X-RAY STUDIES OF ORGANO-BISMUTH COMPOUNDS AND CARYOPHYLLENE DERIVATIVES.

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

by

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Chemistry Department, March, 1969.

ACKNOWLEDGEMENTS.

It is with pleasure that I thank my supervisors, Dr. George Ferguson and Professor J.M.Robertson, for their expert guidance and sustained interest in the work described in this thesis.

My thanks are due to many friends in the crystal-structure analysis group of Glasgow for their unfailing help and co-operation. In particular I wish to thank Dr. J.G.Sime, Dr. H.H.Mills, and Mr. M.Currie for their critical reading of parts of this thesis.

I am also indebted to Drs. W.Parker, J.S.Roberts, T.F.W.McKillop, and G.S.Harris who supplied crystals of the compounds investigated. Dr. McKillop's collaboration in the initial stages of the analysis of the pseudoclovene-A derivative is gratefully acknowledged.

To Professor D.W.J.Cruickshank, Drs. G.Ferguson, K.W.Muir, W.S.McDonald, D.R.McGregor, W.Oberhänsli, D.R. Pollard, J.G.Sime, and Mr. J.G.F.Smith, I wish to express my gratitude for making available to me their KDF-9 computer programs.

The first two years of these studies were carried out during the tenure of an Anderson Scholarship for which I am sincerely grateful.

SUMMARY.

This thesis is divided into three parts. In the first, some aspects of the theory and methods of X-ray Crystallography are introduced and briefly discussed. The second and final parts are concerned with the applications of these methods in the elucidation of the crystal structures of four molecules.

Accounts of the structural analyses of triphenylbismuth, $(C_6H_5)_3Bi$, and triphenylbismuth dichloride, $(C_6H_5)_3BiCl_2$, are contained in Part II. It has been established that the triphenylbismuth molecule is pyramidal with virtually no hybridisation of the 6s and 6p orbitals of the bismuth. The expected C_3 symmetry has been destroyed by the asymmetric rotations of the phenyl groups about the Bi-C bonds. The proposed trigonal bipyramidal structure for triphenylbismuth dichloride has been confirmed by a crystal-structure analysis. The more electronegative chlorine ligands occupy the apical positions with the phenyl groups attached equatorially to the central bismuth atom. Again the molecule possesses no overall symmetry as a result of the unequal rotations of the benzene rings with respect to the equatorial plane.

Part III describes the analyses of two caryophyllene rearrangement products, viz., caryophyllene 'iodonitrosite' and the mono-p-bromobenzenesulphonyl ester of the diol derived from pseudoclovene-A. The former belongs to the relatively new class of stable aliphatic nitroxide radicals, and has an N-O bond length of 1.308 Å which corresponds to a three-electron bond. The absolute stereochemistries of both derivatives have been established by means of Bijvoet's anomalous dispersion method. Fairly detailed accounts of the conformations of these molecules are given and the ways in which they have undergone distortions, to avoid the severe inherent strain associated with these species in their classical conformations, are discussed.

CONTENTS.

PART I SOME ASPECTS OF THE THEORY AND METHODS OF X-RAY CRYSTALLOGRAPHY.

PART II CRYSTAL STRUCTURE ANALYSES OF TWO ORGANO-BISMUTH COMPOUNDS.

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIPHENYLBISMUTH.

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIPHENYLBISMUTH DICHLORIDE.

PART III CRYSTAL STRUCTURE ANALYSES OF TWO CARYOPHYLLENE REARRANGEMENT PRODUCTS.

PART I

SOME ASPECTS OF THE THEORY AND METHODS OF X-RAY CRYSTALLOGRAPHY.

1. INTRODUCTION.

The discovery of X-rays by Röntgen (1895), followed by Laue's demonstration (1912) that crystals act as three-dimensional diffraction gratings, marked the birth of X-ray Crystallography as a new branch of physical science.

X-ray crystallography is mainly concerned with the interpretation of the diffraction patterns produced by crystals when exposed to an X-ray beam. From the positions and the intensities of the diffracted beams, it is possible to gain knowledge of the intimate structure of crystals. In the early days only the structures of metals and simple salts could be attempted with any degree of success. With the introduction of newer methods and the advent of fast electronic computers, the structures of more complicated substances, many of which defied the traditional methods of chemistry, have been solved.

Perhaps one of the greatest triumphs of crystal-structure analysis in recent years has been the unravelling of the intricate structural details of the proteins, haemoglobin (Perutz et. al., 1960), myoglobin (Kendrew et. al., 1960), lysozyme (Phillips et. al., 1965), and chymotrypsin (Matthews et. al., 1967).

With continued interest in biological materials, and in particular the nucleic acids, the X-ray crystallographer may provide an answer or at least a part answer to that formidable question, "What is Life?"

2. CRYSTAL SYMMETRY.

Even in the ancient civilisations, symmetry played an important role in creating objects of artistic beauty. The classical crystallographer analysed this notion and developed a complete geometrical theory of symmetry in space some time before the discovery of X-rays.

An object is said to have symmetry if an operation applied to it produces a form which cannot be distinguished from the original. From a study of crystalline form it has been found that the symmetry elements about a point in a crystal are limited to one-, two-, three-, four-, and six-fold rotation axes plus the corresponding axes of rotatory inversion. Hessel (1830) and Gadolin (1867) independently derived the 32 distinct point groups, which are self-consistent sets containing the symmetry elements outlined above.

It has long been accepted that crystals are built on a lattice structure, that is, a regular repetition in space of identical units. Bravais (1850) demonstrated that only

14 types of lattice are possible. When such lattices are combined with the 32 point groups additional elements of symmetry known as screw axes and glide planes are introduced. They involve rotation about an axis or reflexion through a mirror plane coupled with a translational movement. With these new symmetry elements Barlow (1894, 1895), Federow (1885, 1888), and Schoenflies (1891) independently derived the 230 space groups, thus completing the geometrical theory of crystal symmetry. It was not until Laue's discovery in 1912 that irrefutable proof of the theory was provided.

One of the first tasks of a crystal-structure analysis is to determine the space group to which the crystal belongs. An unambiguous determination from an examination of the X-ray diffraction spectra is only possible for 70 of the 230 space groups. The reason for this is that the diffraction pattern exhibits a centre of symmetry, no matter whether one is present in the space group or not. It is, however, often possible to distinguish between centrosymmetric and non-centrosymmetric space groups by studying piezo- and pyro-electric effects in the crystal or by a statistical investigation of the observed intensity data. Moreover it may happen that the compound is optically active in which case the possibility of it belonging to a centrosymmetric space group or one containing a mirror or glide plane is immediately ruled out.

3. X-RAY DIFFRACTION BY A LATTICE.

Consider a periodic row of points (Figure 1.1) with spacing $\underline{a}$, and an incident monochromatic X-ray beam of wavelength λ, whose direction is defined by the vector $\underline{s}_0$ of magnitude $1/\lambda$. The X-ray beam diffracted by the row of points has the direction given by the vector $\underline{s}$ and magnitude $1/\lambda$. The path difference between the waves diffracted by successive points along the row is given by,

$$\lambda(\underline{a}.\underline{s} - \underline{a}.\underline{s}_0) = \lambda\underline{a}.(\underline{s} - \underline{s}_0) = \lambda\underline{a}.\underline{S} \qquad (1)$$

where $\underline{S} = \underline{s} - \underline{s}_0$. In order that the waves be in phase, this path difference must equal a whole number of waves, and thus $\underline{a}.\underline{S}$ must be equal to an integral number, i.e.,

$$\underline{a}.\underline{S} = h. \qquad (2)$$

The diffracted beam $\underline{S}$ may be regarded as forming a cone about the row of points for a fixed direction of the incident beam (Figure 1.2).

Extending this notion to a triply periodic array of points having three non-coplanar translations $\underline{a}$, $\underline{b}$, and $\underline{c}$, the conditions that points along the second and third rows

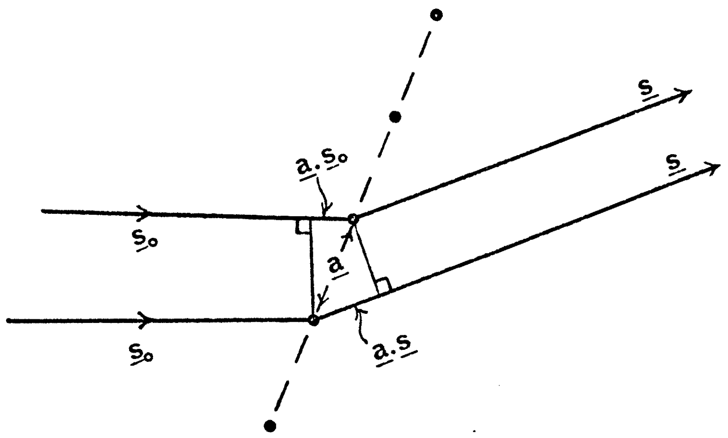

Figure 1.1

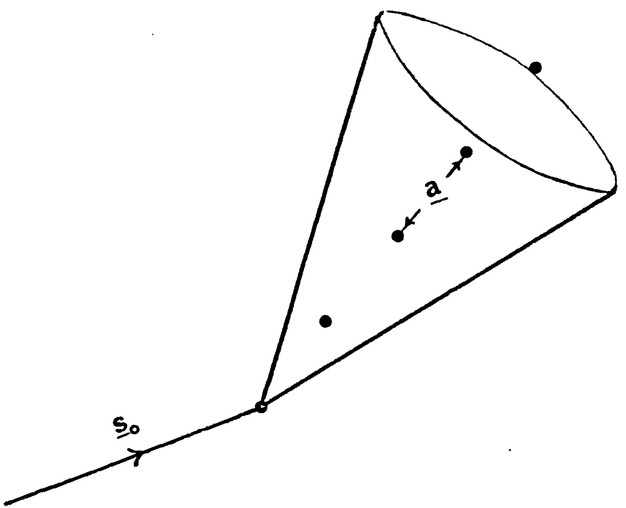

Figure 1.2

diffract in phase are,

$$\underline{b}\cdot\underline{S} = k$$
$$\underline{c}\cdot\underline{S} = \ell, \qquad (3)$$

where k and ℓ are integers. The conditions expressed in (2) and (3) are known as the Laue equations. When all three are satisfied simultaneously the diffracted beam has only one direction defined by the line of intersection of the three diffraction cones.

The Laue equations as they stood proved to be unsuitable for the interpretation of experimental results, until W.L. Bragg (1913) placed them on a physical basis. Rewriting the Laue equations in the following form,

$$(\underline{a}/h)\cdot\underline{S} = 1, \quad (\underline{b}/k)\cdot\underline{S} = 1, \quad (\underline{c}/\ell)\cdot\underline{S} = 1, \qquad (4)$$

and subtracting the first two equations in (4) we obtain the expression,

$$(\underline{a}/h - \underline{b}/k)\cdot\underline{S} = 0. \qquad (5)$$

This means that the vector $\underline{S}$ is perpendicular to the vector $(\underline{a}/h - \underline{b}/k)$. Similarly $\underline{S}$ is perpendicular to the vector $(\underline{a}/h - \underline{c}/\ell)$, and both $(\underline{a}/h - \underline{b}/k)$ and $(\underline{a}/h - \underline{c}/\ell)$ are vectors in the plane with Miller indices $hk\ell$ (Figure 1.3). Essentially Bragg's contribution was to identify the integers h, k, and ℓ, with the Miller indices of the lattice

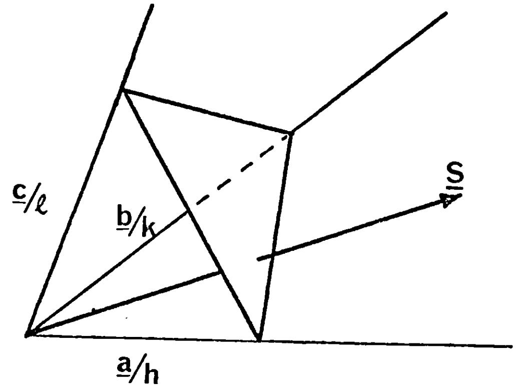

Figure 1.3

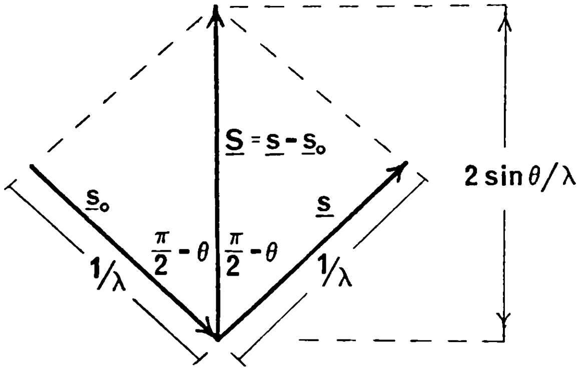

Figure 1.4

planes.

The vector $\underline{S}$ is in the direction of the bisector of the angle made by the incident and diffracted beams, since the magnitudes of $\underline{s}$ and $\underline{s}_0$ are both equal to $1/\lambda$ (Figure 1.4). Thus justification for the notion that diffraction may be regarded as a 'reflexion' of rays from lattice planes, is provided by identifying the bisector of the incident and diffracted beams with the normal to the $hk\ell$ plane. In order to place Bragg's law on a quantitative basis the spacing, d, of the planes, $hk\ell$, must be introduced; it is the perpendicular distance of the plane, $nk\ell$, from the origin and is the projection of $\underline{a}/h$, $\underline{b}/k$, and $\underline{c}/\ell$ on the vector $\underline{S}$, i.e.

$$d = \frac{(\underline{a}/h)\cdot\underline{S}}{|\underline{S}|} \tag{6}$$

But from equation (4), $(\underline{a}/h)\cdot\underline{S} = 1$, hence,

$$d = 1/|\underline{S}|. \tag{7}$$

From Figure 1.4 we see that,

$$|\underline{S}| = (2\sin\theta)/\lambda. \tag{8}$$

Substituting (7) in (8) and rearranging we obtain Bragg's Law,

$$\lambda = 2d\sin\theta. \tag{9}$$

Mathematical methods of solving the Laue equations may be expressed in terms of the reciprocal lattice. Such methods are concerned with finding values of $\underline{S}$ which simultaneously satisfy the Laue equations. It is evident from equation (2) that the projection of $\underline{S}$ on $\underline{a}$ is a constant for a fixed value of h, and that the ends of the vector $\underline{S}$ lie on a plane perpendicular to $\underline{a}$. A set of planes of constant spacing is produced, each plane of the set corresponding to a particular value of h. Similarly another two sets of equidistant planes will be set up, one perpendicular to $\underline{b}$ and the other perpendicular to $\underline{c}$. The intersections of these planes form an array of points called the reciprocal lattice. The lattice points defined by the integers h, k, and ℓ, represent the end points of vectors which simultaneously satisfy the Laue equations.

Each of the reciprocal lattice vectors, defined as $\underline{a}^*$, $\underline{b}^*$, and $\underline{c}^*$, is formed by the intersection of two planes perpendicular to two crystal axes, i.e. $\underline{a}^*$ is perpendicular to $\underline{b}$ and $\underline{c}$. Representing this in terms of vector algebra,

$$\underline{a}^* = p(\underline{b} \times \underline{c}), \tag{10}$$

where p is a constant to be determined. Similarly $\underline{b}^*$ and $\underline{c}$ may be represented thus,

$$\underline{b}^* = q(\underline{c} \times \underline{a}),$$

$$\text{and } \underline{c}^* = r(\underline{a} \times \underline{b}), \tag{11}$$

where q and r are constants.

The diffraction vector $\underline{S}$ to the reciprocal lattice points may be expressed as,

$$\begin{aligned} \underline{S} &= h\underline{a}^* + k\underline{b}^* + \ell\underline{c}^*, \\ &= hp(\underline{b} \times \underline{c}) + kq(\underline{c} \times \underline{a}) + \ell r(\underline{a} \times \underline{b}). \end{aligned} \tag{12}$$

But $\underline{a}.\underline{S} = h$, therefore,

$$h = \underline{a}.\{hp(\underline{b} \times \underline{c}) + kq(\underline{c} \times \underline{a}) + \ell r(\underline{a} \times \underline{b})\}. \tag{13}$$

Since $\underline{a}.\underline{c} \times \underline{a}$ and $\underline{a}.\underline{a} \times \underline{b} = 0$, then,

$$1 = p\ \underline{a}.\underline{b} \times \underline{c}. \tag{14}$$

Rearranging expression (14) and noting that $\underline{a}.\underline{b} \times \underline{c}$ is a representation of the volume of the unit cell of the real space lattice, we find that the constant p has the value,

$$p = 1/V. \tag{15}$$

Similarly $q = r = 1/V$. Hence substituting (15) in equations(10) and (11), we obtain the following expressions for the reciprocal lattice vectors,

$$\begin{aligned} \underline{a}^* &= (\underline{b} \times \underline{c})/V, \\ \underline{b}^* &= (\underline{c} \times \underline{a})/V, \\ \underline{c}^* &= (\underline{a} \times \underline{b})/V. \end{aligned} \tag{16}$$

4. THE STRUCTURE FACTOR.

So far we have discussed the geometry of X-ray diffraction in terms of scattering from lattice points without regard to the specific nature of these scattering points. It is convenient to think of the scattering units of a crystal as its constituent atoms, remembering of course, that the electrons of an atom are responsible for its scattering power.

We define $\rho_n(\underline{r})$ as the electron density of the nth atom at a vector distance $\underline{r}$ relative to an origin chosen at the centre of this atom. The scattering power of a single atom may then be expressed as,

$$f_n(\underline{S}) = \int_{-\infty}^{\infty} \rho_n(\underline{r}) \exp(2\pi i \underline{r}.\underline{S}) dV. \qquad (17)$$

The quantity $f_n(\underline{S})$ is called the atomic scattering factor. In this treatment it is assumed that the atom is spherically symmetric i.e. $\rho_n(\underline{r})$ is a function of $|\underline{r}|$ only. $f_n(S)$ therefore, also has spherical symmetry and so is a function of $|\underline{S}| = (2\sin\theta)/\lambda$.

The wavelets scattered by the individual electrons within the volume of the atom have different phases, and this results in destructive interference which increases as the angle of diffraction increases. Hence the scattering factor of an atom will decrease with increasing angles of diffraction. Approximate values of the scattering factors for various elements have been calculated on the basis of quantum theory and extensive lists of these are available in "International Tables for X-ray Crystallography" Vol.III(1962).

Let us now consider a unit cell in which there are N atoms each with a scattering factor $f_n(\underline{S})$. If the vector distance of the nth atom from the origin of the unit cell is $\underline{r}_n$, then the total wave scattered by the entire contents of the unit cell is given by $G(\underline{S})$ where,

$$G(\underline{S}) = \sum_{n=1}^{N} f_n(\underline{S})\exp 2\pi i\underline{r}_n.\underline{S}. \qquad (18)$$

$2\pi\underline{r}_n.\underline{S}$ is the phase difference between the beam scattered by the nth atom relative to that scattered by an atom at the origin. The summation sign is used in (18) since a finite number of atoms is being considered.

If the nth atom has coordinates x_n, y_n, z_n expressed as fractions of the unit cell edges, then the vector $\underline{r}_n$ may be written as,

$$\underline{r}_n = x_n\underline{a} + y_n\underline{b} + z_n\underline{c}. \qquad (19)$$

Substituting (19) in (18) results in the following expression for $G(\underline{S})$,

$$G(\underline{S}) = \sum_{n=1}^{N} f_n(\underline{S}) \exp 2\pi i (x_n \underline{a} \cdot \underline{S} + y_n \underline{b} \cdot \underline{S} + z_n \underline{c} \cdot \underline{S}). \qquad (20)$$

The wave scattered by the crystal will only have an appreciable amplitude when the Laue equations are satisfied. Equation (20) then reduces to,

$$G(\underline{S}) = F(hk\ell) = \sum_{n=1}^{N} f_n(hk\ell) \exp 2\pi i (hx_n + ky_n + \ell z_n). \qquad (21)$$

$F(hk\ell)$ is known as the structure factor and is defined only when h, k, and ℓ have integral values. It is a description of the amplitude and phase of the complete wave scattered by the unit cell and also by the crystal since all the unit cells are assumed to scatter in phase.

The structure factor is a complex quantity and may be expanded into real and imaginary parts i.e.,

$$F(hk\ell) = A + iB, \qquad (22)$$

where $$A = \sum_{n=1}^{N} f_n(hk\ell) \cos 2\pi (hx_n + ky_n + \ell z_n),$$

and $$B = \sum_{n=1}^{N} f_n(hk\ell) \sin 2\pi (hx_n + ky_n + \ell z_n). \qquad (23)$$

The amplitude $|F(hk\ell)|$ and phase $\alpha(hk\ell)$ of the structure factor can be evaluated by means of the following expressions,

$$|F(hk\ell)| = (A^2 + B^2)^{\frac{1}{2}} \text{ and } \alpha(hk\ell) = \tan^{-1}(B/A). \qquad (24)$$

So far we have assumed that the crystal structure is a static one, but in actual fact every atom undergoes some type of thermal motion. The effect of this is to make the electrons of each atom sweep out a larger volume than they would otherwise occupy if the atom were at rest. The atomic scattering factor is modified by multiplication by a factor $q_n(hk\ell)$ which takes into account the thermal motion. Thus,

$$f_T(hk\ell) = f_n(hk\ell)q_n(hk\ell). \tag{25}$$

When the atomic vibration is isotropic then,

$$q_n(hk\ell) = \exp\{-B(\sin\theta/\lambda)^2\}, \tag{26}$$

where the Debye-Waller factor $B = 8\pi^2 U$; U is the mean square amplitude of vibration. Usually an atom executes an anisotropic motion such that the electron density is smeared over an ellipsoid. In such a case the function $q_n(hk\ell)$ may be expressed in the form,

$$q_n(hk\ell) = \exp[-2\pi^2(U_{11}h^2\underline{a}^{*2} + U_{22}k^2\underline{b}^{*2} + U_{33}\ell^2\underline{c}^{*2}$$

$$+ 2U_{23}k\ell\underline{b}^*\underline{c}^* + 2U_{31}\ell h\underline{c}^*\underline{a}^* + 2U_{12}hk\underline{a}^*\underline{b}^*)], \tag{27}$$

where $U_{ij}(i,j = 1,2,3)$ are referred to the reciprocal axes of the crystal.

Taking the thermal motion into account expression (21) becomes,

$$F(hk\ell) = \sum_{n=1}^{N} f_n(hk\ell)q_n(hk\ell)\exp 2\pi i(hx_n + ky_n + \ell z_n), \qquad (28)$$

which is a more complete description of the structure factor.

5. ANOMALOUS SCATTERING OF X-RAYS.

It has already been pointed out that for normal scattering of X-rays, the diffraction pattern from a crystal will always exhibit a centre of symmetry. This is a direct consequence of Friedel's law (1913) which states that,

$$|F(hk\ell)| = |F(\bar{h}\bar{k}\bar{\ell})|. \qquad (29)$$

This implies that the structure obtained by reversing the direction of the axes used to define the original one is still consistent with the observed diffraction pattern. In other words, provided the scattering of X-rays is normal, it is impossible to distinguish between optical enantiomers.

Coster et. al. (1930) discovered, however, that Friedel's law was violated when a structure contains an atom (or atoms) which scatter the primary beam anomalously. When the frequency of the incident radiation is close to the critical absorption frequency of the scattering atom, the atomic scattering factor becomes a complex quantity of the form,

$$f = f_o + \Delta f' + i\Delta f'', \qquad (30)$$

where f_o is the normal scattering factor and $\Delta f'$ and $\Delta f''$ are correction terms which arise due to dispersion effects. The correction factors are regarded to be independent of the scattering angle since the electrons responsible for these effects are those confined to a small volume around the nucleus. The quantity $\Delta f''$ is always positive which implies that the phase of the scattered radiation is advanced relative to that for an atom which scatters normally. An extensive table of values of $\Delta f'$ and $\Delta f''$ for various elements is given in "International Tables for X-ray Crystallography" Vol.III.

Bijvoet (1949), realising the deeper implications of this effect, pointed out that anomalous scattering could be used in the determination of absolute configuration. This was carried out on sodium rubidium tartrate (Peerdeman, van Bommel, and Bijvoet, 1951) and the results showed that Emil Fischer's arbitrary convention does in fact correspond to reality. In order to use the anomalous dispersion method successfully it is imperative that one coordinate system e.g. a right-handed one, be adopted and adhered to throughout the analysis (Peerdeman and Bijvoet, 1956). Indexing of the reflexions must also be consistent with the chosen coordinate system.

In view of Bijvoet's pioneering work in this field, a pair of reflexions whose intensities become unequal when anomalous scattering is present, is known as a Bijvoet pair.

Ueki, Zalkin, and Templeton (1966) have pointed out that in some non-centrosymmetric space groups in which the origins are not fixed by symmetry, errors in the positional parameters of the anomalous scattering atoms may be introduced if the correction for $\Delta f''$ is neglected. This effect has been dealt with in much greater detail by Cruickshank and McDonald (1967).

6. THE DERIVATION OF STRUCTURE AMPLITUDES FROM INTENSITIES.

Consider a small crystal rotating with uniform velocity in an X-ray beam. When a set of $hk\ell$ planes passes through the reflecting position, the total energy, $E(hk\ell)$, of the diffracted beam is given by,

$$E(hk\ell) = K\, L(hk\ell)p(hk\ell)\,|F(hk\ell)|^2, \qquad (31)$$

where K is a constant for the experiment. The energies of the diffracted beams are proportional to their intensities which can be recorded on photographic films. In practice the maximum range of intensities which can be measured on one film is 1 to 50, but a much greater range of diffraction intensities emanates from a single crystal. Therefore it is desirable that the multiple-film technique (Robertson, 1943) be employed in which several films, one behind the other, are placed in the cassette and exposed simultaneously. The intensity of each reflexion can then be determined by visual comparison with a calibrated intensity wedge, or by employing a microdensitometer. Intensities can also be measured by the direct counting of the diffracted photons. Under favourable conditions such counter techniques tend to be superior to photographic methods in terms of cost, time and accuracy (Arndt and Willis, 1966).

Two important corrections which must be made to the observed intensities are the polarisation, $p(hk\ell)$, and the Lorentz, $L(hk\ell)$, factors. Polarisation which occurs in reflexion diminishes the intensity of the diffracted beam, and the correction factor takes the form,

$$p(hk\ell) = \tfrac{1}{2}(1 + \cos^2 2\theta). \tag{32}$$

It is a function only of the scattering angle 2θ and is thus independent of the method used for the data collection. The Lorentz factor $L(hk\ell)$, on the other hand, varies with the technique employed in data collection. It expresses the relative time any crystal plane spends within the narrow angular range over which reflexion occurs. For equi-inclination geometry (Tunnel, 1939) it takes the form,

$$L(hk\ell) = 1/\{2\cos\theta(\cos^2\mu - \cos^2\theta)^{\frac{1}{2}}\}, \qquad (33)$$

where μ is the equi-inclination angle.

The physical factors of absorption and extinction are more difficult to deal with than the above mentioned geometrical factors, and should only be neglected when a minute crystal is employed. Absorption causes diminution of the primary X-ray beam on passing through a crystal and is dependent on the material of the crystal, and the thickness through which the beam passes. Reliable absorption corrections can only be applied with any degree of simplicity to cylindrical or spherical specimens. Extinction also results in attenuation of the incident beam when the crystal is in the diffracting position and is related to the mosaic nature of the crystal. Darwin (1922) recognised two different kinds of extinction which he termed primary and secondary extinction. The former occurs when a reflected beam emerging from the crystal is reflected back into the crystal. The double-reflected beam is parallel to, but out of phase, with the incident beam. This results in destructive interference thus reducing the intensity of the primary beam. Secondary extinction, on the other hand, arises when the surface planes of the crystal reflect away an appreciable amount of the incident radiation, and consequently the lower planes receive a beam of much weaker intensity.

Normally structures are solved by interpretation of a set of relative intensities but for some purposes absolute values are necessary. The latter may be obtained by comparison with some standard crystal from which absolute measurements have been derived (Robinson, 1933; Robertson, 1934). Alternative methods (Wilson, 1942; Yü, 1942; Beevers and Cochran, 1947) based on statistics can also be used to obtain absolute intensities. In Wilson's method the structure amplitudes are divided into groups covering small ranges of $\sin\theta$. For each group the mean values of the squares of the structure amplitudes $\langle|F_o|^2\rangle$, and the scattering factors of the atoms $\langle f_n^2\rangle$ are determined. $\mathrm{Log}(\langle|F_o|^2\rangle/\langle f_n^2\rangle)$ is plotted against $\sin^2\theta/\lambda^2$ and the 'best' straight line through the experimental points is drawn. From the intercept on the ordinate axis an absolute scale factor can be obtained and the slope of the line provides an overall temperature factor.

7. FOURIER SERIES.

Since a crystal consists of an infinitely repeating array of unit cells and is therefore triperiodic, Bragg

(1915) suggested its electron density can be represented by a triple Fourier series. Assigning the integral indices h', k', and ℓ' to each Fourier coefficient A, the electron density $\rho(xyz)$ may be expressed thus,

$$\rho(xyz) = \sum_{h'}\sum_{k'}^{\infty}\sum_{\ell'} A(h'k'\ell')\exp 2\pi i(h'x + k'y + \ell'z). \qquad (34)$$
$$-\infty$$

The structure factor when expressed in terms of the electron density takes the form,

$$F(hk\ell) = \int_0^1\int_0^1\int_0^1 V\rho(xyz)\exp\{2\pi i(hx + ky + \ell z)\}dxdydz, \qquad (35)$$

where $\rho(xyz)Vdxdydz$ is the amount of scattering matter in the volume element Vdxdydz. Substituting (34) in expression (35) we obtain,

$$F(hk\ell) = \int_0^1\int_0^1\int_0^1 \sum_{h'}\sum_{k'}^{\infty}\sum_{\ell'} A(h'k'\ell')\exp\{2\pi i(hx + ky + \ell z)\}$$
$$-\infty$$

$$\times \exp\{2\pi i(h'x + k'y + \ell' z)\}Vdxdydz. \qquad (36)$$

The exponential functions in equation (36) are periodic and the integral will only have a value when $h = -h'$, $k = -k'$ and $\ell = -\ell'$. In such circumstances expression (36) reduces to,

$$F(hk\ell) = \int_0^1\int_0^1\int_0^1 A(h'k'\ell')Vdxdydz = A(\bar{h}\bar{k}\bar{\ell})V. \qquad (37)$$

Hence $F(hk\ell)/V$ is the Fourier coefficient of the electron density which may now be expressed as,

$$\rho(xyz) = \frac{1}{V}\sum_{h}\sum_{k}\sum_{\ell}{}_{-\infty}^{\infty} F(hk\ell)\exp\{-2\pi i(hx + ky + \ell z)\}. \qquad (38)$$

The result of summing this series is a direct representation of the crystal structure. It is more advantageous to express the electron-density function in the form,

$$\rho(xyz) = \frac{1}{V}\sum_{h}\sum_{k}\sum_{\ell}{}_{-\infty}^{\infty} |F(hk\ell)| \cos\{2\pi(hx + ky + \ell z) - \alpha(hk\ell)\}, \qquad (39)$$

since the phase angle $\alpha(hk\ell)$ associated with the amplitude $|F(hk\ell)|$ appears explicitly.

8. THE PHASE PROBLEM.

After the preliminary routines of an X-ray analysis which involve the determination of the unit cell parameters, the space group, and the collection of adequate intensity data, we are confronted with the fundamental difficulty in crystal-structure analyses, that is, the Phase Problem. From the observed intensities, values for the structure amplitudes $|F(hk\ell)|$ may be derived, but there is no direct experimental method of obtaining the corresponding phases, $\alpha(hk\ell)$. Consequently an infinite number of combinations of phase angles would yield an electron-density distribution consistent with the observed intensities. Lacking a general solution to the phase problem, many methods have been devised to circumvent it. Some of these methods will be briefly discussed.

8.1 Trial and Error Methods.

When the chemical structure is not in doubt, it may be possible to postulate the atomic positions within the unit cell. The validity of the trial structure may then be evaluated from the agreement between the observed and calculated structure amplitudes.

A study of space-group symmetry, physical properties (morphology, optical and magnetic properties), or dominant features of the diffraction pattern may in favourable cases provide a promising trial model.

One of the earliest applications of trial and error methods was in the determination of the structure of hexamethylbenzene (Lonsdale, 1929). Other classical examples include the structure elucidations of coronene (Robertson and White, 1945) and pyrene (Robertson and White, 1947). Trial and error methods are of rather limited application and a great deal of experience is necessary to use them effectively.

8.2 The Patterson Function.

The inability to synthesise an electron-density distribution from the measured intensities led A.L. Patterson (1934, 1935) to devise a Fourier expression in which the phaseless quantities $|F(hk\ell)|^2$ - the squares of the structure amplitudes - are used as coefficients. The resulting synthesis has been shown to be related in a simple way to the crystal structure, and gives evidence concerning atomic positions.

Patterson defined the function P(uvw) such that

$$P(uvw) = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\rho(x + u,\ y + v,\ z + w)dxdydz, \qquad (40)$$

where u, v, and w are fractional coordinates. P(uvw) will be a maximum when the vector with components u, v, and w connects the electron density of one atom with that of another. Consequently the Patterson function displays all the interatomic vectors present in the real crystal.

Substituting in (40) the values for the electron densities given by expression (38) we obtain,

$$\begin{aligned} P(uvw) = \frac{1}{V}\int_0^1\int_0^1\int_0^1 \sum_h\sum_k\sum_\ell\sum_{h'}^{\infty}\sum_{k'}\sum_{\ell'}{}_{-\infty} & F(hk\ell)\exp\{-2\pi i(hx + ky + \ell z)\} \\ & \times F(h'k'\ell')\exp\{-2\pi i(h'x + k'y + \ell' z)\} \\ & \times \exp\{-2\pi i(h'u + k'v + \ell' w)\}dxdydz. \qquad (41) \end{aligned}$$

Applying similar reasoning to (41) as we did to expression (36) the triple integral will be zero unless $h = -h'$, $k = -k'$, and $\ell = -\ell'$. Noting that $F(hk\ell)$ and $F(\bar{h}\bar{k}\bar{\ell})$ are complex conjugates, the Patterson function reduces to the form,

$$P(uvw) = \frac{1}{V}\sum_{h}\sum_{k}^{\infty}\sum_{\ell}|F(hk\ell)|^{2}\exp 2\pi i(hu + kv + \ell w). \qquad (42)$$
$$-\infty$$

For a structure in which there are N atoms in the unit cell, the Patterson vector map will be composed of $N(N - 1)$ distinct atomic vectors. Consequently only simple structures containing a few atoms can be solved directly from the Patterson function, and even then, the solution may not be unique. The chances of interpreting a Patterson function are improved when the individual peaks are resolved to the greatest possible extent. This can be achieved by modifying the structure amplitudes such that they correspond to scattering from point atoms at rest.

Harker (1936) pointed out that much useful information can be gleaned from certain planes and lines of the three-dimensional Patterson function, by making use of certain space-group symmetry elements. Consider for example the space group $P2_1$. The presence of the two-fold screw axis parallel to the <u>b</u> axis of the crystal, implies that for an atom at x,y,z, there will be another at -x, $\frac{1}{2}$ + y, -z. A peak corresponding to the vector between these symmetry related atoms will have coordinates 2x, $\frac{1}{2}$, 2z. The section through the Patterson function at v = $\frac{1}{2}$ is known as a Harker section.

8.3 The Heavy Atom and Isomorphous Replacement Methods.

When a molecule contains an atom (or atoms) of relatively high atomic number, then this 'heavy' atom will tend to dominate the structure factor magnitudes and phases. Its position is normally determined from the three-dimensional Patterson function and a set of phases based on the heavy atom alone can be deduced. These phase angles, although approximate, are often sufficiently close to the true values to enable one to couple them with the observed structure amplitudes in a Fourier synthesis. It may be possible to recognise other atoms of the structure in the resulting electron-density distribution and with the inclusion of these atoms a new set of phases can be calculated. The iteration process of phase angle calculations and Fourier syntheses is continued until the complete structure is revealed.

For a successful application of the heavy atom method it is desirable, though not essential, that the square of the atomic number of the heavy atom be approximately equal to the sum of the squares of the atomic numbers of the light atoms. An unfortunate disadvantage of this method arises from the fact that the major contribution to each structure amplitude comes from the heavy atom and consequently the accuracy in determining the light atom positions is reduced.

Despite this limitation there can be no doubt that the heavy atom method is one of the most popular and most successful ways of overcoming the phase problem, since the literature abounds with practical illustrations of it. The first direct application of the heavy atom method was by Robertson and Woodward (1940) in their structure determination of platinum phthalocyanine. Further outstanding illustrations are given by the crystal-structure analyses of cholesteryl iodide (Carlisle and Crowfoot, 1945) and Vitamin B_{12} (Hodgkin et. al., 1957).

In favourable cases the method of isomorphous replacement provides an even more direct way of determining the phases. It is assumed in this technique that corresponding atoms in isomorphous crystals occupy practically the same position in the unit cell, but the interchangeable atoms differ in scattering power. Evidence concerning the phases can be obtained by comparing the intensities from a pair or a series of isomorphous crystals. This method was first used by Cork (1927) and later developed independently by Robertson in his work on the phthalocyanines (Robertson, 1935, 1936; Robertson and Woodward, 1937), but its widest application has been in the field of protein crystallography.

An alternative approach to solving structures by way of the heavy atom, is embodied in the Minimum function method (Buerger, 1951) which involves the superposition of Patterson functions. One vector map is placed with its origin at the derived heavy atom position, while the origin of the second superimposes a symmetry-related heavy atom position. A third map is then drawn over the minimum contours of the coincident peaks. Further superpositions may be required depending on the number of heavy atoms in the unit cell, but the final composite minimum function may reveal the structure or an appreciable amount of it. Such a method is particularly favourable in that the images being superimposed involve vectors between heavy and light atoms which stand out from the background of light atom-light atom vectors. Successful applications of this technique include the structure determination of Vitamin B_1 (Kraut and Reed, 1962).

8.4 Direct Methods.

The term 'direct' is usually reserved for those methods in which the phases of structure factors are derived directly by mathematical means from the diffraction data. The origin of these methods may be traced back to the inequality relationships between structure factors, first expounded by Harker and Kasper (1948), and later by Karle and Hauptman (1950). Sayre (1952) initiated the next development, in the derivation of an equality relationship between structure factors,

$$F_H = (\varphi_H/V)\sum_{H'} F_{H'}\, F_{H-H'}\,, \qquad (43)$$

where H is shorthand for hkℓ and H' is a particular value of H; φ_H is a scaling factor. As it stands Sayre's equation appears to be of little value, since to determine one structure factor the magnitudes and phases of all the others must be known. This led Zachariasen (1952) to the development of a sign relationship between structure factors,

$$s(H) \sim s\left\{\sum_{H'} s(H')\, s(H-H')\right\}, \qquad (44)$$

which implies that the sign of the structure factor F_H is probably equal to the product of the signs of $F_{H'}$ and $F_{H-H'}$. Structure factor magnitudes, however, fall off rapidly with increasing $\sin\theta$ and consequently it would be difficult to find many large structure factors which could be used in the sign relationship. This difficulty was overcome by the introduction of the unitary structure factor and later the normalised structure factor. The latter is now more commonly used and is defined as,

$$E_H = F_H/\epsilon^{\frac{1}{2}}(\sum_{i=1}^{N} f_i{}^2)^{\frac{1}{2}}, \qquad (45)$$

where ϵ is a multiplicity factor; for example, in the space group $P2_1/c$, $\epsilon = 2$ for the $h0\ell$ and the $0k0$ reflexions and 1 for all others.

In the initial stages of a direct phase determination the formula,

$$sE_H \sim s\sum_{H'} E_{H'}E_{H-H'}\ , \qquad (46)$$

introduced by Karle and Hauptman (1953) and known as the Σ_2 relationship, is normally used. It is a modification of Sayre's equation and implies that the sign of the combination $E_{H'}E_{H-H'}$ is probably equal to that of E_H. The probability that equation (46) is correct is given by,

$$P = \tfrac{1}{2} + \tfrac{1}{2}\tanh\{(|E_HE_{H'}E_{H-H'}|)/N^{\frac{1}{2}}\}, \qquad (47)$$

(Cochran and Woolfson, 1955). It is assumed that the N atoms in the unit cell are equal.

The signs of three strong reflexions must then be specified in order to define the origin of the unit cell. Subject to certain restrictions it is advantageous to choose those reflexions which make many combinations in the Σ_2 relationship. This allows further signs to be determined and the process snowballs until no further relationships exist involving two reflexions of known sign with one of unknown sign. At this point, letters may be assigned to certain useful reflexions in order to continue the phase determination. It is often possible to reduce the number of symbols of unknown sign by considering the relationships which are produced between them. For example there may be strong indications that ab = +1 and that abc = -1 in which case it is likely that the sign of c is -1. Other probability formulae such as Karle and Hauptman's (1953) Σ_1 relationship,

$$sE_{2H} \sim s(E_H^{\,2} - 1), \qquad (48)$$

may also prove helpful in deducing signs for some of the symbols.

When the phase determination has been completed for a suitable number of reflexions (usually about 10 to 15 per atom in the asymmetric unit) a Fourier synthesis using E's as coefficients can be computed and the structure may be revealed in the resulting E-map. Normalised structure factors are used in the Fourier summation in preference to F's since they correspond to completely sharpened atoms, and hence the peaks in the E-map will be sharply defined.

Karle and Karle have undoubtedly played the major role in demonstrating the full potential of this procedure which they have called the 'symbolic addition' method (Karle and Karle, 1963, 1964a, 1966a). Although it has been applied in the main to centrosymmetric space groups, a number of structures belonging to non-centrosymmetric space groups have been solved (Karle and Karle, 1964b, 1966b, 1968).

Germain and Woolfson (1968) have recently introduced a multi-solution symbolic addition procedure which we have used in the structure determination of a nematicide, $C_{16}H_{14}S_3$ (Curtis et. al., 1969), which is described in a published paper presented at the end of this thesis.

Direct methods have made giant strides since their introduction in 1948 and now rival other powerful methods of phase determination.

9. METHODS OF REFINEMENT.

9.1 Correctness of Structure.

Once the phase problem has been successfully overcome and a structure has been postulated, it is important that some criterion be established to assess the correctness of the trial model, thus giving some measure of the agreement between the calculated and the observed structure factors. Many functions have been devised but perhaps the most popular of these is the following,

$$R = \frac{\sum \big| |F_o| - |F_c| \big|}{\sum |F_o|} . \tag{49}$$

R is called the residual or discrepancy factor and $|F_o|$ and $|F_c|$ are respectively the magnitudes of the observed and calculated structure factors. The summations are over all the reflexions used in the analysis. There is no precise value of R below which the validity of the trial structure is guaranteed, but generally if R is less than 0.25 then the structure is probably correct.

9.2 Fourier Refinement.

When a set of coordinates for the atoms in the trial structure have been found, phases based on this model can be determined and used along with the observed structure amplitudes in computing a Fourier synthesis. Any errors in the initial assignment of the phases will cause the peaks in the resulting electron-density distribution to deviate slightly from the postulated positions. New phase angles can then be calculated from the revised atomic locations. The iteration procedure is continued until no further adjustment to the atomic parameters can be made.

Since only a finite number of terms are used in the Fourier summation, errors caused by termination of series are present in the resulting electron-density distribution. Booth (1946, 1947) has proposed a method which virtually eliminates such errors, and it involves computation of both F_o and F_c Fourier syntheses. The atomic positions resulting from an F_c synthesis will probably differ from those used for its calculation, and these deviations with reversed signs are the corrections which should be applied to the atomic parameters derived from the F_o synthesis.

Difference syntheses, which are essentially Fourier series with $(F_o - F_c)$ as coefficients, are particularly useful in revealing any errors in the positional and thermal parameters of the atoms. When there is a gradient at an atomic site, the atom should be moved in the direction of the gradient's steepest ascent. If an atom vibrates isotropically and provided it has been correctly positioned, a single peak at that position indicates that the assigned temperature factor is too high. Moreover if an atom vibrates anisotropically when its motion is assumed to be isotropic, characteristic peaks and troughs are revealed in the difference map in the vicinity of this atom. Various analytical corrections have been devised to remove these errors.

Nowadays the difference synthesis is used primarily to locate hydrogen atoms, and to check the final results after least-squares refinement. When the atomic parameters are satisfactory the difference map will be flat with only a few random fluctuations due to experimental errors.

9.3 Least-squares Refinement.

The least-squares procedure for refining crystal-structure models was first employed by Hughes (1941) and consists of varying the atomic parameters in order to minimise some function of the difference between the observed and calculated structure amplitudes. The function most commonly used is,

$$M = \sum_{hk\ell} w(|F_o| - |F_c|)^2 = \sum_{hk\ell} w\Delta^2, \qquad (50)$$

where the summation is over all the structure amplitudes from independent observations. Ideally, the weight $w(hk\ell)$ allotted to an observation should be taken as the inverse of the square of the standard deviation of that observation. The standard deviations may be estimated from the agreement between independent measurements or from the method by which the observation was made. If, in practice, adequate weights cannot be obtained by these methods then an artificial weighting scheme incorporating a fair degree of flexibility is usually applied. Cruickshank and Smith's least-squares program (1965), currently in use at the University of Glasgow, outputs an analysis of the weighting scheme after each cycle of refinement. The structure amplitudes are batched according to magnitude and $\sin\theta/\lambda$, and if the average values of $w\Delta^2$ in each batch are approximately constant then the weighting scheme is considered to be satisfactory.

The calculated structure factor is a function of the parameters $p_1, p_2, \ldots p_n$, and the problem in the least-squares technique is to determine the values of these parameters which minimise M. For M to be a minimum the expression,

$$\frac{dM}{dp_j} = 0 \qquad (j = 1,2,\ldots n) \qquad (51)$$

must hold. Applying this condition to (50) we obtain,

$$\sum_{hk\ell} w\,\Delta\,\frac{\partial|F_c|}{\partial p_j} = 0 \qquad (j = 1,2,\ldots n). \qquad (52)$$

Since these equations, in n unknowns, are non-linear they cannot be solved directly to give the values of the parameters p_j.

Nevertheless, if we have a trial set of parameters we can determine the corrections ϵ, which, when applied to these parameters will give the best values. Δ may then be expanded as a Taylor series,

$$\Delta(p+\epsilon) = \Delta(p) - \sum_{i=1}^{n} \epsilon_i \frac{\partial|F_c|}{\partial p_i} + 0(\epsilon_i^{\,2}), \qquad (53)$$

where ϵ_i is a correction in parameter p_j. Provided the corrections are known to be small the second and higher order terms of the Taylor series can be neglected. Hence, on substituting (53) in (52) we obtain,

$$\sum_{i=1}^{n} \Big(\sum_{hk\ell} w\,\frac{\partial|F_c|}{\partial p_i}\,\frac{\partial|F_c|}{\partial p_j}\Big)\epsilon_i = \sum_{hk\ell} w\,\Delta\,\frac{\partial|F_c|}{\partial p_j}, \qquad (54)$$

a set of n equations called the normal equations which are linear in the correction terms and thus soluble for them.

The normal equations can be conveniently expressed in matrix notation as,

$$\sum_i a_{ij}\epsilon_i = b_j, \qquad (55)$$

where $a_{ij} = \sum_{hk\ell} w \frac{\partial|F_c|}{\partial p_i}\frac{\partial|F_c|}{\partial p_j}$ and $b_j = \sum_{hk\ell} w\Delta\frac{\partial|F_c|}{\partial p_j}$, (56)

and their solution is given by,

$$\epsilon_i = \sum_i (a^{-1})_{ij} b_j \ , \qquad (57)$$

where $(a^{-1})_{ij}$ is the matrix inverse of a_{ij}.

As we have seen, the least-squares procedure involves purely mathematical operations and thus lends itself particularly well to electronic computers. Because of storage capacity and time-factor limitations, the full-matrix least-squares can only be used when the number of parameters being refined is small. When the number is large approximations must be made in which some or all of the off-diagonal elements of the matrix are neglected.

Since high-order terms of the Taylor series are neglected in the least-squares method, several successive cycles of refinement are necessary before a true minimum has been attained. Convergence is reached when the atomic parameters after two successive cycles are not significantly different. The progress of the least-squares refinement may be followed by observing changes in $\Sigma w\Delta^2$ and R' where,

$$R' = \sum_{hk\ell} w\,\Delta^2 / \sum_{hk\ell} wF_o^2 \;. \qquad (58)$$

10. ACCURACY.

Often the object of a crystal-structure analysis is to establish the broad features of the gross structure, but an increasing number of investigations, in which bond lengths and bond angles are measured with some degree of precision, are undertaken. It is essential, therefore, that an assessment of the refined parameters must be made before one can embark on a valid discussion of the results of a crystal-structure analysis. The least-squares method allows estimates to be made of the standard deviations of the atomic parameters.

If correctly chosen relative weights have been used in the least-squares refinement, then the variance (the square of the standard deviation) of a parameter p_i is given by,

$$\sigma^2(p_i) = (a^{-1})_{ii}(\Sigma\, w\,\Delta^2)/(m - n), \qquad (59)$$

where $(a^{-1})_{ii}$ is a diagonal element of the inverse matrix, and m and n are respectively the number of observations and refined parameters. If there is a correlation between the parameters then the covariance of the parameters p_i and p_j for relative weights can be estimated as,

$$\mathrm{cov}(p_i,p_j) = (a^{-1})_{ij}(\Sigma w \Delta^2)/(m - n). \qquad (60)$$

The standard deviation in a bond length AB between atoms A and B is given by the expression,

$$\sigma(AB) = \left\{\sigma^2(A) - 2\mathrm{cov}(A,B) + \sigma^2(B)\right\}^{\frac{1}{2}}, \qquad (61)$$

where $\sigma^2(A)$ and $\sigma^2(B)$ are the variances of A and B in the direction AB. When there is no correlation between the atoms, cov(A,B) = 0. The standard deviation in the angle β between the bonds AB and BC is,

$$\sigma(\beta) = \left\{\frac{\sigma^2(A)}{AB^2} + \frac{AC^2\sigma^2(B)}{AB^2BC^2} + \frac{\sigma^2(C)}{BC^2}\right\}^{\frac{1}{2}}, \qquad (62)$$

where $\sigma^2(A)$ and $\sigma^2(C)$ are the variances of A and C in the plane of the three atoms and perpendicular to AB and BC respectively, and $\sigma^2(B)$ is the variance of B in the direction of the centre of the circle passing through atoms A, B and C (Darlow, 1960).

Before conclusions can be drawn from a comparison of two different experimental measurements of a bond length or angle, proper statistical significance tests should be applied (Cruickshank and Robertson, 1953). As a general rule, if the difference between two bond lengths or angles is greater than about three times the estimated standard deviation, then this difference is probably significant.

PART II

CRYSTAL STRUCTURE ANALYSES OF TWO ORGANO-BISMUTH COMPOUNDS.

INTRODUCTION.

The study of the chemistry of organo-bismuth compounds was inaugurated in 1850 by Löwig and Schweizer, with the synthesis of triethylbismuth. Originally these compounds were prepared and studied with a view to finding substances of pharmacological importance, but the principle objection to their use as such, lay in their high toxicity.

Although bismuth forms numerous organic derivatives in which it exhibits covalencies of 3, 4, and 5, its organic chemistry is less extensive than the other members of Group VB. Moreover organo-bismuth compounds tend to be much less stable than their Group VB analogues, which is in accord with the general chemistry of these elements.

A relatively small amount of work has been carried out on the structural aspects of organo-bismuth compounds particularly by X-ray diffraction methods. It was with this general theme in mind that the crystal structures of triphenylbismuth and triphenylbismuth dichloride were investigated.

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIPHENYLBISMUTH.

1.1 INTRODUCTION.

Wetzel (1942) has reported cell data and space group for triphenylbismuth, $(C_6H_5)_3Bi$, and in addition describes a structure which involves a planar distribution of the Bi-C bonds with the phenyl groups inclined at an angle of 60° to (010). Wetzel's analysis is based on quantitative intensity data for 210 ($h0\ell$) planes with qualitative data for 324 ($h1\ell$) and ($h2\ell$) planes.

Iveronova and Roitburd (1952) have also reported unit cell parameters and space group as part of a study on the possible isomorphism of triphenyl derivatives of the Group V elements, but make no mention of Wetzel's earlier work. The cell data which have been determined in the present work are presented in Table 1.1 below, along with that of the earlier work for the purposes of comparison.

Table 1.1

Source	a Å	b Å	c Å	β	Space Group
Wetzel	26.74	5.78	20.44	109° 34'	I2/c
Iveronova and Roitburd	26.7	5.78	20.4	109° 24'	C2/c or Cc
Present work	27.70	5.82	20.45	114° 29'	C2/c

Wetzel's unit cell is consistent with his space group assignment but Iveronova and Roitburd's cell is incorrect for C2/c and Cc.

Quite apart from the lack of a quantitative foundation, the structure proposed by Wetzel is inconsistent with the short b axis. Moreover the Bi-C bond length (2.30 Å) which appears in "International Tables for X-ray Crystallography", Vol.III, and has been reported by Sutton (1958), is based on this erroneous structure. It was decided therefore to reinvestigate the structure of triphenylbismuth with full three-dimensional data.

1.2 EXPERIMENTAL.

Crystal Data.

Triphenylbismuth, $C_{18}H_{15}Bi$, M = 440.3. Monoclinic,

$\underline{a} = 27.70 \pm 0.03$, $\underline{b} = 5.82 \pm 0.02$, $\underline{c} = 20.45 \pm 0.03$ Å,

$\beta = 114.48^{\circ}$, $\underline{U} = 3000$ A^3, $\underline{D}_m = 1.95$ (Wetzel, 1942),

$\underline{Z} = 8$, $\underline{D}_c = 1.95$, F(000) = 1648.

Space group C2/c (C_{2h}^{6}, No. 15). Linear absorption coefficient for X-rays ($\lambda = 0.7107$ Å), $\mu = 111.6\text{cm}^{-1}$.

Triphenylbismuth, crystallised from acetonitrile afforded fine white needle-shaped crystals elongated along b.

Crystallographic Measurements.

The unit cell parameters were obtained from rotation and equatorial layer-line Weissenberg photographs (Cu-Kα radiation, $\lambda = 1.5418$ Å) and checked on a Hilger and Watts linear diffractometer (Arndt and Phillips, 1961). Systematic absences indicated space groups C2/c and Cc; C2/c was chosen and is confirmed by the analysis.

Intensity data, used in solving the structure in the

(010) projection, were estimated visually from Weissenberg photographs of the h0ℓ reciprocal lattice net. The observed intensities were reduced to structure amplitudes by applying the appropriate Lorentz and polarisation corrections (Tunnel, 1939). For the three-dimensional analysis, the intensity data were collected from a small (0.01 x 0.01 mm^2 cross section) needle crystal, on a Hilger and Watts linear diffractometer, using balanced ZrO_2-SrO filters with Mo radiation. In all five reciprocal nets (h0ℓ - h4ℓ) were surveyed and the usual angle correction factors (Lorentz, polarisation and rotation) were applied to the intensities. A total of 1980 independent structure amplitudes were thus obtained. No absorption corrections were applied and no account was taken of reflexions of zero intensity. During the refinement stages of the analysis all reflexions corresponding to an intensity count of 25 or less were discarded as being unreliable, thus reducing the total number of independent reflexions to 1353.

Initially the data were placed on an approximately absolute scale by ensuring that $\Sigma k|F_o| = \Sigma |F_c|$ for each layer. The layer-scale factors were later refined by least-squares methods.

Structure Determination.

The structure was first solved in the $(h0\ell)$ projection. The plane group of this projection is p2 (both the a and c axes are halved) with the two equivalent positions, (x,z) and (-x,-z). A heavy atom situated at a general position will give rise to a single weight vector at (2x,2z). A Patterson synthesis using unsharpened data was computed with the aid of Beevers-Lipson strips (Lipson and Beevers, 1936). The Bi...Bi vector peak was easily located in the resulting Patterson distribution which is shown in Figure 1.1. The positions of the carbon atoms were found by minimum function methods (Buerger, 1951) and difference syntheses. The structural parameters of all the non-hydrogen atoms were then refined by minimum residual methods (Bhuiya and Stanley, 1963; Muir, 1967) and after six cycles of refinement the R-factor took the value 0.104 for 274 $(h0\ell)$ data.

For the three-dimensional analysis the y coordinate of the bismuth atom was determined from the Harker line section at $u = 0$ and $w = \frac{1}{2}$, to be 0.25. This implies that the bismuth atom does not contribute to those $hk\ell$ reflexions for which $(k + \ell)$ is odd and consequently such reflexions were removed from the preliminary calculations. A three-dimensional difference synthesis showing the expected pseudo-mirror planes parallel to (010) at $y = \frac{1}{4}$ and $\frac{3}{4}$, revealed quite clearly two of the phenyl groups (rings A and C in Figure 1.2) and their false mirror images. Ring B and its ghost were not clearly resolved since they lay across the mirror plane at $y = \frac{1}{4}$. One of the ring C images was arbitrarily chosen as being the true location of that benzene ring, and one of the ring A images was rejected on the grounds that the molecular packing arrangement resulting from such a choice would have led to impossibly short intermolecular contacts. An electron-density synthesis, using all the structure amplitudes as coefficients and phased on the bismuth atom and the carbon atoms constituting rings A and C, resulted in the unambiguous location of the third phenyl group. Inclusion of the 19 atoms in a structure-factor calculation reduced the R-factor from 0.46 (with heavy atom phases only) to 0.33. Four cycles of full-matrix least-squares calculations were then carried out to refine the positional and isotropic thermal parameters of the bismuth atom; the carbon atom parameters were included in these calculations, but not refined. The discrepancy factor fell to 0.17 and the y coordinate of the bismuth atom moved from 0.250 to 0.273. A further difference synthesis provided more accurate values for the y coordinates of the ring B carbon atoms.

Structure Refinement.

The structure was refined by eleven cycles of full-matrix least-squares calculations to a final R value of 0.069. In the first two cycles of refinement, unit weights were applied, but in the remaining cycles a weighting scheme of the form,

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

was employed. Appropriate values of p_1 and p_2 were obtained from an examination of the weighting scheme analysis after each cycle of refinement. The final values of p_1 and p_2 were 75 and 0.03 respectively. Before anisotropic refinement of the bismuth atom was introduced, the data were placed on a common scale using the refined layer-scale factors. At the end of the seventh cycle it was noted that a large number of the weaker reflexions showed poor agreement with the calculated structure factors. All those reflexions corresponding to an intensity count of 25 or less were removed from subsequent calculations. Apart from a substantial reduction in the discrepancy index, improvements in bond lengths and angles, and estimated standard deviations were also noted. In the last refinment cycle, no shifts were larger than one fifth of the estimated standard deviations. The progress of the refinement is outlined in Table 1.2 and the agreement between the observed amplitudes and final calculated structure factors can be seen in Table 1.3. In the structure-factor calculations values for the atomic scattering factors were taken from "International Tables for X-ray Crystallography", Vol.III.

The final fractional coordinates and thermal parameters with estimated standard deviations are given in Table 1.4. Bonded distances and valence angles with estimated standard deviations calculated from these data are listed in Table 1.5, which also contains some relevant non-bonded intramolecular distances, and all intermolecular contacts < 3.8 Å. Table 1.6 contains equations of planes through various portions of the molecule.

The numbering scheme adopted in the analysis is illustrated in Figure 1.2, and the arrangement of the molecules in the unit cell when viewed down the short b axis is shown in Figure 1.3.

Table 1.2

Progress of Refinement.

Parameters refined	Cycle No.	Final R	Final $\Sigma w\Delta^2 \times 10^{-5}$	Final R′
x,y,z,Uiso, for Bi and C, layer-scale factors, full matrix, unit weights.	1-2	0.147	6.17	0.0216
As above plus changes to weighting scheme	3-5	0.139	4.55	0.0190
x,y,z,Uij(i,j=1,2,3) for Bi, x,y,z,Uiso for C, one scale factor, full matrix.	6-7	0.116	3.53	0.0149
As above but structure amplitudes corresponding to small counts eliminated. Changes to weighting scheme.	8-11	0.069	1.28	0.0074

Table 1.3

Observed structure amplitudes and calculated values of the structure factors.

h	k	l	Fo	Fc
10	0	-24	64	-69
14	0	-24	76	66
6	0	-22	85	101
10	0	-22	99	-103
14	0	-22	80	89
18	0	-22	70	-73
2	0	-20	79	-79
4	0	-20	78	94
6	0	-20	103	101
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11	3	3	185	177
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12	4	-8	96	96
14	4	-8	90	-89
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Table 1.4

Fractional co-ordinates and isotropic temperature factors ($\mathring{A}^2$) with estimated standard deviations.

	x/a	y/b	z/c	Uiso
Bi	0.11448 ± 4	0.27180 ± 20	0.03017 ± 5	*
C(1)	0.0845 ± 9	0.4770 ± 47	0.0965 ± 12	0.048 ± 6
C(2)	0.0916 ± 12	0.4008 ± 57	0.1664 ± 16	0.071 ± 8
C(3)	0.0729 ± 13	0.5179 ± 65	0.2089 ± 18	0.082 ± 9
C(4)	0.0468 ± 10	0.7162 ± 54	0.1850 ± 14	0.061 ± 7
C(5)	0.0376 ± 12	0.8226 ± 64	0.1160 ± 17	0.078 ± 9
C(6)	0.0575 ± 11	0.6917 ± 59	0.0736 ± 15	0.070 ± 8
C(7)	0.1991 ± 10	0.3149 ± 51	0.1105 ± 13	0.055 ± 7
C(8)	0.2155 ± 11	0.5171 ± 56	0.1530 ± 15	0.066 ± 8
C(9)	0.2678 ± 9	0.5251 ± 49	0.2049 ± 13	0.050 ± 6
C(10)	0.3041 ± 10	0.3478 ± 49	0.2125 ± 14	0.054 ± 7
C(11)	0.2882 ± 13	0.1536 ± 60	0.1651 ± 17	0.076 ± 9
C(12)	0.2339 ± 12	0.1355 ± 54	0.1143 ± 15	0.066 ± 8
C(13)	0.1177 ± 11	0.5667 ± 52	-0.0392 ± 14	0.058 ± 7
C(14)	0.1650 ± 11	0.6646 ± 57	-0.0313 ± 16	0.067 ± 8
C(15)	0.1619 ± 13	0.8546 ± 58	-0.0780 ± 17	0.073 ± 9
C(16)	0.1162 ± 12	0.9314 ± 61	-0.1311 ± 17	0.074 ± 9
C(17)	0.0699 ± 11	0.8200 ± 56	-0.1360 ± 15	0.065 ± 8
C(18)	0.0695 ± 11	0.6550 ± 55	-0.0901 ± 15	0.065 ± 8

* The anisotropic vibration of the Bi atom is described by the following expression:

$$\exp[\,-2\pi^2\,(\,0.051\,h^2a^{*2} + 0.051\,k^2b^{*2} + 0.046\,\ell^2c^{*2} - 0.014\,k\ell b^*c^* + 0.027\,\ell hc^*a^* - 0.017\,hka^*b^*\,)\,].$$

Table 1.5

Interatomic distances and angles

(a) Intramolecular bonded distances (Å) with e.s.d.s.

Bi - C(1)	2.21 ± 2	C(9) - C(10)	1.40 ± 4
Bi - C(7)	2.25 ± 2	C(10) - C(11)	1.43 ± 4
Bi - C(13)	2.25 ± 3	C(11) - C(12)	1.43 ± 4
C(1) - C(2)	1.43 ± 4	C(7) - C(12)	1.40 ± 4
C(2) - C(3)	1.37 ± 5	C(13) - C(14)	1.38 ± 4
C(3) - C(4)	1.34 ± 5	C(14) - C(15)	1.44 ± 5
C(4) - C(5)	1.46 ± 4	C(15) - C(16)	1.36 ± 5
C(5) - C(6)	1.43 ± 5	C(16) - C(17)	1.40 ± 4
C(1) - C(6)	1.43 ± 4	C(17) - C(18)	1.35 ± 4
C(7) - C(8)	1.42 ± 4	C(13) - C(18)	1.41 ± 4
C(8) - C(9)	1.40 ± 4		

(b) Valency angles (°) with e.s.d.s.

C(1)- Bi -C(7)	92 ± 1	C(7) -C(8) -C(9)	117 ± 3
C(1)- Bi -C(13)	96 ± 1	C(8) -C(9) -C(10)	122 ± 3
C(7)- Bi -C(13)	94 ± 1	C(9) -C(10)-C(11)	120 ± 2
Bi -C(1)-C(2)	121 ± 2	C(10)-C(11)-C(12)	119 ± 3
Bi -C(1)-C(6)	123 ± 2	C(7) -C(12)-C(11)	118 ± 3
C(2)-C(1)-C(6)	116 ± 2	Bi -C(13)-C(14)	122 ± 2
C(1)-C(2)-C(3)	123 ± 3	Bi -C(13)-C(18)	118 ± 2
C(2)-C(3)-C(4)	119 ± 3	C(14)-C(13)-C(18)	120 ± 3
C(3)-C(4)-C(5)	125 ± 3	C(13)-C(14)-C(15)	117 ± 3
C(4)-C(5)-C(6)	114 ± 3	C(14)-C(15)-C(16)	124 ± 3
C(1)-C(6)-C(5)	123 ± 3	C(15)-C(16)-C(17)	115 ± 3
Bi -C(7)-C(8)	121 ± 2	C(16)-C(17)-C(18)	123 ± 3
Bi -C(7)-C(12)	116 ± 2	C(13)-C(18)-C(17)	120 ± 3
C(8)-C(7)-C(12)	123 ± 2		

(c) Some intramolecular non-bonded distances (Å).

Bi...C(2)	3.19	C(1)...C(18)	3.81
Bi...C(6)	3.23	C(2)...C(7)	3.64
Bi...C(8)	3.22	C(2)...C(8)	3.62
Bi...C(12)	3.13	C(6)...C(13)	3.44
Bi...C(14)	3.20	C(6)...C(18)	3.51
Bi...C(18)	3.17	C(7)...C(13)	3.30
C(1)...C(7)	3.21	C(7)...C(14)	3.34
C(1)...C(8)	3.33	C(8)...C(13)	3.75
C(1)...C(13)	3.31	C(8)...C(14)	3.54

(d) Intermolecular Contacts (<3.80 Å).

C(2)...C(5)$_{\mathrm{I}}$	3.65
C(3)...C(10)$_{\mathrm{II}}$	3.65
C(3)...C(11)$_{\mathrm{II}}$	3.72
C(3)...C(17)$_{\mathrm{III}}$	3.76
C(4)...C(18)$_{\mathrm{IV}}$	3.69
C(8)...C(10)$_{\mathrm{II}}$	3.58
C(9)...C(9)$_{\mathrm{II}}$	3.79
C(9)...C(10)$_{\mathrm{II}}$	3.62
C(9)...C(11)$_{\mathrm{II}}$	3.67
C(9)...C(12)$_{\mathrm{II}}$	3.77
C(10)...C(15)$_{\mathrm{V}}$	3.69
C(10)...C(16)$_{\mathrm{V}}$	3.51
C(12)...C(8)$_{\mathrm{I}}$	3.76

The subscripts refer to the following equivalent positions:

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

Table 1.6

Atoms in plane	Equation of plane	RMSD
C(1)....C(6)	$-0.869X' - 0.492Y - 0.062Z' = -3.289$	0.009
C(7)....C(12)	$0.252X' + 0.456Y - 0.854Z' = 2.146$	0.020
C(13)...C(18)	$0.073X' - 0.660Y - 0.748Z' = -0.369$	0.027
C(1),C(7),C(13)	$-0.380X' - 0.891Y - 0.248Z' = -3.531$	

X', Y, and Z' (in Å) are referred to the orthogonal axes a', b, and c. RMSD is the root mean square deviation of the atoms from the plane.

Figure 1.1

The Patterson distribution projected on to (C1C) showing clearly the Bi...Bi vector peak. Contour levels are at equal arbitrary intervals.

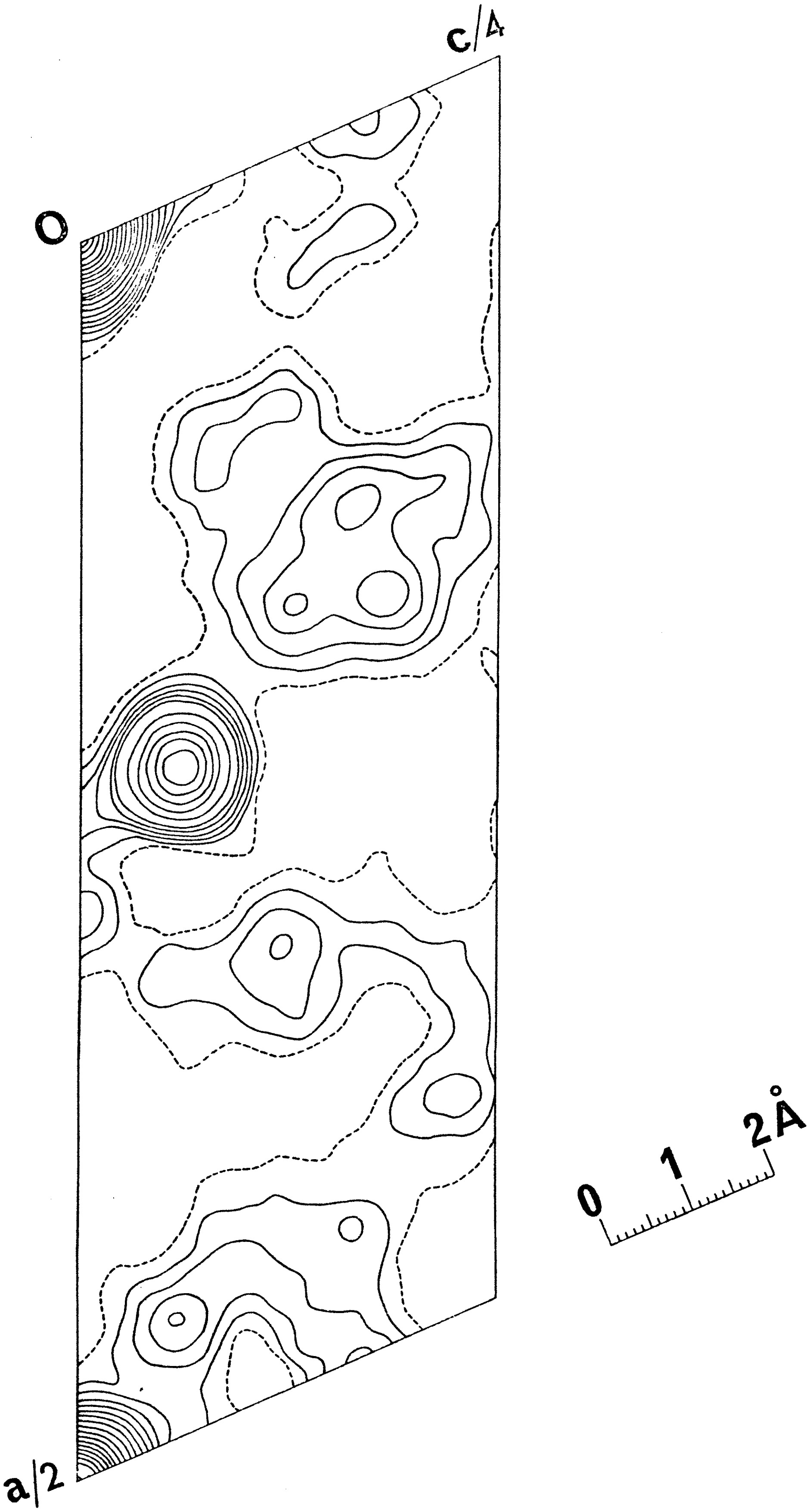
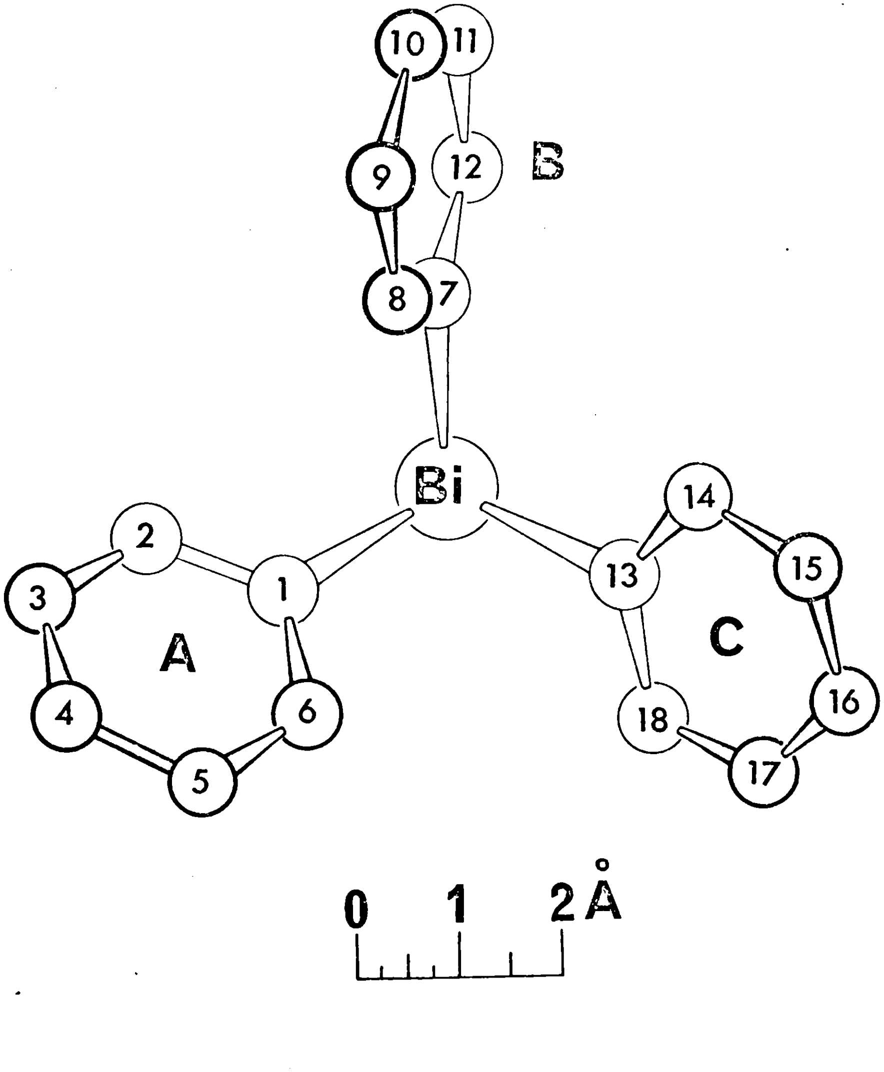
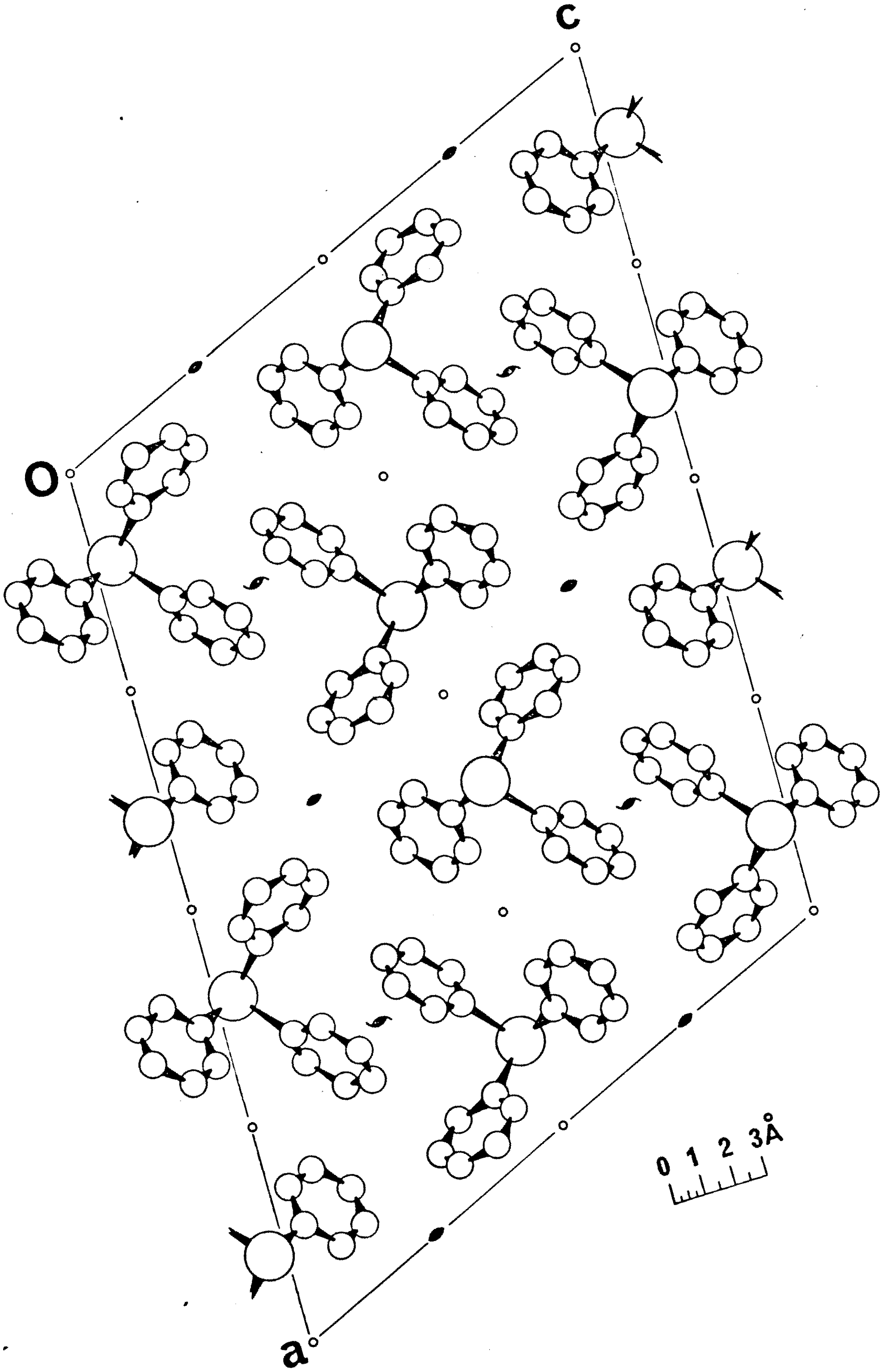

O
c/4
a/2
0
1
2Å

Figure 1.2

A view of the triphenylbismuth molecule along the vector joining the centroid of the C(1), C(7), C(13) triangle and the Bi atom. The numbering scheme adopted in the analysis is also shown.


10
11
9
12
B
8
7
Bi
14
2
13
15
3
1
A
C
6
16
4
18
5
17
0
1
2 Å


c
O
a
0 1 2 3Å

1.3 DISCUSSION.

One of the main problems with which we were confronted in the crystal-structure analysis of triphenylbismuth arose from the dominating effect of the bismuth atom on the scattering of X-rays. Assuming that on average the contribution made by any one atom of the structure to the diffracted intensity is proportional to the square of its scattering factor, then the bismuth atom contribution amounts to 91%. Consequently, Fourier syntheses would tend to show only the heavy atom, the lighter ones being lost in diffraction ripples emanating from the bismuth atom. This was overcome to a certain extent by using difference syntheses techniques in the initial stages of the analysis. Plausible sites for the light carbon atoms were thus obtained, but their accuracy is not, and could not be expected to be, high.

It may be argued that the crystal structure ought to have been determined from a neutron diffraction analysis, in which case the bismuth atom makes a contribution of only 8% to the average intensity. This in principle appears to be a viable proposition, but there is the major difficulty in obtaining a large crystal which is necessary in neutron diffraction work in view of the relative weakness of the beam.

This analysis has established that triphenylbismuth adopts a pyramidal configuration about the bismuth atom. The average C-Bi-C valency angle of 94° is significantly smaller than the tetrahedral angle, indicating that there is virtually no hybridisation of the 6s and 6p orbitals. This is not altogether unexpected in view of the high stability of the 6s orbital. The mean Bi-C distance is 2.24 ± 0.02 Å, and is fortuitously close to the value of 2.30 Å given by Wetzel (1942) and quoted in various tables ("International Tables for X-ray Crystallography", Vol.III, 1962; Sutton, 1958). The average aromatic C-C bond length of 1.40 Å and the mean valency angle of 120° at sp^2 hybridised carbon atoms are in accord with accepted values.

The triphenylbismuth molecule as a whole possesses no symmetry because of the asymmetric rotations of the phenyl groups about their respective Bi-C bonds. The Bi, C(1), C(7), and C(13) pyramid however, has within experimental error C_{3v} symmetry. In triphenylphosphine (Daly, 1964), on the other hand, the symmetry of the corresponding group of atoms is closer to C_s rather than to C_{3v}. Although in triphenylbismuth similar deviations from C_{3v} symmetry are observed - the C(1)BiC(7) bond angle (92°)

is less than the other two C-Bi-C angles (96° and 94°) and the intramolecular contacts C(1)...C(13) (3.31 Å) and C(7)...C(13) (3.30 Å) are longer than the C(1)...C(7) contact (3.21 Å) - the accuracy of the analysis does not render them significant.

The dihedral angles between the best planes through the phenyl groups A, B, and C and the plane defined by C(1), C(7) and C(13) which constitutes the base of the pyramid, are 38°, 73°, and 42° respectively. Each ring is rotated about the appropriate Bi-C bond in the same sense. This is illustrated in Figure 1.2 which is a view of the molecule along the vector joining the bismuth atom to the centroid of the C(1), C(7), C(13) triangle. In triphenylphosphine (Daly, 1964) the phenyl groups are rotated about the P-C bonds by 68°, 36°, and 65°, but tri-p-tolylarsine (Trotter, 1963) has crystallographic C_3 symmetry with each ring rotated by 36° about the As-C bond. Ring B, in triphenylbismuth is twisted by approximately 30° from the position it would occupy if the molecule had a three-fold axis of symmetry. It would appear that the deviation from a symmetrical C_3 environment is governed to a large extent by the intermolecular forces within the crystal, rather than the intramolecular repulsions, since twisting the B-ring to the symmetrical position would tend to reduce such repulsions.

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIPHENYLBISMUTH DICHLORIDE.

2.1 INTRODUCTION.

A notable feature of bismuth chemistry is the relative lack of Bi(V) compounds which may well be attributed to the high stability of the 6s orbital. A few of general formula R_3BiX_2 (R = aryl group; X = halogen, acetate etc.) as well as bismuth pentafluoride and pentaphenyl, have however been reported in the literature.

It has been shown, as part of a general study of organometallic halides of Group VB elements (Beveridge, and Harris, 1964; Beveridge, Harris, and Inglis, 1966) that triphenylbismuth dichloride has a negligible molar conductance even in solvents of high dielectric constant, such as methyl cyanide, which implies that a molecular species is present. Jensen (1943) found that triphenylbismuth dichloride has a zero dipole moment in benzene and he has suggested a trigonal bipyramidal structure which has been confirmed by this crystal-structure analysis.

Stroganov (1959) has reported the space group and unit cell data for this molecule which are in agreement with our results.

1.2 EXPERIMENTAL.

Crystal Data.

Triphenylbismuth dichloride, $C_{18}H_{15}BiCl_2$, M = 511.2.

Orthorhombic,

$\underline{a} = 9.18 \pm 0.02$, $\underline{b} = 17.11 \pm 0.03$, $\underline{c} = 22.30 \pm 0.03$ Å.

$\underline{U} = 3503$ Å^3, $\underline{D}_m = 1.96$ (Stroganov, 1959), $\underline{Z} = 8$, $\underline{D}_c = 1.94$,

F(000) = 1920. Space group $P2_12_12_1$ (D_2^4, No. 19).

Linear absorption coefficient for X-rays ($\lambda = 1.542$ Å),

$\mu = 220 \mathrm{cm}^{-1}$.

Crystals of triphenylbismuth dichloride, similar in appearance to those of triphenylbismuth, consisted of fine white needles elongated along a.

Crystallographic Measurements.

The lattice parameters were obtained from oscillation, rotation, and zero-layer Weissenberg photographs taken with Cu-Kα radiation. The space group was determined uniquely from the systematic absences (h00, 0k0, and 00ℓ

absent when h, k, and ℓ are odd). The three-dimensional intensity data, consisting of layer-line spectra $0k\ell$-$5k\ell$ were collected by means of equi-inclination multiple-film Weissenberg exposures (Robertson, 1943), taken with Cu-Kα radiation. A small needle-shaped crystal of 0.04 x 0.02mm^2 cross section was used in the data collection. The intensities of 1247 reflexions were measured visually by comparison with a calibrated step wedge. Reflexions with intensities too small to be measured were not included in any of the calculations. Corrections for Lorentz, polarisation and the rotation factors (Tunnel, 1939) appropriate to the upper layers, were applied to the observed intensities, but no absorption corrections were made.

The data were initially set on an approximately absolute scale by correlation with the calculated structure amplitudes.

Structure Determination.

The structure determination commenced with an analysis in the (100) projection. The plane group for this projection is pgg with four equivalent positions, $\pm(y,z)$ and $\pm(\frac{1}{2} + y, \frac{1}{2} - z)$. Since there are two bismuth atoms in the asymmetric unit the (100) Patterson distribution, illustrated in Figure 2.1, contains two distinct types of Bi...Bi vector peaks. There are those peaks (marked 'A' and 'B' in Figure 2.1) derived from symmetry related atoms, which are described by the following analytical expressions,

$$2y_i, \quad 2z_i \quad \text{(single weight)}$$

$$\tfrac{1}{2}, \quad \tfrac{1}{2} - 2z_i \quad \text{(double weight)}$$

$$\tfrac{1}{2} - 2y_i, \quad \tfrac{1}{2} \quad \text{(double weight)}$$

where the subscript i refers to Bi or Bi'. In addition there are four vector peaks (marked by a cross) which result from interactions between non-symmetry related bismuth atoms. Coordinates consistent with the peaks in the asymmetric unit of the projected Patterson function were obtained for both bismuth atoms. A structure-factor calculation phased on these positions gave an R-factor of 0.35. The chlorine atoms were then located in the ensuing electron-density distribution. Refinement of the positional and isotropic thermal parameters of the six heavy atoms by minimum residual methods (Bhuiya and Stanley, 1963; Muir, 1967) reduced R to 0.17.

For the three-dimensional analysis the x coordinates of the bismuth atoms were found from the Harker section at $v = \frac{1}{2}$ (Figure 2.1) and a Patterson line section through one of the Bi...Bi' vectors. The first electron-density distribution clearly revealed the chlorine atoms but the resolution of the light carbon atoms was poor as one might expect. Using difference Fourier techniques plausible sites for these atoms were eventually obtained. Calculation of structure factors based on the forty-two non-hydrogen atoms in the asymmetric unit resulted in an agreement index, R, of 0.114. A further round of structure factors and Fourier calculations, with back-shift corrections for termination of series errors (Booth, 1946) derived from an F_c synthesis, reduced R slightly to 0.107.

Structure Refinement.

Refinement was by seven cycles of full-matrix and block-diagonal least-squares calculations minimising the function $\Sigma w(|F_o| - |F_c|)^2$. Initially positional and isotropic thermal parameters, as well as layer-scale factors, were refined, but before anisotropic refinement of the bismuth and chlorine atoms, the data were placed on a common scale using the layer-scale factors obtained at the end of the isotropic refinement. The weighting scheme applied was of the form,

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

The parameters p_1, p_2, and p_3 were assigned the values 200, 0.01, and 0.0001 respectively since such a choice gave constant averages of $w\Delta^2$ for reflexions batched according to $|F_o|$ and $\sin\theta/\lambda$. The least-squares refinement which is summarised in Table 2.1, reduced R to its final value of 0.077. Values of the observed and final calculated structure amplitudes are listed in Table 2.2. The atomic scattering factors used in all structure-factor calculations throughout the analysis are those given in "International Tables for X-ray Crystallography", Vol.III(1962).

The final fractional coordinates and thermal parameters are contained in Table 2.3. The anisotropic temperature parameters are the values of U_{ij} in the expression,

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2}$$
$$+ 2U_{23}k\ell b^*c^* + 2U_{31}\ell hc^*a^* + 2U_{12}hka^*b^*)] .$$

Estimated standard deviations derived from the inverse of the least-squares matrix are also included in Table 2.3. Bonded distances, valency angles, some intramolecular non-bonded distances and intermolecular contacts (<3.7 Å) are presented in Table 2.4 together with average estimated standard deviations in bond lengths and angles. Table 2.5 contains equations of the best planes through the phenyl groups and the planes containing Bi, C(1), C(7), and C(13), and Bi', C(1'), C(7'), and C(13').

The atom numbering scheme adopted in the analysis is explained in Figure 2.2 which is a view of the two crystallographically independent molecules in the asymmetric unit, projected on (100). The molecular packing arrangement in the unit cell as viewed down the a axis is illustrated in Figure 2.3.

Table 2.1

Progress of Refinement.

Parameters refined	Cycle No.	Final R	Final $\Sigma w\Delta^2 \times 10^{-4}$	Final R′
x,y,z,Uiso, for Bi and Cl, carbons included but not refined; layer-scale factors; full matrix.	1-2	0.107	9.43	0.021
x,y,z,Uiso for Bi, Cl and C; layer-scale factors; block diagonal.	3-4	0.094	6.47	0.016
x,y,z,Uij(i,j=1,2,3) for Bi and Cl, carbons included but not refined; one scale factor; full matrix.	5-7	0.077	3.94	0.011

Table 2.2

Observed and final calculated values of the structure amplitudes.

H	K	L	Fo	Fc
0	0	2	78	65
0	0	4	352	342
0	0	6	230	204
0	0	8	61	60
0	0	10	234	228
0	0	12	30	23
0	0	14	89	83
0	0	16	92	93
0	0	18	79	92
0	0	20	45	41
0	0	22	61	74
0	1	2	42	37
0	1	3	347	327
0	1	4	192	183
0	1	5	181	179
0	1	6	85	83
0	1	7	140	137
0	1	8	111	101
0	1	9	37	33
0	1	10	136	137
0	1	11	43	48
0	1	12	82	74
0	1	13	183	197
0	1	14	177	175
0	1	16	106	117
0	1	17	90	92
0	1	18	99	115
0	1	20	62	68
0	1	22	45	57
0	2	0	36	26
0	2	1	123	103
0	2	2	596	558
0	2	4	140	137
0	2	5	315	318
0	2	6	92	90
0	2	7	142	136
0	2	8	314	311
0	2	9	28	24
0	2	10	92	97
0	2	11	165	160
0	2	12	198	206
0	2	13	61	65
0	2	15	50	40
0	2	17	71	84
0	2	18	67	78
0	2	20	64	84
0	3	1	311	303
0	3	2	112	106
0	3	3	72	74
0	3	4	114	102
0	3	5	349	365
0	3	6	147	151
0	3	7	59	58
0	3	8	66	66
0	3	9	184	168
0	3	10	72	68
0	3	11	144	139
0	3	12	204	212
0	3	14	38	35
0	3	15	121	141
0	3	16	110	120
0	3	18	46	48
0	3	20	44	48
0	4	0	86	81
0	4	1	219	195
0	4	3	221	191
0	4	4	147	130
0	4	5	102	93
0	4	6	195	175
0	4	7	27	2
0	4	8	75	84
0	4	9	286	311
0	4	10	279	277
0	4	11	52	57
0	4	12	75	75
0	4	13	139	152
0	4	14	59	63
0	4	15	97	112
0	4	16	45	38
0	4	17	42	36
0	4	18	53	66
0	4	19	70	79
0	4	20	45	52
0	4	22	49	41
0	4	23	53	53
0	5	1	167	143
0	5	2	28	27
0	5	3	264	270
0	5	4	277	260
0	5	5	38	36
0	5	6	125	126
0	5	7	330	352
0	5	8	149	136
0	5	9	144	125
0	5	10	33	35
0	5	11	75	69
0	5	12	42	37
0	5	13	117	121
0	5	14	98	105
0	5	15	54	62
0	5	17	58	61
0	5	23	40	19
0	6	0	64	69
0	6	1	189	180
0	6	2	83	79
0	6	3	37	31
0	6	4	126	116
0	6	5	67	67
0	6	6	40	39
0	6	7	264	250
0	6	8	121	116
0	6	10	87	87
0	6	11	196	221
0	6	12	59	65
0	6	13	51	46
0	6	15	94	95
0	6	17	111	129
0	6	21	77	96
0	7	1	274	259
0	7	2	224	196
0	7	3	149	176
0	7	4	161	149
0	7	5	253	243
0	7	6	169	175
0	7	7	38	24
0	7	8	100	92
0	7	9	145	124
0	7	11	95	85
0	7	14	114	123
0	7	15	79	85
0	7	16	54	54
0	8	0	116	100
0	8	1	189	164
0	8	2	171	157
0	8	3	129	116
0	8	4	58	51
0	8	5	109	107
0	8	6	72	72
0	8	8	64	66
0	8	9	159	163
0	8	11	45	39
0	8	12	39	40
0	8	13	120	133
0	8	15	86	83
0	9	1	152	152
0	9	2	150	152
0	9	3	179	160
0	9	4	84	82
0	9	5	63	67
0	9	6	197	183
0	9	7	185	118
0	9	9	56	55
0	9	10	39	40
0	9	11	39	38
0	9	12	123	143
0	9	14	46	43

H	K	L	Fo	Fc
0	9	16	127	142
0	10	0	155	147
0	10	1	145	134
0	10	2	154	147
0	10	3	96	82
0	10	4	90	88
0	10	6	108	103
0	10	7	79	77
0	10	8	56	55
0	10	9	62	62
0	10	10	73	59
0	10	11	126	134
0	10	14	55	52
0	11	2	57	58
0	11	4	149	154
0	11	6	45	48
0	11	7	42	35
0	11	8	127	147
0	11	10	77	80
0	11	14	124	149
0	12	0	103	106
0	12	1	77	69
0	12	2	64	70
0	12	3	53	47
0	12	4	108	117
0	12	6	101	95
0	12	7	69	73
0	12	8	61	63
0	12	9	82	82
0	12	10	88	92
0	12	11	76	75
0	13	2	69	69
0	13	4	42	41
0	13	6	125	141
0	13	7	56	60
0	13	12	75	84
0	14	0	52	52
0	14	1	71	62
0	14	2	81	93
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3	13	10	62	61
3	14	0	66	75
4	0	1	101	137
4	0	3	53	63
4	0	4	183	168

H	K	L	Fo	Fc
4	0	5	230	255
4	0	6	175	214
4	0	8	57	63
4	0	9	110	126
4	0	10	178	207
4	0	11	104	118
4	0	15	75	70
4	1	1	35	48
4	1	2	128	158
4	1	3	143	163
4	1	4	64	68
4	1	5	141	153
4	1	7	169	200
4	1	8	116	121
4	1	9	98	95
4	1	10	93	97
4	1	11	94	97
4	1	12	105	102
4	1	13	130	137
4	1	14	81	66
4	1	15	100	102
4	1	17	80	65
4	2	0	41	29
4	2	1	85	91
4	2	2	215	238
4	2	3	241	215
4	2	4	43	34
4	2	6	63	53
4	2	7	159	173
4	2	8	145	162
4	2	9	57	57
4	2	10	74	72
4	2	11	101	84
4	2	12	121	125
4	2	13	96	87
4	2	14	58	36
4	2	15	71	48
4	2	16	87	64
4	2	17	75	63
4	2	18	81	69
4	3	0	222	241
4	3	1	160	154
4	3	2	130	112
4	3	3	39	32
4	3	4	135	133
4	3	5	186	214
4	3	6	155	148
4	3	7	85	90
4	3	9	80	81
4	3	10	104	105
4	3	11	130	126
4	3	12	76	60
4	3	13	67	56
4	3	15	105	104
4	3	16	88	80
4	3	17	80	72
4	3	18	70	48
4	4	0	214	200
4	4	1	143	139
4	4	2	81	67
4	4	3	141	143
4	4	4	142	136
4	4	5	146	156
4	4	6	63	60
4	4	8	90	90
4	4	9	107	96
4	4	10	110	116
4	4	12	78	53
4	4	13	72	65
4	4	14	96	106
4	4	15	87	77
4	5	0	81	84
4	5	1	125	118
4	5	2	234	208
4	5	3	196	200
4	5	4	154	152
4	5	6	106	89
4	5	7	120	109
4	5	8	116	111
4	5	9	70	74
4	5	10	62	51
4	5	11	64	48
4	5	12	87	75
4	5	13	101	104
4	5	14	86	32
4	5	16	69	47
4	6	0	101	98
4	6	1	140	132
4	6	2	88	83
4	6	3	93	75
4	6	5	72	63
4	6	6	117	107
4	6	7	107	96
4	6	8	100	83
4	6	10	108	94
4	6	11	112	100
4	6	12	119	118
4	6	15	74	56
4	6	16	90	90
4	6	17	81	85
4	7	0	147	147
4	7	1	112	97
4	7	2	85	87
4	7	3	91	80
4	7	4	158	145
4	7	5	151	142
4	7	6	132	132
4	7	7	60	39
4	7	8	91	81
4	7	9	137	131
4	7	10	80	85
4	7	12	71	38
4	7	14	84	75
4	8	1	91	85
4	8	2	53	34
4	8	3	93	89
4	8	4	100	109
4	8	7	76	63
4	8	8	110	106
4	8	9	139	146
4	8	10	69	69
4	8	12	67	63
4	8	13	84	85
4	8	14	59	91
4	9	0	65	56
4	9	1	80	89
4	9	2	73	80
4	9	3	74	83
4	9	4	107	112
4	9	6	116	111
4	9	7	107	94
4	9	8	73	60
4	9	11	87	85
4	9	12	97	95
4	9	13	75	47
4	10	0	65	69
4	10	1	104	117
4	10	3	86	72
4	10	4	30	75
4	10	5	72	67
4	10	6	94	93
4	10	7	103	94
4	10	8	76	64
4	10	9	87	80
4	10	11	89	84
4	11	3	70	53
4	11	4	34	38
4	11	5	66	37
4	11	5	78	72
4	11	9	89	84
4	12	0	36	35
4	12	1	94	111
4	12	2	72	64
4	12	3	73	66
4	12	4	68	70
4	12	5	74	71

H	K	L	Fo	Fc
5	0	2	40	58
5	0	3	41	49
5	0	4	112	138
5	0	5	54	38
5	0	6	179	153
5	0	7	117	111
5	0	8	150	139
5	0	9	171	154
5	0	10	50	45
5	0	11	125	160
5	0	13	110	103
5	0	14	109	113
5	0	15	68	70
5	0	16	53	43
5	1	0	26	41
5	1	1	118	171
5	1	2	28	47
5	1	3	115	154
5	1	4	44	45
5	1	5	151	134
5	1	6	85	73
5	1	7	201	179
5	1	9	197	172
5	1	10	50	52
5	1	11	153	140
5	1	13	58	56
5	2	0	34	47
5	2	1	35	45
5	2	2	86	112
5	2	3	77	98
5	2	4	162	184
5	2	5	83	81
5	2	6	192	198
5	2	7	106	98
5	2	8	90	77
5	2	9	76	63
5	2	11	100	82
5	2	12	115	95
5	2	13	72	67
5	2	14	61	56
5	2	15	62	64
5	2	16	78	84
5	2	17	57	61
5	3	0	34	41
5	3	1	151	183
5	3	2	85	89
5	3	3	136	164
5	3	4	45	36
5	3	5	91	104
5	3	7	86	79
5	3	8	94	85
5	3	9	142	133
5	3	10	79	84
5	3	11	86	80
5	3	12	81	69
5	3	13	80	74
5	3	14	72	68
5	4	0	149	171
5	4	1	68	79
5	4	2	151	170
5	4	3	37	30
5	4	4	177	183
5	4	5	120	117
5	4	6	113	105
5	4	8	109	98
5	4	9	51	49
5	4	10	61	56
5	4	11	59	47
5	4	12	53	48
5	4	13	60	58
5	4	14	37	32
5	4	15	63	62
5	4	16	57	55
5	5	0	123	125
5	5	1	124	146
5	5	2	93	96
5	5	3	47	51
5	5	4	92	84
5	5	5	60	56
5	5	6	66	66
5	5	7	104	93
5	5	8	88	72
5	5	9	45	41
5	5	10	103	96
5	5	11	100	90
5	5	12	80	74
5	5	14	77	67
5	5	15	31	73
5	6	0	111	129
5	6	2	150	158
5	6	3	124	124
5	6	4	134	139
5	6	5	93	79
5	6	6	127	121
5	6	7	125	111
5	6	8	92	85
5	6	10	53	59
5	6	12	54	52
5	6	13	76	68
5	6	14	57	50
5	6	15	64	54
5	7	0	122	122
5	7	1	67	54
5	7	2	73	75
5	7	3	38	29
5	7	4	76	71
5	7	5	63	49
5	7	6	71	61
5	7	8	104	103
5	7	9	85	76
5	7	10	111	109
5	7	12	38	96
5	7	13	63	57
5	7	14	57	59
5	8	0	72	73
5	8	1	63	58
5	8	2	90	96
5	8	3	64	63
5	8	4	34	87
5	8	5	133	142
5	8	5	84	91
5	8	7	72	81
5	8	8	58	60
5	8	9	53	53
5	8	10	64	60
5	8	11	62	62
5	8	13	57	61
5	9	0	62	64
5	9	1	60	56
5	9	2	103	102
5	9	3	79	70
5	9	5	57	62
5	9	6	52	47
5	9	7	73	79
5	9	8	100	105
5	9	10	34	86
5	9	12	67	66
5	10	0	49	48
5	10	3	102	91
5	10	5	95	87
5	10	7	75	82
5	10	11	64	54
5	11	0	105	113
5	11	1	86	87
5	11	3	75	72
5	11	4	52	42
5	11	5	68	79
5	11	6	59	52
5	11	7	49	44
5	11	8	57	47
5	11	10	54	67
5	13	0	43	47
5	13	1	57	63
5	13	2	67	53
5	13	3	64	63

Table 2.3

Fractional co-ordinates and thermal parameters ($\AA^2$) with estimated standard deviations.

(a) Molecule 1.

	x/a	y/b	z/c	Uiso
Bi	0.08946±28	0.04135±13	0.01371±9	*
Cl(1)	-0.0039 ±20	0.1669 ± 8	0.0684 ±6	*
Cl(2)	0.1994 ±23	-0.0769 ±10	-0.0371 ±7	*
C(1)	-0.032 ± 9	-0.033 ± 4	0.081 ± 3	0.06 ± 2
C(2)	-0.060 ± 14	-0.006 ± 7	0.135 ± 5	0.13 ± 4
C(3)	-0.118 ± 11	-0.062 ± 5	0.173 ± 4	0.09 ± 3
C(4)	-0.151 ± 13	-0.135 ± 6	0.161 ± 4	0.13 ± 4
C(5)	-0.128 ± 12	-0.165 ± 5	0.100 ± 4	0.11 ± 3
C(6)	-0.078 ± 11	-0.109 ± 5	0.059 ± 3	0.08 ± 3
C(7)	-0.030 ± 11	0.075 ± 5	-0.071 ± 4	0.09 ± 3
C(8)	0.009 ± 12	0.043 ± 6	-0.119 ± 5	0.13 ± 4
C(9)	-0.057 ± 12	0.072 ± 5	-0.171 ± 4	0.11 ± 3
C(10)	-0.181 ± 13	0.119 ± 6	-0.165 ± 4	0.13 ± 4
C(11)	-0.248 ± 14	0.147 ± 6	-0.118 ± 5	0.14 ± 4
C(12)	-0.132 ± 12	0.128 ± 5	-0.064 ± 4	0.09 ± 3
C(13)	0.277 ± 7	0.061 ± 3	0.037 ± 2	0.02 ± 2
C(14)	0.358 ± 10	0.137 ± 4	0.021 ± 3	0.13 ± 2
C(15)	0.496 ± 12	0.165 ± 6	0.042 ± 4	0.10 ± 3
C(16)	0.587 ± 10	0.109 ± 4	0.074 ± 3	0.08 ± 3
C(17)	0.559 ± 12	0.039 ± 6	0.091 ± 4	0.10 ± 3
C(18)	0.388 ± 9	0.025 ± 4	0.070 ± 3	0.07 ± 2

(b) Molecule 2.

	x/a	y/b	z/c	Uiso
Bi′	0.64814±29	0.22579±13	0.30119±9	*
Cl(1′)	0.7413 ±22	0.1098 ± 9	0.2381 ±7	*
Cl(2′)	0.5318 ±24	0.3357 ±11	0.3626 ±8	*
C(1′)	0.758 ± 8	0.191 ± 3	0.382 ± 2	0.04 ± 2
C(2′)	0.795 ± 10	0.109 ± 5	0.387 ± 3	0.08 ± 3
C(3′)	0.871 ± 12	0.067 ± 5	0.434 ± 4	0.10 ± 3
C(4′)	0.905 ± 13	0.112 ± 6	0.480 ± 4	0.13 ± 3
C(5′)	0.873 ± 15	0.191 ± 6	0.481 ± 5	0.17 ± 4
C(6′)	0.795 ± 10	0.234 ± 5	0.428 ± 3	0.07 ± 2
C(7′)	0.767 ± 12	0.305 ± 5	0.238 ± 4	0.11 ± 3
C(8′)	0.787 ± 11	0.385 ± 5	0.262 ± 4	0.09 ± 3
C(9′)	0.858 ± 13	0.444 ± 6	0.224 ± 4	0.14 ± 3
C(10′)	0.894 ± 13	0.415 ± 6	0.168 ± 4	0.11 ± 3
C(11′)	0.863 ± 10	0.342 ± 4	0.150 ± 3	0.07 ± 2
C(12′)	0.817 ± 12	0.282 ± 6	0.189 ± 4	0.09 ± 3
C(13′)	0.445 ± 10	0.192 ± 4	0.282 ± 3	0.06 ± 2
C(14′)	0.394 ± 10	0.183 ± 4	0.226 ± 3	0.06 ± 2
C(15′)	0.217 ± 11	0.166 ± 5	0.206 ± 4	0.09 ± 3
C(16′)	0.137 ± 11	0.151 ± 4	0.250 ± 3	0.08 ± 3
C(17′)	0.179 ± 12	0.166 ± 6	0.312 ± 4	0.12 ± 3
C(18′)	0.322 ± 9	0.180 ± 4	0.324 ± 3	0.05 ± 2

* Anisotropic thermal parameters U_{ij} ($\mathring{A}^2$) with e.s.d.s.

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Bi	0.0552	0.0641	0.0513	-0.0021	-0.0125	0.0026
	23	13	11	24	28	30
Cl(1)	0.086	0.065	0.074	0.016	0.073	0.014
	16	9	9	16	20	19
Cl(2)	0.106	0.097	0.084	-0.038	-0.006	-0.009
	19	11	10	18	23	25
Bi′	0.0529	0.0628	0.0523	-0.0229	-0.0035	0.0017
	24	13	11	23	27	30
Cl(1′)	0.090	0.082	0.084	-0.017	0.001	-0.019
	17	10	11	19	23	23
Cl(2′)	0.100	0.107	0.112	-0.068	0.029	0.052
	18	14	13	23	27	27

Table 2.4

Interatomic distances and angles

(a) Bonded distances (Å) with average e.s.d.s.

	Mol.1	Mol.2
Bi -Cl(1)	2.615	2.579
Bi -Cl(2)	2.530	2.560
Bi -C(1)	2.25	2.14
Bi -C(7)	2.25	2.23
Bi -C(13)	1.83	2.00
C(1)-C(2)	1.33	1.45
C(2)-C(3)	1.38	1.47
C(3)-C(4)	1.31	1.31
C(4)-C(5)	1.49	1.39
C(5)-C(6)	1.39	1.56
C(6)-C(1)	1.46	1.31
C(7)-C(8)	1.25	1.49
C(8)-C(9)	1.41	1.48
C(9)-C(10)	1.41	1.37
C(10)-C(11)	1.30	1.34
C(11)-C(12)	1.64	1.41
C(12)-C(7)	1.32	1.25
C(13)-C(14)	1.54	1.33
C(14)-C(15)	1.43	1.71
C(15)-C(16)	1.45	1.24
C(16)-C(17)	1.28	1.46
C(17)-C(18)	1.66	1.37
C(18)-C(13)	1.41	1.48

Bi-Cl ± 0.017 Bi-C ± 0.08 C-C ± 0.13 Å

(b) Valency angles (°) with average e.s.d.s.

	Mol.1	Mol.2		Mol.1	Mol.2
Cl(1)-Bi-Cl(2)	176	175	C(1)-C(6)-C(5)	120	117
Cl(1)-Bi-C(1)	89	95	Bi -C(7)-C(8)	117	113
Cl(1)-Bi-C(7)	91	88	Bi -C(7)-C(12)	116	123
Cl(1)-Bi-C(13)	91	88	C(8)-C(7)-C(12)	127	123
Cl(2)-Bi-C(1)	93	87	C(7)-C(8)-C(9)	116	118
Cl(2)-Bi-C(7)	91	95	C(8)-C(9)-C(10)	118	113
Cl(2)-Bi-C(13)	84	86	C(9)-C(10)-C(11)	132	124
C(1)-Bi-C(7)	117	118	C(10)-C(11)-C(12)	102	123
C(1)-Bi-C(13)	113	123	C(7)-C(12)-C(11)	121	115
C(7)-Bi-C(13)	130	120	Bi -C(13)-C(14)	123	124
Bi -C(1)-C(2)	121	116	Bi -C(13)-C(18)	139	127
Bi -C(1)-C(6)	115	129	C(14)-C(13)-C(18)	98	109
C(2)-C(1)-C(6)	124	115	C(13)-C(14)-C(15)	130	126
C(1)-C(2)-C(3)	113	130	C(14)-C(15)-C(16)	117	113
C(2)-C(3)-C(4)	130	113	C(15)-C(16)-C(17)	131	123
C(3)-C(4)-C(5)	118	121	C(16)-C(17)-C(18)	104	119
C(4)-C(5)-C(6)	114	124	C(13)-C(18)-C(17)	141	129

Cl-Bi-Cl ±0.6° Cl-Bi-C ± 2° C-Bi-C ± 3°

Bi-C-C ± 6° C-C-C ± 8°

(c) Some intramolecular non-bonded distances (Å).

	Mol.1	Mol.2		Mol.1	Mol.2
Bi...C(2)	3.15	3.07	Cl(1)...C(14)	3.53	3.44
Bi...C(6)	3.17	3.13	Cl(2)...C(1)	3.46	3.26
Bi...C(8)	3.04	3.14	Cl(2)...C(6)	3.38	3.32
Bi...C(12)	3.06	3.09	Cl(2)...C(7)	3.43	3.55
Bi...C(14)	2.97	2.96	Cl(2)...C(8)	3.25	3.35
Bi...C(18)	3.03	3.13	Cl(2)...C(13)	2.97	3.15
Cl(1)...C(1)	3.44	3.49	Cl(2)...C(18)	3.43	3.39
Cl(1)...C(2)	3.35	3.35	C(1)...C(7)	3.85	3.74
Cl(1)...C(7)	3.49	3.34	C(1)...C(13)	3.41	3.64
Cl(1)...C(12)	3.25	3.22	C(7)...C(13)	3.71	3.66
Cl(1)...C(13)	3.23	3.22			

(d) Intermolecular Contacts (<3.70 Å).

Cl(1)...C(15$'$)$_{\mathrm{I}}$	3.68	C(8$'$)...C(3)$_{\mathrm{V}}$	3.48
Cl(1$'$)...C(2)$_{\mathrm{II}}$	3.53	C(9$'$)...C(3)$_{\mathrm{V}}$	3.33
Cl(1$'$)...C(3)$_{\mathrm{II}}$	3.53	C(9$'$)...C(16$'$)$_{\mathrm{V}}$	3.60
Cl(2)...C(18$'$)$_{\mathrm{III}}$	3.57	C(10$'$)...C(11)$_{\mathrm{VI}}$	3.63
Cl(2$'$)...C(4)$_{\mathrm{IV}}$	3.57	C(11$'$)...C(11)$_{\mathrm{VI}}$	3.65
Cl(2$'$)...C(18)$_{\mathrm{V}}$	3.64	C(17)...C(4$'$)$_{\mathrm{VII}}$	3.59
C(5)...C(5$'$)$_{\mathrm{III}}$	3.51	C(17$'$)...C(4)$_{\mathrm{IV}}$	3.47
C(6)...C(4$'$)$_{\mathrm{III}}$	3.48	C(18)...C(4$'$)$_{\mathrm{VII}}$	3.62
C(6)...C(5$'$)$_{\mathrm{III}}$	3.52	C(18$'$)...C(4)$_{\mathrm{IV}}$	3.54
C(6$'$)...C(5)$_{\mathrm{V}}$	3.56	C(18$'$)...C(5)$_{\mathrm{IV}}$	3.62

The subscripts refer to the following equivalent positions:

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

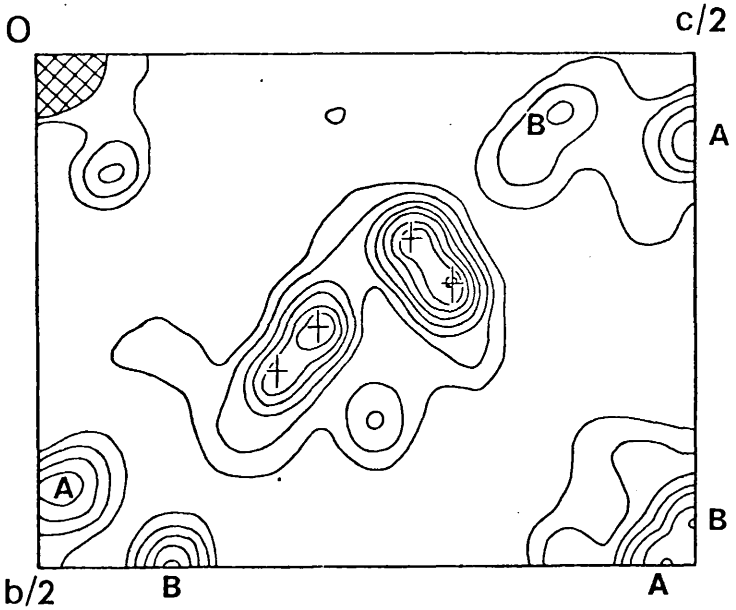
Table 2.5

Atoms in plane	Equation of plane	RMSD
Bi,C(1),C(7),C(13)	$0.316X - 0.834Y - 0.453Z = -0.448$	0.012
C(1).....C(6)	$-0.923X + 0.297Y - 0.246Z = -0.278$	0.038
C(7).....C(12)	$0.602X + 0.787Y - 0.133Z = 1.073$	0.085
C(13)....C(18)	$0.361X - 0.380Y - 0.852Z = -0.169$	0.040
Bi′,C(1′),C(7′),C(13′)	$0.364X - 0.799Y - 0.478Z = -4.144$	0.059
C(1′).....C(6′)	$0.883X + 0.191Y - 0.428Z = 3.129$	0.087
C(7′).....C(12′)	$-0.906X + 0.243Y - 0.346Z = -6.997$	0.055
C(13′)....C(18′)	$-0.210X + 0.977Y - 0.037Z = 2.126$	0.039

X, Y, and Z (in Å) are referred to the orthogonal axes a, b, and c. RMSD is the root mean square deviation of the atoms from the plane.

Figure 2.1

The Patterson distribution projected on to (100) and a Harker section at v = 1/2. Vector peaks designated A and B arise from symmetry related Bi and Bi$'$ atoms respectively; those marked by a cross arise from interactions between non-symmetry related bismuth atoms. Contour levels are arbitrary.


O
c/2
B
A
A
B
b/2
B
A

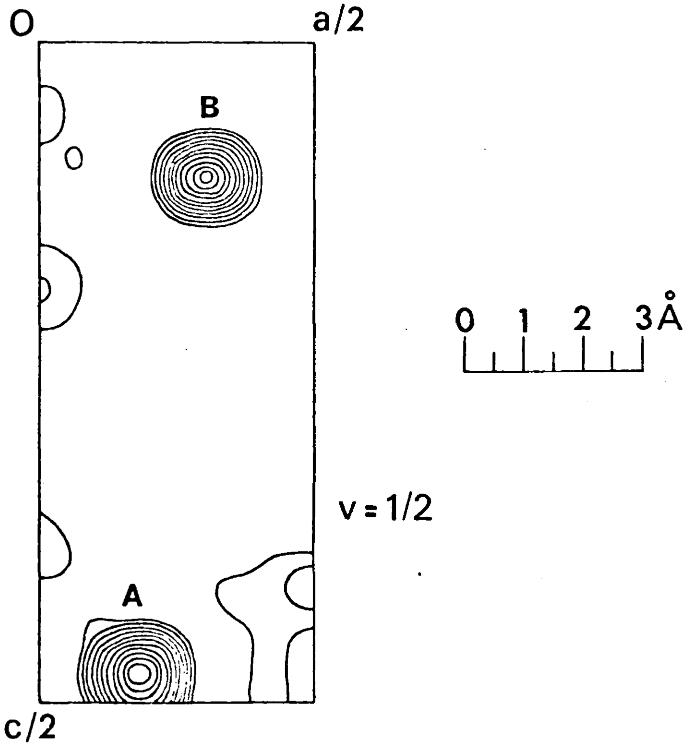

O
a/2
B
0 1 2 3Å
v = 1/2
A
c/2

Figure 2.2

A view of the two triphenylbismuth dichloride molecules in the asymmetric unit, projected on (100). The numbering scheme adopted in the analysis is also shown.

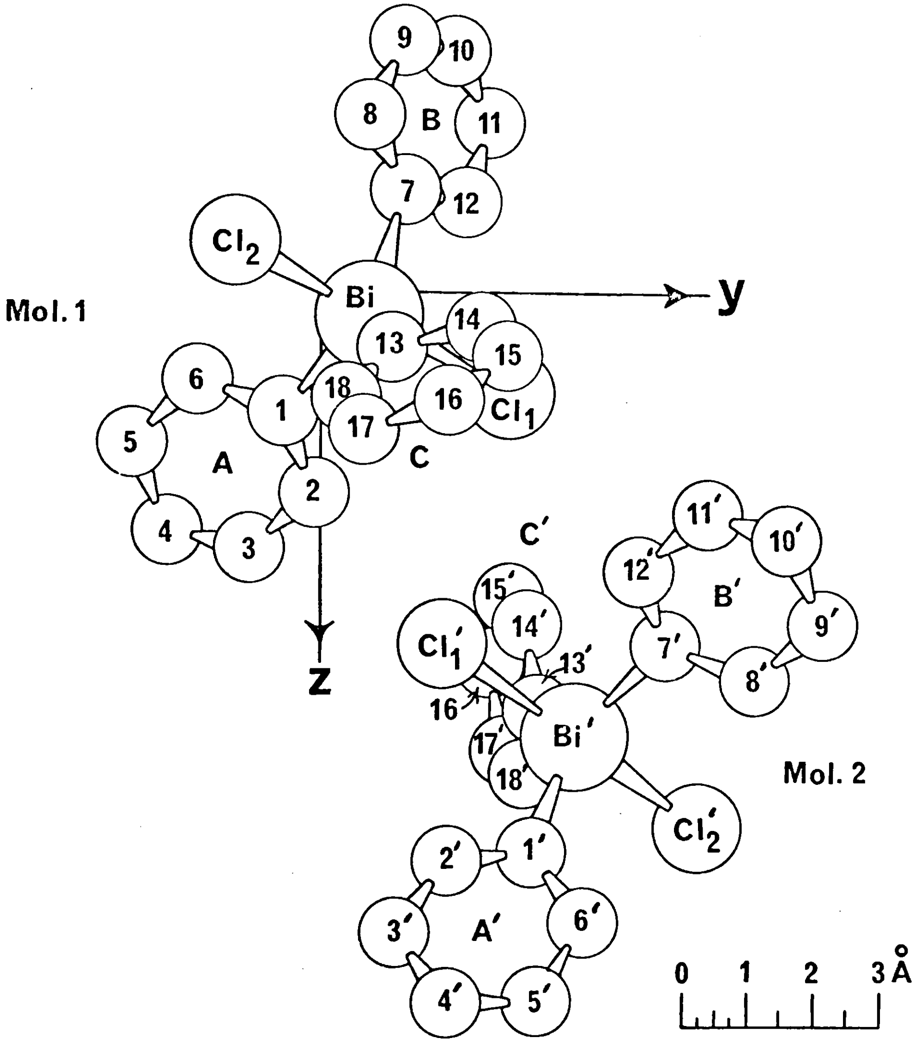

Mol. 1
Mol. 2
y
z
Bi
Bi'
Cl2
Cl1
Cl1'
Cl2'
A
B
C
A'
B'
C'
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
1'
2'
3'
4'
5'
6'
7'
8'
9'
10'
11'
12'
13'
14'
15'
16'
17'
18'
0 1 2 3 Å

Figure 2.3

The crystal structure as viewed along the a axis.

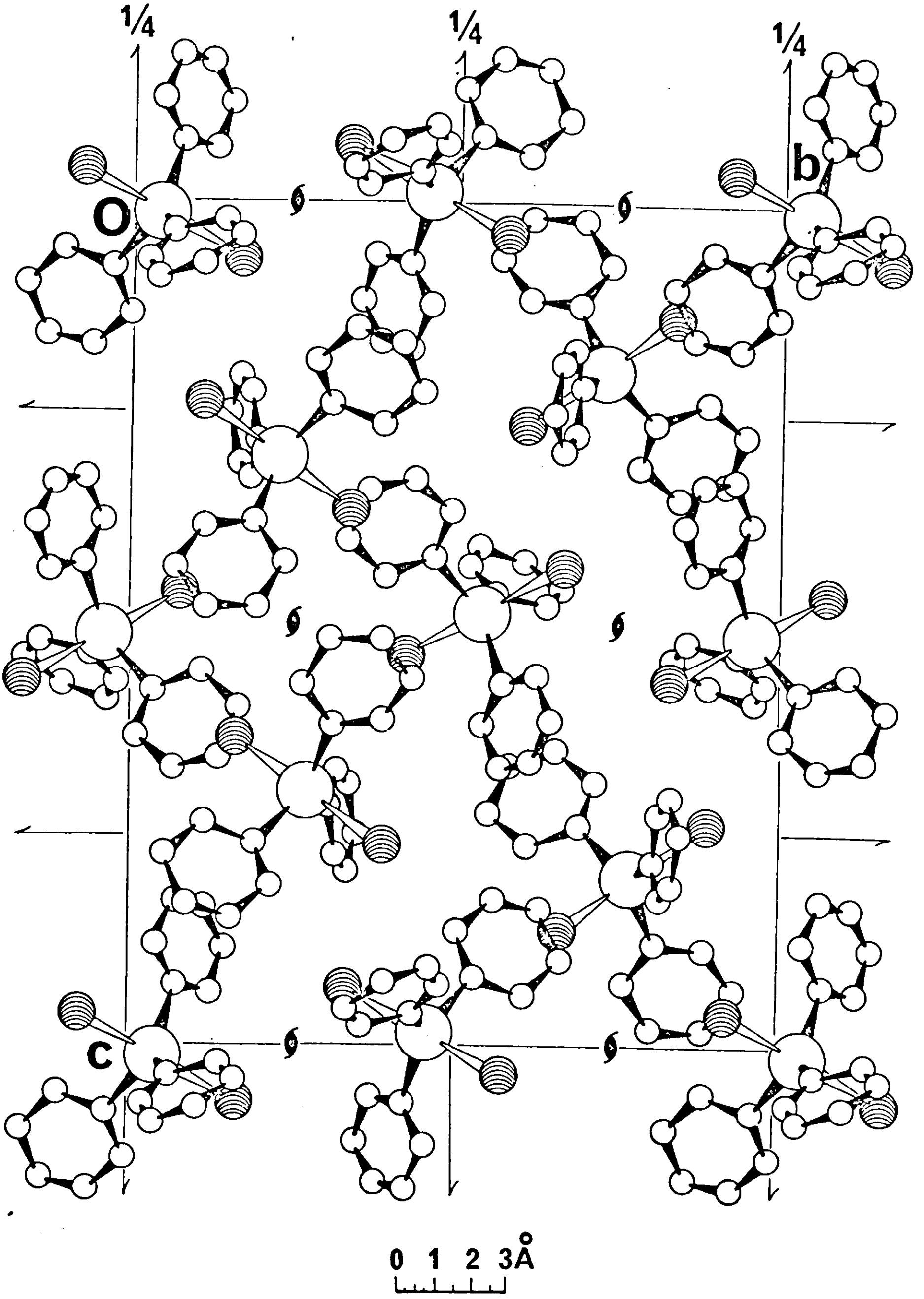
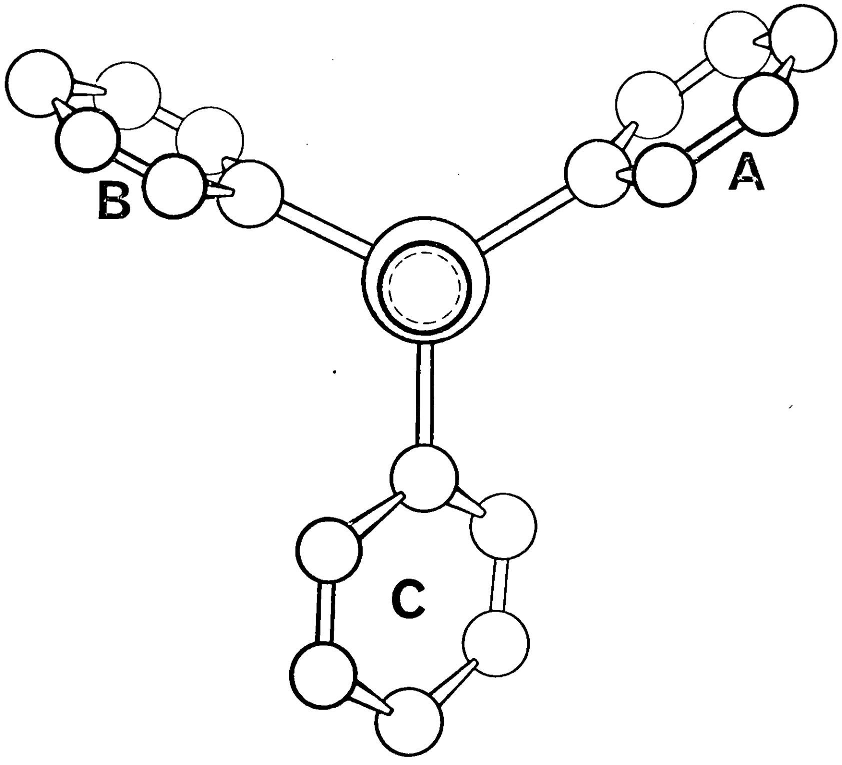

1/4
1/4
1/4
O
b
c
0 1 2 3Å

Figure 2.4

An 'average' molecule as viewed down the Cl(1)...Cl(2) vector.


B
A
C

2.3 DISCUSSION.

The problem caused by the dominant scattering power of the bismuth atom in the crystal-structure analysis of triphenylbismuth also occurs in this analysis. In addition to the bismuth atom there are a further two chlorine atoms per molecule and the contribution of these heavy atoms to the average intensity amounts to 92%. Difference syntheses were again used in the initial stages of the analysis, in order to locate the carbon atoms, in preference to electron-density syntheses which would tend to reveal the heavy atoms, the lighter ones being seen only with difficulty. Although acceptable positions for the carbon atoms were eventually found, their accuracy is not high.

The analysis has established that both molecules of triphenylbismuth dichloride in the asymmetric unit, although crystallographically independent, adopt virtually the same trigonal bipyramidal configuration. The phenyl groups are attached equatorially to the central bismuth atom, with the more electronegative chlorine atoms occupying the apical positions. Studies by Muetterties, Mahler, and co-workers (1963, 1964) indicate that the more electronegative ligands tend to assume the axial sites in trigonal bipyramidal structures in which the central atom is a light element.

They point out that there is no firm basis to extend this generality to the heavier elements. Nevertheless, in any structures of penta-coordinate species which have been reported, the more electronegative groups invariably occupy axial positions and clearly the triphenylbismuth dichloride molecule is no exception to this rule.

The phenyl groups adopt conformations such that the triphenylbismuth dichloride molecule as a whole, possesses no symmetry. The rotation of the benzene rings in each molecule about the Bi-C bonds are given by the dihedral angles between the plane of the phenyl group and the plane containing Bi, C(1), C(7), and C(13). Rings A, B, and C in molecule 1 are twisted about the appropriate Bi-C bonds by 65°, 66°, and 35° respectively while the corresponding values for the second molecule are 68°, 69°, and 37°. A view of an 'average' molecule of triphenylbismuth dichloride down the Cl(1)...Cl(2) vector, illustrated in Figure 2.4, shows clearly the asymmetric rotations of the phenyl groups with respect to the equatorial plane. One further point of interest also illustrated in this diagram is the fact that the rings are not all rotated in the same sense; rings A and C are rotated in one direction while ring B is rotated in the opposite sense. A similar asymmetric rotation of the equatorial benzene rings has been observed in pentaphenylphosphorus (Wheatley, 1964) although the magnitude of these rotations is considerably less than those found in triphenylbismuth dichloride; presumably this is a result of the bulky nature of the apical phenyl groups. In contrast with the afore-mentioned molecules, triphenylantimony dichloride (Polynova and Porai-Koshits, 1966) adopts a regular trigonal bipyramidal configuration in which the phenyl groups assume a "propeller type" arrangement with each ring rotated in the same sense by about 45°. It appears that the molecular packing forces within the crystal play a large part in dictating the orientations of the phenyl groups in these compounds.

Both Cl-Bi-Cl bond angles (175°, $176^{\circ} \pm 0.06^{\circ}$) in triphenylbismuth dichloride are significantly less than 180° which indicates a slight distortion from a regular trigonal bipyramidal structure. From an examination of the appropriate intramolecular distances in Table 2.4(c) we see that the Bi-Cl bonds are bent towards ring C. This is also illustrated quite clearly in Figure 2.4. Benzene rings A and B are rotated from the equatorial plane by about twice as much as ring C, and the distortion in the molecule probably results from the greater interference between the apical chlorine atoms and rings A and B, than there is between the chlorines and the remaining phenyl group. A similar deviation from a true trigonal bipyramidal structure has been observed in pentaphenylphosphorus (Wheatley, 1964) where the angle between the axial P-C bonds is 176.9°.

The mean Bi-Cl bond length in triphenylbismuth dichloride of 2.57 ± 0.02 Å is significantly longer than that reported for the Bi^{III}-Cl distance (2.48 ± 0.02 Å) in bismuth trichloride (Skinner and Sutton, 1940), but such lengthening of the apical bonds is common in trigonal bipyramidal structures. The average Bi^{V}-C distance found in this analysis is 2.12 ± 0.08 Å which compares favourably with the value of 2.24 Å found in triphenylbismuth (Hawley and Ferguson, 1968). The C-Bi-C bond angles vary from 113° to 130° (± 3°) while the Cl-Bi-C angles lie within the range 84° - 95° (± 2°). The mean C-C bond length in the benzene rings is 1.41 Å and the average angle at sp^2 hybridised carbon atoms is 120° in accord with accepted values (Sutton et. al., 1958). Although there are some large departures from the mean values none of these is significant.

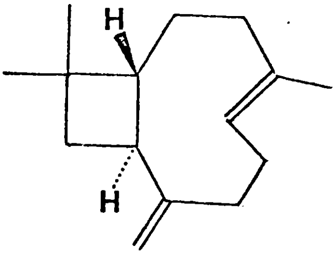
PART III

CRYSTAL STRUCTURE ANALYSES OF TWO CARYOPHYLLENE REARRANGEMENT PRODUCTS.

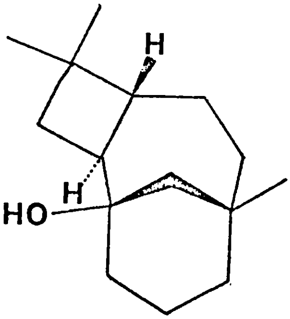
INTRODUCTION.

X-ray crystallography has played a vital role in unravelling the extremely complex rearrangements of caryophyllene (I), the major constituent of oil of cloves. The method has been used, on the one hand, to confirm structures proposed by the organic chemist, and on the other, to elucidate structures which had completely defied solution by the traditional methods of organic chemistry.

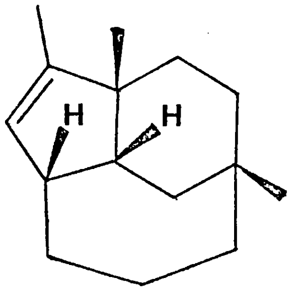
The crystal structure analysis of a derivative of caryolan-1-ol (II) (Robertson and Todd, 1955), which is obtained by treating caryophyllene with sulphuric acid, not only provided confirmation of the proposed chemical structure but also yielded valuable information of stereochemical interest. Dehydration of caryophyllene results in a complex mixture of products but the structures of the two main components, isoclovene (III) and pseudoclovene-A (IV), have been determined from the analyses of suitable heavy atom derivatives (Clunie and Robertson, 1961; Ferguson et.al., 1967). Another unexpected structure in the caryophyllene series, which was resolved by X-ray diffraction methods, is that of the stable nitroxide radical, caryophyllene 'iodonitrosite' (V) (Hawley, Roberts, Ferguson, and Porte, 1967; Hawley, Ferguson, and Robertson, 1968). The latter



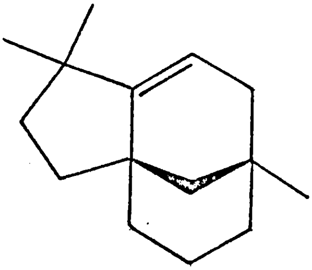
I



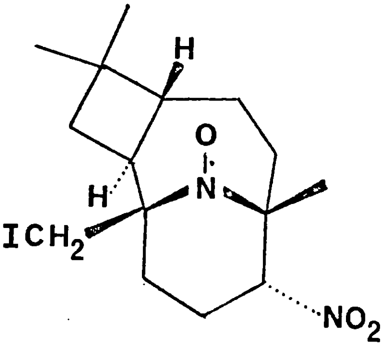
II



III



IV



V

analysis also confirmed Barton and Nickon's (1954) assignment of the absolute configuration for caryophyllene.

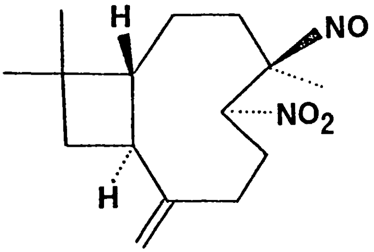
The final part of the thesis describes in detail the crystal-structure analyses of caryophyllene 'iodonitrosite' and of a derivative of pseudoclovene-A.

Although the application of X-ray crystallographic methods to the field of caryophyllene chemistry has resulted in a number of unambiguous structure determinations, it has not removed the need for additional chemical work, as has sometimes been suggested, but has in fact stimulated further research in the field.

THE CRYSTAL STRUCTURE AND ABSOLUTE STEREOCHEMISTRY OF CARYOPHYLLENE 'IODONITROSITE'.

1.1 INTRODUCTION.

The structure of caryophyllene nitrosite (VI), an important derivative once used in the characterisation of caryophyllene (I), has never been satisfactorily established (Ramage, Whitehead, and Wilson, 1954). In the course of a re-examination of the chemistry of this compound, Dr. J.S. Roberts prepared a stable crystalline 'iodonitrosite' by treatment of the nitrosite with iodine in chloroform solution at room temperature according to Deussen's (1926) method.



VI

The proton magnetic resonance spectrum of the 'iodonitrosite' when examined over the range 0≤ τ ≤10 revealed only a broad hump in the region 7-9τ which suggested that a paramagnetic species might be present. This was confirmed when a solution of the compound in a chloroform/toluene mixture exhibited a very intense paramagnetic resonance spectrum consisting of a 1:1:1 triplet, which was found to be virtually identical to that given by the ditertiarybutyl nitroxide radical under the same experimental conditions. The spectrum arises from the coupling of the odd electron with the nuclear spin of the nitrogen atom.

Caryophyllene 'iodonitrosite' therefore belongs to the relatively new class of stable aliphatic nitroxide radicals which have received fairly close attention over the past few years in view of their unusual properties.

The presence of the iodine atom in the compound made it particularly amenable to a crystal-structure investigation by X-ray diffraction using the phase-determining heavy atom method, and also enabled the absolute configuration to be determined.

1.2 EXPERIMENTAL.

Crystal Data.

Caryophyllene 'iodonitrosite', $C_{15}H_{24}N_2O_3I$, M = 407.3.

Orthorhombic,

$\underline{a} = 6.78 \pm 0.02$, $\underline{b} = 8.24 \pm 0.02$, $\underline{c} = 30.49 \pm 0.05$ Å.

$\underline{U} = 1705.0$ Å^3, $\underline{D}_m = 1.60$ (by flotation), $\underline{Z} = 4$, $\underline{D}_c = 1.59$.

F(000) = 820. Space group $P2_12_12_1$ (D_2^4, No. 19).

Linear absorption coefficient for X-rays ($\lambda = 0.7107$ Å),

$\mu = 19.1$ cm^{-1}.

Orange-red crystals of caryophyllene 'iodonitrosite' in the form of prisms were grown from ethyl acetate.

Crystallographic Measurements.

Oscillation, Weissenberg and precession photographs, taken with Cu-Kα ($\lambda = 1.542$ Å) and Mo-Kα ($\lambda = 0.7107$ Å) radiations indicated that the crystals belonged to the orthorhombic system with space group $P2_12_12_1$ which was established uniquely from the systematic absences (h00, 0k0, and 00ℓ absent when h, k, and ℓ are odd). The unit cell parameters were evaluated from rotation and equatorial layer-line Weissenberg photographs and checked on a Hilger and Watts linear diffractometer (Arndt and Phillips, 1961). Intensity data, consisting of the seven reciprocal lattice nets $0k\ell$ - $6k\ell$, were collected on the linear diffractometer using balanced ZrO_2-SrO filters with Mo radiation. Two small crystals mounted about a were employed in the data collection, since they decompose slightly on prolonged exposure to the X-ray beam. Since the random background count was of the order 20 counts per minute, all reflexions corresponding to a count of 25 or less were not included in any of the calculations. The remaining 1041 reflexions were reduced to structure amplitudes by applying the appropriate Lorentz, polarisation and rotation factors (Tunnel, 1939). No corrections for absorption were made to the intensities.

The data were initially placed on an approximate absolute scale by comparison with the calculated structure amplitudes. The final scale factors were determined by least-squares refinement.

Structure Determination.

Initial coordinates for the iodine atom were derived from a Patterson synthesis in the (100) projection (Figure 1.1) together with a line section through the three-dimensional Patterson distribution. The first set of structure factors phased on the heavy atom alone resulted in an R-factor of 0.29. The observed structure amplitudes were coupled with phases associated with the iodine atom, in a Fourier summation, and the resulting electron-density distribution revealed the positions of all the non-hydrogen atoms, but it was difficult at this stage to distinguish between carbon, nitrogen, and oxygen atoms. In the next round of structure-factor calculations all the atoms, apart from the iodine, were included as carbon atoms. From a consideration of peak height and integrated peak density, in the ensuing electron-density distribution, it was possible to distinguish between the atom types and thus establish the constitution and structure of caryophyllene 'iodonitrosite'. Two further rounds of structure-factor and Fourier calculations led to new improved coordinates for all of the atoms and reduced R to 0.17.

Structure Refinement.

Refinement of the positional and vibrational (isotropic and anisotropic) parameters and scale factors by least-squares methods converged after eleven cycles with R at 0.069. Details of the refinement are given in Table 1.1. Before the anisotropic refinement the data were placed on a common scale using the layer-scale factors obtained at the end of the isotropic refinement. The non-methyl hydrogen atoms were placed in calculated positions and their contributions, with assumed isotropic thermal parameters of 0.06 Å^2, were included in all structure-factor calculations after cycle 4. The hydrogen atoms were not refined but their positions were adjusted after cycle 7 to allow for the shifts in the positions of the carbon atoms in the previous cycles.

A weighting scheme of the form,

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

was applied throughout the refinement. Initially p_1 was set at 500 and p_2 at zero, but the parameters were adjusted so that constant averages for $w\Delta^2$, for reflexions batched according to $|F_o|$ and $\sin\theta/\lambda$, were obtained. The final values of p_1 and p_2 were 80 and 0.008 respectively.

The observed structure amplitudes and final calculated structure amplitudes are listed in Table 1.2. The theoretical scattering factors used in all the structure-factor calculations are those given in "International Tables for X-ray Crystallography", Vol.III.

Structure factors phased on the final atomic parameters were used to evaluate an electron-density distribution which is shown in Figure 1.2 as superimposed contour sections drawn parallel to (100). An explanation of the atom numbering system is also contained in this diagram. Excluding contributions from the hydrogen atoms, a further set of structure factors were calculated and used in a difference-Fourier synthesis. The resulting map revealed only some diffuse maxima which occurred in positions stereochemically acceptable for hydrogen atoms, but it was impossible to determine their coordinates with any degree of accuracy.

The final fractional coordinates and e.s.d.s for the non-hydrogen atoms are given in Table 1.3, and their thermal parameters in Table 1.4. The latter are the values of U_{ij} in the expression,

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{23}k\ell b^*c^* + 2U_{31}\ell hc^*a^* + 2U_{12}hka^*b^*)].$$

Table 1.5 contains the final calculated hydrogen atom coordinates. The hydrogen atoms have the same number as the carbon atoms to which they are bonded. Figures 1.3 and 1.4 give details of intramolecular bonded distances and valence angles respectively. Average e.s.d.s in bond lengths and angles are given in Table 1.6. Some intramolecular non-bonded distances and all intermolecular contacts <4.0 Å are listed in Table 1.7. Table 1.8 contains the displacements of atoms from, and equations of various planes in the molecule. The packing arrangement of the molecules in the crystal projected down the a axis is illustrated in Figure 1.5.

Absolute Configuration.

The absolute configuration of caryophyllene 'iodonitrosite' was established by means of the anomalous-dispersion method (Bijvoet, 1949). The iodine atom scatters X-rays anomalously which results in a breakdown of Friedel's Law. Consequently for the space group $P2_12_12_1$ we have,

$$I(hk\ell) = I(\bar{h}\bar{k}\ell) = I(h\bar{k}\bar{\ell}) = I(\bar{h}k\bar{\ell})$$

$$\neq I(\bar{h}\bar{k}\bar{\ell}) = I(\bar{h}k\ell) = I(h\bar{k}\ell) = I(hk\bar{\ell}).$$

The reflexions were indexed with respect to a right-handed set of axes (Peerdeman and Bijvoet, 1956) and the intensities of 101 Bijvoet pairs ($hk\ell$ and $hk\bar{\ell}$) were measured on the linear diffractometer. Using the complex scattering curve for iodine ("International Tables for X-ray Crystallography", Vol.III, 1962) structure factors were calculated and the ratio of the observed intensities was compared with the ratio of the squares of the corresponding calculated structure factors for each pair of reflexions. Results of this calculation, shown in Table 1.9, reveal that all the Bijvoet pairs, with the exception of 12 (marked by an asterisk), have both ratios consistently greater or less than unity, which implies that the molecule chosen (structure (V) and Figure 1.2) is the one with the correct absolute configuration.

Table 1.1

Progress of Refinement.

Parameters refined	Cycle No.	Final R	Final $\Sigma w\Delta^2 \times 10^{-4}$	Final R′
x,y,z,Uiso for all non-hydrogen atoms, layer-scale factors, full-matrix.	1-4	0.108	1.67	0.011
x,y,z,Uij(i,j=1,2,3) for all non-hydrogen atoms; hydrogens included but not refined, one scale factor, block diagonal.	5-7	0.073	0.64	0.007
As above but hydrogen positions revised.	8-11	0.069	0.56	0.006

Table 1.2

Observed and final calculated values of the structure amplitudes.

H	K	L	Fo	Fc
0	0	6	79.4	72.4
0	0	8	164.0	170.0
0	0	12	131.6	136.1
0	0	14	73.4	73.5
0	0	16	56.2	61.3
0	0	18	25.1	28.1
0	0	20	18.3	17.0
0	0	22	18.5	20.5
0	0	24	26.7	26.7
0	0	28	8.8	7.5
0	0	30	45.3	41.9
0	0	32	12.7	10.3
0	0	34	15.5	12.7
0	1	1	4.0	16.3
0	1	3	38.6	23.8
0	1	5	76.0	76.5
0	1	7	54.2	46.5
0	1	8	77.8	70.3
0	1	9	82.3	83.0
0	1	10	75.9	73.5
0	1	11	23.3	24.2
0	1	12	56.0	55.5
0	1	13	73.4	70.9
0	1	14	60.3	58.8
0	1	15	23.1	14.9
0	1	16	23.0	20.8
0	1	17	57.8	55.1
0	1	18	48.2	43.6
0	1	20	53.9	52.1
0	1	21	66.2	65.0
0	1	22	41.3	38.2
0	1	26	8.1	9.1
0	1	27	8.1	5.0
0	1	28	24.6	23.4
0	1	32	14.8	11.2
0	1	36	15.2	12.3
0	2	0	5.3	0.8
0	2	1	137.5	137.3
0	2	2	80.0	76.5
0	2	3	74.5	80.0
0	2	4	82.0	80.3
0	2	5	34.1	36.9
0	2	6	4.7	1.4
0	2	7	167.1	165.9
0	2	8	15.0	16.2
0	2	9	68.8	72.2
0	2	11	95.2	92.6
0	2	12	7.0	7.2
0	2	13	16.5	19.8
0	2	14	23.6	23.1
0	2	15	103.6	102.9
0	2	18	23.3	26.2
0	2	19	42.9	42.8
0	2	20	12.6	5.6
0	2	21	8.9	6.1
0	2	22	12.3	10.8
0	2	23	37.8	34.7
0	2	24	19.0	17.2
0	2	27	27.0	27.7
0	2	28	12.7	11.3
0	2	29	9.0	9.4
0	2	31	12.1	11.1
0	2	32	13.9	12.6
0	3	1	106.4	107.4
0	3	2	75.1	76.7
0	3	3	67.5	69.0
0	3	4	5.7	6.6
0	3	5	99.2	102.3
0	3	6	53.8	55.0
0	3	7	93.0	90.2
0	3	8	20.4	23.3
0	3	9	69.6	70.3
0	3	12	27.7	27.2
0	3	13	81.3	82.3
0	3	14	50.1	52.6
0	3	15	13.6	12.5
0	3	16	40.3	39.0
0	3	17	43.9	46.6
0	3	20	42.0	41.7
0	3	21	37.1	36.4
0	3	22	9.7	11.2
0	3	23	16.5	16.9
0	3	25	24.2	24.8
0	3	26	9.7	5.9
0	3	29	11.4	13.8
0	3	32	15.6	14.4
0	4	0	57.6	62.0
0	4	4	68.3	73.3
0	4	5	20.7	21.0
0	4	6	19.3	19.4
0	4	7	31.3	33.3
0	4	8	92.5	91.8
0	4	9	16.3	15.2
0	4	10	43.6	44.0
0	4	11	50.5	53.2
0	4	12	57.8	56.9
0	4	14	53.2	52.5
0	4	15	29.4	29.3
0	4	16	59.8	53.1
0	4	17	20.0	19.9
0	4	18	23.1	21.9
0	4	19	35.3	40.6
0	4	20	50.2	51.0
0	4	22	32.1	28.4
0	4	23	22.2	21.3
0	4	24	14.7	12.7
0	4	25	14.1	11.1
0	4	26	32.5	30.1
0	4	30	9.3	4.9
0	5	1	19.9	18.3
0	5	2	113.5	111.6
0	5	4	28.3	26.5
0	5	5	42.3	40.1
0	5	6	73.9	72.4
0	5	7	23.5	21.2
0	5	8	8.5	10.5
0	5	9	15.4	10.9
0	5	10	42.5	38.8
0	5	12	26.9	28.0
0	5	14	48.8	45.2
0	5	16	30.2	33.5
0	5	17	9.0	13.8
0	5	18	23.2	19.7
0	5	20	7.7	4.3
0	5	28	16.2	14.2
0	6	0	11.2	12.7
0	6	1	36.3	33.5
0	6	4	28.7	30.1
0	6	5	35.7	30.9
0	6	6	12.7	14.8
0	6	7	34.7	31.6
0	6	8	34.8	33.5
0	6	9	20.0	17.9
0	6	10	15.0	17.5
0	6	11	33.9	31.2
0	6	13	30.2	27.3
0	6	15	23.3	22.7
0	6	19	27.1	24.0
0	6	22	14.1	17.3
0	6	23	13.3	14.9
0	7	1	40.6	36.1
0	7	3	26.6	23.7
0	7	5	35.5	33.4
0	7	6	17.4	19.1
0	7	7	14.6	9.8
0	7	9	40.9	40.4
0	7	11	10.1	5.9
0	7	13	39.8	36.3
0	7	17	22.5	19.5
0	7	21	15.1	13.8
0	7	25	13.6	9.7
0	8	0	24.9	19.0
0	8	1	15.8	15.2
0	8	3	19.0	19.7
0	8	5	13.3	13.7
0	8	7	16.5	17.4
0	8	8	11.6	9.8
0	8	9	13.9	12.9
0	8	12	16.3	11.3
0	8	15	10.7	12.5
0	8	16	13.6	10.0
0	9	2	11.0	10.9
0	9	6	14.1	11.2
0	9	10	16.5	14.1
0	9	14	13.2	10.4
1	0	3	140.6	146.6
1	0	4	18.3	15.2
1	0	5	159.5	155.3
1	0	6	94.5	93.9
1	0	7	133.7	125.5
1	0	8	67.8	56.1
1	0	9	14.3	14.4
1	0	10	79.5	80.5
1	0	11	119.1	119.9
1	0	13	39.8	44.1
1	0	14	51.9	58.2
1	0	15	37.1	35.2
1	0	16	34.6	36.3
1	0	17	10.9	8.7
1	0	18	40.3	43.2
1	0	19	66.0	74.5
1	0	20	49.5	52.0
1	0	21	17.1	10.7
1	0	22	21.0	22.0
1	0	23	32.2	34.0
1	0	24	20.9	22.7
1	0	25	24.9	27.7
1	0	26	10.6	10.2
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2	0	16	37.3	37.4
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3	9	0	16.9	13.0
3	9	4	11.6	10.1
3	9	8	13.0	9.8
4	0	2	10.7	15.3
4	0	3	34.6	41.3
4	0	4	68.3	71.4
4	0	5	27.7	28.4
4	0	6	23.3	22.1
4	0	7	29.7	30.5
4	0	8	56.4	56.5
4	0	9	34.4	35.4
4	0	10	6.4	0.1
4	0	11	19.9	19.5
4	0	12	41.0	41.3
4	0	13	45.2	46.8
4	0	14	13.2	12.7
4	0	15	26.2	25.1
4	0	16	19.1	13.7
4	0	17	43.9	45.3
4	0	18	11.8	12.3
4	0	19	10.6	10.7
4	0	20	8.6	7.3
4	0	21	24.9	25.4
4	0	29	11.0	10.5
4	1	2	41.9	45.2
4	1	3	25.3	32.4
4	1	4	22.2	25.1
4	1	5	24.7	23.5
4	1	6	53.5	50.0
4	1	7	33.3	31.2
4	1	8	32.5	31.6
4	1	9	44.7	43.8
4	1	10	38.3	36.3
4	1	11	29.5	26.3
4	1	12	28.9	29.1
4	1	13	30.5	30.2
4	1	14	13.1	13.2
4	1	15	26.1	25.6
4	1	16	14.5	16.4
4	1	17	29.4	29.5
4	1	18	19.1	19.8
4	1	19	18.6	13.0
4	1	20	15.9	14.9
4	1	21	25.2	25.5
4	1	22	16.6	14.6
4	1	23	14.2	12.6
4	1	24	14.4	17.0
4	1	25	10.3	7.8
4	2	0	12.7	10.2
4	2	1	40.6	39.2
4	2	2	50.0	50.9
4	2	3	49.8	49.4
4	2	4	24.0	20.9
4	2	5	30.4	29.9
4	2	6	38.3	37.7
4	2	7	41.8	40.7
4	2	8	14.7	14.9
4	2	9	17.7	17.2
4	2	10	35.1	35.2
4	2	11	44.7	44.1
4	2	12	20.5	23.0
4	2	14	30.2	30.8
4	2	15	43.9	43.0
4	2	18	19.4	20.0
4	2	19	24.7	24.5
4	2	20	12.6	10.8
4	2	22	10.7	11.5
4	2	23	16.9	16.4
4	2	26	11.8	6.6
4	2	27	10.6	9.0
4	2	28	9.3	7.3
4	3	0	27.4	26.6
4	3	1	45.4	43.8
4	3	3	43.1	44.0
4	3	4	29.9	29.3
4	3	5	41.1	42.4
4	3	6	20.9	19.1
4	3	7	28.4	29.0
4	3	8	37.3	37.0
4	3	9	41.1	39.1
4	3	10	21.6	19.8
4	3	11	17.8	15.2
4	3	12	14.4	12.0
4	3	13	30.4	30.3
4	3	14	15.5	17.3
4	3	15	17.9	19.0
4	3	16	21.6	21.3
4	3	17	24.4	24.0
4	3	19	10.7	12.5
4	3	20	15.5	14.3
4	3	21	14.0	12.6
4	3	23	9.5	9.7
4	3	25	9.5	9.3
4	3	26	8.9	6.5
4	3	30	11.5	4.4
4	4	0	13.3	14.1
4	4	1	28.7	29.5
4	4	2	6.5	6.9
4	4	3	38.2	36.9
4	4	4	36.4	36.4
4	4	5	25.9	27.3
4	4	7	27.8	26.3
4	4	8	24.4	22.5
4	4	9	23.6	23.6
4	4	10	18.0	20.8
4	4	11	21.7	21.7
4	4	12	17.1	14.9
4	4	13	22.7	22.5
4	4	14	14.2	19.2
4	4	15	14.3	15.6
4	4	16	18.3	16.4
4	4	17	15.6	14.1
4	4	19	17.1	19.4
4	4	20	16.0	12.9
4	4	21	12.3	10.8
4	4	22	9.7	10.3
4	4	23	9.7	10.6
4	5	1	23.8	22.7
4	5	2	42.5	43.1
4	5	3	8.1	9.8
4	5	4	11.0	13.5
4	5	5	10.5	10.9
4	5	6	31.5	31.2
4	5	7	12.2	12.7
4	5	8	18.5	18.4
4	5	9	15.7	13.7
4	5	10	27.9	27.2
4	5	11	13.1	13.6
4	5	12	13.0	12.5
4	5	13	10.0	10.9
4	5	14	22.4	21.3
4	5	15	13.5	14.4
4	5	16	17.9	17.3
4	5	19	11.8	9.6
4	6	0	25.5	27.6
4	6	1	8.1	10.3
4	6	2	20.2	18.8
4	6	3	13.4	17.9
4	6	4	25.0	25.7
4	6	5	11.1	12.5
4	6	6	21.7	22.6
4	6	8	19.3	20.0
4	6	9	8.2	8.2
4	6	10	17.7	17.0
4	6	11	10.2	10.9
4	6	12	11.7	14.2
4	6	14	11.8	11.4
4	6	15	13.0	10.0
4	6	18	9.2	8.6
4	7	0	11.8	16.4
4	7	1	15.1	14.4
4	7	3	10.9	11.3
4	7	4	15.9	13.3
4	7	5	12.5	11.7
4	7	7	8.3	9.9
4	7	8	12.4	10.5
4	7	9	15.2	14.4
4	8	1	13.9	13.6
4	8	5	11.3	9.9
4	8	7	11.6	11.8
5	0	4	6.6	0.6
5	0	5	39.6	41.3
5	0	7	37.7	37.3
5	0	9	11.5	9.4
5	0	10	10.8	11.8
5	0	11	43.6	40.0
5	0	13	9.7	7.7
5	0	15	18.1	13.8
5	0	19	17.2	15.9
5	0	20	9.4	12.2
5	0	23	17.1	14.0
5	1	5	19.8	27.1
5	1	6	23.0	24.6
5	1	7	11.6	9.8
5	1	8	15.1	17.7
5	1	9	27.9	23.1
5	1	10	30.0	27.8
5	1	11	13.5	13.9
5	1	12	17.2	17.4
5	1	13	24.3	25.6
5	1	14	20.0	20.7
5	1	16	22.9	20.2
5	1	17	23.3	22.1
5	1	18	18.2	20.0
5	1	20	12.1	13.2
5	1	21	10.4	10.5
5	2	1	7.7	11.0
5	2	2	20.5	18.8
5	2	3	7.5	9.5
5	2	4	51.8	56.0
5	2	6	8.5	3.9
5	2	7	19.0	19.7
5	2	8	46.2	45.1
5	2	10	9.2	10.2
5	2	12	35.5	34.0
5	2	13	9.2	15.4
5	2	14	15.8	16.0
5	2	15	13.5	13.2
5	2	16	22.9	20.7
5	2	18	17.6	16.8
5	2	19	12.3	11.2
5	2	20	12.9	11.0
5	3	3	15.4	15.3
5	3	4	6.9	5.8
5	3	5	9.9	6.0
5	3	6	32.7	32.0
5	3	8	14.7	13.4
5	3	9	20.4	22.1
5	3	10	31.8	31.0
5	3	13	10.1	11.1
5	3	14	19.1	19.5
5	3	17	11.3	10.2
5	3	19	15.4	11.6
5	3	20	12.9	13.4
5	3	22	13.3	11.9
5	3	24	9.7	10.0
5	4	0	19.0	16.8
5	4	1	22.6	21.8
5	4	2	8.7	7.8
5	4	3	31.4	30.6
5	4	4	8.3	5.1
5	4	5	15.3	14.6
5	4	6	7.9	5.3
5	4	7	26.9	24.3
5	4	9	12.7	15.5
5	4	11	16.3	19.3
5	4	15	24.9	25.7
5	4	19	12.3	12.3
5	5	1	22.5	23.1
5	5	2	16.9	17.4
5	5	3	22.7	20.9
5	5	5	28.2	29.5
5	5	6	8.1	5.5
5	5	7	20.0	16.4
5	5	9	23.0	23.0
5	5	13	16.5	15.9
5	5	17	10.7	13.5
5	6	0	10.9	13.1
5	6	1	12.5	13.5
5	6	3	13.0	14.1
5	6	4	10.6	11.8
5	6	8	16.1	14.3
5	7	2	19.0	16.6
5	7	6	14.2	14.8
5	7	10	14.6	13.3
5	8	5	11.7	6.0
6	0	3	5.4	9.4
6	0	6	6.2	3.6
6	0	9	9.9	15.6
6	0	12	13.1	10.9
6	0	13	14.9	11.2
6	0	14	10.8	11.2
6	0	16	20.0	19.5
6	0	17	12.4	9.0
6	1	0	5.2	8.3
6	1	3	15.7	20.8
6	1	4	11.4	11.8
6	1	5	10.6	12.9
6	1	6	10.6	14.5
6	1	7	16.4	15.3
6	1	8	12.9	12.6
6	1	9	12.4	14.4
6	1	10	13.6	14.2
6	1	11	18.2	14.4
6	1	12	13.9	13.5
6	1	13	17.4	16.2
6	1	17	9.0	9.2
6	1	19	12.7	8.0
6	2	1	11.3	16.3
6	2	2	10.9	13.1
6	2	5	10.7	16.2
6	2	6	7.8	6.6
6	2	7	17.4	20.8
6	2	8	11.5	11.9
6	2	9	19.3	18.5
6	2	10	12.1	12.0
6	2	11	14.0	13.7
6	2	12	11.4	10.7
6	2	13	9.5	8.5
6	2	15	18.0	14.3
6	2	17	12.0	7.1
6	3	0	11.9	15.4
6	3	1	11.5	13.7
6	3	2	16.6	17.5
6	3	3	17.6	16.0
6	3	4	17.1	17.0
6	3	5	9.9	11.3
6	3	7	15.9	15.6
6	3	8	15.8	13.3
6	3	9	9.4	11.1
6	3	10	8.6	11.3
6	3	11	15.7	12.3
6	3	12	12.9	11.1
6	3	13	10.9	10.2
6	3	14	13.0	12.6
6	3	16	11.9	8.9
6	4	0	16.3	15.5
6	4	4	18.1	19.6
6	4	6	15.5	14.9
6	4	8	18.5	17.4
6	4	9	13.7	9.9
6	4	10	14.3	15.0
6	4	12	16.3	13.5
6	4	14	11.2	8.6
6	4	18	14.4	10.4
6	5	1	12.4	9.8
6	5	2	18.4	14.7
6	5	3	11.9	10.4
6	5	6	14.2	11.8
6	5	10	14.0	11.7
6	6	3	17.0	14.6

Table 1.3

Fractional co-ordinates with e.s.d.s.

	x/a	y/b	z/c
I	-0.09981 ± 25	0.60874 ± 20	0.38193 ± 5
O(1)	-0.0744 ± 22	0.1822 ± 16	0.3655 ± 4
O(2)	0.5564 ± 21	0.1356 ± 23	0.2565 ± 5
O(3)	0.3430 ± 27	0.2413 ± 21	0.2152 ± 4
N(1)	0.0891 ± 27	0.2450 ± 17	0.3504 ± 4
N(2)	0.4093 ± 25	0.2157 ± 18	0.2515 ± 4
C(1)	0.2176 ± 27	0.3361 ± 20	0.3824 ± 6
C(2)	0.3414 ± 25	0.2151 ± 19	0.4083 ± 5
C(3)	0.3365 ± 35	0.1759 ± 27	0.4586 ± 5
C(4)	0.4004 ± 44	0.0024 ± 23	0.4488 ± 6
C(5)	0.3097 ± 35	0.0364 ± 22	0.4023 ± 6
C(6)	0.3884 ± 41	-0.0357 ± 21	0.3591 ± 6
C(7)	0.2520 ± 34	-0.0072 ± 23	0.3209 ± 6
C(8)	0.1735 ± 26	0.1649 ± 20	0.3110 ± 5
C(9)	0.3103 ± 28	0.2896 ± 22	0.2904 ± 5
C(10)	0.4627 ± 27	0.3608 ± 24	0.3210 ± 5
C(11)	0.3480 ± 28	0.4478 ± 22	0.3566 ± 6
C(12)	0.0790 ± 36	0.4290 ± 21	0.4132 ± 6
C(13)	-0.0123 ± 30	0.1445 ± 27	0.2785 ± 6
C(14)	0.2967 ± 53	-0.1321 ± 31	0.4739 ± 7
C(15)	0.6267 ± 39	-0.0141 ± 27	0.4468 ± 6

Table 1.4

(a) Anisotropic thermal parameters U_{ij} (Å^2).

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
I	0.086	0.081	0.094	-0.017	-0.019	0.049
O(1)	0.061	0.074	0.086	-0.032	0.073	-0.044
O(2)	0.074	0.132	0.072	-0.083	0.026	0.005
O(3)	0.122	0.108	0.044	-0.031	0.023	-0.007
N(1)	0.064	0.050	0.056	-0.013	0.019	-0.015
N(2)	0.063	0.079	0.030	-0.023	0.011	-0.008
C(1)	0.055	0.053	0.052	-0.038	0.016	0.006
C(2)	0.050	0.040	0.034	-0.008	-0.012	0.004
C(3)	0.106	0.090	0.021	-0.023	-0.023	0.001
C(4)	0.118	0.060	0.046	-0.006	0.024	0.002
C(5)	0.096	0.044	0.050	0.031	-0.046	0.008
C(6)	0.103	0.042	0.065	0.004	0.007	0.012
C(7)	0.087	0.045	0.053	-0.019	0.007	-0.027
C(8)	0.054	0.050	0.040	-0.028	-0.024	-0.023
C(9)	0.059	0.055	0.036	0.025	-0.021	-0.011
C(10)	0.060	0.071	0.044	0.010	-0.019	-0.022
C(11)	0.054	0.063	0.053	0.026	-0.019	-0.013
C(12)	0.085	0.049	0.069	0.000	-0.015	-0.031
C(13)	0.055	0.080	0.069	-0.025	-0.026	-0.037
C(14)	0.227	0.084	0.053	0.064	-0.027	-0.111
C(15)	0.097	0.089	0.052	0.002	-0.058	0.055

(b) Average e.s.d.s. in the thermal parameters.

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
I	0.001	0.001	0.001	0.002	0.002	0.002
O	0.012	0.011	0.008	0.016	0.016	0.021
N	0.010	0.009	0.007	0.014	0.018	0.020
C	0.016	0.012	0.010	0.019	0.022	0.025

Table 1.5

Calculated hydrogen co-ordinates.

	x/a	y/b	z/c
H(2)	0.459	0.282	0.394
$H(3)_1$	0.414	0.249	0.481
$H(3)_2$	0.204	0.198	0.477
H(5)	0.165	-0.011	0.397
$H(6)_1$	0.523	0.021	0.352
$H(6)_2$	0.399	-0.163	0.363
$H(7)_1$	0.340	-0.036	0.293
$H(7)_2$	0.125	-0.077	0.328
H(9)	0.219	0.388	0.281
$H(10)_1$	0.559	0.440	0.304
$H(10)_2$	0.555	0.268	0.334
$H(11)_1$	0.256	0.534	0.341
$H(11)_2$	0.451	0.500	0.378
$H(12)_1$	0.169	0.491	0.436
$H(12)_2$	-0.019	0.343	0.427

Table 1.6

Average e.s.d.s. in bond lengths and angles.

C - I	± 0.020 Å	I - C - C	± 1.2°
N - O	± 0.021	O - N - C	± 1.5
C - N	± 0.022	O - N - C	± 1.4
C - C	± 0.027	N - C - C	± 1.4
		C - N - C	± 1.5
		C - C - C	± 1.6

Table 1.7

(a) Some intramolecular non-bonded distances(Å).

I ...N(1)	3.40	N(2)...C(7)	3.00
I ...C(11)	3.40	N(2)...C(13)	3.03
O(1)...C(2)	3.12	C(1)...C(6)	3.35
O(1)...C(5)	3.08	C(1)...C(7)	3.40
O(1)...C(6)	3.62	C(1)...C(8)	2.61
O(1)...C(7)	3.03	C(2)...C(4)	2.18
O(1)...C(12)	2.71	C(2)...C(7)	3.29
O(1)...C(13)	2.70	C(2)...C(8)	3.20
O(2)...C(7)	3.08	C(2)...C(10)	3.03
O(2)...C(8)	3.09	C(2)...C(14)	3.50
O(2)...C(10)	2.78	C(2)...C(15)	2.95
O(3)...C(7)	3.87	C(3)...C(5)	2.07
O(3)...C(8)	3.20	C(3)...C(12)	3.05
O(3)...C(10)	3.47	C(5)...C(8)	3.12
O(3)...C(13)	3.19	C(6)...C(10)	3.50
N(1)...C(5)	2.77	C(6)...C(14)	3.64
N(1)...C(6)	3.09	C(6)...C(15)	3.13
N(1)...C(10)	2.85	C(7)...C(10)	3.35

(b) Intermolecular distances (<4.0 Å).

$I \ldots O(3)_{I}$	3.56	$O(3) \ldots C(11)_{III}$	3.88
$O(1) \ldots C(10)_{II}$	3.72	$N(2) \ldots C(10)_{III}$	3.77
$O(1) \ldots C(15)_{II}$	3.59	$C(6) \ldots O(3)_{III}$	3.44
$O(2) \ldots O(3)_{III}$	3.43	$C(7) \ldots O(2)_{III}$	3.99
$O(2) \ldots N(2)_{III}$	3.48	$C(7) \ldots O(3)_{III}$	3.61
$O(2) \ldots C(9)_{III}$	3.31	$C(7) \ldots N(2)_{III}$	3.92
$O(2) \ldots C(10)_{III}$	3.27	$C(13) \ldots O(2)_{II}$	3.00
$O(2) \ldots C(11)_{III}$	3.83	$C(14) \ldots C(15)_{IV}$	3.96
$O(3) \ldots C(10)_{III}$	3.58		

The subscripts refer to the following equivalent positions:

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

Table 1.8

Distances (Å) of atoms from various planes in the molecule.

Atoms included in calculation of planes.

Plane 1		Plane 2		Plane 3		Plane 4		Plane 5	
N(1)	0.000	C(2)	0.167	N(1)	-0.004	C(1)	-0.004	O(2)	0.004
C(1)	0.000	C(3)	-0.164	C(8)	0.004	C(11)	0.004	O(3)	0.004
C(8)	0.000	C(4)	0.163	C(5)	0.004	C(8)	0.004	N(2)	-0.010
		C(5)	-0.166	C(6)	-0.004	C(9)	-0.004	C(9)	0.003

Atoms not included in calculation of planes.

Plane 1		Plane 2		Plane 3		Plane 4	
O(1)	-0.527	C(14)	-0.773	C(7)	0.539	N(1)	0.518
		C(15)	1.662	C(1)	-1.155	C(10)	-0.736
				C(2)	-1.130		

Plane Equations.

Plane 1: $-0.135X + 0.840Y - 0.526Z = -4.003$ Å

Plane 2: $0.980X + 0.104Y - 0.172Z = 0.142$

Plane 3: $-0.752X - 0.660Y - 0.002Z = -1.801$

Plane 4: $-0.793X + 0.554Y - 0.253Z = -2.587$

Plane 5: $0.569X + 0.818Y - 0.088Z = 2.370$

X, Y and Z are co-ordinates in Å referred to the orthogonal axes a, b and c.

Table 1.9

Bijvoet pairs used in the anomalous dispersion calculation.

h	k	l	$I_{\ell}/I_{\bar{\ell}}$	$F^2_{\ell}/F^2_{\bar{\ell}}$	h	k	l	$I_{\ell}/I_{\bar{\ell}}$	$F^2_{\ell}/F^2_{\bar{\ell}}$	h	k	l	$I_{\ell}/I_{\bar{\ell}}$	$F^2_{\ell}/F^2_{\bar{\ell}}$
1	1	25	0.84	0.92	1	7	10	1.11	1.03	3	3	15	1.14	1.08
1	1	21	1.50	1.15	1	7	2	0.90	0.99	3	3	12	1.12	1.09
1	1	16	0.90	0.93	2	2	23	0.85	0.98	3	4	9	1.19	1.11
1	1	14	0.86	0.93	2	2	22	1.12	1.02	3	5	12	0.76	0.92
1	1	10	0.90	0.87	*2	2	5	0.89	1.02	3	5	2	1.13	1.03
1	1	9	1.14	1.11	2	3	24	1.11	1.02	*3	6	13	0.73	1.04
1	1	7	1.10	1.09	2	3	22	0.84	0.96	3	6	9	1.13	1.09
1	1	6	1.12	1.06	2	3	20	1.25	1.10	3	6	5	0.76	0.91
1	1	3	1.10	1.16	2	3	11	0.90	0.94	*4	1	19	0.80	1.01
1	2	24	0.82	0.80	2	3	9	1.23	1.38	4	1	18	0.90	0.99
*1	2	15	1.27	0.95	2	3	7	0.90	0.90	4	1	17	1.10	1.06
1	2	13	1.14	1.16	2	3	3	0.79	0.85	4	1	16	0.52	0.67
1	2	6	1.12	1.16	2	4	20	0.87	0.99	4	1	8	0.90	0.93
1	3	24	1.41	1.03	*2	4	14	1.31	0.98	4	1	5	1.12	1.05
*1	3	20	0.80	1.05	2	4	12	0.90	0.90	4	2	9	0.78	0.85
1	3	12	0.79	0.93	2	4	10	0.78	0.80	4	2	5	0.87	0.98
1	3	4	0.87	0.67	2	4	8	0.81	0.89	4	3	17	0.87	0.95
1	4	19	1.26	1.08	2	4	6	0.65	0.71	4	3	6	1.36	1.17
*1	4	16	1.23	0.97	2	4	2	1.17	1.21	4	4	13	0.89	0.99
1	4	14	1.16	1.10	2	5	19	0.89	0.94	4	4	11	0.90	0.90
1	4	13	1.10	1.11	2	5	15	1.13	1.02	4	4	10	1.14	1.07
1	4	9	1.15	1.23	2	5	10	1.36	1.04	4	4	9	0.89	0.96
1	5	15	1.22	1.02	2	5	6	1.20	1.10	4	4	5	0.84	0.94
1	5	12	1.17	1.04	2	5	2	0.88	0.92	4	4	4	1.13	1.09
*1	5	10	1.35	0.88	*2	6	13	1.13	0.95	4	5	10	1.12	1.09
1	5	4	1.13	1.02	2	6	5	0.81	0.90	5	1	9	1.26	1.01
1	5	1	1.11	1.08	2	6	2	1.26	1.01	5	1	8	1.33	1.03
1	6	14	1.12	1.01	2	7	12	0.87	0.92	5	2	12	0.80	0.96
*1	6	12	1.14	0.85	3	2	25	1.16	1.18	5	4	15	1.10	1.03
*1	6	9	1.20	0.98	3	2	17	0.90	0.93	5	4	7	1.26	1.07
1	6	5	1.17	1.06	3	2	11	0.86	0.94	5	4	3	1.10	1.07
1	6	4	1.13	1.07	3	2	8	0.86	0.91	5	5	7	1.27	1.02
1	6	3	1.15	1.12	3	2	4	0.88	0.90	6	1	7	0.82	0.83
*1	6	1	0.88	1.04	3	3	23	0.89	0.87					

Figure 1.1

The Patterson distribution projected on to (100). The iodine vector peaks are marked with a cross. Contour levels are at equal arbitrary intervals.

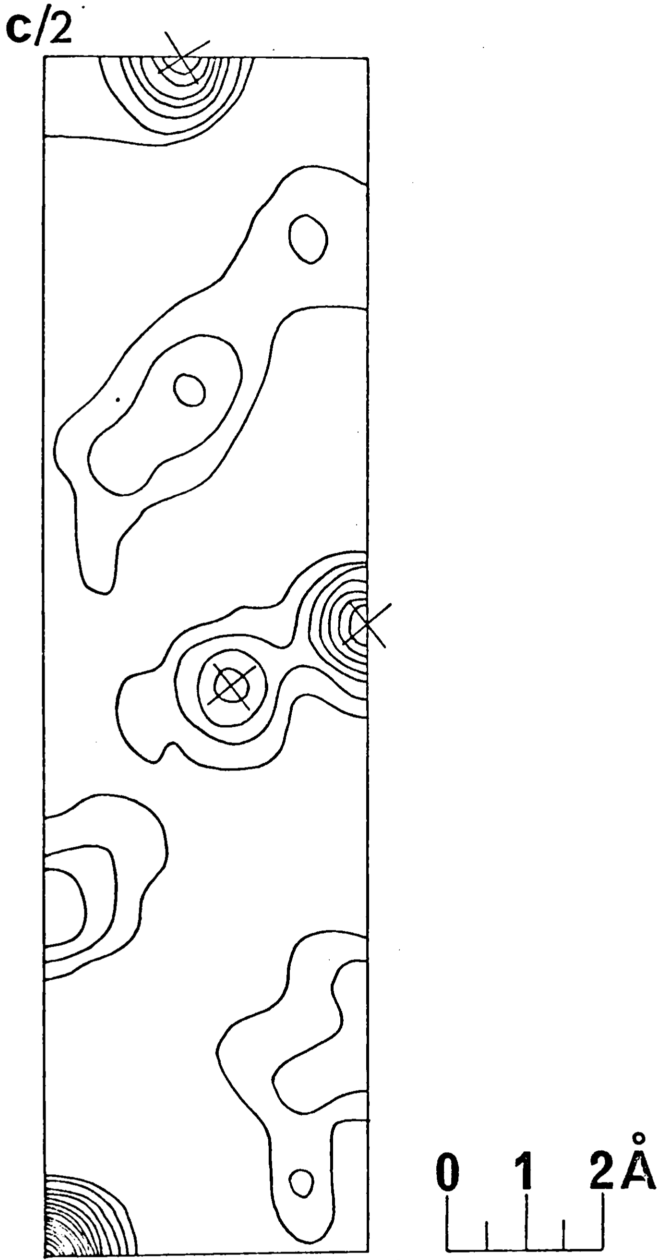

c/2
O
b/2
0 1 2Å

Figure 1.2

The final three-dimensional electron-density distribution shown by means of superimposed contour sections drawn parallel to (100). Contour intervals are of 1e $\mathring{A}^{-3}$ for the carbon, nitrogen and oxygen atoms, and of 10e $\mathring{A}^{-3}$ for the iodine atom. The arrangement of the atoms corresponding to the electron-density distribution contains an explanation of the numbering scheme adopted in the analysis.

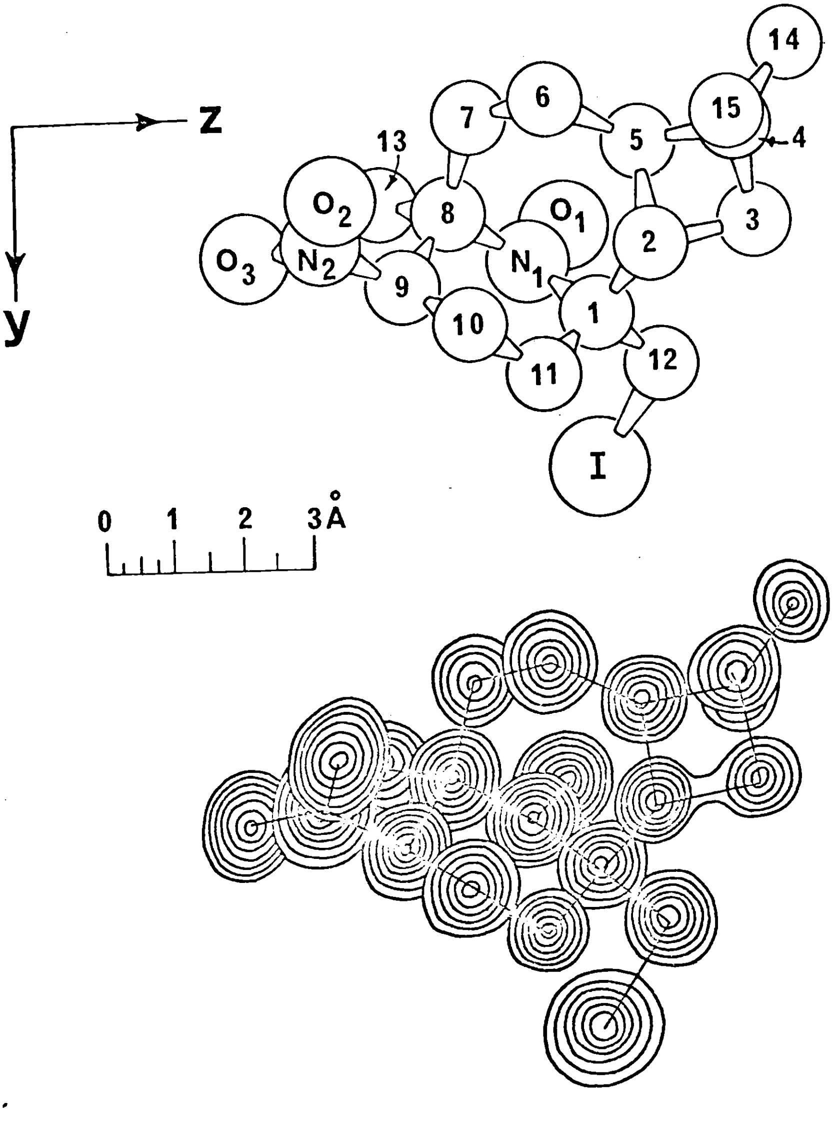

z
y
14
6
15
7
5
4
13
O2
8
O1
3
2
O3
N2
N1
9
1
10
12
11
I
0
1
2
3Å

Figure 1.3

Bond lengths (Å).

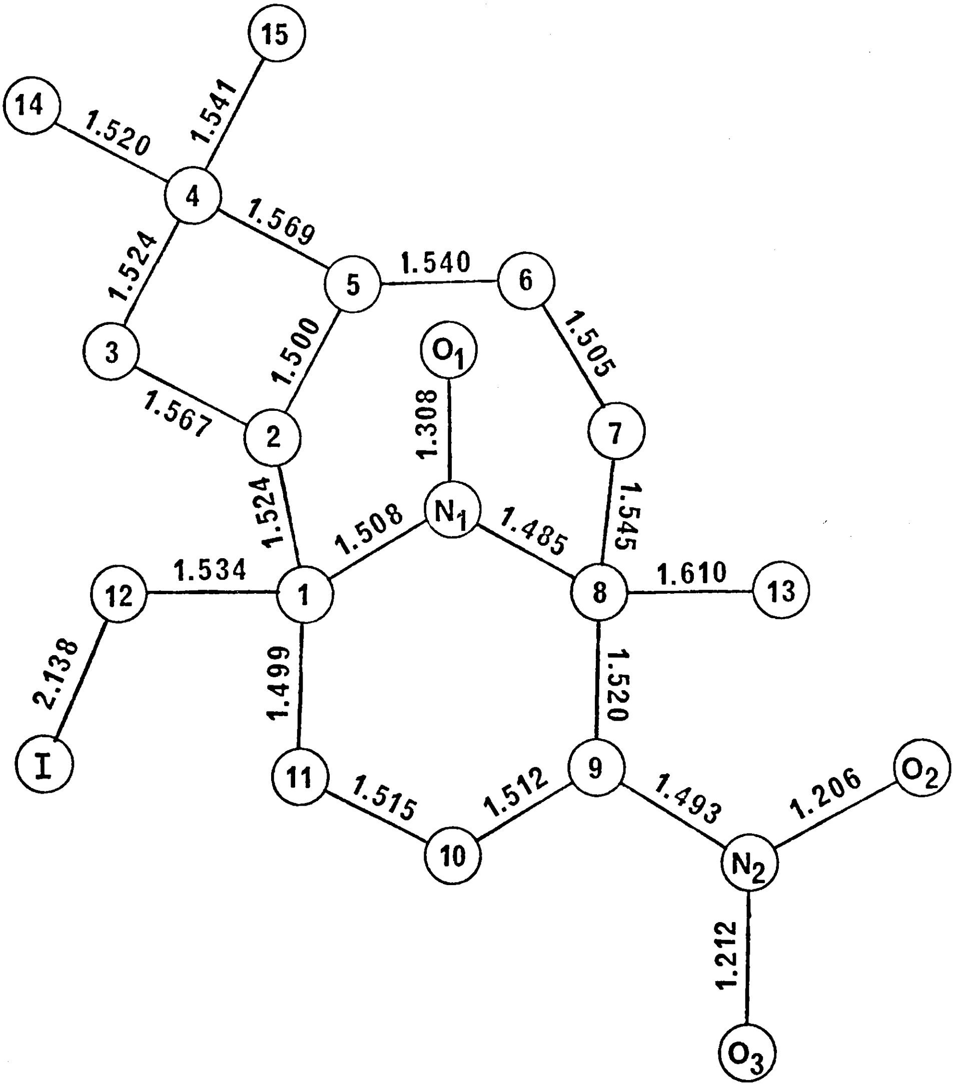

15
14
1.520
1.541
4
1.569
1.524
5
1.540
6
3
1.500
O1
1.505
1.567
2
1.308
7
1.524
N1
1.545
1.508
1.485
12
1.534
1
8
1.610
13
2.138
1.499
1.520
I
11
1.515
1.512
9
1.493
1.206
O2
10
N2
1.212
O3

Figure 1.4

Bond angles (degrees).

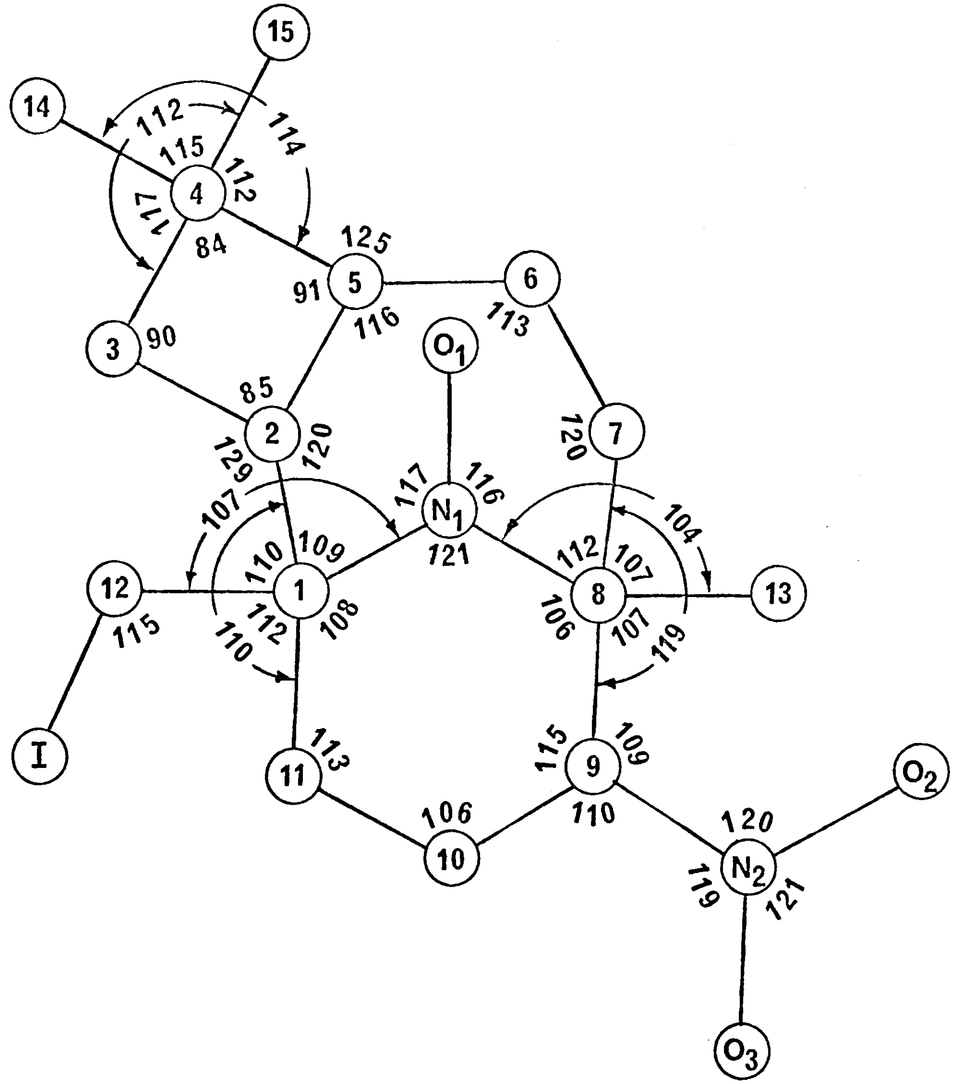
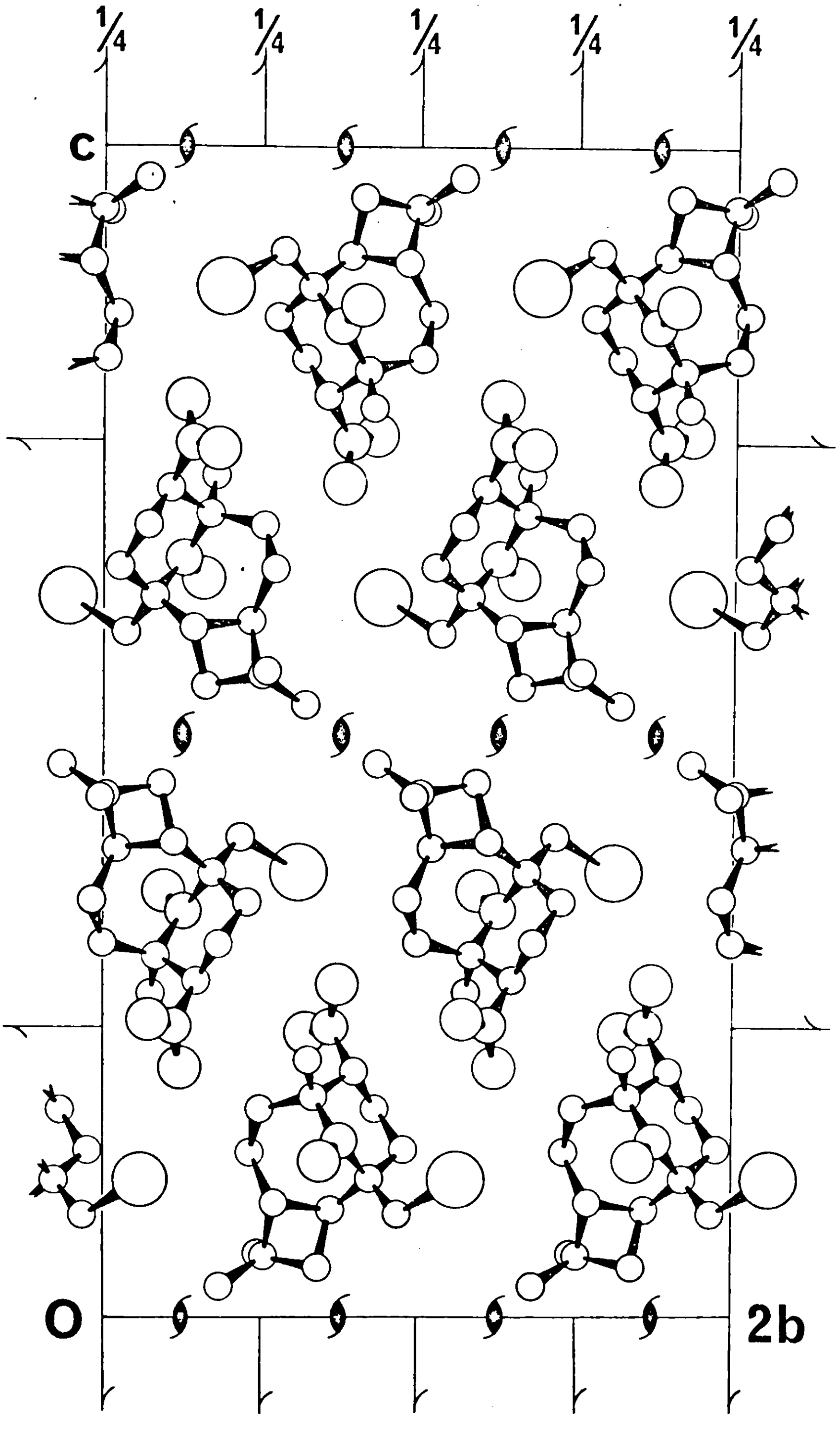

15
14
112
114
115
112
117
4
84
125
5
91
6
113
116
O1
3
90
85
2
129
120
7
120
107
117
116
N1
104
110
109
121
112
107
12
1
8
13
115
112
108
106
107
110
119
I
11
113
115
9
109
O2
106
110
120
10
N2
119
121
O3

Figure 1.5

A molecular-packing diagram viewed along the a axis.


1/4
1/4
1/4
1/4
1/4
c
O
2b

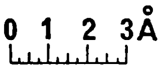

0 1 2 3Å

Figure 1.6

A stereoscopic view of a molecule of caryophyllene iodonitrosite. The oxygen atoms are hatched while the nitrogen atoms are cross hatched.

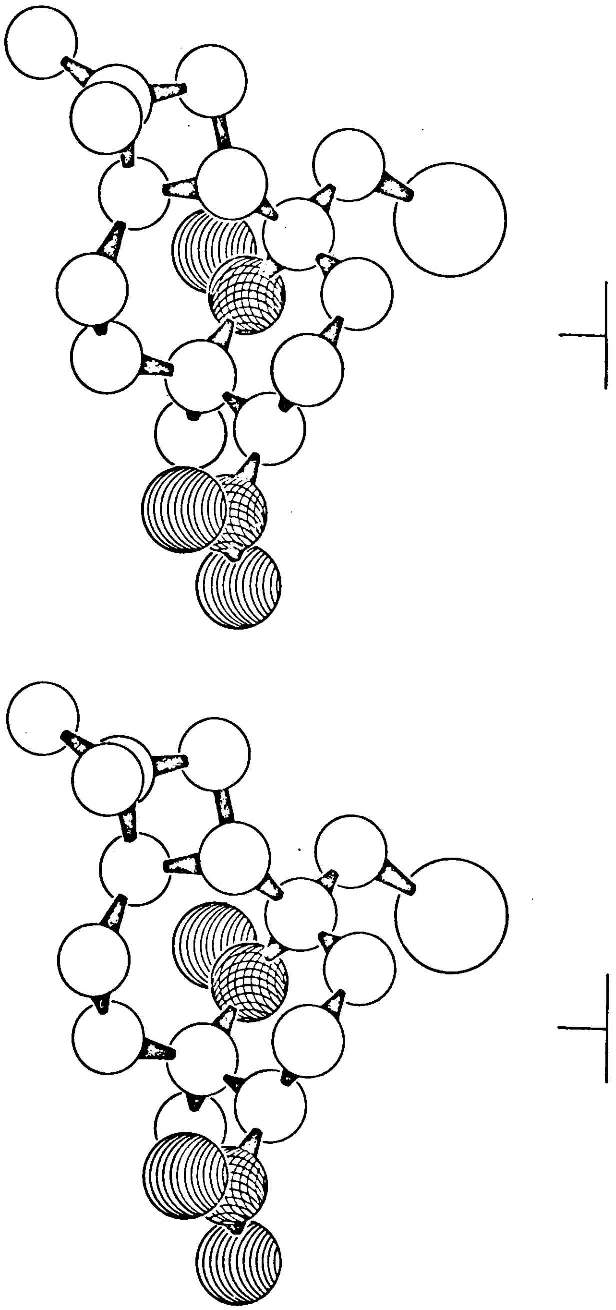
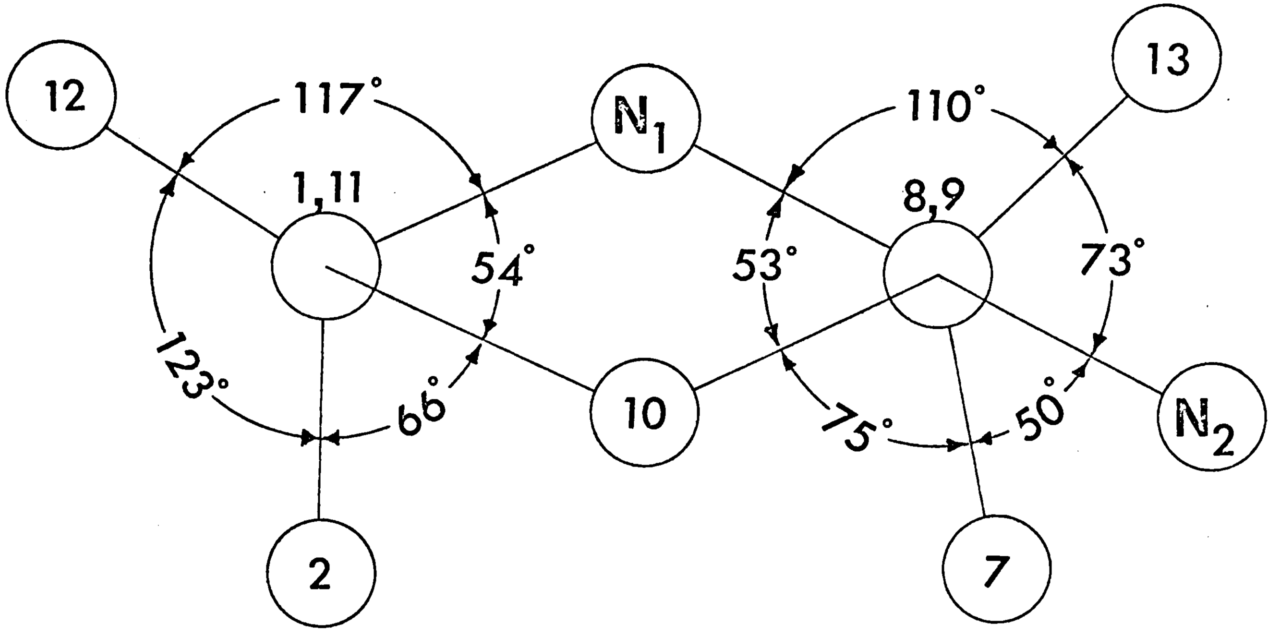


Figure 1.7

A Newman projection along the C(11)-C(1) and C(9)-C(8) bonds showing the torsional angles about these bonds.

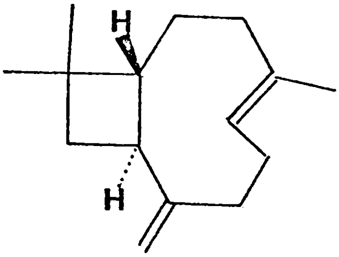

12
117°
1,11
N$_1$
110°
13
8,9
54°
53°
73°
123°
66°
10
75°
50°
N$_2$
2
7

1.3 DISCUSSION.

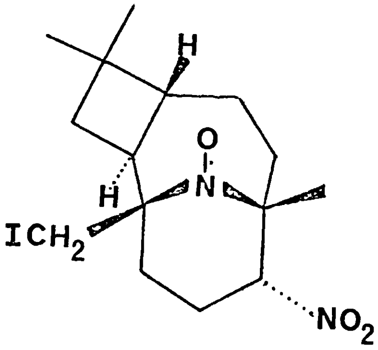
The X-ray analysis has established that caryophyllene 'iodonitrosite' has the structure and absolute stereochemistry shown in (V), from which it follows that the absolute stereochemistry of caryophyllene itself must be (I) as deduced earlier by Barton and Nickon (1954). Moreover on the basis of this crystallographic analysis and spectroscopic and chemical (Roberts, 1967) evidence, structure (VI) is inferred for the parent caryophyllene nitrosite. A mechanism for the formation of the nitroxide radical has been formulated (Hawley, Roberts, Ferguson, and Porte, 1967) and involves the addition of $I^{\cdot}$ to the exo-methylene group in (VI) thus forming a tertiary alkyl radical which then undergoes transannular addition to the nitroso group, generating the nitroxide radical.

Caryophyllene 'iodonitrosite' is tricyclic with a cyclobutane ring <u>trans</u>-fused to a seven-membered ring which is in turn <u>cis</u>-bridged to a six-membered ring. The molecular structure and overall stereochemistry are clearly illustrated in Figure 1.6, a stereoscopic view of the molecule.

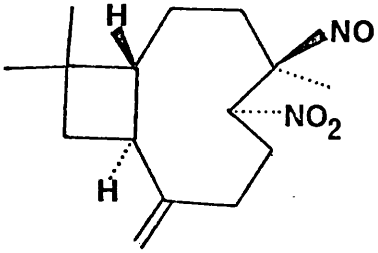
Perhaps the most interesting feature associated with caryophyllene 'iodonitrosite' is the fact that it is a



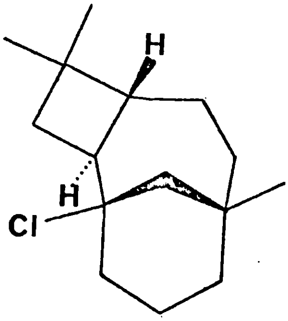
I



V



VI



VII

stable free radical. Although aromatic nitroxide radicals were known prior to 1961, they contained groups attached to the nitrogen, capable of delocalising the odd electron, thus imparting a high degree of stability to these compounds The stability of aliphatic nitroxide radicals such as di-t-butylnitroxide and caryophyllene 'iodonitrosite' cannot however be ascribed to electron delocalisation over a conjugated system. The explanation lies in the intrinsic stability of an N-O three electron bond (Linnett, 1961). Hoffmann and Henderson (1961) have suggested that additional stabilisation in many of these radicals is afforded by steric inhibition of N-N and N-O bond formation, thus preventing the formation of a dimer.

The N-O bond length of 1.308 Å agrees well with that of 1.28 ± 0.02 Å found in an electron diffraction study of di-t-butylnitroxide (Andersen and Andersen, 1966), but it is somewhat elongated in comparison with the values of 1.26 Å and 1.23 Å observed in 2,2,6,6-tetramethylpiperidin-4-ol-1-oxide (Lajzérowicz-Bonneteau, 1968) and di-p-anisyl nitroxide (Hanson, 1953) respectively. Pauling (1960) quotes 1.44 Å and 1.20 Å for the normal N-O single and double bond lengths, hence a value of 1.308 Å seems a very reasonable length for a three-electron N-O bond. The oxygen atom deviates from the plane defined by atoms C(1), N(1), and C(8) by 0.53 Å which corresponds to an angle of 24° between the N-O bond and the CNC plane. A similar feature has been observed in tetramethylpiperidinol-oxide, but in di-t-butylnitroxide, Andersen and Andersen found no evidence to suggest that the N-O and N-C bonds were not coplanar. The C(1)N(1)C(8) bond angle (121°) in caryophyllene 'iodonitrosite' is considerably smaller than the corresponding angle of 136° in di-t-butylnitroxide. This discrepancy probably results from the constraint placed on these atoms by their inclusion in both six- and seven-membered ring systems.

Turning to the conformational aspects of the 'iodonitrosite' we find that the cyclobutane ring is severely puckered with each atom alternately above and below the mean plane through the four ring atoms. The perpendicular distance between the diagonals of the cyclobutane ring is 0.33 Å, somewhat greater than the corresponding distance of 0.25 Å observed in caryophyllene chlorohydrin (Rogers and Mazhar-ul-Haque, 1963). The dihedral angle between the plane through C(2), C(4), and C(3) and that defined by C(2), C(4), and C(5) is 145° which is consistent with ring dihedral angles of 149° in cis-cyclobutane-1,3-dicarboxylic acid (Adman and Margulis, 1967), and 150° and 153° in *cis*- and *trans*-1,2-dibromo-1,2-dimethoxycarbonylcyclobutane (Karle, Karle and Britts, 1966). The conformation of the highly strained cyclobutane ring in organic compounds is of considerable interest but it has, only recently, been seriously investigated by X-ray diffraction methods. Greenberg and Post (1968) have surveyed a number of crystallographic studies of compounds containing cyclobutane rings and it appears that the cyclobutane ring is buckled in some cases and planar (e.g. tetra-phenylcyclobutane (Dunitz, 1949; Margulis, 1965)) in others; there seems to be no clear-cut conditions favouring one conformation over the other.

The seven-membered ring adopts a chair conformation in which N(1), C(8), C(5), and C(6) are planar; carbon atoms 7, 1, and 2 are displaced by + 0.54, -1.16 and -1.13 Å respectively from this plane. This ring conformation is in contrast to that found in caryolanyl chloride (VII) (Robertson and Todd, 1955) in which a boat arrangement is favoured, although these compounds have basically the same skeleton apart from the nitroxide group. An examination of a Dreiding model reveals that the steric interaction between O(1) and the hydrogen attached to C(5) is only increased if the seven-membered ring in caryophyllene 'iodonitrosite' adopts a boat conformation, and this presumably accounts for the apparent discrepancy. The valence angles in the ring are, with one exception, significantly larger than the tetrahedral angle (the mean value is 116°) and the inherent ring flattening further diminishes the repulsion between O(1) and the C(5) hydrogen. X-ray studies have disclosed flattened seven-membered rings in a number of compounds which include isoclovene hydrochloride (Clunie and Robertson, 1961), isophotosantonic lactone (Asher and Sim, 1965) and a taxadiene-tetraol derivative (Bjåmer, Ferguson, and Robertson, 1967) where the mean valence angles in the ring are 116.5°, 115°, and 115.7° respectively.

The fusion of the cyclobutane and the seven-membered rings has resulted in appreciable strain which is reflected in the considerable increase, from the tetrahedral value, in the exocyclic angles, C(1)C(2)C(3) (129°) and C(4)C(5)C(6) (125°), at the rings' junction. The torsional strain about the C(1)-C(2) bond and the C(3)...C(12) steric interaction obviously play a large part in increasing the C(1)C(2)C(3) angle. The C(2)-C(3) and C(1)-C(12) bonds are almost fully eclipsed (the torsional angle C(3)C(2)-C(1)C(12) is 2°) and consequently the C(3)...C(12) non-bonded separation of 3.05 Å is significantly greater than the theoretica value of 2.57 Å in which a fully eclipsed situation is assumed. The C(5)-C(6) and C(4)-C(15) bonds, on the other hand, are only partially eclipsed, the torsional angle C(15)C(4)-C(5)C(6) being 36°. The strain is thus relieved by a proportionately smaller increase in the C(4)C(5)C(6) angle.

The six-membered ring assumes a chair conformation with C(1), C(11), C(8), and C(9) in a planar arrangement, and N(1) and C(10) are displaced from this plane in opposite directions. Carbon atoms 2 and 7 occupy axial positions of the six-membered ring and are bent away from each other in order to accommodate the seven-membered ring in its chair form. In an idealised situation the C(2)...C(7 non-bonded distance would have been identical to the C(1)...C(8) distance of 2.61 Å but here it has been increased to 3.29 Å. An examination of Figure 1.7 reveals that C(7) is displaced from its true axial position much more than is C(2) since the torsion angle C(10)C(9)-C(8)C(9) is 9° greater than the torsion angle C(10)C(11)-C(1)C(2). The steric interaction between the nitro-group and C(7) (the C(7)...N(2) and C(7)...O(2) non-bonded distances are 3.00 and 3.08 Å respectively) is diminished by the increase in the C(7)C(8)C(9) bond angle from the normal tetrahedral value to 119°.

The bond lengths observed in caryophyllene 'iodo-nitrosite' do not deviate significantly from accepted values. The C(sp^3)-C(sp^3) bond lengths vary from 1.499 to 1.610 Å with a mean value of 1.533 Å which is in reasonable agreement with the value of 1.545 Å found in diamond (Lonsdale, 1947). The average C-N single bond length of 1.495 Å is close to the value, 1.51 Å, observed by Andersen and Andersen (1966) in di-t-butylnitroxide.

The atoms which constitute the nitro-group and C(9) are planar within experimental error and the mean N-O bond length of 1.209 Å compares favourably with the value 1.216 Å found in p-nitro-benzoic acid (Sakore and Pant, 1966).

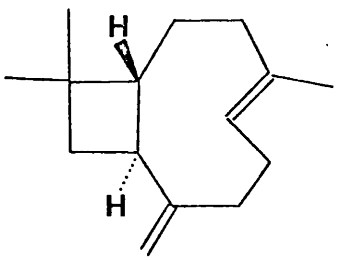
All the intermolecular distances less than 4.0 Å were calculated and three of the oxygen-carbon contacts were found to be shorter than the oxygen-carbon van der Waals distance of 3.4 Å (Pauling, 1960). It is unlikely, however, that there is any C-H...O hydrogen bonding since none of the hydrogen atoms attached to the carbons in these short contacts is activated.

THE CRYSTAL STRUCTURE AND ABSOLUTE STEREOCHEMISTRY OF THE MONO-p-BROMOBENZENESULPHONYL ESTER OF PSEUDOCLOVENE-A DIOL.

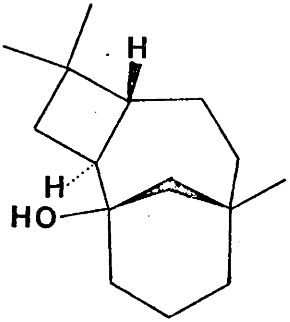
2.1 INTRODUCTION.

When caryophyllene (I) is treated with concentrated sulphuric acid in ether, a mixture of three products (Parker, Raphael, and Roberts, 1965) is produced, one of which, caryolan-1-ol (II), has been reported (Lutz and Reid, 1954; Henderson, McCrone, and Robertson, 1929) to yield pseudoclovene and isoclovene (III) on dehydration with phosphorus pentoxide. Although the complete structure of isoclovene has been established by an X-ray crystallographic analysis of the corresponding hydrochloride (Clunie and Robertson, 1961), little evidence has been produced to support the proposed structure for pseudoclovene (VIII).

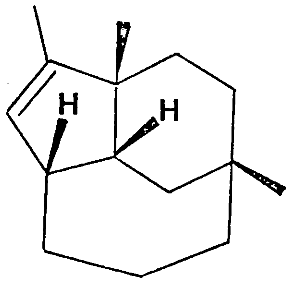
Recent work (McKillop, 1968) has shown that treatment of (II) with polyphosphoric acid yields a complex mixture mixture of at least ten hydrocarbons, pseudo- and isoclovene being the main components. An extensive g.l.c. examination of the pseudoclovene fraction revealed that it was a two component mixture. One of the components, labelled pseudoclovene-A, was isolated pure and from infra-red and



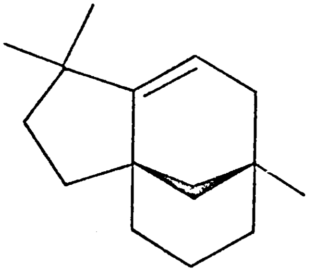
I



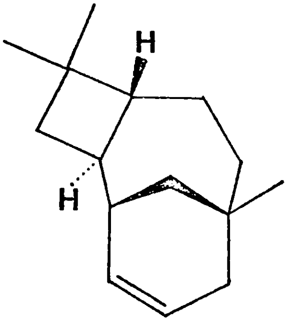
II



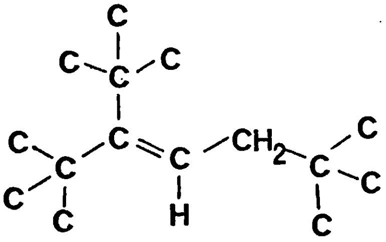
III



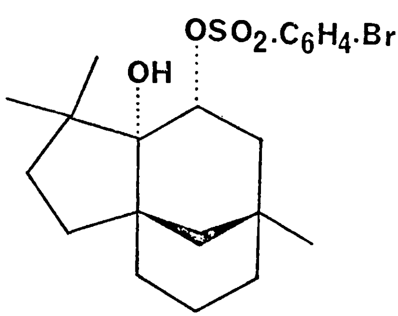
IV



VIII



IX



X

proton magnetic resonance spectra only a partial structure (IX) could be formulated, but this was enough to discount (VIII) as a structural possibility for pseudoclovene-A. Crystals of the mono-p-bromobenzenesulphonate ester of pseudoclovene-A diol were prepared and a three-dimensional X-ray analysis of this derivative (Ferguson et.al., 1967) shows it to have the structure and absolute stereochemistry shown in (X). From this it has been inferred that (IV) represents the structure and absolute stereochemistry of the parent hydrocarbon, pseudoclovene-A.

Although the analysis of the pseudoclovene-A derivative was undertaken primarily to determine the gross molecular structure, the results are of a sufficient accuracy to allow for a fairly detailed discussion of the geometry of the molecule.

2.2 EXPERIMENTAL.

Crystal Data.

Pseudoclovene-A diol mono-p-bromobenzenesulphonate,

$C_{21}H_{29}O_4SBr$, M = 457.5. Monoclinic,

$a = 9.97 \pm 0.02$, $b = 21.41 \pm 0.03$, $c = 9.97 \pm 0.02$ Å,

$\beta = 90.0 \pm 0.2°$. $U = 2128$ Å^3, $D_m = 1.42$ (by flotation),

$Z = 4$, $D_c = 1.43$. F(000) = 952. Space group $P2_1$ (C_2^2, No. 4).

Linear absorption coefficient for X-rays ($\lambda = 1.542$ Å),

$\mu = 39.7$ cm^{-1}.

Recrystallisation from petroleum ether afforded well-formed, clear coloured prisms elongated along b.

Crystallographic Measurements.

The unit cell parameters were derived from oscillation and Weissenberg photographs obtained from crystals rotated about a and b, using Cu-Kα radiation ($\lambda = 1.542$ Å), and from precession photographs taken with Mo-Kα radiation ($\lambda = 0.7107$ Å). The systematic absences (0k0 only present if k = 4n), cell dimensions, and the number of molecules in the unit cell originally led us to believe that the crystals were tetragonal, space group $P4_1$ or $P4_3$. The $1k\ell$ Weissenberg photograph, however, on detailed examination, revealed some significant differences in intensity between $1k\ell$ and $1k\bar{\ell}$ reflexions which were too large to be caused by anomalous dispersion effects. Hence the crystals must therefore be monoclinic, space group $P2_1$, but masquerading to a large extent as tetragonal. The alternative possibility of the space group, viz. $P2_1/m$ was ruled out in view of the optically active nature of the compound.

For the intensity measurements a small crystal (0.3 x 0.2 x 0.2 mm^3) was used, completely bathed in a uniform X-ray beam; absorption corrections were neglected. The intensity data, consisting of the reciprocal lattice nets $0k\ell$ - $8k\ell$ were collected by means of equi-inclination, multiple-film, Weissenberg exposures (Robertson, 1943) taken with Cu-$K\alpha$ radiation. Two independent estimations of the intensities of 3072 reflexions were made, by visual comparison with a calibrated step wedge. By comparing the time of exposure for each set of Weissenberg films the intensity data (averaged over the two estimations) were placed on approximately the same scale and corrected for

Lorentz, polarisation and the rotation factors (Tunnel, 1939) appropriate to the upper layers. The absolute scale was obtained at a later stage by correlation of the measured structure amplitudes with the calculated values. Unobserved reflexions were not included in any of the calculations.

Structure Determination.

In the space group $P2_1$ the equivalent positions, (x,y,z) and $(-x,\frac{1}{2}+y,-z)$, are such that an atom situated in a general position will give rise to a vector peak of double weight at $(2x, \frac{1}{2}, 2z)$ in the Patterson distribution. The data were sharpened to point atom at rest with respect to bromine and used to compute the three-dimensional Patterson function, from which it was evident that the four molecules in the unit cell, or at least their heavy atoms were closely related by a pseudo four-fold screw axis. In addition to vector peaks appearing on the true Harker section at $v = \frac{1}{2}$, other correlating peaks lay on or near the sections at $v = 0$ and $\frac{1}{4}$. These sections of the three-dimensional Patterson distribution are shown in Figure 2.1.

Since there are two types of heavy atoms present and two molecules in each asymmetric unit, we expect the vector peaks to belong to one of five different classes which have been designated A, A', B, B', and C in Figure 2.1. There are those peaks (A) arising from the bromine atoms in symmetry related positions and those (B) arising from non-symmetry related atoms. A similar situation prevails with the sulphur atoms although it was found that these peaks (A' and B') were coincident with the Br...Br vectors. The other type of vector peak viz. C results from an interaction between bromine and sulphur atoms. A set of coordinates for the four heavy atoms, consistent with the maxima in the Patterson distribution, were determined; the y coordinate of one of the bromine atoms was arbitrarily chosen as zero since the space group is a polar one.

The structure analysis was continued by the heavy atom method of phase determination (Robertson and Woodward, 1940) and in the first Fourier synthesis the structure factors were weighted in order to reduce phase-angle errors (Sim, 1961). The atoms constituting molecule 2 in the asymmetric unit were clearly revealed in the ensuing electron-density distribution, but the other molecule was not well resolved apart from the p-bromobenzene sulphonate moiety. A further round of structure-factor and Fourier calculations however provided coordinates for all 54 non-hydrogen atoms in the asymmetric unit. Another two cycles of Fourier refinement led to improved coordinates for these atoms and the R-factor was reduced to 0.25.

Structure Refinement.

Thirteen cycles of least-squares calculations followed and a block-diagonal approximation to the least-squares matrix was used throughout. During the first seven cycles positional and isotropic thermal parameters were refined, but thereafter the anisotropic vibration of the atoms was taken into account. Before commencing the anisotropic refinement the data were placed on a common scale using the layer-scale factors obtained at the end of the isotropic refinement. The weighting scheme used in the refinement was of the form,

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

The parameters p_1, p_2, and p_3 were varied in order to maintain constant averages of $w\Delta^2$ for reflexions batched according to $|F_o|$ and $\sin\theta/\lambda$; the final values of p_1, p_2, and p_3 were 20, 0.0001, and 0.0008 respectively. At convergence, when the shifts in the coordinates were all less than one fifth of the estimated standard deviations, R was 0.087. The shifts in the scale factor and thermal parameters were also insignificant. The progress of the refinement is outlined in Table 2.1 while the agreement between the observed and final calculated structure amplitudes can be seen in Table 2.2. The atomic scattering factors used in all the structure-factor calculations were those taken from "International Tables for X-ray Crystallography", Vol.III.

A composite view of the final electron-density distribution over molecule 1 is shown in Figure 2.2 together with a diagram illustrating the corresponding atomic arrangement and numbering scheme adopted in the analysis. A three-dimensional difference synthesis phased on the final atomic parameters revealed no errors in the structure.

Table 2.3 contains the final values of the fractional coordinates with their e.s.d.s. The anisotropic thermal parameters in Table 2.4 are values of U_{ij} in the expression,

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{23}k\ell b^*c^* + 2U_{31}\ell hc^*a^* + 2U_{12}hka^*b^*)] .$$

Bonded distances and valence angles in both molecules are shown in Figures 2.3 and 2.4 respectively. The average values of bond lengths and angles over the two molecules in the asymmetric unit are presented in Table 2.5, along with their e.s.d.s in parentheses. Some intramolecular non-bonded distances and all intermolecular contacts <3.8 Å are listed in Table 2.6. Table 2.7 contains the displacements of atoms from various planes through portions of the molecular framework and the equations of these planes. The contents of the unit cell when viewed along the a axis are illustrated in Figure 2.5.

Absolute Configuration.

The absolute configuration of the mono-p-bromobenzenesulphonyl ester of pseudoclovene-A diol was determined by the anomalous dispersion method (Bijvoet, 1949). Values of $\Delta f'$ and $\Delta f''$ for sulphur and bromine were taken from "International Tables for X-ray Crystallography", Vol.III. The intensities of 28 Bijvoet pairs ($hk\ell$ and $h\bar{k}\ell$) were estimated visually from equi-inclination Weissenberg photographs taken with Cu-Kα radiation. With the anomalous-dispersion corrections included, structure factors were calculated and the ratios $I_o(hk\ell)/I_o(h\bar{k}\ell)$ and $F_c^2(hk\ell)/F_c^2(h\bar{k}\ell)$ determined. The results are presented in Table 2.8 and show that for each Bijvoet pair, the ratios of intensities and of the squares of the calculated structure factors, are either both greater or both smaller than unity with the exception of two pairs of reflexions which are marked by an asterisk. It follows, therefore, that structure (X) and Figure 2.2 correctly represent the absolute stereochemistry of the mono-p-bromobenzenesulphonyl ester of pseudoclovene-A diol.

Table 2.1

Progress of Refinement.

Parameters refined	Cycle No.	Final R	Final $\Sigma w\Delta^2 \times 10^{-3}$	Final R′
x,y,z,Uiso for all non-hydrogen atoms; layer-scale factors; block diagonal.	1-7	0.179	39.5	0.048
x,y,z,Uij(i,j=1,2,3) for all non-hydrogen atoms; one scale-factor;block diagonal.	8-11	0.087	7.4	0.012

Table 2.2

Observed and final calculated values of the structure amplitudes.

H	K	L	Fo	Fc
1	0	-12	7.4	6.0
1	1	-12	6.5	5.9
1	2	-12	5.4	5.9
1	3	-12	6.0	5.3
1	4	-12	3.6	2.9
1	5	-12	7.3	6.6
1	6	-12	6.4	7.0
1	9	-12	3.8	3.9
2	0	-12	11.1	10.5
2	1	-12	11.7	12.4
2	2	-12	9.6	8.9
2	3	-12	11.4	10.6
2	4	-12	8.3	8.2
2	5	-12	5.9	6.7
2	6	-12	4.6	3.5
2	7	-12	4.9	5.0
2	8	-12	5.7	6.4
3	0	-12	4.9	4.5
3	1	-12	3.8	3.6
3	2	-12	7.1	7.4
3	3	-12	2.6	3.7
3	4	-12	4.7	5.2
3	5	-12	4.2	4.5
3	6	-12	7.7	8.6
1	0	-11	13.8	12.3
1	1	-11	10.6	14.6
1	2	-11	10.9	10.8
1	3	-11	15.7	12.8
1	4	-11	11.2	10.7
1	5	-11	15.2	14.2
1	6	-11	14.0	13.4
1	7	-11	9.0	7.8
1	8	-11	6.1	7.0
1	9	-11	13.9	13.3
1	10	-11	13.9	13.5
1	13	-11	9.2	9.2
2	0	-11	19.5	19.8
2	1	-11	12.4	12.6
2	2	-11	3.4	3.9
2	3	-11	18.3	17.6
2	4	-11	18.7	15.8
2	5	-11	11.4	11.4
2	6	-11	3.1	4.1
2	7	-11	14.5	14.4
2	8	-11	11.9	10.9
2	9	-11	12.5	13.1
2	10	-11	6.4	5.9
2	11	-11	9.5	9.1
2	12	-11	5.9	5.7
2	13	-11	7.7	9.2
3	0	-11	8.9	8.3
3	1	-11	10.4	10.7
3	2	-11	11.3	10.6
3	3	-11	4.9	5.0
3	4	-11	11.0	11.1
3	5	-11	13.9	12.6
3	6	-11	10.5	14.4
3	8	-11	11.9	11.7
3	9	-11	9.1	8.9
3	10	-11	9.8	9.9
4	3	-11	11.8	11.6
4	4	-11	8.4	7.4
4	5	-11	7.1	7.1
4	6	-11	9.9	10.4
4	7	-11	9.5	9.5
4	9	-11	6.8	7.8
4	10	-11	8.6	10.0
5	5	-11	8.3	9.3
5	6	-11	6.9	6.1
5	7	-11	4.9	4.2
1	0	-10	4.2	4.1
1	1	-10	12.0	12.8
1	2	-10	7.0	7.5
1	3	-10	11.1	12.0
1	5	-10	8.3	8.6
1	6	-10	8.9	8.8
1	7	-10	8.6	10.3
1	9	-10	6.1	5.9
1	10	-10	5.9	6.6
1	11	-10	5.7	6.4
1	13	-10	4.3	4.8
1	14	-10	3.6	4.9
2	0	-10	7.3	7.6
2	1	-10	14.2	15.3
2	2	-10	15.2	16.4
2	3	-10	13.9	15.5
2	4	-10	8.1	8.8
2	5	-10	8.0	9.0
2	6	-10	9.1	8.0
2	7	-10	5.5	4.8
2	8	-10	7.4	7.8
2	9	-10	6.5	6.5
2	10	-10	3.8	4.2
2	13	-10	9.7	9.2
2	14	-10	4.0	4.7
2	15	-10	4.1	3.4
3	0	-10	12.7	12.7
3	1	-10	11.6	13.4
3	3	-10	14.0	14.2
3	4	-10	7.9	8.3
3	5	-10	7.1	8.9
3	7	-10	7.8	7.8
3	9	-10	6.0	7.8
3	10	-10	4.1	4.1
3	12	-10	4.0	5.9
3	13	-10	3.9	4.7
3	15	-10	3.9	4.0
3	16	-10	2.8	5.2
4	0	-10	13.9	15.4
4	2	-10	11.7	11.2
4	3	-10	4.2	4.5
4	4	-10	7.3	8.5
4	5	-10	5.1	6.9
4	6	-10	10.7	11.4
4	8	-10	3.8	4.7
4	9	-10	5.2	5.8
4	10	-10	6.6	8.2
4	12	-10	4.9	6.6
4	13	-10	4.0	4.9
5	0	-10	7.1	8.8
5	1	-10	13.3	14.4
5	3	-10	13.1	14.2
5	4	-10	4.4	6.8
5	5	-10	13.3	12.8
5	6	-10	3.8	3.4
5	7	-10	11.7	12.2
5	8	-10	6.9	7.6
5	9	-10	6.4	7.9
5	11	-10	7.5	8.3
5	12	-10	3.7	5.0
5	13	-10	3.8	4.8
6	2	-10	5.7	10.6
6	4	-10	13.7	17.1
6	6	-10	4.0	6.5
6	8	-10	6.5	11.6
6	10	-10	5.9	7.9
1	0	-9	21.0	19.0
1	1	-9	6.9	7.6
1	2	-9	15.5	16.6
1	4	-9	25.4	26.5
1	5	-9	5.8	6.3
1	6	-9	19.0	20.3
1	8	-9	21.4	21.6
1	9	-9	9.1	9.5
1	10	-9	11.9	11.8
1	12	-9	10.2	11.3
1	13	-9	3.3	3.9
1	14	-9	5.2	6.2
1	15	-9	8.2	8.1
1	16	-9	8.1	8.5
2	0	-9	4.5	4.0
2	1	-9	14.3	14.9
2	2	-9	27.3	29.1
2	3	-9	22.3	23.1
2	5	-9	12.7	11.9
2	6	-9	16.3	16.9
2	7	-9	18.5	19.7
2	8	-9	4.0	4.1
2	9	-9	18.5	20.7
2	10	-9	9.4	8.2
2	11	-9	5.9	6.4
2	12	-9	5.1	6.1
2	13	-9	12.3	14.9
2	14	-9	5.5	6.4
2	15	-9	4.7	3.9
2	16	-9	6.7	6.1
2	17	-9	3.4	4.7
2	18	-9	4.0	4.0
3	0	-9	10.6	9.8
3	1	-9	8.8	6.5
3	2	-9	12.5	13.3
3	3	-9	11.4	11.7
3	4	-9	19.2	21.6
3	5	-9	5.4	4.4
3	6	-9	8.2	9.5
3	7	-9	11.9	12.8
3	8	-9	22.6	25.4
3	9	-9	6.0	6.6
3	10	-9	8.2	8.5
3	11	-9	7.3	5.3
3	12	-9	13.1	14.9
3	14	-9	6.4	5.7
3	15	-9	7.5	7.3
4	0	-9	10.4	10.4
4	1	-9	15.5	16.4
4	2	-9	14.0	13.4
4	3	-9	6.6	7.6
4	4	-9	8.0	8.1
4	5	-9	17.2	17.9
4	6	-9	16.8	19.1
4	7	-9	6.0	5.8
4	8	-9	6.3	5.8
4	9	-9	12.3	13.9
4	10	-9	13.3	14.3
4	12	-9	3.9	6.2
4	13	-9	3.7	5.4
4	14	-9	6.7	7.3
5	0	-9	10.3	9.5
5	1	-9	13.0	14.0
5	3	-9	16.5	18.4
5	4	-9	9.9	10.5
5	5	-9	12.7	14.1
5	6	-9	7.3	8.1
5	7	-9	15.7	15.7
5	8	-9	6.7	9.1
5	9	-9	11.4	12.5
5	10	-9	5.7	5.9
5	11	-9	7.2	6.2
5	12	-9	5.1	6.2
5	13	-9	4.5	4.0
5	14	-9	4.7	5.6
6	0	-9	8.5	9.2
6	1	-9	8.9	7.3
6	4	-9	5.0	9.2
6	5	-9	9.9	9.6
6	7	-9	4.8	4.4
6	8	-9	6.9	7.6
6	9	-9	7.4	8.9
6	12	-9	6.2	7.3
6	13	-9	5.0	6.9
7	2	-9	5.1	3.1
7	3	-9	5.4	4.5
7	4	-9	4.0	2.8
7	6	-9	5.5	6.7
7	7	-9	4.6	5.1
7	9	-9	4.3	6.5
7	10	-9	5.0	6.7
7	12	-9	2.9	5.4
8	5	-9	6.7	7.8
8	7	-9	4.4	4.0
1	0	-8	54.9	54.2
1	1	-8	25.2	23.4
1	2	-8	14.0	14.8
1	3	-8	15.6	13.2
1	4	-8	42.0	42.0
1	5	-8	19.2	20.3
1	6	-8	13.0	12.7
1	7	-8	5.3	5.1
1	8	-8	26.0	25.6
1	9	-8	10.7	10.0
1	10	-8	7.6	8.0
1	11	-8	6.2	5.4
1	12	-8	17.0	16.9
1	13	-8	10.3	12.1
1	14	-8	5.0	4.3
1	15	-8	5.3	4.8
1	16	-8	10.1	10.9
1	17	-8	3.6	4.0
1	19	-8	5.4	4.7
1	20	-8	6.1	7.0
1	21	-8	5.9	6.5
2	0	-8	16.4	15.8
2	1	-8	15.0	17.3
2	2	-8	24.1	21.5
2	3	-8	25.0	25.7
2	4	-8	10.9	12.1
2	5	-8	12.3	14.3
2	6	-8	9.8	9.6
2	7	-8	15.3	20.2
2	8	-8	6.7	6.7
2	9	-8	10.7	11.5
2	10	-8	11.4	11.8
2	12	-8	6.8	6.8
2	13	-8	8.2	8.2
2	14	-8	12.5	13.4
2	17	-8	3.9	4.9
2	18	-8	11.3	11.9
3	0	-8	29.4	29.3
3	1	-8	30.1	30.2
3	2	-8	27.5	28.2
3	3	-8	26.8	25.1
3	4	-8	25.0	24.8
3	5	-8	22.2	23.6
3	6	-8	11.8	10.1
3	7	-8	12.5	15.4
3	8	-8	17.2	15.2
3	9	-8	17.4	18.3
3	10	-8	6.5	5.4
3	11	-8	5.8	5.5
3	12	-8	12.0	12.6
3	13	-8	9.6	11.0
3	14	-8	6.0	7.1
3	15	-8	5.0	4.8
3	16	-8	4.8	5.1
3	17	-8	3.9	4.0
3	18	-8	4.1	4.1
3	19	-8	5.9	5.3
4	0	-8	14.1	13.8
4	2	-8	14.1	13.5
4	3	-8	10.5	9.8
4	4	-8	6.7	6.3
4	6	-8	10.0	11.6
4	7	-8	10.0	11.1
4	10	-8	7.3	6.1
4	15	-8	4.8	8.0
4	17	-8	3.7	5.6
5	0	-8	7.2	5.9
5	1	-8	10.1	10.9
5	2	-8	15.8	13.9
5	3	-8	5.3	7.8
5	4	-8	8.2	8.5
5	5	-8	10.6	11.1
5	6	-8	10.3	10.4
5	8	-8	5.7	7.5
5	9	-8	11.3	9.6
5	10	-8	9.3	9.3
5	13	-8	3.5	5.6
5	14	-8	4.7	7.1
5	15	-8	3.1	5.1
6	0	-8	15.6	13.2
6	1	-8	15.6	14.0
6	3	-8	10.3	9.5
6	4	-8	16.5	17.5
6	5	-8	16.7	17.5
6	7	-8	8.0	8.0
6	8	-8	12.3	12.3
6	9	-8	12.0	11.6
6	12	-8	4.6	4.5
6	13	-8	6.2	6.6
7	0	-8	8.1	8.0
7	1	-8	5.7	7.8
7	2	-8	10.9	12.7
7	3	-8	6.1	7.2
7	4	-8	8.9	8.4
7	5	-8	7.2	8.2
7	6	-8	7.1	9.4
7	7	-8	4.4	6.0
7	8	-8	6.1	6.8
7	9	-8	5.9	6.5
7	10	-8	6.0	7.3
7	11	-8	3.8	4.6
7	12	-8	5.0	5.5
7	13	-8	3.3	4.5
7	14	-8	3.6	4.3
8	0	-8	10.5	9.4
8	1	-8	9.2	10.1
8	2	-8	7.4	7.8
8	3	-8	4.5	4.9
8	4	-8	8.7	7.9
8	5	-8	12.1	13.8
8	6	-8	5.6	6.8
8	7	-8	6.4	7.0
8	8	-8	5.9	5.0
8	9	-8	6.2	7.6
1	0	-7	15.3	15.4
1	1	-7	44.2	42.3
1	3	-7	34.5	33.3
1	4	-7	14.1	11.4
1	5	-7	24.5	24.8
1	6	-7	20.0	20.7
1	7	-7	5.1	7.3
1	8	-7	11.5	12.1
1	9	-7	18.1	17.4
1	10	-7	18.6	17.4
1	11	-7	8.4	9.6
1	12	-7	11.2	12.2
1	13	-7	12.4	13.2
1	14	-7	4.3	4.5
1	15	-7	9.6	11.3
1	16	-7	3.6	4.4
1	17	-7	12.4	12.8
1	21	-7	4.1	4.9
2	0	-7	25.7	23.4
2	1	-7	15.2	15.4
2	2	-7	53.4	57.3
2	3	-7	13.8	15.1
2	4	-7	20.0	19.9
2	5	-7	9.6	10.3
2	6	-7	11.7	13.4
2	7	-7	16.2	16.6
2	8	-7	13.3	11.4
2	9	-7	5.6	5.9
2	10	-7	6.3	9.5
2	11	-7	8.6	9.1
2	13	-7	6.1	6.5
2	14	-7	15.2	16.8
2	16	-7	4.0	4.4
2	18	-7	8.4	9.5
2	19	-7	7.5	7.3
2	20	-7	3.8	4.6
3	0	-7	6.7	6.7
3	1	-7	21.4	17.9
3	2	-7	16.2	14.9
3	3	-7	12.0	13.5
3	4	-7	10.0	9.6
3	5	-7	19.0	21.2
3	6	-7	20.6	20.9
3	7	-7	17.7	16.6
3	8	-7	17.9	17.5
3	9	-7	17.5	19.2
3	10	-7	10.2	10.7
3	11	-7	6.9	8.6
3	12	-7	9.3	9.6
3	13	-7	4.6	5.0
3	16	-7	3.8	4.1
3	20	-7	5.6	4.9
4	0	-7	50.5	51.0
4	1	-7	21.2	21.4
4	2	-7	29.6	27.7
4	3	-7	9.6	10.6
4	4	-7	37.4	35.1
4	5	-7	16.1	19.8
4	6	-7	11.3	10.7
4	7	-7	4.0	2.8
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1	14	-3	11.2	12.3
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1	16	-3	27.4	26.6
1	17	-3	21.7	19.6
1	18	-3	12.4	13.2
1	20	-3	12.2	11.4
1	21	-3	5.8	5.2
2	0	-3	[illegible]	[illegible]
2	1	-3	20.7	19.5
2	2	-3	10.5	9.6
2	3	-3	45.2	43.4
2	4	-3	[illegible]	43.0
2	5	-3	22.0	21.1
2	6	-3	30.8	33.6
2	7	-3	33.7	27.4
2	8	-3	34.7	31.2
2	9	-3	16.7	15.2
2	10	-3	24.6	21.9
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2	12	-3	47.5	50.8
2	13	-3	15.8	16.4
2	15	-3	9.6	11.5
2	16	-3	[illegible]	20.2
2	17	-3	8.3	6.7
2	18	-3	6.4	7.4
2	19	-3	9.0	6.9
2	20	-3	14.2	14.7
2	22	-3	4.7	6.6
2	24	-3	4.7	4.3
3	0	-3	65.6	22.2
3	1	-3	[illegible]	[illegible]
3	2	-3	37.6	30.6
3	3	-3	44.9	41.3
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3	6	-3	34.0	33.0
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3	12	-3	3.6	3.0
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3	16	-3	6.5	7.3
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3	21	-3	5.4	5.2
3	22	-3	4.4	5.3
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4	1	-3	37.9	37.7
4	2	-3	23.7	23.7
4	3	-3	25.3	25.9
4	4	-3	27.2	25.0
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2	14	0	29.3	29.3
2	15	0	14.5	11.5
2	16	0	24.1	24.3
2	17	0	26.1	26.0
2	18	0	19.6	20.8
2	19	0	16.7	15.0
2	20	0	12.1	12.0
2	21	0	13.7	13.4
2	22	0	5.4	6.6
2	25	0	4.8	4.4
3	2	0	15.7	15.0
3	3	0	53.2	56.2
3	4	0	110.8	108.3
3	5	0	75.3	75.1
3	6	0	7.9	4.1
3	7	0	10.0	11.2
3	8	0	21.4	20.9
3	9	0	28.5	30.1
3	10	0	21.7	17.8
3	11	0	5.4	6.5
3	12	0	13.7	14.3
3	13	0	16.2	16.6
3	14	0	9.0	9.4
3	15	0	16.1	15.7
3	16	0	32.0	34.8
3	17	0	11.6	11.1
3	18	0	15.0	14.5
3	19	0	15.3	14.8
3	20	0	15.2	15.5
3	23	0	5.6	4.8
4	2	0	20.2	31.6
4	3	0	37.7	43.9
4	4	0	19.5	17.5
4	5	0	15.8	11.3
4	6	0	28.3	27.3
4	7	0	21.8	17.0
4	8	0	22.6	19.8
4	9	0	29.5	24.6
4	10	0	22.7	22.2
4	11	0	24.4	22.6
4	12	0	3.9	3.0
4	13	0	8.5	6.9
4	14	0	13.3	12.4
4	15	0	3.2	4.7
4	16	0	4.6	4.8
4	17	0	14.1	14.9
4	18	0	7.8	9.7
4	19	0	8.5	9.1
4	20	0	4.6	5.3
4	21	0	5.4	6.5
4	22	0	7.2	9.6
4	23	0	2.7	1.1
5	2	0	9.5	10.9
5	3	0	29.5	37.3
5	4	0	37.2	36.8
5	5	0	72.4	75.1
5	6	0	10.3	9.5
5	7	0	36.2	33.7
5	8	0	10.0	10.7
5	9	0	46.9	43.9
5	10	0	17.4	15.7
5	11	0	11.8	10.4
5	12	0	10.6	9.6
5	13	0	29.4	27.2
5	14	0	22.5	21.2
5	15	0	13.1	11.5
5	16	0	5.3	6.4
5	17	0	20.5	20.0
5	18	0	12.6	13.1
5	19	0	7.0	6.4
5	21	0	5.6	5.6
6	2	0	8.9	16.3
6	3	0	20.6	29.5
6	4	0	4.7	4.9
6	5	0	25.2	28.3
6	6	0	23.7	23.5
6	7	0	27.2	26.5
6	8	0	17.3	18.9
6	9	0	33.1	31.8
6	10	0	32.2	30.5
6	11	0	6.4	5.3
6	12	0	10.2	9.3
6	13	0	15.4	13.0
6	14	0	15.8	15.2
6	15	0	5.5	5.6
6	16	0	7.9	7.2
6	17	0	11.4	9.9
7	2	0	8.6	13.8
7	3	0	11.1	15.3
7	4	0	15.0	17.4
7	5	0	22.5	26.3
7	6	0	20.8	21.0
7	7	0	35.9	35.3
7	8	0	9.8	7.8
7	9	0	20.1	19.2
7	10	0	18.5	19.4
7	11	0	30.0	30.1
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7	13	0	7.5	6.8
7	14	0	11.3	12.1
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7	16	0	8.7	10.4
7	17	0	4.7	5.3
7	18	0	5.5	5.3
8	2	0	3.7	5.4
8	3	0	15.9	21.5
8	4	0	26.7	34.7
8	5	0	15.0	14.8
8	6	0	4.2	4.8
8	7	0	12.3	9.5
8	8	0	36.6	39.1
8	9	0	9.2	6.8
8	10	0	7.0	6.2
8	12	0	18.3	17.0
8	13	0	8.9	7.0
8	14	0	7.8	6.9
8	18	0	5.2	5.9
0	1	1	62.5	73.8
0	2	1	13.2	13.6
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0	4	1	63.3	66.2
0	5	1	76.7	71.9
0	6	1	34.2	35.7
0	7	1	30.0	25.5
0	8	1	20.1	23.4
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0	14	1	13.8	12.3
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0	17	1	33.0	31.5
0	18	1	13.4	12.7
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0	21	1	18.3	17.0
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1	9	1	48.6	49.8
1	10	1	62.1	56.9
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1	19	1	6.3	3.9
1	22	1	6.8	7.1
1	26	1	7.9	7.8
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2	2	1	27.4	28.1
2	3	1	75.1	87.7
2	4	1	43.9	40.9
2	5	1	29.9	35.9
2	6	1	65.6	65.6
2	7	1	59.1	62.2
2	8	1	12.1	12.5
2	9	1	11.3	12.7
2	10	1	71.5	59.0
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2	12	1	14.7	13.9
2	14	1	37.7	37.5
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2	17	1	14.2	13.2
2	18	1	16.7	14.2
2	19	1	9.8	7.8
2	20	1	15.7	14.8
2	21	1	6.3	4.9
2	22	1	5.6	5.0
2	24	1	6.2	6.6
2	26	1	4.1	4.7
3	0	1	50.3	66.1
3	2	1	46.2	52.3
3	3	1	40.6	51.7
3	4	1	66.3	73.7
3	5	1	43.4	52.0
3	6	1	28.8	28.0
3	7	1	21.7	20.4
3	8	1	47.5	54.2
3	9	1	12.8	13.4
3	10	1	20.0	14.7
3	11	1	18.7	17.1
3	12	1	31.9	33.0
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3	14	1	13.1	11.5
3	15	1	6.8	5.4
3	16	1	30.3	28.8
3	17	1	23.2	20.6
3	18	1	12.7	12.4
3	20	1	12.0	10.5
3	21	1	9.0	7.8
4	0	1	8.5	9.5
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4	2	1	34.4	40.1
4	3	1	87.7	101.3
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4	5	1	42.7	39.5
4	6	1	76.4	68.9
4	7	1	31.6	36.2
4	8	1	29.3	24.8
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4	11	1	9.2	6.3
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4	14	1	22.1	20.7
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4	18	1	8.2	8.8
4	19	1	3.3	3.5
4	20	1	6.9	6.0
4	21	1	10.3	11.0
4	23	1	3.3	2.2
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5	3	1	33.3	37.6
5	4	1	69.0	64.3
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5	8	1	41.0	37.8
5	9	1	33.5	31.5
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5	13	1	17.7	17.4
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5	16	1	19.5	19.4
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5	18	1	10.3	10.2
5	19	1	5.7	4.6
5	20	1	7.1	8.2
5	21	1	5.2	4.8
5	23	1	4.3	3.9
6	1	1	21.1	31.7
6	2	1	13.7	16.4
6	3	1	33.3	41.1
6	4	1	57.0	72.2
6	5	1	21.2	21.9
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6	8	1	51.5	53.3
6	9	1	16.9	10.8
6	10	1	12.4	11.0
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6	12	1	33.0	32.2
6	14	1	9.4	10.1
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6	18	1	8.1	6.9
6	20	1	4.9	4.2
7	0	1	10.1	12.4
7	1	1	25.7	35.7
7	2	1	3.3	3.6
7	3	1	22.6	29.0
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7	5	1	20.3	20.7
7	6	1	19.0	21.7
7	7	1	5.2	5.4
7	8	1	11.8	10.4
7	9	1	17.4	15.4
7	10	1	17.1	16.8
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7	12	1	12.4	10.3
7	13	1	12.7	11.4
7	15	1	9.7	10.2
7	17	1	11.0	11.0
8	0	1	30.7	39.7
8	1	1	13.5	19.7
8	2	1	9.0	11.3
8	3	1	11.1	10.0
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8	5	1	15.4	17.7
8	6	1	11.8	12.0
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8	8	1	24.6	22.9
8	9	1	15.7	15.0
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8	11	1	5.9	6.0
8	12	1	16.7	15.1
8	13	1	9.9	10.9
8	14	1	4.9	3.0
8	15	1	5.9	4.1
8	16	1	9.4	7.5
8	20	1	4.1	4.4
0	0	2	120.6	157.4
0	1	2	97.0	126.0
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0	3	2	82.0	83.4
0	4	2	80.3	99.4
0	5	2	53.5	57.4
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0	7	2	66.3	66.5
0	8	2	50.6	45.7
0	9	2	34.7	37.7
0	10	2	42.5	40.5
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0	12	2	51.1	48.6
0	13	2	26.0	23.3
0	14	2	32.2	30.4
0	15	2	16.9	13.0
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0	17	2	29.4	27.0
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0	19	2	18.0	16.1
0	20	2	14.4	13.2
0	21	2	16.2	14.2
0	22	2	7.8	7.8
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1	2	2	16.9	12.9
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1	4	2	95.6	116.9
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1	8	2	79.2	73.8
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1	13	2	4.0	5.3
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1	16	2	18.4	16.7
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1	19	2	4.8	3.4
1	20	2	10.4	9.6
1	21	2	6.6	6.9
1	22	2	10.0	10.9
1	26	2	2.8	3.3
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2	1	2	46.4	56.2
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2	4	2	15.4	15.2
2	5	2	68.9	76.4
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2	10	2	26.2	28.8
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3	1	2	19.8	21.0
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3	3	2	44.3	41.8
3	4	2	85.9	92.9
3	5	2	20.2	20.9
3	6	2	31.0	32.1
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3	9	2	17.3	16.2
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3	12	2	52.3	51.9
3	13	2	18.9	20.1
3	15	2	12.5	12.8
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0	2	3	23.3	16.3
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3	10	3	21.1	23.3
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4	12	3	11.6	10.9
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5	9	3	30.7	29.5
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5	12	3	6.3	4.3
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5	22	3	3.6	6.6
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H	K	L	Fo	Fc
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0	21	4	7.0	6.6
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0	12	5	10.0	9.0
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0	15	5	12.6	11.3
0	16	5	7.6	8.9
0	17	5	24.5	22.1
0	18	5	14.6	15.6
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2	1	12	12.1	10.2
2	2	12	9.2	9.0
2	3	12	11.2	9.7
2	4	12	3.5	2.9
2	5	12	7.4	7.1
2	6	12	8.1	7.2
2	7	12	4.8	4.0
2	8	12	5.0	4.5
3	0	12	9.1	7.3
3	1	12	9.3	9.6
3	2	12	16.0	13.5
3	3	12	8.9	7.3
3	4	12	9.4	9.3
3	5	12	8.7	5.3
3	6	12	9.3	8.4
3	7	12	3.2	3.5
4	0	12	5.4	6.9
4	1	12	5.9	11.7
4	3	12	5.9	9.1
4	4	12	5.2	6.9

Table 2.3

Fractional co-ordinates with e.s.d.s.

Molecule 1

	x/a	y/b	z/c
Br	0.23542± 21	0.00000± 0	-0.85570± 14
S	0.12167± 30	0.01567±15	-0.23035± 25
O(1)	0.1915 ± 8	0.0649 ± 4	-0.1747 ± 9
O(2)	0.1380 ± 10	-0.0459 ± 4	-0.1729 ± 8
O(3)	-0.0316 ± 7	0.0360 ± 4	-0.2234 ± 7
O(4)	-0.2782 ± 9	0.0743 ± 4	-0.1785 ± 10
C(1)	-0.3841 ± 14	-0.0266 ± 6	-0.2040 ± 14
C(2)	-0.4403 ± 12	-0.0543 ± 7	-0.0739 ± 14
C(3)	-0.3804 ± 15	-0.0165 ± 7	0.0361 ± 13
C(4)	-0.2311 ± 13	-0.0064 ± 6	-0.0065 ± 11
C(5)	-0.2561 ± 12	0.0086 ± 5	-0.1625 ± 12
C(6)	-0.1371 ± 12	-0.0077 ± 5	-0.2546 ± 10
C(7)	-0.1750 ± 14	-0.0028 ± 7	-0.4009 ± 12
C(8)	-0.2941 ± 14	-0.0475 ± 7	-0.4342 ± 13
C(9)	-0.4091 ± 18	-0.0076 ±10	-0.5010 ± 16
C(10)	-0.4615 ± 18	0.0398 ±10	-0.4067 ± 22
C(11)	-0.4906 ± 13	0.0149 ± 8	-0.2653 ± 15
C(12)	-0.3516 ± 14	-0.0763 ± 6	-0.3103 ± 13
C(13)	-0.1528 ± 13	-0.0656 ± 7	0.0134 ± 12
C(14)	-0.1666 ± 16	0.0446 ± 9	0.0709 ± 15

C(15)	-0.2481 ± 24	-0.0999 ±10	-0.5307 ± 17
C(16)	0.2019 ± 13	0.0028 ± 7	-0.6694 ± 10
C(17)	0.1994 ± 14	-0.0496 ± 7	-0.5996 ± 11
C(18)	0.1795 ± 14	-0.0479 ± 5	-0.4581 ± 11
C(19)	0.1583 ± 12	0.0096 ± 6	-0.4019 ± 9
C(20)	0.1585 ± 14	0.0644 ± 6	-0.4768 ± 13
C(21)	0.1823 ± 14	0.0599 ± 7	-0.6128 ± 14

Molecule 2

Br′	-0.85512± 18	0.25036±14	-0.23529± 20
S′	-0.23030± 30	0.26561±15	-0.12214± 23
O(1′)	-0.1710 ± 9	0.3159 ± 5	-0.1914 ± 8
O(2′)	-0.1729 ± 8	0.2040 ± 4	-0.1355 ± 8
O(3′)	-0.2253 ± 8	0.2866 ± 4	0.0297 ± 6
O(4′)	-0.1762 ± 12	0.3241 ± 4	0.2799 ± 8
C(1′)	-0.2059 ± 15	0.2236 ± 5	0.3846 ± 11
C(2′)	-0.0743 ± 18	0.1955 ± 7	0.4421 ± 13
C(3′)	0.0342 ± 15	0.2339 ± 6	0.3809 ± 13
C(4′)	-0.0087 ± 15	0.2450 ± 6	0.2334 ± 11
C(5′)	-0.1583 ± 13	0.2585 ± 5	0.2552 ± 9
C(6′)	-0.2534 ± 12	0.2418 ± 5	0.1402 ± 9
C(7′)	-0.4028 ± 15	0.2449 ± 7	0.1723 ± 12
C(8′)	-0.4348 ± 15	0.2038 ± 7	0.2947 ± 14

C(9')	-0.5045 ± 15	0.2418 ±10	0.4068 ± 14
C(10')	-0.4029 ± 20	0.2909 ± 9	0.4621 ± 15
C(11')	-0.2646 ± 16	0.2659 ± 8	0.4946 ± 11
C(12')	-0.3093 ± 14	0.1730 ± 6	0.3502 ± 13
C(13')	0.0149 ± 17	0.1834 ± 7	0.1557 ± 14
C(14')	0.0761 ± 19	0.2956 ± 8	0.1661 ± 17
C(15')	-0.5313 ± 20	0.1524 ±10	0.2501 ± 21
C(16')	-0.6616 ± 14	0.2538 ± 7	-0.2041 ± 11
C(17')	-0.5982 ± 14	0.2011 ± 7	-0.2029 ± 12
C(18')	-0.4597 ± 15	0.2021 ± 6	-0.1763 ± 12
C(19')	-0.4050 ± 10	0.2596 ± 6	-0.1567 ± 10
C(20')	-0.4781 ± 17	0.3144 ± 6	-0.1649 ± 13
C(21')	-0.6110 ± 16	0.3094 ± 7	-0.1828 ± 12

Table 2.4

(a)Anisotropic thermal parameters Uij (Å^2).

Molecule 1

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Br	0.113	0.156	0.044	0.025	0.020	0.009
S	0.043	0.059	0.043	-0.002	0.004	-0.001
O(1)	0.031	0.078	0.066	-0.041	-0.006	-0.038
O(2)	0.076	0.062	0.050	0.030	0.010	0.052
O(3)	0.033	0.049	0.045	-0.008	0.007	-0.004
O(4)	0.052	0.032	0.100	0.004	0.009	0.025
C(1)	0.060	0.041	0.080	0.008	0.030	-0.002
C(2)	0.023	0.079	0.082	0.020	0.019	-0.019
C(3)	0.071	0.069	0.059	-0.024	0.050	-0.038
C(4)	0.061	0.044	0.052	-0.018	0.005	0.006
C(5)	0.053	0.034	0.066	-0.024	0.005	0.007
C(6)	0.049	0.043	0.048	-0.008	-0.022	0.005
C(7)	0.061	0.073	0.054	0.009	-0.016	-0.023
C(8)	0.052	0.077	0.059	-0.015	-0.003	-0.015
C(9)	0.074	0.116	0.078	0.062	-0.038	-0.045
C(10)	0.060	0.103	0.126	0.094	0.012	0.028
C(11)	0.040	0.094	0.082	0.037	0.011	0.005
C(12)	0.063	0.055	0.058	-0.011	-0.014	-0.033
C(13)	0.044	0.073	0.056	0.008	0.005	0.032
C(14)	0.071	0.098	0.068	-0.060	0.038	-0.045

C(15)	0.137	0.128	0.062	-0.093	0.027	-0.107
C(16)	0.057	0.079	0.044	0.008	0.024	0.009
C(17)	0.070	0.076	0.036	0.001	-0.006	-0.010
C(18)	0.072	0.040	0.045	0.001	-0.002	0.012
C(19)	0.055	0.048	0.037	0.022	0.027	0.010
C(20)	0.057	0.058	0.062	0.023	0.010	0.020
C(21)	0.057	0.065	0.070	0.054	0.036	0.003

Molecule 2

Br′	0.065	0.153	0.094	-0.007	-0.022	0.029
S′	0.053	0.058	0.032	0.006	-0.002	0.000
O(1′)	0.054	0.078	0.048	0.029	0.010	-0.032
O(2′)	0.038	0.062	0.056	-0.014	-0.001	0.041
O(3′)	0.061	0.048	0.028	0.012	-0.008	-0.009
O(4′)	0.127	0.032	0.043	-0.010	-0.028	0.011
C(1′)	0.084	0.044	0.040	0.017	0.004	0.016
C(2′)	0.107	0.057	0.051	0.030	-0.053	0.026
C(3′)	0.077	0.059	0.061	0.026	-0.039	-0.020
C(4′)	0.088	0.039	0.048	0.006	0.007	-0.008
C(5′)	0.074	0.032	0.037	0.014	-0.032	-0.025
C(6′)	0.071	0.035	0.030	0.010	-0.001	-0.015
C(7′)	0.078	0.069	0.049	0.025	0.027	0.031
C(8′)	0.067	0.073	0.066	0.042	0.027	0.000

C(9')	0.049	0.152	0.062	0.026	0.034	0.067
C(10')	0.113	0.097	0.060	-0.028	0.021	0.094
C(11')	0.090	0.092	0.035	0.007	-0.019	0.060
C(12')	0.061	0.057	0.056	0.029	0.002	-0.003
C(13')	0.093	0.057	0.057	-0.015	-0.019	0.004
C(14')	0.106	0.074	0.078	0.038	-0.060	-0.073
C(15')	0.082	0.109	0.103	0.042	0.018	-0.036
C(16')	0.075	0.065	0.042	-0.005	-0.024	0.020
C(17')	0.055	0.075	0.056	-0.022	-0.003	-0.013
C(18')	0.072	0.050	0.055	-0.007	-0.030	0.001
C(19')	0.035	0.050	0.046	0.016	-0.013	-0.001
C(20')	0.099	0.042	0.059	0.007	0.008	0.025
C(21')	0.073	0.085	0.050	0.016	-0.001	0.080

(b) Average e.s.d.s. in thermal parameters (Å^2).

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Br	0.001	0.002	0.001	0.002	0.001	0.002
S	0.002	0.002	0.001	0.002	0.002	0.003
O	0.006	0.005	0.004	0.007	0.007	0.008
C	0.009	0.008	0.007	0.012	0.012	0.014

Table 2.5

(a) Average bond lengths with e.s.d.s.(Å).

Br -C(16)	1.921(12)	C(4)-C(14)	1.506(21)
S -O(1)	1.394(10)	C(5)-C(6)	1.535(16)
S -O(2)	1.445(9)	C(6)-C(7)	1.517(17)
S -O(3)	1.584(7)	C(7)-C(8)	1.549(20)
S -C(19)	1.766(10)	C(8)-C(9)	1.562(23)
O(3)-C(6)	1.464(13)	C(8)-C(12)	1.506(19)
O(4)-C(5)	1.435(14)	C(8)-C(15)	1.537(25)
C(1)-C(2)	1.542(21)	C(9)-C(10)	1.519(27)
C(1)-C(5)	1.552(16)	C(10)-C(11)	1.524(26)
C(1)-C(11)	1.525(19)	C(16)-C(17)	1.307(20)
C(1)-C(12)	1.534(19)	C(16)-C(21)	1.335(21)
C(2)-C(3)	1.488(21)	C(17)-C(18)	1.415(18)
C(3)-C(4)	1.555(18)	C(18)-C(19)	1.365(17)
C(4)-C(5)	1.570(17)	C(19)-C(20)	1.387(18)
C(4)-C(13)	1.525(18)	C(20)-C(21)	1.360(21)

(b) Average valency angles with e.s.d.s.(°)

O(1) S O(2)	118.9(5)	C(4)C(5)C(6)	115.6(9)
O(1) S O(3)	104.4(5)	O(3)C(6)C(5)	106.7(8)
O(1) S C(19)	110.9(5)	O(3)C(6)C(7)	109.2(9)
O(2) S O(3)	109.8(5)	C(5)C(6)C(7)	113.8(10)
O(2) S C(19)	107.4(5)	C(6)C(7)C(8)	110.4(11)
O(3) S C(19)	104.5(5)	C(7)C(8)C(9)	109.7(13)
S O(3)C(6)	121.1(7)	C(7)C(8)C(12)	111.6(11)
C(2)C(1)C(5)	104.4(11)	C(7)C(8)C(15)	109.4(13)
C(2)C(1)C(11)	107.4(10)	C(9)C(8)C(12)	108.4(11)
C(2)C(1)C(12)	112.6(10)	C(9)C(8)C(15)	109.0(13)
C(5)C(1)C(11)	114.3(10)	C(12)C(8)C(15)	108.7(13)
C(5)C(1)C(12)	110.7(10)	C(8)C(9)C(10)	109.8(13)
C(11)C(1)C(12)	107.3(11)	C(9)C(10)C(11)	114.8(16)
C(1)C(2)C(3)	104.9(11)	C(1)C(11)C(10)	114.9(12)
C(2)C(3)C(4)	105.4(11)	C(1)C(12)C(8)	110.3(11)
C(3)C(4)C(5)	98.8(9)	Br C(16)C(17)	118.2(11)
C(3)C(4)C(13)	108.8(10)	Br C(16)C(21)	116.8(11)
C(3)C(4)C(14)	111.9(11)	C(17)C(16)C(21)	125.0(13)
C(5)C(4)C(13)	112.2(10)	C(16)C(17)C(18)	119.1(13)

C(5)C(4)C(14)	116.4(11)	C(17)C(18)C(19)	116.2(11)
C(13)C(4)C(14)	108.3(11)	S C(19)C(18)	119.4(9)
O(4)C(5)C(1)	107.8(9)	S C(19)C(20)	117.6(9)
O(4)C(5)C(4)	109.2(10)	C(18)C(19)C(20)	123.0(11)
O(4)C(5)C(6)	106.1(9)	C(19)C(20)C(21)	117.6(13)
C(1)C(5)C(4)	107.8(10)	C(20)C(21)C(16)	119.1(13)
C(1)C(5)C(6)	110.0(10)		

Table 2.6

(a) Some intramolecular non-bonded distances (Å).

	Mol.1	Mol.2		Mol.1	Mol.2
S...C(5)	3.83	3.83	O(3)...C(20)	3.22	3.23
S...C(7)	3.43	3.43	O(4)...C(7)	2.95	3.02
O(1)...C(6)	3.71	3.76	O(4)...C(10)	3.01	2.98
O(1)...C(20)	3.03	3.07	O(4)...C(11)	2.62	2.63
O(2)...C(6)	2.97	2.97	O(4)...C(14)	2.80	2.82
O(2)...C(7)	3.97	3.93	C(5)...C(9)	3.72	3.78
O(2)...C(13)	3.47	3.48	C(5)...C(10)	3.25	3.27
O(2)...C(18)	2.87	2.89	C(6)...C(12)	2.65	2.62
O(3)...O(4)	2.63	2.67	C(6)...C(13)	2.95	2.96
O(3)...C(4)	3.07	3.10	C(7)...C(10)	3.00	3.05
O(3)...C(13)	3.43	3.49	C(7)...C(11)	3.44	3.52
O(3)...C(14)	3.23	3.30			

(b) Intermolecular contacts (<3.8 Å).

$\mathrm{Br}...\mathrm{O}(1)_{\mathrm{I}}$	3.50	$\mathrm{O}(4)...\mathrm{C}(18')_{\mathrm{V}}$	3.28
$\mathrm{O}(1')...\mathrm{Br}'_{\mathrm{II}}$	3.47	$\mathrm{C}(18)...\mathrm{O}(4')_{\mathrm{IV}}$	3.26
$\mathrm{Br}...\mathrm{O}(2)_{\mathrm{I}}$	3.45	$\mathrm{C}(13)...\mathrm{C}(14)_{\mathrm{IV}}$	3.55
$\mathrm{O}(2')...\mathrm{Br}'_{\mathrm{II}}$	3.46	$\mathrm{C}(14)...\mathrm{C}(13')_{\mathrm{V}}$	3.58
$\mathrm{O}(1)...\mathrm{C}(11)_{\mathrm{II}}$	3.46	$\mathrm{C}(19)...\mathrm{C}(11)_{\mathrm{II}}$	3.76
$\mathrm{O}(1')...\mathrm{C}(11')_{\mathrm{I}}$	3.44	$\mathrm{C}(19')...\mathrm{C}(11')_{\mathrm{I}}$	3.75
$\mathrm{O}(1)...\mathrm{C}(17')_{\mathrm{II}}$	3.60	$\mathrm{C}(20)...\mathrm{C}(2')_{\mathrm{I}}$	3.73
$\mathrm{O}(1')...\mathrm{C}(17)_{\mathrm{III}}$	3.57	$\mathrm{C}(20')...\mathrm{C}(2)_{\mathrm{VI}}$	3.77
$\mathrm{O}(2)...\mathrm{O}(4')_{\mathrm{IV}}$	3.00	$\mathrm{C}(21)...\mathrm{C}(15')_{\mathrm{VII}}$	3.73
$\mathrm{O}(4)...\mathrm{O}(2')_{\mathrm{V}}$	3.00	$\mathrm{C}(21')...\mathrm{C}(15)_{\mathrm{VIII}}$	3.73

The subscripts refer to the following equivalent positions:

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

Table 2.7

Distances (Å) of atoms from various planes in the molecules.

Molecule 1.

Atoms included in calculation of planes.

Plane 1		Plane 2		Plane 3		Plane 4	
C(1)	0.060	C(1)	0.021	C(1)	0.039	Br	0.003
C(5)	-0.059	C(11)	-0.020	C(2)	-0.025	S	0.031
C(7)	0.058	C(8)	-0.020	C(4)	0.024	C(16)	0.011
C(8)	-0.059	C(9)	0.020	C(5)	-0.038	C(17)	0.019
						C(18)	-0.028
						C(19)	-0.026
						C(20)	-0.008
						C(21)	-0.003

Atoms not included in calculation of planes.

C(6)	-0.645	C(10)	-0.537	C(3)	-0.636
C(12)	-0.658	C(12)	0.743		

Plane equations.

Plane 1: $-0.483X + 0.824Y - 0.298Z = 1.925$ Å

Plane 2: $-0.596X - 0.801Y - 0.059Z = 2.839$

Plane 3: $0.504X - 0.837Y - 0.214Z = -1.056$

Plane 4: $-0.982X - 0.090Y - 0.169Z = -0.863$

Molecule 2.

Atoms included in calculation of planes.

Plane 1		Plane 2		Plane 3		Plane 4	
C(1')	-0.048	C(1')	-0.024	C(1')	0.032	Br'	-0.024
C(5')	0.046	C(11')	0.023	C(2')	-0.020	S'	-0.029
C(7')	-0.047	C(8')	0.023	C(4')	0.021	C(16')	0.010
C(8')	0.049	C(9')	-0.022	C(5')	-0.033	C(17')	0.021
						C(18')	0.001
						C(19')	-0.002
						C(20')	0.042
						C(21')	-0.020

Atoms not included in calculation of planes.

C(6')	0.590	C(10')	0.560	C(3')	-0.615
C(12')	0.717	C(12')	-0.755		

Plane equations.

Plane 1': $0.293X - 0.842Y - 0.454Z = -6.320$ Å

Plane 2': $0.062X + 0.805Y - 0.590Z = 1.489$

Plane 3': $-0.201X - 0.837Y - 0.509Z = -5.576$

Plane 4': $0.173X + 0.077Y - 0.982Z = 1.263$

X, Y and Z are co-ordinates in Å referred to the orthogonal axes a, b and c.

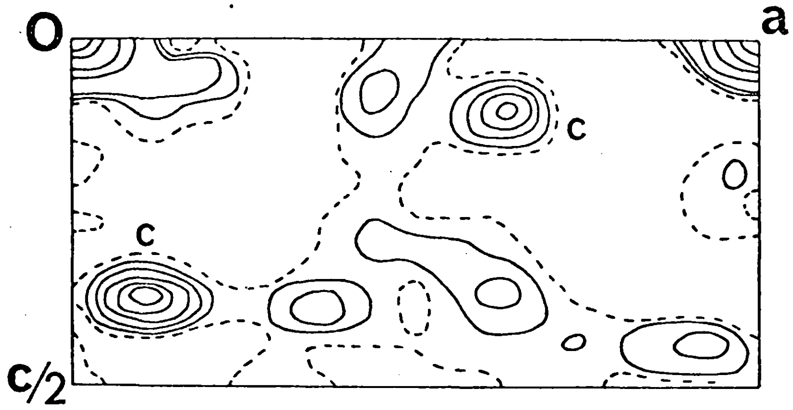
Table 2.8

Bijvoet pairs used in the anomalous-dispersion calculations.

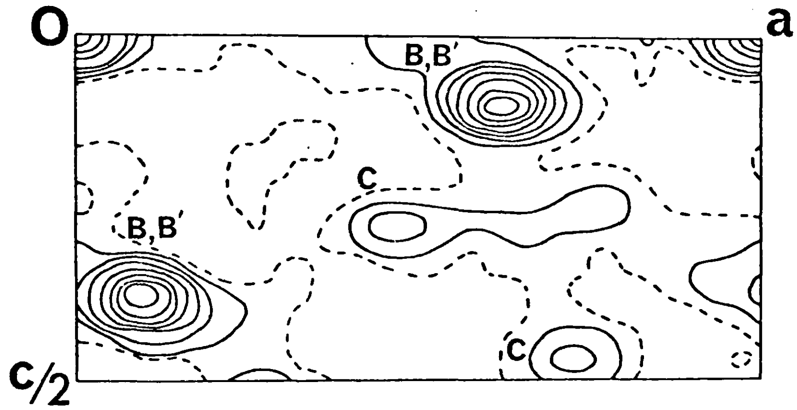
h	k	l	$I_k/I_{\bar{k}}$	$F_k^2/F_{\bar{k}}^2$	h	k	l	$I_k/I_{\bar{k}}$	$F_k^2/F_{\bar{k}}^2$
1	2	3	0.54	0.75	3	4	-7	1.33	1.69
1	6	4	0.73	0.88	4	3	-2	0.64	0.58
2	1	9	1.24	1.24	4	3	-7	0.77	0.91
2	1	7	1.22	1.09	4	4	5	0.83	0.98
2	1	-6	0.50	0.49	4	4	3	0.76	0.99
2	1	-7	0.80	0.99	4	5	4	0.73	0.92
2	1	-8	1.50	1.49	5	1	3	0.42	0.66
2	3	4	0.50	0.57	5	3	4	0.74	0.74
2	3	-6	1.10	1.05	5	3	3	1.30	1.26
2	4	3	0.69	0.85	5	3	2	0.50	0.51
3	1	8	0.85	0.78	5	4	4	0.57	0.81
*3	1	6	1.25	0.96	6	1	2	0.64	0.50
3	1	-5	0.55	0.74	*6	5	4	0.81	1.04
3	3	-5	1.40	1.31	7	2	-2	0.63	0.76

Figure 2.1

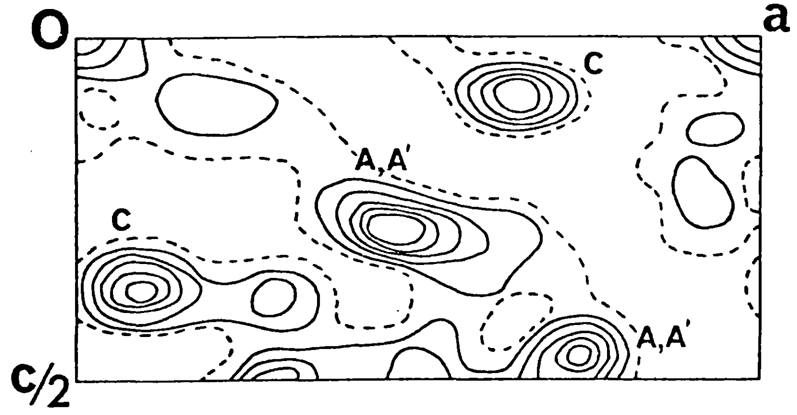
Sections at $v = 0$, 1/4, and 1/2 through the three-dimensional Patterson distribution. Explanations of the marked peaks are contained in the text. Contour levels are at equal arbitrary intervals.



V = 0



V = 1/4



V = 1/2

Figure 2.2

Superimposed sections parallel to the (C1C) plane, of the three-dimensional electron-density distribution over molecule 1. The contours start at 1e Å^{-3} and are drawn at intervals of 1e Å^{-3} except around the bromine and sulphur atoms, where the intervals are 5e Å^{-3} and 2e Å^{-3} respectively.

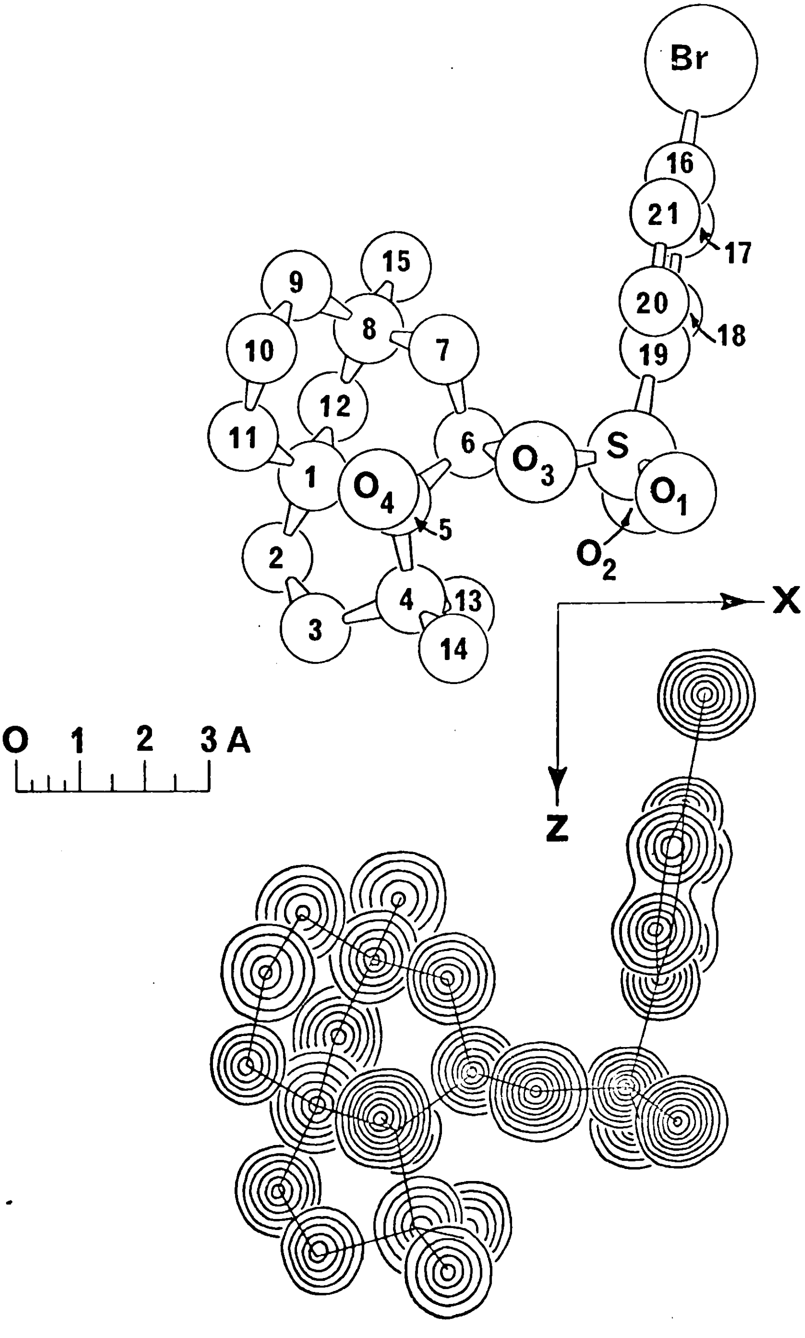
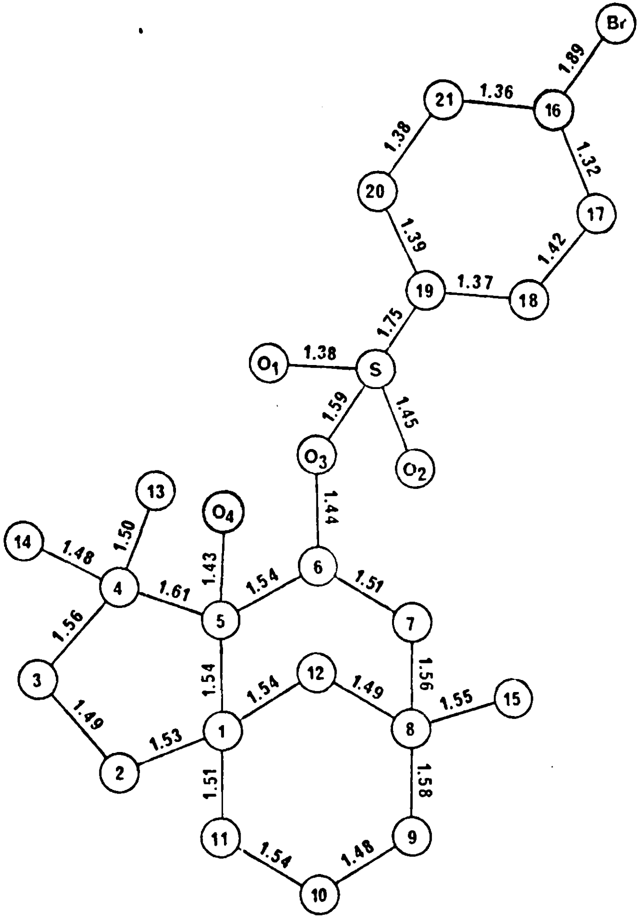
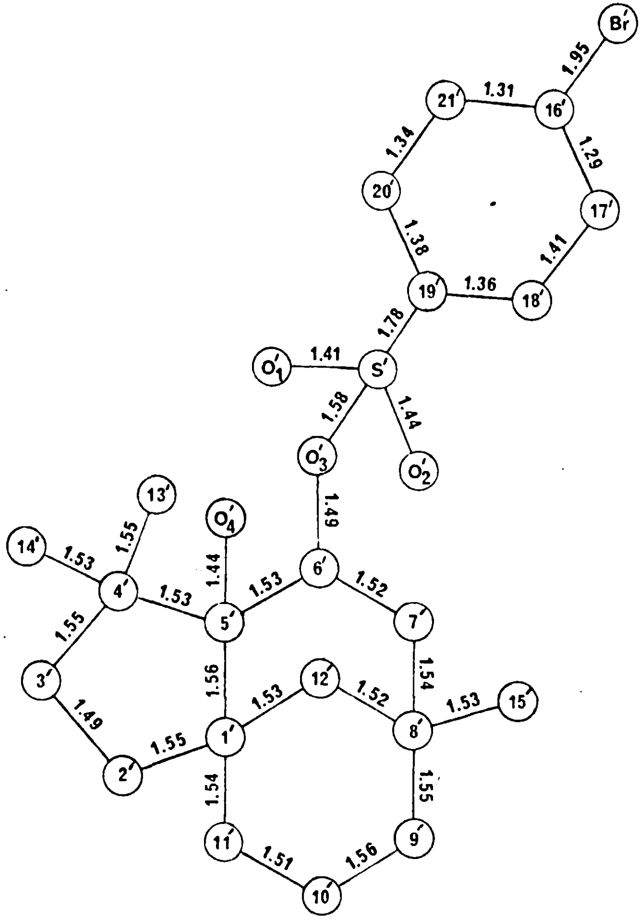

Br
16
21
17
15
9
8
10
7
20
18
19
12
11
6
O_3
S
1
O_4
O_1
5
O_2
2
X
4
13
3
14
O 1 2 3 A
Z

Figure 2.3

Bond lengths (Å).



Molecule 1

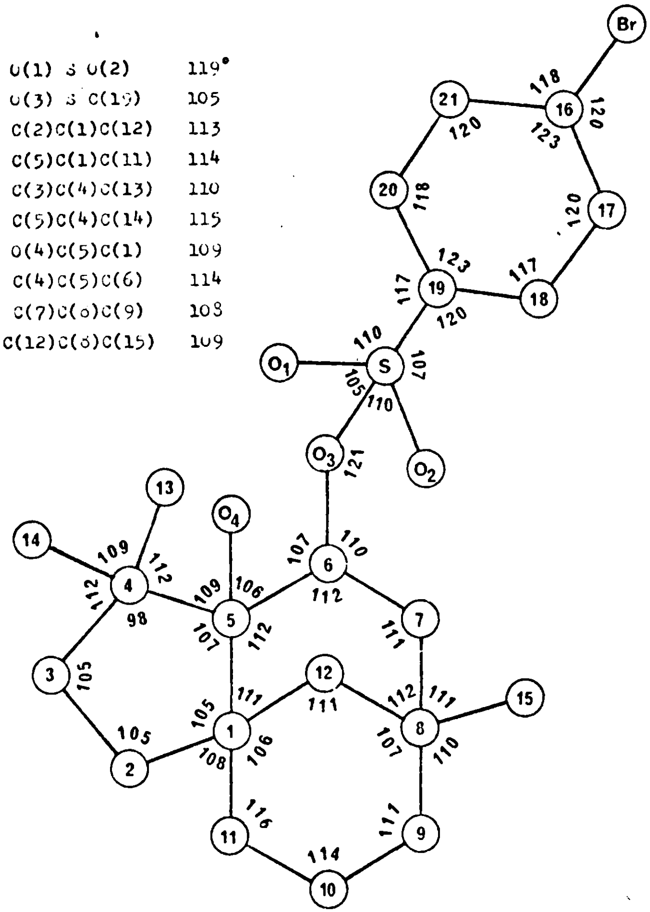


Molecule 2

Figure 2.4

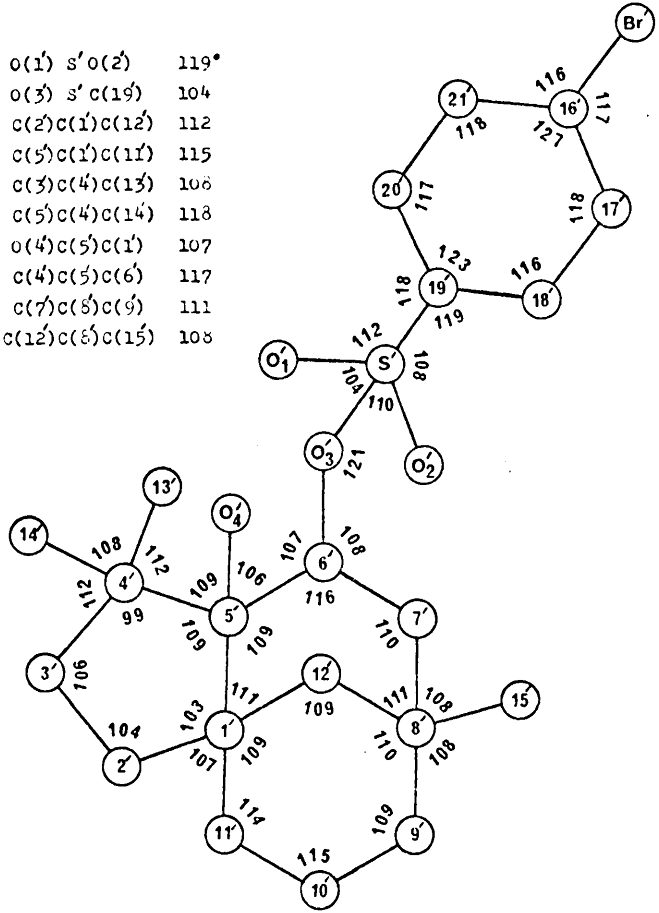
Bond angles (degrees).

o(1) s o(2)	119°
o(3) s c(19)	105
c(2)c(1)c(12)	113
c(5)c(1)c(11)	114
c(3)c(4)c(13)	110
c(5)c(4)c(14)	115
o(4)c(5)c(1)	109
c(4)c(5)c(6)	114
c(7)c(8)c(9)	108
C(12)C(8)C(15)	109



Molecule 1

o(1′) s′o(2′)	119°
o(3′) s′ c(19′)	104
c(2′)c(1′)c(12′)	112
c(5′)c(1′)c(11′)	115
c(3′)c(4′)c(13′)	108
c(5′)c(4′)c(14′)	118
o(4′)c(5′)c(1′)	107
c(4′)c(5′)c(6′)	117
c(7′)c(8′)c(9′)	111
c(12′)c(8′)c(15′)	108



Molecule 2

Figure 2.5

The crystal packing as seen in projection along the a axis. The hydrogen bonds are shown by broken lines.

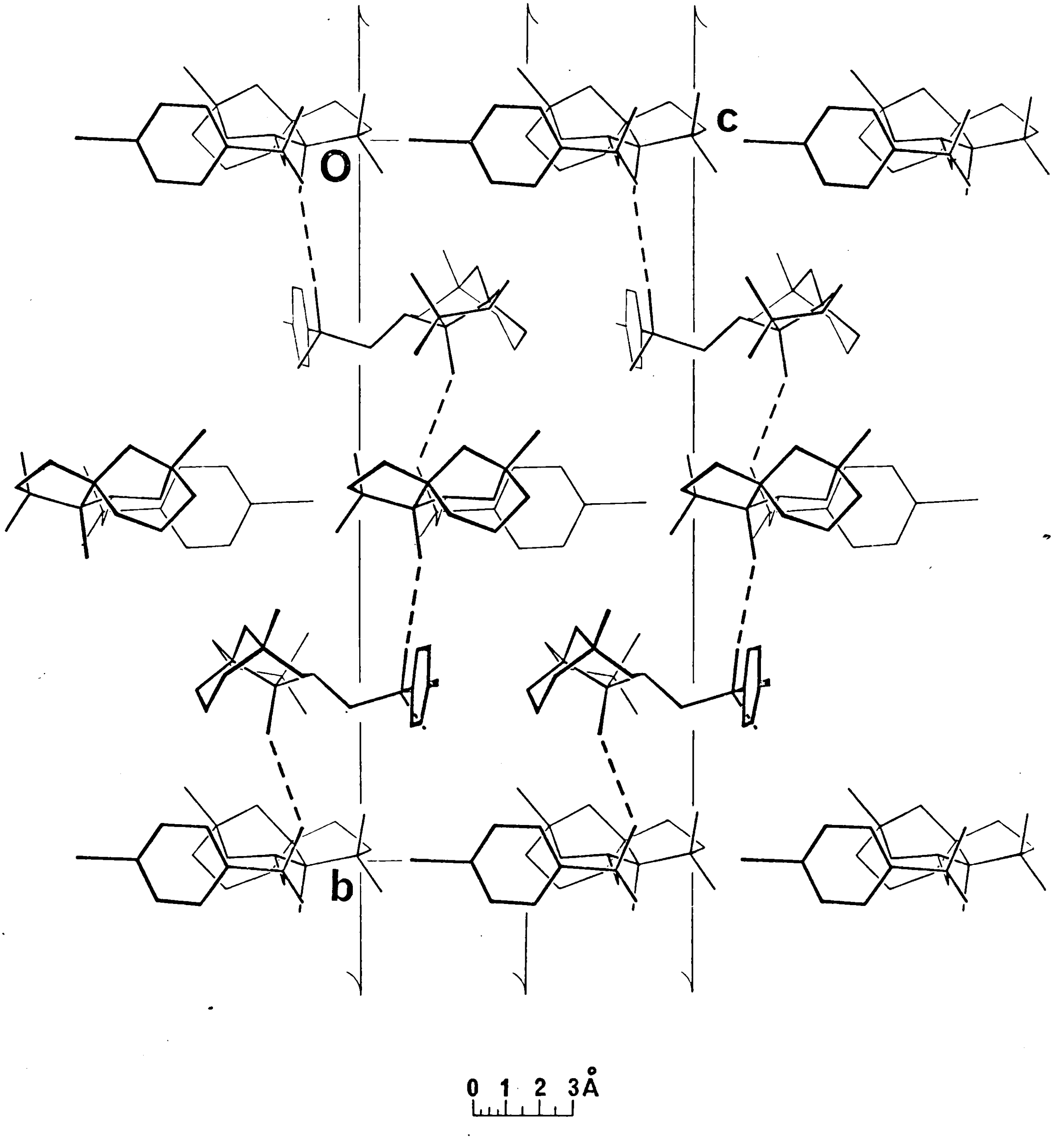

O
c
b
0 1 2 3Å

Figure 2.6

The proposed mechanism rationalising the formation of pseudoclovene-A and isoclovene from caryolan-1-ol.

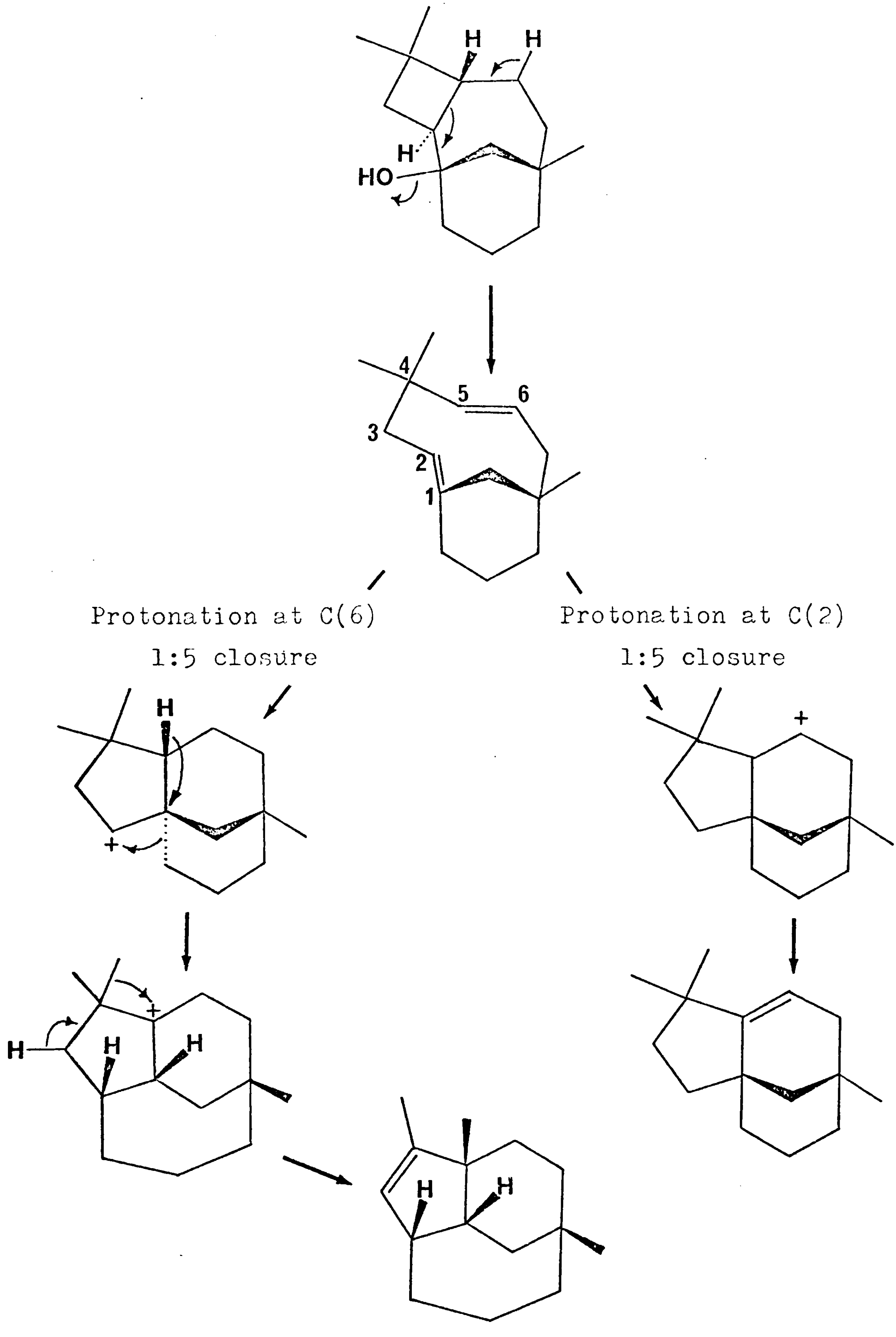
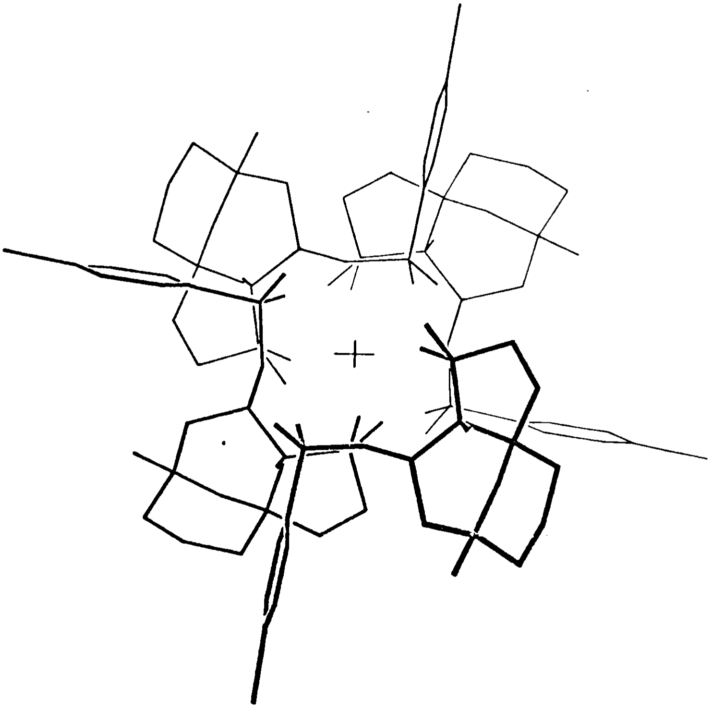
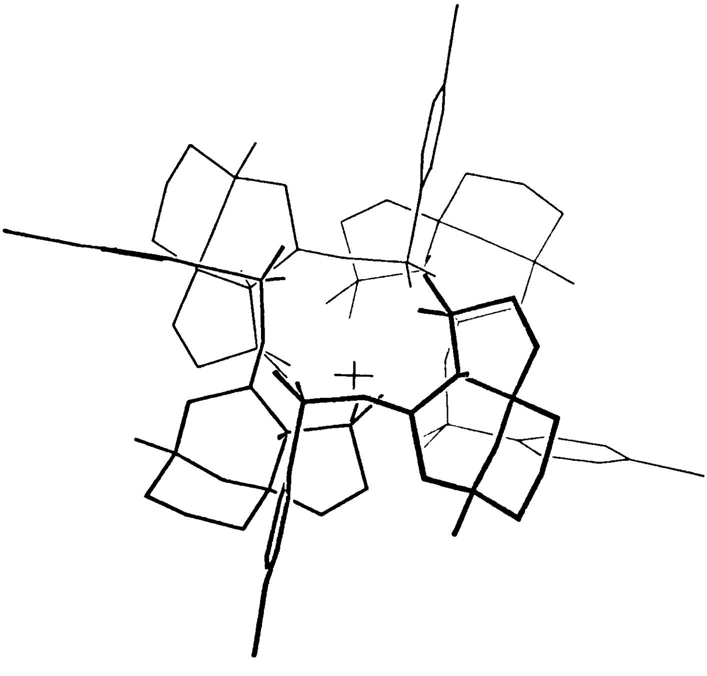

H
H
H
HO
4
5
6
3
2
1
Protonation at C(6)
1:5 closure
Protonation at C(2)
1:5 closure
H
+
+
H
H
H
H
H

Figure 2.7

A stereoscopic view of four molecules of the pseudo-clovene-A derivative showing the presence of the pseudo four-fold screw axis.





2.3 DISCUSSION.

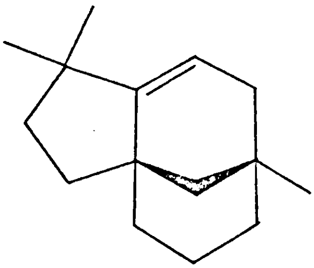
The X-ray analysis of the mono-p-bromobenzenesulphonyl ester of pseudoclovene-A diol has established that formula (X) is a true representation of its structure and absolute stereochemistry. It is inferred from this, that the parent olefin, pseudoclovene-A, has the structure and absolute stereochemistry shown in (IV). The latter has been confirmed by a synthesis of (IV) in its racemic form (Ferguson et.al., 1967; McKillop, 1968). A mechanism which has been proposed (Ferguson et.al., 1967; McKillop, 1968) to rationalise the formation of pseudoclovene-A, also encompasses the co-formation of isoclovene with the correct stereochemistry; it is outlined in Figure 2.6.

Both molecules in the asymmetric unit adopt essentially the same conformation and are closely related by a pseudo four-fold screw axis. If we take the coordinates pertaining to the bromine atom in molecule 1 viz.,

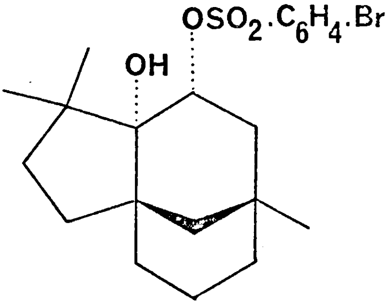
$$0.23542 \quad 0.00000 \quad -0.85570,$$

and transform them by a symmetry operation appropriate to a four-fold screw axis ($x,y,z \longrightarrow z,\frac{1}{4} + y,-x$) we generate the following position,

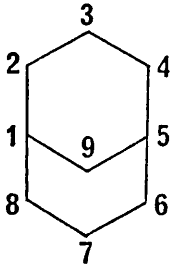
$$-0.85570 \quad 0.25000 \quad -0.23542,$$



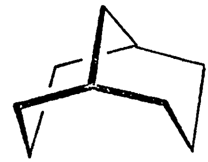
IV



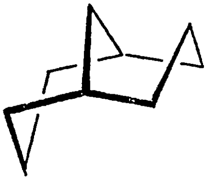
X



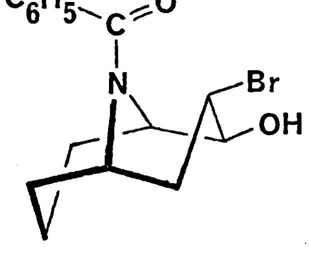
XI



XII



XIII



XIV

which is virtually the same as the position of the bromine atom in molecule 2 viz.,

$$-0.85512 \quad 0.25036 \quad -0.23529.$$

For the most part the corresponding bond lengths and angles in both molecules are not significantly different. One or two differences which appear to be significant in terms of the estimated standard deviations are more likely to indicate a slight underestimation of errors rather than inherent differences between the two molecules in the asymmetric unit. Since no correction for anomalous dispersion was made, errors in the y coordinates of the atoms are expected (Cruickshank and McDonald, 1967), and this may well account for the slight discrepancies. The corresponding dimensions in both molecules have been averaged and these values are given in Table 2.5. In the following discussion mean values are quoted where appropriate.

The pseudoclovene-A derivative is a substituted tricyclo(6,3,1,$0^{1,5}$)dodecane system and reveals some interesting conformational properties. The five-membered ring adopts an envelope conformation and is cis-fused to a cyclohexane ring in a boat arrangement. The latter ring is in turn cis-bridged to a cyclohexane ring in a chair form. In idealised conformations these rings would constitute a highly strained species and the deformations undergone by the molecule to relieve this strain are marked as is evidenced by the large distortions in many of the bond angles (Figure 2.4 and Table 2.5). Bond length extension plays little or no part in strain minimisation, as might be expected, particularly in the light of recent strain calculations (Westheimer, 1956). The C(sp^3)-C(sp^3) distances vary from 1.49 to 1.57 Å but are not significantly different from the usual value of 1.537 Å (Sutton, 1958).

The two cyclohexane rings constitute a bicyclo(3,3,1)-nonane system (XI) which has provided the chemist with some rather interesting conformational problems (Eliel, 1962). There are two possible conformations for this system, namely the twin-chair (XII) and chair-boat (XIII). In the twin-chair conformer an intolerably short transannular contact (0.75 Å) between the axial hydrogens attached to C(3) and C(7) results if it is constructed from regular cyclohexane rings with normal tetrahedral valency angles. Despite this, a number of studies on carbocyclic (Brown, Martin, and Sim, 1965; Webb and Becker, 1967) and heterocyclic (Dobler and Dunitz, 1964) bicyclo(3,3,1)nonanes, by X-ray diffraction methods, reveals the rather unexpected result that the twin-chair conformation is adopted in preference to the chair-boat form. In these molecules the H...H interaction is diminished by a flattening of the three-carbon bridges. In contrast to this the bicyclo(3,3,1)nonane moiety in the derivative of pseudoclovene-A assumes a chair-boat conformation. The twin-chair arrangement is precluded by the presence of the p-bromobenzene sulphonate group and the cis-fusion of the cyclopentane ring at C(1) and C(5), since this would result in an impossibly short contact between O(3) and the C(10) endomethylene hydrogen. A similar feature has been observed by Tamura and Sim (1968) in 9-benzoyl-3α-bromo-2β-hydroxy-9-azabicyclo(3,3,1)nonane (XIV) where the molecule has evaded the severe Br...H interaction which is associated with the alternative twin-chair conformation.

Even in the boat-chair conformation, adopted in the pseudoclovene-A derivative, there is still considerable strain resulting from the close proximity of the C(5) hydroxyl group and the endomethylene hydrogens attached to C(7) and C(10). There is also a severe interaction between the 'bow-sprit' hydrogens bonded to carbon atoms 6 and 12. The interactions of C(10) with O(4) and C(7) are partially relieved by a flattening of the cyclohexane chair, the extent of which can be described in terms of the deviation of C(10) (0.55 Å) from the best plane through C(1), C(11), C(8), and C(9). In a molecule with ideal cyclohexane chair geometry this displacement would be 0.73 Å (Brown, Martin, and Sim, 1965). The deviation of the bridge atom, C(12), from the same plane is not significantly different from the ideal value and reflects the constraint placed on this atom by the adjacent boat ring. Ring flattening effects similar to this have been observed in the tricyclo-(5,3,1,$1^{2,6}$)dodecane system (Macrossan and Ferguson, 1968) in addition to the other bicyclo(3,3,1)nonane systems mentioned previously.

Interaction between the 'bow-sprit' hydrogens is relieved by a slight flattening of the boat ring but greater relief is afforded by a significant twisting of the two cyclohexane rings. Evidence for this can be found in the non-equality of the C(9)...C(5) (3.75 Å) and the C(11)...C(7) (3.49 Å) distances. The twist conformation also minimises the overcrowding of the C(5) hydroxyl group and the endo-methylene hydrogen bonded to C(10). It is probable that the latter interaction is responsible for the twisting since no such effect has been observed in the chair-boat conformation adopted in (XIV) (Tamura and Sim, 1968), nor has it been found in the twin-chair conformations of the aforementioned carbocyclic and heterocyclic(3,3,1)nonane systems. A necessary consequence of the ring flattening and twisting in the bicyclo(3,3,1)nonane skeleton is the appreciable increase in the valency angles at carbon atoms 10 and 11 to an average value of 114.9°.

The cyclopentane ring has an envelope conformation with C(3) displaced 0.63 Å from the best plane through carbon atoms 1, 2, 4, and 5. The average valency angle in the ring of 104.3° is in good agreement with the usual mean angle (105°) associated with five-membered rings (Sim, 1965). The C(3)C(4)C(5) angle (98.8°), however, is distinctly smaller than the others and the contraction is probably a result of the steric interaction between the C(4) and C(5) substituents. Similar angle deformations have been found in ring D of numerous steroids, e.g. 4-bromo-estradiol (98.5°) (Norton, Kartha, and Lu, 1964) and 3-keto-4,4-dimethyl-5α-androstane-17β-iodoacetate (97.7°) (Macauley, 1968).

The C(5)C(1)C(11) valency angle (114.3°) has been increased to minimise the steric interaction between the hydroxyl group O(4), and C(11), and the torsional interaction about the C(5)-C(1) bond (the non-bonded separation O(4)...C(11) is 2.62 Å while the torsional angle O(4)C(5)-

C(1)C(11) is 5°). The non-bonded interaction of the hydroxyl O(4) with the methyl group C(14) (O(4)...C(14) is 2.81 Å) has been relieved by an enlargement of the C(14)C(4)C(5) angle to 116.4°. It is not surprising that there is no accompanying increase in the C(4)C(5)O(4) angle (109.2°) since such an increase would push the hydroxyl group closer to the endomethylene hydrogen on C(10), and so worsen the severe steric strain already present between these centres. The steric interaction between C(13) and C(6), on the other hand, is diminished by increases in both the C(13)C(4)C(5) (112.2°) and C(4)C(5)C(6) (115.6°) angles.

The benzene ring and the bromine and sulphur atoms bonded to it, may be regarded as planar within experimental error. Bond lengths in this part of the molecule are normal (the average aromatic C-C, C-Br, and C-S distances are 1.36, 1.92, and 1.77 Å respectively while the corresponding mean values quoted by Sutton et.al. (1958) for such bonds are 1.395, 1.85, and 1.80 Å) with perhaps the exception of those around C(16'). These discrepancies may well be a result of the uncertainty in the position of C(16') caused by diffraction effects emanating from the adjacent bromine atom.

All the intermolecular contacts are close to or greater than the normal van der Waals contacts with the exception of O(2)...O(4') and O(2')...O(4) which both have a value of 3.00 Å probably as a result of intermolecular O...H-O hydrogen bonding. Such a conclusion is supported by a difference in the S-O(1) (1.394 Å) and S-O(2) (1.445 Å) bond lengths. The lengthening of the S-O(2) bond, if significant, is presumably caused by a partial loss in the double bond character as a result of its participation in hydrogen-bond formation. The molecules in the crystal are linked together by the hydrogen bonds and form spirals parallel to the b direction. Figure 2.7, a stereoscopic drawing, shows four molecules of the pseudoclovene-A derivative spiralling round the pseudo four-fold screw axis.

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