(7)	C(1)-C(7)-C(4)	92.5(5)
O(1)-C(2)-C(1)	128.4(6)	C(1)-C(7)-C(8)	112.9(6)
O(1)-C(2)-C(3)	128.7(6)	C(1)-C(7)-C(9)	114.1(6)
C(1)-C(2)-C(3)	102.9(5)	C(4)-C(7)-C(8)	115.1(6)
N(1)-C(3)-C(2)	123.4(6)	C(4)-C(7)-C(9)	113.4(6)
N(1)-C(3)-C(4)	127.0(6)	C(8)-C(7)-C(9)	108.4(7)

Table 2.6 (contd.)

(c) Intramolecular Non-bonded Distances < 3.5 Å

O(1)...N(1)	2.93	C(2)...C(8)	2.92
O(1)...C(6)	3.33	C(3)...C(6)	2.80
O(1)...C(10)	2.95	C(3)...C(8)	2.90
N(1)...C(5)	3.33	C(5)...C(9)	2.94
N(2)...C(2)	3.42	C(6)...C(9)	2.96
C(1)...C(4)	2.26	C(8)...C(10)	3.19
C(2)...C(5)	2.94	C(9)...C(10)	3.26

(d) Intermolecular Distances

O(1)...N(1^{I})	3.71	N(2)...C(6^{I})	3.79
O(1)...N(1^{II})	3.98	N(2)...C(8^{II})	3.85
O(1)...N(2^{I})	3.89	N(2)...C(9^{IV})	3.83
O(1)...C(3^{I})	3.91	N(2)...C(10^{II})	3.93
O(1)...C(3^{II})	3.98	N(2)...C(10^{IV})	3.97
O(1)...C(4^{III})	3.65	C(5)...C(8^{V})	3.80
O(1)...C(5^{I})	3.74	C(6)...C(8^{V})	3.73
O(1)...C(6^{I})	3.87	C(6)...C(10^{VI})	3.93
O(1)...C(8^{II})	3.54	C(9)...C(10^{VII})	3.90

Roman numerals as superscripts refer to the equivalent positions which should be applied to the coordinates of the second atom :

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

Table 2.7

Least-squares Planes

given in the form $\ell X' + mY' + nZ' = d$,
where X', Y' and Z' are coordinates in Å

(a) Plane equations

Plane (1) : $-0.0541\ X' + 0.9932\ Y' - 0.1033\ Z' = 1.8648$

Plane (2) : $-0.5358\ X' + 0.2412\ Y' - 0.8092\ Z' = -3.7355$

Plane (3) : $-0.0342\ X' + 0.9946\ Y' - 0.0976\ Z' = 1.9669$

Plane (4) : $-0.0602\ X' + 0.9982\ Y' + 0.0001\ Z' = 1.9309$

(b) Deviation of atoms (Å) from planes (starred atoms not used to define plane)

Plane (1) : O(1)* 0.045, N(1)* 0.231, N(2)* 0.420, C(1) -0.001, C(2) 0.001, C(3) -0.001, C(4) 0.001

Plane (2) : C(1) -0.013, C(4) 0.013, C(5) -0.019, C(6) 0.019

Plane (3) : O(1) 0.006, C(1) 0.004, C(2) -0.013, C(3) 0.004

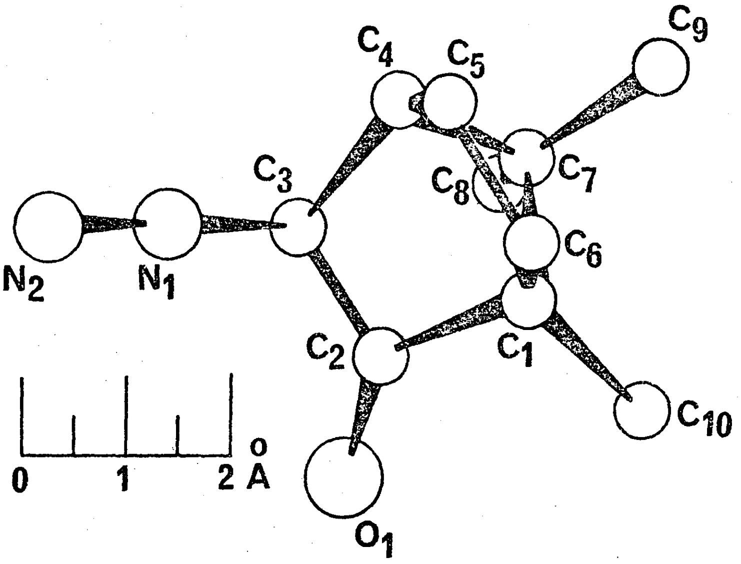
Plane (4) : N(1) -0.028, C(2) -0.021, C(3) 0.071, C(4) -0.021

(c) Dihedral angles between planes (°)

(1) - (2) 69.4, (3) - (4) 5.8

Figure 2.1

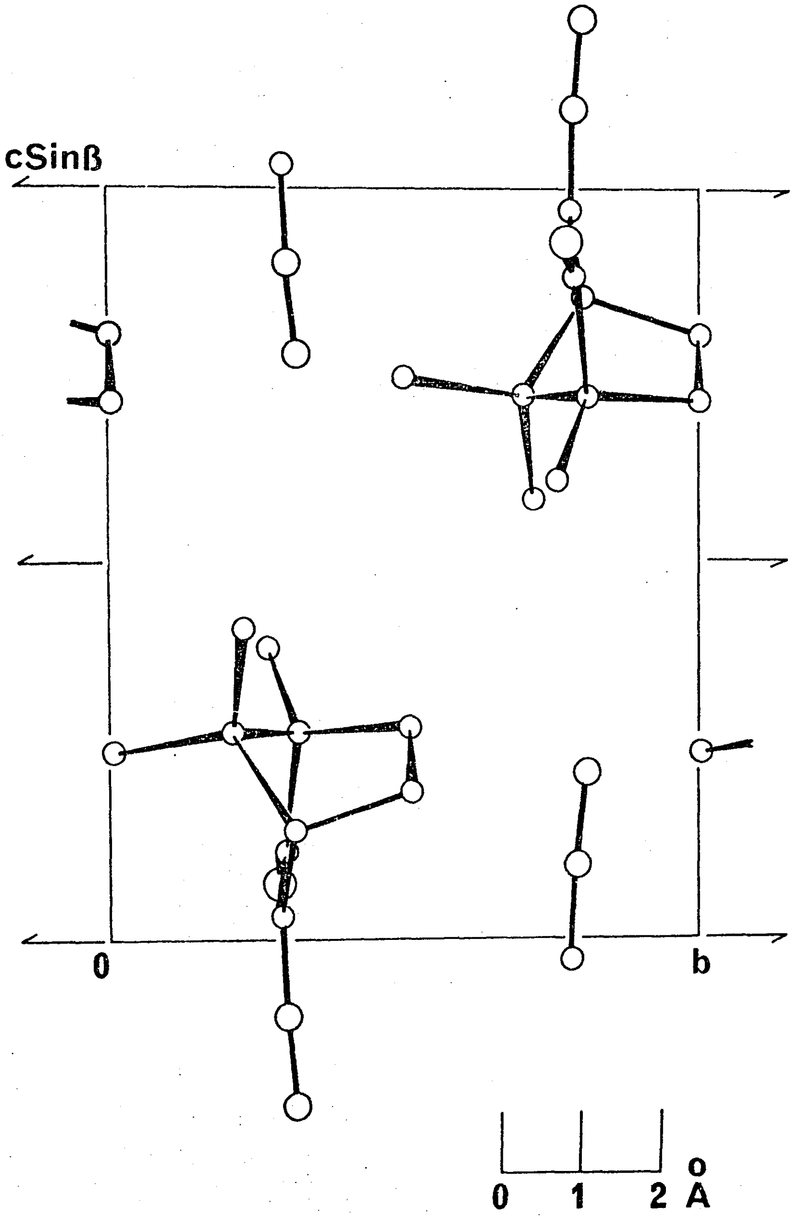
Atomic numbering scheme



C9
C4
C5
C3
C7
C8
N2
N1
C6
C1
C2
C10
0
1
2
Å
O1

Figure 2.2

Molecular packing arrangement
viewed along the a-axis


cSinß
0
b
0 1 2 Å

2.3 DISCUSSION

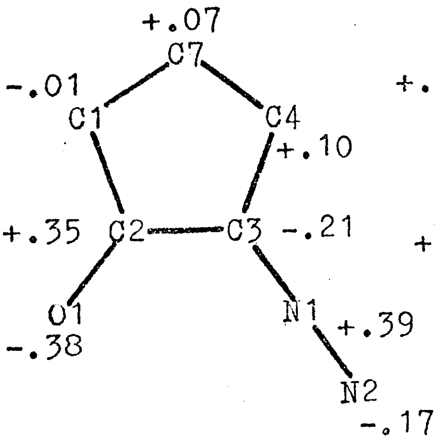
The structure analysis of compound (III) has not only confirmed that the crystal structure of (+)-3-diazocamphor is isomorphous with the structures of the other three camphor derivatives listed in Table 2.1, but has also yielded information regarding the bonding and mode of stabilisation which may be expected for diazoketones.

Examination of the geometry of the diazonium moiety reveals that the atoms C(3), N(1) and N(2) adopt a virtually linear arrangement [angle C(3)-N(1)-N(2) = 177.8(8)°], in which the relevant bonding distances C(3)-N(1) and N(1)-N(2) are 1.296(8) and 1.125(8) Å respectively. These values are comparable to the corresponding lengths of 1.332 and 1.113 Å quoted recently for the diazoketone moiety in 5-diazo-6-methoxy-6(H)-uracil (IV).[95] However, in order to assess the importance of the diazo-function in the stabilisation of diazoketones, it is necessary to make comparisons with the corresponding data for diazoalkanes. For diazomethane, a linear structure has been established[96] with C-N and N-N bonds of 1.32 and 1.12 Å respectively, while values of 1.32(3) and 1.12(3) Å for the corresponding bonds have been more recently reported for 2-bromo-9-diazofluorene.[94] By comparison, a close similarity between the diazo-groupings in both diazoketones and diazoalkanes is indicated, which suggests comparable electronic structures within these residues of the different molecules. A possible conclusion, therefore, is that the stabilisation of the negative charge in the diazoketone(III), *via* delocalisation into the diazo-function, has occurred to an extent comparable to that in diazoalkanes.

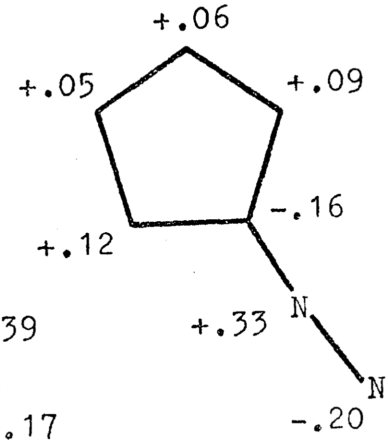
In accordance with this conclusion, the geometry of the C(3)-C(2)-O(1) system appears to indicate a predominance of the keto form (Ia) over the enolate form (Ib). The carbonyl bond [1.215(8) Å] is not significantly longer than reported values for aliphatic ketones,[66] and although it has been shown that, in conjugated systems, the length of a carbonyl bond is relatively insensitive to change,[70,71] slight, but significant lengthening has been observed both in the *N*-ammonio-amidate (V) [61,62] and the ammonium ylide (VI) [74] [1.243(5) and 1.27 Å respectively]. It may therefore be inferred that any delocalisation of the negative charge onto the oxygen atom O(1) of (III) is likely to be minimal. Moreover, comparison of both the C(2)-C(3) bond [1.448(9) Å] of the potential enolate system and the corresponding bond [1.436 Å] in (IV) [95] with the value of 1.476 Å calculated for a single bond between two sp^2-hybridised carbon atoms,[97] and with the experimental values of 1.483 and 1.475 Å found for butadiene [98] and 1,3-cyclo-octadiene,[99] indicates only slight shortening, consistent with the introduction of no more than a limited amount of double-bond character into the C(2)-C(3) bond in (III) and the corresponding bond in (IV). This view is further supported by comparison with the corresponding bond [1.36 Å] in the ammonium ylide (VI),[74] where charge delocalisation into the enolate system has definitely occurred. However, the possibility that increased strain in the bicyclo[2.2.1]heptyl system could limit the introduction of double-bond character into the C(2)-C(3) bond of the present molecule is remote, since a comparable value for the corresponding bond was obtained in the unstrained system (IV).[95]

Nevertheless, support for at least a minor contribution from the enolate form (Ib) in diazoketones can be taken from a comparison of the infra red carbonyl frequency ν_{max}(CCl$_4$) [illegible] cm^{-1} for (III) [C(2)-O(1)] and with the value of ν_{max}, 1751 cm.$^{-1}$, for norcamphor.[100] Thus to the extent that bond extension [C(2)-O(1)] and bond contraction [C(2)-C(3)] within the C(3)-C(2)-O(1) system may be taken as a measure of the delocalisation of the formal negative charge on C(3) within this potential enolate system, it may possibly be concluded, since both diazoketones and diazoalkanes are apparently stabilised to a similar extent <u>via</u> their respective diazo-functions, that it is the minor additional delocalisation into the enolate groupings of diazoketones which is at least in part responsible for their enhanced stability.

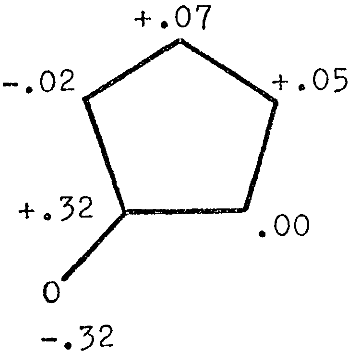
In order to further investigate the charge delocalisation which takes place in diazoketones, theoretical INDO calculations,[72] based on the determined coordinates for molecule (III), were carried out [73] both for the model compound (VII) and also for the two related molecules (VIII) and (IX) for comparison purposes. The calculated atomic charge densities are shown below :-



(VII)



(VIII)



(IX)

The most obvious feature of the calculated charge distribution of (VII) is the delocalisation of the formal negative charge on C(3) apparently into both the carbonyl and diazo functional groups. However, comparison with (IX) indicates that the extra charge transference into the carbonyl moiety, although probably still significant, is less than at first appears. Nevertheless, coupled with a smaller amount of charge being delocalised into the diazo-function in (VII) as compared to (VIII), probably as a result of the additional presence of the carbonyl group in the former, the overall conclusion to be drawn from the charge density calculations seems to support the involvement of a significant, though perhaps small, contribution from the enolate resonance form (Ib).

In PART II, Section 1.3, the cis-conformations common to the carbonyl-stabilised and nitro-stabilised first-row ylides (V) and (X) [61,62] have already been discussed. Both compounds exhibit evidence of slight delocalisation of the negative charge onto their respective oxygen atoms, and the effect of the cis-conformations is to produce short $\overset{+}{N}\ldots\overset{-}{O}$ intramolecular contacts of 2.74 Å (V) and 2.65 Å (X). Similar conclusions result from the study of (VI).[74] However, although (+)-3-diazocamphor is a first-row ylide, the constraints placed by the bicyclic skeleton on the overall conformation render any direct comparisons with the conformations of the other molecules difficult, since the diazonium and carbonyl functions are in this case restricted to be cis. Nevertheless, the dihedral angle between the planes of atoms [C(1), C(2), C(3), O(1)] and [C(2), C(3), C(4), N(1)] is almost 6°, representing a larger degree of twist about the C(2)-C(3) bond than is observed for the corresponding bonds in (V) [2°] and (X) [0°]. Similar twisting has been observed in other norbornane derivatives,[93] and its significance has also been discussed.[101] Furthermore, the N(1)...O(1) [2.93 Å] separation in (III) is significantly longer than the corresponding distances in (V) and (X), although this may also result from the constraints placed upon the exocyclic angles of the bicyclic system.

It has been predicted that, by regarding bicyclo [2.2.1] heptyl systems as two fused cyclopentane rings with three carbon atoms in common, the endocyclic bond angles should have values of *ca*. 100°.[102] In accord with this suggestion, the mean value of the relevant bond angles in the fused cyclopentane ring bearing the diazoketone moiety is 101.0°, while the corresponding value for the unsubstituted fused ring is 100.8°. Furthermore, for diazocamphor the bridge angle C(1)-C(7)-C(4) has a value [92.5°] which is comparable to those reported for other norbornane derivatives.[93]

The two bonds C(1)-C(2) and C(3)-C(4), connecting the diazoketone moiety to the bridgehead positions, have lengths [1.520(9) and 1.514(9) Å respectively] which are in good agreement with the literature value [1.510 Å] for bonds between *sp*^{2} and *sp*^{3} centres.[66] The remaining C(sp^3) - C(sp^3) bonds of the fused ring system [mean 1.553(12) Å] and C-H bonds [mean 0.98(10) Å] have values which compare well with quoted values for similar bond types.[66]

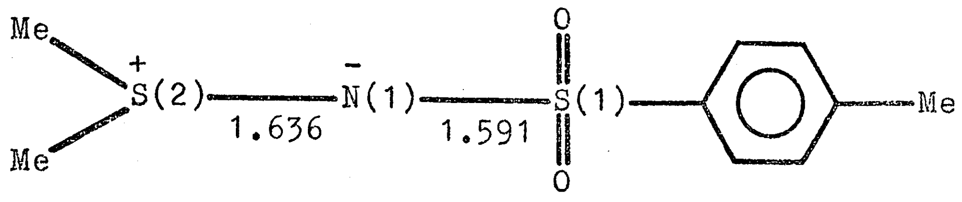
The absence of any short intermolecular non-bonded distances in the crystal indicates that the crystal packing is determined by van der Waals' forces.

3. THE CRYSTAL AND MOLECULAR STRUCTURE OF N-(p-TOLUENESULPHONYL)-IMINODIMETHYLSULPHUR(IV) : A SULPHONYL-STABILISED SECOND-ROW YLIDE.

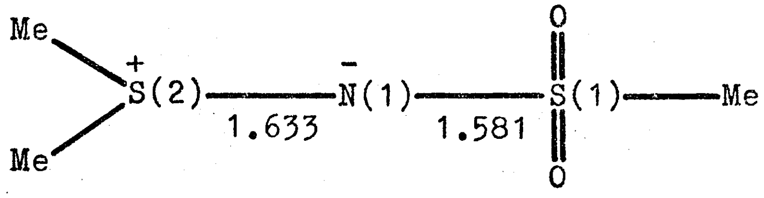
3.1 INTRODUCTION

For ylides ($\overset{+}{X} - \overset{-}{Y}$) in which the 'onium group X is a second or higher row element, it has been postulated that a bonding interaction, formally of the $d_{\pi} - p_{\pi}$ type, may occur between the empty d-orbitals of the 'onium group and a lone-pair of electrons of the vicinal atom (see PART II, Introduction). However, despite the stabilising effect of such an interaction, almost all examples, with the exceptions of the sulphoxides (X = S; Y = O) and the phosphine oxides (X = P; Y = O), require that an electron-withdrawing group such as -COR or $-SO_2R$ be attached to the atom Y in order to provide further stabilisation. Moreover, in ylides where such stabilisation has resulted from the presence of a sulphonyl moiety, there is the additional possibility of d-orbital involvement in the bonding between the sulphonyl grouping and the vicinal atom Y.

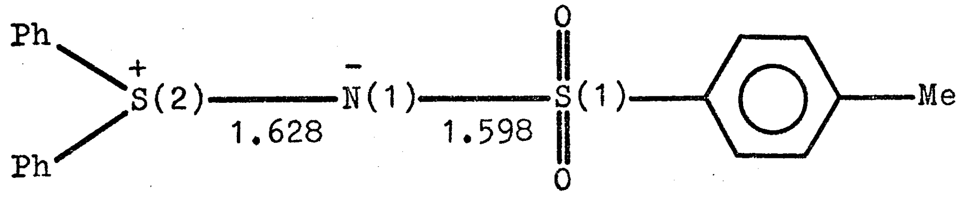
As part of a study of the bonding and conformations of second-row ylides, the crystal structure of N-(p-toluenesulphonyl)-iminodimethylsulphur(IV) (I), which is representative of the class of ylides (X = S; Y = N—), has been determined.[103] The choice of this compound for study was influenced by the recent analyses of the two related compounds (II)[50] and (III),[51] with which geometrical comparisons may be made.


Me
Me
S(2)
N(1)
S(1)
O
O
Me
1.636
1.591

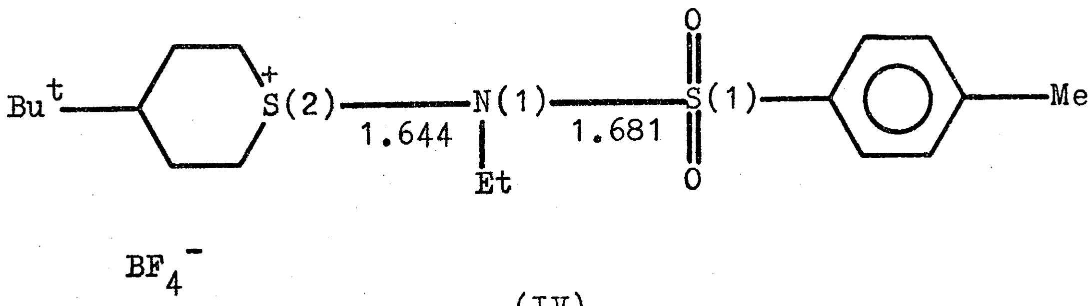
(I)


Me
Me
S(2)
N(1)
S(1)
O
O
Me
1.633
1.581

(II)


Ph
Ph
S(2)
N(1)
S(1)
O
O
Me
1.628
1.598

(III)


Bu^t
S(2)
N(1)
Et
S(1)
O
O
Me
1.644
1.681
BF_4^-

(IV)

3.2 EXPERIMENTAL

Crystal Data

(I); N-(p-toluenesulphonyl)-iminodimethylsulphur(IV),

$C_9H_{13}NO_2S_2$, M = 231.3.

Monoclinic, a = 12.93(2), b = 7.17(1), c = 12.50(2) Å,

β = 104.2(1)°, U = 1123.4 Å^3.

D_m = 1.34 g.cm.$^{-3}$ (by flotation in aqueous KI), Z = 4,

D_c = 1.37 g.cm.$^{-3}$, F(000) = 488.

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

Linear absorption coefficient for X-rays (λ = 1.5418 Å),

μ = 47.5 cm.$^{-1}$.

Crystallographic Measurements

The unit cell parameters were determined from oscillation and Weissenberg photographs taken with Cu-K_α (λ = 1.5418 Å) radiation, and from precession photographs taken with Mo-K_α (λ = 0.7107 Å) radiation. The space group is uniquely determined by systematic absences in the 0k0 and h0ℓ spectra.

A small, needle-shaped crystal, rotating about b, was exposed to Cu-K_α radiation, and 1085 independent reflexions from the reciprocal lattice nets h0-6ℓ were recorded on equatorial and equi-inclination Weissenberg photographs using the multiple-film technique.[3] The intensities, which were measured visually by comparison with a calibrated strip, were then corrected for the appropriate Lorentz and polarisation factors, the set of structure amplitudes, thus obtained, being subsequently placed on an approximate absolute scale by equating $k\sum|F_o|$ and $\sum|F_c|$ for each layer. Absorption effects were not considered.

Structure Determination

The positions of both sulphur atoms, S(1) [0.791, 0.321, 0.311] and S(2) [0.856, 0.680, 0.371], were determined from a three-dimensional Patterson synthesis, and the analysis thereafter proceeded on the basis of the phase-determining heavy-atom method.[11] A structure-factor calculation based on the coordinates of the sulphur atoms yielded an R-value of 48 %, and the initial electron-density distribution, calculated with the appropriate phasing, revealed the entire structure. Three further rounds of structure-factor and electron-density calculations effected a preliminary refinement of positional parameters. After each of the previous structure-factor calculations, in which an overall isotropic thermal parameter $U_{iso} = 0.05$ Å^2 was assumed, the data were placed on an approximate absolute scale by making $k\sum|F_o| = \sum|F_c|$ for each of the layers $h0-6\ell$.

Structure Refinement

The refinement of positional, vibrational and scale parameters by three-dimensional least-squares calculations converged after 12 cycles when R was 0.107 and R' ($= \sum w\Delta^2 / \sum w|F_o|^2$) was 0.019. Full details of the refinement are given in Table 3.1. The concurrent refinement of layer-scale factors and anisotropic thermal parameters was avoided by prior conversion to an overall-scale factor.

A weighting scheme of the form

$$\sqrt{w} = \left\{ \left[1 - \exp(-p_1(\sin\theta/\lambda)^2)\right] / \left[1 + p_2|F_o| + p_3|F_o|^2\right] \right\}^{1/2}$$

was applied in all cycles, the p-parameters being initially chosen to give unit weights to all reflexions. In later cycles they were adjusted, according to an ($|F_o|$ and $\sin\theta/\lambda$) analysis of $w\Delta^2$, to the final values $p_1 = 100$, $p_2 = 0.001$, and $p_3 = 0.01$, in order to give the same average $w\Delta^2$ value to various batches of the data.

The refinement was assumed complete when the parameter-shifts calculated by a least-squares cycle were insignificant compared to the corresponding estimated standard deviations. The subsequent calculation of an electron-density distribution and a difference synthesis revealed no errors in the structure. Although there were diffuse peaks evident in the difference synthesis in positions stereochemically acceptable for hydrogen atoms, it proved impossible to determine their coordinates with any accuracy. In all the structure-factor calculations, the atomic scattering factors used were taken from 'International Tables for X-Ray Crystallography,' Vol.III.[65] Observed and final calculated structure factors are listed in Table 3.2.

The final fractional coordinates and anisotropic thermal parameters are given in Table 3.3, the values of U_{ii} and $2U_{ij}$ referring to the anisotropic temperature factor expression given in PART I, Section 3. All bond lengths, valency angles, and pertinent intra- and inter-molecular non-bonded distances are listed in Table 3.4. The appropriate estimated standard deviations, σ, derived from the inverse of the least-squares normal equation matrix are included in Tables 3.3 and 3.4, the average values for S-O, S-N, S-C and C-C bonds being 0.007, 0.008, 0.011 and 0.013 Å respectively, and for valency angles 0.6°. In view of the block-diagonal approximation used in the latter stages of the refinement, these are best regarded as minimum values.

Details of least-squares planes calculated for various portions of the molecular framework are given in Table 3.5. The atomic numbering scheme, used in every table, and the molecular packing, viewed along the b-axis, are shown in Figures 3.1 and 3.2 respectively.

Table 3.1

Course of Refinement

Cycles	Parameters refined	Final R	Final R'
1 - 3	x, y, z, U_{iso} for S, O, N, C, Layer scale factors, Full matrix, unit weights.	0.147	0.036
4 - 5	x, y, z, U_{iso} for S, O, N, C, Layer scale factors, Full matrix, weighting scheme adjusted.	0.141	0.034
6 - 10	x, y, z, U_{ij} for S, O, N, C, Overall scale factor, Block diagonal, weighting scheme applied.	0.107	0.019

Table 3.2

Observed structure amplitudes and final calculated structure factors

H	K	L	F OBS	F CALC
-15	0	0	10.4	12.7
-14	0	0	10.5	12.1
-13	0	0	8.3	-7.9
-12	0	0	11.3	-11.6
-11	0	0	25.9	-25.6
-10	0	0	4.9	5.5
-9	0	0	15.8	15.1
-8	0	0	10.3	10.2
-7	0	0	8.5	7.0
-6	0	0	58.3	59.1
-5	0	0	29.1	25.5
-4	0	0	56.1	-59.0
-2	0	0	23.2	-33.7
-16	0	2	13.0	15.7
-14	0	2	12.7	-13.0
-13	0	2	8.5	-7.8
-10	0	2	8.3	9.4
-9	0	2	9.3	7.3
-8	0	2	47.0	48.4
-7	0	2	42.7	46.6
-6	0	2	38.4	-43.1
-4	0	2	67.2	-77.0
-3	0	2	55.9	80.5
0	0	2	39.0	-56.7
2	0	2	52.9	-51.8
3	0	2	16.6	17.1
4	0	2	23.1	-21.0
5	0	2	19.0	20.3
6	0	2	14.0	11.9
7	0	2	4.1	4.1
8	0	2	7.8	-8.4
10	0	2	42.4	-43.8
11	0	2	11.4	11.9
-15	0	4	5.1	-6.1
-15	0	4	5.5	-5.5
-13	0	4	8.5	-7.3
-12	0	4	5.1	-2.6
-10	0	4	33.5	31.3
-9	0	4	16.7	19.4
-8	0	4	32.4	-37.7
-7	0	4	49.7	-46.6
-6	0	4	80.5	-80.8
-5	0	4	45.6	49.7
-4	0	4	48.1	60.1
-3	0	4	17.6	24.4
-2	0	4	16.8	-17.9
-1	0	4	60.0	-61.5
0	0	4	37.5	-53.9
2	0	4	31.4	31.2
3	0	4	27.7	24.4
4	0	4	6.2	4.4
5	0	4	11.0	9.1
6	0	4	17.5	-17.0
7	0	4	4.6	-6.5
8	0	4	13.7	-13.2
9	0	4	10.1	-9.2
10	0	4	12.5	11.2
11	0	4	23.0	21.5
-14	0	6	6.2	-5.6
-12	0	6	14.3	14.5
-9	0	6	26.9	-26.8
-8	0	6	25.5	-24.9
-7	0	6	19.9	22.6
-6	0	6	45.7	44.7
-5	0	6	40.4	49.1
-3	0	6	35.1	-33.1
-2	0	6	61.7	-67.0
-1	0	6	21.4	21.1
2	0	6	17.8	19.7
3	0	6	15.0	-14.4
4	0	6	20.0	21.5
5	0	6	15.7	-14.6
6	0	6	16.5	-15.0
7	0	6	17.3	-16.0
9	0	6	28.5	29.9
10	0	6	13.6	11.6
-13	0	8	10.1	9.1
-11	0	8	12.4	-11.3
-10	0	8	19.0	-17.8
-8	0	8	20.1	20.9
-7	0	8	53.9	57.6
-5	0	8	37.1	-33.9
-4	0	8	36.1	-40.7
-3	0	8	4.2	-6.4
-2	0	8	17.3	18.7
-1	0	8	32.5	29.9
0	0	8	17.7	-18.9
2	0	8	23.2	22.8
4	0	8	27.7	-26.0
5	0	8	28.4	-23.5
7	0	8	18.9	18.5
8	0	8	18.2	20.2
9	0	8	7.8	-7.7
10	0	8	13.0	-13.1
-14	0	10	5.7	5.6
-13	0	10	11.2	-10.3
-12	0	10	18.2	-17.5
-11	0	10	6.7	-7.3
-10	0	10	17.9	16.3
-9	0	10	14.4	13.5
-8	0	10	14.4	12.4
-7	0	10	35.1	-32.5
-6	0	10	23.5	-20.5
-4	0	10	5.5	7.0
-3	0	10	9.5	-9.0
-2	0	10	8.5	-7.5
0	0	10	14.9	14.0
2	0	10	8.8	-8.8
3	0	10	35.3	-34.1
4	0	10	12.4	14.5
5	0	10	11.1	11.5
6	0	10	8.2	10.5
8	0	10	8.4	-9.0
9	0	10	7.1	-7.3
-13	0	12	6.4	-6.3
-12	0	12	9.6	9.0
-11	0	12	9.5	10.6
-9	0	12	9.2	-9.0
-6	0	12	12.2	10.9
-4	0	12	7.1	-7.1
-3	0	12	8.9	8.6
-2	0	12	12.4	11.5
0	0	12	12.2	-10.9
2	0	12	4.5	-5.5
3	0	12	17.2	15.7
4	0	12	10.6	10.0
5	0	12	5.6	-5.0
6	0	12	7.7	-6.7
-3	0	14	4.3	4.0
-2	0	14	9.4	-8.7
-1	0	14	5.8	-5.1
1	0	14	6.4	5.4
2	0	14	7.6	6.7
-14	1	0	7.4	6.3
-12	1	0	19.0	-19.7
-10	1	0	13.8	-11.5
-9	1	0	65.2	53.4
-8	1	0	36.5	26.9
-7	1	0	23.2	-27.9
-6	1	0	84.4	-46.9
-5	1	0	26.4	-15.7
-4	1	0	52.4	37.7
-3	1	0	78.3	65.4
-2	1	0	82.6	40.5
-13	1	1	10.5	-9.4
-12	1	1	6.4	-5.3
-10	1	1	22.8	19.5
-9	1	1	14.1	-11.3
-8	1	1	7.4	6.2
-7	1	1	13.4	-6.0
-6	1	1	35.4	25.9
-5	1	1	23.6	-15.5
-4	1	1	55.3	-44.9
-3	1	1	35.3	-28.9
-2	1	1	35.9	32.2
1	1	1	45.9	-63.2
2	1	1	17.6	-18.1
3	1	1	12.6	-12.6
4	1	1	8.7	7.9
5	1	1	8.0	-8.3
7	1	1	14.1	12.1
8	1	1	13.5	15.7
9	1	1	13.2	12.1
10	1	1	17.7	-16.7
-14	1	2	11.1	-12.5
-13	1	2	17.3	-15.3
-11	1	2	32.3	27.7
-10	1	2	22.7	19.0
-9	1	2	9.8	-7.7
-8	1	2	49.1	-37.6
-7	1	2	59.3	-44.5
-6	1	2	53.4	38.6
-5	1	2	29.0	-11.9
-4	1	2	42.3	-30.2
-3	1	2	22.5	-19.5
-2	1	2	24.4	28.0
-1	1	2	16.0	-16.4
0	1	2	43.5	60.8
2	1	2	49.7	-54.7
3	1	2	19.2	19.6
4	1	2	39.0	41.0
5	1	2	20.0	15.8
6	1	2	13.4	-10.8
7	1	2	35.5	-32.6
8	1	2	16.0	-14.4
9	1	2	21.3	18.5
10	1	2	21.9	19.8
-15	1	3	5.7	-7.6
-10	1	3	4.1	-5.9
-9	1	3	16.0	12.6
-8	1	3	11.7	8.5
-7	1	3	6.8	-5.6
-6	1	3	54.6	-43.4
-5	1	3	9.7	-11.6
-4	1	3	27.2	28.2
-3	1	3	30.5	31.1
-2	1	3	22.7	24.4
0	1	3	36.4	-45.0
1	1	3	19.4	19.7
2	1	3	33.4	-46.9
5	1	3	31.5	29.1
6	1	3	17.4	15.2
8	1	3	8.3	-7.6
9	1	3	15.2	-15.1
10	1	3	11.0	-9.6
-15	1	4	13.5	-15.0
-13	1	4	13.7	14.3
-12	1	4	12.7	11.0
-10	1	4	22.8	-20.6
-9	1	4	10.0	-7.2
-8	1	4	9.2	8.6
-6	1	4	6.4	-6.5
-5	1	4	17.2	-16.4
-4	1	4	29.3	27.7
-3	1	4	29.6	28.5
-2	1	4	28.4	25.8
-1	1	4	25.6	-35.0
0	1	4	7.7	2.8
1	1	4	8.0	4.6
2	1	4	29.4	38.6
3	1	4	42.7	52.6
4	1	4	34.7	-37.2
5	1	4	17.1	-16.6
6	1	4	20.1	-19.3
7	1	4	12.9	13.1
8	1	4	26.7	28.0
9	1	4	17.9	17.4
10	1	4	12.7	-13.3
-10	1	5	10.7	9.9
-9	1	5	8.3	-9.5
-8	1	5	12.3	-11.6
-7	1	5	17.8	-14.6
-5	1	5	22.7	21.2
-4	1	5	17.3	15.3
-3	1	5	14.9	15.7
-2	1	5	3.9	5.4
-1	1	5	32.1	-37.9
0	1	5	18.4	-17.6
1	1	5	11.6	-12.0
2	1	5	15.3	15.3
3	1	5	8.0	7.4
4	1	5	23.3	21.0
7	1	5	10.5	-9.1
9	1	5	15.4	-15.6
10	1	5	13.9	14.1
-14	1	6	9.4	9.8
-10	1	6	8.9	9.3
-9	1	6	10.4	11.9
-8	1	6	8.1	7.5
-5	1	6	9.8	17.9
-3	1	6	9.9	-10.4
-1	1	6	13.1	-13.8
0	1	6	41.9	55.0
1	1	6	26.0	27.0
2	1	6	11.8	-10.1
3	1	6	38.6	-44.2
4	1	6	37.0	-44.4
5	1	6	12.5	12.0
6	1	6	24.1	24.4
7	1	6	21.7	23.1
9	1	6	6.3	-7.7
-10	1	7	9.0	-9.1
-9	1	7	6.2	-4.6
-8	1	7	14.5	-14.2
-7	1	7	9.8	9.5
-6	1	7	25.3	26.7
-5	1	7	12.7	9.3
-4	1	7	5.0	-3.7
-3	1	7	18.3	-20.0
-2	1	7	22.7	-20.6
-1	1	7	10.9	11.8
1	1	7	9.1	7.3
3	1	7	19.2	19.7
5	1	7	13.6	-13.4
6	1	7	12.6	-12.3
8	1	7	8.9	10.6
9	1	7	10.4	10.6
-14	1	8	8.9	-9.2
-13	1	8	7.9	-7.3
-10	1	8	6.4	6.8
-8	1	8	17.4	-18.2
-7	1	8	11.9	12.4
-5	1	8	20.8	-21.0
-4	1	8	27.7	-35.4
-2	1	8	18.4	22.5
-1	1	8	33.4	44.4
1	1	8	31.6	-44.2
2	1	8	29.4	-37.3
3	1	8	6.0	8.6
4	1	8	17.4	17.5
5	1	8	15.5	15.2
7	1	8	6.3	-6.5
-11	1	9	10.7	-9.3
-10	1	9	6.4	-7.1
-9	1	9	6.4	6.5
-8	1	9	14.1	12.8
-7	1	9	10.7	9.6
-6	1	9	14.9	-13.6
-5	1	9	10.3	-11.2
-1	1	9	5.8	-7.3
0	1	9	8.4	9.4
1	1	9	6.0	7.2
2	1	9	6.7	9.2
3	1	9	15.4	-15.2
4	1	9	14.2	-14.1
6	1	9	6.3	8.4
-9	1	10	6.3	7.7
-6	1	10	29.6	-33.3
-4	1	10	23.2	26.3
-3	1	10	23.0	25.5
-1	1	10	15.2	-17.0
0	1	10	17.7	-18.0
2	1	10	23.8	20.1
-10	1	11	5.9	7.9
-7	1	11	9.0	-8.8
-2	1	11	6.4	7.5
-1	1	11	6.4	6.3
1	1	11	9.0	-8.7
2	1	11	8.9	-8.1
4	1	11	10.4	9.3
-11	1	12	7.0	7.4
-10	1	12	7.6	7.3
-9	1	12	5.7	-5.0
-8	1	12	6.0	-4.7
-6	1	12	10.6	10.2
-5	1	12	15.4	17.1
-3	1	12	15.5	-16.8
-2	1	12	6.3	-7.0
0	1	12	5.8	7.8
1	1	12	6.6	7.6
3	1	12	9.8	-11.7
-5	1	14	5.2	-5.8
-4	1	14	10.5	-12.0
-15	2	0	5.2	-6.1
-14	2	0	3.4	-3.9
-12	2	0	5.9	5.6
-10	2	0	4.2	3.8
-9	2	0	5.9	-9.1
-8	2	0	9.0	7.9
-6	2	0	38.8	-32.8
-5	2	0	13.7	-12.0
-4	2	0	16.3	19.8
-3	2	0	6.3	9.5
-2	2	0	10.1	10.9
-1	2	0	12.9	-10.9
-15	2	1	7.9	9.7
-13	2	1	14.8	-15.3
-12	2	1	14.6	-14.4
-11	2	1	6.0	-6.6
-10	2	1	25.9	26.5
-9	2	1	33.0	36.0
-8	2	1	5.1	-4.2
-7	2	1	42.3	-46.5
-6	2	1	22.8	-23.4
-5	2	1	14.9	13.8
-4	2	1	26.4	30.8
-3	2	1	10.0	10.0
-2	2	1	11.2	-8.4
-1	2	1	23.9	-28.6
2	2	1	12.5	-17.0
3	2	1	18.1	-20.9
4	2	1	56.2	60.9
5	2	1	36.0	39.6
6	2	1	4.4	3.4
7	2	1	44.4	-53.4
8	2	1	26.2	-26.3
9	2	1	7.0	-6.6
10	2	1	29.3	33.1
-11	2	2	8.5	7.9
-10	2	2	7.2	-7.6
-8	2	2	15.3	-15.4
-7	2	2	27.7	-26.7
-6	2	2	8.4	6.9
-5	2	2	27.5	29.9
-4	2	2	30.2	26.7
-3	2	2	7.2	5.3
-2	2	2	38.2	-41.6
0	2	2	30.9	-22.8
3	2	2	18.2	-17.5
4	2	2	4.6	4.2
5	2	2	5.2	-2.4
6	2	2	16.8	14.7
7	2	2	13.5	18.6
10	2	2	14.5	14.3
-15	2	3	9.0	-10.3
-14	2	3	13.5	-14.5
-12	2	3	14.7	15.4
-11	2	3	21.3	21.4
-9	2	3	32.9	-35.0
-8	2	3	10.3	-8.4
-7	2	3	3.3	3.2
-6	2	3	31.4	30.8
-5	2	3	2.7	-4.3
-4	2	3	11.7	10.4
-3	2	3	15.7	16.7
-2	2	3	21.6	-21.7
-1	2	3	15.4	-18.1
0	2	3	38.4	-39.5
2	2	3	53.9	57.2
3	2	3	41.7	41.4
4	2	3	8.2	-7.6
5	2	3	33.1	-33.9
6	2	3	29.4	-30.5
7	2	3	13.1	-12.4
8	2	3	19.0	18.8
9	2	3	26.4	28.2
-11	2	4	8.5	9.7
-10	2	4	10.2	-8.9
-9	2	4	7.9	-7.4
-7	2	4	14.1	11.6
-6	2	4	36.1	38.9
-4	2	4	12.6	-11.2
-3	2	4	9.4	-10.1
-2	2	4	33.7	34.2
-1	2	4	20.1	30.8
0	2	4	20.2	19.6
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-6	5	3	16.0	-16.5
-5	5	3	13.8	-14.3
-4	5	3	5.2	5.7
-3	5	3	17.2	21.1
-2	5	3	26.0	32.8
-1	5	3	12.4	-10.8
0	5	3	27.3	-32.1
1	5	3	18.7	-18.0
2	5	3	10.6	9.3
3	5	3	14.4	12.4
4	5	3	9.3	8.7
8	5	3	6.7	-5.5
9	5	3	11.1	-10.1
-9	5	4	14.3	13.8
-8	5	4	9.5	-8.3
-7	5	4	8.0	-7.0
-4	5	4	6.8	-5.9
-2	5	4	5.0	4.5
-1	5	4	16.4	17.9
0	5	4	24.6	26.1
2	5	4	24.5	-25.7
3	5	4	14.4	-12.9
5	5	4	19.0	16.0
6	5	4	19.6	16.4
8	5	4	8.0	-8.3
-11	5	5	7.4	7.1
-9	5	5	6.7	7.4
-8	5	5	18.5	-16.9
-7	5	5	17.5	-17.2
-5	5	5	27.2	28.7
-4	5	5	19.6	18.9
-2	5	5	20.1	-21.4
-1	5	5	13.6	-17.6
0	5	5	5.6	-5.0
1	5	5	23.6	24.7
2	5	5	16.0	-14.8
3	5	5	10.9	10.1
4	5	5	4.6	4.2
5	5	5	4.7	4.8
7	5	5	6.1	-6.1
8	5	5	9.9	-8.5
9	5	5	5.7	5.7
-12	5	6	8.2	7.1
-11	5	6	4.2	5.3
-7	5	6	6.7	5.0
-5	5	6	12.9	-11.1
-4	5	6	4.4	2.6
-3	5	6	17.9	16.1
-2	5	6	20.1	16.3
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1	5	6	27.7	-30.1
2	5	6	6.4	4.7
3	5	6	16.2	13.7
4	5	6	8.2	7.2
6	5	6	6.6	-6.6
7	5	6	7.5	-7.0
-12	5	7	6.4	8.2
-10	5	7	10.7	-7.6
-9	5	7	10.3	-9.7
-8	5	7	6.7	-5.8
-7	5	7	19.7	17.1
-6	5	7	14.2	17.2
-4	5	7	13.9	-11.9
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0	5	7	6.5	4.8
1	5	7	4.7	-4.2
2	5	7	6.7	5.9
3	5	7	4.6	5.2
5	5	7	11.4	-10.4
8	5	7	6.4	6.6
-7	5	8	6.7	-7.0
-6	5	8	4.8	-5.6
-5	5	8	4.6	3.8
-4	5	8	14.3	13.2
-2	5	8	14.2	-13.7
-1	5	8	16.4	-19.4
1	5	8	5.3	9.5
2	5	8	14.3	13.3
4	5	8	7.0	-8.8
-9	5	9	7.2	6.7
-8	5	9	4.4	4.6
-5	5	9	11.6	-9.3
3	5	9	6.3	-5.9
6	5	9	6.1	8.0
-7	5	10	6.1	6.3
-6	5	10	6.3	6.4
-5	5	10	4.5	3.4
-4	5	10	10.2	-9.6
-3	5	10	11.3	-10.0
-1	5	10	10.2	9.1
0	5	10	12.8	10.5
2	5	10	6.0	-5.2
1	5	11	3.9	-5.2
2	5	11	3.7	-4.3
-8	5	12	4.1	5.4
-7	5	12	4.6	4.4
-6	5	12	4.9	-5.8
-5	5	12	6.2	-5.7
-3	5	12	6.4	5.5
-2	5	12	5.2	5.0
-6	6	0	17.4	15.4
-5	6	0	6.4	4.2
-4	6	0	11.6	-11.0
-3	6	0	20.9	-22.0
-2	6	0	17.2	-19.5
-1	6	0	10.6	13.3
-2	6	1	11.0	-11.6
0	6	1	2.1	3.7
2	6	1	4.6	5.7
3	6	1	5.4	-4.2
-8	6	2	11.2	11.0
-7	6	2	7.0	6.9
-6	6	2	8.3	-7.6
-5	6	2	20.1	-19.9
-4	6	2	10.1	-9.0
-2	6	2	25.8	34.1
-1	6	2	12.7	14.8
0	6	2	8.5	-8.2
1	6	2	23.0	-27.3
2	6	2	9.8	-9.3
3	6	2	11.7	10.2
4	6	2	16.2	14.7
5	6	2	10.7	9.7
-3	6	3	5.6	-5.4
-1	6	3	5.1	4.1
1	6	3	9.4	-10.0
2	6	3	5.9	5.6
4	6	3	6.7	5.6
6	6	3	7.1	-6.9
7	6	3	4.6	-6.6
-7	6	4	16.0	-19.2
-6	6	4	13.0	-12.6
-5	6	4	9.5	9.7
-4	6	4	21.2	23.1
-3	6	4	15.3	19.5
-2	6	4	4.2	-4.3
-1	6	4	17.4	-19.3
0	6	4	17.7	-23.3
1	6	4	18.3	19.6
2	6	4	6.4	5.9
-8	6	5	6.5	8.7
-1	6	5	6.4	-6.3
1	6	5	10.5	10.1
2	6	5	6.5	5.9
4	6	5	7.1	-6.0
-8	6	6	17.5	-17.5
-6	6	6	15.9	15.0
-5	6	6	13.1	13.4
-4	6	6	9.8	-10.1
-3	6	6	15.4	-14.8
-2	6	6	10.8	-9.5
0	6	6	8.4	8.4
2	6	6	11.1	-10.7
3	6	6	7.1	8.4
-4	6	7	7.1	-6.7
2	6	7	8.6	-9.1
-5	6	8	13.9	-14.6
2	6	8	8.3	6.6

Table 3.3

(a) Fractional Coordinates

	x/a	y/b	z/c
S(1)	0.79981(17)	0.32531(35)	0.31025(19)
S(2)	0.85792(18)	0.67855(36)	0.37083(20)
O(1)	0.78093(52)	0.39580(104)	0.19945(51)
O(2)	0.84364(58)	0.14311(101)	0.33323(74)
N(1)	0.87640(57)	0.45611(110)	0.39800(66)
C(1)	0.67605(63)	0.32173(120)	0.34454(66)
C(2)	0.58695(69)	0.41133(137)	0.27602(79)
C(3)	0.48981(71)	0.40611(145)	0.30350(87)
C(4)	0.47769(73)	0.31729(139)	0.39683(86)
C(5)	0.56633(76)	0.22768(159)	0.46520(77)
C(6)	0.66554(73)	0.23120(141)	0.43741(74)
C(7)	0.37127(87)	0.31236(186)	0.42632(118)
C(8)	0.97817(106)	0.75244(171)	0.33481(104)
C(9)	0.88381(81)	0.77898(169)	0.50629(93)

Table 3.3 (contd.)

(b) Anisotropic Temperature Factors $(\mathring{A}^2)$

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
S(1)	0.0435	0.0546	0.0571	-0.0034	0.0210	0.0029
S(2)	0.0458	0.0553	0.0590	0.0060	0.0005	0.0033
O(1)	0.0672	0.0870	0.0522	0.0066	0.0457	-0.0110
O(2)	0.0689	0.0510	0.1231	-0.0082	0.0602	0.0160
N(1)	0.0440	0.0544	0.0730	0.0200	-0.0230	-0.0105
C(1)	0.0421	0.0445	0.0484	-0.0089	0.0027	-0.0177
C(2)	0.0449	0.0577	0.0609	0.0171	0.0026	0.0133
C(3)	0.0421	0.0621	0.0778	0.0085	0.0083	0.0076
C(4)	0.0478	0.0555	0.0819	-0.0377	0.0250	-0.0234
C(5)	0.0566	0.0821	0.0527	0.0103	0.0183	-0.0256
C(6)	0.0548	0.0581	0.0504	0.0092	0.0135	-0.0119
C(7)	0.0589	0.0951	0.1276	-0.0854	0.0805	-0.0576
C(8)	0.1075	0.0722	0.0928	0.0100	0.1195	-0.0401
C(9)	0.0565	0.0829	0.0776	-0.0451	0.0326	-0.0042

Average estimated standard deviations $(\mathring{A}^2)$

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
S	0.0012	0.0016	0.0012	0.0023	0.0019	0.0023
O	0.0042	0.0047	0.0050	0.0077	0.0073	0.0074
N	0.0038	0.0051	0.0049	0.0080	0.0069	0.0074
C	0.0056	0.0073	0.0073	0.0107	0.0096	0.0102

Table 3.4

Interatomic Distances (Å) and Angles (°) with estimated standard deviations in parentheses

(a) Bonded Distances

S(1)-O(1)	1.438(7)	C(1)-C(2)	1.411(12)
S(1)-O(2)	1.425(8)	C(1)-C(6)	1.366(13)
S(1)-N(1)	1.591(8)	C(2)-C(3)	1.382(13)
S(1)-C(1)	1.755(8)	C(3)-C(4)	1.371(15)
S(2)-N(1)	1.636(8)	C(4)-C(5)	1.406(14)
S(2)-C(8)	1.801(13)	C(4)-C(7)	1.510(15)
S(2)-C(9)	1.794(12)	C(5)-C(6)	1.409(13)

(b) Interbond Angles

O(1)-S(1)-O(2)	118.8(5)	S(1)-C(1)-C(2)	120.2(7)
O(1)-S(1)-N(1)	112.8(4)	S(1)-C(1)-C(6)	120.1(7)
O(1)-S(1)-C(1)	106.9(4)	C(2)-C(1)-C(6)	119.7(8)
O(2)-S(1)-N(1)	104.6(4)	C(1)-C(2)-C(3)	119.6(9)
O(2)-S(1)-C(1)	106.2(4)	C(2)-C(3)-C(4)	121.7(9)
N(1)-S(1)-C(1)	106.9(4)	C(3)-C(4)-C(5)	118.9(9)
N(1)-S(2)-C(8)	104.3(5)	C(3)-C(4)-C(7)	121.3(9)
N(1)-S(2)-C(9)	102.2(5)	C(5)-C(4)-C(7)	119.8(9)
C(8)-S(2)-C(9)	98.4(5)	C(4)-C(5)-C(6)	119.9(9)
S(1)-N(1)-S(2)	113.4(5)	C(1)-C(6)-C(5)	120.3(9)

Table 3.4 (contd.)

(c) Intramolecular Non-bonded Distances

S(1)...C(8)	3.80	O(2)...C(6)	2.98
S(2)...O(1)	2.94	N(1)...C(2)	3.69
S(2)...O(2)	3.87	N(1)...C(6)	3.31
S(2)...C(1)	3.44	C(1)...C(4)	2.80
S(2)...C(2)	3.91	C(2)...C(5)	2.78
O(1)...C(2)	2.90	C(2)...C(7)	3.79
O(1)...C(6)	3.83	C(3)...C(6)	2.77
O(1)...C(8)	3.71	C(6)...C(7)	3.82
O(2)...C(2)	3.75		

(d) Intermolecular Distances

S(2)...O(2^{I})	3.36	C(2)...C(4^{III})	3.60
O(1)...C(5^{II})	3.62	C(4)...C(4^{V})	3.62
O(1)...C(6^{II})	3.37	C(4)...C(5^{V})	3.80
O(1)...C(7^{III})	3.71	C(4)...C(7^{V})	3.69
O(2)...C(8^{IV})	3.29	C(5)...C(7^{V})	3.58
O(2)...C(9^{IV})	3.35	C(6)...C(7^{V})	3.77
C(2)...C(3^{III})	3.75	C(7)...C(9^{V})	3.66

Roman numerals as superscripts refer to the equivalent positions which should be applied to the coordinates of the second atom :

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

Table 3.5

Least-squares Planes

given in the form $\ell X' + mY' + nZ' = d$,
where X', Y' and Z' are coordinates in Å

(a) Plane equations

Plane (1) : $-0.2373\,X' - 0.8437\,Y' - 0.4815\,Z' = -4.9956$

Plane (2) : $0.6806\,X' - 0.0301\,Y' - 0.7321\,Z' = 5.7711$

Plane (3) : $-0.4542\,X' + 0.8439\,Y' - 0.2857\,Z' = -1.3259$

(b) Deviation of atoms (Å) from planes (starred atoms not used to define plane)

Plane (1) : S(1) 0.003, O(1)* 0.271, C(1) -0.003, C(2) -0.003, C(3) 0.003, C(4) -0.004, C(5) -0.001, C(6) 0.001, C(7) 0.003

Plane (2) : S(1) 0.000, S(2) 0.000, N(1) 0.000

Plane (3) : S(2) 0.000, C(8) 0.000, C(9) 0.000

(c) Dihedral angles between planes (°)

(1) - (2) 77.5, (1) - (3) 62.2, (2) - (3) 82.8

Figure 3.1

Atomic numbering scheme

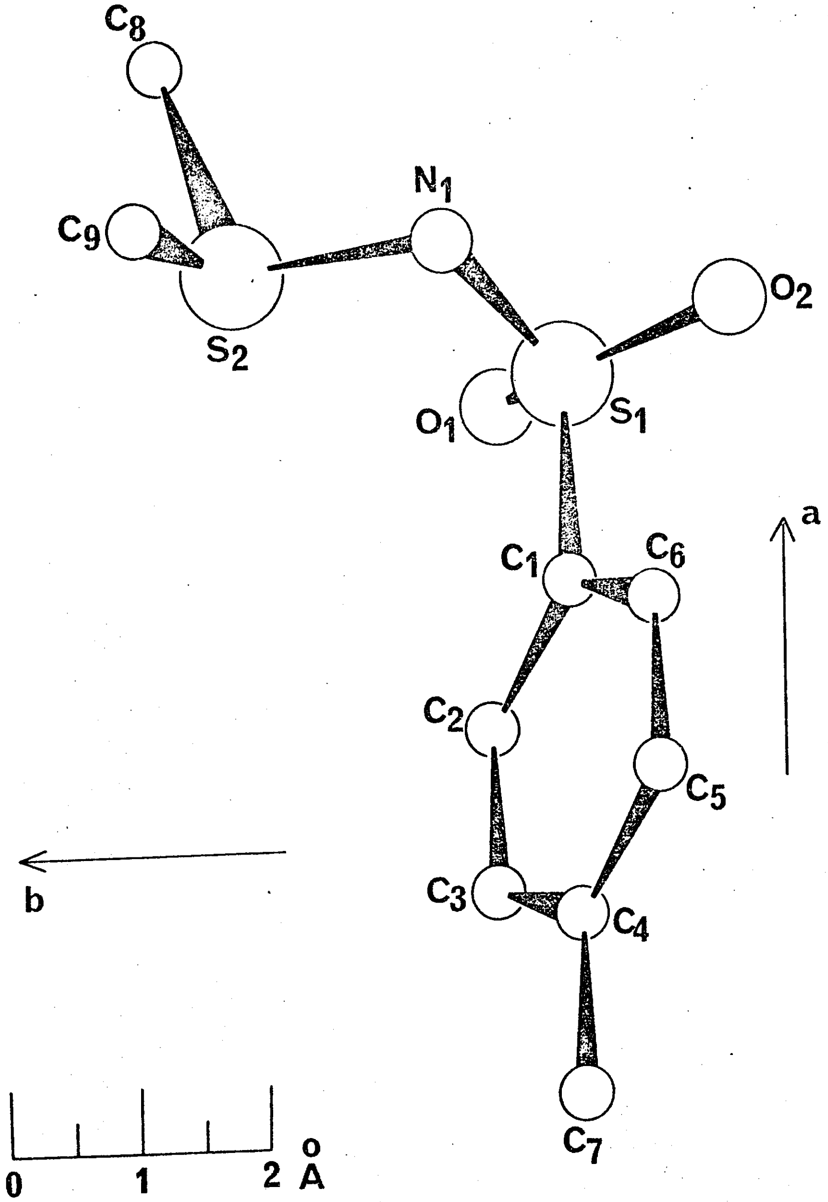

C8
C9
S2
N1
O2
O1
S1
a
C1
C6
C2
C5
b
C3
C4
C7
0
1
2 Å

Figure 3.2

Molecular packing arrangement viewed along the b-axis

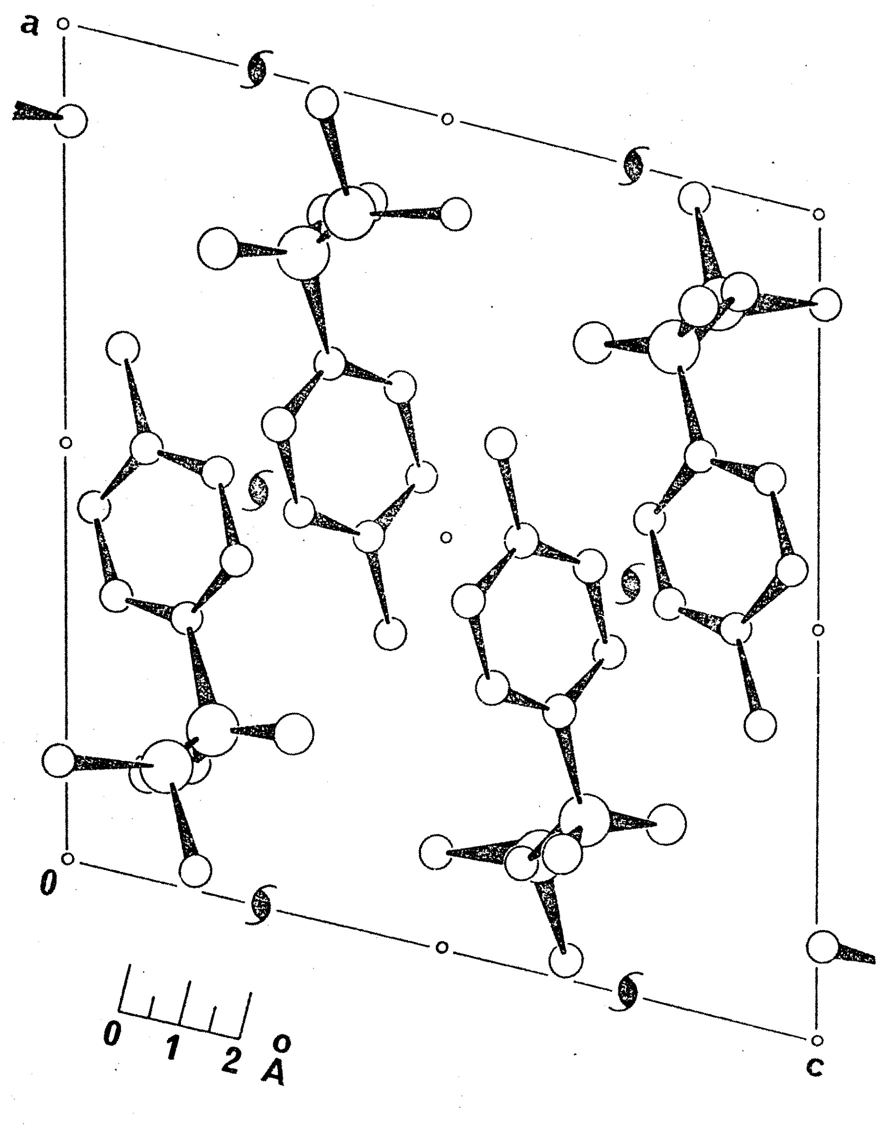
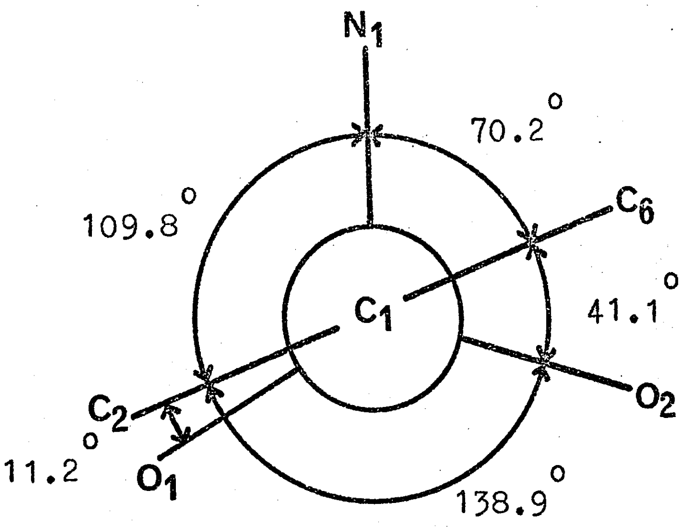

a
0
c
0 1 2 Å

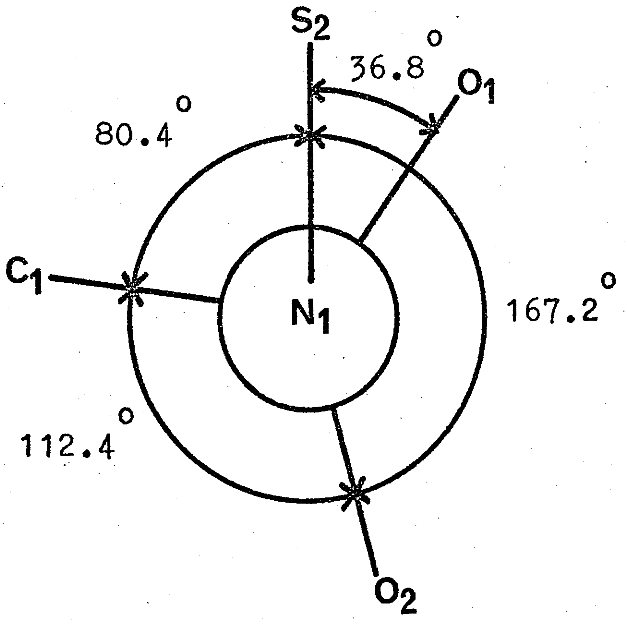
Figure 3.3

Newman projections illustrating the solid-state conformation of (I)



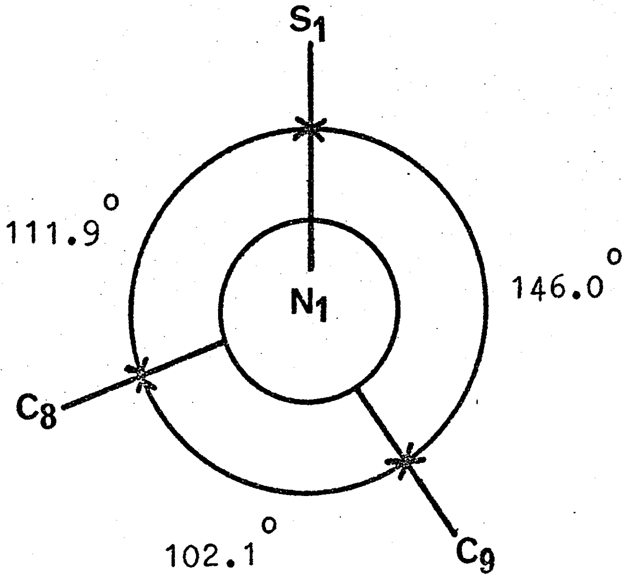
C(1) - S(1)

Projection



N(1) - S(1)

Projection



N(1) - S(2)

Projection

3.3 DISCUSSION

The structure analysis of compound (I) has not only provided evidence supporting the involvement of d-orbitals in the bonding systems of second-row ylides, but has also revealed various geometrical features apparently peculiar to the class of sulphonyl-stabilised ylide (X = S; Y = N—). Moreover, the results obtained allow useful comparisons to be made with the bonding systems of several similar molecules.

The occurence of d-orbital involvement in the S-N-S bonding system of molecule (I) should be accompanied by a shortening of the two relevant sulphur - nitrogen bonds. Thus, to the extent that the N(1)-S(1) [1.591(8) Å] and N(1)-S(2) [1.636(8) Å] bonds are considerably shorter than the value which might be expected for an S-N single bond (1.74 Å from Pauling's covalent radii,[69] and 1.76(2) Å for sulphamic acid [104]), the observed dimensions are consistent with significant involvement of the d-orbitals of the sulphonyl-sulphur S(1) and the 'onium-sulphur S(2) in delocalisation of the nitrogen lone-pair electrons through the S(1)-N(1)-S(2) system.

Comparison of the dimensions of (I) with those of the similar ylides (II) [N(1)-S(2) 1.633(9); N(1)-S(1) 1.581(10) Å][50] and (III) [N(1)-S(2) 1.628(7); N(1)-S(1) 1.598(8) Å][51] reveals that, in all three molecules, the N(1)-S(1) and N(1)-S(2) bonds are experimentally equal. This similarity in the dimensions of (I), (II) and (III) therefore suggests, contrary to a previous postulate,[105] that, within the errors of the three structure determinations, interchanging aliphatic and aromatic substituents does not produce significant changes in the bonding of the three S-N-S systems. Further evidence of the non-interaction of the π-system of the S-N-S moiety with that of the aromatic ring in (I) may be inferred from the essentially normal dimensions of the ring (mean C-C 1.39(1) Å) and the length of the connecting S(1)-C(1) bond [1.755(8) Å] which is comparable to that expected for S-C(sp^2) bonds.[66]

It is noticeable that in each of the molecules (I), (II) and (III) the S(1)-N(1) bond is significantly shorter [24] than the respective S(2)-N(1) bond, and although the different bonding environments of the two sulphur atoms, S(1) and S(2), render difficult any direct comparison of these two bonds, it has been suggested [51] that the greater effectiveness of the S(1)-N(1) bond can be attributed to the higher electronegativity of the S(1) atom [oxidation state (VI)] relative to the S(2) atom [oxidation state (IV)]. However, inherent in such previous descriptions of the S-N-S bonding system has been a neglect of the possible involvement of the second lone-pair of electrons of the nitrogen atom, except in steric considerations. When involvement of the two nitrogen lone-pairs is considered, it is possible to visualise delocalisation *via* both an overlap component which involves appropriate linear combinations of the sulphur *d*-orbitals lying perpendicular to the S-N-S plane (π-bonding) and also an overlap component (σ'-bonding) involving combinations of sulphur *d*-orbitals lying in the S-N-S plane (see Introduction to PART II). Moreover, theoretical calculations on thionylimide (H-N-S=O) predict significant interactions of the π and σ' type when the *d*-orbitals of the sulphur atom are included in the calculations.[106] However, in the particular cases of (I), (II) and (III), the existence of a lone-pair of electrons on S(2) located approximately in the S-N-S planes of all three molecules will possibly destabilise the in-plane d-orbitals of the respective S(2) atoms, as has been suggested in the analogous cases of $(S-N)_n$ cyclic compounds,[55] and will therefore tend to inhibit σ' bonding in the S(2)-N(1) bonds relative to the S(1)-N(1) bonds. In accord with this suggestion, the S(2)-N(1) bonds are significantly longer [24] than the S(1)-N(1) bonds, although it is probably unjustified to ascribe this feature solely to such an effect.

An interesting comparison may be made, in this context, with the appropriate dimensions of the N-alkylated compound (IV),[105] since alkylation of ylides such as (I → III) would be expected to remove the σ' component of the bonding as a result of the single lone-pair of electrons of the nitrogen atom being located in a p-type orbital approximately perpendicular to the S-N-S plane, as is suggested by the geometry of (IV). Such a comparison reveals that the major effect of the N-alkylation is to produce a lengthening of the S(1)-N(1) bond [1.681(5) Å], while leaving the S(2)-N(1) length unchanged [1.644(5) Å], and is thus consistent with the lone-pair of electrons in each of molecules (I), (II) and (III), which is not bonded to an additional alkyl substituent, being involved in the formation of at least a weak σ' interaction only in the respective S(1)-N(1) bonds. Furthermore, the possibly significant lengthening [24] of the S(1)-O bonds in (I) [mean 1.432(7) Å] compared to the corresponding values in (IV) [mean 1.411(5) Å] appears to support the suggested increase in charge delocalisation into the N-sulphonyl system of (I). The former value has been taken to indicate a π-bond order of ca. 0.66 for S-O bonds.[57]

It is perhaps worthy of comment that, in (IV) where only a π-type d-orbital interaction is possible, the greater effectiveness of the S(2)-N(1) bond may be rationalised in terms of the relative electronegativities of the two sulphur atoms. Truter has suggested that S(VI) [S(1)] is more electronegative than S(IV) [S(2)] ,[107] thus, if the d-orbital involvement is represented by a "back-bonding" model as has been proposed for systems involving second-row elements bonded to electronegative atoms,[43] a greater inductive withdrawal via the σ-bond framework can be predicted to occur from S(IV) as a result of the greater electronegativity difference between S(IV) and N(1) than between S(VI) and N(1). This presents a better opportunity for back-donation of the nitrogen p-type lone-pair of electrons into vacant d-orbitals via a π-overlap component in S(IV) than in S(VI), and thus the N(1)-S(IV) bond would be predicted to be the more effective bond, in agreement with the observed dimensions.[105]

Further discussion of the relative efficiencies of different stabilising groups, and comparison of second-row ylides belonging to the class (X = S; Y = O, N—, C<) will be made subsequently in Section 5.

The solid-state conformation of molecule (I), which is similar to that of (II)[50] and (III),[51] is best described in terms of the three Newman projections along the C(1)-S(1), N(1)-S(1) and N(1)-S(2) bonds (Figure 3.3). The main feature of the C(1)-S(1) projection is the asymmetric disposition of the aromatic ring plane relative to the sulphonyl grouping [O(1)...C(2) 2.90 Å; O(2)...C(6) 2.98 Å], the C(2)-C(1)-S(1)-O(1) torsion angle being -11.2°, and it is possible that this conformation is favoured in order to reduce steric interactions between C(2) and S(2). Although the C(2)...S(2) contact [3.91 Å] is not anomalously short, the lone-pair of electrons on S(2) appears to be so located that it could possibly repel C(2), and therefore cause the observed twist of the aromatic ring. Further interest arises from the semi-gauche relationship of O(1) and S(2), the S(2)-N(1)-S(1)-O(1) torsion angle being +36.8°, similar values having been obtained for the corresponding angles in (II) [31.7°] and (III) [34.0°]. The possible importance of this conformation in the S-N-S bonding systems of these molecules will be discussed in Section 5.

Examination of the N(1)-S(2) projection of (I) reveals an asymmetric orientation of the S(1)-N(1) bond with respect to the two methyl substituents of S(2), and it is possible that this arrangement has been determined by the S(2) lone-pair of electrons in order to minimise not only steric repulsions with both methyl groups, but also electronic repulsions with both nitrogen lone-pairs. Accordingly, a recent theoretical treatment of rotation about the N(1)-S(2) bond in sulphonyl-stabilised second-row ylides of the type (X = S; Y = N—) has suggested that the rotational characteristics of the N(1)-S(2) π-bond seem to be controlled mainly by steric effects.[108]

Further features of the conformation of (I) are the approximately tetrahedral and pyramidal arrangements around S(1) and S(2) respectively, which are similar to those observed in comparable molecules.[2,3,18,19] Examination of the previously undiscussed regions of molecule (I) reveals dimensions which do not differ significantly from normally accepted values.[66] In particular, both S(2)-C(sp^3) bonds [mean 1.798(12) Å] are essentially pure single bonds [66] and do not differ significantly from each other, contrary to the effect observed in similar compounds.[51] Apart from those already mentioned, the only other short intramolecular non-bonded distance of interest is S(2)...O(1) [2.94 Å], and while shorter than the sum of the van der Waals' radii [~3.25 Å], it is probably of much less significance than the corresponding short contacts observed in first-row ylides (see Section 1.3).

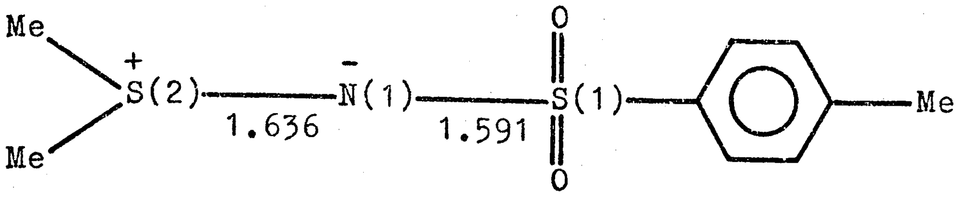
Since there are no anomalously short intermolecular contacts, it may be assumed that the crystal-packing has been determined by van der Waals' forces.

4. THE CRYSTAL AND MOLECULAR STRUCTURE OF N-(p-TOLUENESULPHONYL)-IMINOTRIPHENYLPHOSPHORANE : A SULPHONYL-STABILISED SECOND-ROW YLIDE.

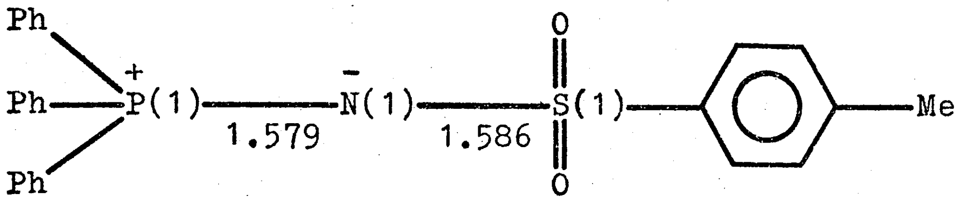
4.1 INTRODUCTION

It has already been suggested in Section 3.3, from the structure analysis of the sulphonyl-stabilised ylide (I)[103] which represents the class of ylides (X = S; Y = N—), that d-orbitals of the 'onium group X may be involved in the bonding systems of such second-row ylides, and moreover that, in molecules where extra stabilisation is achieved *via* further delocalisation of the Y atom lone-pairs of electrons into a vicinal sulphonyl grouping, there is the additional possibility of involvement of the d-orbitals of the sulphonyl-sulphur atom in the overall bonding pattern.

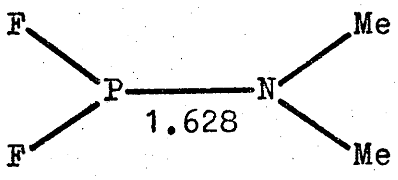
In order to further investigate the bonding and stereochemistry of such systems, and also to examine an ylidic bond $\overset{+}{X} - \overset{-}{Y}$ in which both π and σ' overlap components are feasible, the crystal structure of N-(p-toluenesulphonyl)-iminotriphenylphosphorane (II), which is representative of ylides of the type (X = P; Y = N—), has been determined.[103]


Me
Me
S(2)
N(1)
S(1)
O
O
Me
1.636
1.591

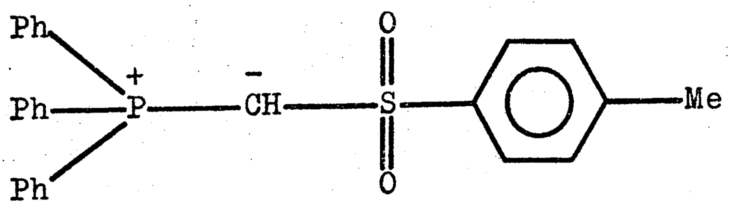
(I)


Ph
Ph
Ph
P(1)
N(1)
S(1)
O
O
Me
1.579
1.586

(II)


F
F
P
N
Me
Me
1.628

(III)


Ph
Ph
Ph
P
CH
S
O
O
Me

(IV)

4.2 EXPERIMENTAL

Crystal Data

(II); N-(p-toluenesulphonyl)-iminotriphenylphosphorane,

$C_{25}H_{22}NO_2PS$, M = 433.5.

Triclinic, a = 11.582(8), b = 9.049(19), c = 13.144(23) Å,

α = 99.99(9), β = 113.34(8), γ = 60.57(6)°, U = 1101.4 $Å^3$.

D_m = 1.28 $g.cm.^{-3}$ (by flotation in aqueous KI), Z = 2,

D_c = 1.30 $g.cm.^{-3}$, F(000) = 452.

Space group $P\bar{1}$ (C_i^1 , No.2).

Linear absorption coefficient for X-rays (λ = 0.7107 Å),

μ = 2.37 $cm.^{-1}$.

Crystallographic Measurements

The unit cell dimensions were initially determined from oscillation and Weissenberg photographs taken with Cu-K_α (λ = 1.5418 Å) radiation, and from precession photographs taken with Mo-K_α (λ = 0.7107 Å) radiation. Refined values for these parameters were subsequently obtained, by least-squares techniques, from the Busing and Levy orientation-matrix program [63] prior to the data collection. The lack of reciprocal lattice symmetry and systematic extinctions restricted the choice of space group to either P1 or $P\bar{1}$. Statistical tests indicating a centric distribution of the data, and also the presence of two molecules in the unit cell, implied that the space group should be $P\bar{1}$, a choice which was later vindicated by the least-squares refinement of the crystal structure.

Table 4.1 contains details of the crystal morphology and data collection for compound (II). Intensity measurements were made on a Hilger and Watts Y290 computer-controlled diffractometer using Mo-K_α radiation, structure amplitudes on an overall non-absolute scale being obtained by applying the appropriate Lorentz and polarisation factors. Absorption effects were considered small and were ignored.

Structure Determination

The structure was solved by a combination of methods, namely, the phase-determining heavy-atom method,[11] and the symbolic addition method [19] using programs developed by Stewart et al.[64] and modified by the Glasgow group.

At first it proved difficult to solve a three-dimensional Patterson synthesis, and it was therefore decided to attempt a concurrent solution by the symbolic addition method. The data were initially placed on an absolute scale using the "K-curve" method,[6] normalised structure amplitudes subsequently being derived (see PART I, Section 2). A statistical analysis of the data, shown in Table 4.2, indicates a centric distribution appropriate to the centrosymmetric space group $P\bar{1}$.

$\sum_2$ relationships for use in the symbolic addition procedures were then generated for the 211 reflexions with $|E| \geq 1.90$. The phasing procedure, applied to the basic starting set shown in Table 4.3, determined the signs of the 211 reflexions in terms of the symbol 'a'. In order to depart from the trivial solution (i.e. all signs positive), the symbol 'a' was assigned the value -1, and an E-map, computed with the 211 signed E-values (101+, 110-) as coefficients, revealed 18 possible atomic sites. Each of the 211 signs determined subsequently proved to be correct.

The positions of the two highest peaks were found to coincide with the two heavy-atom positions which, meanwhile, had been derived from the Patterson function, thus indicating a good agreement between the two methods. Inclusion of the eighteen atomic positions in a structure-factor calculation yielded an R-value of 47 %, the entire structure being revealed in the electron-density distribution subsequently calculated. An improved set of coordinates, for refinement by least-squares methods, was obtained by performing two further rounds of structure-factor and electron-density calculations. After each structure-factor calculation, in which an overall isotropic thermal parameter $U_{iso} = 0.05\ \mathring{A}^2$ was assumed, the data were placed on an approximate absolute scale by equating $k\sum|F_o|$ and $\sum|F_c|$.

Structure Refinement

The refinement of positional, vibrational and overall-scale parameters by three-dimensional least-squares calculations converged after 13 cycles when R was 0.072 and R' ($= \sum w\Delta^2 / \sum w|F_o|^2$) was 0.004. Full details of the refinement are given in Table 4.4.

A difference synthesis, calculated at the end of the isotropic refinement, revealed the positions of all 22 hydrogen atoms. In later cycles, the hydrogen atom parameters were refined, individual isotropic thermal parameters $U_{iso} = 0.08 \mathring{A}^2$ being assumed as starting values.

In the initial stages of the refinement all reflexions were assigned unit weights. Moreover, since in later cycles it was found, from an ($|F_o|$ and $\sin\theta/\lambda$) analysis of $w\Delta^2$, unnecessary to apply a weighting scheme to the data, the system of unit weights was maintained throughout the refinement process.

The refinement was judged to be complete when the calculated parameter shifts for a least-squares cycle were insignificant compared to the corresponding estimated standard deviations. The subsequent calculation of an electron-density distribution and a difference synthesis revealed no errors in the structure. Observed and final calculated structure factors are listed in Table 4.5. In all the structure-factor calculations, the atomic scattering factors used were taken from 'International Tables for X-Ray Crystallography,' Vol.III.[65]

The final fractional coordinates and thermal parameters are given in Table 4.6, the hydrogen atoms being numbered according to the numbering of the attached atoms. In Table 4.6 the values of U_{ii} and $2U_{ij}$ refer to the anisotropic temperature factor expression given in PART I, Section 3. All bond lengths, valency angles, and pertinent intra- and inter-molecular non-bonded distances are shown in Table 4.7. Included in Tables 4.6 and 4.7 are the appropriate estimated standard deviations, σ, derived from the inverse of the least-squares normal equation matrix. The average σ for S-O, S-N, S-C, P-N, P-C, C-C and C-H bonds are 0.003, 0.004, 0.004, 0.004, 0.004, 0.006 and 0.05 Å respectively, while for valency angles the average σ is 0.4°. These are probably best regarded as minimum values, since the block-diagonal approximation was used in the latter stages of the refinement owing to computer-storage limitations.

Details of least-squares planes calculated for various portions of the molecular framework are given in Table 4.8. The atomic numbering scheme, used in every table, and the molecular packing projected onto the *ac*-plane are shown in Figures 4.1 and 4.2 respectively.

Table 4.1

Details of Crystal Morphology and Data Collection

	Compound(II)
Crystal shape	Flat plate
Crystal size (mm.)	0.5 × 0.2 × 0.1
Rotation axis	$\underline{b}^*$
Scan technique	2θ
Step size (°)	0.02
Number of steps	40
Step time (secs)	2
Total background count (secs)	40
Radiation filter	Zr
2θ range (°)	$0 \rightarrow 50$
Independent reflexions	3276 (with $I > 0$)

Table 4.2

Statistical Analysis of the Data

	Theoretical		Experimental
	Centric	Acentric	Compound (II)
Average $\|E\|$	0.798	0.886	0.796
Average $\|E\|^2$	1.000	1.000	1.000
Average $\|E^2 - 1\|$	0.968	0.736	0.965
$\|E\| > 1$	31.73	36.79	32.15
$\|E\| > 2$	4.55	1.83	4.82
$\|E\| > 3$	0.27	0.01	0.25

Table 4.3

Origin-defining and Variable Reflexions

h	k	ℓ		Sign	E
9	2	-7	O.D.	+1	3.47
6	1	-4	O.D.	+1	3.33
7	0	-8	O.D.	+1	3.29
-4	3	7	Variable	a	3.14

Correct solution has the symbol 'a' equal to -1.

Table 4.4

Course of Refinement

Cycles	Parameters refined	Final R	Final R'
1 - 3	x, y, z, U_{iso} for S, P, O, N, C, Overall scale factor, Full matrix, unit weights.	0.143	0.017
4 - 8	x, y, z, U_{ij} for S, P, O, N, C, Overall scale factor, Block diagonal, unit weights, H-atom contributions included but not refined.	0.080	0.006
9 - 11	x, y, z, U_{iso} for H only, Overall scale factor, Block diagonal, unit weights, other atom contributions included but not refined.	0.074	0.005
12 - 13	x, y, z, U_{ij} for S, P, O, N, C, x, y, z, U_{iso} for H, Overall scale factor, Block diagonal, unit weights.	0.072	0.004

Table 4.5

Observed structure amplitudes and
final calculated structure factors

H	K	L	F OBS	F CALC
11	2	-3	11.1	-11.6
11	2	-5	16.1	16.0
11	2	-6	6.2	-6.5
11	2	-8	4.4	-5.6
11	2	-9	10.1	-11.8
11	2	-11	6.7	7.1
11	1	2	7.9	8.0
11	1	1	11.6	12.2
11	1	0	1.8	-1.6
11	1	-1	2.8	-2.5
11	1	-3	4.5	-3.3
11	1	-4	10.4	10.6
11	1	-5	11.0	11.0
11	1	-6	10.8	-11.9
11	1	-7	20.2	-20.6
11	1	-8	8.6	-8.5
11	1	-9	3.4	2.8
11	1	-11	2.9	-2.5
11	1	-12	6.4	-6.1
11	0	0	6.1	-5.0
11	0	-1	8.6	-8.7
11	0	-2	4.3	4.2
11	0	-3	6.6	6.5
11	0	-4	2.2	-2.2
11	0	-5	1.2	-0.2
11	0	-6	6.1	-4.4
11	0	-7	14.9	-15.7
11	0	-9	10.3	10.9
11	0	-10	2.2	-1.1
10	10	-2	7.7	5.6
10	10	-3	3.1	-2.9
10	10	-4	2.4	-2.8
10	10	-5	1.9	-1.3
10	10	-7	7.1	5.4
10	9	1	3.7	2.0
10	9	-1	2.9	3.3
10	9	-2	3.9	1.5
10	9	-3	11.0	-9.2
10	9	-4	5.1	-5.0
10	9	-5	8.3	8.1
10	9	-6	1.7	2.9
10	9	-7	4.3	3.7
10	9	-9	5.7	-5.4
10	9	-10	5.2	-4.3
10	8	3	4.5	-5.0
10	8	1	1.7	2.9
10	8	-1	6.3	-4.5
10	8	-2	2.6	-3.2
10	8	-3	3.8	-4.4
10	8	-4	3.1	-2.9
10	8	-5	7.5	8.0
10	8	-6	2.7	2.5
10	8	-7	4.9	-3.6
10	8	-8	5.1	-4.7
10	8	-9	1.2	1.2
10	8	-10	5.1	3.7
10	8	-11	9.8	7.9
10	7	4	2.3	1.0
10	7	3	7.6	-7.3
10	7	2	2.5	2.0
10	7	1	8.5	7.9
10	7	0	6.0	-4.4
10	7	-1	14.8	-14.2
10	7	-2	5.6	-5.2
10	7	-3	5.2	-5.6
10	7	-5	3.1	-1.6
10	7	-6	4.1	4.3
10	7	-7	0.6	-1.8
10	7	-8	5.6	-5.4
10	7	-9	6.7	5.7
10	7	-10	10.5	10.0
10	6	4	1.0	4.1
10	6	2	3.8	-5.2
10	6	1	4.9	3.7
10	6	0	3.1	0.3
10	6	-1	17.1	-16.0
10	6	-2	11.6	-12.0
10	6	-3	3.9	-4.4
10	6	-4	19.0	19.3
10	6	-5	5.5	-5.0
10	6	-6	3.9	4.3
10	6	-7	5.2	-4.9
10	6	-8	8.9	-7.9
10	6	-9	13.8	13.9
10	6	-10	19.4	18.7
10	6	-11	13.1	-12.6
10	6	-12	3.5	-3.1
10	6	-13	4.2	1.3
10	5	5	7.5	-5.6
10	5	2	5.6	-4.2
10	5	1	5.6	6.1
10	5	0	3.5	2.8
10	5	-1	10.4	-10.6
10	5	-2	2.8	-2.3
10	5	-3	14.7	15.1
10	5	-4	13.2	13.9
10	5	-5	14.4	-13.9
10	5	-6	3.2	-3.6
10	5	-7	10.6	11.3
10	5	-8	6.7	6.3
10	5	-9	3.8	-3.2
10	5	-10	3.5	-3.5
10	5	-11	9.7	-9.4
10	5	-12	5.7	-5.1
10	5	-13	3.8	3.0
10	5	-14	4.6	5.1
10	4	5	7.6	-7.1
10	4	4	2.4	0.0
10	4	3	13.8	13.4
10	4	2	0.9	1.1
10	4	1	5.5	-4.3
10	4	0	1.4	-2.0
10	4	-1	15.1	14.7
10	4	-2	1.0	-3.1
10	4	-3	13.4	13.8
10	4	-4	4.8	3.9
10	4	-5	7.6	-9.0
10	4	-6	6.4	-4.2
10	4	-7	13.9	14.4
10	4	-8	10.2	-10.9
10	4	-9	15.3	-16.0
10	4	-10	6.4	6.9
10	4	-11	5.5	3.7
10	4	-12	8.1	-7.7
10	4	-13	4.0	3.2
10	4	-14	8.4	7.2
10	3	5	3.5	0.2
10	3	4	4.8	6.2
10	3	3	6.3	5.6
10	3	2	3.6	-0.5
10	3	1	11.4	-12.4
10	3	0	9.2	-10.1
10	3	-1	26.4	27.5
10	3	-2	2.6	2.9
10	3	-3	0.8	1.3
10	3	-4	1.0	1.7
10	3	-5	22.1	-23.3
10	3	-6	9.1	-9.3
10	3	-7	21.7	23.2
10	3	-8	10.4	9.9
10	3	-9	4.9	-4.6
10	3	-10	6.0	-6.4
10	3	-11	2.9	2.0
10	3	-12	2.7	3.8
10	3	-13	2.9	-1.8
10	3	-14	5.4	3.0
10	2	3	6.6	-7.2
10	2	2	2.1	-2.4
10	2	1	13.0	-13.9
10	2	0	2.4	3.0
10	2	-1	21.1	21.3
10	2	-2	4.2	-4.1
10	2	-3	14.8	-15.1
10	2	-4	4.7	4.1
10	2	-5	2.7	1.5
10	2	-6	8.4	8.5
10	2	-7	16.5	18.1
10	2	-9	16.0	-15.1
10	2	-10	6.1	-5.9
10	2	-11	9.5	9.3
10	2	-12	2.3	1.5
10	2	-13	7.9	-8.2
10	2	-14	4.8	-3.9
10	1	4	5.8	-4.4
10	1	3	11.6	-11.7
10	1	1	3.2	4.6
10	1	-1	3.4	-3.2
10	1	-2	4.8	5.4
10	1	-3	2.0	-2.9
10	1	-4	6.7	7.2
10	1	-5	17.0	17.6
10	1	-6	7.6	-9.2
10	1	-7	9.1	-9.5
10	1	-8	2.5	2.6
10	1	-9	4.5	-4.9
10	1	-11	6.2	4.8
10	1	-12	2.7	-0.4
10	1	-13	11.1	-11.7
10	0	3	12.1	-11.6
10	0	2	2.7	3.8
10	0	1	9.3	9.5
10	0	0	1.2	-0.4
10	0	-1	3.1	1.6
10	0	-3	4.0	-3.8
10	0	-4	4.1	5.1
10	0	-5	9.9	9.8
10	0	-6	2.3	-2.1
10	0	-7	11.2	-11.2
10	0	-8	8.8	-8.2
10	0	-9	5.6	6.4
10	0	-10	7.1	6.4
10	0	-11	0.7	1.8
10	0	-12	7.2	-7.7
9	10	0	6.8	-8.1
9	10	-1	2.9	2.1
9	10	-4	6.5	4.4
9	10	-5	5.7	-5.7
9	10	-6	11.4	-10.0
9	10	-7	2.4	2.7
9	9	2	0.7	2.9
9	9	1	7.7	-7.6
9	9	0	6.4	-6.6
9	9	-1	7.2	7.2
9	9	-2	6.9	7.5
9	9	-3	6.2	-5.3
9	9	-4	6.8	-5.8
9	9	-5	4.3	-4.8
9	9	-6	3.2	-1.5
9	9	-7	8.4	7.5
9	9	-9	2.0	-3.4
9	9	-10	8.6	-7.6
9	8	4	6.4	5.9
9	8	3	3.1	-1.2
9	8	2	3.3	-3.0
9	8	1	1.9	-2.3
9	8	0	2.5	2.3
9	8	-1	7.7	6.7
9	8	-2	9.3	9.1
9	8	-3	7.4	-6.9
9	8	-4	5.9	-4.2
9	8	-5	2.8	2.4
9	8	-6	1.8	2.0
9	8	-7	4.6	-5.0
9	8	-8	0.7	0.8
9	8	-9	1.5	-2.6
9	8	-10	7.4	-6.4
9	8	-11	4.4	1.7
9	8	-12	10.7	9.4
9	7	5	5.5	5.0
9	7	4	5.5	6.3
9	7	3	5.4	-5.8
9	7	1	7.8	7.4
9	7	0	6.4	6.0
9	7	-1	2.8	2.5
9	7	-2	3.3	3.0
9	7	-5	13.1	-14.4
9	7	-6	12.4	10.9
9	7	-7	6.5	-5.6
9	7	-10	1.1	0.8
9	7	-11	5.6	4.5
9	7	-12	9.1	8.6
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9	6	3	6.7	-5.9
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7	1	4	15.5	-15.6
7	1	3	4.7	3.1
7	1	2	17.7	18.0
7	1	1	11.7	-12.4
7	1	0	12.7	-12.9
7	1	-1	12.1	16.0
7	1	-2	3.5	4.3
7	1	-3	2.5	-3.7
7	1	-4	3.7	4.0
7	1	-5	2.7	-3.9
7	1	-6	23.1	-23.5
7	1	-7	2.2	2.0
7	1	-8	32.0	32.1
7	1	-9	9.2	-9.0
7	1	-10	19.0	-20.2
7	1	-11	10.1	9.7
7	1	-12	11.9	-11.7
7	1	-13	4.4	-3.0
7	1	-14	13.4	13.0
7	0	8	4.4	3.7
7	0	7	2.1	1.6
7	0	6	1.7	1.7
7	0	5	5.5	-5.6
7	0	4	17.4	-17.6
7	0	3	8.2	8.5
7	0	2	16.4	16.0
7	0	1	3.1	2.4
7	0	0	11.0	-11.2
7	0	-1	8.5	-8.3
7	0	-2	26.7	26.7
7	0	-3	10.1	-9.6
7	0	-4	1.3	1.9
7	0	-5	2.7	2.8
7	0	-6	23.4	-24.0
7	0	-7	4.5	-5.1
7	0	-8	39.9	41.4
7	0	-9	15.0	-15.9
7	0	-10	12.2	-13.3
7	0	-11	10.7	-11.7
7	0	-13	7.4	7.1
7	0	-14	10.3	9.9
6	10	2	2.0	-1.3
6	10	1	7.3	-6.8
6	10	0	5.6	4.0
6	10	-1	6.3	5.5
6	10	-3	4.9	-6.9
6	10	-4	4.4	-2.4
6	10	-5	2.0	-2.4
6	10	-7	3.4	1.7
6	9	5	7.0	6.7
6	9	4	4.5	-3.5
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6	9	1	2.6	-1.9
6	9	0	3.6	2.3
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6	9	-2	12.2	-11.7
6	9	-3	11.2	-13.5
6	9	-4	1.8	2.6
6	9	-5	6.4	6.8
6	9	-6	1.5	-0.2
6	9	-8	2.0	-2.4
6	9	-9	4.2	-2.9
6	8	7	5.1	-3.0
6	8	6	8.9	7.4
6	8	5	3.1	4.0
6	8	4	9.0	-8.5
6	8	2	1.7	1.2
6	8	1	4.4	-2.5
6	8	0	10.5	-9.5
6	8	-1	11.5	10.3
6	8	-2	1.3	0.5
6	8	-3	9.5	-10.3
6	8	-5	17.9	18.2
6	8	-6	10.2	-9.3
6	8	-7	5.4	-3.9
6	8	-8	2.3	1.9
6	8	-11	1.0	2.6

H	K	L	F OBS	F CALC
6	7	8	2.6	4.0
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6	7	5	3.6	2.8
6	7	4	9.1	-7.5
6	7	3	6.4	-6.9
6	7	1	22.5	23.1
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6	7	-1	2.0	-2.7
6	7	-2	2.1	2.4
6	7	-3	11.1	-10.9
6	7	-4	1.7	-1.6
6	7	-5	20.5	20.3
6	7	-6	14.4	-14.5
6	7	-7	11.6	-11.9
6	7	-8	12.5	11.6
6	7	-9	5.3	4.5
6	7	-10	4.9	-5.8
6	7	-11	4.1	-2.8
6	7	-12	3.7	2.6
6	6	9	2.7	-3.3
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6	6	7	7.9	6.9
6	6	6	3.9	-3.0
6	6	5	4.0	-5.4
6	6	4	3.6	-2.5
6	6	2	37.3	38.0
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6	6	0	29.5	-29.8
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6	6	-5	11.1	-10.9
6	6	-6	7.4	-6.6
6	6	-7	8.2	-7.6
6	6	-8	14.2	14.8
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6	6	-10	3.3	-1.2
6	6	-11	2.2	2.7
6	6	-12	5.9	4.7
6	6	-13	3.7	0.9
6	6	-14	3.0	1.6
6	5	9	1.2	-0.8
6	5	8	10.0	9.5
6	5	7	6.2	7.1
6	5	6	6.4	-7.2
6	5	5	4.4	-3.9
6	5	4	15.4	15.9
6	5	3	2.8	2.4
6	5	2	2.2	1.5
6	5	1	10.2	-10.5
6	5	0	11.6	-12.4
6	5	-1	2.3	-2.2
6	5	-2	1.9	3.6
6	5	-3	2.0	0.3
6	5	-4	21.7	-21.6
6	5	-5	10.0	-10.0
6	5	-6	7.0	8.1
6	5	-7	4.4	-3.4
6	5	-8	12.6	14.1
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6	5	-10	5.6	-4.9
6	5	-11	17.8	-18.0
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6	5	-14	1.9	1.0
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6	4	9	3.8	4.0
6	4	8	2.7	2.0
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6	4	5	3.6	-3.2
6	4	4	10.0	10.5
6	4	3	2.8	2.7
6	4	2	15.6	-17.8
6	4	1	3.3	2.5
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6	4	-1	10.7	-10.7
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6	4	-3	1.4	1.9
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6	4	-5	7.4	-6.5
6	4	-6	1.2	-1.5
6	4	-7	13.7	15.0
6	4	-8	1.4	-2.2
6	4	-9	8.2	-8.3
6	4	-10	11.0	-11.0
6	4	-11	4.0	-4.4
6	4	-12	6.9	6.2
6	4	-13	12.7	12.0
6	4	-14	8.0	-7.1
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6	3	10	10.9	11.5
6	3	9	3.2	3.2
6	3	8	11.4	-11.0
6	3	7	4.0	-4.3
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6	3	5	2.4	2.9
6	3	4	12.5	11.9
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6	3	-3	12.1	-11.0
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6	3	-5	10.9	9.9
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6	3	-8	19.8	-19.3
6	3	-9	13.8	-13.7
6	3	-10	4.8	5.0
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6	3	-13	11.0	11.6
6	3	-14	6.7	-6.3
6	3	-15	2.7	-3.4
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6	2	9	1.5	-2.8
6	2	8	6.5	-7.6
6	2	7	1.7	-2.6
6	2	6	1.8	3.5
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6	2	-12	10.2	-10.0
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6	1	1	19.4	-20.0
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6	1	-1	15.9	17.0
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6	1	-4	72.3	73.1
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6	1	-9	2.3	-3.2
6	1	-10	22.6	24.0
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6	1	-12	10.1	-9.1
6	1	-13	14.4	-15.4
6	1	-14	2.6	-2.0
6	1	-15	1.9	1.7
6	0	9	2.8	1.9
6	0	8	2.0	-1.5
6	0	6	9.0	9.3
6	0	5	1.0	-1.1
6	0	4	23.2	-24.5
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6	0	-8	31.5	32.8
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6	0	-13	7.7	-7.2
6	0	-14	3.7	3.9
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5	9	-3	3.4	-4.1
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5	6	2	19.6	18.6
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4	8	3	4.3	-3.2
4	8	2	3.2	3.1
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4	7	7	14.1	-14.2
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4	5	9	4.8	-5.5
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H	K	L	F OBS	F CALC
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-9	2	1	8.6	-7.5
-9	2	0	4.6	4.6
-9	2	-1	9.4	9.6
-9	2	-2	1.2	-1.2
-9	1	11	6.8	7.2
-9	1	10	4.1	5.9
-9	1	9	11.1	11.7
-9	1	8	11.5	-11.8
-9	1	7	11.0	-12.0
-9	1	6	11.0	10.5
-9	1	5	4.9	6.8
-9	1	4	2.3	-1.3
-9	1	3	10.1	-10.0
-9	1	2	3.2	-4.3
-9	1	0	1.3	-0.8
-9	1	-1	6.4	5.4
-9	1	-2	2.5	-1.8
-9	1	-3	11.4	-10.9
-10	2	8	2.8	-3.5
-10	2	7	7.3	8.4
-10	2	5	12.5	-11.9
-10	2	4	4.2	2.5
-10	2	3	8.9	9.6
-10	2	2	2.3	1.3
-10	2	1	6.0	-5.4
-10	1	11	8.6	-9.3
-10	1	9	18.3	19.4
-10	1	8	7.5	-7.0
-10	1	7	11.8	-11.4
-10	1	5	3.6	2.6
-10	1	4	4.8	4.4
-10	1	3	9.1	9.1
-10	1	1	6.3	-6.0
-10	1	0	4.5	-2.3
-10	1	-1	9.1	9.9
-11	1	8	2.1	-1.0
-11	1	7	6.5	5.3
-11	1	6	3.3	1.7
-11	1	5	10.2	-9.5
-11	1	4	4.1	-4.3
-11	1	3	6.4	6.1
-11	1	2	2.6	4.4

Table 4.6

(a) Fractional Coordinates

	x/a	y/b	z/c
S(1)	1.05811(11)	-0.11894(13)	0.29974(9)
P(1)	0.78551(11)	0.14530(13)	0.18735(9)
O(1)	1.08501(32)	-0.16824(43)	0.19756(26)
O(2)	1.11035(32)	-0.25453(39)	0.37512(28)
N(1)	0.89472(35)	0.00088(43)	0.27985(29)
C(1)	1.14208(43)	0.00882(52)	0.37038(34)
C(2)	1.23489(54)	0.02035(70)	0.33588(42)
C(3)	1.29832(61)	0.12073(79)	0.39190(47)
C(4)	1.26783(58)	0.21538(69)	0.48112(42)
C(5)	1.17577(61)	0.20020(68)	0.51531(41)
C(6)	1.11078(52)	0.10101(62)	0.46106(37)
C(7)	1.33449(76)	0.33107(89)	0.53855(56)
C(8)	0.85471(43)	0.26943(52)	0.16149(34)
C(9)	0.90966(50)	0.22783(61)	0.07667(38)
C(10)	0.97805(57)	0.31097(70)	0.06789(44)
C(11)	0.99561(60)	0.43352(74)	0.14237(48)
C(12)	0.94327(63)	0.47281(67)	0.22757(47)
C(13)	0.87147(53)	0.39401(57)	0.23586(41)
C(14)	0.64298(41)	0.28581(48)	0.23746(34)
C(15)	0.66035(45)	0.25343(60)	0.34404(35)
C(16)	0.54806(51)	0.35402(65)	0.38264(39)
C(17)	0.42295(47)	0.47808(59)	0.31543(41)
C(18)	0.40678(48)	0.51094(58)	0.21048(41)
C(19)	0.51738(46)	0.41252(56)	0.17095(38)

Table 4.6 (contd.)

	x/a	y/b	z/c
C(20)	0.70906(44)	0.06294(55)	0.05729(35)
C(21)	0.62789(56)	0.16059(69)	-0.03971(39)
C(22)	0.56603(62)	0.08878(89)	-0.13724(44)
C(23)	0.58739(65)	-0.07334(86)	-0.13397(49)
C(24)	0.66799(62)	-0.16876(74)	-0.03764(52)
C(25)	0.72932(53)	-0.10123(62)	0.05898(44)

Table 4.6 (contd.)

(b) H-atom Fractional Coordinates and Isotropic Thermal Parameters ($\mathring{A}^2$)

	x/a	y/b	z/c	U_{iso}
H(2)	1.2478(55)	-0.0371(66)	0.2736(43)	0.049(16)
H(3)	1.3507(58)	0.1451(70)	0.3563(45)	0.059(18)
H(5)	1.1546(61)	0.2714(73)	0.5857(48)	0.065(19)
H(6)	1.0463(47)	0.0860(56)	0.4884(36)	0.027(13)
H(71)	1.2665(71)	0.4355(84)	0.5058(55)	0.101(24)
H(72)	1.4389(65)	0.2611(78)	0.5568(51)	0.087(21)
H(73)	1.3231(81)	0.3637(98)	0.6051(64)	0.117(29)
H(9)	0.8966(44)	0.1373(52)	0.0234(34)	0.019(12)
H(10)	1.0142(49)	0.2818(58)	0.0076(38)	0.031(13)
H(11)	1.0504(53)	0.4939(63)	0.1412(41)	0.041(15)
H(12)	0.9604(58)	0.5514(70)	0.2800(46)	0.054(18)
H(13)	0.8383(52)	0.4124(62)	0.2946(40)	0.039(15)
H(15)	0.7514(46)	0.1555(54)	0.3933(35)	0.022(12)
H(16)	0.5697(57)	0.3143(69)	0.4678(45)	0.056(17)
H(17)	0.3428(56)	0.5422(67)	0.3367(43)	0.047(17)
H(18)	0.3199(55)	0.5996(66)	0.1602(43)	0.045(16)
H(19)	0.5073(56)	0.4536(67)	0.0949(43)	0.053(17)
H(21)	0.6214(48)	0.2697(57)	-0.0399(37)	0.028(13)
H(22)	0.5118(57)	0.1761(68)	-0.1896(45)	0.056(17)
H(23)	0.5393(74)	-0.1186(89)	-0.2069(58)	0.099(26)
H(24)	0.6854(68)	-0.2989(82)	-0.0363(53)	0.087(23)
H(25)	0.7940(75)	-0.1762(91)	0.1413(59)	0.088(26)

Table 4.6 (contd.)

(c) Anisotropic Temperature Factors (Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
S(1)	0.0327	0.0392	0.0486	-0.0064	0.0387	-0.0139
P(1)	0.0327	0.0369	0.0418	-0.0064	0.0413	-0.0206
O(1)	0.0437	0.0695	0.0569	-0.0384	0.0578	-0.0348
O(2)	0.0441	0.0466	0.0715	0.0220	0.0357	-0.0163
N(1)	0.0330	0.0429	0.0547	0.0020	0.0479	-0.0173
C(1)	0.0351	0.0430	0.0463	0.0051	0.0361	-0.0204
C(2)	0.0577	0.0823	0.0619	-0.0460	0.0743	-0.0686
C(3)	0.0737	0.1000	0.0734	-0.0456	0.0846	-0.1133
C(4)	0.0703	0.0761	0.0563	-0.0227	0.0465	-0.0926
C(5)	0.0843	0.0737	0.0513	-0.0384	0.0730	-0.0913
C(6)	0.0593	0.0660	0.0475	-0.0142	0.0598	-0.0593
C(7)	0.1078	0.1074	0.0943	-0.0567	0.0938	-0.1492
C(8)	0.0364	0.0441	0.0452	0.0052	0.0358	-0.0239
C(9)	0.0525	0.0626	0.0505	-0.0058	0.0569	-0.0514
C(10)	0.0661	0.0768	0.0665	0.0028	0.0811	-0.0614
C(11)	0.0690	0.0831	0.0809	0.0069	0.0746	-0.0852
C(12)	0.0872	0.0601	0.0801	-0.0279	0.0827	-0.0880
C(13)	0.0666	0.0459	0.0677	-0.0208	0.0834	-0.0508
C(14)	0.0334	0.0340	0.0510	-0.0135	0.0474	-0.0257
C(15)	0.0368	0.0639	0.0398	0.0010	0.0314	-0.0238
C(16)	0.0501	0.0702	0.0508	-0.0200	0.0620	-0.0316
C(17)	0.0412	0.0542	0.0706	-0.0304	0.0661	-0.0287
C(18)	0.0390	0.0479	0.0663	0.0065	0.0413	-0.0072
C(19)	0.0392	0.0467	0.0552	0.0133	0.0463	-0.0032
C(20)	0.0402	0.0521	0.0487	-0.0221	0.0532	-0.0435

Table 4.6 (contd.)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(21)	0.0664	0.0762	0.0467	-0.0081	0.0480	-0.0670
C(22)	0.0691	0.1274	0.0481	0.0009	0.0429	-0.0884
C(23)	0.0800	0.1155	0.0743	-0.0695	0.0873	-0.1238
C(24)	0.0751	0.0769	0.0939	-0.0632	0.0796	-0.0964
C(25)	0.0546	0.0567	0.0764	-0.0436	0.0755	-0.0560

Average estimated standard deviations ($\mathring{A}^2$)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
S,P	0.0005	0.0005	0.0006	0.0009	0.0009	0.0009
O,N	0.0018	0.0020	0.0021	0.0032	0.0032	0.0030
C	0.0031	0.0033	0.0031	0.0050	0.0052	0.0054

Table 4.7

Interatomic Distances (Å) and Angles (°) with estimated standard deviations in parentheses

(a) Bonded Distances

S(1)-O(1)	1.445(3)	C(10)-C(11)	1.385(8)
S(1)-O(2)	1.439(3)	C(11)-C(12)	1.391(8)
S(1)-N(1)	1.586(4)	C(12)-C(13)	1.376(7)
S(1)-C(1)	1.778(4)	C(14)-C(15)	1.396(6)
P(1)-N(1)	1.579(4)	C(14)-C(19)	1.377(6)
P(1)-C(8)	1.804(4)	C(15)-C(16)	1.406(6)
P(1)-C(14)	1.812(4)	C(16)-C(17)	1.368(7)
P(1)-C(20)	1.808(4)	C(17)-C(18)	1.382(7)
C(1)-C(2)	1.373(6)	C(18)-C(19)	1.396(6)
C(1)-C(6)	1.396(6)	C(20)-C(21)	1.384(6)
C(2)-C(3)	1.379(8)	C(20)-C(25)	1.388(7)
C(3)-C(4)	1.384(8)	C(21)-C(22)	1.421(8)
C(4)-C(5)	1.379(7)	C(22)-C(23)	1.368(9)
C(4)-C(7)	1.523(8)	C(23)-C(24)	1.369(9)
C(5)-C(6)	1.377(7)	C(24)-C(25)	1.390(8)
C(8)-C(9)	1.404(6)	average C-H(Ph)	1.02(5)
C(8)-C(13)	1.395(6)	average C-H(Me)	0.94(7)
C(9)-C(10)	1.377(7)		

Table 4.7 (contd.)

(b) Interbond Angles

O(1)-S(1)-O(2)	116.4(2)	P(1)-C(8)-C(13)	119.3(3)
O(1)-S(1)-N(1)	112.7(2)	C(9)-C(8)-C(13)	119.1(4)
O(1)-S(1)-C(1)	107.0(2)	C(8)-C(9)-C(10)	119.6(4)
O(2)-S(1)-N(1)	108.1(2)	C(9)-C(10)-C(11)	121.2(5)
O(2)-S(1)-C(1)	107.2(2)	C(10)-C(11)-C(12)	119.3(5)
N(1)-S(1)-C(1)	104.6(2)	C(11)-C(12)-C(13)	120.3(5)
N(1)-P(1)-C(8)	115.2(2)	C(8)-C(13)-C(12)	120.5(4)
N(1)-P(1)-C(14)	105.2(2)	P(1)-C(14)-C(15)	117.5(3)
N(1)-P(1)-C(20)	111.9(2)	P(1)-C(14)-C(19)	121.8(3)
C(8)-P(1)-C(14)	108.1(2)	C(15)-C(14)-C(19)	120.5(4)
C(8)-P(1)-C(20)	108.5(2)	C(14)-C(15)-C(16)	118.8(4)
C(14)-P(1)-C(20)	107.5(2)	C(15)-C(16)-C(17)	120.3(4)
S(1)-N(1)-P(1)	126.4(2)	C(16)-C(17)-C(18)	120.7(4)
S(1)-C(1)-C(2)	121.1(3)	C(17)-C(18)-C(19)	119.7(4)
S(1)-C(1)-C(6)	119.2(3)	C(14)-C(19)-C(18)	119.9(4)
C(2)-C(1)-C(6)	119.7(4)	P(1)-C(20)-C(21)	122.0(4)
C(1)-C(2)-C(3)	119.9(5)	P(1)-C(20)-C(25)	117.3(3)
C(2)-C(3)-C(4)	121.6(5)	C(21)-C(20)-C(25)	120.6(4)
C(3)-C(4)-C(5)	117.5(5)	C(20)-C(21)-C(22)	118.4(5)
C(3)-C(4)-C(7)	120.6(5)	C(21)-C(22)-C(23)	120.1(5)
C(5)-C(4)-C(7)	121.9(5)	C(22)-C(23)-C(24)	121.0(6)
C(4)-C(5)-C(6)	122.2(5)	C(23)-C(24)-C(25)	120.1(5)
C(1)-C(6)-C(5)	119.0(4)	C(20)-C(25)-C(24)	119.8(5)
P(1)-C(8)-C(9)	121.0(3)		

Table 4.7 (contd.)

(c) Intramolecular Non-bonded Distances

S(1)...P(1)	2.82	C(1)...C(8)	3.39
S(1)...C(8)	3.45	C(1)...C(13)	3.48
S(1)...C(20)	3.78	C(2)...C(8)	3.71
P(1)...O(1)	3.19	C(2)...C(9)	3.80
P(1)...C(1)	3.54	C(2)...C(13)	3.75
O(1)...C(2)	2.93	C(3)...C(12)	3.77
O(1)...C(8)	3.51	C(6)...C(13)	3.53
O(1)...C(9)	3.43	C(8)...C(19)	3.51
O(1)...C(20)	3.57	C(8)...C(21)	3.32
O(1)...C(25)	3.56	C(9)...C(20)	3.24
O(2)...C(2)	3.62	C(9)...C(21)	3.32
O(2)...C(6)	3.22	C(13)...C(14)	3.25
N(1)...C(2)	3.80	C(13)...C(19)	3.77
N(1)...C(6)	3.08	C(14)...C(21)	3.58
N(1)...C(9)	3.74	C(14)...C(25)	3.79
N(1)...C(13)	3.57	C(19)...C(20)	3.35
N(1)...C(15)	2.89	C(19)...C(21)	3.50
N(1)...C(25)	3.06		

Table 4.7 (contd.)

(d) Intermolecular Distances

S(1)...C(17^{I})	3.95	C(18)...C(23^{V})	3.89
O(1)...C(17^{I})	3.55	C(18)...C(24^{V})	3.76
O(1)...C(18^{I})	3.37	C(19)...C(21^{VII})	3.79
O(2)...C(7^{II})	3.77	C(19)...C(23^{V})	3.72
O(2)...C(12^{II})	3.69	C(19)...C(24^{V})	3.59
O(2)...C(17^{I})	3.54	C(20)...C(23^{V})	3.90
C(7)...C(16^{III})	3.88	C(20)...C(24^{V})	3.89
C(11)...C(24^{IV})	3.92	C(21)...C(24^{V})	3.91
C(11)...C(25^{IV})	3.82	C(22)...C(24^{V})	3.95
C(12)...C(25^{IV})	3.89	C(22)...C(25^{V})	3.89
C(14)...C(23^{V})	3.73	C(23)...C(24^{V})	3.98
C(15)...C(23^{V})	3.91	C(23)...C(25^{V})	3.68
C(16)...C(16^{VI})	3.84	C(24)...C(24^{V})	3.97
C(16)...C(17^{VI})	3.94	C(24)...C(25^{V})	3.92
C(18)...C(21^{VII})	3.80		

Roman numerals as superscripts refer to the equivalent positions which should be applied to the coordinates of the second atom :

I	1+x,	-1+y,	z	V	1-x,	-y,	-z
II	x,	-1+y,	z	VI	1-x,	1-y,	1-z
III	1+x,	y,	z	VII	1-x,	1-y,	-z
IV	x,	1+y,	z				

Table 4.8

Least-squares Planes

given in the form $\ell X' + mY' + nZ' = d$,
where X', Y' and Z' are coordinates in Å

(a) Plane equations

Plane (1) : $-0.7603\,X' + 0.4704\,Y' - 0.4479\,Z' = -5.2834$
Plane (2) : $-0.8674\,X' + 0.3387\,Y' - 0.3646\,Z' = -3.9073$
Plane (3) : $-0.3601\,X' - 0.9284\,Y' - 0.0913\,Z' = -7.4834$
Plane (4) : $0.8175\,X' + 0.0367\,Y' - 0.5748\,Z' = 7.0930$

(b) Deviation of atoms (Å) from planes (starred atoms not used to define plane)

Plane (1) : S(1)* 0.022, O(1)* 0.308, C(1) 0.000,
C(2) 0.004, C(3) -0.010, C(4) 0.013, C(5) -0.010,
C(6) 0.003, C(7)* 0.057

Plane (2) : P(1)* -0.238, C(8) -0.001, C(9) -0.007,
C(10) 0.005, C(11) 0.011, C(12) -0.012, C(13) 0.010

Plane (3) : P(1)* 0.122, C(14) 0.000, C(15) 0.004,
C(16) -0.009, C(17) 0.011, C(18) -0.007, C(19) 0.002

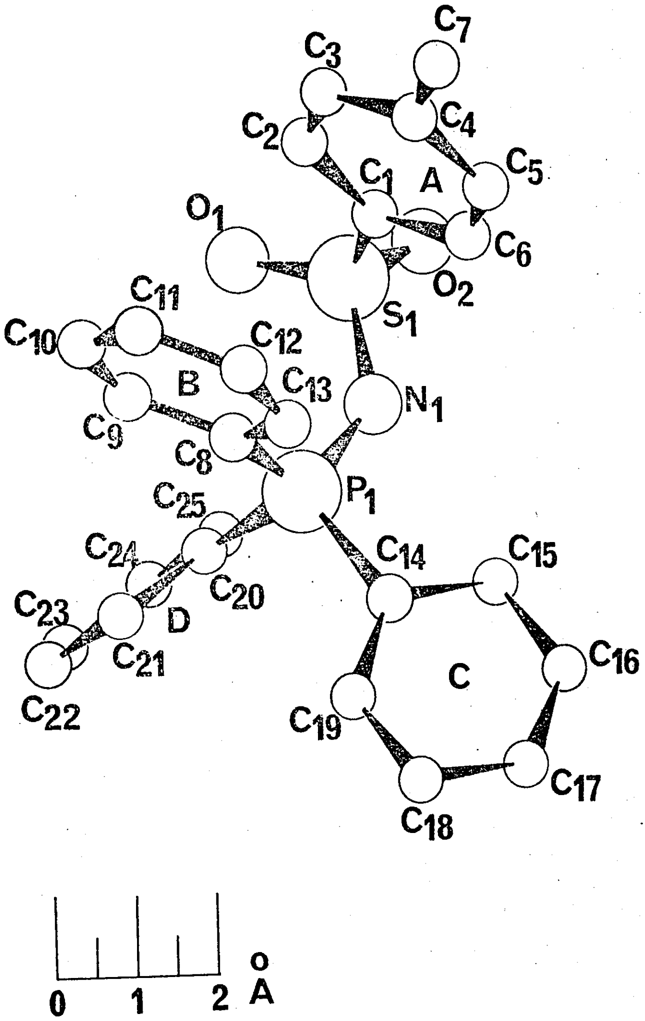
Plane (4) : P(1)* -0.078, C(20) 0.000, C(21) 0.001,
C(22) -0.001, C(23) 0.000, C(24) 0.001, C(25) -0.001

(c) Dihedral angles between planes (°)

(1) - (2) 10.9, (1) - (3) 83.0, (1) - (4) 69.7,
(2) - (3) 88.2, (2) - (4) 60.9, (3) - (4) 74.0

Figure 4.1

Atomic numbering scheme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C_3
C_4
C_2
C_5
C_1
A
O_1
C_6
O_2
S_1
C_{11}
C_{10}
C_{12}
B
C_{13}
N_1
C_9
C_8
P_1
C_{25}
C_{24}
C_{14}
C_{15}
C_{20}
C_{23}
D
C_{21}
C_{16}
C_{22}
C
C_{19}
C_{17}
C_{18}
0
1
2
Å

Figure 4.2

Molecular packing arrangement projected on to the ac-plane

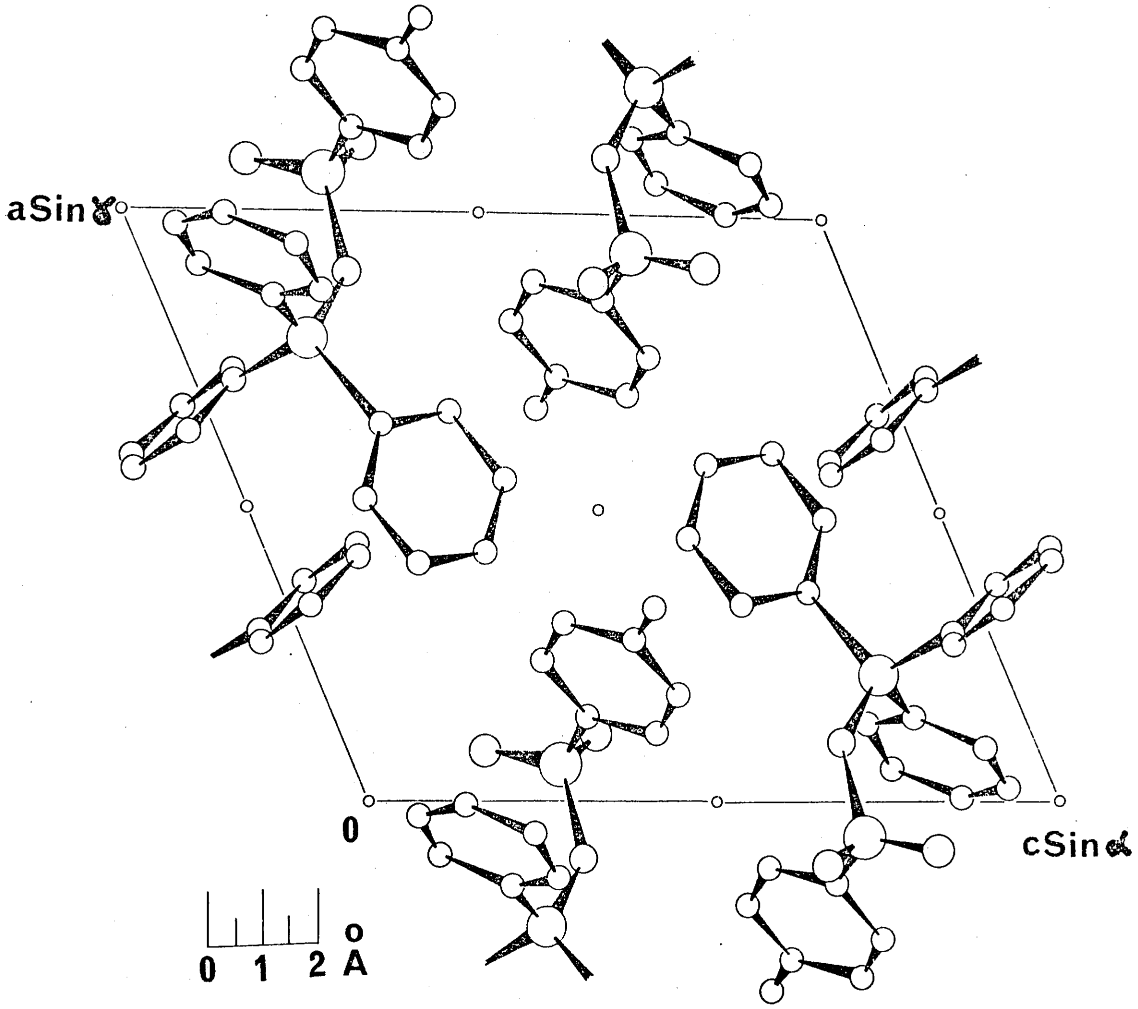
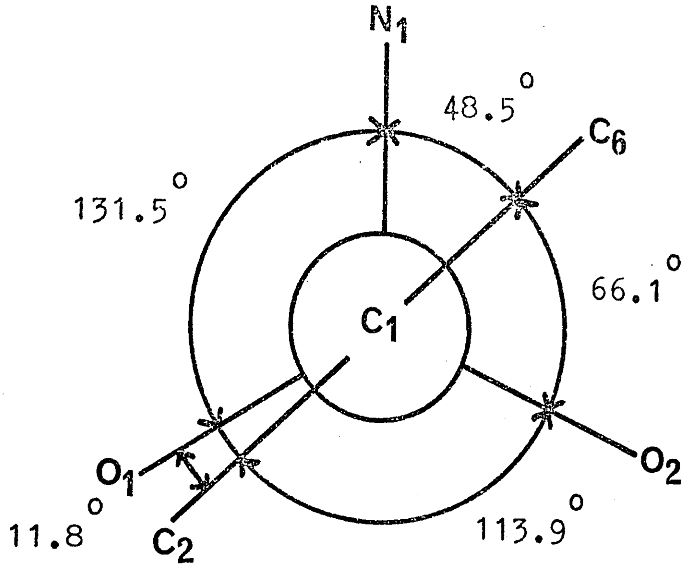

aSinγ
0
cSinα
0 1 2 Å

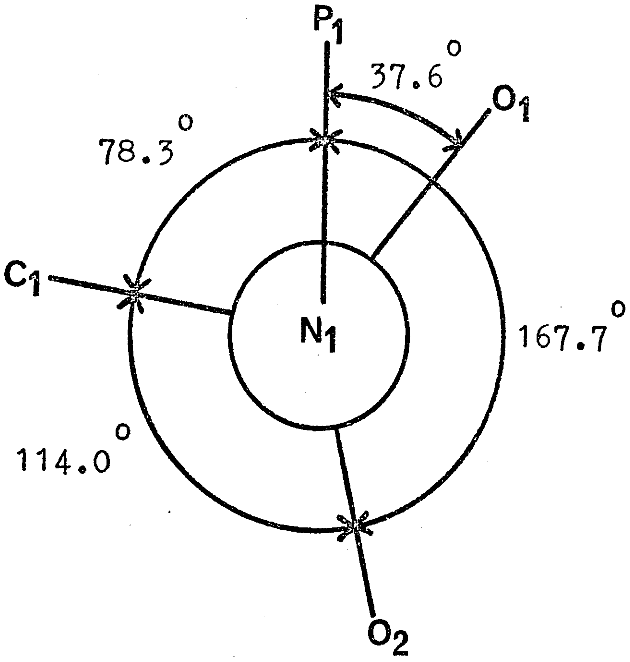
Figure 4.3

Newman projections illustrating
the solid-state conformation of (II)



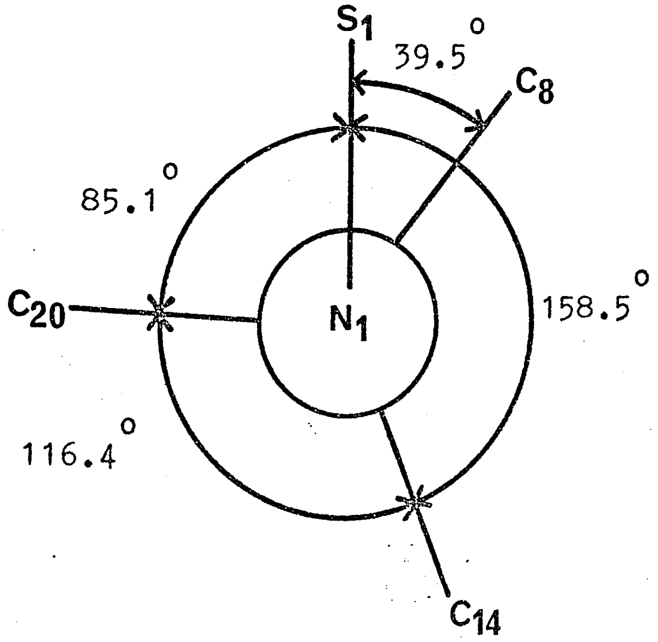
C(1) - S(1)

Projection



N(1) - S(1)

Projection



N(1) - P(1)

Projection

4.3 DISCUSSION

The structure analysis of compound (II) has not only revealed structural similarities to molecule (I) [see Section 3.3] which may therefore be common to all second-row sulphonyl-stabilised ylides for which (Y = N—), but has also yielded information on the bonding and conformations adopted by the little-studied iminophosphoranes (X = P; Y = N—). Moreover, the results of the analysis have made possible relevant comparisons with other bonding systems.

The presence of d-orbital participation in the electron delocalisation achieved through the P(1)-N(1)-S(1) bonding system of molecule (II) is suggested, as in the similar case of (I), by the considerable shortening of the P(1)-N(1) [1.579(4) Å] and N(1)-S(1) [1.586(4) Å] bonds from the values which might be expected for the respective single bonds [1.80 from Pauling's covalent radii[69] and 1.77(2) Å in sodium phosphoramide;[110] 1.74[69] and 1.76(2) Å in sulphamic acid[104]]. The virtual duplication of the N(1)-S(1) distances in (I) [1.591(8) Å] and (II) suggests that both molecules have similar opportunities to form comparable π and σ' bonding-components in their respective N-sulphonyl stabilising systems. Further support for such similar delocalisation is provided by the experimentally identical mean S(1)-O lengths observed in both molecules [1.432(8) Å in (I); 1.442(3) Å in (II)]. Moreover, the possibility of interaction between the π-systems of the P-N-S moiety and the sulphonyl-bonded aromatic ring (A) may be again discounted (see Section 3.3) on consideration of the essentially normal dimensions observed for the ring [mean C-C 1.381(7) Å] and for the connecting S(1)-C(1) bond [1.778(4) Å].[66]

However, despite such similarities in (I) and (II), comparison of the N(1)-P(1) [1.579(4) Å] and N(1)-S(2) [1.636(8) Å] bonds in (II) and (I) respectively reveals that not only are both bonds shortened relative to their respective single bond values, but also that the shortening is more pronounced in the case of the former. That the N(1)-P(1) bond is relatively more shortened implies a more effective *d*-orbital involvement in the iminophosphorane (II), perhaps arising simply from the better 'back-bonding' [43] possibilities afforded by the greater electronegativity difference between P and N than between S and N (see Section 3.3), although it is possible that other factors may be involved. For example, the stronger interaction in (II) could possibly be attributed to *d*-orbital contraction resulting from participation of the three phosphorus-bonded electron-withdrawing phenyl groups, although this is unlikely to be a significant factor since negligible differences have been observed between the $\overset{+}{S} - \overset{-}{N}$ systems of (I) and its diphenyl analogue [51] (see Section 3.3).

A possibly more significant effect may, however, arise from a more fundamental difference between (I) and (II). It has already been suggested in Section 3.3 that the S(2) lone-pair of electrons of (I) may destabilise the *d*-orbitals of S(2) lying in the S-N-S plane thus inhibiting a σ' bonding component, whereas in (II) P(1) has no such lone-pair. It may therefore be inferred that, in the latter case, there should be no such barrier to the presence of a σ' component which could contribute to the formation of a more effective

$\overset{+}{P} - \overset{-}{N}$ bond. Such involvement of both nitrogen lone-pairs of electrons in the formation of two bonding components, one parallel and the other perpendicular to the P-N-S plane, has been postulated to account for the bonding features observed in the $(P - N)_n$ systems of cyclic phosphonitriles,[55,56] although comparable P-N distances [range 1.558 - 1.641 Å] have been reported in similar, but not directly comparable, systems where σ' bonding was considered unlikely.[53,54,111] Nevertheless, it is worthy of comment that the P-N bond in molecule (III),[112] in which no σ' component is possible since the nitrogen lone-pair of electrons probably occupies a pure p significantly longer [1.628(5) Å] than the corresponding

significantly longer [1.628(5) Å] than the corresponding

bond in (II). The presence of two electronegative fluorine atoms, which may plausibly simulate a near positive charge on P in (III), renders this comparison not too inappropriate. Further support for the suggestion of phosphorus d-orbital involvement in two mutually perpendicular planes may be inferred from theoretical calculations for the phosphonium ylide $H_3\overset{+}{P} - \overset{-}{C}H_2$,[113,114] which imply the presence of both π and σ' components, the latter having been postulated to result from a hyperconjugative effect involving both C-H bonds.[113]

Further discussion of the relative efficiencies of different stabilising groups and comparison of second-row ylides belonging to the series (X = P; Y = O, N—, C<) will be made in Section 5.

Comparable regions of (I) (see Section 3.3) and (II) display similar solid-state conformations which are again best described in terms of the three Newman projections along the C(1)-S(1), N(1)-S(1) and N(1)-P(1) bonds (Figure 4.3). Whereas in (I) the C(1)-S(1) projection showed the aromatic ring plane asymmetrically disposed to the sulphonyl grouping [C(2)-C(1)-S(1)-O(1) torsion angle -11.2°], the corresponding aromatic ring (A) in (II) has been rotated counterclockwise by 23°, the relevant torsion angle being +11.8°. As a result of this reverse twisting in (II), the O(2)...C(6) contact has increased [3.22 Å in (II); 2.98 Å in (I)] while the O(1)...C(2) contact has remained almost unaltered [2.93 Å in (II); 2.90 Å in (I)], in comparison with the corresponding distances in (I).

Examination of the N(1)-S(1) projection reveals that O(1) and S(2) take up the <u>semi-gauche</u> arrangement which was also observed for (I), the P(1)-N(1)-S(1)-O(1) torsion angle being +37.6°. It has already been suggested that, for compound (I) [see Section 3.3], the steric requirements of the S(2) lone-pair of electrons are of considerable importance in determining the orientation of substituents about the N(1)-S(2) bond in that compound. However, the possible involvement of such factors in the conformation of the N(1)-S(1) bond in (I) may now be discounted since virtually the same conformation is observed for (II), there being no lone-pair available on P(1). Thus the <u>semi-gauche</u> conformations observed about the N(1)-S(1) bonds of (I) and (II), and other similar ylides,[50,51] possibly constitute a common feature in such compounds which may be intimately connected with the electron delocalisation through the respective S-N-S and P-N-S systems, and will subsequently be discussed in this context in Section 5.

The main feature of the N(1)-P(1) projection is the deviation of the N(1)-S(1) bond from the expected staggered arrangement with respect to the three P-C(phenyl bonds, possibly in an attempt to satisfy the steric requirements of the two nitrogen lone-pairs of electrons.

Of particular interest is the enlargement of the P(1)-N(1)-S(1) angle in (II) [126.4(2)°] relative to the corresponding S(2)-N(1)-S(1) angle in (I) [113.4(5)°], this increase being reflected in the considerable lengthening of the P(1)...O(1) contact [3.19 Å] compared to the S(2)...O(1) contact [2.94 Å] in (I). It has been suggested by Cruickshank [57] that, in various P-O-P bridged systems, enlargement of the P-O-P bridge angle achieves an effective participation of both mutually perpendicular oxygen lone-pairs of electrons in the electron delocalisation, and moreover, in three recent structure determinations of the bis(triphenylphosphine)iminium cation,[118] P-N-P angles within the range 137 - 142° have been reported, perhaps reflecting the presence of such an effect in systems comparable to second-row ylides. However, in the similar ylide (IV), which shows evidence of steric repulsion [P...O 3.14 Å compared to the van der Waals' separation 3.30 Å], the central P-C-S angle has a value of 124°.[115] Thus it is difficult to assess whether the enlarged angle in (II) results from the presence of an effective σ' bonding component in (II), which is less probable in (I), or simply from steric effects.

On closer examination, the molecular conformation of (II) suggests that steric effects may have at least some influence on the magnitude of the P(1)-N(1)-S(1) angle. The sulphonyl-aromatic ring (A) and the phenyl ring (B), which are almost parallel (dihedral angle 10.9°), are in such close

proximity that the perpendicular distance between the centre of (A) and the plane of (B) [3.54 Å] is considerably shorter than the van der Waals' separation for two parallel aromatic rings [3.70 Å]. Considered in this context, the reverse twisting of ring (A) relative to the S(1)-O(1) bond can now be interpreted as an attempt by the molecule to reduce such steric interactions. Moreover, several fairly short intramolecular contacts are noticeable between O(1) and phenyl groups (B) and (D) [see Table 4.7] which suggest steric crowding in this region of (II). The enlargement of other involved angles on the same side of the molecule, namely the Nangles relative to N(1)-P(1)-C(14) [105.2(2)°] further)°]
angles relative to N(1)-P(1)-C(14) [105.2(2)°] further support this suggestion.

Further features of the conformation of (II) are the approximately tetrahedral arrangements found for both S(1) and P(1). Moreover, the three phosphonium-bonded phenyl groups, which are planar within experimental error (Table 4.8), are arranged in the familiar "propellor-type" configuration (interplanar angles: 88.2°, 60.9°, and 74.0°) with the phosphorus atom lying slightly out of plane relative to each ring (B -0.24 Å; C 0.12 Å; D -0.08 Å), as has been previously reported for various triphenylphosphine derivatives.[49,53,54, 115-117] Examination of the previously undiscussed dimensions of (II), in particular the P-C(phenyl) [mean 1.808(4) Å], phosphonium-bonded phenyl C-C [mean 1.388(7) Å] and C-H [aromatic 1.02(5) Å; methyl 0.94(7) Å] bonds, reveals lengths which do not differ significantly from normally accepted values.[66]

The absence of short intermolecular contacts infers that the crystal packing arrangement has been determined by van der Waals' forces.

5. OVERALL DISCUSSION

It was possible from the studies of first-row ylides in Section 1 to compare the stabilities of the series of compounds ($X = R_3N$; $Y = O$, $N\!-\!-$, $C\!<$) in relation to the electronegativities of the central negatively charged atom, and it was shown that, as the electronegativity of this atom decreased, the evidence of stabilisation via delocalisation of the negative charge into the stabilising group became more apparent.

It must be appreciated, however, that first-row ylides represent relatively simplified cases since, in general, only an electrostatic interaction is possible between the 'onium and vicinal groups, and also, in those compounds examined in Section 1, only a $p_\pi - p_\pi$ delocalising interaction may occur between the negatively charged atom and the stabilising group. In second-row ylides, moreover, there are additional factors which must be considered - firstly, d-orbital involvement of the 'onium group, and, depending on the choice of stabilising group, d-orbital involvement of the latter in the overall bonding. Furthermore, and in the same context, there may be differing numbers of lone-pairs of electrons on the central atom Y which are available for bonding interactions. As a result, comparisons of second-row ylides are necessarily rather complicated.

Nevertheless, it should be possible to regard the bonding interactions in second-row ylides as resulting from competition between the 'onium and stabilising groups to delocalise the available lone-pairs of electrons on the negatively charged carbon or nitrogen atoms. Since, in the latter case of nitrogen-containing compounds, the bonding may be rendered more complex by the possible presence of both π and σ' interactions (see Sections 3.3 and 4.3), the relative efficiencies of stabilising groups which can form only bonding interactions (e.g. $>C=O$), as compared with those stabilising groups which may form an additional σ' bonding component (e.g. $>SO_2$), can be examined by comparing the dimensions of compounds (1→3),[49,115,48] each of which may have only π-type components involved in the bonding. Thus (1) [49] exhibits an extremely short $\overset{+}{P} - \overset{-}{C}$ bond [mean 1.661(8) Å] which has been ascribed to a very strong $d_\pi - p_\pi$ interaction in the absence of a stabilising group, whereas in compound (2),[115] which has the additional possibility of delocalising part of the negative charge via an analogous π stabilising group, the $\overset{+}{P} - \overset{-}{C}$ bond is lengthened [1.709(19) Å]. Moreover, the further increase in the corresponding bond in (3) [1.736(14) Å] [48] results presumably from the presence of a carbonyl stabilising group in this compound, although the carbon-bonded chlorine may also have some effect on the molecular dimensions. It is possible that this trend in $\overset{+}{P} - \overset{-}{C}$ lengths reflects the relative efficiencies of sulphonyl and carbonyl stabilising groups, the latter being more effective since orbitals of more comparable size and energy are available for interaction with the carbon p-type lone-pair of electrons.* Furthermore, the relative lengthening of the $\overset{+}{P} - \overset{-}{C}$ bonds in (2) and (3) with respect to

stabilising group, the $\overset{+}{P} - \overset{-}{C}$ bond is lengthened [1.709(19) Å

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* It is known that the $p_\pi - d_\pi$ bonds in phosphoryl compounds are weaker than their $p_\pi - p_\pi$ counterparts in carbonyl compounds.[56]

(1) may possibly afford a measure of the respective stabilising group participation.

Further support for this interpretation may be obtained from a comparison of the $\overset{+}{S} - \overset{-}{N}$ lengths in (4) [1.673 Å][52] and (5) [1.636(8) Å][103] which, despite the additional possibility of a σ' interaction in the N-S(sulphonyl) bond in (5), again reflects the greater effectiveness of the carbonyl grouping, although there is less evidence of delocalisation into the $\bar{N}$-C=O moiety of (4) [$\bar{N}$-C 1.344 Å; C=O 1.212 Å] than in the corresponding grouping of the carbonyl-stabilised first-row ylide (6) [$\bar{N}$-C 1.313(6) Å; C=O 1.243(5) Å].[61,62]

Since it has been suggested in Section 3.3 that the lone-pair of electrons on nitrogen are not apparently involved to any great extent in the formation of a σ' overlap component with the 'onium group d-orbitals when (X = S), then comparisons of the bonding in the series of ylides (X = S; Y = O, N—, C<) would seem to be valid. Accordingly, not only is the $\overset{+}{S} - \overset{-}{C}$ bond in (7) [119] more shortened relative to single bond values than the corresponding $\overset{+}{S} - \overset{-}{N}$ bond in (4),[52] but evidence of charge delocalisation into the carbonyl group of (7) is also more apparent. It is possible that this may result from the fact that negatively charged carbon is inherently less stable than negatively charged nitrogen, as reflected in the lower electronegativity of the former. Comparison of the isoelectronic pair (2) [115] and (8) [105] reveals a similar trend, the $\bar{C}$-S(sulphonyl) bond in (2) [1.686(19) Å] being relatively more shortened than the corresponding N-S(sulphonyl) bond in (8) [1.681(5) Å]. Thus the series of compounds (X = S; Y = O, N—, C<), representative of second-row ylides in which only π-type interactions are possible, shows an increasing requirement for stabilisation, <u>via</u> both 'onium and stabilising group participation, on progressing from ($O^{*} \rightarrow C<$), as was previously observed for the simplified first-row systems.

In contrast to the latter series, comparison of compounds in the series (X = P; Y = O, N—, C<) is complicated by the possibility of the additional lone-pairs of electrons on nitrogen and oxygen participating in σ' interactions with the phosphonium grouping. Nevertheless, examination of the relative shortening of the $\overset{+}{P} - \overset{-}{Y}$ bonds in (2) [1.709(19)],[115] [1.579(4)][103] and triphenylphosphine oxide [1.46(1) Å][120] respectively (i.e. progressing along the series Y = C<, N—, O) reveals a marked increase in the effectiveness of the <u>d</u>-orbital participation in the $\overset{+}{P} - \overset{-}{Y}$ bonds, which is ultimately reflected in the high stability of Ph_3PO itself. This trend may be correlated both with the increasing possibilities of π and σ' bonding, and also with the greater electronegativity differences between P and Y which will afford better opportunities for 'back-bonding'.[43]

Unfortunately, comparison of the relative efficiencies of different 'onium residues raises difficulties, since a σ' is unlikely in the $\overset{+}{X} - \overset{-}{Y}$ bond when (X = S) see Section 3.3 , whereas it appears to be more feasible when (X = P). Nevertheless, this problem can be circumvented by examining systems in which σ' components are not possible i.e. (Y = C) or <u>N</u>-alkylated systems. Thus comparing the $\overset{+}{X} - \overset{-}{C}$ bonds of (3) [1.736(14) Å][48] and (7) [1.707(4) Å][119] reveals a more

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* Dimethyl sulphoxide (X = S; Y = O) is a stable compound without need for further stabilisation.

effective 'onium-anion bond in the former, from which it may be suggested that the phosphonium group overlaps more effectively in the plane of the π overlap component. While this implied difference in the π-bonding efficiencies of P and S 'onium groups could partly account for the anomalously short $\overset{+}{P} - \overset{-}{N}$ bond in (9) [1.579(4) Å][103] compared to the corresponding $\overset{+}{S} - \overset{-}{N}$ bond in (5) [1.636(8) Å],[103] the operation of a further effect is possibly necessary. Thus it is quite plausible that the presence of the postulated σ' bonding component, which is unlikely in (5) as a result of the destabilisation effect of the $\overset{+}{S}$ lone-pair of electrons (see Section 3.3), could explain the extra shortening which occurs in (9).

Perhaps most intriguing is the possible relationship between the bonding systems of ylides and the conformations adopted by these molecules. Considerable importance has been attached to the value of the torsion angle $(X\overset{+}{Y}\overset{-}{Z}/Y\overset{-}{Z}O_{cis})$ [defined in Table 5.1], values for the four sulphonyl-stabilised imines (Y = N—) [5,9→11] [103,50,51] being very similar (36.8°, 37.6°, 31.7°, 34.0°), thus suggesting that this aspect of the conformation may be a property of the molecule, rather than an effect of crystal packing forces. A striking difference is found, however, when the conformations of the carbonyl-stabilised second-row ylides (3, 4, 7) [48,52,119] and first-row ylides (6, 12→14) [62,74,91] are examined, the corresponding values for the torsion angles in those molecules being close to zero.

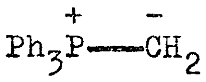
First impressions therefore suggest grouping the ylides, on conformational grounds, into two general classes, namely those with ($>SO_2$) and those with ($>C{=}O$ or $-NO_2$) stabilising groups. However, it is apparent that compound (2) [115] and the N-alkylated derivative (8) [105] possibly also belong to the latter category since both have one sulphonyl oxygen atom approximately coplanar with their respective $\overset{+}{X}\overset{-}{Y}Z$ groupings, the relevant oxygen being cis in (2) and trans in (8). Moreover, from symmetry considerations, a coplanar oxygen arrangement is likely to afford similar overlap possibilities between the p-type lone-pair of electrons on the anion and a particular linear combination of sulphonyl d-orbitals irrespective of a cis or trans conformation, the choice of cis or trans possibly being controlled by steric factors in particular molecules.

A possibly more correct classification would therefore be to divide ylides into two categories according to the inclination of the $Z{=}O_{cis}$ $[Z = C, N, S]$ (or $Z{=}O_{trans}$ for $Z = S$) bond to the $\overset{+}{X}\overset{-}{Y}Z$ ($X = N, P, S$; $Y = C, N$; $Z = C, N, S$) plane. Moreover, subdivision of the compounds (2→14) into those in which a σ' interaction may or may not occur between the anions and the stabilising groups, reveals that the additional σ' bonding may take place only in ylides (5, 9→11), thus revealing complete correspondence between this subdivision and that previously suggested on the basis of conformation. Although this cannot be taken as direct proof of the existence of σ' bonding, it is nevertheless significant that, of all the compounds so far examined, the two classifications according either to bonding or to conformation should correspond so exactly, and a plausible interpretation is that the coplanar or semi-gauche conformations, adopted respectively by the two categories, afford the best opportunities to form extended π (and σ')

bonding through the respective systems. Furthermore, the large variety of substituents in the discussed molecules also suggests that the conformations adopted are not simply an effect of steric requirements alone, but may also be influenced by the bonding interactions. It has already been suggested in Section 1.3 that the syn-planar relationships in the first-row ylides (6, 12, 13) result in the maximising of electrostatic interactions between the 'onium group X and the vicinal oxygen atom.

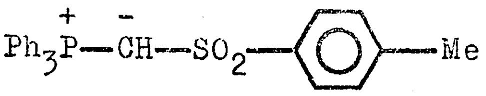
Despite the many comparisons which can be made, it is nevertheless clear that further useful information would undoubtedly derive from the determinations of the structures of compounds such as (15→18), the dimensions and conformations of which would provide further opportunities for more valid comparisons of bonding and conformational relationships in ylides.

(1)



$\mathrm{Ph_3\overset{+}{P}-\overset{-}{C}H_2}$

(2)



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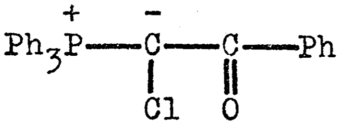
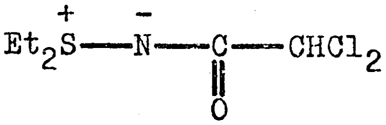


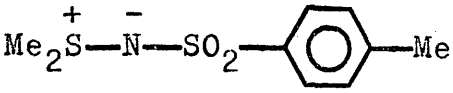
$\mathrm{Ph_3\overset{+}{P}-\underset{Cl}{\overset{-}{C}}-\underset{\Vert}{\overset{}{C}}(=O)-Ph}$

(4)



$\mathrm{Et_2\overset{+}{S}-\overset{-}{N}-C(=O)-CHCl_2}$

(5)



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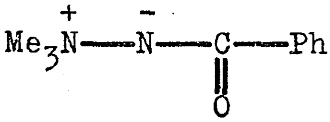
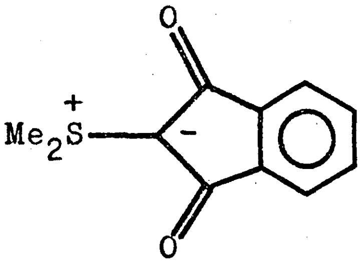
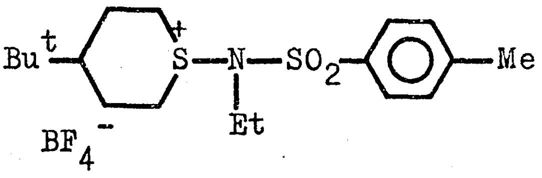


$\mathrm{Me_3\overset{+}{N}-\overset{-}{N}-C(=O)-Ph}$

(7)



(8)



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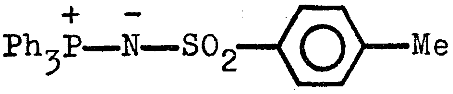

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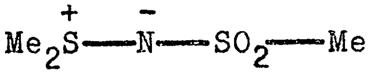
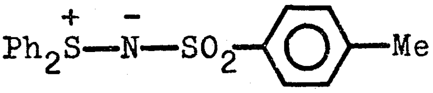


$\mathrm{Me_2\overset{+}{S}-\overset{-}{N}-SO_2-Me}$

(11)



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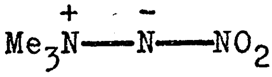
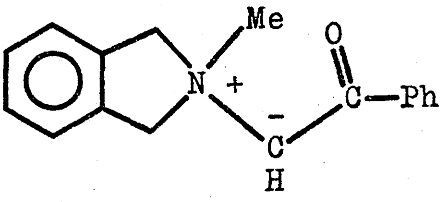
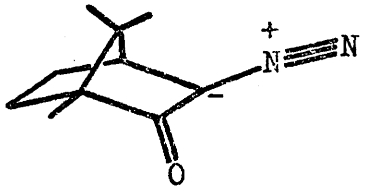


$\mathrm{Me_3\overset{+}{N}-\overset{-}{N}-NO_2}$

(13)



(14)



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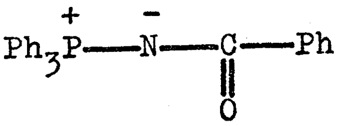
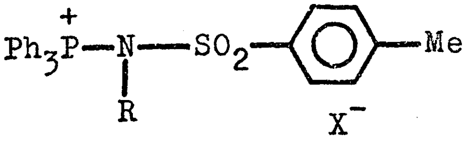


$\mathrm{Ph_3\overset{+}{P}-\overset{-}{N}-C(=O)-Ph}$

(16)



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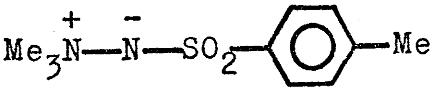

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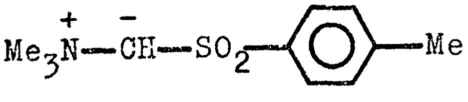
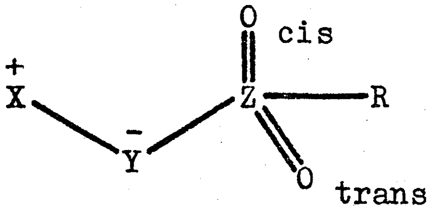


Table 5.1

Comparison of $\overset{+}{X} - \overset{-}{Y}$, $\overset{-}{Y} - Z$, $Z = O$ Bonds and Torsion Angles (φ) defined as $\left[\overset{+}{X} - \overset{-}{Y} - Z \,/\, \overset{-}{Y} - Z = O\right]$



X = N, P, S

Y = C, N

Z = S, C, N

Compound	Ref.	$\overset{+}{X} - \overset{-}{Y}$	$\overset{-}{Y} - Z$	$Z = O$	φ
(1)	49	1.661(8)*	-	-	-
(2)	115	1.709(19)	1.686(19)	1.457(15)*	8.3° (c)
(3)	48	1.736(14)	1.361(20)	1.301(19)	4.8° (c)
(4)	52	1.673	1.344	1.212	0° (c)
(5)	103	1.636(8)	1.591(8)	1.432(8)*	36.8°
(6)	61,62	1.471(5)	1.313(6)	1.243(5)	2.2° (c)
(7)	119	1.707(4)	1.429(5)*	1.232(5)*	7.3° (c)*
(8)	105	1.644(5)	1.681(5)	1.411(5)*	180° (tr)
(9)	103	1.579(4)	1.586(4)	1.442(3)*	37.6°
(10)	50	1.633(9)	1.581(10)	1.447(11)*	31.7°
(11)	51	1.628(7)	1.598(8)	1.433(8)*	34.0°
(12)	61,62	1.470(8)	1.323(8)	1.259(8)*	0° (c)
(13)	74	1.48(1)	1.36(1)	1.27(1)	0° (c)
(14)	91	1.296(8)	1.448(9)	1.215(8)	5.8° (c)

* :- mean value; c :- cis; tr :- trans .

PART III

STRUCTURAL INVESTIGATIONS OF TWO RELATED SYNTHETIC INTERMEDIATES

1. THE CRYSTAL AND MOLECULAR STRUCTURES OF 2β-CARBOMETHOXY-5α,6α-DIHYDROXY-7,7-DIMETHYLTRICYCLO [6.2.1.$0^{1,6}$] UNDECANE AND 2α-CARBOMETHOXY-5β-CHLOROACETOXY-7,7-DIMETHYLTRICYCLO [6.2.1.$0^{1,6}$] UNDECAN-6β-OL.

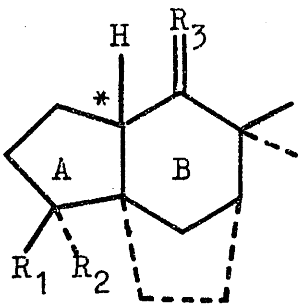
1.1 INTRODUCTION

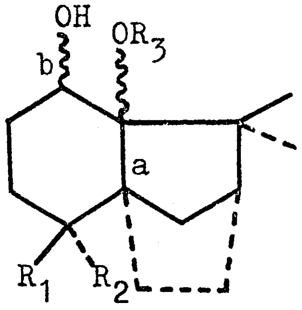
Recently there have been several studies of the various structural types of sesquiterpenes which may be derived from Oil of Vetiver.[121-124] One such study was concerned with the possible synthesis of tricyclovetivene (1) via rearrangement of the tricyclo [6.2.1.$0^{1,6}$] undecane derivative (2).[124] In order to test the feasibility of this rearrangement, a similar scheme was devised [125] in which the key stages were the conversion of (3) to (4), followed by a ring-expansion rearrangement yielding a zizanoic acid derivative (5).

While the only prerequisite for a concerted rearrangement of (4) to (5) is that bonds a and b in (4) are *trans* and coplanar, it was realised that the stereochemistry of the introduced chiral centre (marked *) would depend entirely on the stereochemistry, α or β, of the *cis* diol system in (4). Previously it had been shown [126] that *exo*-face attack of the *cis*-hydroxylating agent osmium tetroxide occurs in bicyclo [3.2.1] oct-2-ene systems, hence implying that in the present case (3)⟶(4) the β-diol should be preferentially formed. However, if the concerted rearrangement (4)⟶(5) proceeds *via* an S_N2 attack with inversion of configuration at the centre involved, the β-diol could conceivably not yield (5) but the epimer with *cis* A/B ring junction and α-hydrogen.

Further complications arose from an earlier reaction stage at which a mixture of epimers (3) and (6) was obtained, since the subsequent hydroxylations (3)⟶(4) and (6)⟶(7) could possibly yield diol systems with different relative stereochemistries. If this does occur, as is suggested by the different reaction times required by (4) and (7) for the rearrangement, then it might be expected that each diol system would yield products differing in A/B ring junction and, therefore, also at the chiral centre (marked *), providing both rearrangements proceed by similar mechanisms.

Since the stereochemistries of the rearrangement products are known by comparison with natural products,[125] a knowledge of the stereochemistries of (4) and (7) i.e. α or β diols, should afford sufficient information to allow a detailed investigation of the ring expansion rearrangement mechanism. In an attempt to resolve this problem, the structures of the molecules (4) and (8), derived from (3) and (6) respectively, were investigated by crystal structure analysis, (4) proving to have absolute stereochemistry (9), and (8) absolute stereochemistry (10).





(1) $R_1 = Me$, $R_2 = H$, $R_3 = CH_2$

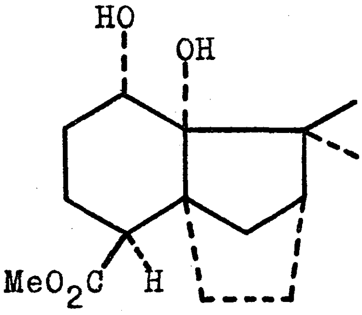
(5) $R_1 = CO_2Me$, $R_2 = H$,
$R_3 = O$

(2) $R_1 = Me$, $R_2 = H$, $R_3 = Me$

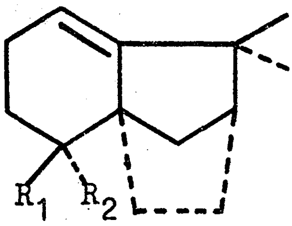
(4) $R_1 = CO_2Me$, $R_2 = H$, $R_3 = H$

(7) $R_1 = H$, $R_2 = CO_2Me$, $R_3 = H$

(8) $R_1 = H$, $R_2 = CO_2Me$,
$R_3 = COCH_2Cl$

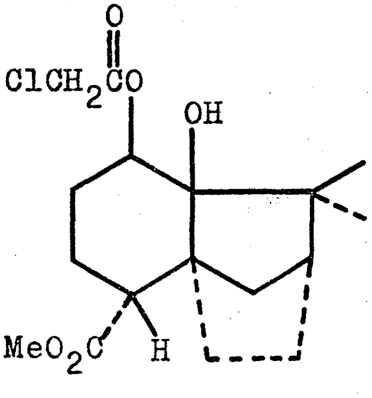


(9)

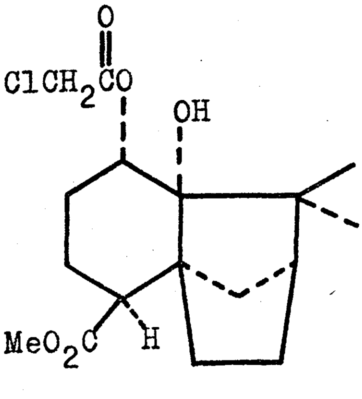


(3) $R_1 = CO_2Me$, $R_2 = H$

(6) $R_1 = H$, $R_2 = CO_2Me$



(10)



(11)

1.2 EXPERIMENTAL

Crystal Data

(9); 2β-carbomethoxy-5α,6α-dihydroxy-7,7-dimethyltricyclo [6.2.1.0^{1,6}]undecane, $C_{15}H_{24}O_4$, M = 268.4.

Monoclinic, a = 10.886(3), b = 7.766(4), c = 8.591(2) Å,

β = 100.93(2)°, U = 713.1 Å^3.

D_m = 1.24 g.cm.$^{-3}$ (by flotation in aqueous KI), Z = 2,

D_c = 1.25 g.cm.$^{-3}$, F(000) = 292.

Space group $P2_1$ (C_2^2 , No.4).

Linear absorption coefficient for X-rays (λ = 0.7107 Å),

μ = 0.96 cm.$^{-1}$.

(10); 2α-carbomethoxy-5β-chloroacetoxy-7,7-dimethyltricyclo [6.2.1.0^{1,6}]undecan-6β-ol, $C_{17}H_{25}O_5Cl$, M = 344.8.

Orthorhombic, a = 14.270(6), b = 7.541(5), c = 15.824(8) Å,

U = 1702.8 Å^3.

D_m = 1.33 g.cm.$^{-3}$ (by flotation in aqueous KI), Z = 4,

D_c = 1.34 g.cm.$^{-3}$, F(000) = 736.

Space group $P2_12_12_1$(D_2^4 , No.19).

Linear absorption coefficient for X-rays (λ = 0.7107 Å),

μ = 2.50 cm.$^{-1}$.

Crystallographic Measurements

The unit cell dimensions of both compounds were initially determined from oscillation and Weissenberg photographs taken with Cu-K_α (λ = 1.5418 Å) radiation, and from precession photographs taken with Mo-K_α (λ = 0.7107 Å) radiation. Refined values for these parameters were subsequently obtained, by least-squares techniques, from the Busing and Levy orientation-matrix program [63] prior to the diffractometer data collections. Although the systematic absences in the h00, 0k0 and 00ℓ spectra uniquely determine the space group of (10) as $P2_12_12_1$, the absences in the 0k0 spectra of (9) result in the possible choice of either space group $P2_1$ or $P2_1/m$. However, the correctness of the space group $P2_1$ was indicated by statistical tests and also by the known optical activity of (9).

Table 1.1 contains details of the crystal morphologies and data collections for compounds (9) and (10). Both sets of intensity data, which were collected on a Hilger and Watts Y290 computer-controlled diffractometer using Mo-K_α radiation, were corrected for the appropriate Lorentz and polarisation factors, but absorption effects were considered negligible in both cases and were ignored.

Structure Determinations

Both structures were solved by the application of non-centrosymmetric direct methods,[19] using programs developed by Stewart et al.,[64] and incorporated into the X-Ray 70 suite of programs.[127] Firstly, both sets of data were placed on absolute scales, normalised structure amplitudes, $|E(hk\ell)|$, subsequently being derived (see PART I, Section 2). Statistical analyses of both data sets, shown in Table 1.2, indicate acentric distributions appropriate to the non-centosymmetric space groups $P2_1$ and $P2_12_12_1$ of molecules (9) and (10) respectively. The tendency towards almost intermediate E-statistics of compound (10) is probably an effect of the pseudo-special position occupied by the chlorine atom.

Σ_2 relationships for use in the initial symbolic addition procedures were then generated for the 201 reflexions of (9) and the 262 reflexions of (10) with $|E| > 1.50$. The phasing process, which involves the phase-refinement techniques of the tangent formula reiteration procedure,[21] was applied to the basic starting sets outlined in Tables 1.3(a) and 1.3(b) for (9) and (10) respectively, and from each of these starting sets was derived a trial set of phases. The reliability of each trial solution can be judged from its corresponding Karle R-index (see PART I, Section 5.3).[19] However, for compound (9), the range of values obtained for the twelve different starting sets only varied from 0.16 to 0.25, thus making the choice of the correct solution very difficult. Fortunately, symbolic addition calculations, carried out by hand, had previously indicated that the sum of (E) and (V) should equal π, therefore reducing the number of possible correct solutions, for the sets examined, to two. In the case of (10), the range of Karle R-indices for the four sets examined was wide i.e. 0.19 to 0.33, hence indicating that the set ($E = \pi/2$; $V = 3\pi/4$) with $R = 0.19$ should afford the correct solution. In the latter case, introduction of the variable reflexion merely enhanced the convergence of the iteration process, and did not significantly alter the set of phases obtained from the origin set plus enantiomorph reflexion alone.

E-maps subsequently calculated for (9), with phases derived from the set ($E = 3\pi/4$; $V = \pi/4$), and for (10), with phases from the appropriate set, revealed the entire structure in both cases. Inclusion of both sets of atomic positions in structure-factor calculations yielded conventional R-values of 32 % and 30 % for (9) and (10) respectively, and after each calculation, in which overall isotropic thermal parameters $U_{iso} = 0.05$ Å^2 were assumed, the two sets of data were placed on approximate absolute scales by equating $k\sum|F_o|$ and $\sum|F_c|$. In both cases, the atomic positions were judged to be sufficiently accurate as to warrant immediate refinement by least-squares methods.

Structure Refinements

The positional, vibrational and overall-scale parameters for both structures were refined by three-dimensional least-squares calculations, which in the case of (9) converged after 12 cycles when R was 0.066 and R' ($= \sum w\Delta^2 / \sum w|F_o|^2$) was 0.006, and for (10) converged after 15 cycles when R was 0.058 and R' was 0.005. Full details of both refinements, in which only statistically significant data ($I > 2\sigma_I$) were included, are given in Table 1.4. Throughout the refinement of (9), the y-coordinate of atom O(1) was not allowed to vary in order to fix the origin on the 2-fold screw axis of space group $P2_1$.

Difference syntheses, calculated after the isotropic refinement stages, revealed all the hydrogen atoms of the two structures. Positional parameters for the hydrogen atoms were refined in later cycles, isotropic thermal parameters $U_{iso} = 0.05 \text{Å}^2$ being assumed throughout. In the initial cycles of the refinements of (9) and (10), unit weights were assigned to all reflexions, but in later cycles it was found necessary, from an $|F_o|$ analysis of $w\Delta^2$, to apply weighting schemes to both sets of data. In both cases, since it was essential to downweight observations of high $|F_o|$, a weighting scheme of the following form was found to be suitable

$$\sqrt{w} = 1 \text{ for } |F_o| \leq p; \quad \sqrt{w} = p/|F_o| \text{ for } |F_o| > p,$$

the optimum value of the parameter p being 10.0 for (9) and 20.0 for (10).

Both refinements were judged to be complete when the parameter shifts calculated by a least-squares cycle were insignificant compared to the corresponding estimated standard deviations. The subsequent calculation of electron-density distributions and difference syntheses revealed no errors in either structure. Observed and final calculated structure factors for compounds (9) and (10) are listed in Tables 1.5 and 1.6 respectively. In all the structure-factor calculations, the atomic scattering factors used were taken from 'International Tables for X-Ray Crystallography,' Vol.III.[65]

Final fractional coordinates and anisotropic thermal parameters for both compounds are given in Table 1.7, the hydrogen atoms being numbered according to the numbering of the attached atoms. In Table 1.7 the values of U_{ii} and $2U_{ij}$

refer to the anisotropic temperature factor expression given in PART I, Section 3. All bond lengths, valency angles, and pertinent intra- and inter-molecular non-bonded distances are shown in Table 1.8. The appropriate estimated standard deviations, σ, derived from the inverses of the respective least-squares normal equation matrices are included in Tables 1.7 and 1.8. In the case of (9), the average σ for C-O and C-C, and C-H bonds are 0.008 and 0.08 Å, while for valency angles σ is 0.5°. The corresponding values for (10) are 0.005 Å, 0.06 Å and 0.3°. These are probably best regarded as minimum values since the block-diagonal approximation to the normal equation matrix was used in the final stages of both refinements owing to computer-storage limitations.

Details of least-squares planes calculated for various portions of the molecular frameworks of (9) and (10) are given in Table 1.9. The atomic numbering schemes, used in every table, are shown in Figures 1.1 and 1.2 for (9) and (10) respectively, while Figures 1.3 and 1.4 show projected views of the molecular packing of (9) and (10), the former illustrating the O-H...O intermolecular hydrogen bonding which associates molecules of (9) related by the 2-fold screw axis of space group $P2_1$, and the latter showing a system of intermolecular hydrogen bonding which extends in the *a*-direction through the crystal.

Table 1.1

Details of Crystal Morphologies and Data Collections

	Compound(9)	Compound(10)
Crystal shape	Flat plate	Plate
Crystal size (mm.)	0.6 × 0.2 × 0.1	0.8 × 0.4 × 0.3
Rotation axis	b	b
Scan technique	2θ	2θ
Step size (°)	0.02	0.02
Number of steps	40	40
Step time (secs)	2	2
Total background count (secs)	40	40
Radiation filter	Zr	Zr
2θ range (°)	0→56	0→56
Independent reflexions	1824 (1240 with $I > 2\sigma_I$*)	2345 (2057 with $I > 2\sigma_I$*)

* σ_I , the standard deviation in the measured intensity, I, is derived from counting statistics

$$\text{i.e.} \quad \sigma_I = \sqrt{(P + B_1 + B_2)}$$

where P, B_1 and B_2 are the peak and two background counts respectively.

Table 1.2

Statistical Analyses of both Data Sets

	Theoretical		Experimental	
	Centric	Acentric	(9)	(10)
Average $\|E\|$	0.798	0.886	0.857	0.855
Average $\|E\|^2$	1.000	1.000	1.000	1.000
Average $\|E^2 - 1\|$	0.968	0.736	0.778	0.819
$\|E\| > 1$	31.73	36.79	37.20	34.34
$\|E\| > 2$	4.55	1.83	1.91	3.17
$\|E\| > 3$	0.27	0.01	0.03	0.17

Table 1.3

(a) Origin-defining and Variable Reflexions for (9)

h	k	ℓ		Phase	E
1	0	-4	O.D.	0	3.13
2	0	-1	O.D.	0	2.21
7	5	-1	O.D.	0	2.86
1	4	-6	Enantimorph	$(\pi/4, \pi/2, 3\pi/4)$	2.82
2	6	1	Variable	$(\pi/4, 3\pi/4, 5\pi/4, 7\pi/4)$	2.91

Correct solution : ($E = 3\pi/4$; $V = \pi/4$), $R = 0.17$.

(b) Origin-defining and Variable Reflexions for (10)

h	k	ℓ		Phase	E
0	3	12	O.D.	$\pi/2$	3.56
3	0	14	O.D.	π	3.06
17	0	7	O.D.	$\pi/2$	2.80
1	4	0	Enantiomorph	$\pi/2$	2.17
9	3	5	Variable	$(\pi/4, 3\pi/4, 5\pi/4, 7\pi/4)$	3.19

Correct solution : ($E = \pi/2$; $V = 3\pi/4$), $R = 0.19$.

Table 1.4

(a) Course of Refinement for (9)

Cycles	Parameters refined	Final R	Final R'
1 - 3	x, y, z, U_{iso} for O, C, Overall scale factor, Full matrix, unit weights.	0.145	0.022
4 - 7	x, y, z, U_{ij} for O, C, Overall scale factor, Block diagonal, weighting scheme adjusted, H-atom contributions included but not refined.	0.084	0.009
8 - 12	x, y, z, U_{ij} for O, C, x, y, z for H, Overall scale factor, Block diagonal, weighting scheme applied.	0.066	0.006

Table 1.4 (contd.)

(b) Course of Refinement for (10)

Cycles	Parameters refined	Final R	Final R'
1 - 4	x, y, z, U_{iso} for Cl, O, C, Overall scale factor, Full matrix, unit weights.	0.184	0.027
5 - 10	x, y, z, U_{ij} for Cl, O, C, Overall scale factor, Block diagonal, weighting scheme adjusted, H-atom contributions included but not refined.	0.071	0.008
11 - 13	x, y, z for H only, Overall scale factor, Block diagonal, weighting scheme applied, other atom contributions included but not refined.	0.061	0.005
14 - 15	x, y, z, U_{ij} for Cl, O, C, x, y, z for H, Overall scale factor, Block diagonal, weighting scheme applied.	0.058	0.005

Table 1.5

Observed and final calculated structure amplitudes (×10)

(9)

```
    13,1,L

 -1    24    20
 -2    30    11

    13,0,L

 -2    34    39

    12,5,L

  0    26    17
 -3    33    36

    12,4,L

  1    32    26

    12,3,L

  3    31    31
  0    44    41
 -3    24    17
 -6    30    28

    12,2,L

 -2    29    29
 -4    23    17
 -5    31    13
 -6    29    31
 -7    24    26

    12,1,L

  0    26    23
 -1    28    18
 -2    33    33
 -3    53    48
 -4    31    37
 -5    27    23
 -6    41    42
 -7    41    44

    12,0,L

  4    39    34
  1    23    18
 -3    35    32
 -5    25    20
 -7    24     4

    11,6,L

  1    30    24
 -3    31    24

    11,5,L

  1    27    25
  0    30    27
 -2    32    21
 -4    30    24

    11,4,L

  2    35    26
  1    54    52
 -2    24    18
 -3    24    28
 -4    27    17
 -6    28    29
 -7    35    36

    11,3,L

  4    30    32
  3    30    30
  2    67    62
  0    44    42

    11,2,L

  2    35    22
  1    23     4
  0    46    52
 -1    34    34
 -2    56    53
 -4    29     9
 -6    46    51
 -7    37    39
 -8    27    22

    11,1,L

  2    23    17
 -2    59    65
 -3    54    43
 -5    50    48
 -6    44    39
 -8    25     4

    11,0,L

  4    26    10
  2    36    37
 -1    82    84
 -2    33    38
 -5    26    29
 -7    33    34

    10,7,L

  1    39    32
  0    38    36
 -1    24    22

    10,6,L

  2    25     6
  1    25    19

    10,5,L

  4    32    25
  2    33    34
 -3    38    40
 -4    50    45
 -6    31    41
 -7    36    36

    10,4,L

  5    51    49
  4    27    31
  2    45    43
 -2    41    33
 -3    34    28
 -5    23    19

    10,3,L

  4    47    45
  3    47    48
  2    22     7
  1    34    32
  0    52    56
 -1    43    45
 -2    30    27
 -3    39    38
 -4    31    27
 -5    22    10

    10,2,L

  4    36    38
  3    54    52
  1    41    46
  0    80    79
 -1    61    55
 -2    76    76
 -3    48    46
 -4    47    53
 -5    51    54
 -6    27    25

    10,1,L

  2    72    76
  1    27    31
  0    47    46
 -1    49    44
 -2    81    84
 -3    49    53
 -4    33    38
 -5    46    47
 -7    35    33
 -8    29    30

    10,0,L

  2    26    24
  1    26    34
  0    28    12
 -1    36    33
 -2    35    37
 -3    22    22
 -4    50    53
 -6    34    31
 -9    41    41

    9,7,L

  2    28    28
  1    35    33
 -3    24    28
 -5    29    15

    9,6,L

  1    36    31
 -5    25    21
 -6    24    16

    9,5,L

 -1    34    27
 -2    73    71
 -3    53    56
 -5    40    41
 -6    32    20
 -8    25    14

    9,4,L

  6    35    32
  1    32    39
  0    38    34
 -1    58    63
 -2    58    58
 -3    35    32
 -5    30    30
 -6    48    42
 -7    44    49

    9,3,L

  6    39    40
  5    44    38
  4    32    30
  3    24    25
  1    71    71
 -1    44    36
 -2    45    41
 -3    44    46
 -4    43    53
 -5    34    37
 -6    28    16

    9,2,L

  7    40    33
  5    38    38
  4    54    56
  3    61    62
  2    67    69
  1    71    73
  0   106   111
 -1    86    84
 -2    65    71
 -3    80    84
 -4    43    43
 -8    27    16

    9,1,L

  3    44    49
  2    93    99
  1    81    82
  0   130   132
 -1   100   104
 -2    72    74
 -3    39    34
 -4    85    87
 -5    72    72
 -6    30    20
 -7    23    31
 -8    31    34
 -9    49    44

    9,0,L

  7    30    31
  3    77    73
  2    64    59
  1    29    30
  0   104   106
 -1    58    63
 -2    35    30
 -3    27    35
 -5    60    66
 -6    29    27
 -7    49    47
-10    34    29

    8,8,L

  2    47    45
  1    38    36
  0    40    40
 -1    45    43

    8,7,L

 -2    39    31
 -4    37    24

    8,6,L

 -1    46    46
 -2    43    39
 -3    24    22
 -5    47    48
 -6    30    35
 -7    25    21

    8,5,L

  3    31    30
  1    76    75
  0    45    41
 -1    22    15
 -2    32    37
 -3    43    40
 -4    68    71
 -5    90    89
 -6    55    55
 -7    26    27

    8,4,L

  6    38    36
  3    28    29
  2    22    21
  0    47    50
 -1   124   129
 -2    88    91
 -3    99   101
 -4    32    17
 -5    55    58

    8,3,L

  6    28    23
  5    46    41
  4    36    36
  3    31    30
  2    33    38
  1    24    23
  0    80    82
 -1    47    45
 -2    50    46
 -3    59    60
 -4    58    54
 -6    26    24
 -8    29    22
 -9    26    24

    8,2,L

  5    50    47
  4    33    41
  3    34    38
  2   104   106
  1    87    88
  0    89    95
 -1    53    53
 -2    59    63
 -3    88    87
 -4   103   106
 -5    56    53
 -6    44    38
 -8    32    25
 -9    27    17

    8,1,L

  5    41    40
  4    79    80
  3    74    73
  2    59    61
  1   102   102
  0   102   104
 -1    56    53
 -2    54    52
 -3    36    38
 -4    62    61
 -5    78    74
 -6    22    25
 -7    67    71
 -8    41    36

    8,0,L

  6    50    41
  5    59    61
  4   116   116
  3    21    22
  2    24    20
  1    74    70
  0    73    68
 -1    55    54
 -2    23    21
 -6    36    38
 -7    25    26
 -8    57    58
 -9    32    34
-10    33    31

    7,8,L

  1    34    30
  0    38    32
 -5    37    11

    7,7,L

 -1    36    37
 -6    27    15

    7,6,L

  6    31    16
  3    28    24
  2    45    42
  0    25    25
 -4    34    33
 -5    38    45

    7,5,L

  7    51    46
  6    28    26
  3    27    36
  2    61    67
  1    70    68
  0    78    87
 -1   160   167
 -2   118   123
 -3    57    60
 -5    63    68
 -6    56    57
 -7    28    23

    7,4,L

  6    36    33
  3    26    33
  2    46    53
  1    52    48
  0    29    28
 -1    77    84
 -2    84    83
 -3    53    61
 -4    84    90
 -6    29    24

    7,3,L

  7    24    22
  6    50    47
  5    51    52
  4    43    49
  3    27    24
  2    60    57
  1    66    70
  0    67    68
 -1    78    80
 -2    33    35
 -3    86    90
 -4    54    57
 -5    91    94
 -6    38    43
 -7    38    33
 -9    30    31

    7,2,L

  6    49    57
  5    53    61
  3    24    36
  2    36    37
  1   180   182
  0   155   156
 -1    80    84
 -2    49    45
 -3   108   105
 -4    85    83
 -5    38    42
 -6    60    62
 -7    45    41
 -8    40    36
 -9    23    28

    7,1,L

  5    53    49
  4    74    76
  3    86    93
  2    43    35
  1   125   129
  0   124   117
 -1    42    41
 -2    94    89
 -3    91    85
 -4    45    43
 -6    98    96
 -7    26    17
 -8    27    15
 -9    25    27
-10    38    35

    7,0,L

  6    27    21
  5    22     3
  4    52    47

  3   122   122
  2    22    19
  1    27    23
  0   103   105
 -1    25    26
 -2    63    61
 -3   111   108
 -4    27    26
 -6    89    92
 -7    79    76
 -8    47    49
-10    24    21

    6,9,L

 -2    26    15
 -3    29    20

    6,8,L

  3    41    40
  2    42    29
  0    30    31
 -1    29    24
 -5    32    20

    6,7,L

  5    24    19
  4    31    15
  3    28    24
  2    29    26
  1    39    41
 -7    31    25

    6,6,L

  6    38    29
  4    34    33
  3    46    45
  0    42    46
 -1    61    65
 -2    37    43
 -4    74    83
 -5    62    68
 -6    31    33
 -7    27    29

    6,5,L

  4    32    36
  3    55    57
  2    38    42
  1    69    68
  0    78    75
 -1    83    82
 -2    21    18
 -3    43    46
 -4    59    59
 -6    36    37
 -8    24    18

    6,4,L

  7    34    27
  6    24    15
  5    25    24
  4    42    41
  3    69    70
  2    61    57
  1    87    92
  0    89    96
 -1    84    87
 -2    24    28
 -3    59    59
 -4    98   104
 -5    77    79
 -6    25    16
 -7    33    36
-10    29    19

    6,3,L

  8    29    22
  6    28    25
  5    31    37
  4    41    43
  3    23    19
  2    23    22
  1    41    48
  0    91    91
 -1   127   134
 -2    23    18
 -3    77    73
 -4    80    91
 -5    44    45
 -6    48    46
 -7    23    12

    6,2,L

  7    33    36

  6    78    78
  5    58    60
  4    43    44
  3    72    73
  2    46    47
  1   122   114
  0   108    98
 -1    49    46
 -2   150   152
 -3   130   125
 -4    75    69
 -5    78    74
 -6    33    43
 -7    61    70
 -8    49    46
-10    37    30

    6,1,L

  8    28    19
  6    35    40
  5   104   105
  4   121   125
  3    69    71
  2    48    49
  1    85    84
  0   101   100
 -1   103    93
 -2   182   178
 -3    76    74
 -4    60    65
 -5   131   126
 -6   155   157
 -7    68    71
-10    34    29

    6,0,L

  8    33    29
  5   100   103
  4    35    31
  3   133   134
  2    30    23
  1   158   161
  0    85    85
 -1   186   177
 -2   211   191
 -3   104   104
 -4    44    41
 -5    52    57
 -6    38    38
 -7    39    35
 -8    27    26
 -9    45    49
-10    36    37

    5,9,L

  1    30    32
 -4    25    25

    5,8,L

  5    51    47
  2    50    48
  1    41    41
  0    23    24
 -1    32    30
 -2    23    18
 -3    27    24
 -5    30    20
 -6    30    30

    5,7,L

  6    26    21
  5    24    22
  1    23    25
 -1    52    50
 -3    42    47
 -4    27    22
 -5    34    36
 -6    35    47
 -7    28    22

    5,6,L

  3    64    66
  2    43    46
  1    37    41
  0    56    58
 -1    82    86
 -2    84    85
 -3    28    25
 -4    50    41
 -5    35    46
 -6    33    32
 -7    48    43
 -8    32    29

    5,5,L

  8    35    29
  7    26    25
  4    51    55
  1    34    44
  0    84    87
 -1    53    55
 -2    47    54
 -4    56    63
 -5    26    26
 -7    31    37

    5,4,L

  8    27    29
  7    45    29
  6    26    28
  5    57    58
  3    40    38
  2    61    61
  1   112   115
  0   172   175
 -1   109   108
 -2   105   110
 -3    31    34
 -4    40    47
 -5    64    71
 -6    59    65
 -7    45    51
-10    27    25

    5,3,L

  7    28    26
  6    22    21
  4    91    92
  3    71    75
  2    57    52
  1   105    99
  0   123   123
 -1   155   147
 -2    29    37
 -3   108   107
 -4    56    62
 -5    37    34
 -6   117   122
 -7    58    61

    5,2,L

  9    35    29
  7    46    47
  6    84    84
  5    47    53
  4    57    55
  3   101    97
  2    99    93
  1   178   176
  0   137   126
 -1    55    57
 -2    63    61
 -3    75    81
 -5   116   113
 -6    51    57
 -7    46    49
 -8    56    65
 -9    47    55
-10    50    40

    5,1,L

  6    48    48
  5   100   105
  4    42    39
  3    31    27
  2    67    73
  1   170   159
  0    83    79
 -1   186   174
 -2   234   221
 -3   177   171
 -4   149   144
 -5    19    25
 -6   120   122
 -7    26    25
 -8    41    43
 -9    42    41
-10    33    29

    5,0,L

  7    42    49
  6    35    38
  4    81    82
  3    51    54
  2   154   156
  1   164   160
  0    77    75
 -1    25    24
 -2   260   266
 -4   142   136
 -5   116   105
```

5,0,L

-6	165	168
-7	27	34
-11	25	7

4,9,L

3	32	30
2	33	20
-1	29	25
-4	29	15

4,8,L

5	37	40
0	27	27
-1	23	25
-2	23	20
-4	35	31
-5	23	16

4,7,L

6	31	32
5	25	16
3	41	48
2	41	42
1	43	42
-1	67	73
-2	25	41
-3	33	32
-4	30	21
-5	29	21
-7	58	52
-8	37	28

4,6,L

5	22	10
3	39	40
2	73	71
1	48	44
-1	35	43
-2	82	84
-3	90	92
-4	96	100
-5	27	17
-6	52	51
-7	25	24
-8	30	14

4,5,L

7	38	28
5	51	49
4	88	94
3	96	102
2	57	57
1	55	61
0	182	182
-1	89	91
-2	81	89
-3	43	43
-4	39	38
-5	32	29
-6	50	55
-7	65	61
-8	30	14

4,4,L

8	34	26
7	24	23
5	58	61
4	111	114
3	35	40
2	57	60
1	70	73
0	124	125
-1	126	126
-2	19	23
-3	71	73
-4	30	28
-5	24	22
-6	50	50
-7	30	34
-8	42	39

4,3,L

8	41	38
6	40	39
5	72	69
4	101	99
3	39	35
2	52	52
1	87	72
0	145	142
-1	25	37
-2	106	104
-3	33	34
-4	86	83
-5	31	33
-7	65	76
-8	52	52
-9	27	24
-10	26	17

4,2,L

9	46	45
8	34	31
7	30	33
6	95	101
5	83	83
4	96	90
3	108	103
2	59	64
1	312	303
0	106	106
-1	257	242
-2	149	141
-3	120	114
-4	78	80
-5	61	60
-6	77	83
-7	54	59
-11	34	31

4,1,L

10	26	17
6	71	78
5	94	97
4	93	93
3	140	136
2	91	95
1	139	147
0	124	128
-1	85	80
-2	56	54
-3	137	136
-4	36	35
-5	125	123

4,0,L

7	92	100
6	54	57
4	35	36
3	128	127
2	64	63
1	68	68
0	226	208
-1	137	133
-2	115	116
-4	203	188
-5	38	35
-6	59	62
-7	98	103
-9	64	66
-10	25	23

3,10,L

-1	32	35

3,9,L

4	32	27
3	27	26
0	26	27
-1	57	54
-4	26	25
-5	30	21

3,8,L

6	39	29
5	43	42
1	29	22
0	33	28
-1	29	25
-2	25	23
-5	25	17

3,7,L

5	41	33
4	31	29
1	39	37
-2	48	53
-3	86	89
-4	27	35
-5	25	30
-6	41	40
-7	32	29

3,6,L

6	31	22
5	26	10
4	38	42
3	44	47
2	58	59
1	145	148
0	99	98
-1	65	63
-3	92	94
-4	63	64
-5	43	46
-6	33	25
-7	44	43

3,5,L

8	27	13
7	37	28
6	29	40
5	23	24
4	89	93
3	27	34
2	30	37
1	22	24
0	122	117
-1	60	58
-2	38	38
-3	41	46
-4	60	64
-6	55	51
-7	31	19
-8	37	37
-9	31	19

3,4,L

6	24	27
5	66	64
4	60	66
3	27	32
2	134	129
1	52	52
0	146	137
-1	97	95
-2	57	48
-3	37	32
-4	26	27
-5	47	50
-6	65	66
-7	57	58
-8	29	11
-9	46	42

3,3,L

7	50	50
6	58	61
5	65	65
4	64	66
3	167	161
2	56	58
1	344	328
0	64	71
-1	69	67
-2	213	208
-3	92	92
-4	221	214
-5	34	30
-6	135	146
-7	57	61
-8	32	29
-10	45	41

3,2,L

8	47	52
7	75	81
6	76	80
5	123	129
4	177	169
3	179	164
2	294	271
1	330	325
0	234	225
-1	44	42
-2	123	120
-3	246	244
-4	96	92
-5	63	58
-6	129	130
-7	71	80
-8	58	61
-11	28	28

3,1,L

10	34	39
9	25	31
8	24	18
7	35	35
6	106	110
5	85	85
4	45	54
3	104	102
2	65	48
1	202	197
0	92	90
-1	159	158
-2	27	34
-3	81	76
-4	99	96
-5	108	112
-6	92	96
-7	102	103
-8	21	21

3,0,L

6	79	77
5	146	143
4	100	93
3	144	141
2	224	215
1	84	83
0	76	84
-1	77	78
-2	450	450
-3	280	269
-4	45	50
-5	264	255
-6	160	158
-7	35	30
-9	33	32

2,10,L

-1	45	43
-2	36	29

2,9,L

3	25	24
2	29	28
-1	39	36
-2	33	19
-5	40	31

2,8,L

6	28	25
5	25	28
3	27	23
1	29	23
0	22	20
-1	26	28
-4	27	24
-7	30	29

2,7,L

7	24	22
6	35	27
5	27	33
3	31	31
2	53	51
1	69	69
0	56	62
-1	26	23
-2	33	32
-3	46	47
-4	40	39
-5	33	29
-6	32	26
-7	24	27

2,6,L

8	25	18
6	55	56
5	62	64
4	49	60
3	51	49
2	83	84
1	209	210
0	150	151
-1	49	51
-3	85	96
-4	72	74
-5	44	51
-6	61	59
-7	32	29
-8	29	17

2,5,L

8	32	21
7	26	22
5	107	112
4	98	106
3	57	56
2	81	79
1	127	128
0	80	78
-1	35	39
-2	52	50
-3	73	76

2,5,L

-6	30	36
-8	24	30

2,4,L

9	26	19
7	46	43
6	30	34
5	78	76
4	118	123
3	34	33
2	30	30
1	171	172
0	314	296
-1	53	47
-2	171	168
-3	51	42
-4	78	84
-5	29	25
-6	66	72
-7	55	51
-9	41	40
-10	59	53

2,3,L

8	30	15
7	42	50
6	63	72
5	78	82
4	102	101
3	153	155
2	175	165
1	88	92
0	272	267
-1	270	270
-2	131	126
-3	69	72
-4	45	45
-5	55	59
-6	70	80
-7	96	100
-8	47	53

2,2,L

10	38	32
9	41	41
7	99	102
6	136	137
5	75	76
4	162	160
3	132	139
2	109	104
1	169	153
0	368	374
-1	98	102
-2	249	243
-3	63	49
-4	51	42
-6	59	62
-7	58	54
-8	29	23
-9	30	29
-10	28	10

2,1,L

10	42	40
9	22	20
8	38	39
7	73	83
6	51	54
5	150	148
4	88	79
3	107	106
2	347	341
1	271	266
0	484	497
-1	386	374
-2	313	297
-3	287	277
-4	227	211
-5	59	57
-6	53	52
-7	22	15
-8	57	58
-9	34	35
-11	41	36

2,0,L

10	26	15
8	41	36
6	61	61
5	41	36
3	29	23
2	76	80
1	352	355
0	526	558
-1	697	801
-2	200	193
-3	283	283
-4	114	111
-5	35	27
-6	78	80
-8	22	7
-9	52	50
-10	27	6

1,9,L

5	29	20
2	27	22
1	23	21
0	73	65
-1	36	38
-2	35	25
-3	33	35

1,8,L

6	39	27
5	27	17
2	44	42
1	26	23
-1	26	31
-3	31	31
-5	32	41
-6	26	13
-7	30	24

1,7,L

6	39	38
5	27	23
2	56	53
1	85	82
-2	65	69
-3	76	86
-4	44	40
-5	43	45
-6	39	38
-8	33	28

1,6,L

7	26	18
5	84	87
4	113	117
3	44	44
2	58	65
1	137	141
0	48	49
-1	44	40
-2	79	77
-3	48	40
-5	60	61
-6	34	34
-7	48	46
-8	26	14

1,5,L

8	31	25
6	26	26
5	96	100
4	48	44
3	98	99
2	23	32
1	98	96
0	101	97
-2	44	41
-4	88	88
-5	55	59
-6	42	41
-7	34	41
-9	31	28

1,4,L

8	32	29
7	71	79
6	42	43
5	191	198
4	83	83
3	73	74
2	78	75
1	149	139
0	200	193
-1	106	110
-2	79	72
-3	21	23
-4	68	72
-5	92	95
-6	175	182
-8	29	10
-9	51	46
-10	26	32

1,3,L

9	40	40
8	27	21
7	75	77
6	109	107
5	44	49
4	113	120
3	199	200
2	294	266
1	176	160
0	237	225
-1	169	164
-2	97	101
-3	194	190
-4	103	104
-5	187	193
-6	67	73
-7	54	59
-8	54	55
-9	37	36

1,2,L

10	70	69
8	25	14
7	66	65
6	132	138
5	88	90
4	129	125
3	42	41
2	140	136
1	36	37
0	141	131
-1	218	196
-2	167	169
-3	126	118
-4	152	151
-5	43	41
-6	96	93
-7	27	26
-8	46	44
-9	33	35
-11	49	51

1,1,L

10	29	20
9	24	16
7	78	82
6	56	50
5	118	123
4	202	191
3	299	287
2	136	134
1	181	185
0	570	601
-1	413	408
-2	373	356
-3	52	47
-4	230	211
-5	45	35
-8	21	19
-9	34	32

1,0,L

8	40	40
7	44	38
5	38	27
3	162	160
2	368	372
1	425	442
0	145	140
-1	43	46
-2	246	252
-3	335	323
-4	549	530
-5	237	218
-6	32	29
-7	81	86
-10	33	29
-11	39	30

0,10,L

1	42	48
0	59	60

0,9,L

4	34	24
1	26	21

0,8,L

6	25	28
5	32	27
2	25	23
0	46	42

0,7,L

6	51	49
5	31	27
4	26	25
2	53	55
1	115	119

0,6,L

6	25	20
5	70	74
4	21	18
3	89	93
2	106	105
1	43	42
0	78	81

0,5,L

9	37	42
7	62	63
5	65	68
4	54	57
3	41	47
2	55	56
1	28	31

0,4,L

9	28	28
8	31	30
6	52	54
5	121	121
4	121	123
3	100	93
2	107	107
1	111	112
0	151	155

0,3,L

10	36	30
7	90	90
6	95	94
5	48	53
4	83	76
3	53	51
2	326	314
1	370	362

0,2,L

10	52	50
8	58	60
7	105	109
6	21	26
5	36	36
4	102	102
3	95	97
2	169	158
1	227	237
0	167	169

0,1,L

11	48	46
9	40	39
8	28	31
7	56	60
6	6[illegible]	73
5	62	61
4	213	202
3	390	370
2	275	273
1	310	300

0,0,L

8	46	43
7	52	59
6	104	107
5	180	175
4	268	257
3	50	48
2	300	281

Table 1.6

Observed and final calculated
structure amplitudes

(10)

H	K	L	F OBS	F CALC
18	2	3	9.9	8.3
18	2	2	7.2	7.7
18	2	1	7.4	7.0
18	2	0	8.8	9.1
18	1	5	15.6	14.1
18	1	4	7.5	6.5
18	1	3	7.7	7.3
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18	1	1	7.2	6.3
18	0	5	2.6	2.9
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18	0	2	8.7	7.7
18	0	1	10.5	9.9
18	0	0	14.8	13.6
17	4	3	9.4	8.0
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17	4	0	6.6	6.3
17	3	6	11.0	10.4
17	3	5	11.6	9.5
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17	2	7	4.4	3.7
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17	2	4	8.3	8.0
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17	2	1	13.1	11.6
17	2	0	4.5	3.7
17	1	7	9.4	7.9
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17	0	5	2.7	3.0
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17	0	2	2.9	2.8
17	0	1	5.2	4.9
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16	4	2	5.1	4.0
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16	4	0	10.9	10.3
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16	3	8	13.9	12.5
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16	3	3	8.6	9.3
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10	4	7	12.5	11.6
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10	4	2	5.6	4.9
10	4	1	7.9	8.7
10	4	0	23.1	21.2
10	3	15	4.5	4.4
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10	3	8	23.9	22.5
10	3	7	10.1	9.5
10	3	6	9.0	7.8
10	3	5	18.7	17.6
10	3	4	29.2	28.0
10	3	3	18.4	17.2
10	3	2	12.3	11.5
10	3	1	23.0	22.0
10	3	0	17.6	17.0
10	2	17	4.9	4.0
10	2	16	3.4	2.3
10	2	15	6.9	6.0
10	2	13	5.8	5.2
10	2	12	8.1	7.5
10	2	11	9.5	9.1
10	2	9	7.9	8.6
10	2	8	9.0	9.0
10	2	7	34.8	33.7
10	2	6	31.4	29.3
10	2	5	18.3	17.2
10	2	4	25.7	25.2
10	2	3	19.9	19.5
10	2	2	10.6	9.6
10	2	1	15.0	13.8
10	2	0	16.6	15.8
10	1	17	4.1	4.6
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10	1	8	4.4	4.5
10	1	7	37.3	36.0
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10	1	5	45.9	41.4
10	1	4	16.5	14.5
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10	1	1	17.2	15.0
10	1	0	30.4	29.4
10	0	17	6.1	5.4
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10	0	13	9.4	9.4
10	0	12	8.5	8.1
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10	0	10	18.0	16.9
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10	0	2	25.7	25.0
10	0	1	15.4	14.7
10	0	0	63.5	59.6
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9	8	4	3.4	2.4
9	8	3	8.9	8.0
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9	8	1	3.5	3.0
9	7	11	2.8	3.6
9	7	10	6.0	5.8
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9	7	3	8.3	7.1
9	7	2	11.8	11.0
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9	6	11	7.1	6.9
9	6	9	7.3	7.1
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9	6	2	9.5	9.0
9	6	1	11.7	10.0
9	5	15	9.0	8.1
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9	4	11	3.2	3.1
9	4	10	12.5	12.4
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9	4	6	23.2	21.7
9	4	5	4.6	4.0
9	4	4	11.5	10.3
9	4	3	10.3	9.7
9	4	2	21.1	20.5
9	4	1	13.0	12.7
9	4	0	4.1	2.7
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9	3	10	8.0	7.1
9	3	9	5.7	6.1
9	3	8	25.6	24.6
9	3	7	15.8	16.0
9	3	6	28.5	28.0

H	K	L	F OBS	F CALC
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9	2	6	12.1	12.4
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9	2	1	21.0	20.3
9	2	0	14.5	14.1
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9	1	16	4.2	3.8
9	1	15	9.2	8.9
9	1	14	7.8	7.9
9	1	13	4.0	5.3
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9	1	9	19.9	19.7
9	1	8	35.9	35.2
9	1	7	13.4	12.8
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9	1	4	17.3	16.7
9	1	3	23.7	26.9
9	1	2	44.4	46.1
9	1	1	18.4	17.8
9	1	0	37.3	37.2
9	0	18	4.2	3.1
9	0	17	12.9	11.8
9	0	16	2.8	2.5
9	0	15	4.0	3.2
9	0	14	15.9	14.4
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9	0	8	30.4	29.6
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9	0	6	14.9	14.6
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9	0	2	6.4	5.6
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8	9	0	2.9	2.6
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8	6	0	13.3	12.9
8	5	15	6.6	6.1
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8	3	2	23.8	23.5
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8	3	0	8.1	7.7
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8	2	16	5.2	5.7
8	2	15	3.4	3.4
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7	1	11	3.8	4.0
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6	3	13	6.1	5.6
6	3	12	22.5	21.9
6	3	11	7.9	7.9
6	3	10	11.9	11.3
6	3	9	7.3	6.6
6	3	8	12.3	11.3
6	3	7	12.3	12.3
6	3	6	6.2	5.6
6	3	5	12.3	14.5
6	3	4	21.4	19.7
6	3	3	23.1	22.0
6	3	2	8.4	8.4
6	3	1	26.2	24.7
6	3	0	11.0	10.4
6	2	19	4.5	4.3
6	2	18	3.6	3.8
6	2	17	5.3	4.8
6	2	15	9.0	8.7
6	2	14	3.2	4.0
6	2	13	9.8	9.9
6	2	12	8.1	7.9
6	2	10	17.5	19.1
6	2	9	16.4	16.2
6	2	8	13.8	13.4
6	2	7	15.1	17.7
6	2	6	31.5	30.8
6	2	5	22.7	22.2
6	2	4	35.9	34.3
6	2	3	8.3	8.2
6	2	2	44.6	42.7
6	2	1	12.8	11.5
6	2	0	15.0	14.0
6	1	19	3.9	1.5
6	1	17	5.7	5.9
6	1	16	5.4	4.6
6	1	15	5.3	6.0
6	1	14	5.9	5.6
6	1	13	4.1	4.9
6	1	12	2.6	2.0
6	1	11	9.3	10.7
6	1	10	3.8	4.2
6	1	9	9.2	9.7
6	1	8	10.7	11.7
6	1	7	5.2	3.7
6	1	6	17.9	16.6
6	1	5	28.3	24.3
6	1	4	13.6	13.8
6	1	3	14.7	13.7
6	1	2	37.9	35.3
6	1	1	41.5	36.7
6	1	0	53.1	47.3
6	0	19	4.7	4.8
6	0	18	3.8	3.9
6	0	17	2.9	2.3
6	0	15	7.4	7.9
6	0	14	9.5	9.9
6	0	13	15.3	13.7
6	0	12	11.4	10.9
6	0	11	8.0	7.8
6	0	10	4.2	3.9
6	0	9	3.3	4.4
6	0	8	12.9	13.5
6	0	7	42.0	40.9
6	0	6	15.6	14.8
6	0	5	13.0	13.2
6	0	4	65.7	64.0
6	0	3	3.8	4.0
6	0	2	4.9	4.0
6	0	1	12.1	10.9
6	0	0	142.9	155.0
5	9	6	5.3	4.8
5	9	3	4.6	4.6
5	9	2	5.2	4.0
5	9	1	4.9	3.9
5	9	0	9.3	8.6
5	8	11	2.7	3.4
5	8	8	3.2	2.4
5	8	5	3.3	3.1
5	8	3	3.8	3.1
5	8	2	3.8	3.3
5	8	1	5.6	4.9
5	8	0	5.8	4.8
5	7	12	3.7	3.2
5	7	10	4.5	3.2
5	7	9	6.8	6.5
5	7	8	3.4	3.6
5	7	7	6.9	6.3
5	7	6	4.4	4.4
5	7	5	8.6	8.5
5	7	4	5.9	5.0
5	7	3	2.9	3.9
5	7	2	11.7	11.5
5	7	1	2.8	2.5
5	7	0	7.2	5.4
5	6	15	2.5	2.7
5	6	13	2.5	3.2
5	6	12	2.6	1.8
5	6	10	10.0	9.7
5	6	9	5.9	5.7
5	6	7	5.3	4.2
5	6	6	7.5	8.6
5	6	5	3.3	4.2
5	6	4	4.2	4.8
5	6	3	15.0	15.1
5	6	2	12.0	11.3
5	6	1	9.5	9.2
5	6	0	2.2	1.9
5	5	17	2.7	2.0
5	5	16	3.6	2.8
5	5	15	4.8	4.5
5	5	14	4.3	3.9
5	5	13	5.2	4.7
5	5	12	3.9	4.4
5	5	10	8.4	8.4
5	5	9	4.8	4.9
5	5	8	6.3	5.5
5	5	7	6.5	5.0
5	5	6	10.2	10.0
5	5	4	13.2	13.7
5	5	3	3.9	3.3
5	5	2	5.2	4.7
5	5	1	13.8	13.1
5	4	18	4.3	3.6
5	4	17	2.7	2.2
5	4	15	4.0	3.8
5	4	13	6.2	6.3
5	4	12	9.1	8.6
5	4	10	4.3	4.4
5	4	9	10.7	10.7
5	4	8	17.0	16.7
5	4	7	12.4	11.5
5	4	6	4.5	5.3
5	4	5	7.4	6.2
5	4	4	5.3	5.5
5	4	3	34.3	36.1
5	4	2	18.4	19.7
5	4	1	35.0	31.9
5	4	0	20.4	18.6
5	3	18	5.3	4.4
5	3	17	3.1	3.7
5	3	16	5.7	6.0
5	3	15	6.6	6.1
5	3	14	4.2	4.3
5	3	13	12.8	12.3
5	3	12	8.3	8.1
5	3	11	5.4	4.3
5	3	10	11.0	12.0
5	3	9	4.1	4.8
5	3	8	26.3	25.8
5	3	7	10.1	9.0
5	3	6	6.1	5.1
5	3	5	17.4	17.7
5	3	4	25.1	23.1
5	3	3	28.6	26.9
5	3	2	12.2	12.1
5	3	1	7.2	6.8
5	3	0	22.8	20.7
5	2	19	6.6	6.7
5	2	18	5.1	4.0
5	2	16	6.7	6.5
5	2	15	8.9	8.5
5	2	14	6.3	6.6
5	2	13	3.0	2.3
5	2	12	14.0	14.4
5	2	11	8.0	7.7
5	2	10	14.3	13.7
5	2	9	17.9	17.2
5	2	8	12.1	12.1
5	2	7	15.7	15.0
5	2	6	6.9	5.2
5	2	5	56.9	54.9
5	2	4	19.1	16.7
5	2	3	29.6	29.1
5	2	2	14.9	14.6
5	2	1	69.2	66.5
5	2	0	12.1	10.8
5	1	20	4.9	2.8
5	1	19	6.3	5.6
5	1	17	2.3	2.2
5	1	16	2.6	2.7
5	1	15	9.1	9.7
5	1	14	7.5	8.2
5	1	13	3.8	3.3
5	1	12	6.4	7.4
5	1	11	6.0	5.9
5	1	10	17.5	16.6
5	1	9	14.9	14.9
5	1	8	19.0	18.4
5	1	7	6.8	6.1
5	1	6	32.0	33.2
5	1	5	12.5	12.4
5	1	4	7.5	7.4
5	1	3	29.1	27.8
5	1	2	47.9	44.5
5	1	1	17.7	16.7
5	1	0	9.6	8.7
5	0	20	4.6	4.7
5	0	18	3.2	3.9
5	0	17	9.9	10.1
5	0	14	8.3	7.3
5	0	13	8.1	7.4
5	0	12	2.1	2.5
5	0	11	1.8	1.3
5	0	10	7.7	7.5
5	0	9	21.5	22.7
5	0	8	3.7	4.0
5	0	7	39.5	37.3
5	0	6	26.8	23.7
5	0	5	50.4	49.3
5	0	4	4.3	4.7
5	0	3	79.1	75.1
5	0	2	19.3	17.1
5	0	1	46.2	45.1
4	9	7	3.9	3.4
4	9	5	3.8	3.7
4	9	4	5.4	4.5
4	9	3	3.0	2.7
4	9	2	6.8	5.2
4	8	9	5.1	4.5
4	8	8	2.9	2.9
4	8	6	2.3	2.3
4	8	2	7.9	6.7
4	8	0	8.1	6.6
4	7	14	2.8	2.9
4	7	13	3.8	3.1
4	7	12	2.9	3.1
4	7	11	2.9	3.1
4	7	8	4.2	3.2
4	7	7	2.3	2.0
4	7	6	3.8	4.0
4	7	5	9.3	8.7
4	7	2	6.6	6.2
4	7	1	9.0	7.7
4	7	0	15.1	13.7
4	6	16	2.6	1.8
4	6	14	3.9	3.3
4	6	13	4.5	4.2
4	6	11	8.1	7.7
4	6	10	11.6	10.2
4	6	9	2.8	2.8
4	6	8	12.6	12.1
4	6	7	10.0	9.5
4	6	6	13.4	12.0
4	6	5	9.7	9.4
4	6	4	4.9	5.1
4	6	3	7.3	6.1
4	6	2	20.3	19.9
4	6	1	7.9	6.8
4	5	16	3.7	3.5
4	5	15	3.1	2.8
4	5	14	4.8	4.3
4	5	13	7.3	7.0
4	5	12	2.8	2.3
4	5	11	4.0	2.9
4	5	10	9.0	8.4
4	5	9	7.1	6.7
4	5	8	10.4	9.9
4	5	7	18.4	18.3
4	5	6	5.5	5.7
4	5	5	7.5	7.9
4	5	4	9.7	9.5
4	5	3	14.7	13.8
4	5	2	2.4	2.0
4	5	1	8.6	8.3
4	5	0	4.1	4.1
4	4	18	2.5	2.3
4	4	17	2.5	2.6
4	4	16	5.3	5.0
4	4	15	3.1	2.7
4	4	14	5.8	5.1
4	4	13	7.8	7.6
4	4	12	13.2	11.6
4	4	11	8.4	8.7
4	4	10	14.5	14.6
4	4	9	8.3	8.5
4	4	8	16.2	15.2
4	4	7	13.0	12.4
4	4	6	12.0	12.5
4	4	5	2.9	4.1
4	4	4	36.3	39.7
4	4	3	9.2	9.2
4	4	2	8.9	8.9
4	4	1	14.4	15.1
4	4	0	38.7	34.5
4	3	19	2.8	3.4
4	3	17	5.2	5.2
4	3	16	7.6	7.2
4	3	15	7.0	6.0
4	3	14	3.0	1.8

H	K	L	F OBS	F CALC
4	3	13	6.4	6.5
4	3	12	9.0	8.7
4	3	11	14.0	14.0
4	3	10	8.6	7.7
4	3	9	16.5	16.1
4	3	8	11.0	9.8
4	3	7	5.4	6.4
4	3	6	4.1	6.5
4	3	5	39.4	36.8
4	3	4	16.3	16.3
4	3	3	9.7	8.1
4	3	2	15.5	13.6
4	3	1	23.9	21.6
4	3	0	7.6	6.6
4	2	19	7.0	6.2
4	2	17	4.7	4.2
4	2	16	7.9	7.4
4	2	15	6.1	6.0
4	2	14	3.9	4.0
4	2	13	4.2	3.9
4	2	12	12.8	11.5
4	2	11	10.7	10.5
4	2	10	3.8	4.3
4	2	9	12.8	11.8
4	2	8	24.0	21.8
4	2	7	29.3	26.5
4	2	6	41.8	37.3
4	2	5	26.6	24.3
4	2	4	43.0	40.8
4	2	3	21.9	20.6
4	2	2	40.3	38.2
4	2	1	15.7	14.3
4	2	0	39.3	38.2
4	1	20	2.5	2.4
4	1	19	4.0	4.0
4	1	16	4.9	4.4
4	1	15	4.8	5.1
4	1	14	13.7	13.1
4	1	13	6.6	6.4
4	1	12	2.7	1.3
4	1	11	12.5	12.4
4	1	10	4.5	5.4
4	1	9	21.9	22.2
4	1	8	19.4	18.0
4	1	7	55.8	51.8
4	1	6	3.4	3.7
4	1	5	16.2	15.6
4	1	4	9.8	9.9
4	1	3	50.8	48.0
4	1	2	50.9	47.8
4	1	1	35.2	32.4
4	1	0	73.1	70.7
4	0	20	6.2	5.0
4	0	19	4.1	3.4
4	0	18	8.4	8.5
4	0	17	3.1	2.8
4	0	16	2.5	2.2
4	0	15	2.8	2.2
4	0	14	12.9	13.4
4	0	13	2.5	2.3
4	0	12	11.8	12.5
4	0	11	19.4	19.0
4	0	10	22.9	21.6
4	0	9	2.7	2.6
4	0	7	19.8	17.6
4	0	6	43.7	40.4
4	0	5	59.1	56.3
4	0	4	47.3	45.4
4	0	3	27.3	25.3
4	0	2	56.4	58.4
4	0	1	44.1	39.8
4	0	0	57.8	57.7
3	9	7	3.6	3.2
3	9	6	5.2	4.9
3	9	4	3.4	2.6
3	9	3	3.0	2.2
3	9	2	8.8	7.0
3	9	1	4.7	4.3
3	9	0	4.6	4.9
3	8	11	4.5	3.8
3	8	10	4.2	4.7
3	8	9	3.8	3.5
3	8	8	6.2	5.3
3	8	7	5.6	5.1
3	8	6	3.8	2.3
3	8	5	5.2	4.5
3	8	4	3.8	3.9
3	8	3	8.7	8.1
3	8	2	5.9	4.5
3	8	1	4.1	4.6
3	8	0	5.3	5.0
3	7	14	5.2	4.3
3	7	13	3.9	2.8
3	7	12	6.9	6.9
3	7	11	4.2	3.7
3	7	9	7.2	7.3
3	7	8	3.4	3.3
3	7	7	3.6	4.4
3	7	5	3.3	2.5
3	7	4	13.6	12.0
3	7	3	6.1	5.6
3	7	1	3.1	4.0
3	7	0	12.6	12.2
3	6	16	3.3	2.2
3	6	14	6.2	6.0
3	6	13	7.5	6.3
3	6	12	2.6	2.5
3	6	11	3.0	2.9
3	6	9	9.3	9.8
3	6	8	2.2	2.0
3	6	7	9.3	8.4
3	6	5	4.8	4.4
3	6	4	8.3	8.3
3	6	3	17.0	16.0
3	6	2	8.1	7.5

H	K	L	F OBS	F CALC
3	6	1	14.3	14.4
3	6	0	3.0	4.1
3	5	17	3.8	3.6
3	5	15	10.4	9.6
3	5	14	4.6	4.0
3	5	13	3.1	1.6
3	5	12	2.7	2.7
3	5	11	11.7	10.6
3	5	10	9.4	8.7
3	5	9	7.9	6.4
3	5	8	16.8	15.8
3	5	7	13.4	12.3
3	5	6	7.6	7.9
3	5	5	4.5	2.8
3	5	4	28.5	26.0
3	5	3	13.2	13.4
3	5	2	3.2	3.2
3	5	1	21.2	20.3
3	5	0	13.4	12.6
3	4	17	5.1	4.2
3	4	16	7.2	6.7
3	4	15	4.7	4.5
3	4	14	2.6	3.1
3	4	13	7.4	7.1
3	4	12	12.6	11.9
3	4	11	5.1	4.7
3	4	10	11.1	11.1
3	4	9	12.5	12.0
3	4	8	9.2	8.4
3	4	7	6.5	6.6
3	4	6	18.6	18.0
3	4	5	13.3	14.0
3	4	4	13.6	14.0
3	4	3	11.1	10.5
3	4	2	10.5	9.9
3	4	1	12.9	12.2
3	4	0	6.1	5.0
3	3	19	3.0	2.4
3	3	18	5.8	5.3
3	3	16	7.9	7.4
3	3	14	8.2	8.2
3	3	13	3.5	3.4
3	3	12	5.3	5.6
3	3	11	21.6	20.9
3	3	10	16.8	16.5
3	3	9	4.0	3.9
3	3	8	20.3	21.7
3	3	7	23.3	21.2
3	3	6	39.6	38.2
3	3	5	42.3	36.8
3	3	4	35.1	30.2
3	3	3	5.0	3.8
3	3	2	69.1	65.6
3	3	1	11.9	9.9
3	3	0	33.9	29.5
3	2	20	4.2	4.3
3	2	19	3.7	3.0
3	2	18	6.2	5.8
3	2	17	4.8	4.2
3	2	16	11.9	10.5
3	2	15	7.2	6.4
3	2	14	5.1	4.6
3	2	12	18.0	18.0
3	2	11	6.1	6.4
3	2	10	7.2	7.4
3	2	9	10.6	11.4
3	2	8	24.7	22.8
3	2	7	34.1	31.9
3	2	6	21.3	20.3
3	2	5	25.5	23.1
3	2	4	24.1	23.2
3	2	3	53.5	49.2
3	2	2	11.9	11.9
3	2	1	34.2	32.0
3	2	0	33.7	29.8
3	1	20	4.0	3.9
3	1	18	7.8	7.0
3	1	17	9.9	9.0
3	1	15	5.4	5.8
3	1	14	2.8	2.5
3	1	13	6.7	5.9
3	1	12	22.7	22.1
3	1	11	11.1	10.0
3	1	10	21.3	22.0
3	1	9	22.7	21.0
3	1	8	30.9	29.5
3	1	7	14.1	14.3
3	1	6	31.7	29.4
3	1	5	38.1	36.0
3	1	4	41.5	38.6
3	1	3	27.6	26.2
3	1	2	25.9	25.0
3	1	1	28.7	26.4
3	1	0	46.8	44.7
3	0	19	8.7	7.9
3	0	18	3.6	3.7
3	0	15	7.7	6.9
3	0	14	34.3	33.4
3	0	13	7.0	6.7
3	0	12	4.6	4.9
3	0	11	13.5	13.1
3	0	10	29.7	33.7
3	0	9	24.5	22.7
3	0	8	57.8	51.5
3	0	7	66.9	61.7
3	0	6	42.5	40.2
3	0	5	10.6	10.7
3	0	4	5.3	4.4
3	0	2	2.4	3.0
3	0	1	14.2	12.9
2	9	8	5.6	5.9
2	9	7	5.7	5.2
2	9	6	5.3	5.8
2	9	5	7.8	6.3
2	9	4	3.7	2.9

H	K	L	F OBS	F CALC
2	9	3	3.9	2.9
2	9	2	4.1	3.2
2	9	1	5.5	5.1
2	8	12	6.9	6.8
2	8	11	2.5	2.1
2	8	10	2.8	2.8
2	8	9	4.3	3.4
2	8	8	4.8	4.9
2	8	6	6.2	5.7
2	8	4	12.0	11.2
2	8	3	2.7	1.7
2	8	2	4.4	3.7
2	8	1	2.5	2.1
2	8	0	4.1	2.9
2	7	14	3.8	3.0
2	7	13	5.4	4.8
2	7	12	4.1	3.7
2	7	11	6.3	5.4
2	7	10	3.8	3.1
2	7	9	13.5	12.6
2	7	8	7.6	7.5
2	7	7	7.4	6.4
2	7	6	5.1	5.4
2	7	5	14.1	12.5
2	7	4	3.9	4.7
2	7	3	9.8	9.0
2	7	2	3.1	3.1
2	7	1	6.3	5.5
2	7	0	4.3	3.1
2	6	16	4.0	3.1
2	6	15	7.2	6.7
2	6	14	4.6	3.9
2	6	13	5.5	4.0
2	6	12	6.0	5.1
2	6	11	12.3	11.7
2	6	10	6.3	6.4
2	6	9	3.3	3.5
2	6	8	10.6	10.3
2	6	7	7.5	6.8
2	6	6	19.2	18.2
2	6	5	14.8	14.6
2	6	4	19.3	18.7
2	6	2	17.0	16.3
2	6	1	13.7	13.3
2	6	0	7.6	7.6
2	5	17	6.8	6.5
2	5	16	2.6	3.4
2	5	15	5.8	5.4
2	5	14	6.2	5.9
2	5	13	4.8	4.1
2	5	12	8.7	5.7
2	5	11	9.0	7.4
2	5	10	10.0	9.4
2	5	8	12.7	12.1
2	5	7	8.9	7.9
2	5	6	14.3	12.1
2	5	5	8.1	7.2
2	5	4	10.1	10.2
2	5	3	3.3	2.8
2	5	2	16.9	17.2
2	5	1	28.4	26.4
2	5	0	13.2	15.2
2	4	19	7.6	6.5
2	4	17	10.1	9.2
2	4	16	4.1	4.0
2	4	15	5.0	4.5
2	4	14	8.1	6.9
2	4	13	9.6	8.9
2	4	12	5.9	5.8
2	4	11	6.2	5.0
2	4	10	3.5	2.7
2	4	9	13.6	12.3
2	4	8	16.2	15.7
2	4	7	16.2	14.0
2	4	6	1.9	2.8
2	4	5	14.3	13.0
2	4	4	33.0	29.5
2	4	3	25.1	24.5
2	4	2	8.2	7.2
2	4	1	28.1	25.6
2	4	0	7.2	7.8
2	3	19	4.9	3.8
2	3	18	8.7	7.3
2	3	17	6.9	6.0
2	3	16	8.4	7.2
2	3	14	2.5	2.4
2	3	13	4.6	3.9
2	3	12	10.3	9.0
2	3	11	29.3	27.1
2	3	10	10.1	9.8
2	3	9	14.8	13.1
2	3	8	16.2	16.2
2	3	7	16.3	14.5
2	3	6	33.8	30.0
2	3	5	34.0	29.4
2	3	4	45.0	40.7
2	3	3	12.0	9.5
2	3	2	51.4	45.0
2	3	1	27.0	26.3
2	3	0	30.6	27.6
2	2	20	4.5	3.4
2	2	19	3.4	2.6
2	2	17	8.3	7.8
2	2	16	9.0	8.1
2	2	15	12.4	11.5
2	2	14	2.6	1.7
2	2	13	24.2	22.2
2	2	12	14.9	14.3
2	2	11	24.2	22.2
2	2	10	5.0	5.7
2	2	9	13.3	13.3
2	2	8	13.6	12.4
2	2	7	32.9	28.1
2	2	6	16.7	17.0
2	2	5	17.7	15.2

H	K	L	F OBS	F CALC
2	2	4	69.2	63.2
2	2	3	38.2	34.3
2	2	2	61.9	58.2
2	2	1	9.3	8.8
2	2	0	32.7	30.3
2	1	20	4.6	4.7
2	1	19	6.2	4.9
2	1	17	3.9	3.6
2	1	16	12.6	11.2
2	1	15	9.3	9.2
2	1	14	6.1	4.5
2	1	13	4.3	4.4
2	1	12	10.3	10.0
2	1	11	21.2	20.0
2	1	10	21.6	23.2
2	1	9	14.2	12.7
2	1	8	34.3	30.2
2	1	7	48.0	43.5
2	1	6	39.6	34.6
2	1	5	59.3	54.7
2	1	4	5.9	6.4
2	1	3	12.5	12.0
2	1	2	49.3	49.6
2	1	1	30.6	27.3
2	1	0	61.3	63.5
2	0	18	3.9	3.5
2	0	17	12.6	12.2
2	0	16	14.2	13.6
2	0	15	3.3	1.1
2	0	14	30.5	29.4
2	0	13	8.0	7.7
2	0	12	5.8	5.0
2	0	10	5.0	0.0
2	0	9	30.6	27.4
2	0	8	2.2	1.0
2	0	7	36.8	33.1
2	0	6	49.6	46.0
2	0	5	21.8	19.8
2	0	4	10.1	9.4
2	0	3	54.3	56.2
2	0	2	65.6	68.8
2	0	1	42.6	41.3
2	0	0	17.1	16.1
1	9	8	11.5	10.0
1	9	6	4.2	4.1
1	9	5	7.6	7.1
1	9	3	3.0	3.6
1	9	0	3.3	2.3
1	8	12	5.1	4.3
1	8	11	5.7	4.9
1	8	10	4.4	3.2
1	8	8	2.4	2.5
1	8	7	9.2	8.5
1	8	6	3.5	2.2
1	8	4	3.9	3.1
1	8	3	7.9	7.0
1	8	2	9.4	8.3
1	8	0	5.2	5.0
1	7	14	9.0	8.2
1	7	13	4.3	4.2
1	7	12	2.9	1.3
1	7	9	3.9	3.5
1	7	8	4.5	3.9
1	7	7	2.5	3.2
1	7	6	12.7	12.2
1	7	5	7.9	7.1
1	7	4	7.6	7.1
1	7	3	8.9	9.6
1	7	2	19.8	17.9
1	7	1	3.6	3.2
1	7	0	4.9	5.0
1	6	16	5.8	4.7
1	6	15	7.1	6.2
1	6	13	5.0	4.8
1	6	12	3.4	3.5
1	6	11	5.1	4.8
1	6	10	3.0	3.2
1	6	9	10.6	9.6
1	6	7	10.6	9.3
1	6	6	13.9	12.5
1	6	5	7.4	7.7
1	6	4	22.1	21.3
1	6	3	37.8	34.0
1	6	1	22.9	21.3
1	5	18	6.2	4.7
1	5	17	3.7	2.9
1	5	16	4.4	3.9
1	5	14	4.9	4.7
1	5	12	4.3	3.3
1	5	11	6.7	4.9
1	5	10	16.8	15.3
1	5	9	3.7	2.6
1	5	8	10.9	9.1
1	5	7	17.1	17.4
1	5	6	18.2	17.5
1	5	5	19.7	18.2
1	5	4	20.1	19.4
1	5	3	12.5	11.0
1	5	2	10.1	10.5
1	5	1	37.3	41.2
1	5	0	7.1	7.7
1	4	18	5.7	4.9
1	4	17	3.8	3.4
	4	16	5.9	5.3
	4	15	3.2	2.4
	4	14	14.2	12.2
	4	13	11.2	10.5
	4	12	6.1	5.0
	4	11	16.6	15.1
	4	10	34.9	32.4
	4	9	10.1	9.2

H	K	L	F OBS	F CALC
1	4	8	12.6	12.4
1	4	7	23.6	21.8
1	4	6	22.7	23.8
1	4	5	14.4	12.8
1	4	4	5.3	5.8
1	4	3	36.3	32.0
1	4	2	29.5	26.4
1	4	1	40.1	36.7
1	4	0	59.5	54.0
1	3	18	3.8	3.2
1	3	17	5.1	4.4
1	3	16	6.1	5.0
1	3	15	12.2	11.1
1	3	14	6.4	5.0
1	3	13	24.3	22.3
1	3	12	9.7	8.1
1	3	11	23.8	21.3
1	3	10	29.0	25.4
1	3	9	21.7	18.9
1	3	8	44.3	43.7
1	3	7	18.9	16.3
1	3	6	19.4	15.6
1	3	5	8.6	7.6
1	3	4	44.4	37.3
1	3	3	66.9	60.7
1	3	2	39.7	33.6
1	3	1	34.8	31.7
1	3	0	14.0	13.3
1	2	20	4.5	4.2
1	2	19	7.7	7.1
1	2	18	7.5	7.3
1	2	17	2.7	1.8
1	2	16	7.7	6.8
1	2	15	15.3	13.7
1	2	14	10.4	10.4
1	2	13	21.8	19.5
1	2	12	19.1	18.3
1	2	11	13.6	12.4
1	2	10	4.6	4.5
1	2	9	24.0	22.8
1	2	8	30.7	27.9
1	2	7	13.2	12.1
1	2	6	27.4	24.5
1	2	5	27.8	25.5
1	2	4	17.5	14.8
1	2	3	42.4	37.8
1	2	2	13.7	12.0
1	2	1	115.5	119.7
1	2	0	35.3	33.6
1	1	20	4.9	4.0
1	1	19	3.2	2.2
1	1	18	3.6	3.1
1	1	17	10.8	10.0
1	1	16	9.9	10.0
1	1	15	11.0	10.1
1	1	14	24.5	23.3
1	1	13	4.7	3.7
1	1	12	24.8	25.2
1	1	11	11.5	11.5
1	1	10	4.9	5.0
1	1	9	3.7	3.4
1	1	8	8.6	7.1
1	1	7	6.3	5.3
1	1	6	40.2	35.5
1	1	5	13.7	12.3
1	1	4	10.9	11.7
1	1	3	39.5	36.6
1	1	2	68.7	67.8
1	1	1	51.6	49.2
1	1	0	86.0	97.6
1	0	19	3.5	3.1
1	0	18	4.5	4.6
1	0	17	9.6	8.7
1	0	16	17.4	16.6
1	0	15	4.4	4.1
1	0	14	22.0	21.5
1	0	11	8.2	8.0
1	0	10	4.5	4.7
1	0	9	50.2	46.1
1	0	8	9.7	7.8
1	0	7	38.8	36.4
1	0	6	9.1	7.9
1	0	5	29.5	26.7
1	0	4	8.4	7.2
1	0	3	109.8	141.9
1	0	2	69.8	72.5
1	0	1	11.5	10.0
0	9	7	5.2	5.3
0	9	6	5.8	6.9
0	9	2	4.1	4.5
0	8	12	3.4	3.5
0	8	11	4.9	4.3
0	8	10	5.6	6.6
0	8	9	4.3	4.7
0	8	8	6.3	6.7
0	8	6	2.9	3.3
0	8	4	4.2	4.6
0	8	2	3.4	6.7
0	8	1	2.3	2.2
0	7	14	3.1	4.5
0	7	13	5.4	4.2
0	7	11	8.9	7.6
0	7	9	5.9	5.3
0	7	8	2.5	1.9
0	7	7	3.9	4.1
0	7	6	7.5	7.1
0	7	4	12.5	14.8
0	7	3	3.5	4.5
0	7	2	2.6	4.5
0	7	1	5.1	8.0
0	6	16	3.8	3.4

H	K	L	F OBS	F CALC
0	6	13	2.2	0.8
0	6	12	6.9	6.9
0	6	11	11.9	11.2
0	6	10	5.7	5.3
0	6	8	3.4	2.1
0	6	7	13.0	12.9
0	6	6	16.3	18.7
0	6	5	6.6	8.9
0	6	4	9.5	12.4
0	6	3	10.7	12.5
0	6	2	6.2	9.5
0	6	1	6.1	10.4
0	6	0	7.7	35.2
0	5	18	3.5	2.6
0	5	17	4.3	3.2
0	5	16	2.7	2.6
0	5	15	14.7	12.5
0	5	14	2.5	1.8
0	5	13	4.7	4.1
0	5	12	14.9	13.7
0	5	11	14.2	13.8
0	5	10	3.8	3.7
0	5	9	8.9	8.1
0	5	8	10.8	10.9
0	5	7	5.4	4.4
0	5	6	18.5	18.4
0	5	5	6.6	6.4
0	5	4	14.1	16.4
0	5	3	15.2	16.6
0	5	2	9.6	14.4
0	4	18	4.4	4.3
0	4	17	3.7	3.1
0	4	16	8.3	6.9
0	4	15	2.8	3.5
0	4	13	19.3	17.0
0	4	12	3.7	4.9
0	4	11	2.9	1.4
0	4	10	13.6	12.1
0	4	9	17.7	18.0
0	4	8	9.5	7.4
0	4	7	6.3	6.3
0	4	6	39.9	40.6
0	4	5	32.2	33.1
0	4	4	41.4	44.0
0	4	3	2.1	1.9
0	4	2	17.4	21.4
0	4	1	1.7	2.8
0	4	0	4.3	24.8
0	3	19	4.8	3.4
0	3	16	6.5	5.9
0	3	15	6.1	5.5
0	3	14	25.3	23.6
0	3	13	12.4	12.2
0	3	12	43.3	40.7
0	3	11	11.0	10.7
0	3	10	18.1	16.9
0	3	9	7.1	6.3
0	3	8	7.8	8.5
0	3	7	22.1	20.1
0	3	6	19.6	17.0
0	3	5	14.8	13.1
0	3	4	40.8	37.2
0	3	3	48.4	43.5
0	3	2	29.0	27.8
0	3	1	6.7	8.3
0	2	17	2.5	1.9
0	2	16	5.9	5.4
0	2	15	2.8	3.6
0	2	14	13.1	11.7
0	2	13	12.2	11.1
0	2	12	2.3	1.0
0	2	11	7.0	6.6
0	2	10	52.0	47.9
0	2	9	23.5	21.4
0	2	7	58.5	53.2
0	2	6	68.1	60.5
0	2	5	2.7	4.3
0	2	4	29.7	26.9
0	2	3	84.1	76.5
0	2	2	109.5	102.0
0	2	1	106.7	114.5
0	2	0	2.0	3.3
0	1	20	2.9	3.9
0	1	19	2.9	2.7
0	1	18	2.6	1.3
0	1	17	3.0	1.9
0	1	16	5.0	4.9
0	1	15	13.2	12.6
0	1	14	7.6	6.7
0	1	13	7.6	7.5
0	1	12	2.3	2.0
0	1	11	27.9	25.2
0	1	10	14.7	14.2
0	1	9	9.1	7.6
0	1	8	22.4	20.3
0	1	7	25.0	24.4
0	1	6	21.7	18.5
0	1	5	61.7	57.2
0	1	4	69.6	64.2
0	1	3	105.1	123.6
0	1	2	109.5	131.3
0	1	1	25.7	23.2
0	0	18	3.4	2.7
0	0	16	17.3	17.0
0	0	14	9.8	8.6
0	0	12	29.2	27.2
0	0	10	21.5	19.5
0	0	6	14.8	14.4
0	0	4	56.6	49.8
0	0	2	35.6	33.4

Table 1.7

(a) Fractional Coordinates for (9)

	x/a	y/b	z/c
O(1)	0.46561(32)	0.42980	0.59808(46)
O(2)	0.42861(37)	0.75708(60)	0.63435(47)
O(3)	0.01952(43)	0.26161(89)	0.25172(78)
O(4)	0.18297(44)	0.12790(71)	0.18270(53)
C(1)	0.24774(45)	0.34228(72)	0.52818(61)
C(2)	0.22683(45)	0.37112(75)	0.34756(60)
C(3)	0.19064(53)	0.55936(87)	0.30453(63)
C(4)	0.29815(54)	0.67438(80)	0.38202(67)
C(5)	0.32106(47)	0.66119(76)	0.56090(61)
C(6)	0.34301(44)	0.47243(72)	0.62216(57)
C(7)	0.32519(51)	0.44800(87)	0.80063(60)
C(8)	0.21434(57)	0.31333(94)	0.77872(68)
C(9)	0.25751(73)	0.13246(98)	0.74297(88)
C(10)	0.29133(57)	0.15653(79)	0.57683(70)
C(11)	0.13759(51)	0.36656(86)	0.61628(73)
C(12)	0.44622(69)	0.38072(114)	0.90571(74)
C(13)	0.28540(60)	0.60942(101)	0.87843(72)
C(14)	0.12992(57)	0.24967(91)	0.25812(73)
C(15)	0.10004(90)	0.00442(115)	0.09193(97)

Table 1.7 (contd.)

(b) H-atom Fractional Coordinates for (9)

	x/a	y/b	z/c
H(01)	0.494(6)	0.349(11)	0.615(8)
H(02)	0.462(6)	0.800(11)	0.561(9)
H(2)	0.310(6)	0.352(11)	0.315(8)
H(31)	0.180(6)	0.573(11)	0.185(9)
H(32)	0.113(6)	0.585(11)	0.358(9)
H(41)	0.372(6)	0.648(11)	0.341(9)
H(42)	0.286(6)	0.790(11)	0.368(9)
H(5)	0.249(6)	0.703(11)	0.593(9)
H(8)	0.168(7)	0.323(11)	0.870(9)
H(91)	0.185(7)	0.040(13)	0.743(10)
H(92)	0.333(7)	0.081(13)	0.834(10)
H(101)	0.374(7)	0.133(11)	0.581(9)
H(102)	0.248(7)	0.069(12)	0.503(10)
H(111)	0.071(6)	0.292(11)	0.582(9)
H(112)	0.101(7)	0.488(11)	0.621(9)
H(121)	0.468(7)	0.277(12)	0.879(10)
H(122)	0.421(7)	0.363(12)	1.014(10)
H(123)	0.503(8)	0.473(13)	0.915(10)
H(131)	0.204(7)	0.645(12)	0.835(10)
H(132)	0.340(7)	0.711(13)	0.876(10)
H(133)	0.295(7)	0.569(12)	0.990(10)
H(151)	0.055(7)	0.063(13)	0.005(11)
H(152)	0.136(8)	-0.058(15)	0.026(10)
H(153)	0.059(8)	-0.067(16)	0.162(11)

Table 1.7 (contd.)

(c) Anisotropic Temperature Factors (Å^2) for (9)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O(1)	0.0369	0.0411	0.0530	-0.0103	0.0182	0.0194
O(2)	0.0537	0.0411	0.0453	-0.0074	0.0047	-0.0306
O(3)	0.0472	0.0821	0.1208	-0.0544	0.0032	-0.0322
O(4)	0.0697	0.0645	0.0502	-0.0461	0.0155	-0.0315
C(1)	0.0342	0.0312	0.0420	0.0156	0.0231	-0.0065
C(2)	0.0323	0.0408	0.0376	-0.0132	0.0121	-0.0082
C(3)	0.0480	0.0528	0.0302	0.0121	0.0039	-0.0165
C(4)	0.0493	0.0372	0.0433	0.0127	0.0031	-0.0112
C(5)	0.0367	0.0371	0.0376	-0.0078	0.0192	-0.0065
C(6)	0.0323	0.0350	0.0299	0.0110	0.0099	0.0245
C(7)	0.0500	0.0484	0.0303	0.0057	0.0080	0.0058
C(8)	0.0573	0.0589	0.0415	0.0197	0.0502	-0.0015
C(9)	0.0796	0.0537	0.0630	0.0465	0.0344	0.0019
C(10)	0.0605	0.0305	0.0504	-0.0040	0.0042	0.0034
C(11)	0.0422	0.0433	0.0560	0.0014	0.0418	-0.0160
C(12)	0.0782	0.0797	0.0390	0.0179	-0.0101	0.0364
C(13)	0.0570	0.0676	0.0429	-0.0192	0.0303	0.0161
C(14)	0.0521	0.0496	0.0477	-0.0336	0.0020	0.0001
C(15)	0.1140	0.0615	0.0655	-0.0439	-0.0064	-0.0669

Average estimated standard deviations (Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O	0.0023	0.0029	0.0028	0.0027	0.0020	0.0023
C	0.0034	0.0036	0.0031	0.0028	0.0025	0.0031

Table 1.7 (contd.)

(d) Fractional Coordinates for (10)

	x/a	y/b	z/c
Cl'(1)	-0.08679(8)	-0.00146(25)	0.25464(10)
O'(1)	0.27658(16)	-0.17258(35)	0.49116(14)
O'(2)	0.15173(15)	-0.08406(36)	0.36516(15)
O'(3)	0.59195(20)	-0.20362(56)	0.46862(18)
O'(4)	0.58933(18)	-0.14506(40)	0.33049(17)
O'(5)	0.11902(20)	0.02863(56)	0.23685(18)
C'(1)	0.40211(20)	-0.00219(48)	0.43480(19)
C'(2)	0.44216(23)	-0.17546(52)	0.40110(21)
C'(3)	0.40232(25)	-0.21576(57)	0.31226(22)
C'(4)	0.29420(25)	-0.22127(54)	0.31412(23)
C'(5)	0.25219(21)	-0.05394(49)	0.35298(21)
C'(6)	0.29311(21)	-0.01747(49)	0.44038(20)
C'(7)	0.26489(24)	0.15870(51)	0.48915(23)
C'(8)	0.36205(27)	0.23038(58)	0.51780(27)
C'(9)	0.41247(30)	0.32254(58)	0.44404(34)
C'(10)	0.43071(25)	0.16616(53)	0.38143(26)
C'(11)	0.42268(24)	0.06094(56)	0.52572(24)
C'(12)	0.20935(30)	0.29051(59)	0.43391(31)
C'(13)	0.20479(29)	0.11901(60)	0.56772(27)
C'(14)	0.54854(24)	-0.17531(55)	0.40490(24)
C'(15)	0.69091(26)	-0.13771(60)	0.32852(28)
C'(16)	0.09445(24)	-0.03659(56)	0.30242(23)
C'(17)	-0.00463(25)	-0.08234(72)	0.32937(29)

(e) H-atom Fractional Coordinates for (10)

	x/a	y/b	z/c
H'(01)	0.2201(40)	-0.2194(81)	0.4971(34)
H'(2)	0.4263(39)	-0.2690(81)	0.4424(34)
H'(31)	0.4207(38)	-0.1411(77)	0.2673(35)
H'(32)	0.4279(38)	-0.3326(77)	0.2899(34)
H'(41)	0.2721(39)	-0.2594(79)	0.2584(33)
H'(42)	0.2767(37)	-0.3211(80)	0.3482(35)
H'(5)	0.2602(38)	0.0557(78)	0.3123(34)
H'(8)	0.3556(38)	0.2931(82)	0.5800(34)
H'(91)	0.4761(40)	0.3724(78)	0.4589(35)
H'(92)	0.3718(39)	0.4054(75)	0.4136(36)
H'(101)	0.4998(35)	0.1526(79)	0.3659(36)
H'(102)	0.3946(37)	0.1758(81)	0.3298(35)
H'(111)	0.3996(35)	-0.0149(80)	0.5659(34)
H'(112)	0.4953(38)	0.0909(78)	0.5390(35)
H'(121)	0.1387(38)	0.2453(80)	0.4255(35)
H'(122)	0.2404(39)	0.3027(82)	0.3861(33)
H'(123)	0.2041(40)	0.4113(74)	0.4733(34)
H'(131)	0.2408(39)	0.0500(78)	0.6099(34)
H'(132)	0.1416(37)	0.0536(78)	0.5529(34)
H'(133)	0.1842(38)	0.2479(79)	0.5944(33)
H'(151)	0.7057(39)	-0.1056(76)	0.2765(35)
H'(152)	0.7188(38)	-0.2674(79)	0.3556(34)
H'(153)	0.7091(38)	-0.0990(73)	0.3769(34)
H'(171)	-0.0141(36)	-0.2515(80)	0.3326(37)
H'(172)	-0.0219(36)	-0.0071(81)	0.3790(34)

Table 1.7 (contd.)

(f) Anisotropic Temperature Factors (Å^2) for (10)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Cl'(1)	0.0334	0.1055	0.1092	0.0396	-0.0575	-0.0043
O'(1)	0.0270	0.0394	0.0333	0.0136	0.0033	-0.0071
O'(2)	0.0230	0.0506	0.0354	0.0072	-0.0055	-0.0071
O'(3)	0.0344	0.1065	0.0440	0.0270	-0.0078	0.0416
O'(4)	0.0303	0.0571	0.0445	0.0115	0.0069	-0.0008
O'(5)	0.0413	0.1006	0.0411	0.0331	-0.0176	0.0005
C'(1)	0.0207	0.0331	0.0302	0.0025	-0.0035	-0.0014
C'(2)	0.0270	0.0388	0.0320	0.0006	0.0017	-0.0019
C'(3)	0.0313	0.0510	0.0333	-0.0197	0.0059	0.0025
C'(4)	0.0319	0.0447	0.0369	-0.0226	-0.0056	-0.0037
C'(5)	0.0207	0.0394	0.0336	0.0009	-0.0059	0.0018
C'(6)	0.0245	0.0353	0.0292	0.0023	-0.0027	0.0017
C'(7)	0.0320	0.0353	0.0406	-0.0137	-0.0028	0.0084
C'(8)	0.0329	0.0445	0.0576	-0.0356	-0.0027	-0.0053
C'(9)	0.0422	0.0332	0.0882	-0.0094	0.0077	-0.0105
C'(10)	0.0330	0.0345	0.0558	0.0229	0.0063	-0.0081
C'(11)	0.0300	0.0480	0.0409	-0.0168	-0.0120	0.0001
C'(12)	0.0466	0.0414	0.0657	-0.0061	-0.0056	0.0320
C'(13)	0.0436	0.0543	0.0476	-0.0227	0.0167	0.0144
C'(14)	0.0302	0.0401	0.0424	-0.0011	0.0017	0.0117
C'(15)	0.0308	0.0528	0.0541	0.0091	0.0071	0.0016
C'(16)	0.0376	0.0492	0.0380	-0.0146	-0.0138	0.0106
C'(17)	0.0237	0.0761	0.0584	-0.0062	-0.0141	0.0052

Table 1.7 (contd.)

Average estimated standard deviations ($\mathring{A}^2$)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Cl	0.0004	0.0011	0.0011	0.0021	0.0012	0.0014
O	0.0012	0.0020	0.0013	0.0029	0.0022	0.0028
C	0.0016	0.0021	0.0020	0.0036	0.0031	0.0033

Table 1.8

Interatomic Distances (Å) and Angles (°) with estimated standard deviations in parentheses

(a) Bonded Distances (9)

O(1)-C(6)	1.428(6)	C(4)-C(5)	1.513(8)
O(2)-C(5)	1.429(7)	C(5)-C(6)	1.561(8)
O(3)-C(14)	1.196(8)	C(6)-C(7)	1.593(7)
O(4)-C(14)	1.338(8)	C(7)-C(8)	1.581(9)
O(4)-C(15)	1.441(10)	C(7)-C(12)	1.540(9)
C(1)-C(2)	1.541(7)	C(7)-C(13)	1.522(10)
C(1)-C(6)	1.559(7)	C(8)-C(9)	1.531(10)
C(1)-C(10)	1.551(8)	C(8)-C(11)	1.541(9)
C(1)-C(11)	1.546(8)	C(9)-C(10)	1.551(10)
C(2)-C(3)	1.541(9)	average O-H	0.78(8)
C(2)-C(14)	1.512(8)	average C-H	0.98(8)
C(3)-C(4)	1.522(8)		

Table 1.8 (contd.)

(b) Interbond Angles (9)

C(14)-O(4)-C(15)	116.7(6)	C(1)-C(6)-C(5)	112.9(4)
C(2)-C(1)-C(6)	112.6(4)	C(1)-C(6)-C(7)	103.3(4)
C(2)-C(1)-C(10)	112.7(5)	C(5)-C(6)-C(7)	113.4(4)
C(2)-C(1)-C(11)	119.7(4)	C(6)-C(7)-C(8)	101.2(4)
C(6)-C(1)-C(10)	108.9(4)	C(6)-C(7)-C(12)	110.9(4)
C(6)-C(1)-C(11)	99.7(4)	C(6)-C(7)-C(13)	114.9(5)
C(10)-C(1)-C(11)	102.0(4)	C(8)-C(7)-C(12)	113.2(6)
C(1)-C(2)-C(3)	111.2(4)	C(8)-C(7)-C(13)	108.8(5)
C(1)-C(2)-C(14)	112.1(5)	C(12)-C(7)-C(13)	107.8(5)
C(3)-C(2)-C(14)	110.4(4)	C(7)-C(8)-C(9)	112.0(5)
C(2)-C(3)-C(4)	108.2(5)	C(7)-C(8)-C(11)	101.6(5)
C(3)-C(4)-C(5)	111.7(5)	C(9)-C(8)-C(11)	101.5(5)
O(2)-C(5)-C(4)	112.1(4)	C(8)-C(9)-C(10)	102.1(5)
O(2)-C(5)-C(6)	106.3(4)	C(1)-C(10)-C(9)	104.3(5)
C(4)-C(5)-C(6)	113.0(5)	C(1)-C(11)-C(8)	94.2(4)
O(1)-C(6)-C(1)	108.8(4)	O(3)-C(14)-O(4)	123.7(7)
O(1)-C(6)-C(5)	104.9(4)	O(3)-C(14)-C(2)	125.0(6)
O(1)-C(6)-C(7)	113.6(4)	O(4)-C(14)-C(2)	111.3(5)

Table 1.8 (contd.)

(c) Intramolecular Non-bonded Distances (9)

O(1)...O(2)	2.60	C(2)...C(5)	2.96
O(1)...C(3)	3.67	C(3)...C(6)	2.99
O(1)...C(10)	2.83	C(3)...C(10)	3.94
O(1)...C(11)	3.64	C(3)...C(11)	3.21
O(1)...C(12)	2.72	C(5)...C(10)	3.94
O(2)...C(13)	3.06	C(5)...C(11)	3.13
O(3)...C(3)	2.95	C(5)...C(13)	2.86
O(3)...C(11)	3.26	C(6)...C(9)	3.05
O(3)...C(15)	2.66	C(7)...C(10)	2.95
O(4)...C(3)	3.51	C(9)...C(12)	2.97
O(4)...C(10)	3.38	C(10)...C(14)	3.05
C(1)...C(4)	2.96	C(11)...C(13)	3.14
C(1)...C(8)	2.26	C(11)...C(14)	3.19

Table 1.8 (contd.)

(d) Intermolecular Distances (9)

O(1)...O(2^{I})	2.83	O(3)...C(11^{IV})	3.79
O(1)...C(4^{I})	3.23	O(3)...C(13^{IV})	3.50
O(1)...C(5^{I})	3.58	O(3)...C(15^{V})	3.54
O(1)...C(10^{II})	3.72	O(4)...C(8^{VI})	3.83
O(1)...H(02^{I})	1.98	C(3)...C(15^{VII})	3.86
O(2)...O(1^{II})	2.83	C(4)...C(15^{VII})	3.92
O(2)...C(2^{II})	3.83	C(5)...C(10^{VII})	3.87
O(2)...C(6^{II})	3.99	C(8)...C(15^{VII})	3.98
O(2)...C(9^{III})	3.67	C(9)...C(15^{VII})	3.86
O(2)...C(10^{III})	3.44	H(02)...O(1^{II})	1.98
O(2)...C(10^{II})	3.91		

Roman numerals as superscripts refer to the equivalent positions which should be applied to the coordinates of the second atom :

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

Table 1.8 (contd.)

(e) Bonded Distances (10)

Cl'(1)-C'(17)	1.773(5)	C'(3)-C'(4)	1.544(5)
O'(1)-C'(6)	1.439(4)	C'(4)-C'(5)	1.526(5)
O'(2)-C'(5)	1.464(4)	C'(5)-C'(6)	1.526(5)
O'(2)-C'(16)	1.335(4)	C'(6)-C'(7)	1.588(5)
O'(3)-C'(14)	1.203(5)	C'(7)-C'(8)	1.556(5)
O'(4)-C'(14)	1.333(5)	C'(7)-C'(12)	1.543(6)
O'(4)-C'(15)	1.451(5)	C'(7)-C'(13)	1.540(6)
O'(5)-C'(16)	1.201(5)	C'(8)-C'(9)	1.537(7)
C'(1)-C'(2)	1.523(5)	C'(8)-C'(11)	1.548(6)
C'(1)-C'(6)	1.562(4)	C'(9)-C'(10)	1.562(6)
C'(1)-C'(10)	1.578(5)	C'(16)-C'(17)	1.517(5)
C'(1)-C'(11)	1.544(5)	average O-H	0.89(6)
C'(2)-C'(3)	1.547(5)	average C-H	1.01(6)
C'(2)-C'(14)	1.519(5)		

Table 1.8 (contd.)

(f) Interbond Angles (10)

C'(5)-O'(2)-C'(16)	117.4(3)	C'(5)-C'(6)-C'(7)	119.6(3)
C'(14)-O'(4)-C'(15)	117.5(3)	C'(6)-C'(7)-C'(8)	101.9(3)
C'(2)-C'(1)-C'(6)	109.3(3)	C'(6)-C'(7)-C'(12)	113.2(3)
C'(2)-C'(1)-C'(10)	113.9(3)	C'(6)-C'(7)-C'(13)	111.8(3)
C'(2)-C'(1)-C'(11)	121.3(3)	C'(8)-C'(7)-C'(12)	113.5(3)
C'(6)-C'(1)-C'(10)	110.3(3)	C'(8)-C'(7)-C'(13)	109.2(3)
C'(6)-C'(1)-C'(11)	99.2(3)	C'(12)-C'(7)-C'(13)	107.3(3)
C'(10)-C'(1)-C'(11)	101.6(3)	C'(7)-C'(8)-C'(9)	110.7(3)
C'(1)-C'(2)-C'(3)	110.4(3)	C'(7)-C'(8)-C'(11)	103.6(3)
C'(1)-C'(2)-C'(14)	111.1(3)	C'(9)-C'(8)-C'(11)	100.0(3)
C'(3)-C'(2)-C'(14)	113.8(3)	C'(8)-C'(9)-C'(10)	102.6(3)
C'(2)-C'(3)-C'(4)	110.8(3)	C'(1)-C'(10)-C'(9)	103.0(3)
C'(3)-C'(4)-C'(5)	112.2(3)	C'(1)-C'(11)-C'(8)	94.2(3)
O'(2)-C'(5)-C'(4)	108.0(3)	O'(3)-C'(14)-O'(4)	123.1(3)
O'(2)-C'(5)-C'(6)	106.5(3)	O'(3)-C'(14)-C'(2)	123.2(3)
C'(4)-C'(5)-C'(6)	111.3(3)	O'(4)-C'(14)-C'(2)	113.7(3)
O'(1)-C'(6)-C'(1)	104.8(3)	O'(2)-C'(16)-O'(5)	125.0(3)
O'(1)-C'(6)-C'(5)	107.3(3)	O'(2)-C'(16)-C'(17)	107.5(3)
O'(1)-C'(6)-C'(7)	111.5(3)	O'(5)-C'(16)-C'(17)	127.5(4)
C'(1)-C'(6)-C'(5)	110.1(3)	Cl'(1)-C'(17)-C'(16)	110.6(3)
C'(1)-C'(6)-C'(7)	102.6(3)		

Table 1.8 (contd.)

(g) Intramolecular Non-bonded Distances (10)

Cl'(1)...O'(5)	2.96	C'(1)...C'(8)	2.26
O'(1)...O'(2)	2.76	C'(2)...C'(5)	2.96
O'(1)...C'(3)	3.37	C'(3)...C'(6)	2.96
O'(1)...C'(10)	3.79	C'(3)...C'(10)	3.11
O'(1)...C'(11)	2.78	C'(3)...C'(11)	3.98
O'(1)...C'(13)	2.71	C'(5)...C'(10)	3.07
O'(2)...C'(12)	3.14	C'(5)...C'(11)	3.76
O'(3)...C'(3)	3.67	C'(5)...C'(12)	2.96
O'(3)...C'(11)	3.26	C'(6)...C'(9)	3.08
O'(3)...C'(15)	2.68	C'(7)...C'(10)	2.92
O'(4)...C'(3)	2.74	C'(9)...C'(12)	2.91
O'(4)...C'(10)	3.36	C'(10)...C'(14)	3.10
O'(5)...C'(4)	3.36	C'(11)...C'(13)	3.21
O'(5)...C'(5)	2.72	C'(11)...C'(14)	3.17
C'(1)...C'(4)	2.96		

Table 1.8 (contd.)

(h) Intermolecular Distances (10)

$\mathrm{Cl'(1)\ldots O'(2^{I})}$	3.79	$\mathrm{O'(2)\ldots O'(3^{IV})}$	3.20
$\mathrm{Cl'(1)\ldots O'(5^{II})}$	3.58	$\mathrm{O'(3)\ldots O'(1^{V})}$	2.87
$\mathrm{Cl'(1)\ldots C'(4^{I})}$	3.80	$\mathrm{O'(3)\ldots C'(13^{V})}$	3.57
$\mathrm{Cl'(1)\ldots C'(12^{II})}$	3.80	$\mathrm{O'(3)\ldots H'(01^{V})}$	1.99
$\mathrm{Cl'(1)\ldots C'(15^{III})}$	3.53	$\mathrm{O'(4)\ldots C'(10^{VI})}$	3.65
$\mathrm{Cl'(1)\ldots C'(16^{I})}$	3.62	$\mathrm{O'(5)\ldots C'(11^{VII})}$	3.46
$\mathrm{Cl'(1)\ldots C'(17^{I})}$	3.67	$\mathrm{O'(5)\ldots C'(17^{I})}$	3.52
$\mathrm{O'(1)\ldots O'(3^{IV})}$	2.87	$\mathrm{H'(01)\ldots O'(3^{IV})}$	1.99
$\mathrm{O'(1)\ldots C'(15^{IV})}$	3.42		

Roman numerals as superscripts refer to the equivalent positions which should be applied to the coordinates of the second atom :

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

Table 1.9

(i) Least-squares Planes for (9)

given in the form $\ell X' + mY' + nZ' = d$,
where X', Y' and Z' are coordinates in Å

(a) Plane equations

Plane (1) : $-0.0813\,X' + 0.5867\,Y' - 0.8057\,Z' = -0.5378$

Plane (2) : $0.9401\,X' - 0.2905\,Y' - 0.1785\,Z' = 0.9957$

Plane (3) : $-0.9539\,X' + 0.2665\,Y' - 0.1381\,Z' = -3.2033$

Plane (4) : $-0.2696\,X' - 0.9548\,Y' - 0.1250\,Z' = -3.7347$

Plane (5) : $-0.6791\,X' + 0.7337\,Y' - 0.0212\,Z' = 0.0820$

Plane (6) : $-0.9319\,X' - 0.2987\,Y' - 0.2060\,Z' = -4.1196$

(b) Deviation of atoms (Å) from planes (starred atoms not used to define plane)

Plane (1) : O(3) 0.003, O(4) 0.001, C(2) 0.003, C(14) -0.008, C(15) 0.001

Plane (2) : C(1) 0.003, C(2) -0.003, C(3)* -0.739, C(4) 0.003, C(5) -0.003, C(6)* 0.558

Plane (3) : C(1)* 0.830, C(6) 0.043, C(7) -0.043, C(8)* 0.803, C(9) 0.044, C(10) -0.045

Plane (4) : C(1) -0.021, C(2) 0.014, C(8) 0.013, C(11) -0.006

Plane (5) : C(1) -0.015, C(6) 0.022, C(7) -0.021, C(8) 0.015

Plane (6) : C(1) 0.029, C(8) -0.029, C(9) 0.042, C(10) -0.042

Table 1.9 (contd.)

(c) Dihedral angles between planes (°)

(1) - (4) 64.1, (2) - (3) 18.3, (2) - (4) 87.3,
(2) - (6) 41.2, (3) - (4) 88.9, (4) - (5) 59.0,
(4) - (6) 55.8, (5) - (6) 65.3

(ii) Least-squares Planes for (10)

(a') Plane equations

Plane (1) : $0.0110\,X' - 0.9789\,Y' - 0.2039\,Z' = 0.0785$
Plane (2) : $0.3891\,X' + 0.5180\,Y' - 0.7618\,Z' = -3.0413$
Plane (3) : $-0.5467\,X' + 0.3792\,Y' - 0.7465\,Z' = -7.4655$
Plane (4) : $0.7704\,X' + 0.5103\,Y' - 0.3823\,Z' = 1.7362$
Plane (5) : $-0.0231\,X' + 0.5632\,Y' - 0.8260\,Z' = -5.8669$
Plane (6) : $-0.8990\,X' + 0.0728\,Y' - 0.4319\,Z' = -8.0944$
Plane (7) : $0.0668\,X' - 0.9053\,Y' - 0.4194\,Z' = -1.6920$

(b') Deviation of atoms (Å) from planes (starred atoms not used to define plane)

Plane (1) : O'(3) 0.006, O'(4) 0.019, C'(2) -0.008, C'(14) -0.004, C'(15) -0.013

Plane (2) : C'(1) 0.024, C'(2) -0.024, C'(3)* 0.668 C'(4) 0.024, C'(5) -0.024, C'(6)* -0.708

Plane (3) : C'(1)* -0.814, C'(6) -0.073, C'(7) 0.074, C'(8)* -0.817, C'(9) -0.076, C'(10) 0.075

Table 1.9 (contd.)

Plane (4) : C'(1) 0.046, C'(2) 0.023, C'(3) -0.033, C'(8) -0.002, C'(11) -0.035

Plane (5) : C'(1) 0.042, C'(6) -0.060, C'(7) 0.060, C'(8) -0.042, C'(11)* -0.885

Plane (6) : C'(1) -0.037, C'(8) 0.038, C'(9) -0.055, C'(10) 0.054, C'(11)* -0.887

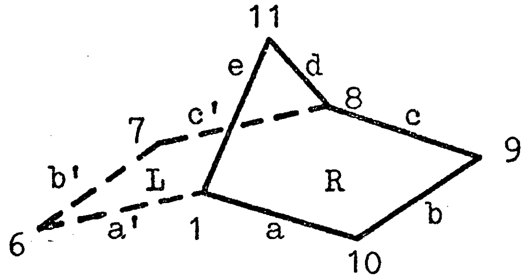
Plane (7) : Cl'(1) -0.071, O'(2) -0.013, O'(5) 0.038, C'(5) -0.042, C'(16) 0.025, C'(17) 0.064

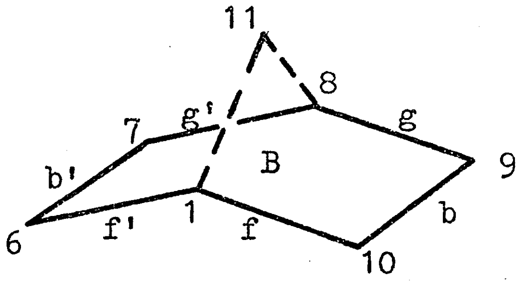
(c') Dihedral angles between planes (°)

(1) - (4) 65.6, (2) - (3) 56.5, (2) - (4) 31.4,
(2) - (6) 89.0, (3) - (4) 86.7, (4) - (5) 54.2,
(4) - (6) 60.6, (5) - (6) 65.3

Table 1.10

Comparison of Skeletal Twisting





Ring L: C(1), C(6), C(7),
C(8), C(11).

Ring R: C(1), C(10), C(9),
C(8), C(11).

Ring B: C(1), C(6), C(7), C(8),
C(9), C(10).

Torsion angles (°)		Bornane[101]	(9)	(10)
Ring L	a'	36	+39.2	+43.6
	b'	0	- 3.4	- 9.6
	c'	36	-33.8	-27.8
	d'	56	+57.8	+54.3
	e'	56	-59.4	-59.3
Ring R	a	36	-29.1	-28.6
	b	0	- 6.9	- 8.7
	c	36	+40.9	+43.0
	d	56	-57.8	-60.0
	e	56	+52.5	+53.8
Ring B	f	71	+75.6	+75.8
	g	71	-66.8	-65.7
	f'	71	-67.1	-62.5
	g'	71	+73.8	+78.5

Figure 1.1

Atomic numbering scheme

(9)

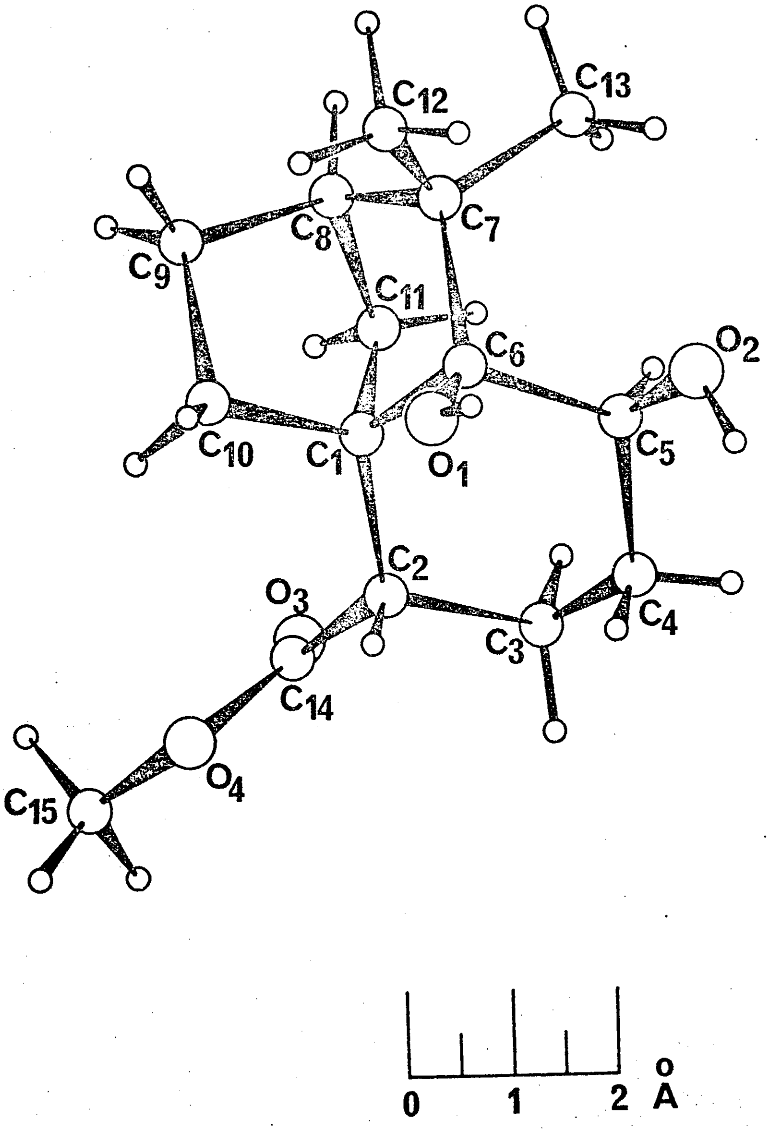

C13
C12
C7
C8
C9
C11
C6
O2
C10
C1
O1
C5
C2
O3
C4
C3
C14
O4
C15
0
1
2
Å

Figure 1.2

Atomic numbering scheme

(10)

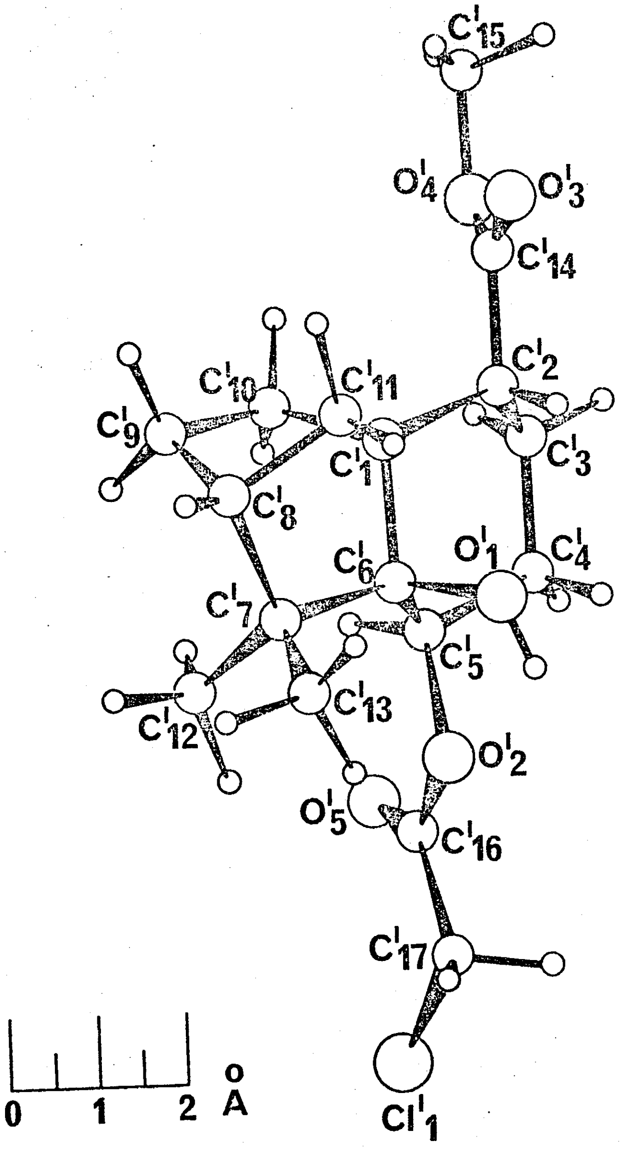

C'_{15}
O'_4
O'_3
C'_{14}
C'_2
C'_{10}
C'_{11}
C'_9
C'_1
C'_3
C'_8
C'_6
O'_1
C'_4
C'_7
C'_5
C'_{13}
C'_{12}
O'_2
O'_5
C'_{16}
C'_{17}
Cl'_1
0
1
2
Å

Figure 1.3

Molecular packing arrangement viewed along the b-axis, illustrating intermolecular O-H...O hydrogen bonding between screw-related molecules

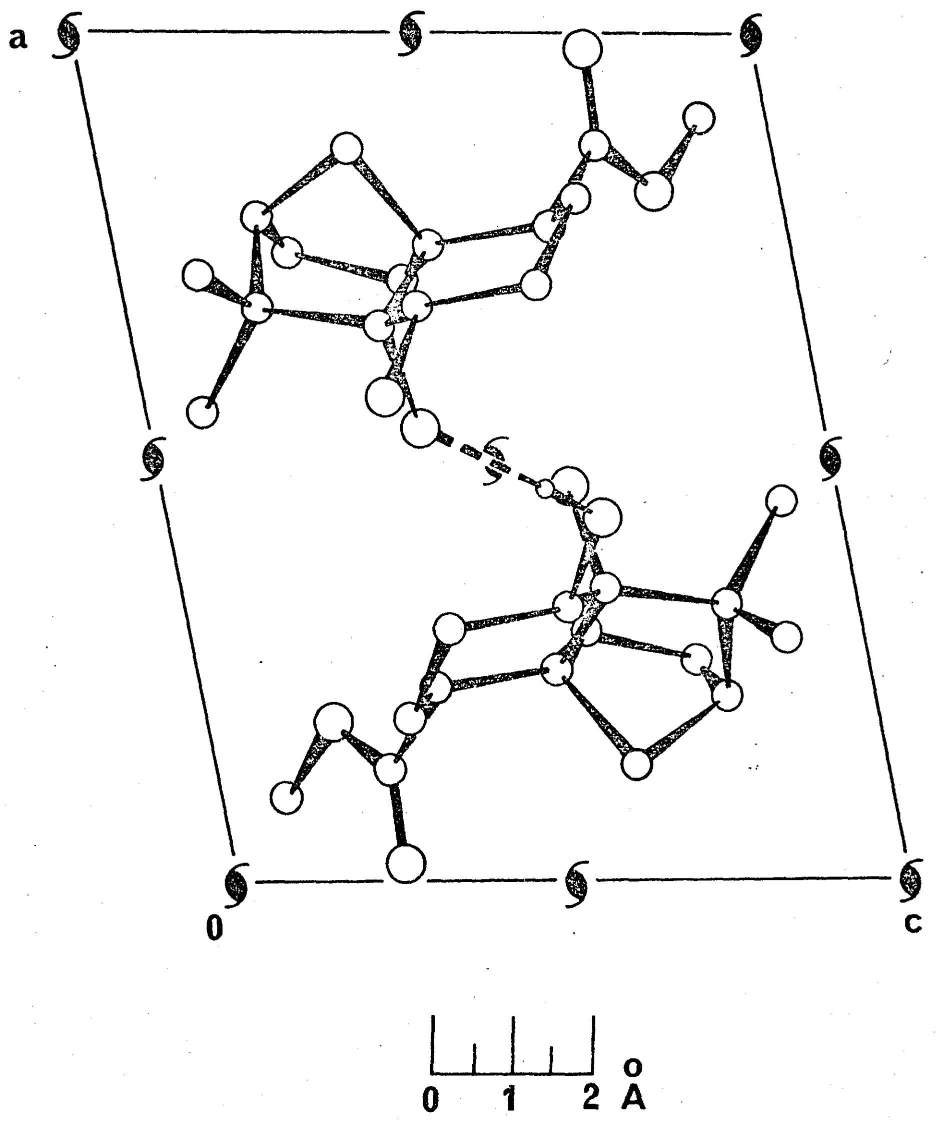

a
0
c
0 1 2 Å

Figure 1.4

Molecular packing arrangement viewed along the b-axis, illustrating intermolecular O-H...O hydrogen bonding extending in the a-direction

(10)

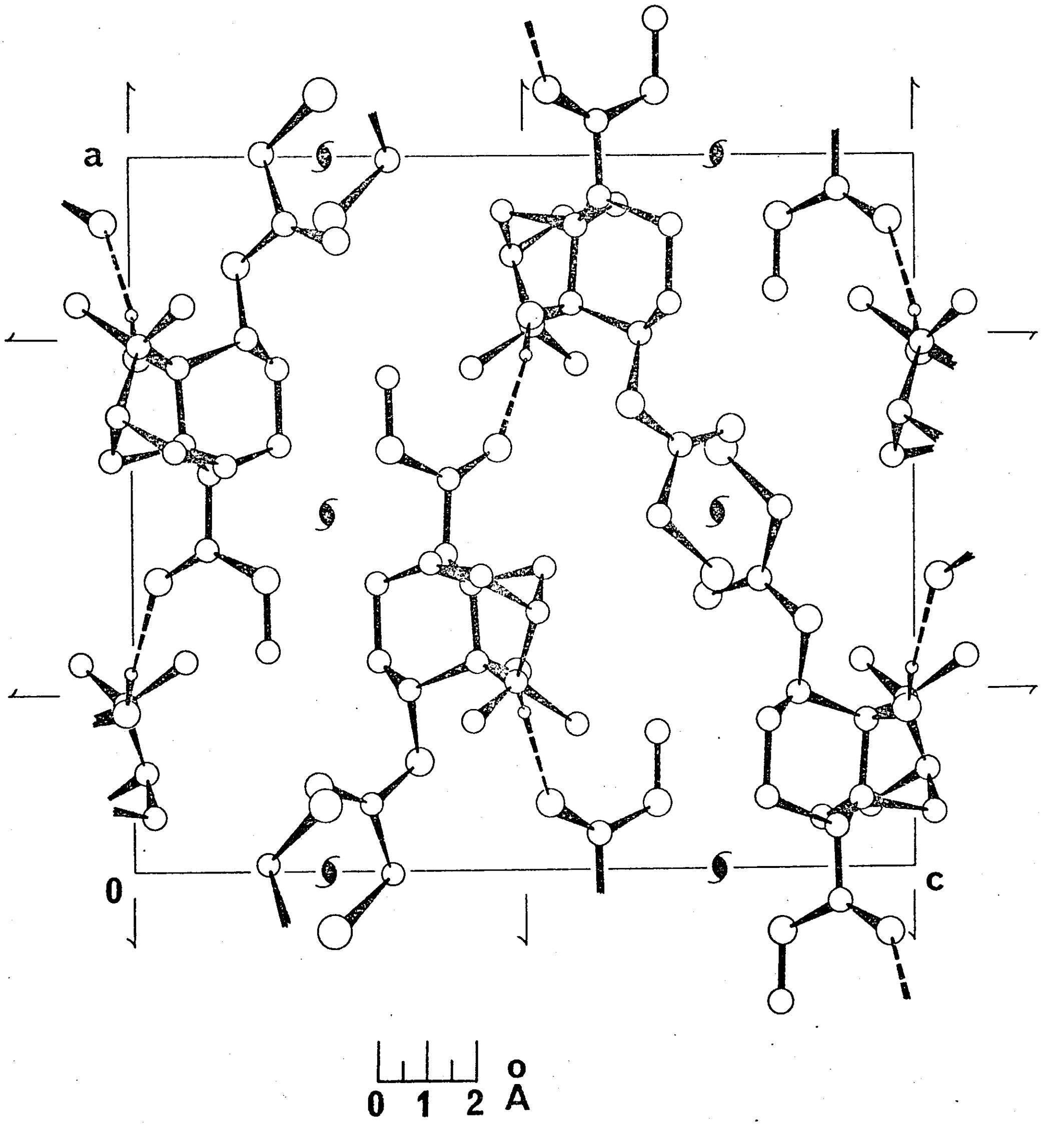
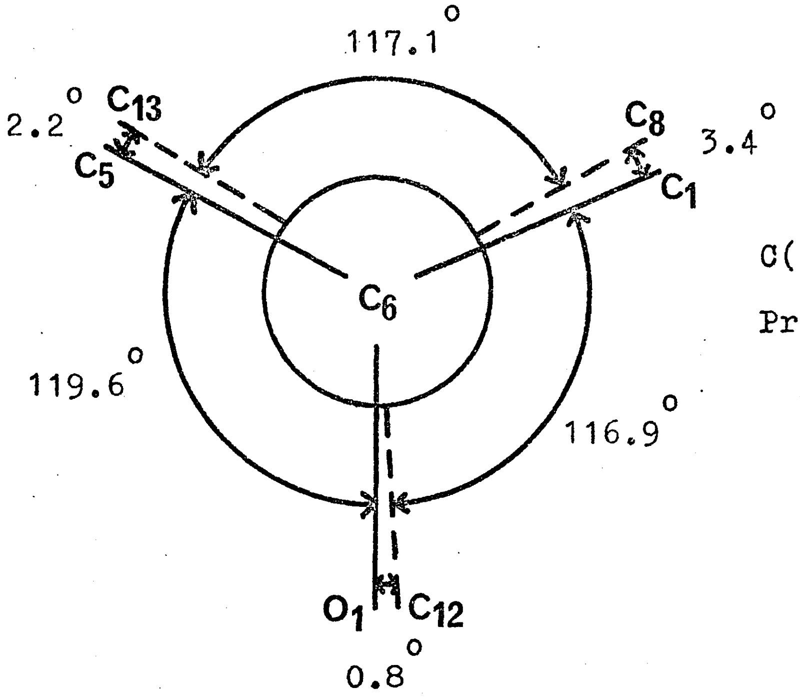
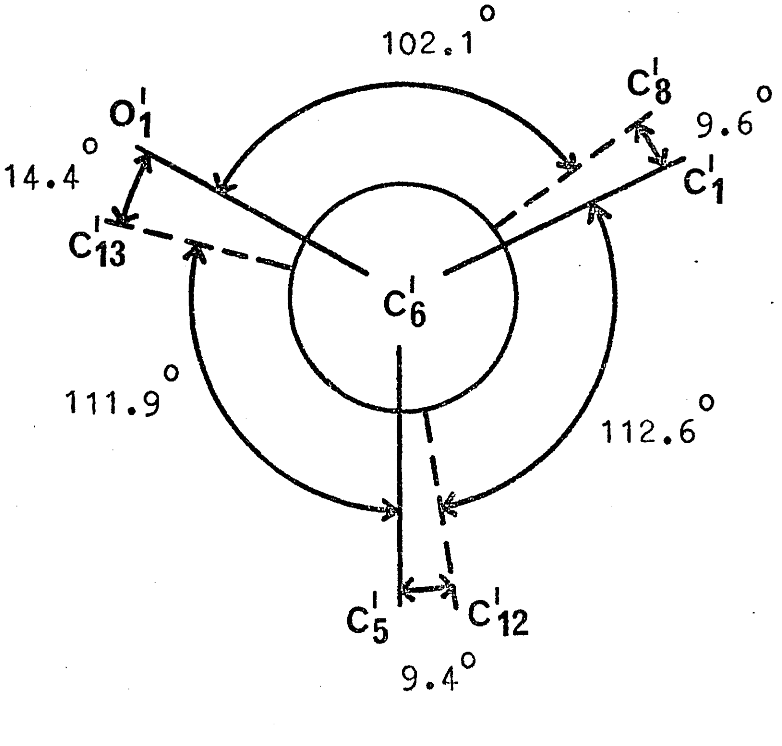

a
0
c
0 1 2
o
A

Figure 1.5

Newman projections illustrating the comparative distortions about the respective C(6)-C(7) bonds of (9) and (10)



C(6) - C(7)
Projection
for (9)



C'(6) - C'(7)
Projection
for (10)

1.3 DISCUSSION

The two crystal structure analyses have shown compounds (4) and (8) to be 2β-carbomethoxy-5α,6α-dihydroxy-7,7-dimethyltricyclo $[6.2.1.0^{1,6}]$ undecane (9) and 2α-carbomethoxy-5β-chloroacetoxy-7,7-dimethyltricyclo $[6.2.1.0^{1,6}]$ undecan-6β-ol (10) respectively, with the stereochemistries indicated. Since (9) is therefore the rearrangement precursor of (5),[125] the most probable mechanism for this rearrangement is via a concerted S_N2 ring expansion with inversion of configuration to give the zizanoic acid derivative. However, a similar mechanism applied to the rearrangement of (10) yields a cis A/B ring junction, and conversion of this product to the epizizanoic acid derivative (C(2) epimer of zizanoic acid) can only be achieved by a subsequent epimerisation of the chiral centre C(5).

It is apparent, from the αα-diol and ββ-diol stereochemistries of (9) and (10) respectively, that the osmium tetroxide hydroxylating agent has preferentially approached the endo-face of (3) to produce (9), and the exo-face of (6) to produce (10), although it has previously been predicted that steric hindrance to approach should be greater on the endo-face.[126] The influence of some other factors, thus implied, led to a consideration of the transition states which would be involved in the formation of the four possible products α(αα), β(αα), α(ββ) and β(ββ), revealing that, in both the α(αα) and β(ββ) cases, there would be severe 1:3 diaxial repulsions between the carbomethoxy group and the approaching osmium tetroxide moiety. Since no such serious interactions are obvious for the β(αα) and α(ββ) transition states, such considerations would predict that (9) and (10) should result from cis-hydroxylations of (3) and (6) respectively, in complete agreement with the X-ray analyses. It is thus reasonable to infer that the β or α orientations of the carbomethoxy groups in (3) and (6) respectively not only control the stereochemical consequences of the cis-hydroxylation reactions, but therefore also control the subsequent rearrangements of (9) to the zizanoic acid series, and of (10) to the C(5) epimer of the epizizanoic acid series.

Although the solution of this mechanistic problem provided the original reason for undertaking both analyses, it was also evident that (9) and (10) have the same basic chemical constitutions (apart from the chloroacetoxy function in (10)), while differing in their relative stereochemistries. The results of the analyses thus also provide an opportunity to study changes which may arise from alterations in the relative stereochemistries of substituents and ring-fusions.

One possible approach to a comparison of the geometries of (9) and (10) is to regard the geometry of (10) as being applicable to its enantiomorph (11). As a result, the skeletons of (9) and (11) differ only in the orientations of the 1- and 2-carbon bridges of the bicyclo [2.2.1] heptyl system relative to the rest of the molecular framework, i.e. β and α respectively in (9) and vice-versa in (11). Since 1- and 2-carbon bridges have different steric requirements, it is reasonable to expect that their opposite orientations in (9) and (11) will result in different molecular conformations. In (9), the inclinations of the 1- and 2-carbon bridges to the plane of atoms [C(1), C(2), C(4), C(5)] are 87.3° and 41.2° respectively, while the corresponding values in (11) are 31.4° and 89.0°, indicating a 10° discrepancy for the α-bridges, rather than the exact reversal which would have resulted had those bridges displayed identical steric requirements. Moreover, by considering corresponding valency angles and non-bonded separations within the two systems, further evidence is provided. The angle O(1)-C(6)-C(1) which has a value of 104.8(3) in (11), increases to 108.8(4)° in (9), thus effecting a release of steric crowding of the α-tertiary hydroxyl group and the α(2-carbon)bridge in the latter molecule. Similarly, the O(4)-C(14)-C(2) angle in (9) [111.3(5)°] opens slightly to a value of 113.7(3)° in (11), relieving interaction between the β(2-carbon)bridge and the β-carbomethoxy grouping in (11). Furthermore, steric repulsion of the α-hydroxyl group by the α(2-carbon)bridge in (9) is evidenced by the larger O(1)...C(3) non-bonded separation in (9) [3.67 Å in (9); 3.37 Å in (11)].

Notable differences resulting from the steric presence of the chloroacetate function in (11) are reflected both in the O(1)...O(2) separation, which is ca. 0.2 Å greater in (11) than in (9), and also in the valency angles C(5)-C(6)-C(7) [119.6(3) in (11); 113.4(4)° in (9)] and O(1)-C(6)-C(5) [107.3(3) in (11); 104.9(4)° in (9)]. These increases are necessarily accompanied by a closing of the angle O(2)-C(5)-C(4) [108.0(3) in (11); 112.1(4)° in (9)].

Yet another approach is to regard (9) and (10) as possessing similar bicyclo[2.2.1]heptyl skeletons fused in differing manners to the cyclohexane ring, with corresponding reorientation of the other bridgehead substituents. While a comparison of the mean bond lengths [1.557(8) Å in (9);

1.559(5) Å in (10)] and endocyclic valency angles [101.1(4)° in (9); 101.0(3)° in (10)] of both bicyclic residues suggests overall similarities, information on detailed skeletal differences may be obtained from comparisons of the torsion angles within the two bicyclo [2.2.1] heptyl systems. Perhaps the most illustrative description of the bicyclo [2.2.1] heptyl system has been as two cyclopentane rings, R and L, fused to give a boat-shaped six-membered ring B.[101] In terms of this description, Table 1.10 lists a comparison of the relevant torsion angles of (9) and (10) with the corresponding theoretical values calculated for the norbornane skeleton.[101] These values show that the skeletal twistings of (9) and (10) differ from each other, and also from the hypothetical case. Both molecules exhibit twisting of the Synchro(- -) type, as evidenced by the negative non-zero values of torsion angles *b* and *b*'. While rings R of (9) and (10), which are only indirectly involved in the ring fusion to the cyclohexane ring, appear to be reasonably similar, both rings L and B, which are directly involved, exhibit marked differences in their torsion angles, *a*', *b*', *c*' and *d*' of ring L, and *f*' and g' of ring B being most altered. Moreover, compound (10) shows the greater deviation from the theoretical model, which possibly infers that the ring fusion in (10) is potentially more strained than in (9), resulting in more noticeable skeletal twisting in the former molecule.

In the absence of distortion, the C(6) and C(7) substituents of both molecules would be completely eclipsed. However, the twisting of the bicyclo [2.2.1] heptyl skeletons, as demonstrated by the Newman projections along the C(6)-C(7) bonds of (9) and (10) [Figure 1.5], has the effect of slightly relieving this potential eclipsing. Greater relief is again obtained in the case of (10), although this may only reflect that the C(6)-C(7) bond in (10) is more amenable to twisting. Further evidence for the strain present in the C(6)-C(7) bond and its substituents may be taken from the lengths of 1.593(7) and 1.588(5) Å observed for this bond in (9) and (10) respectively, both values being significantly longer than the average C(sp^3)-C(sp^3) length for each molecule [1.546(8) Å in (9); 1.548(5) Å in (10)]. Since this lengthening is reproduced in both molecules, it is likely to be a genuine effect. Similar lengthening has also been observed in other polycyclic structures, in particular for C(sp^3)-C(sp^3) bonds which either radiate from bridgehead positions,[128] or bear eclipsed substituents.[129] It is probably worthy of note that possibly significant[24] differences in the corresponding C(1)-C(10) [1.551(8) and 1.578(5) Å] and C(7)-C(8) [1.581(9) and 1.556(5) Å] bonds are observed, although a correlation between possible molecular strain and stereochemical differences is not clear. It is also of interest that (7), which has the same stereochemistry as (10), undergoes more rapid rearrangement than does (4), which has the same stereochemistry as (9), although the same general steric requirements for the ring-expansion are met by both molecules. Thus, it is possible that the difference in reactivities of (7) and (4) may well be related to the detailed conformational differences and resulting strain differences between the two molecules.

Apart from the specific dimensions previously discussed, both systems do not differ greatly, good agreement being obtained with corresponding literature values.[66] A feature of both molecules is the staggered conformations adopted by each methyl group, the average C-H lengths being 0.98(8) and 1.01(6) Å for (9) and (10) respectively. Despite environmental and crystal-packing differences, the dimensions of the three acetate groupings of (9) [short(C-O) 1.196(8) Å; long(C-O) 1.338(8) Å] and (10) [(a) short(C-O) 1.203(5) Å, long(C-O) 1.33(5) Å; (b) short(C-O) 1.201(5) Å, long(C-O) 1.335(4) Å] are found to be virtually duplicated, each acetate adopting an open-chain planar conformation. While in (9) O(3) and H(2) are almost staggered (torsion angle 168°), the corresponding atoms in (10) take up a semi-eclipsed arrangement (torsion angle 38°), as do atoms $O'(5)$ and $H'(5)$ (torsion angle 29°), probably in the latter case to avoid short non-bonded interactions, especially with $O'(1)$. Although appearing to have different conformations, the corresponding acetates of (9) and (10) do, however, maintain similar orientations with respect to the 1- and 2-carbon bridges of their respective bicyclic residues, as evidenced by similar intramolecular contacts i.e. O(3)...C(11) [3.26 Å in both] and O(4)...C(10) [3.38 Å in (9); 3.36 Å in (10)]. It may therefore be inferred that the orientations of either acetate group are determined principally by the non-bonded separations from the bicyclic region of each molecule.

Examination of the crystal packing arrangements of (9) and (10) [Figures 1.3 and 1.4] reveals the presence of O-H...O hydrogen bonding in both cases. For (9) a helix of hydrogen-bonded molecules, extending along the b-direction in the crystal, is produced from the association of screw-related molecules, the relevant dimensions $O(2)\ldots O(1^{II})$, H(02)...O(1^{II}) and angle O(2)-H(02)...O(1^{II}) having values 2.83 Å, 1.98 Å and 173° respectively. However, for (10) a different type of packing results from the non-participation of the secondary hydroxyl oxygen O'(2). The resulting contact distances O'(1)...O'(3^{IV}) and H'(01)...O (3^{IV}) have values of 2.87 Å and 1.99 Å, while the relevant O'(1)-H'(01)...O'(3^{IV}) angle is 169°. The resulting hydrogen-bonded network consists of two independent, unlinked helices of associated molecules extending along the a-direction of the crystal.

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