A Thesis

STUDIES OF LAURENCIA NATURAL PRODUCTS AND SOME SYNTHETIC BICYCLIC MOLECULES BY X-RAY ANALYSIS

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by

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SUMMARY

This thesis is divided into three sections. In Section I some theoretical aspects of the diffraction of X-rays by crystals and some techniques of X-ray structure analysis are introduced and discussed briefly. The structure analyses of two natural products are described in Section II and of three synthetic organic molecules containing bicyclic ring systems are described in Section III.

The natural products described in Section II, laurencin and laurinterol, were both isolated from the Laurencia species of seaweed and were unusual as bromine-containing natural products. Unambiguous determination of their constitutions by chemical and spectroscopic techniques had proved impossible and no details of their stereochemistries were available. In each case the X-ray investigation has established the structure and both absolute stereochemistries were determined by consideration of anomalous dispersion effects. In the case of laurinterol, as a result of the determination of the absolute stereochemistry, the absolute stereochemistries of the chemically related compounds aplysin and aplysinol have been determined, and it has been proved that laurinterol, aplysin and aplysinol have the same absolute stereochemistry at their common centres as the natural products laurene and cuparene. This has allowed speculation on the possibility of a biological precursor common to all five compounds.

The investigations of two bicyclo[2,2,2]octane derivatives and a bicyclo[3,2,2]nonene derivative have been described in Section III. There has been considerable controversy in the literature as to the conformation of the bicyclo[2,2,2]octane molecule, the possibilities being the eclipsed D_{3h} conformation as opposed to the staggered or twisted D_3 conformation. The investigation of one of the bicyclo[2,2,2]octane derivatives was undertaken specifically to study this problem, and the results prove unambiguously that in the solid state the twisted or staggered D_3 conformation is favoured with 5° dihedral angles between substituents on the bridges. The second bicyclo[2,2,2]-octane derivative was an adduct of unknown structure. The analysis has revealed the structure and the results show that despite the presence of many substituents and sp^2 hybridised centres, the second bicyclo[2,2,2]octane skeleton reflects the same conformational trends as the first. The bicyclo[3,2,2]-nonene system was investigated because it was of conformational interest. In this case it has been shown that no twisting of the bicyclic ring system takes place, but that strain is relieved by ring-flattening with accompanying valency-angle distortions. The three conformations have been discussed in one chapter with an accompanying discussion of those strain effects which are generally considered to be conformation-determining.

CONTENTS

PART I SOME THEORETICAL ASPECTS OF CRYSTAL STRUCTURE ANALYSIS

PART II THE CRYSTAL STRUCTURES OF TWO LAURENCIA NATURAL PRODUCTS

page

PART III THE CRYSTAL STRUCTURES OF THREE SYNTHETIC BICYCLIC MOLECULES

PART I

SOME THEORETICAL ASPECTS OF CRYSTAL STRUCTURE ANALYSIS

CHAPTER 1 INTRODUCTION

X-radiation which has a wavelength of about one Angstrom is produced when electrically charged particles are rapidly decelerated by striking a suitable target. In practice electrons are used as particles and the targets, composed of elements such as Cu, Mo or Cr, emit radiation characteristic of these elements. From studies of their external morphologies, it had been proposed before the end of the nineteenth century that crystals were triperiodic arrangements of molecules. It was also known that the number of possible arrangements of molecules in crystals would be limited to 230, corresponding to the 230 space groups. In 1913 von Laue suggested that crystals might act as diffraction gratings for X-rays and acting on this suggestion, Freidrich and Knipping observed the diffraction of X-rays by copper sulphate crystals. This experiment not only proved the wave-nature of X-rays, but also proved that crystals are triperiodic arrangements of matter.

W.L.Bragg (1913) developed and simplified the theory of X-ray diffraction by crystals for practical use. He exposed crystals of several salts, whose structures had previously been proposed from space-group theory, to a monochromatic beam of X-rays and recorded the diffraction patterns. Bragg was able to correlate the observed diffraction intensities with the intensities calculated on the basis of the previously proposed structures. These experiments constituted the first structure analyses of crystalline material by the study of X-ray diffraction patterns.

Since these early days of X-ray crystallography, modern techniques have been developed for recording and measuring diffraction patterns in more convenient forms. The advent of the modern electronic computer has facilitated more rigorous mathematical treatments of the observed data and the experimental results, and has allowed study of more complicated problems.

CHAPTER 2 THE GEOMETRY OF DIFFRACTION BY CRYSTALS

The triperiodicity of a crystal may be expressed in terms of the crystal lattice or crystal space lattice as it is sometimes called. The dimensions of the lattice and the wavelength of the radiation together determine completely the conditions for the diffraction of X-rays by a crystal. Each lattice point may be defined relative to an origin situated at a lattice point by the vector $\underline{r}$

$$\underline{r} = u\underline{a} + v\underline{b} + w\underline{c} \qquad (1)$$

where $\underline{a}$, $\underline{b}$ and $\underline{c}$ are the primitive translations of the lattice and u, v and w are integers.

To simplify the following discussion of diffraction by a lattice it is assumed that each lattice point is capable of scattering X-rays equally in all directions. A parallel beam of X-rays with wavelength λ is allowed to fall on two lattice points A_1 and A_2 which are separated by the vector $\underline{r}$. The direction of the incident beam is defined by the vector $\underline{s}_o$ which has magnitude $1/\lambda$, and another direction defined by the vector $\underline{s}$, also of magnitude $1/\lambda$, is chosen. This is shown in Figure 1.

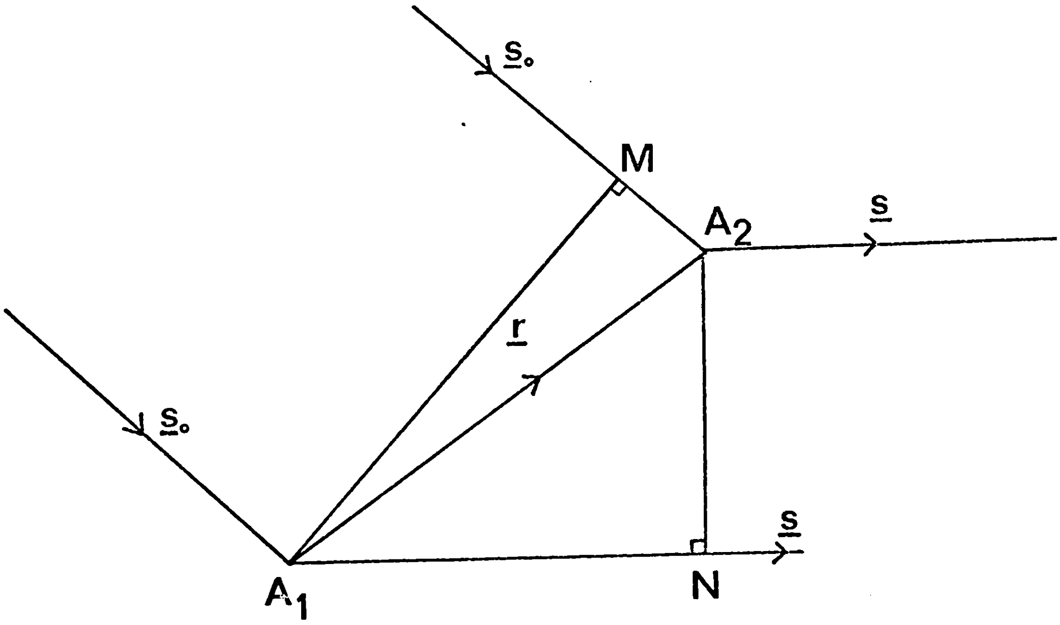

$\underline{s}_0$
M
A_2
$\underline{s}$
$\underline{r}$
$\underline{s}_0$
$\underline{s}$
A_1
N

Figure 1

The path difference between waves scattered by A_1 and A_2 in the direction defined by $\underline{s}$ is given by

$$\begin{aligned} \text{path difference} &= A_1N - A_2M \\ &= \lambda(\, \underline{r}.\underline{s} - \underline{r}.\underline{s}_o \,) \\ &= \lambda \underline{r}.\underline{S} \qquad (2) \end{aligned}$$

where $\underline{S} = \underline{s} - \underline{s}_o$ is called the scattering vector. For the diffracted waves to be in phase $\underline{r}.\underline{S}$ must be integral. Substituting (1) in (2) and imposing integral values gives

$$(u\underline{a} + v\underline{b} + w\underline{c}).\underline{S} = \text{integer} \qquad (3)$$

By definition u, v and w are integers and it therefore follows from (3) that

$$\begin{aligned} \underline{a}.\underline{S} &= \text{integer} = h \\ \underline{b}.\underline{S} &= \text{integer} = k \qquad (4) \\ \underline{c}.\underline{S} &= \text{integer} = \ell \end{aligned}$$

The equations (4) are known as the Laue equations and when they are simultaneously satisfied a diffracted beam of maximum intensity is produced.

Bragg identified the arbitrary integers h, k and ℓ with the Miller indices of the lattice planes. The Laue equations may be rewritten

$$\frac{\underline{a}.\underline{S}}{h} = 1 \tag{5}$$

$$\frac{\underline{b}.\underline{S}}{k} = 1 \tag{6}$$

$$\frac{\underline{c}.\underline{S}}{\ell} = 1 \tag{7}$$

Subtraction of (6) from (5) gives

$$(\underline{a}/h - \underline{b}/k).\underline{S} = 0 \tag{8}$$

The physical interpretation of equation (8) is that the vector $\underline{S}$ is perpendicular to the vector $(\underline{a}/h - \underline{b}/k)$ which lies in the lattice plane defined by the Miller indices h, k and ℓ. Similarly $\underline{S}$ is perpendicular to the vectors $(\underline{a}/h - \underline{c}/\ell)$ and $(\underline{b}/k - \underline{c}/\ell)$ which both are also in the plane (h,k,ℓ). $\underline{S}$ is therefore perpendicular to the plane (h,k,ℓ). Furthermore, if $\underline{s}_o$ makes an angle θ with this plane, then by definition $\underline{S}$ is a vector of magnitude $(2\sin\theta)/\lambda$ in the direction of the bisector of the angle between $\underline{s}_o$ and $\underline{s}$, and therefore $\underline{s}$ also makes an angle θ with the plane. This development is the justification for regarding diffraction as "reflexion" from the lattice planes.

To derive Bragg's Law from this concept, the spacing d of the plane (h,k,ℓ) must be introduced and is given by

$$d = \frac{(\underline{a}.\underline{S})}{h|\underline{S}|} \tag{9}$$

but

$$\frac{\underline{a}.\underline{S}}{h} = 1$$

and

$$|\underline{S}| = 2\sin\theta/\lambda$$

therefore

$$\lambda = 2d\sin\theta \tag{10}$$

Equation (10) may be rewritten generally

$$n\lambda = 2d\sin\theta \tag{11}$$

which is Bragg's Law in the form in which it is normally used.

The derivation of Bragg's Law is only one method of endowing the Laue equations with physical meaning. Another approach is to find the values of $\underline{S}$ which simultaneously satisfy equations (4). The Laue equations state mathematically that the projections of $\underline{S}$ on $\underline{a}$, $\underline{b}$ and $\underline{c}$ are constant for fixed values of h, k and ℓ respectively. Alternatively it may be stated that the ends of the vectors $\underline{S}$ lie at the intersections of planes (not the lattice planes previously discussed) each of which is perpendicular to one of the axes $\underline{a}$, $\underline{b}$ or $\underline{c}$, the values of h, k and ℓ defining the intercepts of these planes on $\underline{a}$, $\underline{b}$ and $\underline{c}$ respectively. The points defined by the intersections of these planes form a lattice of points called the reciprocal lattice, and the values of $\underline{S}$ which simultaneously satisfy the Laue equations are defined by the points of the reciprocal lattice.

The primitive translations of the reciprocal lattice are defined to be $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$. Since $\underline{a}^*$ is perpendicular to both $\underline{b}$ and $\underline{c}$ it must be representable by $p(\underline{b} \times \underline{c})$ where p is a constant to be determined. The corresponding expressions for $\underline{b}^*$ and $\underline{c}^*$ are $q(\underline{c} \times \underline{a})$ and $r(\underline{a} \times \underline{b})$ respectively. The vector $\underline{S}$ may also be represented by

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

but

$$\underline{a}.\underline{S} = h$$

therefore

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

but

$$V = \underline{a}.\underline{b} \times \underline{c}$$

where V is the volume of the real-space unit cell. It therefore follows from equation (13) that

$$p = 1/V \text{ and similarly } q = r = 1/V$$

Therefore

$$\underline{a}^* = \frac{\underline{b} \times \underline{c}}{V} \tag{14}$$

$$\underline{b}^* = \frac{\underline{c} \times \underline{a}}{V} \tag{15}$$

$$\underline{c}^* = \frac{\underline{a} \times \underline{b}}{V} \tag{16}$$

The reciprocal lattice is the Fourier transform of the real-space lattice and since the mathematical definition of a Fourier transform summarises part of the mathematics of diffraction, diffraction is more easily dealt with in terms of the reciprocal lattice.

CHAPTER 3 THE STRUCTURE FACTOR

The wave scattered by the entire contents of one unit cell is given by $G(\underline{S})$ where

$$G(\underline{S}) = \int \rho(\underline{r})\exp(2\pi i\underline{r}.\underline{S})dV_{\underline{r}} \qquad (17)$$

where the integration is over the volume of the unit cell and $\rho(\underline{r})$ is the electron density distribution. By the definition of Fourier transforms, $G(\underline{S})$ is the Fourier transform of $\rho(\underline{r})$.

The electron density $\rho(\underline{r})$ may be regarded as the sum of N independent atomic electron densities and rewriting equation (17) in these terms gives

$$G(\underline{S}) = \sum_{n=1}^{n}\int_{-\infty}^{+\infty}\rho_n(\underline{r}_o)\exp\left\{2\pi i(\underline{r}_o + \underline{r}_n).\underline{S}\right\}dV_{\underline{r}_o} \qquad (18)$$

where $\rho_n(\underline{r}_o)$ is the atomic electron density defined by the vector $\underline{r}_o$ with respect to an origin within the n^{th} atom. The n^{th} atomic origin is defined with respect to the origin of the unit cell by the vector $\underline{r}_n$. The wave scattered by a single atom is given by

$$f_n(\underline{S}) = \int_{-\infty}^{+\infty}\rho_n(\underline{r}_o)\exp(2\pi i\underline{r}_o.\underline{S})dV_{\underline{r}_o} \qquad (19)$$

$f_n(\underline{S})$ is called the atomic scattering factor and is the

Fourier transform of the atomic electron density. The fact that atoms have physical size and that waves scattered from different parts of the same atom will be out of phase, is embodied in equation (19). Substituting (19) into (18) gives

$$G(\underline{S}) = \sum_{n=1}^{N} f_n(\underline{S})\exp(2\pi i\underline{r}_n.\underline{S}) \qquad (20)$$

but

$$\underline{S} = h\underline{a}^* + h\underline{b}^* + \ell\underline{c}^*$$

and

$$\underline{r}_n = x_n\underline{a} + y_n\underline{b} + z_n\underline{c}$$

where (x_n, y_n, z_n) are the coordinates of the n^{th} atom expressed as fractions of the unit cell edges. Equation (20) then becomes

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

The structure factor $F(hk\ell)$ is defined only when h, k and ℓ have integral values thereby satisfying the Laue equations. For a small crystal it may be assumed that all unit cells scatter in phase and that $F(hk\ell)$ is therefore a desription of the total wave scattered in the order h, k, ℓ, by the crystal.

For practical purposes the structure factor $F(hk\ell)$ is rewritten by means of Euler's equation as

$$F(hk\ell) = A + iB \tag{22}$$

where

$$A = \sum_{n=1}^{N} f_n(hk\ell)\cos 2\pi(hx_n + ky_n + \ell z_n) \tag{23}$$

and

$$B = \sum_{n=1}^{N} f_n(hk\ell)\sin 2\pi(hx_n + ky_n + \ell z_n) \tag{24}$$

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

$$\alpha = \tan^{-1}\frac{B}{A} \tag{25}$$

It is assumed in equation (21) that the atoms are at rest. The effect of thermal atomic vibration is to "smear" the electron density over a larger volume than that occupied by the atom at rest. Bloch (1932) , assuming isotropic atomic vibration with a Boltzmann probability distribution of atoms over the energy levels of vibration, showed that the smearing function $t(\underset{\sim}{x})$ is a Gaussian given by

$$t(\underset{\sim}{x}) = (2\pi^2U)^{-3/2}\exp(-x^2/2U) \tag{26}$$

where $U = \bar{U}^2$ is the mean square amplitude of vibration in any direction. The definition of the smearing function is such that the average density in vibration is the convolution of the rest-density with the smearing function. The scattering factor $f_T(hk\ell)$ for an atom in thermal vibration is therefore given by

$$f_T(hk\ell) = f(hk\ell)q(hk\ell) \tag{27}$$

where $f(hk\ell)$ is the scattering factor for an atom at rest and $q(hk\ell)$ is the Fourier transform of the smearing function. Assuming isotropic atomic vibration the expression for $q(hk\ell)$ is

$$q(\underline{S}) = \exp\left[-B\left(\frac{\sin\theta}{\lambda}\right)^2\right] \tag{28}$$

where $B = 8\pi^2 U$ is the Debye factor.

In an anisotropic harmonic potential field the vibrations of an atom are described by a symmetrical tensor $\underline{U}$ with six independent components, such that the mean square amplitude of vibration in the direction of a unit vector $\underline{\ell}$ with components ℓ_1, ℓ_2 and ℓ_3 is

$$\overline{U}^2 = \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}\,\ell_i\,\ell_j \tag{29}$$

In this anisotropic case the Fourier transform of the smearing function is

$$q(\underline{S}) = \exp\left[-2\pi^2\left(\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}\,\underline{s}_i\cdot\underline{s}_j\right)\right] \qquad (30)$$

where $\underline{S} = (\underline{s}_1, \underline{s}_2, \underline{s}_3)$ is the reciprocal vector. At a reciprocal lattice point $\underline{S} = h\underline{a}^* + k\underline{b}^* + \ell\underline{c}^*$, $q(\underline{S})$ becomes

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

Excellent discussions on the treatment of thermal vibration of atoms in crystallography have been given by Cruickshank (1956a, 1956b, 1964, 1965) and by Busing and Levy (1958).

The effect of either isotropic or of anisotropic thermal vibration may be summarised by rewriting the structure factor equation

$$F(hk\ell) = \sum_{n=1}^{N} f_n(hk\ell)q_n(hk\ell)\exp\left[2\pi i(hx_n + ky_n + \ell z_n)\right] \qquad (32)$$

where $q_n(hk\ell)$ is the Fourier transform of the corresponding smearing function.

CHAPTER 4 ANOMALOUS SCATTERING

In equation (19) for the atomic scattering factor it is assumed that each atomic electron behaves as a "free" electron in scattering X-rays. If allowance is made for the constraint placed on atomic electrons by their environment, the atomic scattering factor may be expressed

$$f = f_o + \Delta f' + i\Delta f'' \qquad (33)$$

which is often written

$$f = f' + i\Delta f'' \qquad (34)$$

where f_o is the Fourier transform of the atomic electron density, and $\Delta f'$ and $\Delta f''$ are factors which may be evaluated (Dauben and Templeton, 1955) for various elements and wavelengths. Significant values of $\Delta f'$ and $\Delta f''$ are found only for the innermost electrons and since these electrons occupy a relatively small volume around the nucleus, $\Delta f'$ and $\Delta f''$ are to a good approximation independent of the scattering angle.

Cruickshank and McDonald (1967) have drawn attention to the fact that in analyses involving polar space groups, serious errors in positional parameters can result if $\Delta f''$ is neglected. In particular, $\Delta f''$ may assume significant values when the frequency of the primary radiation is just above the frequency corresponding to an absorption edge of the scattering atom.

Apart from errors in parameters, for crystals in which the atoms are not related by a centre of symmetry significant values of $\Delta f''$ lead to the breakdown of Friedel's Law which states that the reflexion (h,k,ℓ) should have the same intensity as the reflexion $(\bar{h},\bar{k},\bar{\ell})$. This may be demonstrated by substituting the complex expression (34) for the scattering factor into the structure factor expressions:-

$$F(\underline{H}) = \sum_j (f'_j + if''_j)\exp(2\pi i\underline{H}.\underline{r}_j) \qquad (35)$$

$$F(-\underline{H}) = \sum_j (f'_j + if''_j)\exp(-2\pi i\underline{H}.\underline{r}_j) \qquad (36)$$

$$\neq F^*(\underline{H})$$

where $F^*(\underline{H})$ is the complex conjugate of $F(\underline{H})$. It then follows

$$\left|F(\underline{H})\right|^2 \neq \left|F(-\underline{H})\right|^2 \qquad (37)$$

and the pair of reflexions (h,k,ℓ) and $(\bar{h},\bar{k},\bar{\ell})$ thus have different intensities. The effect was first demonstrated by Coster, Knol and Prins (1930). Bijvoet (1949) first suggested that the effects of anomalous scattering could be used to distinguish between enantiomorphic structures in non-centrosymmetric space groups, and subsequently he and his school put this method to great use in the determination of absolute stereochemistries (Bijvoet, 1954; Peerdeman, Bommel and Bijvoet, 1951; Trommel and Bijvoet, 1954; Bijvoet, 1955).

One advantage of the Bijvoet method for the determination of absolute stereochemistries is that it involves the use of few or no more data than are normally collected during the course of a structure analysis. It is therefore quickly and easily attempted and when successful the results are unambiguous.

CHAPTER 5 FOURIER SERIES

W.H.Bragg (1915) first suggested that the triperiodicity of crystals would allow representation of the electron density by a three-dimensional Fourier series. Assigning three integral indices h', k' and ℓ' to each Fourier coefficient, the electron density $\rho(x,y,z)$ may be expressed

$$\rho(x,y,z) = \sum_{h'}\sum_{k'=-\infty}^{+\infty}\sum_{\ell'} C(h'k'\ell')\exp 2\pi i(h'x + k'y + \ell'z) \tag{38}$$

Expressing the structure factor as a function of the electron density gives

$$F(hk\ell) = \int_0^1\int_0^1\int_0^1 V\rho(xyz)\exp 2\pi i(hx + ky + \ell z)dxdydz \tag{39}$$

Substituting (38) into (39) gives

$$F(hk\ell) = \int_0^1\int_0^1\int_0^1 \sum_{h'}\sum_{k'=-\infty}^{+\infty}\sum_{\ell'} C(h'k'\ell')$$

$$\times \exp 2\pi i(h'x + k'y + \ell'z)\exp 2\pi i(hx + ky + \ell z)$$

$$\times Vdxdydz \tag{40}$$

Both exponential functions in equation (40) are periodic, and the integral will therefore be non-zero only when $h = -h'$, $k = -k'$ and $\ell = -\ell'$. Under these circumstances the value of the integral becomes

$$F(hk\ell) = \int_0^1\int_0^1\int_0^1 C(\bar{h},\bar{k},\bar{\ell})\, V dx dy dz$$

therefore

$$F(hk\ell) = C(\bar{h}\bar{k}\bar{\ell})V \tag{41}$$

The Fourier coefficients are therefore directly related to the corresponding structure factors, and the electron density may be expressed

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_{k=-\infty}^{+\infty} \sum_\ell F(hk\ell) \exp\left\{-2\pi i(hx + ky + \ell z)\right\}. \tag{42}$$

Equation (42) gives the basic form of Fourier summation as used in crystal structure analyses.

Woolfson (1956) showed that when a Fourier series is evaluated with the observed amplitudes and the phase angles appropriate to only part of the structure, modification of the Fourier coefficients gives better resolution of the unknown part of the molecule. Sim (1957) has discussed the number of structure factors whose signs are determined by the presence in a molecule of a selected group of atoms. In all the analyses described in this thesis where only part of the molecule has been included in the phase-angle calculations a modification function devised by Sim (1961) was applied to the Fourier coefficients to improve resolution of the rest of the molecule in the resulting electron-density distribution.

CHAPTER 6 THE MEASUREMENT OF STRUCTURE AMPLITUDES

The amount of energy $E(hk\ell)$ diffracted in the order $hk\ell$ as a crystal rotates uniformly about an axis normal to the X-ray beam may be written as

$$E(hk\ell) = K.L(hk\ell).p(hk\ell).\left|F(hk\ell)\right|^2 \qquad (43)$$

K is constant for a given experiment and is given (Buerger, 1960) by

$$K = \left(\frac{I_o \lambda^3 N^2 dV}{\omega}\right)\left(\frac{e^4}{m^2 c^4}\right) \qquad (44)$$

where

I_o = intensity of incident radiation

λ = wavelength of radiation

N = number of unit cells per unit volume

dV = volume of crystal

ω = angular velocity of crystal

e = electronic charge

m = electronic mass

c = velocity of light

The Lorentz factor $L(hk\ell)$ applies a correction for the different speeds with which different points of the reciprocal lattice pass through the sphere of reflexion and hence for the different lengths of time spent by different planes in a reflecting position. This correction depends not only on the reflexion involved but depends also on the specific motion of the crystal relative to the X-ray beam which varies with different techniques of data collection. The form used for equi-inclination Weissenberg data (Tunell, 1939) is given by

$$L(hk\ell)^{-1} = \frac{\sin 2\theta\,(\cos^2\mu - \cos^2\theta)}{\sin\theta} \qquad (45)$$

where μ is the equi-inclination angle.

The incident X-ray beam is unpolarised, but the reflected beam is both polarised and hence reduced in intensity. The polarisation correction $p(hk\ell)$, which depends only on the reflexion and is independent of the motion of the crystal relative to the beam, takes the form

$$p(hk\ell) = \frac{1}{2}(1 + \cos^2\theta) \qquad (46)$$

In practice equation (43) is rewritten

$$F(hk\ell)^2 = \frac{E(hk\ell)}{KLp} \qquad (47)$$

Normally some quantity proportional to $E(hk\ell)$ is measured and since the values thus obtained are on an arbitrary scale the experimental constant K is usually disregarded. The relevant Lorentz-polarisation corrections are then applied to the observed intensities.

Extinction and absorption are additional factors which affect the values of the observed intensities although they are usually neglected in all but the most accurate work. Extinction is attenuation of the primary beam of X-rays which reduces the intensity of the reflected beam. It is a function of the physical perfection of crystals and correction is therefore very difficult. Darwin (1922) has subdivided extinction into "primary extinction" and "secondary extinction". An excellent resumé of Darwin's work has been given by Lonsdale (1947).

The intensity of radiation passing through a crystal is also reduced by absorption which is a function of the material constitution of a crystal and of the path-length of the X-ray beam through the crystal. Absorption is therefore dependent upon the sizes and shapes of crystals and correction hence becomes difficult for all but spherical or cylindrical crystals. Buerger (1960) gives an account of some devices for grinding crystals of minerals until they are spherical or cylindrical. Accounts of absorption corrections have been given by Wells (1960), by Rogers and Moffet (1956) and by Busing and Levy (1957).

The $F(hk\ell)$ values calculated from the observed intensities are on an arbitrary scale. Various methods for putting the amplitudes onto an absolute scale have been given by Yü (1942), by Wilson (1942) and by Beevers and Cochran (1947). In the preliminary stages of an analysis an approximately absolute scale may be achieved by making $k \sum |F_o| = \sum |F_c|$ for various batches of data, and such scale factors may be subsequently refined by least-squares methods.

CHAPTER 7 THE PHASE PROBLEM

The derivation of the experimentally unobservable phases of the structure factors is the fundamental problem of X-ray crystallography. In many cases there is enough information contained in the observed structure amplitudes to allow phase determination to be started. Some of the methods for deriving phase information are described briefly in this chapter.

7.1 THE PATTERSON FUNCTION

Patterson (1934, 1935) defined the function

$$P(uvw) = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\rho\left\{(x+u),(y+v),(z+w)\right\}dxdydz \qquad (48)$$

which is self-convolution of the electron density. Substituting the Fourier expression (42) into (48) gives

$$P(uvw) = \frac{1}{V}\int_0^1\int_0^1\int_0^1 \sum_h\sum_k\sum_\ell\sum_{h'}\sum_{k'}\sum_{\ell'} F(hk\ell)\exp\left\{-2\pi i(hx+ky+\ell z)\right\}$$
$$\times\, F(h'k'\ell')\exp\left\{-2\pi i(h'x+k'y+\ell'z)\right\}$$
$$\times\, \exp\left\{-2\pi i(h'u+k'v+\ell'w)\right\}dxdydz \qquad (49)$$

In equation (49) the exponential factors are all periodic and the integral will hence only have values when $h = -h'$, $k = -k'$, and $\ell = -\ell'$. Also, $F(hk\ell)$ is the complex conjugate of $F(\bar{h}\bar{k}\bar{\ell})$. Equation (49) then reduces to

$$P(uvw) = \frac{1}{V}\sum_{h}\sum_{k}\sum_{\ell}\left|F(hk\ell)\right|^2 \exp\left\{2\pi i(hu + kv + \ell w)\right\} \quad (50)$$

The function P(uvw) therefore gives information about the vectors <u>u</u>, <u>v</u> and <u>w</u> and not directly about atomic positions. P(uvw) will have a significantly large value if the vectors <u>u</u>, <u>v</u> and <u>w</u> are the components of an interatomic vector, and the value of P(uvw) will then be approximately the product of the electron densities of the two atoms involved in the interaction if the observed amplitudes are on an approximately absolute scale. Harker (1936) drew attention to the fact that certain symmetry elements result in peaks being concentrated on certain lines and sections of a P(uvw) plot, and that the positions of these peaks bear special relationships to the coordinates of the atoms which give rise to them.

Since the number of distinct interatomic vectors in a unit cell containing N atoms is N(N-1), it is therefore difficult to obtain the positions of <u>all</u> the atoms in even a moderately complicated structure by inspection of the Patterson synthesis. However, identification of peaks involving heavy atoms is usually possible, especially if the Patterson coefficients have been modified (usually with a function of the scattering factor of the heavy atom) to give additional weight to high-order reflexions. Such modification "sharpens" the peaks due to heavy atom vectors and makes both identification and calculation of coordinates easier.

7.2 THE HEAVY ATOM METHOD AND THE METHOD OF ISOMORPHOUS REPLACEMENT

When a structure contains a small number of heavy atoms whose scattering power is approximately equal to the combined scattering power of the other atoms, it is often possible to find the peaks in the Patterson function corresponding to vectors between the heavy atoms and so to determine the positions of these atoms. The phases of structure factors calculated with the heavy atom contributions alone are often a good approximation to the true (unknown) phases (Sim, 1957). An electron-density distribution evaluated with these approximate phases and with the observed amplitudes will, in all probability, reveal more of the structure and hence allow the phase determination to proceed further. This is currently the most frequently used method for overcoming the phase problem and is often the only method possible for a complicated structure. The main disadvantage is that the major part of each structure amplitude comes from the scattering of the heavy atoms and as a result the accuracy of locating the lighter atoms is reduced.

The last difficulty is minimised in the method of isomorphous replacement, first used by Cork (1927) and later developed by Robertson in his analyses of the phthalocyanines (Robertson, 1935, 1936, 1937; Robertson and Woodward, 1937, 1940). Data are collected for each one of an isomorphous series of compounds, some of which should contain heavy atoms and one of which should be a light atom derivative. The phases of the heavy atom derivatives may be determined by conventional means. The contributions from all the light atoms to the structure factors of both the heavy and light atom derivatives should be the same in each case. It is possible to derive the phases of the light atom derivative directly from the structure factors of the heavy atom derivatives. Refinement of the light atom structure should then be more accurate than the refinement of any of the heavy atom derivatives.

7.3 TRIAL AND ERROR

By consideration of features of a structure such as space-group symmetry, physical or chemical properties, comparison with known structures or dominant features of the diffraction pattern, it may be possible to postulate a model of the crystal structure which has a reasonable chance of being nearly correct. The model may be evaluated by comparison of the observed and calculated amplitudes.

Excellent examples of trial and error methods are the structure determinations of pyrene (Robertson and White, 1947) and of coronene (Robertson and White, 1945). One disadvantage of these methods is that the molecular structure must be known before the structure analysis is undertaken.

7.4 DIRECT METHODS

The aim of this class of methods for solving the phase problem is to derive the phases of the structure factors without prior postulation of any atomic positions. These methods first made an appearance in the form of inequality relationships between structure factors, given notably by Harker and Kasper (1948) and by Karle and Hauptman (1950). The derivation of these inequality relationships depended only on the positivity of electron density. Goedkoop (1950) showed that equality relationships may be derived between structure factors if the electron density is considered to be a superposition of atoms of approximately the same shape. A notable landmark in the development of direct methods was the derivation by Sayre(1952) of a simple form of equality relationship between structure factors. Although Sayre's equations were difficult to handle, they led Cochran (1952) and Zachariasen (1952) to the discovery of a simple probability relationship between structure factors which was both powerful and convenient to handle. Other probability relationships were soon discovered by Karle and Hauptman (1953), and although derived by purely analytical methods, some of their formulae can be given a physical interpretation in terms of the

Patterson function. Karle and Hauptman's sigma-2 relationship is

$$sE_{\underline{h}} \simeq s \sum_{\underline{k}} E_{\underline{k}} \cdot E_{\underline{h}-\underline{k}} \qquad (51)$$

where $sE_{\underline{h}}$ is the sign of the normalised structure factor $E_{\underline{h}}$. This relationship is of use when a strong $E_{\underline{k}}$ tends to dominate the product. It must be noted that normalised structure factors must be used. The probability $P_{+}(E_{\underline{h}})$ that the phase of $E_{\underline{h}}$ is positive is given by

$$P_{+}(E_{\underline{h}}) = \frac{1}{2} + \frac{\frac{1}{2}\tanh\left(\sum_{j=1}^{N} z_j^3\right)\left|E_{\underline{h}}\right| \sum_{\underline{k}} E_{\underline{k}} \cdot E_{\underline{h}-\underline{k}}}{\left(\sum_{j=1}^{N} z_j^2\right)^{3/2}} \qquad (52)$$

Equation (52) is used in conjunction with equation (51).

The greatest stimulus to direct methods has been given by the widespread availability of fast electronic computers. Many methods, particularly those of recent origin, are quite impractical without the aid of a computer in the evaluation of trial sets of phases or in the application of iterative techniques of phase determination.

CHAPTER 8 REFINEMENT

The overall accuracy of the derived structure in relation to the true structure is usually estimated by means of the residual or R-factor defined as

$$R = \frac{\sum\left(k|F_o| - |F_c|\right)}{\sum k|F_o|} \qquad (53)$$

This factor gives an estimate of the agreement between the calculated and observed diffraction patterns. An analytical account of the R-factor has been given by Hamilton (1965).

The purpose of a refinement is to shift the derived atomic parameters slightly to make them agree more with the real structure, the criterion for closer agreement being a lower R-factor. Currently used in a complementary fashion, the two most popular methods of refining a structure are by successive Fourier syntheses and by least-squares refinement.

8.1 SUCCESSIVE FOURIER SYNTHESES

A Fourier synthesis computed with the observed structure amplitudes and the calculated phases will yield a set of coordinates most consistent with these Fourier coefficients. If structure factors are then calculated with the atoms placed at the new positions, it will generally be found that the R-factor is lower and on this criterion the model of the structure has improved. Successive Fourier syntheses will result in more accurate phase determinations until a final cycle has converged on a set of atomic locations which are almost correct. Refinement by this method suffers from certain drawbacks. For example there is the effect of series termination. A Fourier series with a finite number of terms does not give a perfect representation of a point, but gives instead a peak of finite width surrounded by a diffraction ripple. A number of authors (Parry and Pitt, 1949; Ladell and Katz, 1954; Megaw, 1954; and Katz, 1958) have suggested various methods for estimating the centres of Fourier peaks to yield the best estimate of atomic coordinates. In addition, the diffraction ripples which result from series termination add to the peaks of other atoms causing shifts in the centres of these peaks and thus giving rise to further errors in the estimation of coordinates. This effect is particularly noticeable around heavy atoms. Booth (1945, 1946c) has suggested a method for correcting the coordinates estimated from shifted peaks. This method involves the computation of an F_c Fourier synthesis. Comparison of the coordinates resulting from this synthesis and the coordinates used in the structure factor calculation may indicate termination of series errors in the observed atomic parameters. The corrections obtained from this calculation are known as back-shift corrections.

Difference syntheses, which are Fourier series calculated with $(|F_o| - |F_c|)$ as coefficients, are normally computed at the end of a structure refinement as a final check on the accuracy of the parameters. In suitable cases they may reveal the positions of hydrogen atoms. Booth (1948a) and others have suggested the use of the difference synthesis as a refinement technique in its own right.

Bunn's Error Synthesis (Crowfoot, Bunn, Rogers-Low, Turner-Jones, 1949) is a form of difference synthesis. It is used if a structure will not refine below a relatively high R-factor and if it is suspected that there may be something fundamentally wrong with the model. The Error Synthesis is computed using $(|F_o| - |F_c|)$ as amplitudes, but only including terms for which F_o is zero or very small and for which F_c is reasonably large. Such terms should be most sensitive to errors present in the model and may reveal the cause of the high discrepancies.

8.2 DIFFERENTIAL SYNTHESES

In refining a crystal structure by Fourier methods, many summations are made for points which are not actually needed; all that is desired is to find the points where the maxima of $\rho(xyz)$ occur. One such maximum occurs at each atom and at these maxima the first derivative vanishes:-

$$\frac{\partial \rho}{\partial x} = \frac{\partial \rho}{\partial y} = \frac{\partial \rho}{\partial z} = 0 \qquad (54)$$

Booth (1946a, 1946b) devised a refinement method which found the departures in coordinates from the final structure by use of these derivatives.

8.3 LEAST SQUARES

Least squares is applied to crystal structure refinement by minimising some function of the differences between the observed and calculated intensities with respect to the atomic parameters. The function most commonly minimised is

$$\sum_{hk\ell} w(|F_o| - |F_c|)^2 = \sum_{hk\ell} w\Delta^2 \qquad (55)$$

where the summation is over the set of crystallographically independent observed planes, and w is a weight for each term. If the standard deviation for each $F_o(hk\ell)$ is $\sigma(hk\ell)$, then the value of w which gives the lowest standard deviations in the derived parameters may be shown to be

$$w(hk\ell) = \frac{1}{\sigma^2(hk\ell)} \qquad (56)$$

However, since $\sigma^2(hk\ell)$ is unknown in practice, it may be necessary to use a more complicated weighting scheme which also allows more flexibility. It is usual to test a weighting scheme by batching the structure amplitudes according to $|F_o|$ and $\sin\theta/\lambda$. If the weighting scheme be appropriate to the data, the average value of $w\Delta^2$ in each batch should be approximately the same.

If $p_1, p_2, \ldots\ldots, p_n$ are the n parameters (whose values are to be determined) occurring in the F_c, then for R to be a minimum

$$\frac{\partial R}{\partial p_j} = 0 \quad \text{for} \quad j = 1,\ldots\ldots,n \tag{57}$$

where $R = \sum w\Delta^2$. Substituting (55) into (57) gives

$$\sum_{hk\ell} w(|F_o| - |F_c|).\frac{\partial |F_c|}{\partial p_j} = 0 \quad \text{for} \quad j = 1,\ldots\ldots,n \tag{58}$$

The parameters have to be varied until these n conditions are satisfied. For a trial set of p_j close to the correct values, $(|F_o| - |F_c|)$ may be expanded as a first order Taylor series

$$\Delta(\underset{\sim}{p} + \underset{\sim}{\varepsilon}) = \Delta(\underset{\sim}{p}) - \sum_{i=1}^{n} \varepsilon_i \frac{\partial |F_c|}{\partial p_i} \tag{59}$$

where ε_i is a small change in parameter p_i, and $\underset{\sim}{p}$ and $\underset{\sim}{\varepsilon}$ stand for the whole set of parameters and changes. Substitution of (59) into (57) gives

$$\sum_{i=1}^{n} \left\{ \sum_{hk\ell} w \frac{\partial|F_c|}{\partial p_i} \cdot \frac{\partial|F_c|}{\partial p_j} \right\} \varepsilon_i = \sum_{hk\ell} w(|F_o| - |F_c|) \cdot \frac{\partial|F_c|}{\partial p_j} \qquad (60)$$

The equations (60) are known as the normal equations of least squares, and there are n for $j = 1,\ldots,n$.

The normal equations may be conveniently expressed in matrix form

$$\sum_i a_{ij} \varepsilon_i = b_j \qquad (61)$$

where

$$a_{ij} = \sum_{hk\ell} w \frac{\partial|F_c|}{\partial p_i} \cdot \frac{\partial|F_c|}{\partial p_j} \qquad (62)$$

and

$$b_j = \sum_{hk\ell} w(|F_o| - |F_c|) \cdot \frac{\partial|F_c|}{\partial p_j} \qquad (63)$$

Equation (61) may also be rewritten

$$\varepsilon_i = \sum_i (a^{-1})_{ij} b_j \qquad (64)$$

where $(a^{-1})_{ij}$ is the inverse matrix of a_{ij} . The number of independent elements of the matrix a_{ij} is proportional to the square of the number of parameters being refined. Since the capacity of a computer for storing numbers is limited, it is often necessary to make some approximation to a_{ij} . In the diagonal approximation which is used if the crystal axes are orthogonal or nearly so, it is assumed that all elements of a_{ij} involving different parameters of the same atom and all elements involving the parameters of different atoms may be neglected. If the crystal axes are not orthogonal the block-diagonal approximation may be used. In this case it is assumed that all elements of a_{ij} involving parameters of different atoms and all elements involving both the positional and thermal parameters of the same atom may be neglected. Thus the matrix a_{ij} reduces to a number of submatrices in the block-diagonal approximation.

Because of the omission of higher terms in the Taylor series, it is usually necessary to calculate several cycles before a minimum is obtained. The course of a refinement is followed by the reductions in the value of $\sum w\Delta^2$, although the quantities R and R' give an indication of the progress of the refinement. R and R' are defined as follows

$$R' = \frac{\sum w(k|F_o| - |F_c|)^2}{\sum wk^2 |F_o|^2} \qquad (65)$$

$$R = \frac{\sum (k|F_o| - |F_c|)}{\sum k|F_o|} \qquad (66)$$

The criterion used to decide the termination of a refinement is that the calculated shifts should be less than one-half of the estimated standard deviations.

CHAPTER 9 ANALYSIS OF RESULTS

9.1 ESTIMATED STANDARD DEVIATIONS

At the conclusion of a structure analysis it is often important to decide whether some function of the refined parameters, for example a bond length, differs from a theoretical or standard value. Such a problem can be solved by a statistical significance test, the application of which requires a knowledge of the estimated standard deviation of the function in question.

Least squares allows estimated standard deviations to be calculated. The variance of the parameter p_i is given by

$$\sigma(p_i) = (a^{-1})_{ii}\left(\frac{\sum w\Delta^2}{m-n}\right) \qquad (67)$$

and the covariance of the parameters p_i and p_j is given by

$$\mathrm{cov}(p_i p_j) = (a^{-1})_{ij}\left(\frac{\sum w\Delta^2}{m-n}\right) \qquad (68)$$

where m is the number of observations and n is the number of parameters. The covariance may also be written

$$\mathrm{cov}(p_i p_j) = \sigma(p_i)\,\sigma(p_j) r_{ij} \qquad (69)$$

The equations (67), (68), and (69) are valid only if the weighting scheme is appropriate to the data; the usual test applied is that the average $w\Delta^2$ should be approximately constant if the data are examined in a systematic manner.

If the goodness of fit of a set of experimental results to their expected values is under consideration, the χ^2 test may be used. If, for example, d_i is the deviation of the i^{th} of a set of points from the least-squares plane (Schomaker et al., 1959) through the points, then

$$\chi^2 = \sum_{i=1}^{n}\left(\frac{d_i^2}{\sigma^2}\right) \tag{70}$$

where σ is the average positional standard deviation of a point. The probability that the deviations from the plane are due to random errors can then be found by looking up tables of χ^2 for n-3 degrees of freedom (Fisher and Yates, 1953).

CHAPTER 10 COMPUTATION

The many calculations were performed on the Glasgow KDF-9 computer. Some details of the programs used and the authors are given below:-

PROGRAM	AUTHOR
Intensity correction	A.A.Hook R.Truter and M.Wells
Isotropic structure factor and Fourier	J.G.Sime
Fourier search	D.McGregor
Least squares	D.W.J.Cruickshank and J.G.F.Smith (and J.G.Sime)
Bond length and valency angle	K.W.Muir
Data sharpening	K.W.Muir
Hydrogen placing	G.Ferguson
Mean plane	W.Oberhänsli
Standard deviations for bond lengths and valency angles	W.S.Macdonald
Sim weighting	K.W.Muir and D.R.Pollard

Many of the above programs were incorporated into the ASS system of programs which was developed mainly by Drs. D.McGregor, K.W.Muir and Mr. D.R.Pollard.

PART II

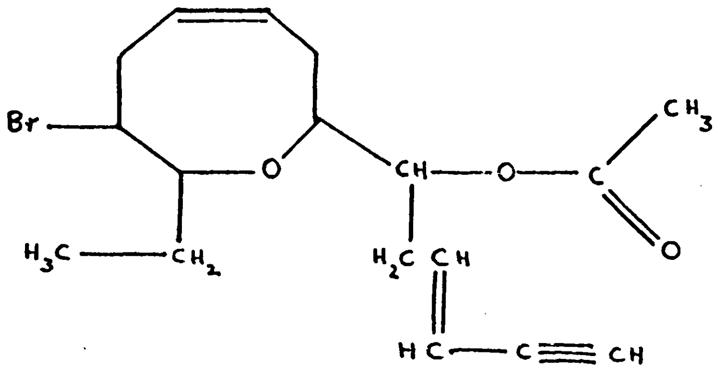
THE CRYSTAL STRUCTURES OF TWO LAURENCIA NATURAL PRODUCTS

CHAPTER 1 THE CRYSTAL STRUCTURE AND ABSOLUTE STEREOCHEMISTRY OF LAURENCIN

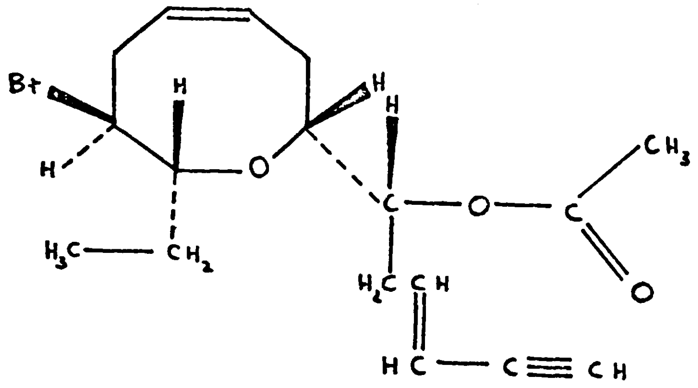
1.1 INTRODUCTION

Irie, Suzuki and Masamune (1965) have described a naturally occurring bromo-compound, laurencin, $C_{17}H_{23}O_3Br$, obtained in low yield from methanol extracts of the seaweed Laurencia glandulifera. From extensive chemical and spectroscopic investigations of laurencin and the related compounds octahydrolaurencin, $C_{17}H_{31}O_3Br$, and deacetyllaurencin, $C_{15}H_{21}O_2Br$, they proposed the eight-membered ring structure I for laurencin. The possibility of a nine-membered ring structure could not be completely eliminated, however, and no details of the stereochemistry were available.

The present single-crystal X-ray analysis using three-dimensional diffraction data has confirmed the structure I proposed by Irie and his co-workers, and determines the absolute stereochemistry as II.



I



II

1.2 EXPERIMENTAL

1.2.1 Crystal Data

Laurencin, $C_{17}H_{23}O_3Br$, M = 355.3,

Orthorhombic, $\underline{a} = 7.70 \pm 0.02$, $\underline{b} = 9.70 \pm 0.02$, $\underline{c} = 22.93 \pm 0.06$ Å,

$\underline{U} = 1713$ Å^3, $\underline{D}_m = 1.36$ g.cm.$^{-3}$ (by flotation in KI/H_2O),

$\underline{z} = 4$, $\underline{D}_x = 1.38$ g.cm.$^{-3}$,

F(000) = 736,

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

Linear absorption coefficient for X-rays ($\lambda = 1.5418$ Å), $\mu = 37\mathrm{cm}^{-1}$

1.2.2 Crystallographic Measurements

The unit cell parameters were determined from oscillation and Weissenberg photographs taken with Cu-Kα radiation ($\lambda = 1.5418$Å) and from precession photographs taken with Mo-Kα radiation ($\lambda = 0.7107$ Å). The dimensions were checked for accuracy when the crystal was mounted on a Hilger and Watts linear diffractometer for the first data collection. The space group was uniquely determined from the systematic halving observed in the h00, 0k0, and 00ℓ spectra.

Two small crystals rotating about b* were exposed to Mo-Kα radiation on a Hilger and Watts linear diffractometer (Arndt and Phillips, 1961) and 1147 independent reflexions from the reciprocal lattice nets h0ℓ - h5ℓ , h6ℓ - h9ℓ were measured. The appropriate Lorentz and polarisation corrections (Tunell, 1939) were applied to the observed intensities, but no absorption corrections were applied and no allowance was made for unobserved reflexions. Rapid and substantial decomposition of the crystals had been observed during this data collection and it was not surprising when the structure, having been established, would not refine below R = 0.24 . It was concluded that the radiation damage had introduced such considerable errors into the data that recollection of the intensity data by photographic methods was necessary for the refinement.

For the second data collection, two small crystals rotating about b were used with less-damaging Cu-Kα radiation and 1152 independent reflexions from the reciprocal lattice nets h0ℓ - h3ℓ , h4ℓ - h7ℓ were recorded on equatorial and equi-inclination Weissenberg photographs using the multiple-film technique with six films in each pack. The intensities were estimated visually by comparison with a calibrated wedge and the appropriate corrections for Lorentz and polarisation factors were applied.

The amplitudes were subsequently placed on an approximately absolute scale by making $k\sum|F_o| = \sum|F_c|$ for each layer. No allowance was made for absorption and unobserved reflexions were not considered. The advantage of Weissenberg photographic methods for relatively slowly decomposing crystals is that the effects of the decomposition on the data are "averaged" for each layer.

1.2.3 Structure Determination

The value of 1.48 for the ratio $f_{Br}^2/\sum_R f_R^2$ indicated a reasonable chance of success (Lipson and Cochran, 1966) for the heavy atom method of phase determination on which basis the analysis subsequently proceeded.

The equivalent positions in the space group $P2_12_12_1$, namely

$$\begin{array}{rrr} x, & y, & z \\ 1/2 - x, & -y, & 1/2 + z \\ 1/2 + x, & 1/2 - y, & -z \\ -x, & 1/2 + y, & 1/2 - z \end{array}$$

are such that an atom placed at the general position (x, y, z) will give rise to the following peaks on the three Harker sections of the Patterson function P(uvw) :-

i) Section at $u = 1/2$

$1/2, \quad 1/2 + 2y, \quad 2z$

ii) Section at $v = 1/2$

$2x, \quad 1/2, \quad 1/2 + 2z$

iii) Section at $w = 1/2$

$1/2 + 2x, \quad 2y, \quad 1/2$

After sharpening to point bromine atom at rest, the diffractometer data were used to compute the three-dimensional Patterson function from which the bromine coordinates (0.4512, 0.1117, 0.7048) were uniquely determined. The three Harker sections are shown in Figure 1.1 .

The first three-dimensional electron-density distribution was calculated with the observed amplitudes and the phase-angles appropriate to the bromine atom, and served to locate a further five atoms. Coordinates were assigned to these atoms and they were included in the second structure-factor calculation. The second electron-density distribution revealed nine further atoms, which were included in the third structure-factor calculation.

With the exception of C(4), the carbon atom bonded to the bromine atom, the complete structure was revealed in the third electron-density distribution evaluated with the observed amplitudes and the phase-angles appropriate to the bromine atom and the fourteen atoms previously located. Including the contributions from all atoms except C(4) a fourth electron-density distribution was evaluated in which the missing atom was located.

In all the previous structure-factor calculations an overall isotropic thermal parameter $U_{iso} = 0.05$ Å^2 was assumed. In all electron-density syntheses evaluated with contributions from only part of the molecule an appropriate modification function (Sim, 1961) was used. After each structure-factor calculation the layers $h0\ell$ - $h7\ell$ were placed on an approximately absolute scale by making $k\sum|F_o| = \sum|F_c|$ for each layer. The oxygen atoms were distinguished from the carbon atoms by their greater integrated peak-density (after being included as carbon atoms in the structure-factor calculations).

1.2.4 Structure Refinement

Because of errors in the diffractometer data arising from radiation damage to the crystals, all attempts to refine the positional and isotropic thermal parameters by full-matrix least-squares methods were unsuccessful. When the photographic data were available the refinement of positional, thermal (isotropic and anisotropic) and scale parameters by least-squares methods proceeded smoothly as outlined in Table 1.1 .

After 11 cycles the least-squares refinement had converged with R = 0.103 and R' = 0.0139. After cycle 3, the data were converted to an overall absolute scale using the refined values of the layer-scale factors, and in all subsequent cycles only an overall scale factor was refined. The Glasgow least-squares program outputs an analysis of the weighting scheme used in a refinement cycle in the form of $w\Delta^2$ batched according to $|F_o|$ and $(\sin\theta)/\lambda$. A weighting scheme of the form

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

was applied in all cycles. Initially the parameters p_1, p_2 and p_3 were chosen to give unit weights to all reflexions, but were subsequently varied to achieve the same average $w\Delta^2$ for the various batches of data, the final values being

$$p_1 = 50, \quad p_2 = 0.01, \quad p_3 = 0.0001$$

After cycle 7 anisotropic vibrations of the atoms were allowed for in the calculations and because of computer-store limitations this necessitated the use of a block-diagonal approximation to the normal-equation matrix in all subsequent cycles. The strategy adopted in the least squares refinement was to refine isotropic thermal parameters and layer-scale factors concurrently. Before introducing anisotropic thermal parameters to the refinement the data were placed on an approximately absolute scale using the refined values of the layer-scale factors, and thereafter only an overall scale factor was refined. Lingafelter and Donohue (1966) have drawn attention to the fact that to refine layer-scale factors and anisotropic thermal parameters when data are available collected about only one axis leads to degeneracy between the scale factors and the thermal parameters. The strategy outlined above was used in an attempt to overcome this difficulty.

The least-squares refinement was terminated when the calculated shifts were less than one-third of the estimated standard deviations. Structure factors calculated with the final parameters were used to evaluate a final electron-density distribution and a three-dimensional difference synthesis. Superimposed sections of the final electron-density map viewed down the a-axis are shown in Figure 1.2 . The difference synthesis revealed no errors in the structure and although there were a number of ill-defined peaks in positions stereochemically acceptable for hydrogen atoms it was impossible to determine their coordinates with any accuracy. The refinement of the structure was therefore considered complete.

In all the structure-factor calculations, the atomic scattering factors used were those given in "International Tables for Crystallography", Vol. III . Values of F_o (photographic data) and the final values of F_c are given in Table 1.2 . The final fractional coordinates are given in Table 1.3 and the anisotropic thermal parameters given in Table 1.4 are the values of U_{ii} and $2U_{ij}$ in the expression :-

$$\exp\left\{-2\pi^2\left(U_{11}h^2\underline{a}^{*2} + U_{22}k^2\underline{b}^{*2} + U_{33}\ell^2\underline{c}^{*2} + 2U_{12}hk\underline{a}^*.\underline{b}^* + 2U_{13}h\ell\,\underline{a}^*.\underline{c}^* + 2U_{23}k\ell\,\underline{b}^*.\underline{c}^*\right)\right\}$$

The appropriate estimated standard deviations derived from the inverse of the least-squares matrix are included in Tables 1.3 and 1.4 . The final coordinates expressed in Angstroms are listed in Table 1.5 .

Intramolecular bond distances are given in Table 1.6 and valency angles are given in Table 1.7 . The average estimated standard deviations for C - C, C - O and C - Br bonds are 0.03, 0.02 and 0.01 Å respectively, and for valency angles is 1.5° . These should be regarded as minimum values. Some intramolecular non-bonded distances are listed in Table 1.8 and all intermolecular distances $<$ 4 Å are listed in Table 1.9 . Details of all best-plane calculations are given in Table 1.10 .

The atomic numbering system used in all the tables is shown in Figure 1.3 , and the molecular packing viewed down the a - axis is shown in Figure 1.4 .

1.2.5 The Determination of the Absolute Stereochemistry

An examination of the $h1\ell$ and $h2\ell$ series of Weissenberg photographs indexed with respect to a right-handed set of axes revealed 20 pairs of $h1\ell$ and $\bar{h}1\ell$ and 5 pairs of $h2\ell$ and $\bar{h}2\ell$ reflexions with differing intensities. This demonstrates the breakdown of Friedel's Law as a result of the anomalous scattering of X-rays by the bromine atoms.

Using a complex scattering curve for bromine (International Tables for Crystallography, Vol. III), structure factors were calculated corresponding to the 25 pairs of reflexions observed to have different intensities. It was found that the ratio of the observed intensities for each pair of reflexions was a correct prediction of the ratio of the squares of the corresponding structure factors for all but three pairs of reflexions. Details of the reflexions and ratios involved are given in Table 1.11 . On the basis of this agreement (Bijvoet, 1949) it was concluded that the atomic parameters represented a model with the correct absolute stereochemistry, and this is shown in all drawings of the molecule.

TABLE 1.1

COURSE OF REFINEMENT

Cycles	Parameters refined	Final R	Final R'	$\sum w\Delta^2$
1 - 3	x, y, z, U_{iso} for Br, O, C, Layer scale factors, Full matrix, unit weights.	0.191	0.0412	30,238
4 - 6	x, y, z, U_{iso} for Br, O, C, Overall scale factor, Full matrix, weighting scheme adjusted.	0.188	0.0338	12,966
7 -11	x, y, z, U_{ij} for Br, O, C, Overall scale factor, Block diagonal, weighting scheme applied.	0.103	0.0139	4,451

TABLE 1.2

Observed and final-calculated structure amplitudes.

H	K	L	Fo	Fc
1	0	1	79.5	80.4
1	0	2	56.3	55.9
1	0	3	89.9	104.0
1	0	4	30.5	25.6
1	0	5	13.0	4.7
1	0	6	12.0	10.4
1	0	7	134.7	133.2
1	0	8	12.7	12.5
1	0	9	43.2	43.2
1	0	10	17.4	14.0
1	0	11	79.8	75.5
1	0	12	25.5	24.5
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1	0	15	22.2	28.7
1	0	16	11.5	10.9
1	0	17	8.8	5.2
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2	0	1	37.4	41.6
2	0	2	31.9	23.9
2	0	3	46.7	43.9
2	0	4	31.1	27.2
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2	0	6	41.2	30.2
2	0	7	5.2	8.5
2	0	8	45.8	39.5
2	0	9	5.8	0.0
2	0	10	56.4	56.6
2	0	11	14.0	14.1
2	0	12	29.8	30.1
2	0	13	21.8	23.3
2	0	14	13.2	11.0
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2	0	16	14.3	16.4
2	0	17	14.8	14.4
2	0	18	12.8	10.0
2	0	19	11.6	10.8
2	0	20	14.0	12.5
2	0	21	5.5	5.2
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2	0	23	3.7	10.7
2	0	24	12.6	13.0
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2	0	26	3.6	4.6
2	0	27	4.1	2.9
3	0	1	20.6	19.7
3	0	2	48.1	47.4
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3	0	22	11.0	8.9
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3	0	26	7.1	5.9
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4	0	11	2.4	2.8
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2	3	14	12.1	14.3
2	3	15	14.5	17.1
2	3	16	9.2	9.3
2	3	17	13.3	15.2
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2	3	19	12.4	12.8
2	3	20	6.8	8.4
2	3	21	6.7	6.9
2	3	22	6.4	5.8
3	3	0	25.0	23.7
3	3	1	27.7	27.6
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3	3	3	30.5	28.3
3	3	4	27.1	27.4
3	3	5	9.0	8.2
3	3	6	62.4	65.5
3	3	7	10.2	12.9
3	3	8	16.8	19.2
3	3	9	27.3	24.5
3	3	10	3.2	13.4
3	3	11	29.5	30.5
3	3	12	17.6	17.5
3	3	13	15.2	16.2
3	3	14	11.7	12.5
3	3	15	3.8	[illegible]
3	3	16	14.4	16.9
3	3	17	12.4	12.4
3	3	18	6.8	6.5
3	3	19	8.7	11.7
3	3	20	7.7	10.4
3	3	21	8.3	10.3
3	3	22	4.1	8.4
4	3	0	21.8	24.1
4	3	1	24.1	23.2
4	3	2	8.5	9.3
4	3	3	12.8	12.6
4	3	4	6.9	8.9
4	3	5	23.0	22.9
4	3	6	7.2	6.7
4	3	7	13.9	[illegible]
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4	3	9	23.9	25.8
4	3	10	28.8	32.7
4	3	11	23.6	27.5
4	3	12	25.8	29.0
4	3	13	5.4	6.6
4	3	15	5.5	6.3
4	3	17	6.8	8.5
4	3	18	5.5	7.3
4	3	19	8.4	10.9
4	3	20	7.3	9.5
4	3	21	4.9	6.9
4	3	22	4.6	5.6
5	3	0	6.9	4.2
5	3	1	16.2	16.1
5	3	2	13.6	21.5
5	3	3	21.0	21.9
5	3	4	8.6	10.0
5	3	5	8.7	10.8
5	3	6	10.2	10.3
5	3	7	10.4	7.6
5	3	8	8.3	7.0
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5	3	10	10.8	11.6
5	3	11	7.7	8.3
5	3	12	6.8	7.2
5	3	13	6.8	8.2
5	3	14	3.9	4.4
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6	3	1	7.7	9.7
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6	3	7	5.5	6.1
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1	4	6	23.0	22.3
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1	4	8	20.5	21.8
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2	4	9	21.6	[illegible]
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2	4	12	37.9	30.0
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2	4	14	21.9	22.4
2	4	15	27.7	20.3
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2	4	19	5.8	5.3
2	4	20	8.7	12.0
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2	4	22	5.1	6.7
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3	4	1	31.5	30.9
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3	4	3	10.1	11.9
3	4	4	31.1	32.3
3	4	5	34.2	35.1
3	4	6	37.4	39.0
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3	4	8	13.4	12.3
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3	4	10	14.1	15.3
3	4	11	7.8	[illegible]
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4	4	0	4.8	3.8
4	4	1	13.3	15.1
4	4	2	12.7	11.6
4	4	3	33.2	[illegible]
4	4	4	10.4	10.8
4	4	5	[illegible]	16.9
4	4	7	19.5	21.3
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5	4	16	6.6	9.2
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6	4	4	5.6	6.8
6	4	5	7.9	10.0
6	4	6	8.8	11.1
6	4	7	8.9	13.1
6	4	8	5.6	6.2
6	4	9	6.8	9.2
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1	5	10	22.9	21.1
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1	5	12	[illegible]	6.2
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1	5	21	4.4	5.9
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2	5	16	3.6	4.7
2	5	17	3.6	5.6
2	5	18	12.6	11.6
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3	5	2	33.2	35.3
3	5	3	23.4	23.1
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3	5	5	24.6	23.7
3	5	6	17.2	16.0
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3	5	8	12.2	9.6
3	5	9	12.4	9.4
3	5	10	16.5	16.8
3	5	11	19.0	18.6
3	5	12	17.6	[illegible]
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3	5	15	9.3	6.7
3	5	16	10.3	7.0
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3	5	20	10.5	9.5
3	5	21	5.4	[illegible]
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4	5	2	15.7	15.0
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4	5	7	9.4	[illegible]
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4	5	11	21.2	21.5
4	5	12	10.2	[illegible]
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4	5	16	5.1	5.1
4	5	17	6.1	6.4
4	5	18	6.3	8.4
4	5	19	7.9	6.1
4	5	20	4.3	4.4
4	5	21	4.9	5.6
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6	5	9	6.0	7.2
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2	6	8	10.8	4.9
2	6	9	12.5	9.7
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2	6	12	16.3	[illegible]
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2	6	14	13.2	13.4
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2	6	16	3.9	6.9
2	6	17	4.4	3.8
2	6	18	10.7	12.2
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3	6	6	12.5	[illegible]
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4	6	12	10.4	[illegible]
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4	6	15	5.3	8.5
4	6	16	5.2	3.3
4	6	17	[illegible]	3.9
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6	6	0	4.9	5.5
6	6	1	4.4	3.0
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1	7	14	17.0	15.3
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2	7	3	27.1	29.5
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2	7	6	11.8	14.1
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2	7	12	7.2	4.9
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4	7	1	9.3	4.7
4	7	2	6.9	5.8
4	7	3	2.8	2.8
4	7	4	10.2	18.0
4	7	5	4.1	3.8
4	7	6	4.1	4.2
4	7	7	4.3	6.4
4	7	8	5.1	4.0
4	7	9	4.2	2.8
4	7	10	10.0	13.3
4	7	11	5.2	2.1
4	7	12	4.2	2.3
4	7	13	7.1	4.0
4	7	14	4.9	4.5
4	7	15	2.8	3.7
4	7	16	3.3	4.7
4	7	17	3.8	4.2
4	7	18	4.7	4.3
4	7	19	3.6	2.1
4	7	20	5.9	6.2
5	7	1	7.3	7.8
5	7	2	5.2	5.2
5	7	3	11.2	9.0
5	7	4	3.0	3.4
5	7	5	10.4	4.9
5	7	6	7.3	6.0
5	7	7	11.1	[illegible]
5	7	9	4.0	3.0
5	7	11	[illegible]	6.3
5	7	12	5.0	4.5
5	7	13	4.3	6.5
5	7	14	2.0	3.5
5	7	15	2.4	3.3
5	7	16	2.3	2.8
5	7	17	4.2	3.1
5	7	18	3.2	3.6
6	7	0	2.2	6.5
6	7	2	6.5	2.0
6	7	4	5.1	[illegible]
6	7	5	2.3	3.5
6	7	6	5.5	4.3
6	7	8	6.6	5.0
6	7	10	2.1	2.5
6	7	11	4.3	4.1
6	7	12	4.1	3.2
6	7	13	3.2	3.0
6	7	14	4.1	3.0
0	7	3	[illegible]	[illegible]
0	7	5	14.9	12.4
0	7	7	21.4	[illegible]
0	7	8	11.0	4.1
0	7	9	15.1	[illegible]
0	7	11	15.4	11.6
0	7	12	14.4	13.1
0	7	13	17.4	12.0
0	7	15	14.0	11.4
0	7	18	5.0	4.0
0	7	19	5.6	4.7
0	7	21	2.6	2.3

TABLE 1.3

FRACTIONAL COORDINATES AND E.S.D.S

ATOM	x/a	y/b	z/c
C(1)	-0.0303 ± 26	0.0320 ± 22	0.7514 ± 7
C(2)	0.1495 ± 20	0.1008 ± 18	0.7543 ± 6
C(3)	0.2809 ± 19	0.0293 ± 17	0.7932 ± 6
C(4)	0.3169 ± 23	-0.1087 ± 20	0.7779 ± 6
C(5)	0.4232 ± 26	-0.1955 ± 20	0.8249 ± 8
C(6)	0.5892 ± 24	-0.1074 ± 22	0.8438 ± 8
C(7)	0.5875 ± 24	-0.0151 ± 22	0.8874 ± 8
C(8)	0.4305 ± 23	0.0172 ± 20	0.9256 ± 7
C(9)	0.2921 ± 21	0.0959 ± 16	0.8951 ± 6
C(10)	0.1439 ± 22	0.1435 ± 18	0.9377 ± 6
C(11)	-0.0020 ± 21	0.2306 ± 16	0.9095 ± 7
C(12)	0.0521 ± 22	0.3737 ± 16	0.8996 ± 6
C(13)	-0.0519 ± 23	0.4712 ± 17	0.9100 ± 7
C(14)	-0.0125 ± 21	0.6169 ± 21	0.9013 ± 6
C(15)	0.0085 ± 26	0.7393 ± 22	0.8945 ± 8
C(16)	0.0058 ± 23	0.0343 ± 21	1.0166 ± 7
C(17)	-0.0616 ± 29	-0.0999 ± 22	1.0367 ± 8
O(1)	0.2036 ± 12	0.0239 ± 10	0.8511 ± 3
O(2)	0.0760 ± 14	0.0250 ± 10	0.9621 ± 4
O(3)	0.0032 ± 17	0.1385 ± 13	1.0415 ± 4
Br	0.45140 ± 33	-0.11014 ± 27	0.70478 ± 9

TABLE 1.4

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S

(in Å^2)

ATOM	U11	U22	U33	2U23	2U31	2U12
C(1)	0.094	0.103	0.069	-0.040	0.013	-0.034
	13	15	9	20	19	25
C(2)	0.079	0.051	0.065	0.041	-0.001	-0.020
	10	11	8	17	15	19
C(3)	0.069	0.065	0.052	-0.015	0.031	0.002
	10	11	7	16	15	17
C(4)	0.108	0.056	0.062	0.004	0.029	0.052
	13	11	8	17	17	24
C(5)	0.088	0.066	0.090	0.025	-0.018	-0.004
	12	13	11	19	21	21
C(6)	0.084	0.061	0.117	0.044	-0.014	0.001
	12	12	13	23	21	22
C(7)	0.070	0.090	0.101	0.055	-0.012	0.018
	11	15	12	22	20	22
C(8)	0.069	0.085	0.075	-0.013	-0.019	0.019
	11	14	9	18	18	22
C(9)	0.085	0.034	0.058	-0.014	0.008	-0.027
	10	10	7	14	14	18
C(10)	0.078	0.059	0.064	-0.019	0.016	-0.012
	11	13	8	15	15	18
C(11)	0.074	0.043	0.082	0.001	-0.022	0.014
	10	11	9	15	16	17
C(12)	0.082	0.037	0.079	0.011	-0.005	0.014
	10	10	9	16	17	19
C(13)	0.079	0.045	0.079	0.020	-0.003	-0.017
	10	10	9	16	18	18
C(14)	0.070	0.093	0.070	0.009	-0.003	0.022
	10	14	9	20	16	23
C(15)	0.096	0.083	0.092	-0.022	-0.015	-0.001
	14	14	11	21	22	25

TABLE 1.4 (contd.)

ATOM	U11	U22	U33	2U23	2U31	2U12
C(16)	0.067	0.101	0.082	-0.039	-0.011	0.035
	11	15	10	21	18	22
C(17)	0.132	0.056	0.113	0.060	0.094	0.014
	16	13	13	22	26	28
O(1)	0.064	0.034	0.049	0.009	0.018	-0.004
	6	6	5	8	9	10
O(2)	0.087	0.035	0.061	0.013	0.047	-0.010
	7	6	5	9	11	11
O(3)	0.110	0.072	0.071	-0.014	0.018	0.025
	9	9	6	11	13	15
Br	0.141	0.109	0.084	-0.003	0.071	0.075
	2	2	1	3	3	3

TABLE 1.5

COORDINATES AND E.S.D.S IN ANGSTROMS WITH RESPECT TO THE CRYSTAL AXES

ATOM	X	Y	Z
C(1)	-0.234 ± 20	0.310 ± 21	17.229 ± 17
C(2)	1.151 ± 15	0.978 ± 18	17.297 ± 14
C(3)	2.163 ± 15	0.284 ± 17	18.188 ± 14
C(4)	2.441 ± 18	-1.054 ± 19	17.837 ± 14
C(5)	3.259 ± 20	-1.896 ± 19	18.915 ± 17
C(6)	4.537 ± 18	-1.041 ± 21	19.347 ± 19
C(7)	4.524 ± 19	-0.146 ± 21	20.347 ± 18
C(8)	3.315 ± 18	0.167 ± 20	21.225 ± 15
C(9)	2.249 ± 16	0.930 ± 16	20.524 ± 13
C(10)	1.108 ± 17	1.392 ± 18	21.501 ± 14
C(11)	-0.016 ± 16	2.237 ± 16	20.856 ± 15
C(12)	0.401 ± 17	3.625 ± 16	20.629 ± 14
C(13)	-0.400 ± 18	4.571 ± 17	20.867 ± 15
C(14)	-0.096 ± 16	5.983 ± 20	20.667 ± 15
C(15)	0.065 ± 20	7.171 ± 21	20.511 ± 18
C(16)	0.045 ± 17	0.333 ± 21	23.311 ± 17
C(17)	-0.474 ± 23	-0.969 ± 21	23.772 ± 19
O(1)	1.568 ± 9	0.232 ± 9	19.516 ± 8
O(2)	0.585 ± 11	0.242 ± 10	22.061 ± 9
O(3)	0.025 ± 13	1.344 ± 12	23.881 ± 10
Br	3.4758± 25	-1.0684± 26	16.1606± 21

TABLE 1.6

INTRAMOLECULAR BONDED DISTANCES AND E.S.D.S (in Å)

ATOM A	ATOM B	A-B	ATOM A	ATOM B	A-B
C(1) -	C(2)	1.54 ± 3Å	C(12)-	C(13)	1.26 ± 2Å
C(2) -	C(3)	1.52 ± 2	C(13)-	C(14)	1.46 ± 3
C(3) -	C(4)	1.41 ± 3	C(14)-	C(15)	1.21 ± 3
C(4) -	C(5)	1.59 ± 3	C(16)-	C(17)	1.48 ± 3
C(5) -	C(6)	1.60 ± 3	O(1) -	C(3)	1.46 ± 2
C(6) -	C(7)	1.34 ± 3	O(1) -	C(9)	1.40 ± 2
C(7) -	C(8)	1.53 ± 3	O(2) -	C(10)	1.38 ± 2
C(8) -	C(9)	1.49 ± 2	O(2) -	C(16)	1.37 ± 2
C(9) -	C(10)	1.57 ± 2	O(3) -	C(16)	1.16 ± 2
C(10)-	C(11)	1.55 ± 2	Br -	C(4)	1.97 ± 1
C(11)-	C(12)	1.47 ± 2			

TABLE 1.7

VALENCY ANGLES AND E.S.D.S (in degrees)

ATOM A	ATOM B	ATOM C	A-B-C	ATOM A	ATOM B	ATOM C	A-B-C
C(1) -	C(2) -	C(3)	115.3° 1.4	C(10)-	C(9) -	O(1)	103.9° 1.2
C(2) -	C(3) -	C(4)	114.8 1.3	C(9) -	C(10)-	C(11)	115.4 1.2
C(2) -	C(3) -	O(1)	106.2 1.1	C(9) -	C(10)-	O(2)	106.4 1.3
C(4) -	C(3) -	O(1)	105.9 1.2	C(11)-	C(10)-	O(2)	110.4 1.3
C(3) -	C(4) -	C(5)	115.7 1.3	C(10)-	C(11)-	C(12)	112.1 1.4
C(3) -	C(4) -	Br	108.8 1.2	C(11)-	C(12)-	C(13)	120.0 1.6
C(5) -	C(4) -	Br	107.6 1.2	C(12)-	C(13)-	C(14)	124.6 1.6
C(4) -	C(5) -	C(6)	108.1 1.5	C(13)-	C(14)-	C(15)	175.6 1.8
C(5) -	C(6) -	C(7)	123.4 1.7	C(17)-	C(16)-	O(2)	111.5 1.6
C(6) -	C(7) -	C(8)	124.9 1.7	C(17)-	C(16)-	O(3)	127.5 1.6
C(7) -	C(8) -	C(9)	113.7 1.3	O(2) -	C(16)-	O(3)	120.9 1.7
C(8) -	C(9) -	C(10)	112.3 1.2	C(3) -	O(1) -	C(9)	116.1 1.1
C(8) -	C(9) -	O(1)	115.6 1.3	C(10)-	O(2) -	C(16)	117.8 1.3

TABLE 1.8

INTRAMOLECULAR NON-BONDED DISTANCES (in Å)

ATOM A ATOM B	A-B	ATOM A ATOM B	A-B
C(1)...C(4)	3.06Å	C(5)...O(1)	2.78Å
C(1)...O(1)	2.91	C(6)...C(9)	3.24
C(2)....Br	3.30	C(6)...O(1)	3.23
C(2)...O(1)	2.38	C(7)...O(1)	3.09
C(3)...C(6)	2.96	C(8)...O(2)	2.86
C(3)...C(7)	3.23	C(10)...O(3)	2.62
C(3)...C(8)	3.25	C(11)...O(1)	2.89
C(4)...C(7)	3.39	C(11)...O(3)	3.15
C(4)...C(9)	3.35	C(11)...C(16)	3.11
C(5)...C(8)	3.10	O(1)...O(2)	2.72
C(5)...C(9)	3.40		

TABLE 1.9

INTERMOLECULAR DISTANCES (in Å) <4 Å

ATOM A ATOM B	E.P.	distance Å
C(1)...C(6)	i	3.86
C(1)...C(12)	i	3.79
C(1)...C(13)	ii	3.80
C(1)...C(14)	ii	3.61
C(1)...C(15)	ii	3.91
C(2)...C(14)	ii	3.72
C(2)...C(15)	ii	3.86
C(4)...C(15)	iii	3.87
C(6)...C(15)	iv	3.74
C(7)...C(11)	v	3.99
C(15)...O(1)	vi	3.29
C(15)...O(2)	vi	3.22
C(15)...C(17)	vi	3.66

Equivalent positions are:-

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

Transformations should be applied to the coordinates of the second atom.

TABLE 1.10

Best-planes calculated through various atoms of the molecule.

Atoms Defining the Planes

PLANE 1	C(5), C(6), C(7), C(8)
PLANE 2	C(4), C(5), C(8), C(9)
PLANE 3	C(11), C(12), C(13), C(14), C(15)
PLANE 4	C(16), C(17), O(2), O(3)

Plane Equations

PLANE 1	$-0.2710X + 0.7203Y - 0.6386Z = -14.3293$
PLANE 2	$0.7829X + 0.4949Y - 0.3769Z = -5.4213$
PLANE 3	$-0.3520X + 0.0594Y - 0.9341Z = -19.6187$
PLANE 4	$-0.8909X + 0.2112Y - 0.4020Z = -9.3399$

Distances of Atoms (in Å) From the Planes

PLANE 1	C(5)	0.0020	C(7)	0.0049
	C(6)	-0.0048	C(8)	-0.0022

TABLE 1.10 (contd.)

PLANE 2	C(4)	0.0879	C(8)	0.1001
	C(5)	-0.0949	C(9)	-0.0930
PLANE 3	C(11)	0.0094	C(14)	-0.0081
	C(12)	-0.0075	C(15)	0.0102
	C(13)	-0.0040		
PLANE 4	C(16)	-0.0014	O(2)	0.0004
	C(17)	0.0004	O(3)	0.0006

TABLE 1.11

DETAILS OF ANOMALOUS SCATTERING CALCULATION

h	k	ℓ	$I(-h)/I(+h)$	$\lvert F(-h)\rvert^2 / \lvert F(+h)\rvert^2$
1	1	8	1.2	1.1
		9	0.8	0.7
		11	1.5	1.1
		15	1.4	1.1
		18	1.3	1.1
		19*	0.7	1.2
		20	1.2	1.1
		23	>1.0	1.2
		24	2.0	1.3
		25*	1.3	1.0
2	1	10	1.2	1.1
		14	1.5	1.1
		19	0.5	0.4
3	1	16	1.3	1.6
		17*	1.3	0.9
		18	1.4	1.1
		19	1.4	1.1
		21	1.5	1.2
		23	2.0	1.2
1	2	5	0.7	0.9
2	2	2	0.6	0.9
		5	>1.0	1.2
3	2	5	0.6	0.9
		3	<1.0	0.9

* denotes a disagreement

TABLE 1.12

INFRA-RED ABSORPTION DATA FOR LAURENCIN

NUJOL MULL		CCl_4 SOLN.	
ν_{C-H}	3252 cm^{-1}	ν_{C-H}	3312 cm^{-1}
$\Delta\nu^{a}_{1/2}$	6	$\Delta\nu^{a}_{1/2}$	16
		ε_a	175 units
$\nu_{C=O}$	1731 cm^{-1}	$\nu_{C=O}$	1749 cm^{-1}
$\Delta\nu^{a}_{1/2}$	8	$\Delta\nu^{a}_{1/2}$	17
		ε_a	550 units
ν_{C-O}	1248 cm^{-1}	ν_{C-O}	1233 cm^{-1}
$\Delta\nu^{a}_{1/2}$	11	$\Delta\nu^{a}_{1/2}$	20
		ε_a	680 units

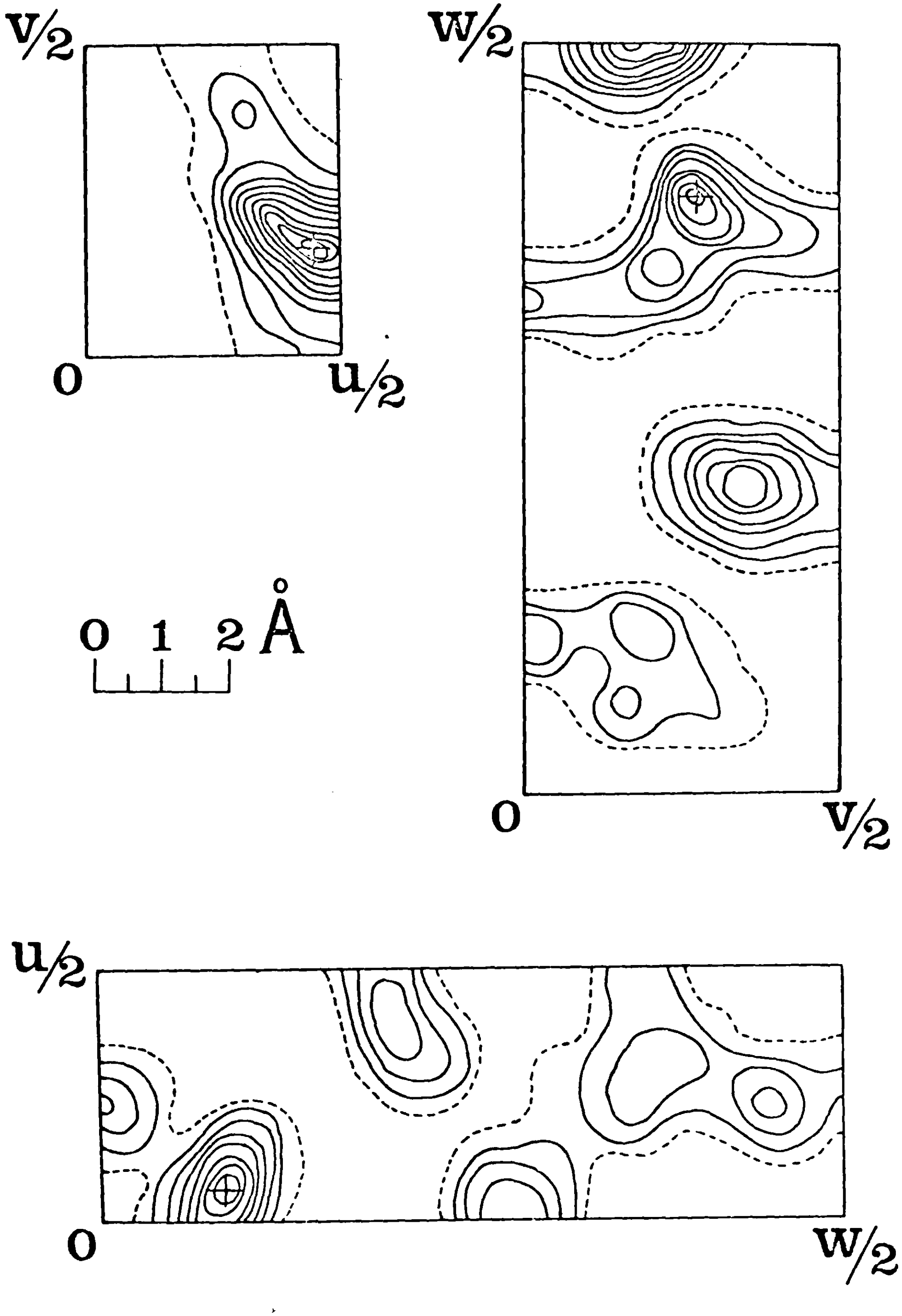
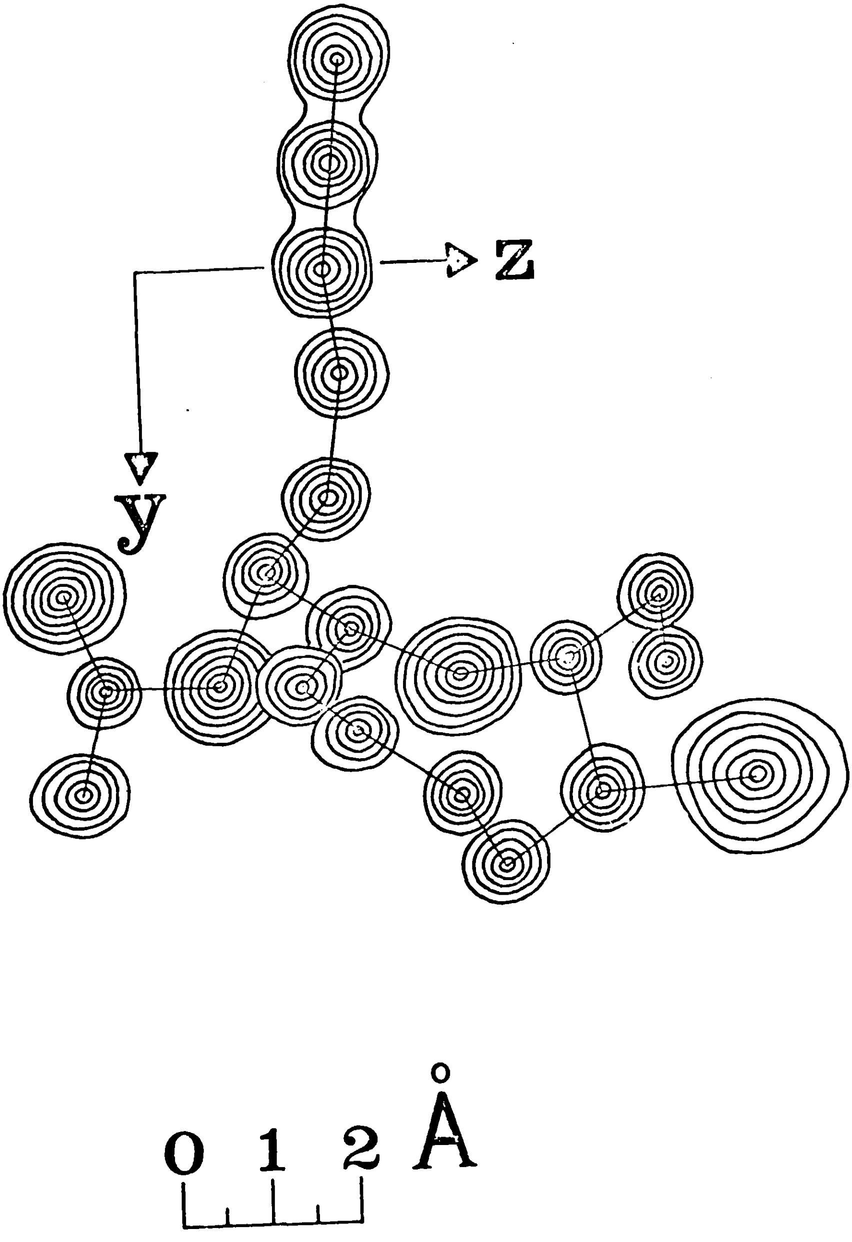

v/2
0
u/2
w/2
0
v/2
0 1 2 Å
u/2
0
w/2

FIGURE 1.2

Superimposed sections of the final electron-density distribution viewed down the a-axis. Contour-levels are at intervals of 1e/Å^3 except around the bromine atom where they are at intervals of 5e/Å^3.



z
y
0 1 2 Å

FIGURE 1.3

Atomic numbering scheme.

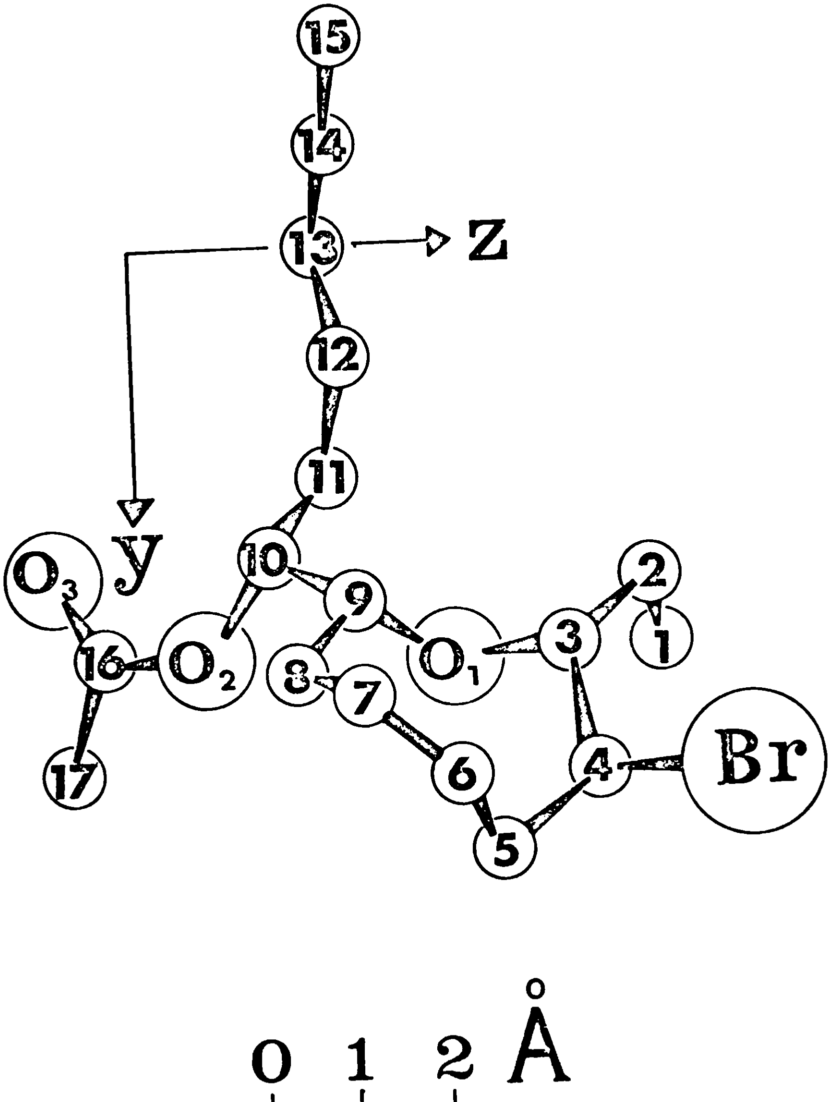

15
14
13
Z
12
11
y
10
O_3
9
2
O_1
3
1
16
O_2
8
7
6
4
Br
5
17
0 1 2 Å

FIGURE 1.4

The molecular packing viewed down the a-axis. The C...O contacts involved in the bifurcated hydrogen bonding are shown by broken lines.

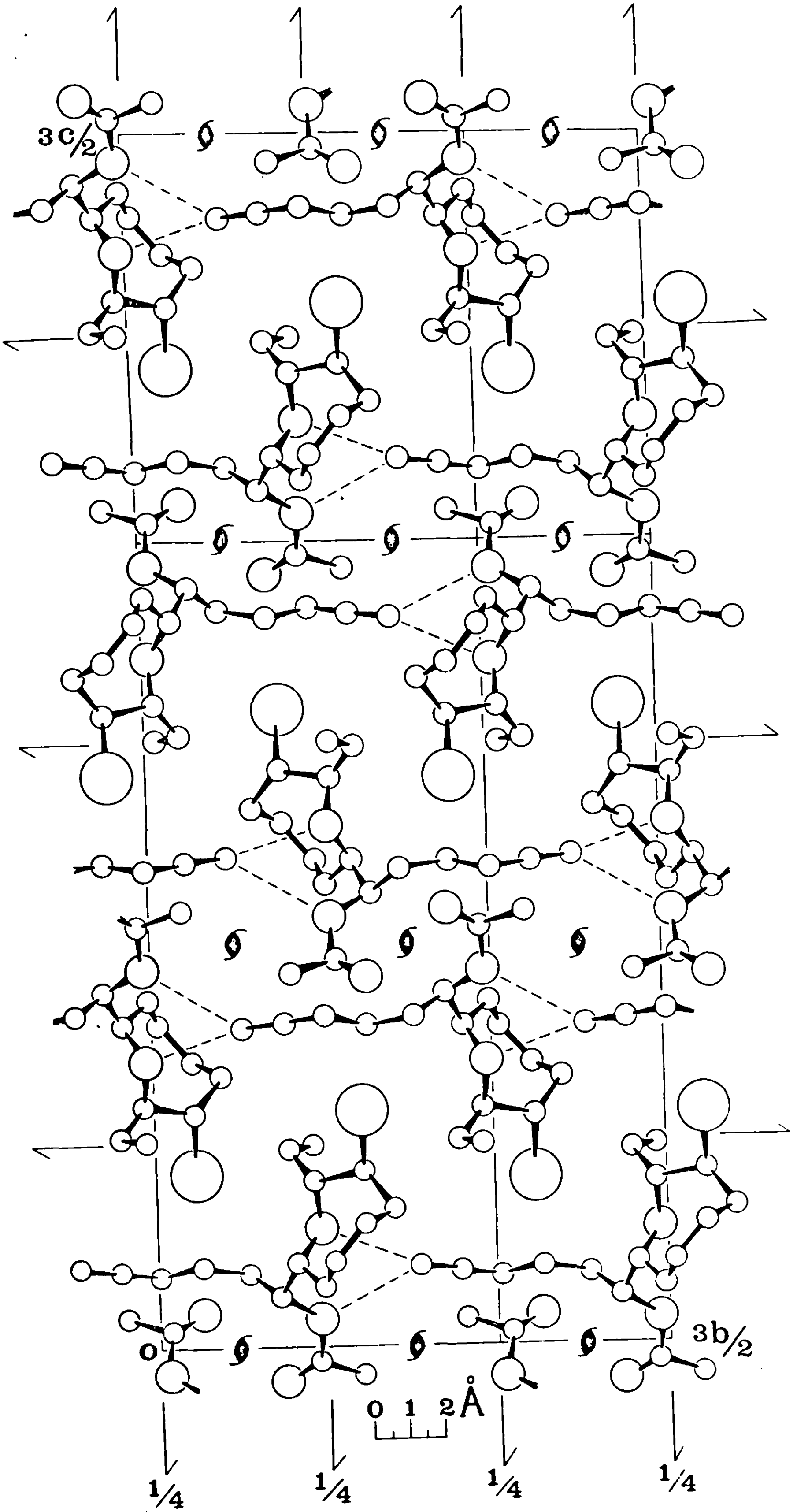

3c/2
0
3b/2
0 1 2 Å
1/4
1/4
1/4
1/4

FIGURE 1.5

Conformation of the eight-membered ring viewed along the best-plane calculated through atoms C(4), C(5), C(8) and C(9).

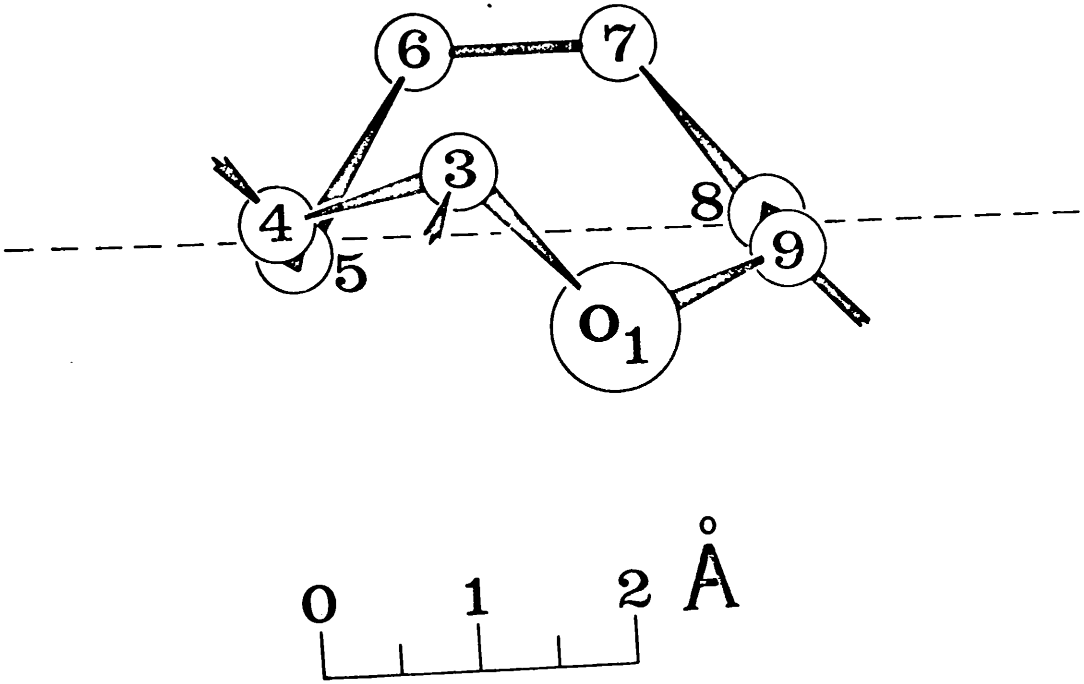

6
7
3
4
5
8
9
O1
0
1
2
Å

FIGURE 1.6

Torsional angles about the bonds of the eight-membered ring.

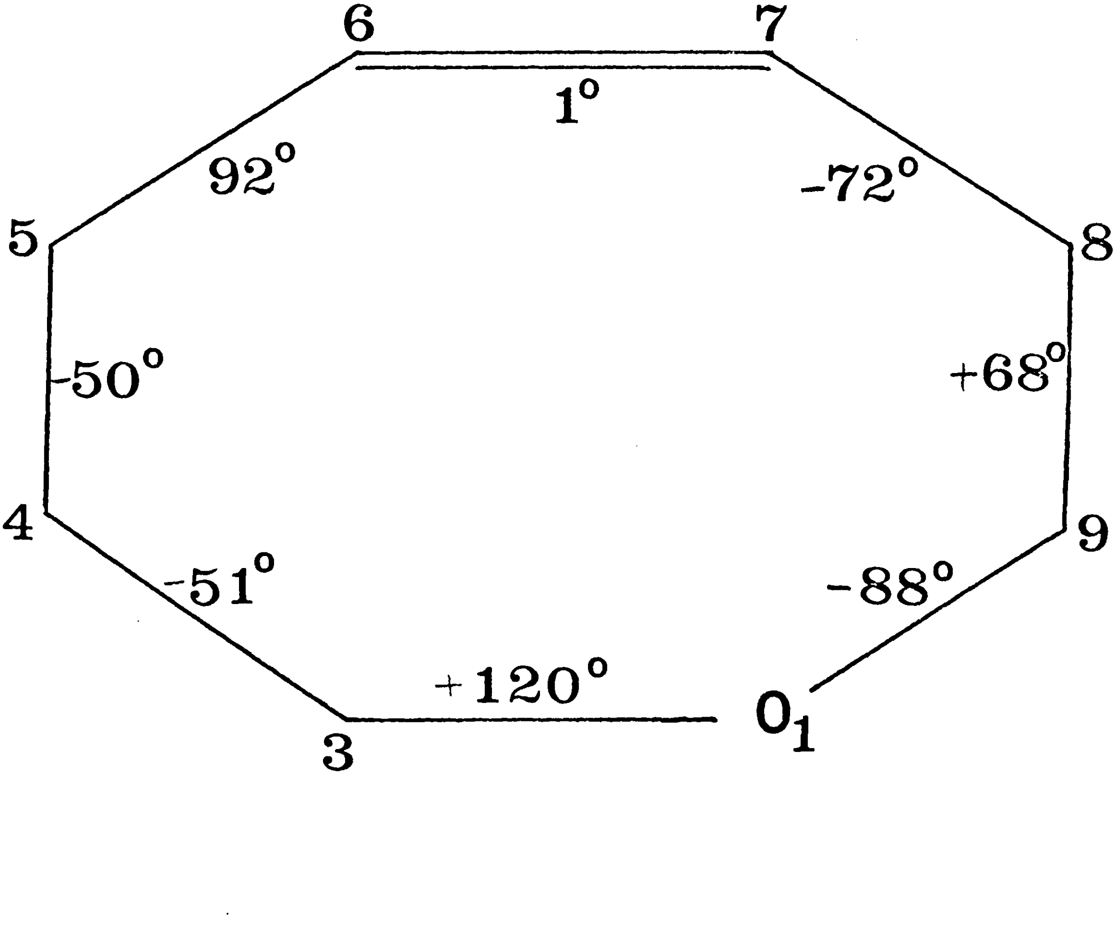
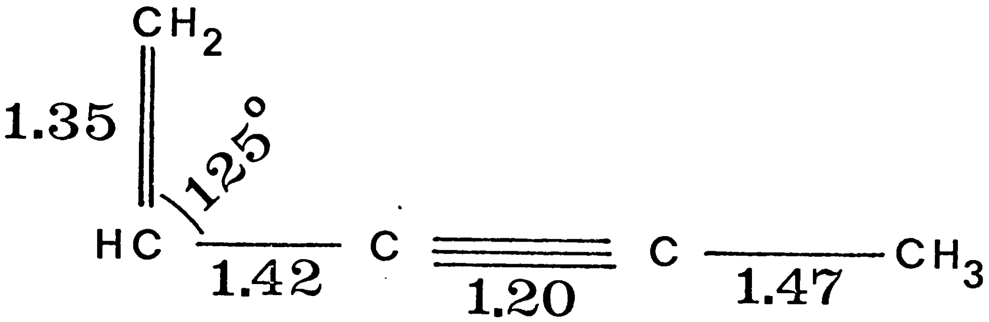
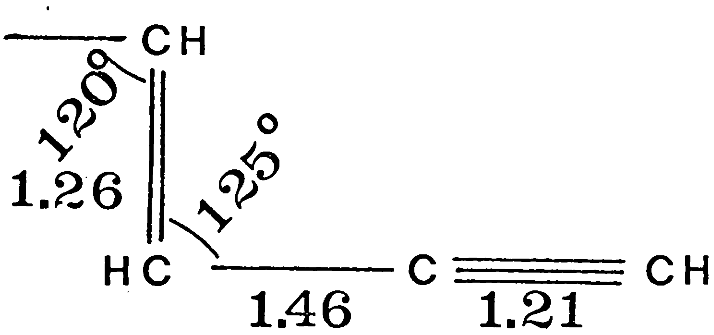

6
7
1°
92°
-72°
5
8
-50°
+68°
4
9
-51°
-88°
+120°
3
0₁

FIGURE 1.7

Comparison of the ethynyl side-chain of laurencin with pirylene.



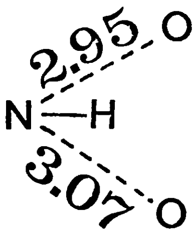
pirylene



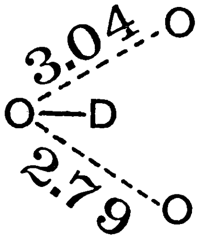
laurencin

FIGURE 1.8

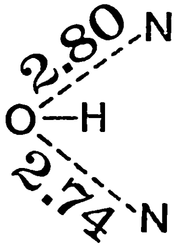
Some contacts involved in bifurcated hydrogen bonding.



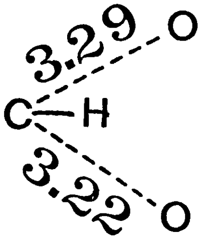
glycine



perdeuterated violuric acid



8-hydroxyquinoline

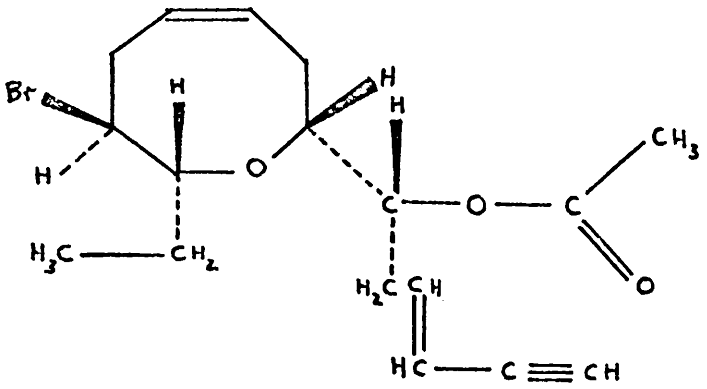


laurencin

1.3 DISCUSSION

The present analysis has established both the structure and the absolute stereochemistry of laurencin as II . With a knowledge of the relative stereochemistry (also from the structure analysis), Irie and his co-workers (1967) were able to deduce that the absolute stereochemistry at C(10) was $\overset{R}{S}$ (Prelog's convention). This is in complete agreement with the crystallographically derived absolute stereochemistry.

The conformation of the eight-membered ring is illustrated in Figure 1.5 , and Figure 1.6 shows the torsional angles around the bonds of the ring. Best-plane calculations (Table 1.10) involving various sets of four atoms within the ring show that, within experimental error, the four atoms of the *cis*-double bond are planar, but that no other combination of four atoms within the ring is planar. That the bond distances, valency angles and planarity of the *cis*-double bond grouping are relatively undistorted indicates that this grouping is the dominant feature of the ring conformation, holding four of the eight atoms in a rigid and predetermined arrangement. The remaining atoms of the ring must then arrange themselves to minimise transannular steric interactions and eclipsing of the substituents about each bond of the ring. Examination of the intramolecular non-bonded distances (Table 1.8) shows that there are no serious transannular interactions, and an examination of the torsional angles on a molecular model reveals



II

that the maximum staggering of all substituents has taken place wherever possible.

The radiation damage which rendered the original set of data unsuitable for the refinement of the structure may also have affected the photographic intensity data. Thus, the carbon atom C(4), which is bonded to the bromine atom and was the last atom to be located in the electron-density distributions calculated with the diffractometer data, is involved in an apparently short bond (C(3) - C(4) 1.41 Å) . All other bond distances and valency angles within the eight-membered ring do not differ significantly from accepted literature values for similar bond types (Sutton et al., 1965) .

The bond lengths and valency angles in the ethynyl side-chain of laurencin may be compared with the corresponding values found in pirylene (buta-1-ene-3-yne) by Spurr and Schomaker (1942). Pirylene and the relevant laurencin moiety with corresponding values of bond distances and angles are shown in Figure 1.7 . The C(12) - C(13) - C(14) valency angle of 125° is remarkably similar in both cases despite the high estimated standard deviation of 1.6° in the case of laurencin. If significant, the deviation from the expected value of 120° can be explained in terms of steric interaction between the hydrogen of C(12) and the acetylene group. An examination of the atomic deviations from the best-plane (Table 1.10) through atoms C(11),.....,C(15) shows that, within experimental error, the ethynyl side-chain is planar.

None of the other bond distances in laurencin differ significantly from accepted values. Slight deviations from expected values of valency angles, if significant, are explicable in terms of non-bonded steric interactions. For example, the C(1) - C(2) - C(3) angle of 115.3° and the C(2) - C(3) - C(4) angle of 114.8° may be explained by interaction between the bromine atom and the ethyl side-chain, increasing the Br...C(2) non-bonded distance to 3.30 Å (Table 1.8). The best-plane (Table 1.10) calculated through atoms O(2), O(3), C(16) and C(17) shows that within experimental error the acetyl group is planar.

The infra-red absorption data given in Table 1.12 (Eglinton, Ferguson, Islam and Glasby, 1968) for laurencin in the solid state and in solution indicate strong $-C\equiv C-H\cdots\cdot O-$ hydrogen bonding in the solid state. The hydrogen bonding was originally interpreted as involving O(3), the only carbonyl oxygen in laurencin, in hydrogen bonding reminiscent of the type found in the benzoyl acetylenes by Ferguson and Islam (1966). This interpretation was based on the fact that marked shifts in carbonyl frequency were observed from solid to solution. However, examination of the molecular packing reveals that the ethynyl side-chain is directed towards the ether oxygens O(1) and O(2) of an adjacent molecule, and is in no way close to the carbonyl oxygen O(3) . The carbon-oxygen intermolecular distances have the values C(15)...O(1) 3.29±0.02 Å and C(15)...O(2) 3.22±0.02 Å , and are shown by broken lines in the molecular packing diagram Figure 1.4. Since the stretching frequency of the acetylenic hydrogen implies hydrogen bonding, this hydrogen must be involved in a bifurcated hydrogen bond with both the ether oxygens O(1) and O(2).

Bifurcated hydrogen bonds have been reported several times in the literature. Albrecht and Corey (1939), Marsh (1958) and Burns and Levy (1958) have reported a bifurcated hydrogen bond in glycine; Craven and Takei (1964) have reported a bifurcated deuterium bond in perdeuterated violuric acid; and Baur (1965) has reported bifurcated hydrogen bonds in acid salts. Recently Prout and Wheeler (1967) have found such a bond in 8-hydroxyquinoline. Unfortunately none of these instances involves an acetylenic hydrogen, but it has been noted (Prout and Wheeler, 1967) that the contacts in each case are longer than would normally be expected for hydrogen bonding. The contacts of 3.29 Å and 3.22 Å in the case of laurencin do not refute this observation. A comparison of the types of contacts involved in bifurcated hydrogen bonding is made in Figure 1.8 .

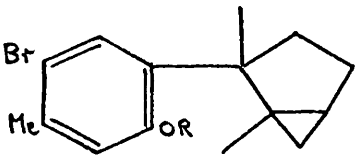
The hydrogen bonding does not, however, explain the observed shift in carbonyl frequency (Table 1.12) for laurencin. Examination of the molecular packing shows that both the ethynyl and to a lesser extent the carbonyl groups are, to a good approximation, always aligned along one crystal direction. This group orientation will result in sharpening of the carbonyl and ethynyl-hydrogen absorptions in the solid state. Polar effects occasioned in the carbonyl group by the adjacent ether oxygens and heightened by the group orientation, could well give rise to the observed shifts in carbonyl frequency from solid to solution.

CHAPTER 2 THE CRYSTAL STRUCTURE OF LAURINTEROL ACETATE, THE STRUCTURE AND ABSOLUTE STEREOCHEMISTRY OF LAURINTEROL, THE ABSOLUTE STEREOCHEMISTRIES OF APLYSIN AND APLYSINOL.

2.1 INTRODUCTION

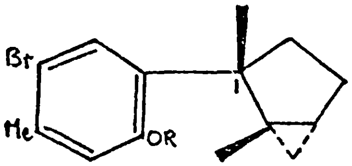
The isolation of another naturally occurring bromo-compound, a sesquiterpene, laurinterol, $C_{15}H_{19}OBr$, from the seaweed Laurencia intermedia is also described by Irie, Suzuki, Kurosawa and Masamune (1966). From extensive chemical and spectroscopic studies they proposed the structure I (R = H) for laurinterol, but were unable to deduce the stereochemistry of the asymmetric centres.

Since laurinterol is an oil, laurinterol acetate, $C_{17}H_{21}O_2Br$, a suitable crystalline derivative was used in the present single-crystal X-ray analysis which has confirmed the constitution I and determined the absolute stereochemistry as II. Furthermore, as a result of showing the absolute stereochemistry of laurinterol to be II, it has been established that laurinterol, aplysin (III), aplysinol (IV), laurene (V) and cuparene (VI) all possess the same absolute stereochemistry at their common asymmetric centre, a factor which allows speculation on the possibility of a biologocal precursor common to all five compounds.



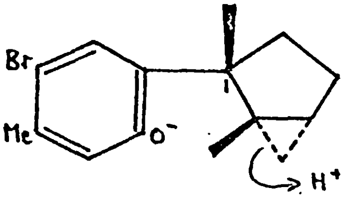
R = H or CH_3CO

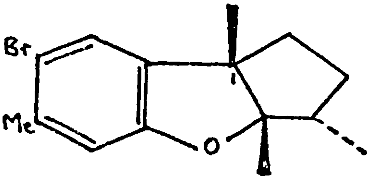
I



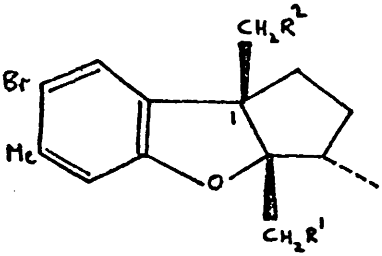
R = H or CH_3CO

II





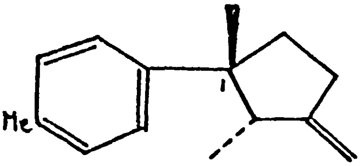
III



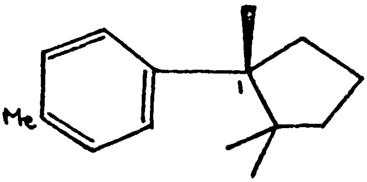
$R^1 = H$, $R^2 = OH$

or $R^1 = OH$, $R^2 = H$

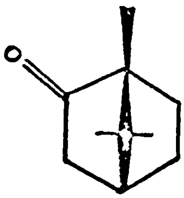
IV



V



VI



VII

2.2 EXPERIMENTAL

2.2.1 Crystal Data

Laurinterol acetate, $C_{17}H_{21}O_2Br$, M = 337,

Monoclinic, $\underline{a} = 10.26 \pm 0.03$, $\underline{b} = 7.28 \pm 0.02$, $\underline{c} = 12.22 \pm 0.03$ Å ,

$\beta = 114.1 \pm 0.3^{\circ}$., $\underline{U} = 833.2$ Å^{3}, $\underline{D}_m = 1.33$ g.cm.$^{-3}$ (by flotation in KI/H_2O), $\underline{z} = 2$, $\underline{D}_x = 1.34$ g.cm.$^{-3}$,

F(000) = 348,

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

Linear absorption coefficient for X-rays ($\lambda = 0.7107$ Å), $\mu = 25 \text{cm}^{-1}$

2.2.2 Crystallographic Measurements

The unit-cell parameters were determined from oscillation and Weissenberg photographs taken with Cu-Kα radiation ($\lambda = 1.5418$ Å) and from precession photographs taken with Mo-Kα radiation ($\lambda = 0.7107$ Å) . The accuracy of these measurements was checked when the crystal was mounted on the diffractometer for the data collection. Systematic halving of the 0k0 spectra indicated the two possible space groups $P2_1$ (C_2^2) or $P2_1/m$ (C_{2h}^2). However, the optical activity of the crystalline material led to the unambiguous choice of space group $P2_1$.

A small crystal rotating about <u>b</u>* was exposed to Mo-Kα radiation on a Hilger and Watts linear diffractometer (Arndt and Phillips, 1961), and 1097 independent reflexions from the reciprocal lattice nets $h0\ell$ - $h8\ell$ were measured. The appropriate Lorentz and polarisation corrections (Tunell, 1939) were applied, but no absorption corrections were made and unobserved reflexions were not considered.

2.2.3 Structure Determination

The value of 1.60 for the ratio $f_{Br}^2 / \sum_R f_R^2$ indicated a reasonable chance of success (Lipson and Cochran, 1966) for the heavy-atom method of phase determination on which basis the analysis subsequently proceeded.

The equivalent positions of space group $P2_1$, namely

$$\begin{array}{ccc} x, & y, & z \\ -x, & 1/2+y, & -z \end{array}$$

are such that an atom placed in the general position (x, y, z) will give rise to a peak at (2x, 1/2, 2z) in the Patterson function P(uvw) . After sharpening to point bromine atom at rest the data were used to compute the three-dimensional Patterson function from which the coordinates (0.1291, 0.2500, 0.2414) were determined for the bromine atom (y coordinate arbitrary) . The Harker section at v = 1/2 of the Patterson function is shown in Figure 2.1 .

The first three-dimensional electron-density distribution was evaluated with the observed amplitudes and the phase-angles appropriate to the bromine atom and served to locate the six atoms of the benzene ring despite the complete mirror pseudo-symmetry inherent in this type of calculation and arising from the incomplete phase contributions from the bromine atom alone. Contributions from the six benzenoid carbon atoms were included in a second structure-factor calculation and the subsequent electron-density distribution revealed the complete structure with a diminished pseudo-mirror image. Contributions from two atoms which were not clearly resolved from their false-mirror peaks were excluded from the third structure-factor calculation. The third electron-density distribution revealed every atom completely resolved from the last traces of the pseudo-mirror image. A fourth round of structure-factor and electron-density calculations yielded an improved set of positional parameters which were subsequently refined by least-squares methods.

In all the previous structure-factor calculations an overall isotropic thermal parameter $U_{iso} = 0.05$ Å ^{2} was assumed, and in all electron-density distributions evaluated with contributions from only part of the molecule, an appropriate modification function was used (Sim, 1961) . After each structure-factor calculation an overall scale factor was derived by equalising $k\sum|F_o|$ and $\sum|F_c|$ for all reflexions.

2.2.4 Structure Refinement

The refinement of positional, vibrational (isotropic and anisotropic) and scale parameters by least-squares methods was completed after 12 cycles with $R = 0.086$ and $R' = 0.0110$.

After cycle 3 a careful examination of the calculated structure factors revealed that the greatest relative discrepancies were systematically occurring in reflexions which had very low counts on the diffractometer. Counting statistics reveal that such low counts are unreliable and on these grounds 82 reflexions were removed from the refinement.

Nine of the twenty-one hydrogen positions were calculated from geometrical considerations and their contributions with assumed isotropic thermal parameters $U_{iso} = 0.05$ Å^2 were included in the structure-factor calculations after cycle 7. The hydrogen parameters were not refined.

A weighting scheme of the form

$$\sqrt{w} = \left[1 - \exp\left(-p_1\left(\frac{\sin\theta}{\lambda}\right)^2\right)\right] / \left[1 + p_2|F_o| + p_3|F_o|^2 + p_4|F_o|^3\right]^{1/2}$$

was applied in all cycles. Initially the parameters $p_1, \ldots, p_4$

were chosen to apply unit weights to all reflexions, but were subsequently varied according to the dictates of the weighting analysis (c.f. Chapter 1, 1.2.4), the final values being

$$p_1 = 100, \quad p_2 = 0.01, \quad p_3 = 0.0001, \quad p_4 = 0.00001$$

After cycle 7 anisotropic vibrational parameters were refined and because of computer-store limitations this necessitated the use of a block-diagonal approximation to the normal-equation matrix in all subsequent cycles.

The least-squares refinement was terminated when the calculated shifts were less than one-third of the estimated standard deviations. Excluding contributions from the hydrogen atoms, structure factors were calculated with the final parameters and used to evaluate a final electron-density distribution and a three-dimensional difference synthesis. Superimposed sections of the final electron-density map viewed down the <u>b</u> - axis are shown in Figure 2.2 . The difference synthesis revealed no errors in the structure and despite a number of diffuse peaks in positions stereochemically acceptable for hydrogen atoms, it was impossible to determine their coordinates with any accuracy. The refinement of the structure was therefore considered complete.

In all the structure-factor calculations the atomic scattering factors used were those given in "International Tables for Crystallography", Vol. III . Values of $|F_o|$ and the final values of $|F_c|$ are given in Table 2.2 . The final fractional coordinates are listed in Table 2.3 , and the anisotropic thermal parameters listed in Table 2.4 are the values of U_{ii} and $2U_{ij}$ in the expression

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

The appropriate estimated standard deviations derived from the inverse of the least-squares matrix are included in Tables 2.3 and 2.4 . Orthogonal coordinates are given in Table 2.5, and the calculated hydrogen positions are given in Table 2.6 .

Intramolecular bond distances are given in Table 2.7 and the valency angles are given in Table 2.8 . The average estimated standard deviations for C - C , C - O and C - Br bonds are 0.03 Å , 0.02 Å and 0.01 Å respectively, and for valency angles is 1.5° . These should be regarded as minimum values. Some intramolecular non-bonded distances are listed in Table 2.9 , and all intermolecular distances < 4 Å are listed in Table 2.10 . Details of all best-plane calculations are included in Table 2.11 .

The atomic numbering system used in all the tables is shown in Figure 2.3 , the hydrogens being numbered as the carbon atoms to which they are bonded. The molecular packing viewed down the b - axis is shown in Figure 2.4 .

2.2.5 Determination of the Absolute Stereochemistry

An examination of the 1kℓ reciprocal lattice net recorded on a Mo-Kα precession photograph and indexed with respect to a right-handed set of axes, revealed 27 1kℓ and 1$\bar{k}\ell$ pairs of reflexions with different intensities demonstrating the breakdown of Friedel's Law as a result of the anomalous scattering of X-rays by the bromine atom.

Using a complex scattering curve for bromine (International Tables for Crystallography, Vol. III), structure factors were calculated corresponding to the 27 pairs of reflexions observed to have different intensities. It was found that the ratio of the observed intensities was a correct prediction of the ratio of the squares of the corresponding structure factors for all but one pair of reflexions. Details of the reflexions and ratios involved are given in Table 2.12 . On the basis of this agreement (Bijvoet, 1949) it was concluded that the atomic parameters described a model with the correct absolute stereochemistry, and this is shown in all drawings of the molecule.

TABLE 2.1

COURSE OF REFINEMENT

Cycles	Parameters refined	Final R	Final R'	$\sum w\Delta^2$
1 - 3	x, y, z, U_{iso} for O, C, x, z, U_{iso} for Br, Overall scale factor, Full matrix, unit weights	0.190	0.0523	24,108
4 - 6	x, y, z, U_{iso} for O, C, x, z, U_{iso} for Br, Overall scale factor, Full matrix, weighting scheme adjusted, data edited.	0.153	0.0310	9,016
7 - 12	x, y, z, U_{ij} for O, C, x, z, U_{ij} for Br, Overall scale factor, Block diagonal, weighting scheme applied, hydrogen atoms included.	0.086	0.0110	2,961

H	K	L	Fo	Fc
12	0	2	8.8	4.6
12	0	0	7.8	8.3
11	0	1	7.2	2.6
10	0	1	14.2	16.0
10	0	-1	8.1	9.1
10	0	-2	8.1	9.5
10	0	-3	18.5	18.2
10	0	-5	17.7	19.0
10	0	-6	9.5	10.0
10	0	-7	13.4	11.3
10	0	-8	9.3	10.5
10	0	-9	9.7	9.4
10	0	-11	7.3	5.0
9	0	-11	10.1	8.3
9	0	-10	6.5	7.7
9	0	-9	16.8	16.1
9	0	-8	6.1	5.4
9	0	-7	12.0	12.5
9	0	-6	8.1	8.4
9	0	-5	5.7	5.0
9	0	-4	5.4	4.9
9	0	-3	5.6	4.4
9	0	1	11.6	12.3
9	0	3	8.0	8.4
8	0	4	9.5	8.4
8	0	2	20.3	21.3
8	0	0	21.6	20.8
8	0	-1	32.4	32.3
8	0	-2	25.8	26.3
8	0	-3	26.6	25.2
8	0	-4	13.4	12.2
8	0	-5	11.7	12.6
8	0	-6	19.2	17.6
8	0	-7	19.4	20.7
8	0	-8	14.7	15.9
8	0	-10	11.3	11.5
8	0	-11	6.2	5.4
8	0	-12	7.2	8.4
7	0	1	18.7	17.5
7	0	-1	19.7	18.2
7	0	-3	19.0	18.6
7	0	-4	35.2	36.3
7	0	-6	19.1	19.5
6	0	7	11.3	9.9
6	0	5	21.2	19.4
6	0	3	16.6	16.2
6	0	2	5.3	5.0
6	0	1	19.4	21.5
6	0	0	4.9	6.9
6	0	-1	50.8	49.8
6	0	-2	17.3	16.1
6	0	-3	23.2	21.8
6	0	-4	12.7	11.9
6	0	-5	25.0	24.4
6	0	-6	19.6	20.3
6	0	-7	15.8	17.9
6	0	-8	6.4	6.8
6	0	-9	1.0	3.4
6	0	-11	9.1	8.5
6	0	-12	7.8	5.8
6	0	-13	10.1	8.8
5	0	-11	13.1	11.6
5	0	-10	6.9	5.9
5	0	-9	31.3	32.3
5	0	-7	39.3	40.7
5	0	-6	23.0	21.9
5	0	-5	49.0	46.3
5	0	-4	28.6	30.0
5	0	-3	43.1	43.5
5	0	-2	22.4	21.3
5	0	-1	27.0	25.0
5	0	0	32.1	31.4
5	0	1	34.1	33.6
5	0	2	18.2	17.6
5	0	3	18.7	19.1
5	0	4	16.8	16.8
5	0	5	20.8	21.0
5	0	7	5.9	3.7
5	0	8	7.6	7.2
4	0	8	5.5	9.1
4	0	6	13.5	11.2
4	0	4	10.2	10.8
4	0	3	6.9	8.5
4	0	2	18.2	16.7
4	0	1	5.5	7.4
4	0	0	52.3	49.8
4	0	-1	5.9	8.3
4	0	-2	44.3	42.3
4	0	-3	16.7	15.1
4	0	-4	32.2	35.6
4	0	-5	4.3	3.3
4	0	-6	25.5	26.8
4	0	-7	6.1	6.8
4	0	-8	17.0	19.0
4	0	-10	8.1	8.5
4	0	-11	8.7	5.8
3	0	-14	5.9	3.2
3	0	-11	6.5	6.7
3	0	-10	9.2	10.4
3	0	-9	8.5	9.4
3	0	-8	26.0	26.7
3	0	-7	23.9	24.5
3	0	-6	20.0	21.0
3	0	-5	32.7	33.6
3	0	-4	38.1	40.7
3	0	-3	18.5	21.1
3	0	-2	34.0	29.4
3	0	-1	34.8	29.1
3	0	0	26.4	26.4
3	0	1	48.5	39.4
3	0	2	42.4	37.9
3	0	4	43.2	43.2
3	0	5	23.6	22.3
3	0	6	22.8	23.3
3	0	7	9.1	10.2
3	0	8	8.4	8.4
3	0	9	7.7	8.3
2	0	11	5.8	9.7
2	0	10	9.2	10.5
2	0	9	9.3	11.6
2	0	8	11.4	12.3
2	0	7	15.1	16.9
2	0	5	38.4	37.5
2	0	4	12.9	17.2
2	0	3	41.3	40.7
2	0	1	57.8	54.8
2	0	0	54.3	40.9
2	0	-1	89.0	106.1
2	0	-2	4.2	2.2
2	0	-3	13.8	14.2
2	0	-4	2.1	4.6
2	0	-5	39.9	43.2
2	0	-6	33.5	31.7
2	0	-7	15.7	15.8
2	0	-8	9.2	9.7
2	0	-9	7.1	6.3
2	0	-10	9.2	8.3
1	0	-11	8.1	7.4
1	0	-10	8.2	9.1
1	0	-8	8.5	9.2
1	0	-6	43.8	44.1
1	0	-5	14.8	14.5
1	0	-4	3.3	4.5
1	0	-3	63.5	69.0
1	0	-2	13.9	12.3
1	0	2	35.7	38.3
1	0	3	31.7	34.8
1	0	4	34.5	32.3
1	0	5	33.6	33.6
1	0	8	19.1	18.7
1	0	9	12.9	11.8
1	0	10	9.4	9.9
1	0	12	7.7	6.7
0	0	10	9.5	10.0
0	0	9	3.9	3.9
0	0	8	12.6	11.9
0	0	6	33.3	32.3
0	0	5	17.1	15.2
0	0	4	56.7	58.6
0	0	3	31.7	30.8
0	0	2	51.7	58.5
0	0	12	7.8	6.1
1	0	-7	28.0	28.6
1	0	6	14.7	13.2
11	1	-1	10.1	11.0
11	1	1	7.4	8.3

H	K	L	Fo	Fc
10	1	1	4.5	4.5
10	1	0	9.7	9.1
10	1	-2	11.4	12.3
10	1	-3	10.3	9.4
10	1	-4	14.6	14.3
10	1	-5	6.1	6.2
10	1	-6	15.5	15.3
10	1	-8	13.9	14.3
10	1	-9	6.2	7.0
10	1	-10	8.5	7.2
9	1	-12	7.1	6.9
9	1	-10	9.9	10.0
9	1	-7	7.0	8.1
9	1	-6	15.4	15.7
9	1	-5	4.1	5.0
9	1	-4	18.6	17.8
9	1	-2	13.9	13.3
9	1	-1	9.7	10.9
9	1	0	16.9	18.5
9	1	1	5.1	4.7
9	1	2	5.1	5.4
8	1	5	6.9	8.8
8	1	3	12.6	13.4
8	1	2	11.3	10.7
8	1	1	9.2	8.4
8	1	0	10.7	11.2
8	1	-1	14.1	14.6
8	1	-2	14.2	14.5
8	1	-3	27.3	26.6
8	1	-4	20.5	20.9
8	1	-5	26.2	26.0
8	1	-6	9.4	10.0
8	1	-7	19.3	19.6
8	1	-8	11.1	12.4
8	1	-9	18.4	18.1
8	1	-10	7.1	7.8
8	1	-11	6.2	7.0
7	1	-11	7.1	6.1
7	1	-9	13.8	14.0
7	1	-8	6.3	6.8
7	1	-7	19.9	19.3
7	1	-6	6.6	6.9
7	1	-5	26.7	27.4
7	1	-4	10.7	11.2
7	1	-3	27.1	27.2
7	1	-2	13.4	13.0
7	1	-1	28.6	28.3
7	1	0	18.8	20.2
7	1	1	33.8	34.6
7	1	2	7.5	8.3
7	1	3	18.6	18.4
7	1	4	7.3	8.5
7	1	5	7.9	9.0
6	1	8	9.0	7.3
6	1	6	12.6	13.9
6	1	4	15.9	15.5
6	1	2	25.6	25.1
6	1	0	18.5	18.4
6	1	-1	8.6	7.8
6	1	-2	30.6	30.9
6	1	-3	11.0	12.4
6	1	-4	36.5	36.6
6	1	-5	7.9	9.0
6	1	-6	20.1	20.1
6	1	-7	9.1	9.6
6	1	-9	7.6	8.4
6	1	-11	12.7	13.1
6	1	-13	6.9	6.3
5	1	-11	7.9	8.6
5	1	-10	14.9	16.7
5	1	-9	11.1	10.4
5	1	-8	27.5	28.9
5	1	-7	12.0	12.9
5	1	-6	34.4	37.4
5	1	-5	8.5	7.1
5	1	-4	43.8	41.3
5	1	-3	29.5	30.8
5	1	-2	51.6	47.0
5	1	-1	26.8	26.7
5	1	0	27.9	28.2
5	1	1	28.2	29.2
5	1	2	35.5	34.7
5	1	3	18.2	17.3
5	1	4	16.3	17.3
5	1	5	10.8	11.3
5	1	6	7.8	9.1
5	1	7	6.9	6.7
5	1	8	6.9	5.3
4	1	9	7.1	5.9
4	1	7	11.5	13.5
4	1	6	7.1	7.3
4	1	5	19.0	17.5
4	1	4	7.8	7.5
4	1	3	30.9	27.7
4	1	2	12.8	12.3
4	1	1	15.9	14.8
4	1	0	37.5	32.0
4	1	-1	37.2	36.4
4	1	-2	13.7	15.1
4	1	-3	51.5	46.7
4	1	-5	37.3	40.5
4	1	-6	9.8	10.4
4	1	-7	25.2	26.6
4	1	-8	4.7	4.2
4	1	-9	10.9	11.0
4	1	-10	6.8	8.3
4	1	-11	9.2	7.9
4	1	-13	7.5	3.5
4	1	-14	7.1	3.9
3	1	-15	7.3	8.5
3	1	-13	6.5	4.5
3	1	-12	2.3	2.6
3	1	-11	6.6	6.1
3	1	-10	9.8	10.6
3	1	-9	14.7	15.3
3	1	-8	11.2	12.5
3	1	-7	18.1	20.3
3	1	-6	17.3	18.5
3	1	-5	40.5	41.9
3	1	-4	38.5	37.2
3	1	-3	41.3	39.1
3	1	-2	46.9	39.0
3	1	-1	33.9	34.0
3	1	0	40.3	42.6
3	1	1	51.4	47.6
3	1	2	53.0	49.2
3	1	3	34.1	34.2
3	1	4	24.2	23.3
3	1	5	14.9	15.2
3	1	6	14.3	15.1
3	1	7	13.0	13.8
3	1	9	2.4	4.3
2	1	11	6.3	5.7
2	1	10	14.1	15.5
2	1	7	7.3	8.2
2	1	6	27.1	28.4
2	1	5	7.7	7.7
2	1	4	37.5	37.5
2	1	3	15.1	16.2
2	1	2	45.4	44.2
2	1	1	41.3	38.3
2	1	0	35.9	37.8
2	1	-1	37.2	33.8
2	1	-2	65.3	67.4
2	1	-3	28.3	29.1
2	1	-4	28.4	28.8
2	1	-5	7.0	7.7
2	1	-6	19.6	20.9
2	1	-7	7.1	8.3
2	1	-8	18.3	20.8
2	1	-9	11.1	12.1
2	1	-10	11.3	10.9
2	1	-11	7.6	9.5
2	1	-12	6.5	5.8
2	1	-13	7.3	3.3
1	1	-12	3.3	6.3
1	1	-1[illegible]	8.0	9.9
1	1	-8	15.1	15.2
1	1	-7	7.8	9.1
1	1	-6	36.3	39.6
1	1	-4	48.9	49.3
1	1	-3	49.3	50.2
1	1	1	79.9	77.9
1	1	2	46.4	44.3
1	1	3	20.6	20.3
1	1	4	14.7	13.9

H	K	L	Fo	Fc
1	1	6	7.1	8.0
1	1	7	22.5	21.9
1	1	8	6.2	7.2
1	1	10	6.9	3.6
1	1	12	6.5	3.2
0	1	13	1.1	2.8
0	1	11	8.8	8.6
0	1	10	9.0	9.5
0	1	9	13.9	14.7
0	1	7	33.4	35.7
0	1	6	9.7	8.3
0	1	5	37.8	38.2
0	1	4	18.7	14.9
0	1	3	105.2	96.0
0	1	2	61.4	55.9
11	2	0	9.9	10.8
10	2	1	9.0	9.4
10	2	0	7.9	6.1
10	2	-1	11.5	10.2
10	2	-2	9.5	9.2
10	2	-3	9.3	10.4
10	2	-4	7.6	10.3
10	2	-5	10.5	12.7
10	2	-6	9.8	10.5
10	2	-7	7.5	9.1
10	2	-8	9.0	6.9
9	2	-13	7.6	4.3
9	2	-11	1.9	6.1
9	2	-9	9.3	10.3
9	2	-7	16.9	17.8
9	2	-6	7.9	6.5
9	2	-5	12.4	11.6
9	2	-3	17.4	19.9
9	2	-2	8.4	9.9
9	2	-1	14.0	14.1
9	2	0	10.1	10.5
9	2	1	10.9	9.6
9	2	3	7.6	6.9
8	2	4	7.4	7.4
8	2	3	7.5	6.6
8	2	2	11.8	13.6
8	2	1	7.2	5.8
8	2	0	14.4	14.2
8	2	-1	10.2	11.8
8	2	-2	15.0	14.7
8	2	-3	7.8	6.5
8	2	-4	26.4	28.3
8	2	-5	11.8	12.1
8	2	-6	22.3	23.7
8	2	-7	8.5	9.7
8	2	-8	17.3	17.9
8	2	-9	8.9	9.6
8	2	-10	7.7	8.4
7	2	-12	6.7	4.9
7	2	-10	12.1	13.4
7	2	-9	6.0	4.6
7	2	-8	11.5	12.4
7	2	-7	6.0	7.6
7	2	-6	25.7	27.2
7	2	-5	8.8	8.8
7	2	-4	13.9	14.2
7	2	-3	11.3	12.3
7	2	-2	23.2	23.7
7	2	-1	9.1	10.9
7	2	0	28.5	27.7
7	2	1	10.8	12.1
7	2	2	19.9	22.0
7	2	3	8.8	11.3
7	2	4	13.1	13.3
6	2	5	12.3	13.8
6	2	4	14.8	14.9
6	2	3	22.9	23.5
6	2	1	18.7	20.3
6	2	0	11.4	10.9
6	2	-1	27.3	27.0
6	2	-2	10.0	11.1
6	2	-3	31.8	32.9
6	2	-4	8.7	8.4
6	2	-5	25.3	25.8
6	2	-7	22.7	21.6
6	2	-8	11.5	12.5
6	2	-9	8.7	9.2
6	2	-10	12.6	14.1
6	2	-11	7.2	6.5
6	2	-12	7.2	8.1
5	2	-11	12.2	13.9
5	2	-10	9.8	11.0
5	2	-9	19.3	20.2
5	2	-8	7.2	9.7
5	2	-7	21.5	23.3
5	2	-6	13.4	13.4
5	2	-5	32.8	33.8
5	2	-4	9.0	9.8
5	2	-3	19.2	18.2
5	2	-2	6.3	5.6
5	2	-1	29.0	27.2
5	2	0	23.8	24.6
5	2	1	37.5	37.7
5	2	2	14.3	15.5
5	2	3	14.3	16.7
5	2	4	11.8	13.6
5	2	5	14.1	15.2
5	2	6	3.5	8.0
5	2	7	8.7	8.7
5	2	8	7.9	6.3
4	2	7	6.5	5.2
4	2	6	7.4	5.9
4	2	5	14.3	15.3
4	2	4	23.0	24.0
4	2	3	5.3	4.7
4	2	2	26.9	27.9
4	2	1	20.0	18.5
4	2	0	45.9	43.3
4	2	-1	36.9	32.6
4	2	-2	50.2	46.6
4	2	-3	24.5	23.8
4	2	-4	44.3	44.4
4	2	-5	19.8	19.0
4	2	-6	16.6	16.3
4	2	-7	6.0	4.9
4	2	-8	15.2	17.4
4	2	-9	6.3	5.5
4	2	-10	8.9	6.6
4	2	-12	7.5	4.6
3	2	-14	7.0	3.8
3	2	-12	8.6	6.2
3	2	-10	7.7	9.5
3	2	-9	11.7	10.5
3	2	-8	17.1	16.0
3	2	-7	11.6	12.1
3	2	-6	29.7	31.3
3	2	-5	23.4	25.6
3	2	-4	19.1	21.3
3	2	-3	26.5	25.2
3	2	-2	48.1	45.0
3	2	-1	42.7	46.9
3	2	0	26.0	27.6
3	2	1	52.9	45.1
3	2	2	29.4	22.2
3	2	3	31.0	30.4
3	2	4	21.2	20.8
3	2	5	11.1	10.1
3	2	6	14.1	15.8
3	2	7	12.0	13.8
3	2	8	9.2	9.4
3	2	9	7.8	5.3
2	2	10	7.8	5.0
2	2	9	17.3	19.6
2	2	7	16.9	19.2
2	2	5	24.5	20.3
2	2	4	10.6	11.7
2	2	3	28.8	28.1
2	2	2	15.8	11.3
2	2	1	56.2	52.0
2	2	0	36.1	32.3
2	2	-1	36.9	41.2
2	2	-2	11.1	9.6
2	2	-3	47.9	50.8
2	2	-4	28.9	27.7
2	2	-5	31.9	33.6
2	2	-6	11.3	11.6
2	2	-7	16.8	16.7
2	2	-8	3.7	9.7
2	2	-9	9.6	10.3
2	2	-10	4.3	3.4
2	2	-11	12.7	13.7

H	K	L	Fo	Fc
1	2	-10	5.8	2.7
1	2	-9	12.4	12.9
1	2	-8	14.3	15.9
1	2	-7	18.9	20.1
1	2	-6	23.1	25.8
1	2	-5	58.8	50.0
1	2	-4	19.6	20.1
1	2	-3	47.8	47.0
1	2	-2	44.7	45.9
1	2	-1	52.4	49.7
1	2	1	14.7	14.6
1	2	2	3.3	3.8
1	2	3	13.7	17.7
1	2	4	45.9	43.4
1	2	5	16.0	15.8
1	2	6	8.0	7.6
1	2	7	11.8	11.4
1	2	8	12.6	12.6
1	2	12	7.2	4.8
0	2	12	7.5	4.0
0	2	10	14.9	16.1
0	2	9	7.1	5.2
0	2	8	14.5	16.7
0	2	7	9.2	8.5
0	2	6	33.6	33.8
0	2	5	25.3	22.6
0	2	4	51.2	48.5
0	2	3	26.5	25.5
0	2	2	57.7	55.4
0	2	1	46.5	42.3
11	3	-9	9.8	8.0
11	3	-3	10.6	13.4
10	3	0	11.1	11.1
10	3	-1	8.5	7.3
10	3	-2	12.3	12.4
10	3	-3	9.5	9.7
10	3	-4	9.2	7.9
10	3	-5	10.4	9.9
10	3	-6	12.0	11.4
10	3	-7	11.7	12.2
10	3	-9	9.0	8.8
9	3	-10	13.4	12.0
9	3	-8	13.6	16.7
9	3	-7	7.6	5.1
9	3	-6	11.9	12.5
9	3	-4	11.5	11.5
9	3	-3	8.9	9.6
9	3	-2	12.1	11.1
9	3	0	10.4	10.8
9	3	2	9.6	10.4
8	3	3	8.3	8.5
8	3	1	19.0	20.8
8	3	-1	19.3	21.1
8	3	-2	12.7	12.8
8	3	-3	10.7	13.5
8	3	-4	13.3	13.6
8	3	-5	18.3	19.0
8	3	-7	12.9	11.6
8	3	-9	10.8	11.4
8	3	-11	9.9	7.2
7	3	-11	8.5	8.6
7	3	-9	15.1	15.6
7	3	-6	9.3	8.9
7	3	-5	15.1	15.5
7	3	-4	7.9	8.0
7	3	-3	20.9	22.7
7	3	-2	15.2	17.4
7	3	-1	14.4	15.8
7	3	0	10.6	11.3
7	3	1	13.0	12.2
7	3	3	9.5	9.9
6	3	6	14.5	13.6
6	3	4	11.2	12.5
6	3	2	19.6	20.6
6	3	1	9.8	11.1
6	3	0	25.1	25.8
6	3	-1	11.4	11.0
6	3	-2	22.1	22.5
6	3	-3	10.2	9.8
6	3	-4	27.0	26.6
6	3	-5	6.4	6.1
6	3	-6	13.3	12.4
6	3	-7	8.9	8.4
6	3	-8	9.0	9.3
6	3	-9	9.9	10.8
6	3	-10	8.7	7.3
5	3	-10	15.1	14.8
5	3	-8	21.0	21.9
5	3	-7	10.8	10.1
5	3	-6	20.7	21.0
5	3	-5	8.1	9.8
5	3	-4	30.4	29.9
5	3	-3	7.6	8.1
5	3	-2	25.3	25.1
5	3	-1	9.5	10.7
5	3	0	13.7	13.0
5	3	1	11.3	12.4
5	3	2	24.3	24.6
5	3	3	13.0	13.2
5	3	4	13.6	15.3
5	3	6	8.6	8.1
5	3	7	8.8	8.5
4	3	8	7.8	3.7
4	3	7	1[illegible].0	9.9
4	3	6	11.7	13.1
4	3	5	13.0	15.3
4	3	4	14.5	15.1
4	3	3	12.1	12.2
4	3	2	21.0	20.9
4	3	1	35.8	36.4
4	3	0	23.2	19.4
4	3	-1	57.9	53.7
4	3	-2	23.8	23.5
4	3	-3	26.5	27.1
4	3	-4	14.2	12.3
4	3	-5	27.4	29.2
4	3	-6	14.3	16.7
4	3	-7	18.9	20.0
4	3	-9	9.6	10.0
4	3	-11	10.1	7.5
3	3	-9	15.4	15.1
3	3	-8	6.6	7.0
3	3	-7	14.6	13.0
3	3	-6	14.3	14.5
3	3	-5	23.5	23.1
3	3	-4	23.3	21.1
3	3	-3	37.3	35.6
3	3	-2	32.0	32.3
3	3	-1	15.9	15.4
3	3	0	25.3	25.0
3	3	1	36.7	35.7
3	3	2	30.9	31.2
3	3	3	28.0	29.1
3	3	4	22.5	26.7
3	3	5	22.7	23.8
3	3	6	17.1	17.2
3	3	7	8.3	11.0
3	3	8	12.5	14.3
2	3	7	14.0	14.6
2	3	6	19.6	19.1
2	3	5	14.3	15.0
2	3	4	17.8	16.5
2	3	3	11.2	12.2
2	3	2	30.4	28.0
2	3	1	8.2	9.6
2	3	0	64.3	57.0
2	3	-1	7.7	7.2
2	3	-2	32.3	32.4
2	3	-3	15.6	17.4
2	3	-4	34.2	38.6
2	3	-6	26.3	26.7
2	3	-7	16.7	13.6
2	3	-8	22.7	21.9
2	3	-9	9.1	9.9
2	3	-10	8.5	8.9
2	3	-11	3.0	4.9
2	3	-12	11.5	5.6
1	3	-10	10.1	9.9
1	3	-9	16.8	16.3
1	3	-8	15.1	18.3
1	3	-7	24.1	21.3
1	3	-6	25.0	23.8
1	3	-5	31.3	29.5
1	3	-4	24.9	21.0
1	3	-3	24.9	26.2
1	3	-2	16.7	13.2

H	K	L	Fo	Fc
1	3	0	22.1	22.0
1	3	1	29.2	27.1
1	3	2	32.4	28.7
1	3	3	29.1	28.8
1	3	4	17.3	16.7
1	3	5	22.6	21.8
1	3	6	12.0	17.7
1	3	7	10.0	9.3
1	3	8	8.8	8.3
1	3	9	9.0	9.5
0	3	11	9.3	7.8
0	3	9	11.5	9.4
0	3	7	12.7	14.5
0	3	6	7.8	8.3
0	3	5	8.4	9.9
0	3	4	11.8	10.5
0	3	3	36.6	36.5
0	3	2	18.9	13.7
0	3	1	50.5	61.2
11	4	-4	10.9	9.5
11	4	0	12.4	10.2
10	4	-1	9.8	7.9
10	4	-4	10.2	10.8
10	4	-7	9.4	9.4
10	4	-8	8.3	7.7
10	4	-9	8.9	5.8
10	4	-10	8.5	7.9
9	4	-11	8.8	7.5
9	4	-9	12.7	10.6
9	4	-7	8.4	7.7
9	4	-1	16.6	13.8
9	4	0	9.6	6.2
8	4	4	10.7	11.5
8	4	2	11.6	10.2
8	4	0	9.8	10.6
8	4	-2	18.4	18.0
8	4	-3	8.3	7.8
8	4	-4	13.2	12.9
8	4	-5	7.4	7.7
8	4	-6	18.2	16.2
7	4	-10	9.2	9.5
7	4	-8	11.3	11.1
7	4	-6	15.1	16.4
7	4	-4	17.5	15.5
7	4	-3	14.9	16.2
7	4	-2	14.5	13.1
7	4	-1	14.0	13.7
7	4	0	14.3	14.9
7	4	1	9.5	9.5
7	4	3	8.2	9.0
7	4	4	10.2	7.6
6	4	7	9.6	9.2
6	4	5	13.1	13.0
6	4	3	9.4	13.1
6	4	2	9.0	9.6
6	4	1	13.7	12.3
6	4	0	12.2	12.8
6	4	-1	22.1	21.2
6	4	-2	7.0	5.6
6	4	-3	14.2	13.6
6	4	-4	8.5	9.8
6	4	-5	16.3	16.3
6	4	-6	6.7	5.5
6	4	-7	14.3	12.6
6	4	-9	11.9	9.0
6	4	-10	7.8	3.8
5	4	-11	8.7	6.7
5	4	-9	8.9	4.7
5	4	-7	14.5	14.7
5	4	-6	9.9	11.3
5	4	-5	25.5	25.5
5	4	-4	8.2	5.3
5	4	-3	23.0	20.3
5	4	-2	11.3	10.9
5	4	0	13.9	12.8
5	4	-1	29.2	27.9
5	4	1	13.2	14.2
5	4	2	16.1	14.5
5	4	3	8.2	9.5
5	4	4	8.5	8.8
5	4	5	13.1	13.7
4	4	8	8.9	5.0
4	4	6	15.4	13.9
4	4	5	7.3	6.3
4	4	4	13.7	15.0
4	4	3	20.8	17.9
4	4	2	19.2	20.0
4	4	1	19.3	20.4
4	4	0	9.1	10.4
4	4	-2	27.0	26.9
4	4	-4	37.1	36.4
4	4	-5	3.6	8.7
4	4	-6	20.3	22.2
4	4	-8	17.9	17.5
4	4	-9	8.5	8.8
4	4	-10	10.4	9.4
3	4	-8	8.4	7.4
3	4	-7	7.9	8.9
3	4	-6	16.2	19.3
3	4	-5	9.2	11.4
3	4	-4	13.3	15.6
3	4	-3	17.2	16.0
3	4	-2	26.3	25.0
3	4	-1	13.8	13.5
3	4	0	34.3	34.0
3	4	1	31.5	31.9
3	4	2	20.4	20.2
3	4	3	31.3	31.6
3	4	5	25.0	23.7
3	4	7	10.4	11.7
2	4	7	11.3	11.1
2	4	6	15.6	16.2
2	4	4	11.9	12.0
2	4	3	28.2	27.5
2	4	2	3.8	3.9
2	4	1	15.0	15.2
2	4	0	22.4	23.2
2	4	-1	27.1	29.2
2	4	-2	3.3	7.7
2	4	-3	27.7	30.8
2	4	-4	10.3	7.2
2	4	-5	22.2	28.3
2	4	-6	8.7	10.1
2	4	-7	21.1	22.6
2	4	-8	11.0	11.4
2	4	-9	20.9	19.9
2	4	-10	11.2	13.5
2	4	-11	3.9	5.1
1	4	-10	9.7	11.2
1	4	-8	12.7	11.5
1	4	-7	12.9	13.2
1	4	-6	18.6	17.0
1	4	-5	14.3	16.1
1	4	-4	6.7	5.7
1	4	-3	22.6	25.0
1	4	-2	25.7	20.9
1	4	-1	19.6	22.6
1	4	0	20.5	21.7
1	4	1	25.0	23.1
1	4	2	33.2	32.2
1	4	3	9.6	9.6
1	4	4	20.3	19.0
1	4	5	15.7	16.5
1	4	6	14.2	15.1
1	4	8	7.3	4.1
1	4	9	7.9	7.7
1	4	10	7.7	5.4
0	4	12	8.3	3.4
0	4	10	3.3	5.0
0	4	9	2.0	5.4
0	4	8	11.3	13.0
0	4	6	16.7	18.0
0	4	5	7.3	9.3
0	4	4	20.7	24.6
0	4	3	13.5	12.3
0	4	2	23.0	24.1
0	4	1	15.8	16.3
9	5	-6	14.0	11.2
9	5	-4	11.0	8.4
9	5	-2	13.2	11.9
8	5	-1	12.1	9.6
8	5	-3	14.9	13.6
8	5	-7	13.2	9.2
7	5	-7	13.9	12.5
7	5	-4	14.0	11.3
7	5	-3	12.7	13.1

H	K	L	Fc	Fc
7	5	-1	12.4	8.2
6	5	-4	20.5	19.6
6	5	-6	15.5	11.8
6	5	-7	8.5	8.7
5	5	-8	13.3	12.9
5	5	-7	11.1	12.6
5	5	-2	17.1	18.1
5	5	3	9.4	7.7
5	5	4	14.2	14.6
5	5	6	10.3	8.0
4	5	3	17.7	17.4
4	5	2	11.5	10.7
4	5	-1	17.6	17.2
4	5	-2	23.5	20.5
4	5	-3	25.1	22.8
4	5	-4	13.8	11.8
4	5	-8	9.0	8.1
4	5	-11	10.2	6.7
3	5	-9	8.9	8.4
3	5	-8	13.9	13.5
3	5	-7	11.5	11.3
3	5	-6	8.7	8.0
3	5	-5	16.9	18.8
3	5	-4	8.2	7.9
3	5	-1	14.7	16.1
3	5	1	18.8	17.2
3	5	2	22.7	18.8
3	5	4	20.8	18.7
3	5	5	13.0	14.0
3	5	6	9.7	9.8
2	5	6	10.3	10.5
2	5	5	12.5	13.8
2	5	4	16.2	14.8
2	5	3	10.3	13.5
2	5	2	18.9	18.5
2	5	0	18.3	19.5
2	5	-1	7.6	9.0
2	5	-2	19.8	22.8
2	5	-3	15.8	16.4
2	5	-4	21.6	24.2
2	5	-6	7.6	6.7
2	5	-7	7.6	9.3
2	5	-8	10.9	10.6
2	5	-9	12.2	13.0
2	5	-10	9.4	10.2
2	5	-12	11.6	5.5
1	5	-8	8.7	9.0
1	5	-7	8.8	6.2
1	5	-6	11.3	13.0
1	5	-5	18.5	16.1
1	5	-4	18.9	18.5
1	5	-3	14.8	14.9
1	5	-2	5.3	7.6
1	5	-1	22.2	23.7
1	5	2	11.6	13.3
1	5	3	12.3	11.4
1	5	4	7.1	7.2
1	5	5	12.3	13.7
1	5	6	12.0	9.3
1	5	7	9.8	8.8
1	5	8	8.7	6.3
0	5	11	9.7	3.6
0	5	9	10.4	7.2
0	5	8	9.0	5.3
0	5	7	11.8	11.2
0	5	6	7.2	2.0
0	5	5	9.9	10.8
0	5	3	14.9	17.1
0	5	2	8.6	10.7
6	6	-1	16.9	14.8
6	6	-5	14.5	13.1
6	6	-6	7.2	3.1
5	6	-9	11.7	8.8
5	6	-3	14.2	11.3
5	6	-2	13.0	10.3
5	6	-1	17.0	14.3
5	6	3	5.6	3.7
4	6	6	11.8	3.9
4	6	2	16.8	16.2
4	6	1	9.4	7.1
4	6	0	24.3	22.9
4	6	-1	16.8	15.5
4	6	-2	15.2	16.6
4	6	-3	5.3	8.7
4	6	-6	11.5	9.3
4	6	-9	11.4	6.1
3	6	-7	11.0	8.5
3	6	-6	11.3	10.9
3	6	-4	7.9	10.1
3	6	-3	10.1	10.7
3	6	-2	13.0	12.6
3	6	-1	10.6	12.7
3	6	0	11.4	13.0
3	6	1	11.1	11.2
3	6	2	9.2	10.2
3	6	5	11.3	5.0
2	6	6	11.3	12.1
2	6	4	12.2	13.8
2	6	3	14.8	13.1
2	6	1	12.5	14.6
2	6	-1	12.6	13.9
2	6	-3	13.3	14.4
2	6	-5	5.9	3.8
2	6	-6	8.3	9.0
1	6	-9	13.9	7.4
1	6	-5	11.6	13.6
1	6	-4	16.1	15.5
1	6	-3	11.0	13.1
1	6	-2	9.9	12.9
1	6	1	11.0	13.4
1	6	2	13.6	14.1
1	6	3	14.9	15.5
1	6	7	10.5	7.1
0	6	6	12.4	11.2
0	6	4	14.3	14.5
0	6	3	3.4	3.6
0	6	2	10.2	15.2
5	7	1	9.6	10.4
5	7	-2	12.0	12.3
5	7	-4	10.3	10.3
5	7	-7	11.1	8.5
4	7	-5	5.3	7.3
4	7	-3	10.1	10.5
4	7	-2	13.6	14.1
4	7	-1	3.1	6.7
4	7	3	11.2	6.2
3	7	2	5.7	5.3
3	7	1	7.7	3.6
3	7	-1	9.5	12.9
3	7	-2	7.0	6.6
3	7	-3	9.2	3.1
3	7	-4	7.1	5.3
2	7	-6	3.1	5.0
2	7	-4	7.3	8.7
2	7	-1	6.6	7.6
2	7	1	7.2	6.9
2	7	3	8.6	9.9
1	7	7	10.5	7.4
1	7	5	9.5	6.7
1	7	3	7.5	10.7
1	7	-4	7.2	11.1
0	7	7	10.2	3.3
0	7	6	9.0	3.6
0	7	5	9.5	7.7
0	7	3	10.9	16.4
0	7	2	5.7	4.3
10	8	-11	5.4	3.3
6	8	3	4.9	5.3
6	8	1	4.7	4.6
5	8	1	5.0	3.6
5	8	2	4.5	4.3
4	8	5	5.7	4.1
4	8	-3	4.1	7.1
4	8	-6	4.4	5.[illegible]
3	8	-4	3.1	6.6
3	8	-1	3.7	4.7
3	8	6	4.3	2.2
3	8	3	5.7	3.9
2	8	3	3.7	7.1
2	8	2	3.5	2.1
1	8	-9	3.5	3.5
1	8	1	6.9	5.2
1	8	12	5.2	4.0
0	8	1[illegible]	5.2	4.7
0	8	4	4.1	7.0

TABLE 2.3

FRACTIONAL COORDINATES AND E.S.D.S

ATOM	x/a	y/b	z/c
C(1)	0.2884 ± 16	-0.1285 ± 22	0.2255 ± 16
C(2)	0.4237 ± 17	-0.0483 ± 21	0.2891 ± 14
C(3)	0.5402 ± 17	-0.1259 ± 21	0.2748 ± 12
C(4)	0.5132 ± 15	-0.2752 ± 24	0.1994 ± 14
C(5)	0.3815 ± 18	-0.3649 ± 31	0.1449 ± 16
C(6)	0.2634 ± 18	-0.2820 ± 30	0.1602 ± 18
C(7)	0.1178 ± 22	-0.3768 ± 45	0.0962 ± 24
C(8)	0.6346 ± 18	-0.3499 ± 22	0.0745 ± 15
C(9)	0.7533 ± 23	-0.4637 ± 38	0.0722 ± 21
C(10)	0.6909 ± 15	-0.0393 ± 26	0.3409 ± 14
C(11)	0.7958 ± 18	-0.1955 ± 26	0.4147 ± 17
C(12)	0.9075 ± 22	-0.0956 ± 28	0.5228 ± 19
C(13)	0.8251 ± 22	0.0559 ± 26	0.5440 ± 16
C(14)	0.6925 ± 17	0.1043 ± 24	0.4325 ± 16
C(15)	0.6781 ± 18	0.0314 ± 32	0.5402 ± 16
C(16)	0.6470 ± 27	0.2938 ± 28	0.3965 ± 22
C(17)	0.7399 ± 19	0.0505 ± 26	0.2463 ± 16
O(1)	0.6269 ± 12	-0.3676 ± 19	0.1817 ± 11
O(2)	0.5532 ± 15	-0.2561 ± 23	-0.0033 ± 13
Br	0.13291 ± 20	0.00000	0.24529 ± 19

TABLE 2.4

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S
(in Å^{2})

ATOM	U11	U22	U33	2U23	2U31	2U12
C(1)	0.037	0.012	0.060	0.051	0.039	0.015
	9	8	11	15	16	15
C(2)	0.047	0.042	0.044	-0.021	0.045	-0.005
	8	10	9	13	14	14
C(3)	0.048	0.014	0.022	-0.029	0.020	-0.020
	9	8	7	13	13	15
C(4)	0.024	0.029	0.042	0.043	0.019	-0.006
	7	9	9	16	13	15
C(5)	0.039	0.050	0.057	0.009	0.020	-0.028
	9	12	11	21	17	20
C(6)	0.037	0.049	0.069	0.003	0.024	-0.057
	9	13	12	21	18	20
C(7)	0.042	0.109	0.110	-0.039	0.029	-0.087
	11	23	19	37	24	29
C(8)	0.055	0.052	0.050	-0.027	0.055	-0.054
	10	8	10	15	16	16
C(9)	0.073	0.064	0.106	-0.058	0.110	-0.018
	13	19	16	32	25	28
C(10)	0.030	0.033	0.044	-0.013	0.007	-0.018
	7	12	9	16	14	16
C(11)	0.032	0.024	0.064	0.010	-0.021	0.006
	9	11	12	18	17	16
C(12)	0.058	0.033	0.072	-0.056	-0.013	0.010
	11	12	13	21	20	20
C(13)	0.080	0.034	0.044	-0.020	-0.023	-0.067
	13	13	10	17	19	22
C(14)	0.030	0.023	0.064	0.043	0.015	-0.025
	8	10	11	17	16	15

TABLE 2.4 (contd.)

ATOM	U11	U22	U33	2U23	2U31	2U12
C(15)	0.048	0.042	0.072	-0.050	0.052	-0.052
	9	14	12	23	18	21
C(16)	0.101	0.011	0.103	-0.018	0.096	0.013
	17	10	17	23	30	23
C(17)	0.057	0.044	0.059	-0.087	0.060	-0.087
	10	13	10	19	17	19
O(1)	0.037	0.037	0.050	-0.028	0.018	-0.008
	6	7	7	13	11	12
O(2)	0.080	0.064	0.059	0.007	0.043	-0.055
	11	11	8	16	17	19
Br	0.048	0.079	0.085	0.047	0.059	0.054
	1	1	1	3	2	3

TABLE 2.5

ORTHOGONALISED COORDINATES AND E.S.D.S (in Å)

ATOM	X'	Y	Z'
C(1)	2.701 ± 15	-0.936 ± 16	1.547 ± 17
C(2)	3.968 ± 16	-0.352 ± 15	1.757 ± 15
C(3)	5.059 ± 16	-0.916 ± 16	1.094 ± 14
C(4)	4.806 ± 14	-2.004 ± 18	0.286 ± 16
C(5)	3.572 ± 17	-2.656 ± 23	0.172 ± 19
C(6)	2.466 ± 17	-2.053 ± 22	0.854 ± 21
C(7)	1.103 ± 21	-2.743 ± 33	0.682 ± 28
C(8)	5.943 ± 17	-2.548 ± 16	-1.749 ± 16
C(9)	7.055 ± 21	-3.376 ± 28	-2.275 ± 22
C(10)	6.470 ± 14	-0.286 ± 19	1.270 ± 16
C(11)	7.452 ± 16	-1.423 ± 19	1.732 ± 21
C(12)	8.499 ± 20	-0.696 ± 21	2.585 ± 24
C(13)	7.727 ± 21	0.407 ± 19	3.190 ± 21
C(14)	6.485 ± 16	0.759 ± 17	2.383 ± 19
C(15)	6.350 ± 17	0.228 ± 23	3.760 ± 18
C(16)	6.059 ± 25	2.139 ± 21	2.134 ± 24
C(17)	6.929 ± 18	0.368 ± 19	-0.092 ± 17
O(1)	5.871 ± 11	-2.676 ± 14	-0.408 ± 12
O(2)	5.181 ± 14	-1.864 ± 17	-2.358 ± 14
Br	1.2380 ± 19	0.0000	2.4434 ± 21

TABLE 2.6

CALCULATED HYDROGEN FRACTIONAL COORDINATES

ATOM	x/a	y/b	z/c
H(2)	0.4332	0.0767	0.3402
H(5)	0.3683	-0.4937	0.0929
H(11)	0.7412	-0.3136	0.4329
H(11')	0.8388	-0.2772	0.3600
H(12)	0.9974	-0.0574	0.5084
H(12')	0.9502	-0.1880	0.6001
H(13)	0.9206	0.0780	0.6071
H(15)	0.6203	-0.0773	0.5648
H(15')	0.6210	0.0569	0.5976

TABLE 2.7

INTRAMOLECULAR BONDED DISTANCES AND E.S.D.S (in Å)

ATOM A	ATOM B	A - B	ATOM A	ATOM B	A - B
C(1)	C(2)	1.41 ± 2	C(10)	C(17)	1.58 ± 2
C(1)	C(6)	1.34 ± 3	C(11)	C(12)	1.53 ± 3
C(2)	C(3)	1.39 ± 2	C(12)	C(13)	1.48 ± 3
C(3)	C(4)	1.38 ± 2	C(13)	C(14)	1.52 ± 3
C(3)	C(10)	1.56 ± 2	C(13)	C(15)	1.50 ± 3
C(4)	C(5)	1.40 ± 2	C(14)	C(15)	1.48 ± 3
C(5)	C(6)	1.43 ± 3	C(14)	C(16)	1.47 ± 3
C(6)	C(7)	1.54 ± 3	O(1)	C(4)	1.44 ± 2
C(8)	C(9)	1.48 ± 3	O(1)	C(8)	1.35 ± 2
C(10)	C(11)	1.57 ± 3	O(2)	C(8)	1.19 ± 2
C(10)	C(14)	1.53 ± 3	Br	C(1)	1.95 ± 1

TABLE 2.8

VALENCY ANGLES AND E.S.D.S (in degrees)

ATOM A	ATOM B	ATOM C	A - B - C	ATOM A	ATOM B	ATOM C	A - B - C
Br	-C(1)	-C(2)	113.9±1.2°	C(3)	-C(10)	-C(14)	111.6±1.2°
Br	-C(1)	-C(6)	120.5±1.2	C(3)	-C(10)	-C(17)	109.5±1.3
C(2)	-C(1)	-C(6)	125.6±1.5	C(11)	-C(10)	-C(14)	105.9±1.3
C(1)	-C(2)	-C(3)	117.6±1.4	C(11)	-C(10)	-C(17)	111.8±1.3
C(2)	-C(3)	-C(4)	117.0±1.4	C(14)	-C(10)	-C(17)	110.0±1.5
C(2)	-C(3)	-C(10)	119.5±1.4	C(10)	-C(11)	-C(12)	104.3±1.5
C(4)	-C(3)	-C(10)	123.5±1.4	C(11)	-C(12)	-C(13)	103.0±1.6
C(3)	-C(4)	-C(5)	125.3±1.5	C(12)	-C(13)	-C(14)	112.5±1.7
C(3)	-C(4)	-O(1)	121.1±1.3	C(12)	-C(13)	-C(15)	123.1±1.8
C(5)	-C(4)	-O(1)	113.3±1.5	C(14)	-C(13)	-C(15)	58.7±1.2
C(4)	-C(5)	-C(6)	116.4±1.8	C(10)	-C(14)	-C(13)	103.7±1.4
C(1)	-C(6)	-C(5)	117.6±1.6	C(10)	-C(14)	-C(15)	115.6±1.6
C(1)	-C(6)	-C(7)	126.1±1.8	C(10)	-C(14)	-C(16)	121.2±1.7
C(5)	-C(6)	-C(7)	116.2±2.0	C(13)	-C(14)	-C(15)	59.9±1.2
O(1)	-C(8)	-O(2)	122.0±1.6	C(13)	-C(14)	-C(16)	123.0±1.7
O(1)	-C(8)	-C(9)	109.8±1.5	C(15)	-C(14)	-C(16)	117.9±1.7
O(2)	-C(8)	-C(9)	128.2±1.7	C(13)	-C(15)	-C(14)	61.4±1.2
C(3)	-C(10)	-C(11)	107.9±1.4	C(4)	-O(1)	-C(8)	118.3±1.3

TABLE 2.9

INTRAMOLECULAR NON-BONDED DISTANCES (in Å)

ATOM A ATOM B	A - B
C(1)...C(4)	2.68 Å
C(2)...C(5)	2.82
C(3)...C(6)	2.84
C(5)...O(2)	3.10
C(7)...Br	3.26
C(10)...O(1)	2.98
C(11)...C(15)	2.84
C(11)...C(16)	3.85
C(12)...C(16)	3.77
C(12)...C(17)	3.28
C(13)...C(17)	3.38
C(15)...C(17)	3.90
C(16)...C(17)	2.97
C(17)...O(1)	3.24

TABLE 2.10

INTERMOLECULAR DISTANCES (in Å) < 4 Å

Transformations should be applied to the coordinates of the second atom.

ATOM A ATOM B	e.p.	distance Å
C(1)...C(9)	i	3.69
C(1)...C(15)	ii	3.69
C(4)...C(16)	iii	3.85
C(5)...C(9)	i	3.81
C(5)...O(2)	iv	3.54
C(6)...C(9)	i	3.61
C(6)...C(15)	ii	3.72
C(7)...C(9)	v	3.68
C(8)...O(2)	iv	3.44
C(9)...O(2)	iv	3.60
C(11)...C(16)	iii	3.99
C(16)...O(1)	vi	3.55
C(17)...O(2)	i	3.54
O(1)...O(2)	iv	3.59
O(2)...O(2)	i	3.81

Equivalent positions are :-

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

TABLE 2.11

Best-planes calculated through various atoms of the molecule.

(Schomaker et al. 1959)

Atoms Defining the Planes

PLANE 1	C(1), C(2), C(3), C(4), C(5), C(6)
PLANE 2	C(8), C(9), O(1), O(2)
PLANE 3	C(10), C(12), C(13), C(14)

Plane Equations

PLANE 1 $-0.1813X' + 0.5790Y - 0.7949Z' = -2.2987$

PLANE 2 $-0.6218X' - 0.7763Y - 0.1034Z' = -1.5320$

PLANE 3 $0.5147X' + 0.6382Y - 0.5726Z' = 2.4345$

Distances of Atoms (in Å) from the Planes

PLANE 1	C(1)	0.0374	C(4)	0.0402
	C(2)	-0.0205	C(5)	-0.0236
	C(3)	-0.0180	C(6)	-0.0155
	C(7)	-0.0318	Br	0.1321
	C(10)	-0.0492	O(1)	0.0088

TABLE 2.11 (contd.)

PLANE 2	C(8)	-0.0045	O(1)	0.0013
	C(9)	0.0013	O(2)	0.0018
PLANE 3	C(10)	-0.0141	C(13)	-0.0244
	C(12)	0.0153	C(14)	0.0231
	C(11)	-0.4991	C(15)	-1.1731

Dihedral Angles Between Planes

PLANE 1 - PLANE 2	75.3°

TABLE 2.12

DETAILS OF ANOMALOUS DISPERSION CALCULATION

h	k	ℓ	I(+k)/I(-k)	$\lvert F(+k)\rvert^2/\lvert F(-k)\rvert^2$
1	5	-3	>1.0	1.3
		-1	0.8	0.9
		1	2.0	1.1
		3	<1.0	0.9
1	4	-7	<1.0	0.6
		-2	1.3	1.1
		1	0.7	0.8
		2	1.3	1.1
1	3	-5	1.3	1.1
		-4	0.6	0.7
		-3	1.7	1.1
		-1	<1.0	0.9
		0	0.6	0.8
		1	1.3	1.3
		2	1.3	1.2
		3	1.3	1.1
		6	0.7	0.9
1	2	-8	1.5	1.2
		-6	1.3	1.2
		-4	1.3	1.2
		-3	0.8	0.8
		1	0.7	0.7
		3	2.0	1.3
		5	0.8	0.9
1	1	2*	1.3	0.8
		3	1.2	1.1
		4	0.7	0.9

* denotes a disagreement

FIGURE 2.1

The Harker section at v = 1/2 of the Patterson function P(uvw). The bromine vector is marked with a cross. Contours are at arbitrary levels.

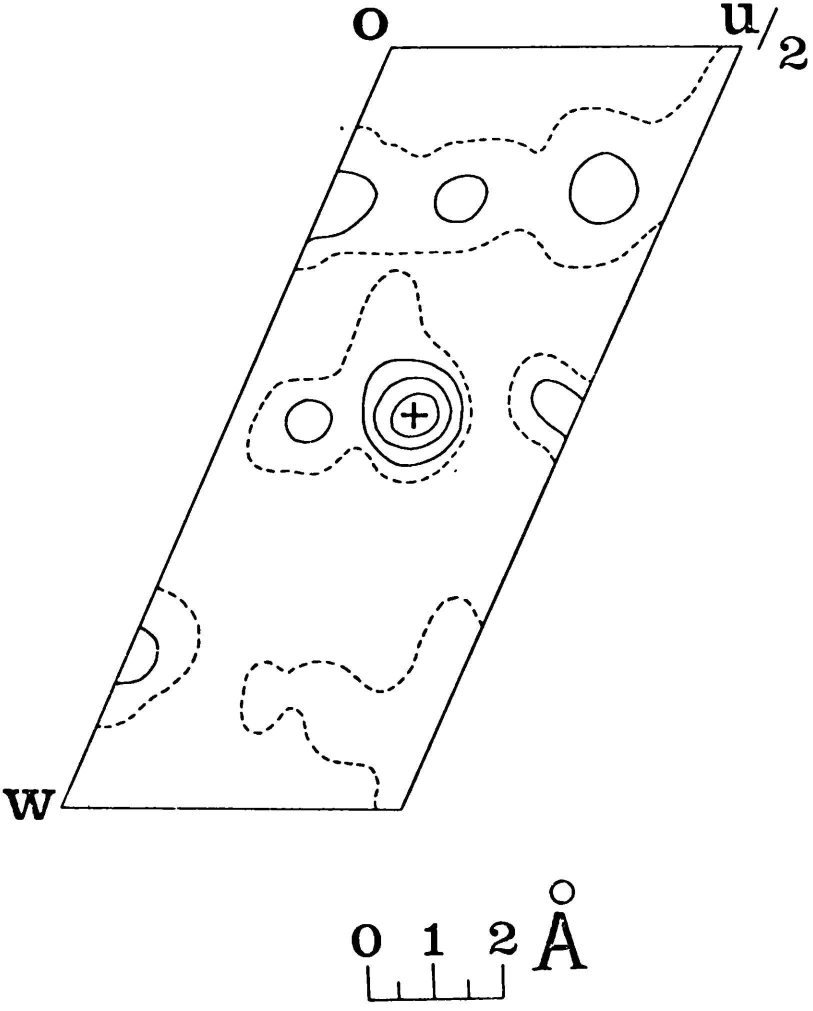

O
u/2
W
0 1 2 Å

FIGURE 2.2

Superimposed sections of the final electron-density distribution viewed down the b-axis. Contour-levels are at intervals of 1e/Å^3 except around the bromine atom where they are at intervals of 5e/Å^3.

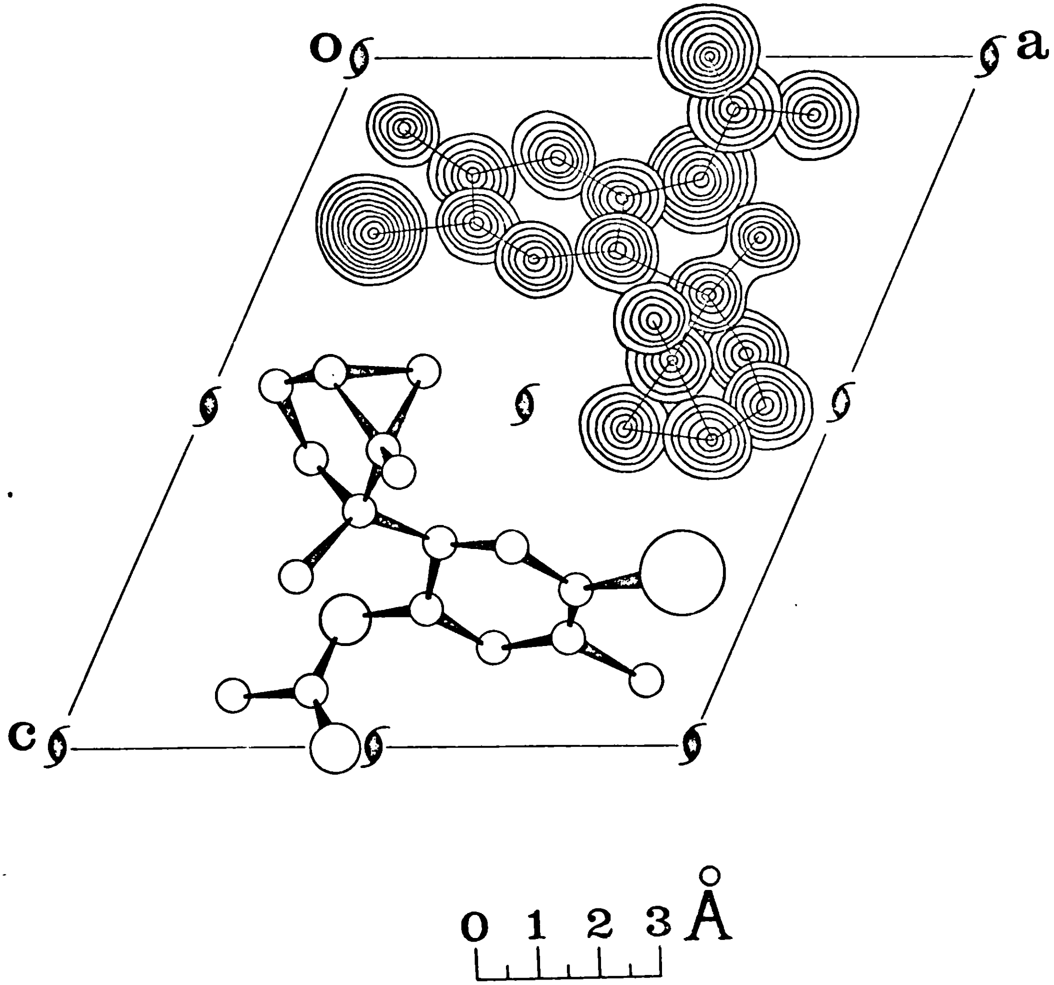

o
a
c
0 1 2 3 Å

FIGURE 2.3

Atomic numbering scheme. Hydrogen atoms are numbered as the carbon atoms to which they are bonded.

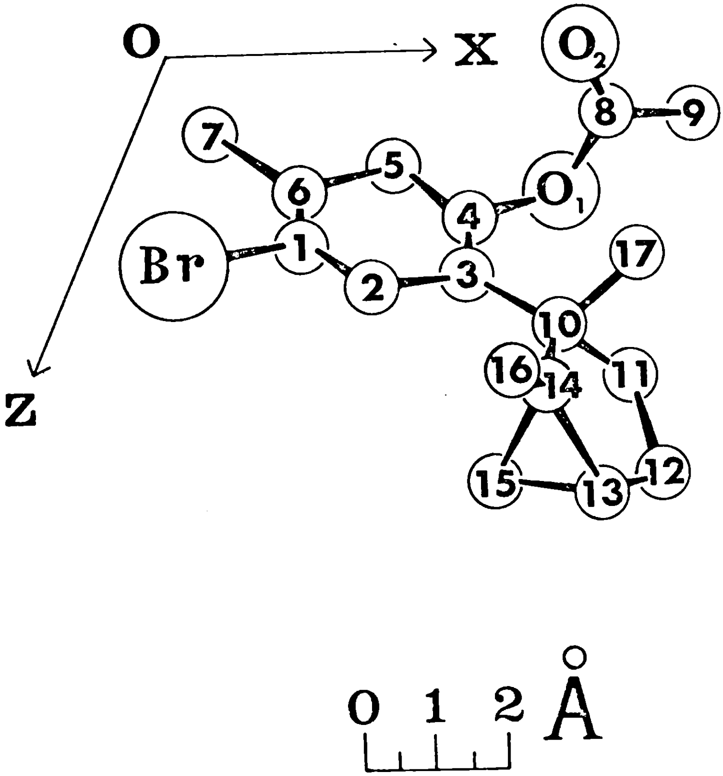
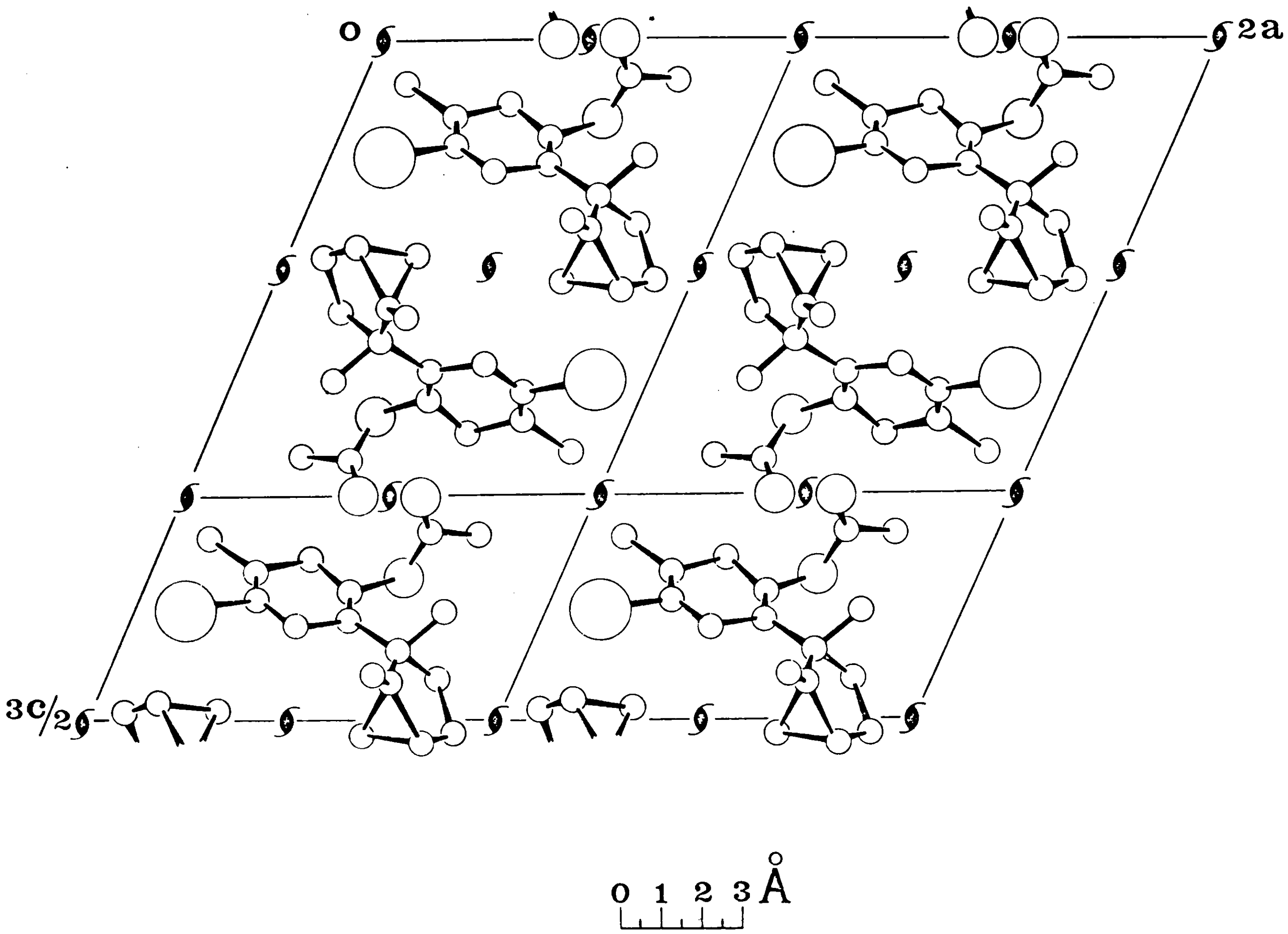

O
X
Z
O₂
8
9
7
5
6
O₁
4
Br
1
2
3
17
10
16
14
11
15
13
12
0 1 2 Å

FIGURE 2.4

Molecular packing viewed down the b-axis.


0
2a
3c/2
0 1 2 3 Å

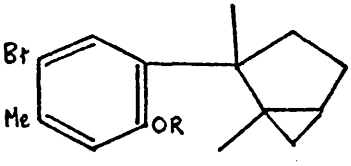
2.3 DISCUSSION

The structure analysis of laurinterol acetate has established both the structure and absolute stereochemistry of laurinterol (II , R = H), and our constitution agrees with that proposed by Irie on the basis of chemical and spectroscopic evidence.

A fundamental step in the elucidation of the structure of laurinterol by Irie was the discovery that treatment with toluene-p-sulphonic acid converted laurinterol into aplysin (III) (Yamamura and Hirata, 1963). The absolute stereochemistry of aplysin must therefore be as shown in IV ($R^1 = H$, $R^2 = H$) . Furthermore, aplysinol must also have the absolute stereochemistry shown in IV ($R^1 = OH$, $R^2 = H$; or $R^1 = H$, $R^2 = OH$) . That the tertiary-methyl and methyl-hydroxyl groups of aplysinol were *cis* had been correctly deduced previously by Yamamura and Hirata (1963).

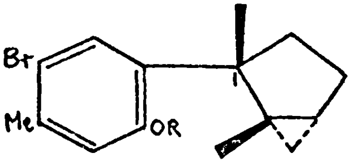
Irie and his co-workers (Irie, Yasunari, Suzuki, Imai, Kurosawa and Masamune, 1965) have determined the structure and stereochemistry of the hydrocarbon laurene (V), also isolated from *Laurencia glandulifera* . They suggest that the methyl groups are trans on the basis of n.m.r. evidence.

The sesquiterpenoid cuparene (VI) has been shown (Enzell and Erdtman, 1958) to have the same absolute stereochemistry at position (1) as (+)-camphor, which has itself been shown (Allen and Rogers, 1966) to have the absolute stereochemistry VII . Laurene has been converted into (+)-cuparene (Irie, personal



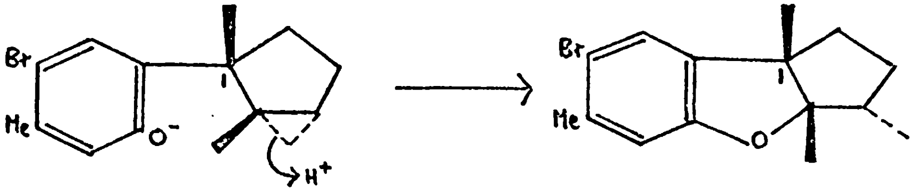
R = H or CH_3CO

I

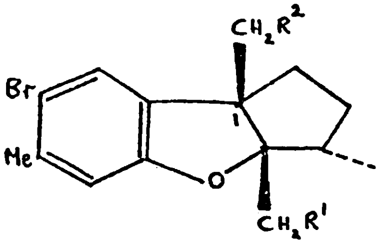


R = H or CH_3CO

II

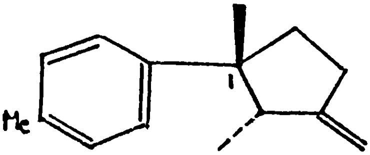


III

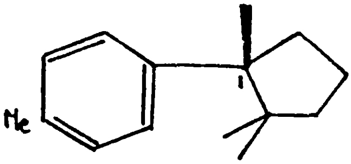


R^1 = H , R^2 = OH
or R^1 = OH, R^2 = H

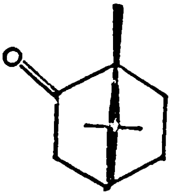
IV



V



VI



VII

communication) and must therefore have the same absolute stereochemistry at position (1) as the latter.

It has been established, therefore, that laurinterol, aplysin, aplysinol, laurene and cuparene all share the same absolute stereochemistry at position (1). This observation adds weight to the possibility of a biological precursor common to all five compounds.

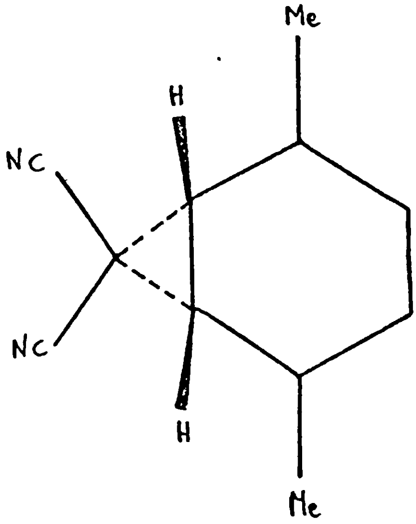
The bond distances (Table 2.7) within the benzene ring do not vary significantly from accepted literature values (Sutton et al., 1965). An examination of the atomic deviations from the best-plane calculated through the six atoms C(1),.......,C(6) of the benzene ring shows that within experimental error the ring must be considered planar. However, the bromine atom and C(7) deviate significantly from this plane. This may be attributed to slight twisting which relieves the steric interaction between the methyl group and the bromine atom, increasing the C(7)...Br non-bonded distance to 3.26 Å. In view of the large estimated standard deviations for atomic positional parameters, the deviations of C(10) and O(1) from the plane of the benzene ring are not entirely significant, but do show the same trend as was observed for the bromine atom and C(7). Again this may presumably be attributed to steric interaction between two <u>ortho</u> substituents, the C(10)...O(1) non-bonded distance being 2.98 Å. Slight deviations from accepted values of valency angles within the benzene ring (Table 2.8), if significant, may also be attributed to the steric interactions between two pairs of ortho substituents.

Calculation of the best-plane (Table 2.11) through the four atoms C(8), C(9), O(1) and O(2) of the acetate group shows that within experimental accuracy this group is planar. The angle between the plane of the acetate group and the plane of the benzene ring is 75° . The bond lengths and valency angles of the acetate group do not differ significantly from accepted literature values.

A study of the conformation of the bicyclo[3,1,0]hexane system reveals that the cyclopentane ring adopts an "envelope" conformation, atoms C(10), C(12), C(13) and C(14) being planar (Table 2.11) with C(11) lying 0.5 Å from this plane and hence forming the "flap" of the envelope. The angle between the plane of the cyclopropane ring and the best-plane through C(10), C(12), C(13) and C(14) is 114° ; also C(11) and C(15) lie on the same side of the latter plane, so that the bicyclo[3,1,0]hexane skeleton adopts an overall "boat" conformation.

The bond distances within the cyclopentane and cyclopropane rings do not differ significantly from accepted values, the mean value for C - C single bonds in the cyclopentane ring being 1.53 Å , and in the cyclopropane ring being 1.50 Å . The average value of valency angle within the cyclopentane ring is 105.8° which compares well with the value of 105° quoted by Sim (1965) . The angles in the cyclopropane ring are not significantly different from 60°. The valency angles at the junction of the two rings are comparable with the angles found for the corresponding centres in 2,5-dimethyl-7,7-dicyano-norcaradiene (VIII) (Fritchie, 1966), the large deviations from tetrahedral values arising from the presence of the cyclopropane ring. However, in the case of laurinterol acetate it is found that there is a marked difference in the valency angles around C(13) and C(14) . For example, C(12)-C(13)-C(14) is 112.5° compared with 103.7° for C(10)-C(14)-C(13) ; and the angle C(12)-C(13)-C(15) is 123.1° compared with 115.6° for C(10)-C(14)-C(15) . An explanation for this is found in the interaction of the <u>cis</u> methyl groups C(16) and C(17) which are separated by 2.97 Å . Further examination of the angles around C(14) reveals that C(10)-C(14)-C(16) and C(13)-C(14)-C(16) have increased to 121.2° and 123.0° respectively, these increases having the effect of moving C(16) away from C(17) and also of reducing the eclipsing of the two groups. Thus the conformation of the bicyclo[3,1,0]hexane system in laurinterol acetate is partly determined by the interaction between the two methyl groups. An additional factor which may affect the conformation is interaction between C(11) and C(15) which are separated by 2.84 Å .

The C(8)...O(2) distance of 3.44 Å is the shortest intermolecular contact, and there is no suggestion of hydrogen bonding as was found in laurencin (Chapter 1).



VIII

PART III

THE CRYSTAL STRUCTURES OF THREE SYNTHETIC BICYCLIC MOLECULES

CHAPTER 1 INTRODUCTION

The three structure analyses which are described separately in this part of the thesis were each undertaken for a different chemical reason and the results have provided the answers for the initial problems in each case. However, all three molecules contain bicyclic ring systems which are of conformational interest, and it has proved possible to compare and contrast the three conformations in Chapter 5 under the general title "Molecular Strain and Conformations in Bicyclic Systems" .

A separate chapter has been devoted to each analysis and in each of these chapters the pertinent problems have been introduced, the experimental work has been described, and the individual molecular geometries have been fully discussed.

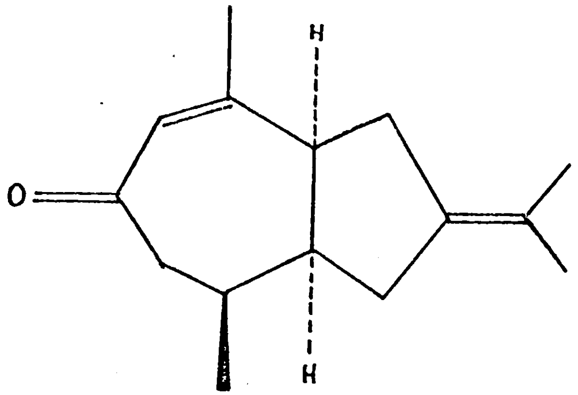
CHAPTER 2 THE CRYSTAL STRUCTURE OF ANTI-3-EXO-BENZOYLOXY-BICYCLO [3,2,2] NON-6-ENE-8,9-ENDO-CIS-DICARBOXYLIC ACID ANHYDRIDE .

2.1 INTRODUCTION

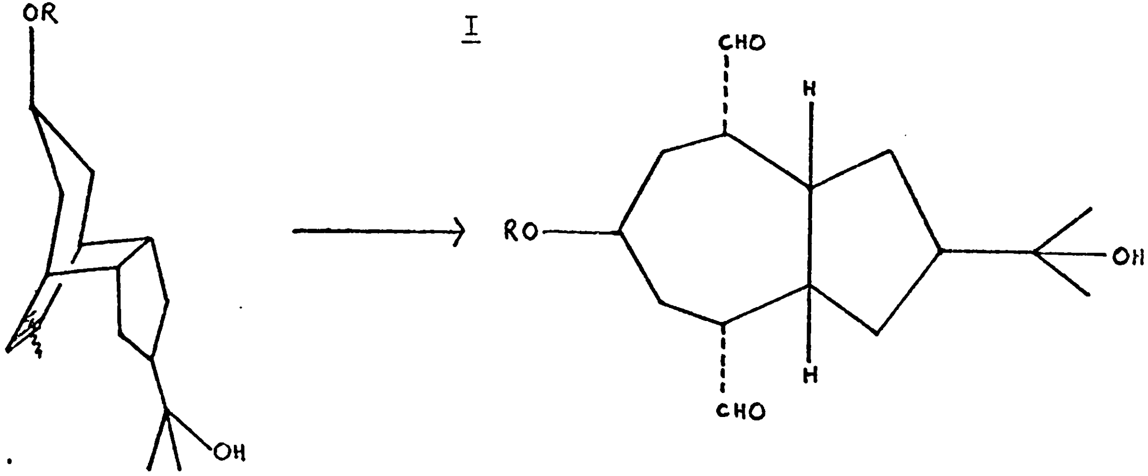
The structure I for β-vetivone, the active constituent of the essential oil of Vetiver (Vetiveria zizanioides Stapf.), was proposed by Pfau and Plattner (1940) . In an attempt to confirm this structure Baker and Chalmers (1967) undertook the synthesis of I by a completely stereoselective route, envisaging a cleavage of the type II → III . In the initial stages of the synthesis of II , 1-benzoyloxycyclohepta-3,5-diene was reacted with maleic anhydride (IV + V) yielding the two epimers VI and VII and in addition the isomeric endo adduct VIII . Although separation of all three products was possible, unambiguous identification of the epimers VI and VII proved impossible despite the fact that one was produced in 34% yield and the other was produced in 11% yield.

Whereas the endo configuration of the anhydride group has been established in the case of compound IX and assumed for compound X , no study has been made of the conformational preference of the three-carbon bridge in the latter type. From theoretical considerations it was expected that in the mixture of products formed in the reaction IV + V , anti-3-exo-benzoyloxy-bicyclo[3,2,2]non-6-ene-8,9-endo-cis-dicarboxylic acid anhydride (VI) should be more stable than the syn-3-exo epimer (VII) , and should hence correspond to the major product (34%) . The argument for this was that the interaction between the 3-endo and the 8,9-exo protons (see Figure 2.3 for numbering) should render VII less stable than VI .

To resolve the difficulty of identifying the epimers, a reaction analogous to IV + V was carried out using 1-p-bromobenzoyloxycyclohepta-3,5-diene and the corresponding bromine-containing products were obtained. A single-crystal X-ray structure analysis of the major product (whose spectral properties were identical to those of the major product of IV + V) proved that, as expected from theoretical considerations, the epimer resulting in 34% yield from the reaction IV + V has the structure VI with the anti-3-exo conformation. The analysis has also confirmed the endo configuration of the anhydride group. It has also been found that steric strain in the bicyclic system has been relieved by ring-flattening with accompanying valency-angle distortions.

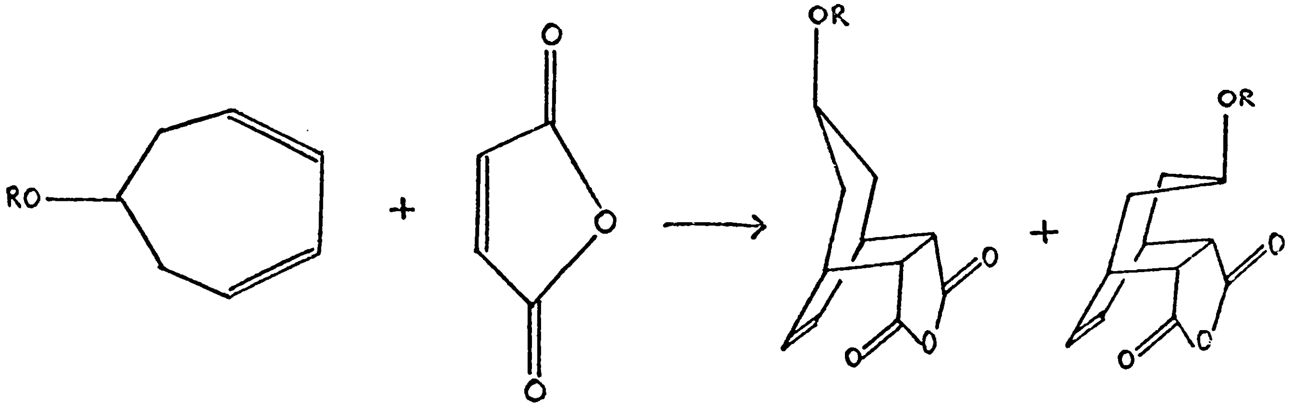


I



II

III

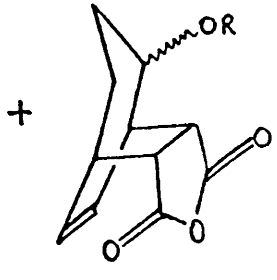


IV

V

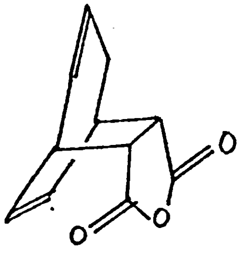
VI

VII

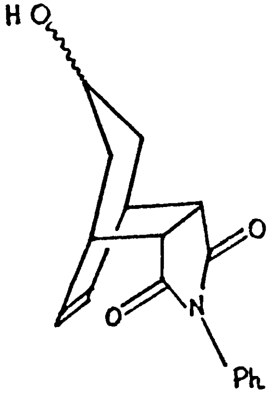


VIII

R = PhCO or BrPhCO



IX



X

2.2 EXPERIMENTAL

2.2.1 Crystal Data

anti-3-exo-p-bromobenzoyloxybicyclo[3,2,2]non-6-ene-8,9-endo-

-dicarboxylic acid anhydride, $C_{18}H_{15}O_5Br$, M = 391 ,

Monoclinic, $a = 13.47\pm0.04$, $b = 12.31\pm0.04$, $c = 10.63\pm0.03$ Å ,

$\beta = 117.5\pm0.2^\circ$, $U = 1563$ Å^3 , $D_m = 1.62$ g.cm.$^{-3}$ (by flotation

in KI/H_2O) , $z = 4$, $D_x = 1.65$ g.cm.$^{-3}$,

F(000) = 792 ,

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

Linear absorption coefficient for X-rays ($\lambda = 1.5418$ Å) $\mu = 42\text{cm}^{-1}$.

2.2.2 Crystallographic Measurements

The unit-cell parameters were determined from oscillation and Weissenberg photographs taken with Cu-Kα radiation ($\lambda = 1.5418$ Å) and from precession photographs taken with Mo-Kα radiation ($\lambda = 0.7107$ Å) . The space group was uniquely determined from systematic absences observed in the 0k0 and h0ℓ spectra.

A small crystal rotating about c was exposed to Cu-Kα radiation and 1,977 independent reflexions from the reciprocal lattice nets hk0 - hk8 were recorded on equatorial and equi-inclination Weissenberg photographs using the multiple-film technique with six films in each pack. The intensities were estimated visually by comparison with a calibrated wedge. The amplitudes were corrected for Lorentz and polarisation factors and were subsequently placed on an approximately absolute scale by making $k\sum|F_o| = \sum|F_c|$ for each layer. No allowance was made for absorption and unobserved reflexions were not considered.

2.2.3 Structure Determination

The value of 1.25 for the ratio $f^2_{Br} / \sum_R f^2_R$ indicated a reasonable chance of success for the heavy atom method of phase determination and the analysis subsequently proceeded on this basis (Lipson and Cochran, 1966).

The equivalent positions of space group $P2_1/c$, namely,

$$\begin{array}{rrr} x, & y, & z \\ -x, & -y, & -z \\ -x, & 1/2+y, & 1/2-z \\ x, & 1/2-y, & 1/2+z \end{array}$$

are such that an atom placed at the general position (x,y,z) will give rise to the following peaks in the Patterson function P(uvw):-

2x ,	1/2 ,	1/2 + 2z
0 ,	1/2 - 2y,	1/2
2x ,	2y,	2z

The data were sharpened to point bromine atom at rest and the three-dimensional Patterson function was computed from which the bromine coordinates (0.2500, 0.2073, 0.0000) were determined. The Harker section at $v = 1/2$ of the Patterson function is shown in Figure 2.1 .

The incomplete contribution to the phasing from the bromine atom alone, arising from the "special" values of the bromine x and z coordinates, results in pseudo-symmetry in the initial electron-density distributions. Despite the pseudo-symmetry, all but five atoms were unambiguously identified in the first electron-density distribution evaluated with the observed amplitudes and the signs appropriate to the bromine atom. Contributions from all atoms whose coordinates were determined were included in the second structure-factor calculation and the subsequent electron-density distribution revealed the complete structure resolved from the last traces of the pseudo-mirror image. Two further rounds of structure-factor and electron-density calculations refined the atomic parameters and reduced the residual R to 0.21. Further refinement of atomic positional and vibrational parameters was carried out by least-squares methods as described in the following section.

After each of the previous structure-factor calculations the layers hk0 - hk8 were put on an approximately absolute scale by making $k \sum |F_o| = \sum |F_c|$ for each layer. An overall isotropic temperature factor $U_{iso} = 0.05$ Å^2 was assumed in all calculations. Where only part of the structure was included in the structure-factor calculations, a suitable modification function (Sim, 1961) was applied to the Fourier coefficients to improve resolution in the electron-density distribution.

2.2.4 Structure Refinement

The refinement of positional, thermal (isotropic and anisotropic) and scale parameters by three-dimensional least-squares methods converged after 14 cycles with $R = 0.089$ and $R' = 0.0132$. Details of the refinement are given in Table 2.1 .

After cycle 5 the data were converted to an overall absolute scale using the refined values of the layer-scale factors, and in all subsequent cycles the overall scale factor was refined. The Glasgow least-squares program outputs an analysis of the weighting scheme used in a refinement cycle in the form of $w\Delta^2$ batched according to $(\sin\theta)/\lambda$ and $|F_o|$. A weighting scheme of the form

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

was applied in all cycles. Initially the parameters $p_1,..,p_3$ were chosen to give unit weights to all reflexions, but were subsequently varied to achieve the same average $w\Delta^2$ within the various batches of the analysis, the final values being

$$p_1 = 50, \quad p_2 = 0.01, \quad p_3 = 0.001$$

Coordinates for 13 of the 15 hydrogen atoms were calculated from geometrical considerations and their contributions with assumed isotropic thermal parameters $U_{iso} = 0.05$ Å^2 were included in all structure-factor calculations after cycle 8. The hydrogen parameters were not refined. Anisotropic thermal parameters were refined, also after cycle 8, and because of computer-store limitations this necessitated the use of a block-diagonal approximation to the normal-equation matrix in all subsequent cycles. The strategy employed in refining anisotropic vibrational parameters was similar to that employed in the refinement of laurencin (c.f. Part II, Chapter 1, 1.2.4) .

The least-squares refinement was terminated when the calculated shifts were less than one-third of the estimated standard deviations. Excluding contributions from the hydrogen atoms, structure factors were calculated with the final parameters and used to evaluate a final electron-density distribution and a three-dimensional difference synthesis. Superimposed sections of the final electron-density distribution viewed down the b-axis are shown in Figure 2.2 . The difference synthesis revealed no errors in the structure, and although there were a few diffuse peaks in positions stereochemically acceptable for hydrogen atoms, it was impossible to determine their coordinates with any accuracy. The refinement was therefore considered complete.

In all the structure-factor calculations, the atomic scattering factors used were those given in "International Tables for Crystallography", Vol. III . Values of $|F_o|$ and the final values of F_c are given in Table 2.2 . The final fractional coordinates are given in Table 2.3 , and the anisotropic thermal parameters in Table 2.4 are the values of U_{ii} and $2U_{ij}$ in the expression

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

The appropriate estimated standard deviations derived from the inverse of the least-squares matrix are included in Tables 2.3 and 2.4 . Orthogonal coordinates are listed in Table 2.5 and the calculated hydrogen coordinates are listed in Table 2.6 .

Table 2.7 contains bond distances and Table 2.8 contains valency angles. The average estimated standard deviations for C - C, C - O and C - Br bonds are 0.012 Å , 0.011 Å and 0.009 Å respectively, and for valency angles is 0.7° .

These should be regarded as minimum values. Some intramolecular non-bonded distances are listed in Table 2.9 and all intermolecular distances <3.6 Å are listed in Table 2.10 . Details of all best-plane calculations are given in Table 2.11 .

The atomic numbering system is shown in Figure 2.3 , the hydrogen atoms being numbered as the carbon atoms to which they are bonded. The molecular packing viewed down the <u>b</u>-axis is shown in Figure 2.4 .

TABLE 2.1

COURSE OF REFINEMENT

Cycles	Parameters refined	Final R	Final R'	$\Sigma w\Delta^2$
1 - 5	x, y, z, U_{iso} for Br, O, C, Layer scale factors, Full matrix, unit weights.	0.187	0.0555	25,077
6 - 7	x, y, z, U_{iso} for Br, O, C, Overall scale factor, Full matrix, weighting scheme adjusted.	0.185	0.0533	25,068
8 - 14	x, y, z, U_{ij} for Br, O, C, Overall scale factor, Block diagonal, weighting scheme applied, hydrogen atoms included.	0.089	0.0132	6,063

TABLE 2.2

Observed amplitudes and calculated (final) structure factors.

H	K	L	Fo	Fc
13	0	0	13.1	-15.0
12	0	0	15.3	16.2
11	0	0	20.1	22.1
10	0	0	28.4	-33.9
9	0	0	20.6	-28.3
8	0	0	29.7	37.5
7	0	0	63.3	73.6
6	0	0	53.1	-61.2
5	0	0	47.0	-48.5
4	0	0	139.2	143.0
3	0	0	6.2	-0.3
13	1	0	19.7	-24.8
12	1	0	17.9	-18.8
11	1	0	16.7	18.4
10	1	0	21.9	30.4
9	1	0	35.9	-44.7
8	1	0	17.2	-24.7
7	1	0	39.0	39.0
6	1	0	11.0	15.7
5	1	0	71.9	-85.6
4	1	0	18.9	-18.1
3	1	0	46.7	49.6
14	2	0	8.1	10.7
13	2	0	9.7	10.2
12	2	0	21.5	-26.6
11	2	0	3.9	-6.8
10	2	0	14.6	18.9
9	2	0	7.4	10.8
8	2	0	50.4	-59.8
7	2	0	7.7	-5.4
6	2	0	36.0	43.4
5	2	0	52.6	50.5
4	2	0	121.2	-108.1
3	2	0	52.2	46.7
2	2	0	99.9	100.5
1	2	0	17.5	16.1
0	2	0	71.9	-65.9
14	3	0	16.4	-19.2
13	3	0	5.8	5.8
12	3	0	9.2	10.0
10	3	0	22.2	-30.6
9	3	0	22.2	28.2
8	3	0	14.1	16.7
7	3	0	38.8	-37.5
6	3	0	20.4	-21.6
5	3	0	67.8	67.6
4	3	0	35.3	29.1
3	3	0	61.5	-59.6
2	3	0	10.0	2.5
1	3	0	112.9	106.8
14	4	0	6.2	-7.3
12	4	0	11.5	12.6
11	4	0	11.0	10.5
10	4	0	9.7	-10.5
9	4	0	10.8	-11.7
8	4	0	22.9	27.4
7	4	0	16.5	-15.3
6	4	0	32.1	-32.5
5	4	0	51.0	-45.4
4	4	0	80.9	69.7
3	4	0	68.0	53.8
2	4	0	36.5	-30.1
1	4	0	23.7	-20.6
0	4	0	136.8	114.5
12	5	0	8.6	-8.7
11	5	0	5.4	3.7
10	5	0	6.8	7.0
9	5	0	15.6	-16.7
8	5	0	12.9	12.0
7	5	0	17.9	15.3
6	5	0	18.5	20.9
5	5	0	12.1	-10.8
2	5	0	71.0	-57.4
1	5	0	30.6	-30.6
7	6	0	6.4	6.5
6	6	0	20.8	20.8
5	6	0	5.6	-5.2
4	6	0	26.0	-24.8
3	6	0	18.8	17.5
2	6	0	20.4	-16.4
1	6	0	13.8	11.2
0	6	0	27.8	-19.9
10	7	0	14.3	15.7
9	7	0	11.1	-9.8
7	7	0	6.6	-4.4
3	7	0	30.2	28.6
2	7	0	39.1	-33.8
1	7	0	14.1	-9.8
10	8	0	10.3	12.2
9	8	0	12.2	12.3
7	8	0	9.6	-11.3
6	8	0	13.3	12.5
5	8	0	6.4	4.4
4	8	0	10.1	-11.5
3	8	0	17.6	17.4
2	8	0	7.5	7.9
1	8	0	28.1	24.4
0	8	0	10.4	-7.1
10	9	0	8.2	-8.1
9	9	0	11.6	13.2
8	9	0	19.7	22.7
7	9	0	18.5	-23.3
6	9	0	11.1	-10.7
3	9	0	47.2	-47.7
1	9	0	34.1	33.2
10	10	0	6.0	-7.0
9	10	0	4.8	-3.6
8	10	0	6.3	7.5
7	10	0	6.7	8.8
4	10	0	40.8	42.6
3	10	0	21.3	23.5
2	10	0	21.1	-20.3
1	10	0	13.2	-14.4
0	10	0	42.8	42.3
9	11	0	13.9	-18.7
8	11	0	5.8	-5.7
7	11	0	7.2	10.0
5	11	0	31.5	-34.3
1	11	0	11.1	-10.9
8	12	0	8.1	-9.7
7	12	0	9.0	-12.1
6	12	0	14.6	17.2
5	12	0	6.3	6.4
4	12	0	24.3	-26.9
2	12	0	23.2	23.9
1	12	0	7.8	8.3
0	12	0	31.7	-31.0
7	13	0	5.9	-7.0
6	13	0	5.1	-4.8
5	13	0	9.1	10.3
4	13	0	5.9	5.1
3	13	0	21.0	-24.3
2	13	0	6.2	-5.0
1	13	0	8.9	10.6
4	14	0	10.6	11.3
3	14	0	5.2	5.9
2	14	0	10.8	-11.3
0	14	0	15.6	15.4
14	1	1	7.5	-9.5
13	1	1	6.9	-7.1
12	1	1	8.6	10.0
11	1	1	8.5	11.8
10	1	1	9.4	-11.2
9	1	1	7.4	6.5
8	1	1	12.0	15.4
7	1	1	10.0	15.5
6	1	1	5.0	2.5
5	1	1	5.1	-4.7
4	1	1	40.8	42.2
3	1	1	61.4	-62.7
1	1	1	84.2	80.0
2	1	1	30.0	0.8
-3	1	1	5.6	6.5
-4	1	1	59.8	-59.0
-5	1	1	5.4	1.7
-6	1	1	12.8	-16.9
-7	1	1	29.3	-24.7
-8	1	1	29.6	28.8
-9	1	1	35.5	-33.0
-10	1	1	11.6	-10.4
-11	1	1	5.4	-4.8
-12	1	1	13.2	10.8
-13	1	1	15.8	16.3
-14	1	1	6.5	5.9
-15	1	1	8.7	9.4
13	2	1	5.2	-5.9
12	2	1	3.5	-2.9
11	2	1	3.8	5.1
10	2	1	18.0	21.0
9	2	1	19.0	-22.9
8	2	1	14.9	-16.7
7	2	1	7.2	-6.3
6	2	1	2.9	3.2
5	2	1	22.4	-24.2
4	2	1	25.3	-30.8
3	2	1	112.4	101.6
2	2	1	56.7	-49.4
1	2	1	125.7	-134.7
-1	2	1	92.5	88.9
-2	2	1	18.6	-16.9
-3	2	1	34.6	-36.5
-4	2	1	12.2	13.7
-5	2	1	37.9	33.3
-6	2	1	44.9	-34.8
-7	2	1	48.3	-42.4
-8	2	1	46.7	36.4
-9	2	1	17.6	12.4
-10	2	1	8.3	-9.8
-11	2	1	15.3	-13.9
-12	2	1	17.8	17.4
-13	2	1	12.3	11.8
13	3	1	5.8	6.8
11	3	1	5.3	-4.4
10	3	1	12.1	12.8
9	3	1	24.4	27.5
8	3	1	9.5	-11.8
6	3	1	38.7	43.5
5	3	1	14.1	14.7
4	3	1	9.3	-10.8
3	3	1	49.5	-43.4
2	3	1	33.3	34.7
1	3	1	27.1	-30.7
0	3	1	85.6	-84.3
-1	3	1	11.2	-6.9
-2	3	1	80.3	78.1
-4	3	1	119.2	-116.6
-6	3	1	19.9	-11.4
-7	3	1	53.8	-48.0
-8	3	1	63.6	-58.1
-9	3	1	7.9	6.8
-10	3	1	30.4	28.7
-11	3	1	23.0	-20.9
-12	3	1	15.9	-16.1
-13	3	1	6.0	5.1
-14	3	1	5.2	5.9
-15	3	1	11.6	-12.8
12	4	1	12.3	14.5
11	4	1	18.7	-23.8
10	4	1	3.8	-4.2
9	4	1	22.8	26.4
8	4	1	23.7	25.0
7	4	1	17.5	-17.9
6	4	1	23.3	-23.2
5	4	1	74.2	71.0
4	4	1	4.6	-2.0
3	4	1	54.0	-55.4
2	4	1	37.1	-32.4
1	4	1	76.2	75.4
-1	4	1	109.6	-107.0
-2	4	1	25.2	16.8
-3	4	1	75.2	76.1
-4	4	1	29.0	-24.6
-5	4	1	51.2	-54.2
-6	4	1	15.7	20.2
-7	4	1	51.4	45.6
-8	4	1	7.6	-9.2
-9	4	1	34.3	-30.1
-10	4	1	19.3	19.2
-11	4	1	8.6	7.3
-12	4	1	8.3	-6.6
-13	4	1	14.3	-16.7
-14	4	1	9.0	9.1
-15	4	1	5.0	6.4
13	5	1	9.4	-10.9
12	5	1	11.7	15.3
11	5	1	10.0	12.5
10	5	1	5.3	-6.7
9	5	1	15.3	-17.8
8	5	1	30.4	37.2
7	5	1	15.1	18.1
6	5	1	46.9	-52.2
4	5	1	63.4	64.8
3	5	1	9.3	-4.2
2	5	1	106.2	-106.5
1	5	1	17.6	16.6
0	5	1	83.8	78.0
-1	5	1	29.6	-31.4
-2	5	1	33.5	-29.8
-3	5	1	17.3	-14.4
-4	5	1	58.4	56.7
-5	5	1	25.1	-23.5
-6	5	1	67.5	-67.6
-7	5	1	34.2	29.1
-8	5	1	29.9	24.5
-9	5	1	31.5	-29.2
-10	5	1	45.9	-40.5
-11	5	1	32.2	31.2
-12	5	1	10.2	8.1
-13	5	1	15.1	-16.5
-14	5	1	9.2	-11.5
12	6	1	5.8	-6.6
11	6	1	8.3	9.7
10	6	1	12.8	13.1
9	6	1	15.3	-17.4
8	6	1	10.8	-11.2
7	6	1	27.1	30.6
6	6	1	24.3	26.2
5	6	1	19.8	-20.8
4	6	1	34.8	-34.4
3	6	1	37.3	41.2
2	6	1	23.6	21.8
1	6	1	76.3	-79.2
0	6	1	15.7	-15.3
-1	6	1	100.0	101.1
-2	6	1	4.6	-5.8
-3	6	1	60.9	-60.5
-4	6	1	21.3	-14.3
-5	6	1	95.8	88.9
-6	6	1	31.0	-28.8
-7	6	1	36.1	-33.5
-8	6	1	26.9	23.7
-9	6	1	32.2	26.9
-11	6	1	35.4	-33.5
-12	6	1	8.5	6.8
11	7	1	7.8	-7.7
10	7	1	14.2	17.8
9	7	1	16.0	20.2
8	7	1	12.1	-14.2
7	7	1	17.8	-21.0
6	7	1	31.1	32.9
5	7	1	8.6	-9.4
4	7	1	42.5	-49.2
2	7	1	51.9	57.4
1	7	1	11.9	12.0
0	7	1	83.2	-75.9
-1	7	1	13.7	-16.9
-2	7	1	37.7	42.5
-3	7	1	28.9	-26.9
-4	7	1	69.7	-63.9
-5	7	1	42.1	38.2
-6	7	1	33.0	29.1
-7	7	1	17.1	-15.3
-8	7	1	53.0	-49.1
-9	7	1	18.0	16.0
-10	7	1	17.7	16.7
-11	7	1	26.4	-24.7
-12	7	1	13.8	-15.7
-13	7	1	11.6	11.4
12	8	1	7.0	8.4
11	8	1	9.1	-10.7
10	8	1	4.7	-5.5
9	8	1	17.0	20.8
8	8	1	8.5	6.8
7	8	1	19.5	-20.3
6	8	1	8.5	-7.4
5	8	1	51.8	58.3
4	8	1	30.2	32.0
3	8	1	32.6	-33.1
2	8	1	6.7	4.9
1	8	1	53.6	50.1
0	8	1	15.8	15.7
-1	8	1	54.6	-54.7
-2	8	1	22.5	22.9
-3	8	1	69.0	67.7
-5	8	1	26.0	-22.8
-6	8	1	10.4	10.4
-7	8	1	26.1	21.2
-8	8	1	16.2	-15.5
-9	8	1	32.3	-27.2
-10	8	1	8.2	7.5
-12	8	1	6.6	-5.8
-13	8	1	9.4	-12.9
10	9	1	9.5	-11.1
9	9	1	4.8	-4.3
8	9	1	12.6	15.4
6	9	1	16.3	-16.3
5	9	1	13.2	-15.4
4	9	1	24.2	26.3
2	9	1	16.0	-16.4
1	9	1	16.5	16.1
0	9	1	12.1	12.4
-1	9	1	17.8	-21.0
-2	9	1	12.2	-10.1
-3	9	1	8.0	9.7
-4	9	1	46.4	44.0
-5	9	1	3.7	5.0
-6	9	1	36.0	-31.8
-7	9	1	3.8	2.7
-8	9	1	32.3	29.6
-11	9	1	12.3	11.4
-12	9	1	8.1	9.2
9	10	1	8.6	-11.4
7	10	1	8.9	7.7
6	10	1	9.2	9.3
5	10	1	21.3	-23.7
4	10	1	15.3	-17.1
3	10	1	17.8	20.2
2	10	1	16.0	19.2
1	10	1	30.3	-30.2
0	10	1	12.9	-13.3
-1	10	1	30.2	27.4
-2	10	1	5.3	4.9
-3	10	1	36.9	-36.2
-4	10	1	14.2	12.9
-5	10	1	28.1	26.1
-7	10	1	19.3	-20.1
-10	10	1	12.5	-12.6
6	11	1	8.7	10.4
5	11	1	8.3	9.1
4	11	1	7.6	-11.1
3	11	1	10.8	11.6
2	11	1	6.6	-8.5
0	11	1	18.0	-19.7
-2	11	1	12.1	12.5
-3	11	1	18.0	-19.3
-4	11	1	12.1	-12.6
-7	11	1	8.0	-8.7
-8	11	1	5.8	-5.6
1	12	1	16.0	18.7
-1	12	1	11.9	12.0
-2	12	1	3.8	-5.2
-4	12	1	5.2	4.2
-5	12	1	10.1	-11.1
-8	12	1	6.6	8.6
-9	12	1	8.1	-9.6
-10	12	1	4.9	-7.1
-1	13	1	10.0	-11.2
-3	13	1	16.1	-17.8
13	0	2	15.0	-10.2
12	0	2	11.3	12.3
11	0	2	11.3	11.5
10	0	2	10.3	-12.0
9	0	2	29.0	-29.7
8	0	2	20.4	21.3
6	0	2	49.8	-54.0
5	0	2	38.8	-45.6
4	0	2	32.5	35.9
3	0	2	5.8	11.5
1	0	2	102.5	-109.6
-7	0	2	37.3	35.8
-8	0	2	93.2	83.9
-9	0	2	53.0	-49.2
10	0	2	15.6	-12.0
-11	0	2	30.4	27.0
-12	0	2	53.7	51.0
-13	0	2	7.1	4.6
-14	0	2	11.8	9.3
-15	0	2	12.6	12.4
-16	0	2	7.7	9.8
13	1	2	6.4	-6.6
12	1	2	7.1	-6.9
11	1	2	9.8	9.0
10	1	2	16.8	15.8
9	1	2	21.4	-23.1
8	1	2	17.0	-18.5
7	1	2	27.4	29.4
6	1	2	25.1	28.4
5	1	2	67.7	-68.0
4	1	2	40.2	36.5
3	1	2	25.0	29.1
2	1	2	21.5	-11.8
-3	1	2	93.6	-103.9
-4	1	2	8.3	13.9
-6	1	2	57.9	-54.9
-7	1	2	84.2	-86.9
-10	1	2	28.8	-27.9
-11	1	2	52.7	-48.5
-12	1	2	19.8	16.7
-13	1	2	11.6	10.7
-14	1	2	21.0	-20.0
-15	1	2	12.5	-12.2
-16	1	2	16.1	19.7
13	2	2	6.8	7.9
12	2	2	4.9	-5.6
11	2	2	16.7	-16.8
10	2	2	19.6	23.0
9	2	2	13.3	13.4
8	2	2	19.0	-22.3
7	2	2	13.1	-14.3
6	2	2	30.7	31.3
5	2	2	29.9	32.6
4	2	2	68.9	-68.8
3	2	2	32.0	-26.4
2	2	2	21.0	20.5
1	2	2	46.9	44.1
0	2	2	176.0	-196.3
-2	2	2	54.6	49.5
-4	2	2	80.7	-86.2
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-14	5	6	7.9	-7.4
-13	5	6	19.9	16.9
-12	5	6	10.4	9.1
-11	5	6	16.5	-12.0
-10	5	6	26.0	-21.4
-9	5	6	6.9	3.9
-8	5	6	29.5	25.0
-7	5	6	4.4	2.9
-6	5	6	17.7	16.7
-5	5	6	20.5	22.8
-4	5	6	3.9	3.9
-3	5	6	22.2	-25.8
-1	5	6	19.6	19.0
0	5	6	12.5	11.6
1	5	6	14.7	-12.6
2	5	6	11.0	10.3
5	5	6	11.6	-9.8
-15	6	6	3.5	3.3
-12	6	6	10.2	-8.8
-11	6	6	7.4	4.5
-10	6	6	7.4	-6.7
-9	6	6	7.2	7.2
-8	6	6	20.8	-17.3
-6	6	6	6.4	-4.5
-5	6	6	6.3	-7.4
-4	6	6	4.4	-1.4
-3	6	6	12.3	11.7
-2	6	6	18.8	18.3
-1	6	6	9.1	8.9
1	6	6	7.0	-6.8
2	6	6	19.0	18.6
7	6	6	7.4	-7.4
-15	7	6	3.0	-2.8
-14	7	6	5.5	-5.8
-13	7	6	9.0	7.9
-12	7	6	4.9	4.2
-11	7	6	11.5	10.8
-10	7	6	29.5	-27.0
-9	7	6	5.2	5.0
-8	7	6	14.5	-12.7
-6	7	6	11.9	-11.5
-5	7	6	15.1	15.7
-1	7	6	4.9	6.8
1	7	6	16.2	-17.6
3	7	6	7.4	8.1
4	7	6	8.9	-9.3
7	7	6	11.0	10.2
-13	8	6	4.1	4.1
-11	8	6	13.9	-11.5
-10	8	6	7.3	6.4
-9	8	6	5.2	-5.0
-8	8	6	11.7	-10.8
-6	8	6	32.4	31.8
-5	8	6	12.4	11.2
-2	8	6	10.1	9.5
-1	8	6	5.1	6.1
0	8	6	5.2	6.3
2	8	6	9.0	8.9
3	8	6	5.1	1.5
5	8	6	7.9	9.1
-13	9	6	6.1	-6.5
-12	9	6	8.3	-7.9
-11	9	6	13.0	12.1
-10	9	6	16.9	16.0
-9	9	6	11.4	-10.4
-6	9	6	7.4	9.1
-5	9	6	30.9	-30.8
-3	9	6	12.8	10.6
-1	9	6	20.9	-19.5
1	9	6	5.2	2.9
2	9	6	5.1	-4.2
3	9	6	8.5	-9.2
4	9	6	6.5	5.2
5	9	6	4.1	4.6
-13	10	6	16.5	-17.7
-12	10	6	14.9	13.8
-11	10	6	11.5	9.2
-10	10	6	14.2	-12.3
-9	10	6	4.8	-5.0
-8	10	6	21.1	18.5
-7	10	6	23.8	21.8
-6	10	6	26.3	-26.1
-5	10	6	5.2	6.3
-4	10	6	9.0	7.8
-3	10	6	9.0	10.3
-2	10	6	14.7	-15.1
-1	10	6	16.3	15.7
0	10	6	23.8	25.5
1	10	6	5.0	-4.1
4	10	6	7.1	8.0
-11	11	6	6.7	-8.1
-10	11	6	6.7	-6.9
-9	11	6	20.0	16.6
-8	11	6	6.4	5.9
-7	11	6	20.1	-17.0
-6	11	6	4.9	-4.9
-5	11	6	13.9	14.3
-4	11	6	9.9	8.7
-3	11	6	15.7	-14.9
-1	11	6	11.9	12.4
1	11	6	14.4	-13.9
3	11	6	5.5	5.2
4	11	6	8.2	-8.7
-10	12	6	14.1	12.1
-9	12	6	12.3	10.2
-8	12	5	9.6	-9.1
-6	12	6	20.3	18.4
-4	12	6	11.0	-10.3
-2	12	6	7.7	7.9
0	12	6	19.5	-15.9
1	12	6	3.9	-6.1
2	12	6	8.7	7.8
-8	13	6	5.8	-4.5
-7	13	6	8.1	7.0
-5	13	6	15.7	-12.9
-3	13	6	9.3	6.8
-1	13	6	16.7	-14.4
1	13	6	5.0	5.0
-14	1	7	17.8	-15.9
-13	1	7	6.2	-4.9
-12	1	7	7.5	6.6
-11	1	7	14.5	14.8
-10	1	7	22.1	-19.3
-9	1	7	11.3	8.8
-8	1	7	4.5	-4.6
-7	1	7	26.9	-24.2
-6	1	7	23.5	-26.5
-5	1	7	11.3	14.0
-3	1	7	9.3	11.8
-1	1	7	4.0	-2.1
0	1	7	6.5	5.2
2	1	7	7.9	-7.7
4	1	7	6.2	-6.3
5	1	7	7.5	-5.3
-15	2	7	8.4	-8.1
-14	2	7	14.4	-12.2
-13	2	7	13.8	11.3
-12	2	7	4.4	2.7
-11	2	7	19.8	-18.6
-10	2	7	39.1	-37.5
-9	2	7	28.5	26.0
-8	2	7	13.8	17.7
-7	2	7	28.9	-29.7
-4	2	7	12.1	15.4
-3	2	7	32.5	-43.7
-2	2	7	9.1	7.8
-1	2	7	15.4	14.9
0	2	7	4.8	5.3
1	2	7	15.8	-16.1
3	2	7	10.4	8.6
4	2	7	12.4	-10.4
5	2	7	13.7	-14.2
6	2	7	7.1	6.0
7	2	7	6.4	7.0
-15	3	7	20.7	-18.6
-14	3	7	20.8	16.9
-13	3	7	22.0	19.9
-12	3	7	18.6	-15.1
-11	3	7	33.2	-29.5
-9	3	7	3.8	-3.0
-8	3	7	44.9	-45.5
-7	3	7	20.3	-20.9
-6	3	7	37.4	37.9
-5	3	7	13.9	15.0
-4	3	7	45.3	-57.2
-3	3	7	15.6	-13.8
-2	3	7	29.2	30.8
-1	3	7	10.3	-10.7
0	3	7	7.2	-8.3
1	3	7	5.5	5.6
2	3	7	17.5	15.5
3	3	7	10.6	-11.0
4	3	7	7.6	-6.9
6	3	7	7.0	6.8
-15	4	7	11.1	10.1
-14	4	7	22.5	20.4
-13	4	7	20.0	-19.2
-12	4	7	35.5	-33.5
-11	4	7	38.4	35.6
-10	4	7	29.2	-26.8
-9	4	7	39.2	-35.9
-8	4	7	33.2	-32.3
-7	4	7	59.6	62.3
-6	4	7	15.5	-14.9
-5	4	7	25.7	-26.1
-3	4	7	31.2	37.0
-1	4	7	18.1	-18.6
0	4	7	5.4	4.8
1	4	7	18.9	15.8
3	4	7	18.5	-16.4
4	4	7	9.8	9.9
5	4	7	11.9	12.3
7	4	7	5.9	-5.4
-15	5	7	12.2	10.6
-14	5	7	19.4	-17.6
-13	5	7	21.1	-22.1
-12	5	7	22.1	19.3
-11	5	7	22.3	21.1
-10	5	7	44.8	-46.1
-9	5	7	28.9	-25.9
-8	5	7	25.9	23.3
-7	5	7	22.8	21.2
-6	5	7	46.5	-50.3
-5	5	7	22.4	-23.1
-4	5	7	28.6	30.1
-3	5	7	8.7	8.3
-2	5	7	25.5	-23.1
-1	5	7	5.4	-5.5
0	5	7	35.5	36.7
1	5	7	5.9	-5.6
2	5	7	20.3	-18.4
3	5	7	18.6	17.8
4	5	7	12.2	11.3
6	5	7	8.3	-8.1
7	5	7	8.9	7.9
-15	6	7	13.7	-14.2
-14	6	7	12.3	-12.3
-13	6	7	20.2	19.8
-12	6	7	29.3	28.5
-11	6	7	32.1	-30.9
-10	6	7	7.6	-8.2
-9	6	7	24.4	24.0
-8	6	7	17.8	14.7
-7	6	7	42.3	-46.9
-6	6	7	25.0	26.3
-5	6	7	40.4	50.4
-4	6	7	14.5	15.5
-3	6	7	28.6	-32.5
-2	6	7	8.9	8.5
-1	6	7	24.5	26.9
1	6	7	20.3	-19.0
2	6	7	6.2	5.5
3	6	7	13.7	12.4
5	6	7	11.1	-10.3
6	6	7	8.5	7.9
-15	7	7	6.8	-8.3
-14	7	7	13.6	13.8
-13	7	7	21.0	19.7
-12	7	7	28.1	-26.3
-11	7	7	20.0	-18.9
-10	7	7	28.3	27.5
-9	7	7	18.6	16.0
-8	7	7	24.5	-25.3
-7	7	7	44.4	-47.0
-6	7	7	21.8	24.9
-4	7	7	36.6	-40.4
-3	7	7	10.2	-10.4
-2	7	7	34.2	35.2
-1	7	7	10.5	-10.4
0	7	7	24.6	-22.8
2	7	7	12.3	10.4
3	7	7	4.2	-5.2
4	7	7	5.7	-3.1
5	7	7	3.6	3.2
6	7	7	6.9	7.2
-14	8	7	6.6	8.1
-13	8	7	27.2	-26.5
-12	8	7	16.0	-14.8
-11	8	7	23.0	22.7
-10	8	7	6.0	4.6
-9	8	7	24.6	-24.2
-8	8	7	6.2	-5.7
-7	8	7	38.6	38.6
-6	8	7	6.2	-6.4
-5	8	7	7.5	-7.0
-4	8	7	4.3	-3.6
-3	8	7	27.4	30.6
-2	8	7	7.6	-9.4
-1	8	7	10.7	-8.5
0	8	7	4.4	1.7
1	8	7	20.3	18.8
3	8	7	15.0	-12.3
5	8	7	9.2	9.1
-12	9	7	9.5	8.8
-11	9	7	8.4	7.3
-10	9	7	16.0	-15.3
-9	9	7	11.8	-11.8
-8	9	7	29.7	30.3
-6	9	7	13.8	-13.2
-5	9	7	6.2	-6.9
-4	9	7	13.8	12.6
-3	9	7	4.4	4.9
-2	9	7	22.3	-22.4
0	9	7	12.1	11.2
2	9	7	12.6	-10.4
3	9	7	3.7	4.3
-12	10	7	8.8	8.8
-11	10	7	15.7	-15.6
-9	10	7	18.2	16.0
-8	10	7	12.8	13.7
-7	10	7	8.3	-9.2
-6	10	7	6.0	-4.1
-5	10	7	13.4	11.8
-3	10	7	10.4	-9.4
-1	10	7	7.2	7.1
0	10	7	5.7	-5.3
1	10	7	16.3	-15.8
-4	11	7	13.7	-13.0
-6	11	7	6.7	7.7
-6	12	7	7.5	-6.4
-4	12	7	7.7	8.1
-14	0	8	19.1	-17.5
-13	0	8	28.1	-30.7
-12	0	8	30.3	29.9
-11	0	8	29.2	27.6
-10	0	8	41.3	-41.9
-9	0	8	21.6	-18.6
-8	0	8	56.8	56.6
-7	0	8	27.2	30.3
-6	0	8	42.5	-59.0
-2	0	8	29.3	-30.1
-1	0	8	5.0	-3.4
0	0	8	25.1	21.8
1	0	8	10.6	-8.3
2	0	8	21.5	-18.2
3	0	8	6.6	3.7
4	0	8	11.4	9.8
5	0	8	13.9	-13.9
6	0	8	7.8	-7.0
7	0	8	5.5	5.2
-15	1	8	30.0	-27.5
-14	1	8	15.5	-15.6
-13	1	8	30.3	28.8
-12	1	8	38.0	39.3
-11	1	8	47.1	-43.6
-10	1	8	18.0	-16.3
-9	1	8	28.4	27.8
-8	1	8	21.6	21.2
-7	1	8	44.4	-50.2
-6	1	8	10.8	-11.2
-4	1	8	9.0	-13.3
-2	1	8	9.8	-8.5
-1	1	8	26.3	30.2
1	1	8	13.5	-17.1
2	1	8	9.2	8.0
3	1	8	9.4	7.1
4	1	8	6.6	-3.8
5	1	8	9.8	-9.4
7	1	8	4.4	3.2
-15	2	8	16.0	-14.3
-14	2	8	26.6	28.0
-13	2	8	25.5	23.2
-12	2	8	23.9	-25.2
-11	2	8	15.8	-10.2
-10	2	8	22.1	18.3
-9	2	8	8.0	-8.6
-8	2	8	50.8	-54.7
-7	2	8	4.5	5.0
-6	2	8	11.2	10.2
-5	2	8	10.2	14.0
-4	2	8	18.0	-24.5
-3	2	8	5.1	-6.3
-2	2	8	21.1	23.9
-1	2	8	5.3	-2.5
0	2	8	15.3	-17.5
1	2	8	6.3	-7.0
2	2	8	14.6	13.2
3	2	8	11.5	-12.4
4	2	8	13.0	-11.6
6	2	8	7.6	8.0
-15	3	8	18.2	16.3
-14	3	8	20.4	18.6
-13	3	8	27.7	-23.6
-12	3	8	22.1	-22.0
-11	3	8	13.1	[illegible]
-10	3	8	6.3	5.8
-9	3	8	46.9	-45.0
-8	3	8	28.4	-28.0
-7	3	8	45.2	53.6
-6	3	8	16.7	18.7
-5	3	8	27.7	-39.7
-4	3	8	16.2	-17.3
-3	3	8	21.3	23.9
-1	3	8	25.2	-28.4
0	3	8	6.1	6.1
1	3	8	16.9	13.7
2	3	8	4.7	-4.1
3	3	8	6.6	-4.9
4	3	8	7.9	7.6
5	3	8	11.9	13.1
-15	4	8	20.9	16.4
-14	4	8	8.4	-11.2
-13	4	8	9.1	-10.3
-12	4	8	28.1	28.1
-11	4	8	13.3	13.9
-10	4	8	7.9	-6.3
-9	4	8	17.5	-13.4
-8	4	8	36.6	35.6
-7	4	8	6.8	6.6
-6	4	8	15.8	-12.8
-5	4	8	23.5	27.2
-4	4	8	20.7	24.3
-3	4	8	3.8	-6.4
-2	4	8	20.3	-22.3
-1	4	8	10.3	10.2
0	4	8	4.5	3.1
2	4	8	8.1	-7.1
4	4	8	7.7	6.6
-15	5	8	7.6	-8.6
-14	5	8	4.0	4.0
-13	5	8	8.8	8.1
-12	5	8	6.5	7.3
-11	5	8	11.5	-12.7
-10	5	8	9.3	8.6
-9	5	8	15.8	14.6
-8	5	8	16.4	14.9
-7	5	8	19.9	-19.7
-6	5	8	11.6	-11.1
-5	5	8	9.9	-9.6
-4	5	8	7.0	7.6
-3	5	8	15.5	-18.3
-1	5	8	6.3	6.6
1	5	8	10.5	-9.5
2	5	8	4.7	-5.7
3	5	8	7.9	8.9
-15	6	8	14.0	12.8
-11	6	8	4.7	3.7
-10	6	8	19.9	17.9
-9	6	8	4.7	-5.0
-8	6	8	14.5	13.0
-7	6	8	6.4	-5.8
-6	6	8	4.4	-4.8
-4	6	8	7.6	7.9
-1	6	8	6.5	4.6
0	6	8	9.4	-9.7
-8	7	8	4.7	4.3
-7	7	8	6.6	9.4
-5	7	8	11.3	10.0
-4	7	8	9.2	8.9
-3	7	8	4.6	3.5
-2	7	8	14.8	-14.9
-14	8	8	14.9	13.7
-12	8	8	9.6	-9.3
-11	8	8	6.0	-5.9
-10	8	8	12.6	12.0
-9	8	8	14.6	13.7
-7	8	8	14.3	15.6
-4	8	8	14.9	-14.9
-3	8	8	4.7	-5.3
-2	8	8	4.7	4.5
0	8	8	11.2	-10.8
-13	9	8	10.2	-7.9
-12	9	8	14.5	-13.0
-11	9	8	5.4	4.1
-10	9	8	13.1	11.9
-9	9	8	16.3	-14.1
-8	9	8	7.8	-6.8
-7	9	8	19.4	18.1
-6	9	8	11.3	10.4
-5	9	8	19.6	-18.5
-3	9	8	11.3	9.2
-1	9	8	8.9	-8.9
0	9	8	4.3	5.0
1	9	8	9.1	9.1
-12	10	8	13.2	11.0
-11	10	8	15.2	12.3
-10	10	8	13.7	-11.3
-9	10	8	7.9	-7.3
-8	10	8	13.1	12.5
-6	10	8	12.3	-11.8
-5	10	8	7.6	-7.8
-4	10	8	17.5	16.8
2	10	8	7.5	-7.7
-10	11	8	2.9	-3.2
-9	11	8	4.7	4.7
-7	11	8	8.4	-7.3
-6	11	8	6.7	-7.5
-5	11	8	16.6	16.6
-4	11	8	3.9	-3.8
-3	11	8	3.8	-3.2
-2	11	8	3.7	-4.0
-1	11	8	9.9	9.0
0	11	8	6.4	-7.3
1	11	8	5.4	-7.3
-8	12	8	13.5	-12.8
-6	12	8	7.6	7.0
-4	12	8	7.1	-7.0
-3	12	8	5.3	-5.4
-2	12	8	7.0	5.8

TABLE 2.3

FRACTIONAL COORDINATES AND E.S.D.S

ATOM	x/a	y/b	z/c
C(1)	-0.35720 ± 67	0.00300 ± 65	0.29988 ± 108
C(2)	-0.28149 ± 71	0.02993 ± 70	0.23169 ± 109
C(3)	-0.19346 ± 64	0.11542 ± 67	0.31403 ± 99
C(4)	-0.24371 ± 68	0.22315 ± 62	0.33019 ± 101
C(5)	-0.31510 ± 64	0.21069 ± 67	0.40804 ± 96
C(6)	-0.27706 ± 72	0.11606 ± 75	0.51328 ± 106
C(7)	-0.29918 ± 75	0.01584 ± 76	0.45802 ± 115
C(8)	-0.46278 ± 69	0.07712 ± 64	0.23908 ± 103
C(9)	-0.43873 ± 62	0.19135 ± 57	0.30360 ± 93
C(10)	-0.50926 ± 74	0.20199 ± 72	0.37893 ± 105
C(11)	-0.54652 ± 74	0.03425 ± 75	0.28399 ± 124
C(12)	-0.04787 ± 68	0.07319 ± 71	0.25511 ± 109
C(13)	0.01917 ± 60	0.11103 ± 65	0.18591 ± 96
C(14)	0.08787 ± 66	0.03379 ± 75	0.16886 ± 100
C(15)	0.15743 ± 64	0.06297 ± 71	0.11043 ± 104
C(16)	0.16052 ± 64	0.17188 ± 74	0.07325 ± 100
C(17)	0.09204 ± 69	0.24912 ± 74	0.09061 ± 100
C(18)	0.02273 ± 69	0.21794 ± 69	0.14787 ± 105
O(1)	-0.03098 ± 55	-0.00939 ± 55	0.32171 ± 85
O(2)	-0.13003 ± 45	0.14329 ± 46	0.23783 ± 70
O(3)	-0.57113 ± 52	0.10770 ± 51	0.36089 ± 82
O(4)	-0.59057 ± 60	-0.05367 ± 58	0.25996 ± 107
O(5)	-0.51761 ± 62	0.27385 ± 56	0.44500 ± 84
Br	0.26025 ± 8	0.21096 ± 8	0.00323 ± 12

TABLE 2.4

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S (in Å^2)

ATOM	U11	U22	U33	2U23	2U31	2U12
C(1)	0.0452	0.0310	0.0766	-0.0184	0.0845	-0.0029
	41	40	68	77	88	63
C(2)	0.0491	0.0450	0.0674	-0.0197	0.0832	-0.0043
	44	47	65	86	89	72
C(3)	0.0397	0.0456	0.0575	0.0021	0.0742	0.0065
	38	45	60	79	79	66
C(4)	0.0467	0.0350	0.0601	-0.0057	0.0722	0.0012
	42	44	61	73	82	63
C(5)	0.0394	0.0421	0.0503	-0.0153	0.0502	-0.0073
	38	42	55	78	72	68
C(6)	0.0487	0.0534	0.0563	0.0110	0.0702	0.0217
	44	52	61	87	84	77
C(7)	0.0529	0.0524	0.0733	0.0134	0.0936	0.0151
	47	54	69	92	94	79
C(8)	0.0475	0.0373	0.0572	-0.0050	0.0723	-0.0030
	43	43	61	76	84	67
C(9)	0.0407	0.0302	0.0498	0.0005	0.0652	0.0064
	38	42	55	64	74	56
C(10)	0.0523	0.0527	0.0526	0.0012	0.0754	0.0088
	46	51	59	84	84	77
C(11)	0.0488	0.0488	0.0926	0.0227	0.0980	0.0156
	45	51	80	98	100	77
C(12)	0.0410	0.0476	0.0674	0.0076	0.0710	0.0029
	40	49	66	87	84	71
C(13)	0.0319	0.0435	0.0536	-0.0076	0.0534	0.0010
	34	44	56	77	70	63
C(14)	0.0404	0.0583	0.0534	0.0058	0.0589	0.0108
	39	55	60	87	78	75
C(15)	0.0357	0.0483	0.0634	0.0024	0.0677	0.0054
	37	47	63	82	78	66

TABLE 2.4 (contd.)

ATOM	U11	U22	U33	2U23	2U31	2U12
C(16)	0.0356	0.0492	0.0546	-0.0068	0.0501	-0.0011
	38	46	59	82	75	68
C(17)	0.0458	0.0455	0.0589	-0.0018	0.0762	0.0032
	43	44	59	88	83	73
C(18)	0.0438	0.0451	0.0613	0.0050	0.0666	0.0090
	41	46	62	81	81	71
O(1)	0.0608	0.0562	0.0941	0.0468	0.1108	0.0341
	37	39	57	74	77	62
O(2)	0.0400	0.0489	0.0660	0.0116	0.0790	0.0112
	27	34	43	58	57	48
O(3)	0.0546	0.0494	0.0925	0.0196	0.1127	0.0009
	35	36	54	68	74	56
O(4)	0.0646	0.0497	0.0831	-0.0043	0.1009	-0.0222
	42	40	82	92	101	68
O(5)	0.0729	0.0660	0.0802	-0.0271	0.1172	0.0056
	44	45	53	74	83	68
Br	0.0571	0.0636	0.0804	-0.0011	0.1024	-0.0092
	5	6	8	10	10	9

TABLE 2.5

ORTHOGONALISED COORDINATES AND E.S.D.S (in Å)

ATOM	X'	Y	Z'
C(1)	-4.2698 ± 80	0.0369 ± 80	5.4057 ± 98
C(2)	-3.3648 ± 85	0.3684 ± 86	4.2107 ± 98
C(3)	-2.3125 ± 77	1.4208 ± 82	4.5394 ± 89
C(4)	-2.9132 ± 81	2.7470 ± 76	5.0232 ± 93
C(5)	-3.7665 ± 77	2.5936 ± 82	6.2940 ± 92
C(6)	-3.3118 ± 86	1.4287 ± 92	7.1765 ± 98
C(7)	-3.5762 ± 90	0.1950 ± 94	6.7265 ±102
C(8)	-5.5318 ± 82	0.9493 ± 79	5.4150 ± 93
C(9)	-5.2443 ± 74	2.3555 ± 70	5.9515 ± 85
C(10)	-6.0874 ± 88	2.4865 ± 89	7.1902 ± 96
C(11)	-6.5328 ± 88	0.4216 ± 92	6.4123 ±111
C(12)	-0.5722 ± 81	0.9010 ± 87	3.0091 ±100
C(13)	0.2291 ± 72	1.3668 ± 80	1.8572 ± 90
C(14)	1.0504 ± 79	0.4160 ± 92	1.2494 ± 94
C(15)	1.8818 ± 77	0.7752 ± 87	0.1963 ± 95
C(16)	1.9188 ± 77	2.1158 ± 91	-0.2181 ± 95
C(17)	1.1002 ± 82	3.0667 ± 91	0.3917 ± 88
C(18)	0.2717 ± 82	2.6828 ± 85	1.4307 ± 98
O(1)	-0.3703 ± 66	-0.1156 ± 68	3.6121 ± 76
O(2)	-1.5543 ± 54	1.7639 ± 57	3.3355 ± 63
O(3)	-6.8270 ± 62	1.3258 ± 63	7.3826 ± 72
O(4)	-7.0594 ± 72	-0.6607 ± 71	6.4304 ± 96
O(5)	-6.1872 ± 74	3.3711 ± 69	7.9444 ± 73
Br	3.1109 ± 10	2.5969 ± 10	-1.5816 ± 11

TABLE 2.6

CALCULATED HYDROGEN FRACTIONAL COORDINATES

ATOM	x/a	y/b	z/c
H(1)	-0.3762	-0.0814	0.2827
H(2)	-0.3330	0.0622	0.1292
H(2')	-0.2397	-0.0420	0.2281
H(3)	-0.1401	0.0793	0.4143
H(4)	-0.2967	0.2528	0.2267
H(4')	-0.1769	0.2771	0.3897
H(5)	-0.3042	0.2840	0.4664
H(8)	-0.4948	0.0795	0.1265
H(9)	-0.4585	0.2503	0.2219
H(14)	0.0860	-0.0480	0.1997
H(16)	0.0928	0.3315	0.0600
H(17)	-0.0271	0.2781	0.1635

TABLE 2.7

INTRAMOLECULAR BONDED DISTANCES AND E.S.D.S (in Å)

ATOM A	ATOM B	A - B	ATOM A	ATOM B	A - B
C(1)	C(2)	1.535 ± 13 Å	C(10)	O(5)	1.167 ± 12 Å
C(1)	C(7)	1.500 ± 14	C(11)	O(3)	1.360 ± 12
C(1)	C(8)	1.557 ± 11	C(11)	O(4)	1.204 ± 12
C(2)	C(3)	1.524 ± 12	C(12)	C(13)	1.479 ± 13
C(3)	C(4)	1.534 ± 11	C(12)	O(1)	1.199 ± 12
C(3)	O(2)	1.464 ± 10	C(12)	O(2)	1.348 ± 10
C(4)	C(5)	1.538 ± 13	C(13)	C(14)	1.396 ± 12
C(5)	C(6)	1.531 ± 13	C(13)	C(18)	1.384 ± 12
C(5)	C(9)	1.536 ± 10	C(14)	C(15)	1.389 ± 13
C(6)	C(7)	1.340 ± 13	C(15)	C(16)	1.404 ± 13
C(8)	C(9)	1.532 ± 11	C(16)	C(17)	1.395 ± 12
C(8)	C(11)	1.505 ± 13	C(17)	C(18)	1.383 ± 13
C(9)	C(10)	1.504 ± 12	Br	C(16)	1.874 ± 9
C(10)	O(3)	1.390 ± 11			

TABLE 2.8

VALENCY ANGLES AND E.S.D.S (in degrees)

ATOM A	ATOM B	ATOM C	A-B-C °	ATOM A	ATOM B	ATOM C	A-B-C °
C(2)-	C(1)-	C(7)	113.0±7	C(9)-	C(10)-	O(5)	130.3±8
C(2)-	C(1)-	C(8)	110.8±7	O(3)-	C(10)-	O(5)	119.9±9
C(7)-	C(1)-	C(8)	107.9±7	C(8)-	C(11)-	O(3)	112.5±7
C(1)-	C(2)-	C(3)	112.9±8	C(8)-	C(11)-	O(4)	127.9±9
C(2)-	C(3)-	C(4)	113.2±7	O(3)-	C(11)-	O(4)	119.5±9
C(2)-	C(3)-	O(2)	110.0±7	C(13)-	C(12)-	O(1)	124.6±8
C(4)-	C(3)-	O(2)	105.1±6	C(13)-	C(12)-	O(2)	112.5±7
C(3)-	C(4)-	C(5)	113.1±7	O(1)-	C(12)-	O(2)	122.9±9
C(4)-	C(5)-	C(6)	112.8±7	C(12)-	C(13)-	C(14)	116.3±8
C(4)-	C(5)-	C(9)	111.4±7	C(12)-	C(13)-	C(18)	123.8±8
C(6)-	C(5)-	C(9)	107.3±7	C(14)-	C(13)-	C(18)	119.7±8
C(5)-	C(6)-	C(7)	116.7±8	C(13)-	C(14)-	C(15)	120.4±8
C(1)-	C(7)-	C(6)	119.0±8	C(14)-	C(15)-	C(16)	119.1±8
C(1)-	C(8)-	C(9)	112.8±7	C(15)-	C(16)-	C(17)	120.4±8
C(1)-	C(8)-	C(11)	109.7±7	C(15)-	C(16)-	Br	118.5±6
C(9)-	C(8)-	C(11)	102.4±7	C(17)-	C(16)-	Br	121.1±7
C(5)-	C(9)-	C(8)	113.6±6	C(16)-	C(17)-	C(18)	119.4±8
C(5)-	C(9)-	C(10)	110.0±7	C(13)-	C(18)-	C(17)	120.9±8
C(8)-	C(9)-	C(10)	105.3±7	C(3)-	O(2)-	C(12)	115.3±7
C(9)-	C(10)-	O(3)	109.9±7	C(10)-	O(3)-	C(11)	110.0±7

TABLE 2.9

INTRAMOLECULAR NON-BONDED DISTANCES (in Å)

ATOM A ATOM B	A-B	ATOM A ATOM B	A-B
C(1)...C(4)	3.05 Å	C(6)...C(10)	2.97 Å
C(1)...C(5)	2.75	C(6)...C(11)	3.46
C(1)...O(4)	3.05	C(7)...C(9)	2.83
C(2)...C(5)	3.07	C(7)...C(10)	3.44
C(2)...C(12)	3.09	C(7)...C(11)	2.98
C(3)...C(6)	2.82	C(13)...C(16)	2.78
C(3)...C(7)	2.81	C(14)...C(17)	2.79
C(3)...C(8)	3.37	C(15)...C(18)	2.78
C(3)...C(9)	3.39	O(1)...C(14)	2.81
C(3)...O(1)	2.64	O(3)...C(1)	3.48
C(5)...O(5)	3.03	O(3)...C(5)	3.49
C(6)...C(8)	2.86		

TABLE 2.10

INTERMOLECULAR DISTANCES (in Å) < 3.6 Å

Transformations should be applied to the coordinates of the second atom.

ATOM A ATOM B	e.p.	distance Å
C(4)...O(4)	i	3.39
C(5)...O(4)	i	3.34
C(7)...O(3)	ii	3.49
C(8)...O(5)	iii	3.40
C(9)...O(4)	i	3.27
C(9)...O(5)	iii	3.48
C(14)...C(15)	iv	3.47
C(15)...O(4)	v	3.34
C(15)...C(11)	v	3.56
C(16)...O(3)	v	3.58
C(17)...O(1)	vi	3.33
C(18)...O(1)	vi	3.37
O(1)...O(1)	vii	3.49

Equivalent positions are:-

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

ii) $-1 - x, \quad - y, \quad 1 - z$

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

iv) $- x, \quad - y, \quad - z$

v) $1 + x, \quad y, \quad z$

vi) $- x, \quad 3/2 + y, \quad 3/2 - z$

vii) $- x, \quad - y, \quad 1 - z$

TABLE 2.11

Best-planes calculated through various atoms of the molecule.

(Schomaker et al., 1959)

Atoms Defining the Planes

PLANE 1	C(13), C(14), C(15), C(16), C(17), C(18)
PLANE 2	C(12), C(13), O(1), O(2)
PLANE 3	C(1), C(2), C(4), C(5)
PLANE 4	C(1), C(5), C(8), C(9)
PLANE 5	C(1), C(5), C(6), C(7)
PLANE 6	C(8), C(9), C(10), C(11), O(3), O(4), O(5)

Plane Equations

PLANE 1	$-0.7279X' - 0.1948Y - 0.6575Z' = -1.6588$
PLANE 2	$-0.6203X' - 0.4816Y - 0.6191Z' = -1.9483$
PLANE 3	$-0.7983X' + 0.3285Y - 0.5047Z' = 0.6877$
PLANE 4	$0.1869X' + 0.2958Y - 0.9368Z' = -5.8419$
PLANE 5	$0.8842X' - 0.0132Y - 0.4669Z' = -6.3017$
PLANE 6	$-0.7485X' + 0.3685Y - 0.5513Z' = 1.5075$

TABLE 2.11 (contd.)

Distances of Atoms (in Å) from the Planes

PLANE 1	C(13)	0.0047	C(16)	-0.0065
	C(14)	-0.0082	C(17)	0.0032
	C(15)	0.0090	C(18)	-0.0022
	Br	-0.0714	C(12)	-0.0786
PLANE 2	C(12)	0.0065	O(1)	-0.0026
	C(13)	-0.0019	O(2)	-0.0020
PLANE 3	C(1)	0.0051	C(4)	0.0054
	C(2)	-0.0054	C(5)	-0.0050
	C(3)	-0.6656		
PLANE 4	C(1)	-0.0090	C(8)	0.0163
	C(5)	0.0092	C(9)	-0.0165
PLANE 5	C(1)	0.0018	C(6)	0.0036
	C(5)	-0.0018	C(7)	-0.0037
PLANE 6	C(8)	-0.0025	O(3)	0.0208
	C(9)	0.0047	O(4)	-0.0123
	C(10)	0.0010	O(5)	-0.0141
	C(11)	0.0024		

TABLE 2.11 (contd.)

Dihedral Angles Between Planes

PLANE 1 - PLANE 2	17.76°
PLANE 3 - PLANE 4	65.12°
PLANE 3 - PLANE 5	61.67°
PLANE 4 - PLANE 5	53.22°
PLANE 4 - PLANE 6	60.95°

FIGURE 2.1

The Harker section at $v = 1/2$ of the Patterson function $P(uvw)$. The bromine vector is marked with a cross. Contours are at arbitrary levels.

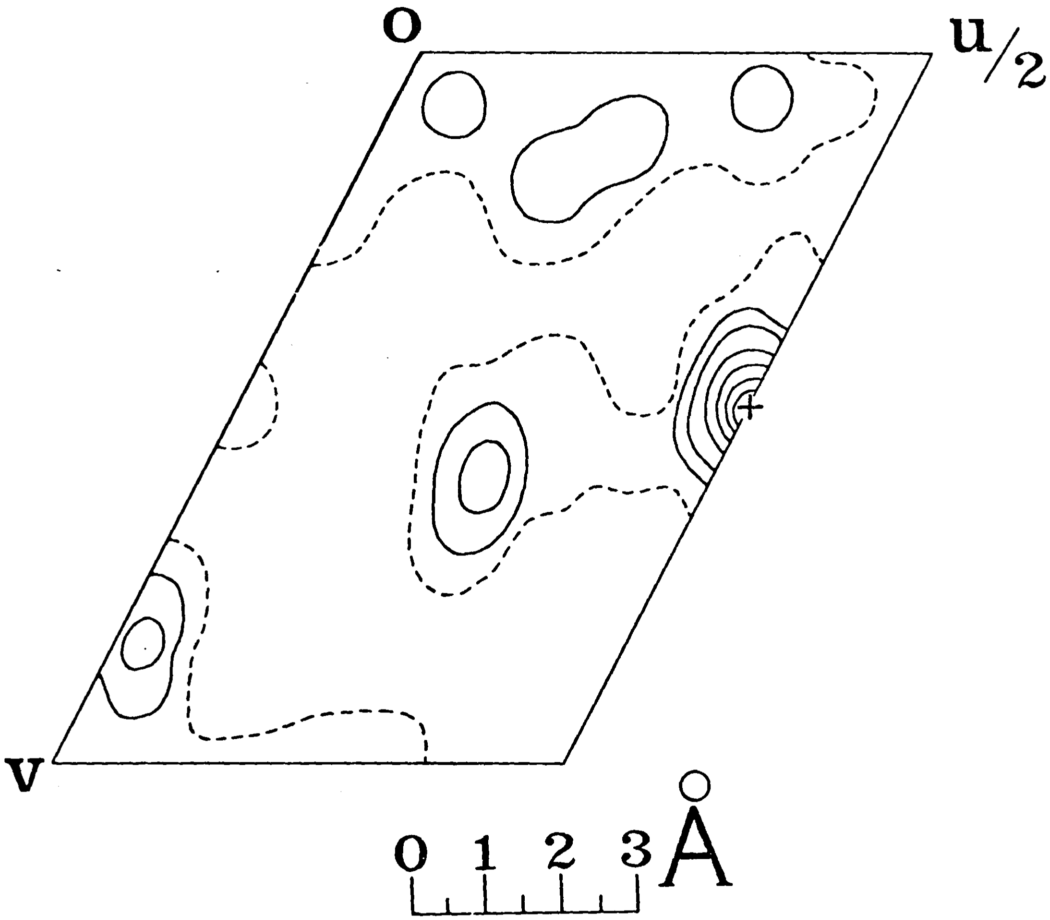

o
u/2
v
0 1 2 3 Å

FIGURE 2.2

Superimposed sections of the final electron-density distribution viewed down the b-axis. Contour-levels are at intervals of 1e/Å^3 except around the bromine atom where they are at intervals of 5e/Å^3.

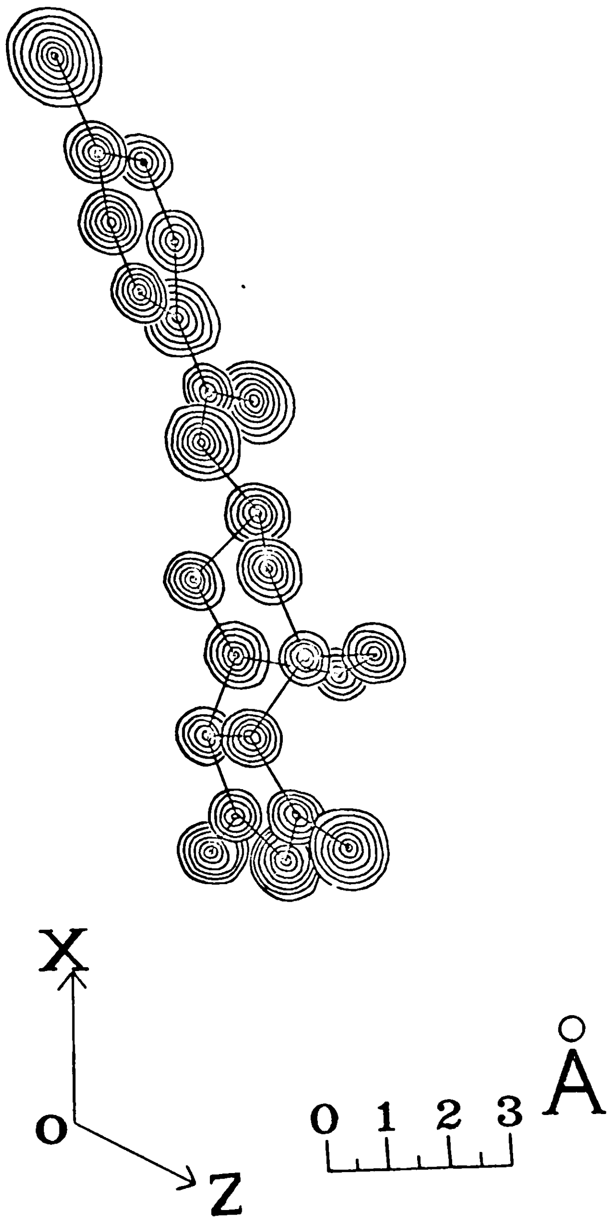

X
O
Z
0 1 2 3 Å

FIGURE 2.3

Atomic numbering scheme. Hydrogen atoms are numbered as the carbon atoms to which they are bonded.

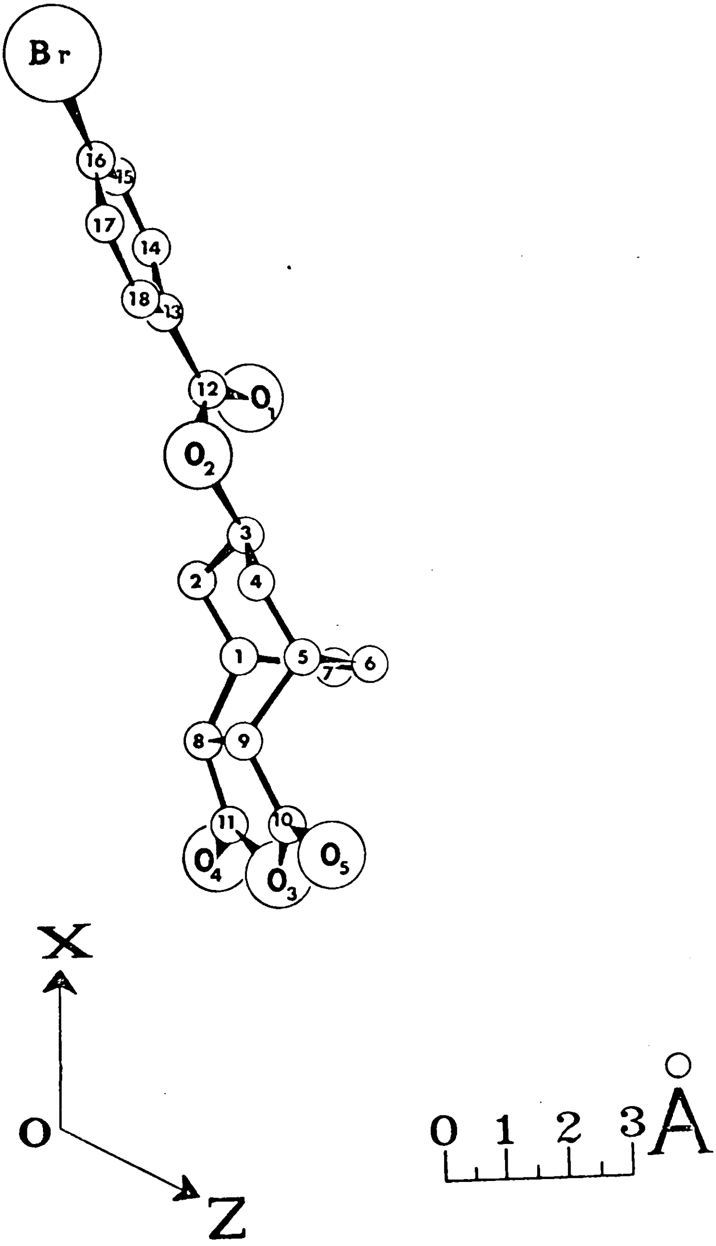

Br
16
15
17
14
18
13
12
O_1
O_2
3
2
4
1
5
7
6
8
9
11
10
O_4
O_3
O_5
X
O
Z
0 1 2 3 Å

FIGURE 2.4

Molecular packing viewed down the b-axis.

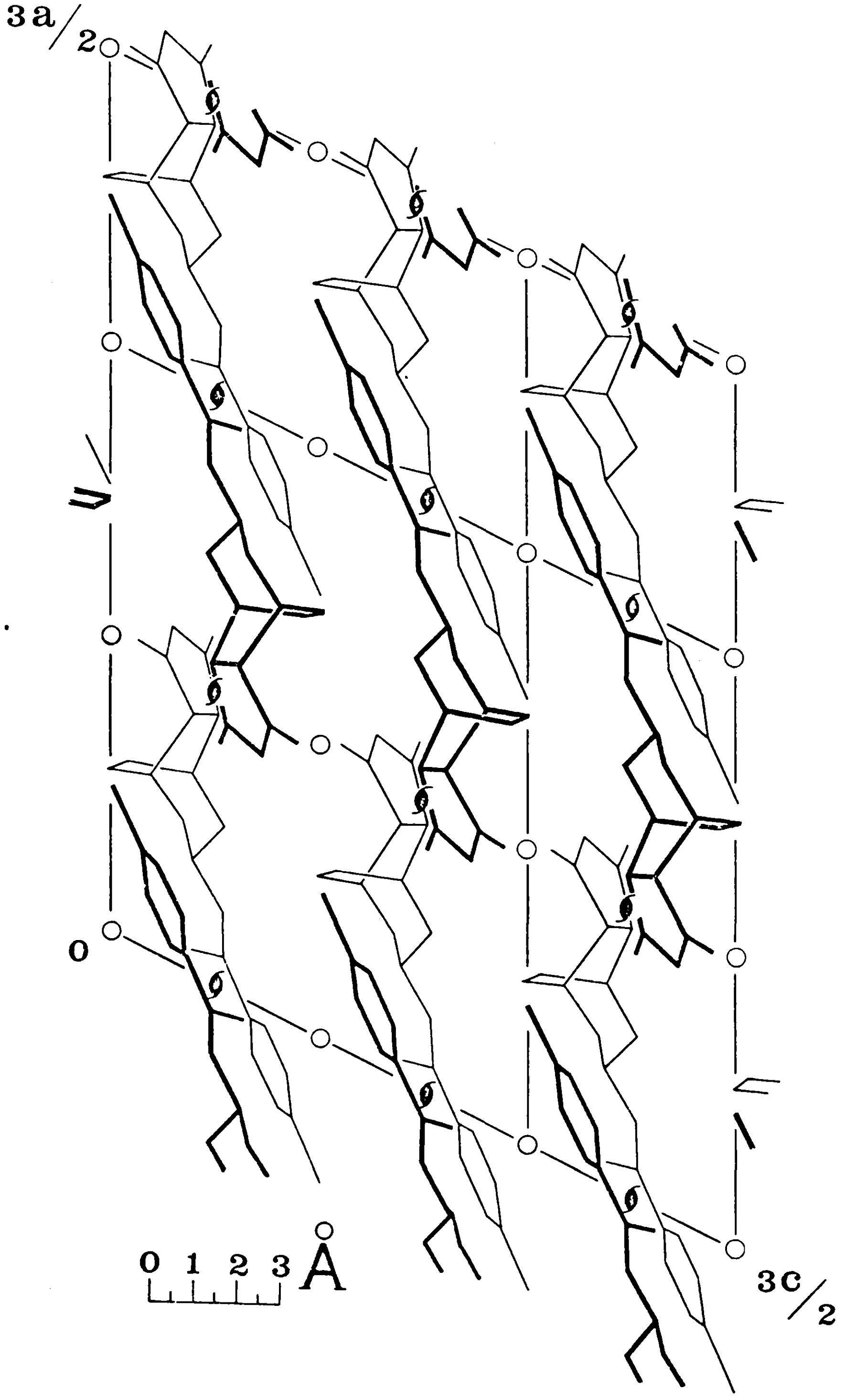
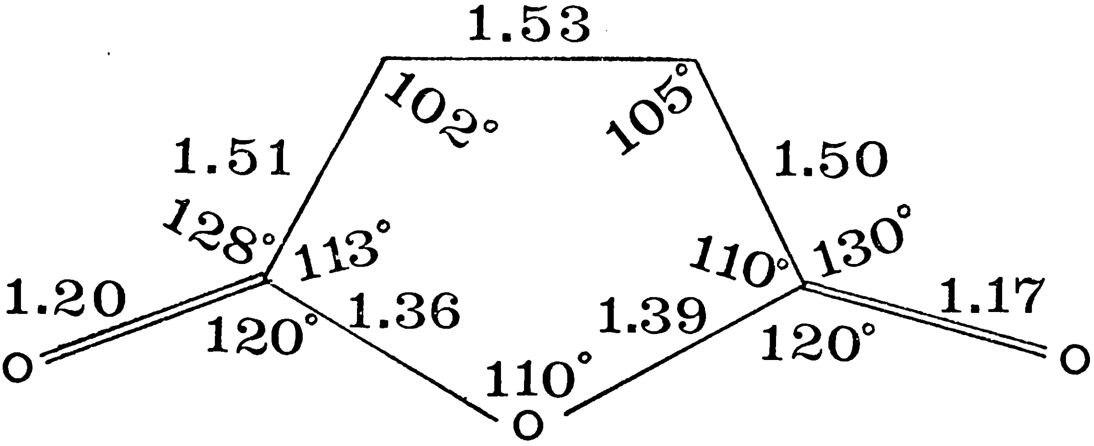
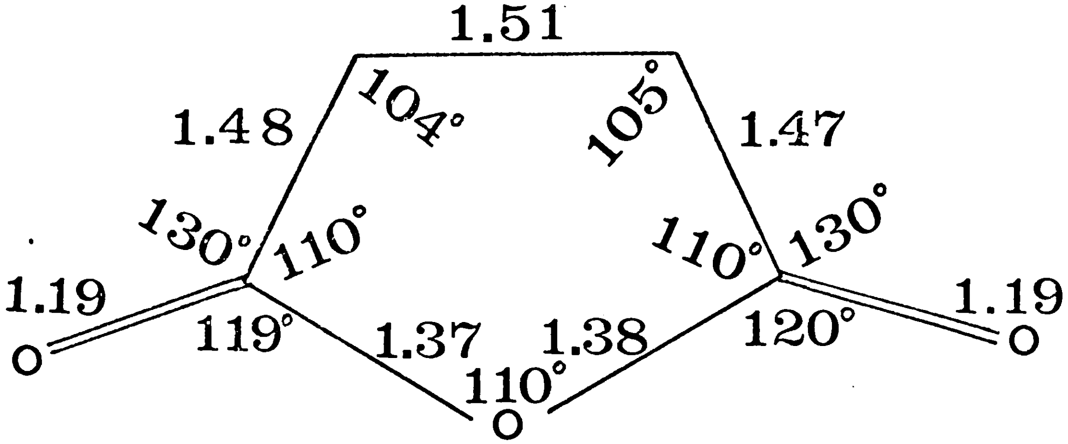

3a/2
0
3c/2
0 1 2 3 Å

FIGURE 2.5

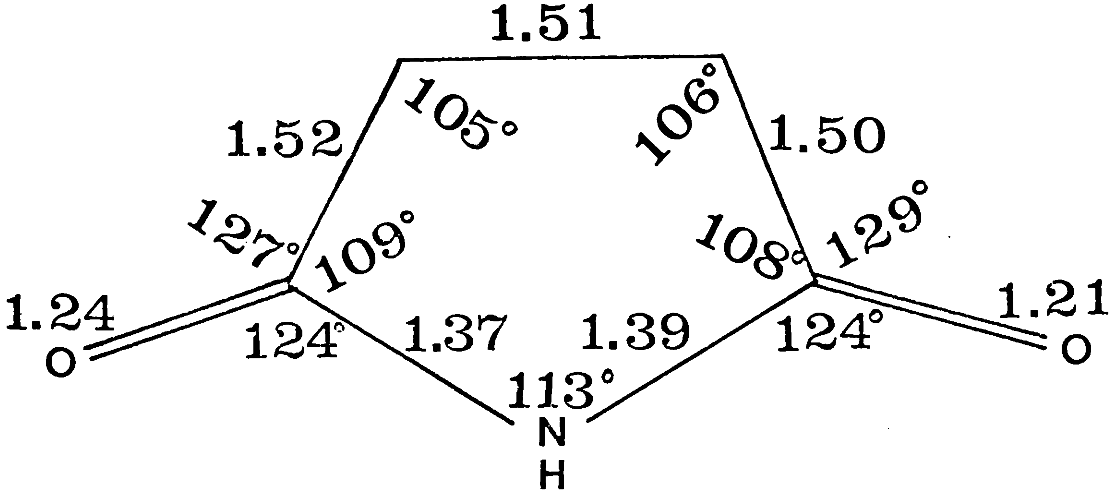
Comparison of the anhydride ring of the present molecule with succinic anhydride and succinimide.



anhydride part of present molecule



succinic anhydride



succinimide

FIGURE 2.6

View of the bicyclic ring system along the axis through C(1) and C(5).

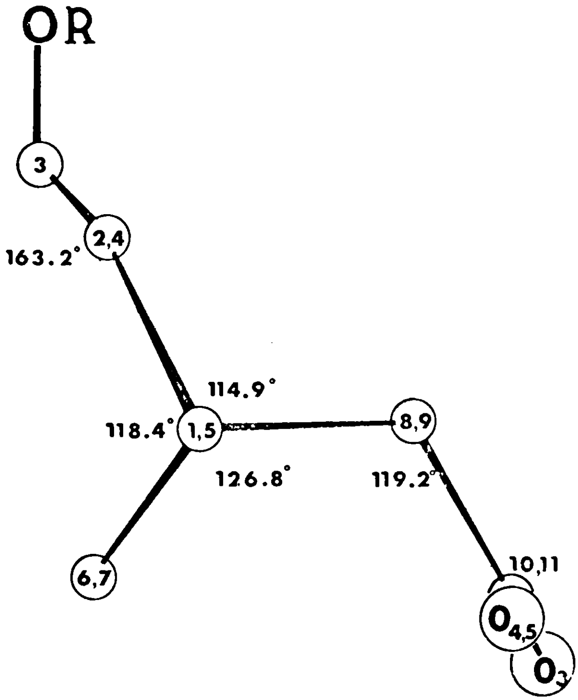

OR
3
2,4
163.2°
114.9°
118.4°
1,5
8,9
126.8°
119.2°
6,7
10,11
$O_{4,5}$
O_3

FIGURE 2.7

Bond lengths (in Å)

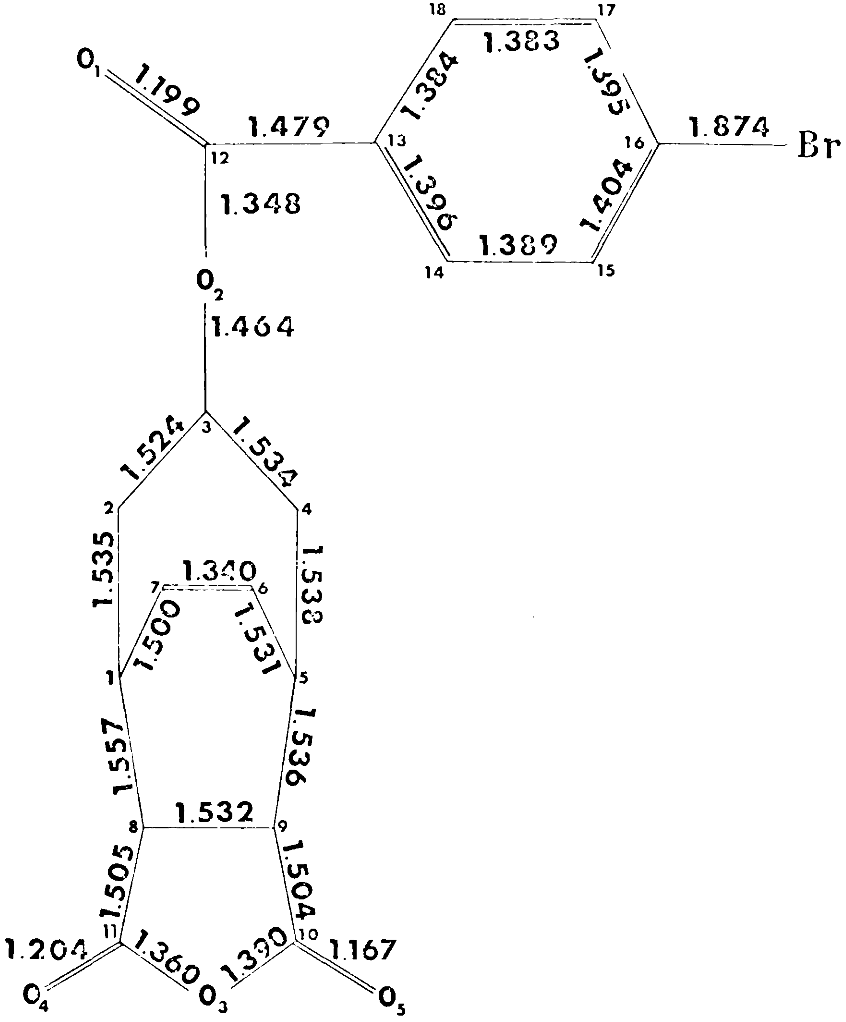
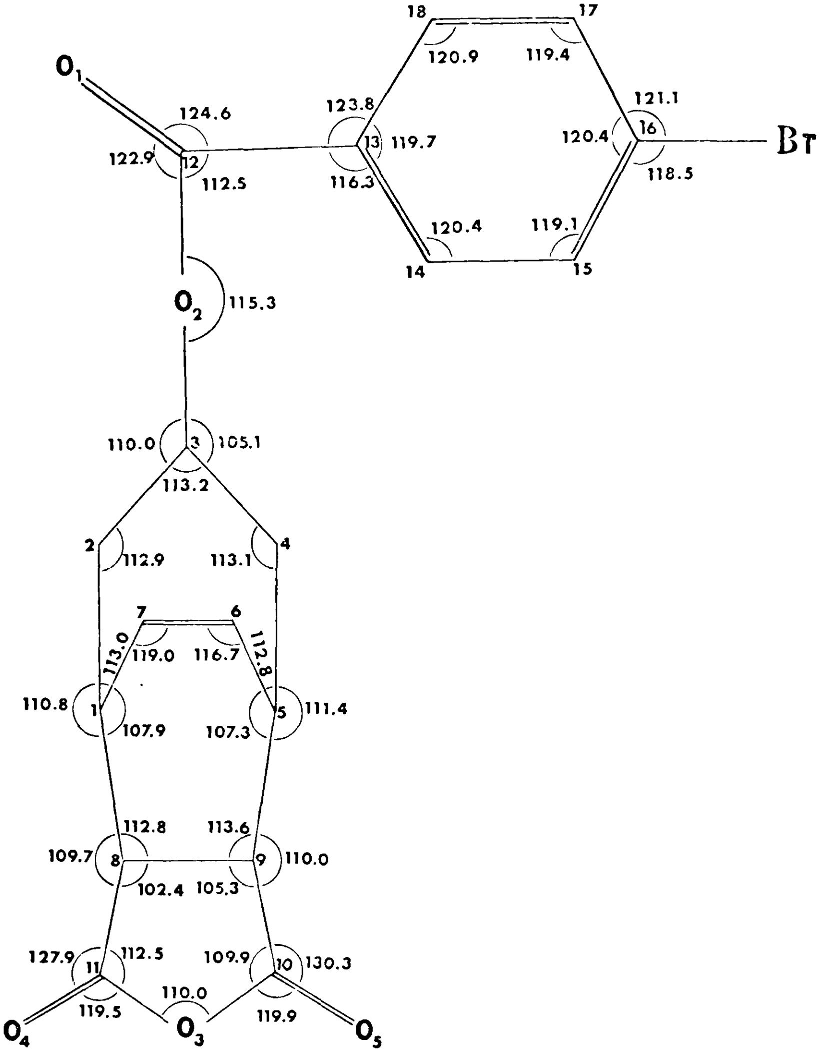

18
17
1.383
O1
1.199
1.384
1.395
1.479
13
16
1.874
Br
12
1.396
1.404
1.348
1.389
14
15
O2
1.464
3
1.524
1.534
2
4
1.535
1.340
1.538
7
6
1.500
1.531
1
5
1.557
1.536
1.532
8
9
1.505
1.504
1.204
11
1.360
1.390
10
1.167
O4
O3
O5

FIGURE 2.8

Valency angles (in degrees)

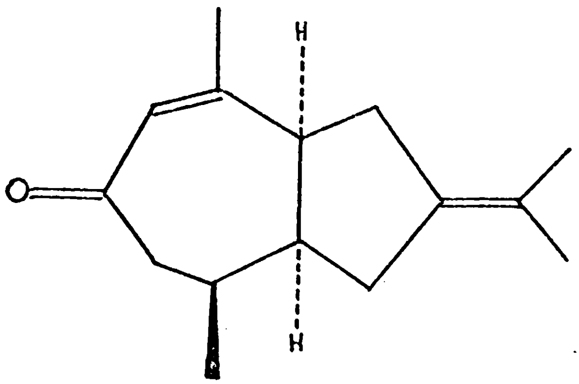

O1
O2
O3
O4
O5
Br
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
124.6
122.9
112.5
115.3
123.8
119.7
116.3
120.9
119.4
121.1
120.4
118.5
120.4
119.1
110.0
105.1
113.2
112.9
113.1
113.0
119.0
116.7
112.8
110.8
107.9
107.3
111.4
112.8
113.6
109.7
110.0
102.4
105.3
127.9
112.5
109.9
130.3
110.0
119.5
119.9

2.3 DISCUSSION

The analysis has resolved the problem of identifying the anti-3-exo and syn-3-exo epimers and has hence confirmed the theoretical prediction that the anti-3-exo epimer should be the more stable and therefore major product of the reaction IV + V . The analysis has also confirmed the endo configuration of the anhydride group relative to the bicyclic system, thus proving that the product VI was suitable for subsequent stages in the synthesis of Pfau and Plattner's proposed structure for β- vetivone (I) . Marshall and his co-workers (1967) have since proved that the true structure of β- vetivone is XI .

In addition , the molecule possesses some stereochemically and conformationally interesting features. Considering the anhydride group, the bond lengths and valency angles compare very well with the corresponding values found for succinic anhydride by Ehrenberg (1965) and for succinimide by Mason (1961) . A comparison is made in Figure 2.5 . Whereas Ehrenberg and Mason both observe slight deviations from planarity in succinic anhydride and succinimide, the anhydride group of the present molecule appears to be almost planar (Table 2.11) . This planarity may possibly be attributed to the constraint placed by the bicyclic system on atoms C(8) and C(9) (see Figure 2.3 for numbering) .

The bond lengths and valency angles in the p-bromobenzoyloxy



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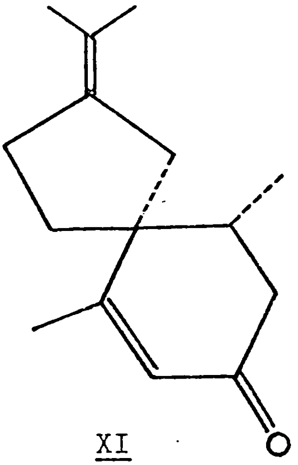
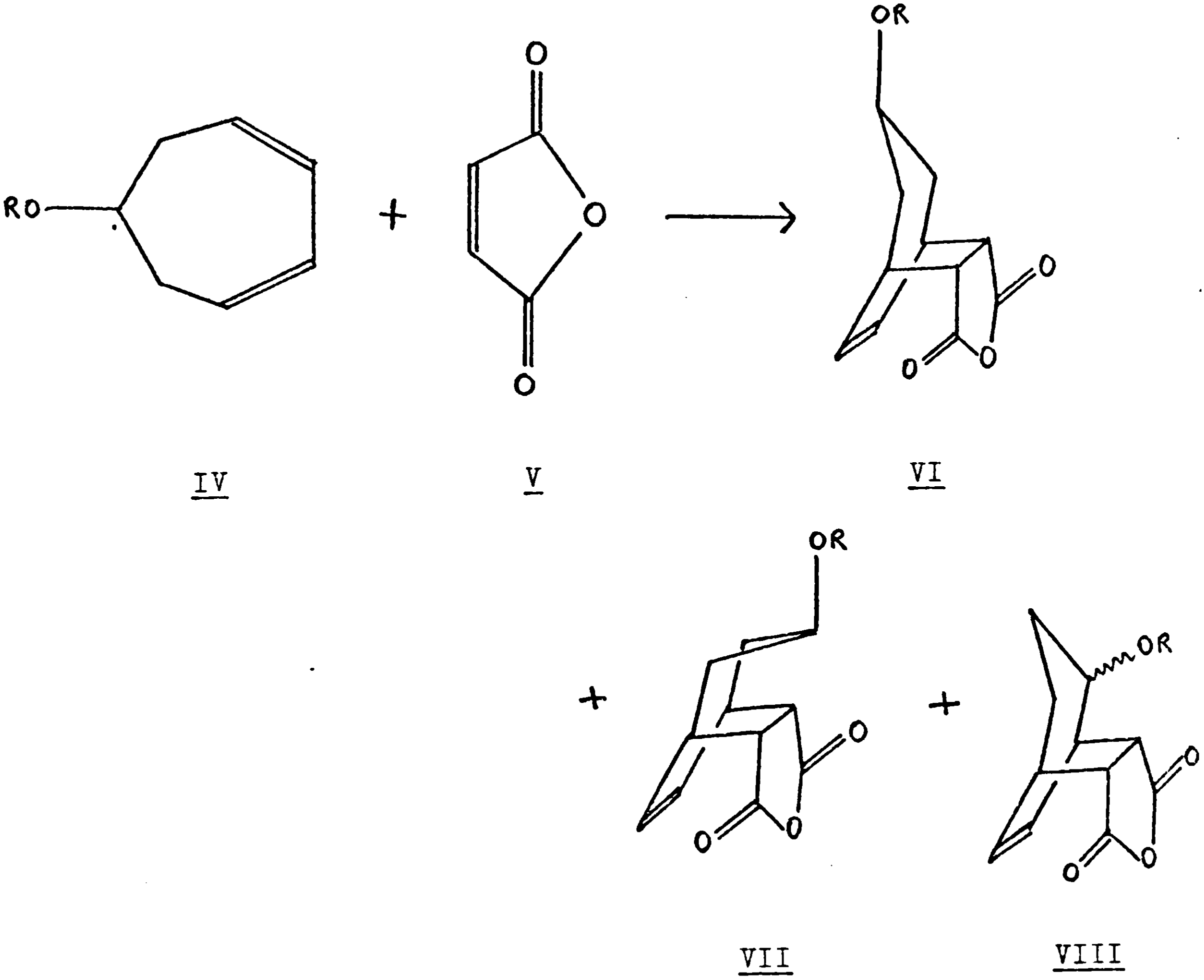


XI



group compare well with values found for the same group in other molecules, and particularly with the values found by Macdonald and Trotter (1965) for anti-7-norbornenyl-p-bromobenzoate which also possesses a bicyclic skeleton. The values of 1.48 Å and 1.35 Å for the C(12) - C(13) and C(12) - O(2) bonds respectively may presumably be attributed to extended conjugation involving the aromatic ring. Within experimental error both the benzene ring and the carboxyl groups are planar (Table 2.11), and the angle between the two planes is 17.8° .

The bond lengths (Table 2.7 and Figure 2.7) of the bicyclo-[3,2,2]non-6-ene ring system are comparable with literature values for similar bond types (Sutton et al., 1965) . However, an examination of the valency angles (Table 2.8 and Figure 2.8) reveals that the valency angles C(1) - C(2) - C(3) , C(2) - C(3) - C(4) and C(3) - C(4) - C(5) are increased to an average value of 113.1° indicating slight flattening of the three-carbon bridge. Such flattening of three-carbon bridges is consistent with that found by Brown, Martin and Sim (1965) for 1-p-bromobenzenesulphonyloxy-methyl-5-methylbicyclo[3,3,1]nonan--9-ol, where the average value of corresponding angles is 114° . Within experimental error the atoms C(1), C(2), C(4) and C(5) are planar (Table 2.11) and the angle between this plane and the plane of atoms C(2), C(3), C(4) is 163° . The valency angles C(2) - C(1) - C(7) and C(4) - C(5) - C(6) are increased to 113.0° and 112.8° respectively. Although the ring-flattening and valency-angle increases are slight, they are manifestations of molecular strain being relieved. The angle increases have a number of effects; the interaction of the C(3) hydrogen with atoms C(6) and C(7) is relieved, the C(3)...C(6) and C(3)...C(7) non-bonded distances being 2.82 Å and 2.81 Å respectively (Table 2.9) . Torsional interactions about the C(1) - C(2) and C(4) - C(5) bonds are also relieved by the three-carbon bridge flattening. The non-bonded interactions between the C(2) and C(8) hydrogens, between the C(4) and C(9) hydrogens and between the C(2) and C(4) hydrogens are all lessened by the ring flattening. There does not appear to be much steric interaction between the anhydride ring and atoms C(6) and C(7) , since the average value for the valency angles C(7) - C(1) - C(8), C(1) - C(8) - C(11), C(6) - C(5) - C(9) and C(5) - C(9) - C(10) is 108.7° . Also, the C(7)...C(11) and C(6)...C(10) non-bonded distances are 2.98 Å and 2.97 Å respectively.

Within experimental error the anhydride group, the bridge formed by atoms C(6) and C(7) , the bridge formed by atoms C(8) and C(9) , and the group of atoms C(1), C(2), C(4) and C(5) are all planar (Table 2.11) . The angles between all these planes are shown in Figure 2.6 , which is a view of the bicyclic system along the C(1),C(5) axis. The flattening of the three-carbon bridge is clearly seen. The planarity of all these groups of atoms demonstrates that this bicyclo[3,2,2]nonene system is not twisted. Further proof of the lack of twisting is found in the symmetry of the intramolecular non-bonded contacts (Table 2.9) on either side of the bicyclic system. For example C(3)...C(6) and C(3)...C(7) are 2.82 Å and 2.81 Å respectively, C(7)...C(11) and C(6)...C(10) are 2.98 Å and 2.97 Å respectively, and C(6)...C(11) and C(7)...C(10) are 3.46 Å and 3.44 Å respectively. Such symmetry of these intramolecular non-bonded distances would not be possible if there were any twisting of the bicyclic system about the C(1),C(5) axis. Within experimental error, the values of bond lengths (Table 2.7 and Figure 2.7) , valency angles (Table 2.8 and Figure 2.8), and intramolecular non-bonded distances on either side of the bicyclic system indicate the presence of a non-crystallographic plane of symmetry within the bicyclic moiety which precludes any possibility of twisting.

Apart from those valency angles already discussed, most of the other angles in the bicyclic system conform to accepted values, and any slight differences, if significant, may be explained by the constraints of the bicyclic system and by the non-bonded intramolecular interactions. The results of the foregoing conformational studies are further discussed in Chapter 5 in comparison with the conformations of the two molecules described in Chapters 3 and 4.

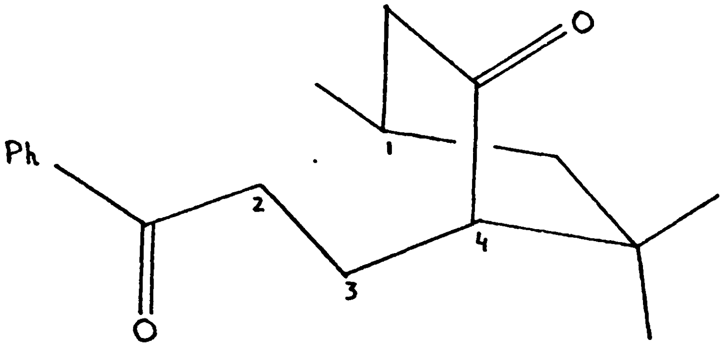
CHAPTER 3 THE CRYSTAL STRUCTURE OF 1,5,5-TRIMETHYL-2(3'-p-BROMOPHENYL-3'-OXOPROPYL)-BICYCLO[2,2,2]OCTAN-6,8-DIONE

3.1 INTRODUCTION

In the course of studies on the scope and mechanism of the Thermal Michael condensation (Buchanan and McLay, 1965; Brown and Buchanan, unpublished), β-dimethylamino-propiophenone was treated with isophorone at its boiling point for 1 hour. Distillation afforded a red oil (71%) which on trituration with ether yielded a colourless crystalline product, $C_{18}H_{22}O_3$, accounting for 35-40% of the distillate. The expected product of the reaction should have had the formula $C_{18}H_{22}O_2$ and the structure I . The product $C_{18}H_{20}O_3$ showed $\nu_{CO}(CCl_4)$ 1733 and 1688 cm^{-1} and Ph.CO absorption in the ultraviolet region. Its n.m.r. spectrum showed three singlet resonances (τ 8.72, 8.91, 9.01) and a sharp 1xH triplet at τ 6.17(J = 8.8c/sec), but no vinylic signal. On this evidence formulation of the product was impossible, and in particular it was impossible to account for the extra oxygen or to assign the low-field triplet signal in the n.m.r. spectrum.

An analogous bromine-containing product, $C_{18}H_{19}O_3Br$, which showed the same spectroscopic features, was then prepared by the reaction of isophorone with β-dimethylamino-p-bromo-propiophenone for examination by single-crystal X-ray structure analysis.

The X-ray analysis showed the structure to be II(R = Br), and its halogen-free analogue thus to be II(R = H) .



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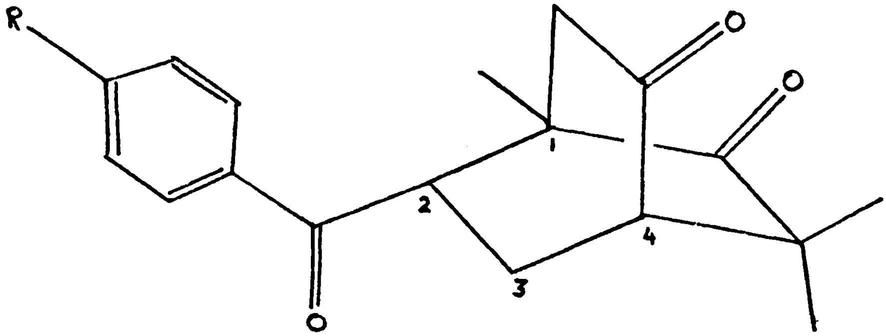

II

3.2 EXPERIMENTAL

3.2.1 Crystal Data

1,5,5-trimethyl-2(3'-p-bromophenyl-3'-oxopropyl)-bicyclo[2,2,2]-octan-6,8-dione, $C_{18}H_{19}O_3Br$, M = 363,

Monoclinic, a = 17.71±0.05, b = 9.25±0.02, c = 10.63±0.03 Å,

β = 106.5±0.2°, U = 1669 Å^3, D_m = 1.44 g.cm.$^{-3}$ (by flotation in KI/H_2O solution), z = 4, D_x = 1.44 g.cm.$^{-3}$,

F(000) = 744,

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

Linear absorption coefficient for X-rays (λ = 1.5418 Å), μ = 38cm^{-1}.

3.2.2 Crystallographic Measurements

The unit-cell dimensions were determined from oscillation and Weissenberg photographs taken with Cu-Kα radiation (λ = 1.5418Å) and from precession photographs taken with Mo-Kα radiation (λ = 0.7107 Å). The space group was uniquely determined from systematic absences observed in the 0k0 and $h0\ell$ spectra.

A small crystal rotating about c was exposed to Cu-Kα radiation and 1828 independent reflexions from the reciprocal lattice nets hk0 - hk8 were recorded on equatorial and equi-inclination Weissenberg photographs using the multiple-film technique with six films in each pack. The intensities, which were estimated visually by comparison with a calibrated wedge, were corrected for Lorentz and polarisation factors and were subsequently placed on an approximately absolute scale by making $k \sum |F_o| = \sum |F_c|$ for each layer. No allowance was made for absorption and unobserved reflexions were not considered.

3.2.3 Structure Determination

The value of 1.37 for the ratio $f^2_{Br} / \sum_R f^2_R$ indicated a reasonable chance of success (Lipson and Cochran, 1966) for the heavy-atom method of phase determination and the analysis subsequently proceeded on this basis.

The data were sharpened to point bromine atom at rest, and the three-dimensional Patterson function was computed from which the bromine coordinates (0.0250, 0.3320, 0.0357) were unambiguously determined (c.f. Chapter 2, 2.2.3 , page 74). The Harker section at v = 1/2 of the Patterson function is shown in Figure 3.1 .

The first electron-density distribution was calculated with the observed amplitudes and the signs appropriate to the bromine atom, and revealed the complete structure. One further round of structure-factor and electron-density calculations yielded an improved set of atomic positional parameters which were subsequently refined by least-squares methods. In both the previous structure-factor calculations an overall isotropic temperature factor $U_{iso} = 0.05$ Å^2 was assumed, and after each calculation the layers hk0-hk8 were put on an approximately absolute scale by making $k\sum|F_o| = \sum|F_c|$ for each layer. A modification function (Sim, 1961) was applied to the Fourier coefficients in the first electron-density distribution to improve the resolution.

3.2.4 Structure Refinement

The refinement of positional, vibrational (isotropic and anisotropic) and scale parameters by three-dimensional least-squares methods converged after 14 cycles with $R = 0.099$ and $R' = 0.0154$. Details of the refinement are given in Table 3.1 .

After cycle 3 the data were converted to an overall absolute scale using the refined values of the layer-scale factors and in all subsequent cycles the overall scale factor was refined. A weighting scheme of the form

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

was applied in all cycles. Initially the parameters $p_1, \ldots, p_3$

were chosen to give unit weights to all reflexions, but were subsequently varied according to the dictates of the weighting analysis (c.f. Chapter 2, 2.2.4 , page 77) , the final values being

$$p_1 = 200, \quad p_2 = 0.01, \quad p_3 = 0.0005$$

Coordinates for 10 of the 19 hydrogen atoms were calculated from geometrical considerations and their contributions with assumed isotropic thermal parameters $U_{iso} = 0.05$ Å^2 were included in all structure-factor calculations after cycle 6 . The hydrogen parameters were not refined. Anisotropic thermal parameters were also refined after cycle 6, and because of computer-store limitations this necessitated the use of a block-diagonal approximation to the normal-equation matrix in all subsequent cycles. The strategy employed in refining anisotropic thermal parameters was similar to that used in the refinement of laurencin (Part II , Chapter 1 , 1.2.4 , page 49) .

The least-squares refinement was terminated when the calculated shifts were much less than the estimated standard deviations. Excluding contributions from the hydrogen atoms, structure factors were calculated with the final parameters and used in the evaluation of a final electron-density distribution and a three-dimensional difference synthesis. Superimposed sections of the final electron-density map viewed down the b - axis are shown in

Figure 3.2 . The difference synthesis revealed no errors in the structure and despite the existence of several diffuse peaks in positions stereochemically acceptable for hydrogen atoms, it was impossible to determine their coordinates with any accuracy. The refinement was therefore considered complete.

In all structure-factor calculations the atomic scattering factors used are those given in "International Tables for Crystallography", Vol. III . Values of $|F_o|$ and the final values of F_c are given in Table 3.2 . The final fractional coordinates are given in Table 3.3 and the anisotropic thermal parameters given in Table 3.4 are the values of U_{ii} and $2U_{ij}$ in the expression

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

The appropriate estimated standard deviations derived from the inverse of the least-squares matrix are included in Tables 3.3 and 3.4 . Orthogonal coordinates are listed in Table 3.5 and the calculated hydrogen coordinates are listed in Table 3.6 .

Table 3.7 contains bond distances and Table 3.8 contains valency angles. The average estimated standard deviations for C - C, C - O and C - Br bonds are 0.02 Å , 0.02 Å and 0.01 Å respectively, and for valency angles is 0.8°. These should be regarded as minimum values. Some intramolecular non-bonded distances are listed in Table 3.9 and all intermolecular distances < 3.5 Å are given in Table 3.10 . Table 3.11 gives details of all best-plane calculations.

The atomic numbering system is shown in Figure 3.3 , the hydrogen atoms being numbered as the carbon atoms to which they are bonded. The molecular packing viewed down the $\underline{b}$ - axis is shown in Figure 3.4 .

TABLE 3.1

COURSE OF REFINEMENT

Cycles	Parameters refined	Final R	Final R'	$\Sigma w\Delta^2$
1 - 3	x, y, z, U_{iso} for Br, O, C, Layer scale factors, Full matrix, unit weights	0.229	0.0616	53,266
4 - 5	x, y, z, U_{iso} for Br, O, C, Overall scale factor, Full matrix, weighting scheme adjusted.	0.202	0.0587	34,734
6 - 14	x, y, z, U_{ij} for Br, O, C, Overall scale factor, Block diagonal, weighting scheme applied, hydrogen atoms included.	0.099	0.0154	8,321

TABLE 5.2

Observed amplitudes and calculated (final) structure factors.

H	K	L	Fo	Fc
1	1	0	57.2	53.9
2	1	0	35.3	-29.3
3	1	0	67.7	-71.1
4	1	0	84.9	-90.4
6	1	0	33.6	-31.2
7	1	0	48.3	-43.6
8	1	0	57.3	-56.2
9	1	0	35.8	-37.0
10	1	0	57.8	-61.9
11	1	0	45.9	-50.3
12	1	0	21.1	-23.2
13	1	0	17.0	-17.4
14	1	0	25.7	-26.0
15	1	0	9.9	-11.7
16	1	0	15.5	-17.3
17	1	0	10.5	-14.3
18	1	0	2.3	-5.8
19	1	0	9.2	-9.2
20	1	0	2.5	1.4
0	2	0	18.3	-6.9
1	2	0	55.4	-66.8
2	2	0	38.0	-34.6
3	2	0	52.9	-46.7
4	2	0	73.8	-76.0
5	2	0	55.9	-55.0
6	2	0	26.7	-32.3
7	2	0	32.3	-26.1
8	2	0	11.1	-12.3
9	2	0	7.6	4.9
10	2	0	21.4	-20.7
11	2	0	8.6	-10.9
12	2	0	8.5	7.8
13	2	0	15.9	12.6
14	2	0	2.5	-5.4
15	2	0	6.1	5.7
16	2	0	5.5	4.9
17	2	0	8.2	8.8
18	2	0	9.7	11.8
19	2	0	2.0	3.1
20	2	0	5.9	8.1
1	3	0	14.7	8.2
2	3	0	1.4	4.5
3	3	0	20.1	-18.2
4	3	0	12.6	-12.1
5	3	0	46.5	-40.9
7	3	0	14.0	-14.0
8	3	0	23.0	21.1
9	3	0	17.7	16.7
10	3	0	6.0	-5.1
11	3	0	6.3	-3.7
12	3	0	5.7	4.9
13	3	0	14.2	14.3
14	3	0	10.8	11.2
15	3	0	12.6	15.5
16	3	0	7.7	-7.2
17	3	0	3.3	-4.1
18	3	0	2.1	-1.7
20	3	0	5.4	6.5
0	4	0	104.1	-104.0
1	4	0	45.9	-41.6
2	4	0	39.5	-33.7
3	4	0	39.1	-40.6
4	4	0	31.8	23.3
5	4	0	4.3	0.4
6	4	0	37.9	-34.1
7	4	0	6.7	-5.3
8	4	0	7.7	5.9
9	4	0	7.5	-5.0
10	4	0	21.4	24.7
11	4	0	12.0	9.9
12	4	0	2.4	-4.2
13	4	0	10.8	11.4
15	4	0	9.8	10.4
16	4	0	13.3	14.9
17	4	0	8.2	9.0
18	4	0	4.8	4.8
2	5	0	37.6	34.5
3	5	0	13.7	14.2
4	5	0	47.8	44.3
5	5	0	35.3	35.6
6	5	0	42.1	40.9
7	5	0	30.5	33.7
8	5	0	27.1	26.2
9	5	0	28.1	26.7
10	5	0	31.2	30.9
11	5	0	25.8	28.7
12	5	0	23.5	24.3
13	5	0	14.0	16.6
14	5	0	11.5	12.1
15	5	0	8.1	9.9
16	5	0	3.1	4.3
17	5	0	6.4	5.7
0	6	0	61.3	56.8
1	6	0	45.6	44.0
2	6	0	42.8	42.4
3	6	0	39.8	41.4
4	6	0	51.7	56.2
5	6	0	48.6	51.8
7	6	0	30.5	30.9
8	6	0	20.4	21.1
9	6	0	19.2	-19.3
13	6	0	9.7	-8.7
14	6	0	9.3	-9.2
15	6	0	9.5	-9.6
16	6	0	10.1	-9.9
17	6	0	7.0	-7.8
1	7	0	2.3	5.2
2	7	0	16.9	-16.0
3	7	0	22.2	-19.8
4	7	0	9.5	-6.9
5	7	0	34.2	-34.6
6	7	0	21.5	-20.9
7	7	0	19.4	-20.1
8	7	0	30.2	-31.8
9	7	0	14.1	-14.4
10	7	0	15.6	-17.0
11	7	0	20.7	-25.6
12	7	0	10.2	-11.8
13	7	0	9.8	-11.3
14	7	0	17.8	-17.3
15	7	0	8.9	-9.5
16	7	0	5.7	-6.9
0	8	0	26.1	-25.8
1	8	0	11.6	-12.3
2	8	0	16.6	-15.1
3	8	0	27.7	-27.6
4	8	0	15.5	-16.6
5	8	0	7.9	-4.4
6	8	0	15.5	-15.3
7	8	0	6.1	-7.1
8	8	0	6.9	-7.9
9	8	0	14.0	-16.4
11	8	0	8.9	-11.2
13	8	0	7.2	6.9
1	9	0	6.9	8.1
4	9	0	7.6	-8.8
5	9	0	2.4	-3.6
6	9	0	5.3	-5.4
8	9	0	7.7	7.3
10	9	0	4.9	4.6
0	10	0	6.3	-6.1
1	10	0	9.7	-8.8
2	10	0	12.8	-10.9
4	10	0	2.1	-2.0
5	10	0	3.6	-4.5
6	10	0	3.1	5.7
9	10	0	6.7	7.4
2	11	0	8.8	8.7
3	11	0	5.3	4.6
5	11	0	8.7	10.0
2	0	0	34.2	43.8
3	0	0	133.7	143.0
4	0	0	37.1	-34.7
5	0	0	68.2	71.8
6	0	0	67.9	73.5
7	0	0	44.7	40.1
8	0	0	3.7	3.0
9	0	0	25.5	21.8
10	0	0	51.1	-50.0
11	0	0	8.3	11.0
12	0	0	34.8	37.5
13	0	0	41.1	-39.5
14	0	0	16.2	-16.0
16	0	0	26.2	-28.4
17	0	0	9.1	-11.4
18	0	0	8.6	-8.4
20	1	1	3.5	4.1
19	1	1	3.0	5.9
18	1	1	5.8	6.7
17	1	1	7.3	6.2
16	1	1	17.0	17.9
15	1	1	6.7	-7.4
14	1	1	10.8	8.1
13	1	1	37.3	31.8
12	1	1	19.7	-19.6
10	1	1	14.9	14.1
9	1	1	45.5	-38.5
8	1	1	23.3	-18.8
7	1	1	38.6	-34.1
3	1	1	88.0	-90.0
2	1	1	34.5	-31.5
0	1	1	75.0	-91.5
-1	1	1	3.8	0.9
-2	1	1	67.6	61.9
-3	1	1	168.4	-174.3
-4	1	1	59.2	-48.1
-5	1	1	111.1	-112.4
-6	1	1	39.3	-35.1
-7	1	1	39.0	31.5
-8	1	1	2.5	-4.1
-10	1	1	13.1	12.8
-11	1	1	15.8	16.2
-12	1	1	2.4	-4.6
-13	1	1	26.6	27.0
-14	1	1	18.6	21.6
-15	1	1	3.8	6.0
-16	1	1	7.7	7.8
-17	1	1	6.6	6.5
-18	1	1	5.7	5.8
-19	1	1	8.2	11.6
16	2	1	9.2	8.9
15	2	1	15.4	17.7
14	2	1	28.7	31.8
13	2	1	31.4	36.9
12	2	1	33.5	35.7
11	2	1	53.4	50.2
10	2	1	40.6	36.4
9	2	1	63.7	58.0
8	2	1	35.5	32.1
7	2	1	32.7	30.3
6	2	1	85.8	76.0
5	2	1	38.3	33.2
4	2	1	14.0	11.6
3	2	1	30.0	19.5
2	2	1	23.7	-11.2
1	2	1	28.4	-37.0
0	2	1	5.4	8.6
-1	2	1	45.9	-34.0
-2	2	1	14.5	-18.9
-3	2	1	33.7	-37.7
-4	2	1	68.0	-71.4
-5	2	1	44.0	-45.9
-6	2	1	10.2	-12.5
-7	2	1	77.1	-77.8
-8	2	1	92.9	-100.5
-9	2	1	49.9	-50.4
-10	2	1	73.7	-73.6
-11	2	1	37.3	-35.5
-12	2	1	17.7	-19.1
-13	2	1	10.2	-11.3
-14	2	1	16.8	-19.9
-15	2	1	12.7	-14.6
-18	2	1	12.8	13.8
19	3	1	7.6	-7.0
17	3	1	9.7	-9.0
16	3	1	11.3	-11.5
15	3	1	15.2	-15.4
14	3	1	13.9	-13.2
13	3	1	23.0	-21.9
11	3	1	13.3	11.9
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-1	3	8	11.8	8.4
0	3	8	5.5	-1.7
1	3	8	12.8	8.7
2	3	8	14.6	10.5
3	3	8	13.8	-12.2
6	3	8	29.0	-30.7
8	3	8	7.7	-5.8
-10	4	8	14.2	15.2
-9	4	8	13.9	11.1
-8	4	8	12.2	8.1
-7	4	8	7.3	6.4
-5	4	8	25.8	31.4
-4	4	8	28.7	30.1
-3	4	8	11.5	-7.1
-2	4	8	23.3	24.2
-1	4	8	8.4	-6.9
1	4	8	8.7	5.4
4	4	8	12.9	-9.1
5	4	8	6.5	-3.5
6	4	8	15.7	-14.5
8	4	8	6.0	-5.5
9	4	8	17.3	-16.7
-8	5	8	6.4	7.5
-7	5	8	18.0	18.1
-6	5	8	20.9	-20.7
-5	5	8	19.4	-21.0
-4	5	8	14.0	13.8
-3	5	8	22.6	-22.1
-1	5	8	17.9	-19.8
0	5	8	23.1	-25.6
1	5	8	19.9	-21.3
2	5	8	21.5	-20.4
3	5	8	10.2	-13.5
4	5	8	9.1	-11.3
5	5	8	10.0	-8.6
6	5	8	27.5	-30.8
9	5	8	11.3	-10.3
-9	6	8	11.1	-15.0
-8	6	8	6.5	-9.2
-6	6	8	18.3	-23.1
-3	6	8	17.1	-20.5
0	6	8	10.2	-10.9
1	6	8	9.1	-7.0
3	6	8	10.9	-8.0
4	6	8	13.7	17.4
5	6	8	16.7	18.5
7	6	8	16.2	17.6
8	6	8	15.8	17.7
-6	7	8	9.9	12.0
-3	7	8	16.6	20.0
-2	7	8	14.0	14.6
0	7	8	8.7	10.8
1	7	8	8.6	8.4
2	7	8	14.5	17.1
3	7	8	11.4	14.1
4	7	8	8.7	9.4
5	7	8	12.6	15.3
6	7	8	10.6	12.6
-9	8	8	8.1	10.9
-2	8	8	8.8	-3.3
0	8	8	5.4	6.4
-8	9	8	6.7	0.3
-2	9	8	6.9	-2.6
-1	9	8	8.4	-9.1

TABLE 3.3

FRACTIONAL COORDINATES AND E.S.D.S

ATOM	x/a	y/b	z/c
C(1)	0.3430 ± 5	-0.3136 ± 9	0.0610 ± 8
C(2)	0.2636 ± 5	-0.3295 ± 9	0.0965 ± 9
C(3)	0.2518 ± 5	-0.4907 ±10	0.1366 ±10
C(4)	0.3279 ± 5	-0.5870 ± 9	0.1408 ± 8
C(5)	0.3406 ± 5	-0.5980 ± 9	0.0140 ± 9
C(6)	0.3426 ± 5	-0.4366 ± 9	-0.0361 ± 8
C(7)	0.4122 ± 5	-0.3556 ± 9	-0.1821 ± 8
C(8)	0.4017 ± 5	-0.5084 ± 9	0.2280 ± 9
C(9)	0.3575 ± 7	-0.1571 ±10	0.0153 ±11
C(10)	0.4230 ± 6	-0.6733 ±12	0.0236 ±10
C(11)	0.2704 ± 7	-0.6871 ±11	-0.0854 ±11
C(12)	0.1919 ± 6	-0.2792 ±11	-0.0132 ± 8
C(13)	0.1532 ± 5	-0.1294 ±10	-0.0142 ± 9
C(14)	0.1636 ± 6	-0.0446 ±11	0.0943 ±10
C(15)	0.1231 ± 6	0.0924 ±12	0.0889 ±10
C(16)	0.0763 ± 5	0.1428 ± 9	-0.0242 ±10
C(17)	0.0659 ± 6	0.0636 ±12	-0.1360 ±10
C(18)	0.1048 ± 6	-0.0767 ±12	-0.1270 ±10
O(1)	0.4464 ± 4	-0.5627 ± 9	0.3235 ± 7
O(2)	0.3453 ± 5	-0.4093 ± 9	-0.1371 ± 7
O(3)	0.1670 ± 5	-0.3633 ± 8	-0.1026 ± 7
Br	0.0245 ± 1	0.3312 ± 1	-0.0361 ± 1

TABLE 3.4

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S (in $\AA^2$)

ATOM	U11	U22	U33	2U23	2U31	2U12
C(1)	0.044	0.046	0.018	-0.001	0.001	0.000
	4	4	5	6	7	7
C(2)	0.046	0.052	0.017	-0.021	0.005	0.026
	5	5	5	8	8	8
C(3)	0.050	0.059	0.027	-0.002	0.042	-0.003
	5	5	6	9	8	9
C(4)	0.057	0.048	0.024	0.000	0.034	0.006
	5	4	5	7	7	8
C(5)	0.055	0.041	0.017	-0.012	0.028	-0.002
	5	4	6	7	8	8
C(6)	0.044	0.050	0.013	0.007	0.008	-0.004
	5	5	5	7	8	7
C(7)	0.054	0.044	0.021	0.011	0.006	0.007
	5	4	5	6	8	7
C(8)	0.050	0.054	0.025	0.007	0.030	0.028
	5	5	6	7	7	8
C(9)	0.079	0.049	0.033	0.020	0.009	-0.023
	7	5	7	9	10	10
C(10)	0.064	0.081	0.030	-0.023	0.055	0.034
	6	7	8	10	10	11
C(11)	0.082	0.058	0.042	-0.047	0.024	-0.028
	8	6	9	10	11	11
C(12)	0.056	0.060	0.010	-0.025	0.016	0.010
	5	5	5	8	8	9
C(13)	0.041	0.062	0.015	0.002	0.015	0.005
	5	5	6	8	8	8
C(14)	0.059	0.065	0.020	-0.006	-0.004	0.040
	6	6	6	9	9	9

TABLE 3.4 (contd.)

ATOM	U11	U22	U33	2U23	2U31	2U12
C(15)	0.071	0.067	0.025	-0.031	-0.012	0.059
	6	6	7	9	10	11
C(16)	0.049	0.045	0.039	-0.005	-0.005	0.014
	5	5	7	8	9	8
C(17)	0.072	0.067	0.028	0.033	0.010	0.040
	7	6	7	9	10	10
C(18)	0.057	0.084	0.021	-0.013	-0.018	0.036
	6	7	6	10	9	11
O(1)	0.079	0.085	0.019	0.035	0.006	0.043
	5	5	4	7	7	8
O(2)	0.093	0.082	0.015	0.033	0.042	-0.009
	5	5	4	7	7	8
O(3)	0.076	0.079	0.030	-0.042	-0.028	0.041
	5	5	4	7	7	8
Br	0.075	0.065	0.069	-0.002	-0.027	0.041
	1	1	1	1	1	1

ORTHOGONAL COORDINATES

The orthogonal axes X', Y and Z' are defined as follows:-

X' is parallel to a*

Z' is parallel to c

Y is normal to X' and Z' so as to complete a right-handed set.

TABLE 3.5

ORTHOGONALISED COORDINATES AND E.S.D.S (in Å)

ATOM	X'	Y	Z'
C(1)	5.825 ± 8	-2.900 ± 8	-1.077 ± 8
C(2)	4.476 ± 9	-3.047 ± 9	-0.300 ± 9
C(3)	4.276 ± 9	-4.539 ±10	0.185 ±10
C(4)	5.569 ± 9	-5.429 ± 9	-0.153 ± 8
C(5)	5.784 ± 9	-5.531 ± 8	-1.564 ± 9
C(6)	5.817 ± 8	-4.038 ± 9	-2.107 ± 9
C(7)	6.999 ± 9	-3.289 ± 8	-0.138 ± 9
C(8)	6.821 ± 9	-4.703 ± 9	0.403 ± 9
C(9)	6.070 ±11	-1.453 ±10	-1.635 ±11
C(10)	7.183 ±11	-6.228 ±11	-1.877 ±10
C(11)	4.592 ±12	-6.355 ±11	-2.268 ±12
C(12)	3.259 ± 9	-2.583 ±10	-1.106 ± 9
C(13)	2.601 ± 9	-1.197 ± 9	-0.922 ± 9
C(14)	2.778 ±10	-0.413 ±10	0.180 ±10
C(15)	2.090 ±11	0.854 ±11	0.325 ±11
C(16)	1.296 ± 9	1.321 ± 9	-0.641 ±11
C(17)	1.120 ±11	0.589 ±11	-1.777 ±11
C(18)	1.780 ±10	-0.709 ±12	-1.878 ±11
O(1)	7.580 ± 8	-5.205 ± 8	1.193 ± 7
O(2)	5.863 ± 8	-3.786 ± 8	-3.194 ± 7
O(3)	2.835 ± 8	-3.360 ± 8	-1.931 ± 8
Br	0.416 ± 1	3.063 ± 1	-0.507 ± 1

TABLE 3.6

CALCULATED HYDROGEN FRACTIONAL COORDINATES

ATOM	x/a	y/b	z/c
H(2)	0.2658	-0.2587	0.1777
H(3)	0.2016	-0.5349	0.0663
H(3')	0.2414	-0.4912	0.2312
H(4)	0.3221	-0.6939	0.1717
H(7)	0.4654	-0.3493	0.1578
H(7')	0.4119	-0.2834	0.2609
H(14)	0.2009	-0.0842	0.1868
H(15)	0.1303	0.1532	0.1783
H(17)	0.0291	0.1016	-0.2264
H(18)	0.0949	-0.1446	-0.2124

TABLE 3.7

INTRAMOLECULAR BONDED DISTANCES AND E.S.D.S (in Å)

ATOM A	ATOM B	A - B	ATOM A	ATOM B	A - B
C(1)	C(2)	1.56 ± 1 Å	C(6)	O(2)	1.12 ± 2 Å
C(1)	C(6)	1.54 ± 2	C(8)	O(1)	1.21 ± 2
C(1)	C(7)	1.55 ± 2	C(7)	C(8)	1.52 ± 1
C(1)	C(9)	1.57 ± 1	C(12)	C(13)	1.55 ± 2
C(2)	C(3)	1.58 ± 2	C(12)	O(3)	1.21 ± 2
C(2)	C(12)	1.53 ± 2	C(13)	C(14)	1.36 ± 2
C(3)	C(4)	1.60 ± 2	C(13)	C(18)	1.35 ± 3
C(4)	C(5)	1.43 ± 2	C(14)	C(15)	1.44 ± 2
C(4)	C(8)	1.55 ± 2	C(15)	C(16)	1.34 ± 2
C(5)	C(6)	1.58 ± 2	C(16)	C(17)	1.36 ± 2
C(5)	C(10)	1.59 ± 2	C(16)	Br	1.95 ± 1
C(5)	C(11)	1.61 ± 2	C(17)	C(18)	1.45 ± 2

TABLE 3.8

VALENCY ANGLES AND E.S.D.S (in degrees)

ATOM A	ATOM B	ATOM C	A-B-C	ATOM A	ATOM B	ATOM C	A-B-C
C(2)-	C(1)-	C(6)	105.0±0.7°	C(1)-	C(6)-	O(2)	119.1±0.8°
C(2)-	C(1)-	C(7)	109.2±0.7	C(5)-	C(6)-	O(2)	123.1±0.8
C(2)-	C(1)-	C(9)	113.4±0.7	C(1)-	C(7)-	C(8)	111.0±0.7
C(6)-	C(1)-	C(7)	103.0±0.6	C(4)-	C(8)-	C(7)	113.7±0.7
C(6)-	C(1)-	C(9)	116.4±0.7	C(4)-	C(8)-	O(1)	123.3±0.8
C(7)-	C(1)-	C(9)	109.1±0.7	C(7)-	C(8)-	O(1)	123.0±0.8
C(1)-	C(2)-	C(3)	110.5±0.7	C(2)-	C(12)-	C(13)	123.2±0.8
C(1)-	C(2)-	C(12)	113.3±0.7	C(2)-	C(12)-	O(3)	116.2±0.9
C(3)-	C(2)-	C(12)	110.3±0.7	C(13)-	C(12)-	O(3)	120.6±0.8
C(2)-	C(3)-	C(4)	110.9±0.7	C(12)-	C(13)-	C(14)	123.9±0.8
C(3)-	C(4)-	C(5)	111.6±0.7	C(12)-	C(13)-	C(18)	119.9±0.9
C(3)-	C(4)-	C(8)	108.3±0.7	C(14)-	C(13)-	C(18)	116.3±0.9
C(5)-	C(4)-	C(8)	105.4±0.7	C(13)-	C(14)-	C(15)	121.5±0.9
C(4)-	C(5)-	C(6)	105.9±0.7	C(14)-	C(15)-	C(16)	120.9±1.0
C(4)-	C(5)-	C(10)	110.9±0.8	C(15)-	C(16)-	C(17)	119.5±0.9
C(4)-	C(5)-	C(11)	110.9±0.8	C(15)-	C(16)-	Br	121.9±0.8
C(6)-	C(5)-	C(10)	108.9±0.7	C(17)-	C(16)-	Br	118.5±0.8
C(6)-	C(5)-	C(11)	110.3±0.7	C(16)-	C(17)-	C(18)	118.4±1.0
C(10)-	C(5)-	C(11)	109.9±0.8	C(13)-	C(18)-	C(17)	123.2±1.0
C(1)-	C(6)-	C(5)	117.8±0.7				

TABLE 3.9

INTRAMOLECULAR NON-BONDED DISTANCES (in Å)

ATOM A ATOM B	A-B	ATOM A ATOM B	A-B
C(1)...C(4)	2.70 Å	C(5)...C(7)	2.92 Å
C(1)...C(10)	3.68	C(6)...C(8)	2.78
C(1)...C(11)	3.86	C(6)...C(12)	3.11
C(1)...O(3)	3.14	C(7)...O(2)	3.30
C(2)...C(5)	3.08	C(8)...C(9)	3.91
C(2)...C(8)	2.96	C(8)...C(10)	2.77
C(2)...C(14)	3.17	C(9)...O(2)	2.81
C(2)...C(18)	3.90	C(11)...O(2)	3.01
C(2)...O(2)	3.29	C(10)...C(3)	3.94
C(3)...C(6)	2.81	C(10)...O(2)	3.07
C(3)...C(7)	3.01	C(13)...C(16)	2.85
C(3)...C(11)	3.07	C(14)...C(17)	2.75
C(3)...C(13)	3.90	C(15)...C(18)	2.72
C(3)...O(3)	2.82	C(18)...O(3)	2.85

TABLE 3.10

INTERMOLECULAR DISTANCES (in Å) < 3.80 Å

ATOM A ATOM B	e.p.	distance Å
C(2)...O(2)	i	3.56
C(7)...O(1)	ii	3.70
C(7)...O(2)	i	3.52
C(8)...C(9)	i	3.69
C(9)...O(1)	ii	3.52
C(14)...O(3)	i	3.32
C(14)...O(2)	i	3.67
C(15)...O(3)	i	3.79
Br...C(18)	iii	3.76
Br...Br	iv	3.39

Equivalent positions are:-

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

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

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

iv) $-x, 1 - y, -z$

Transformations should be applied to the coordinates of the second atom.

TABLE 3.11

Best-planes calculated through various atoms of the molecule and dihedral angles between the bonds of the bicyclic system.

(Schomaker et al., 1959)

Atoms Defining the Planes

PLANE 1	C(13), C(14), C(15), C(16), C(17), C(18)
PLANE 2	C(2), C(12), C(13), O(3)
PLANE 3	C(1), C(2), C(3), C(4)
PLANE 4	C(1), C(4), C(5), C(6)
PLANE 5	C(1), C(4), C(7), C(8)

Plane Equations

PLANE 1 $0.7810X' + 0.4524Y - 0.4306Z' = 1.8900$

PLANE 2 $0.6114X' + 0.3878Y - 0.6898Z' = 1.7597$

PLANE 3 $-0.4361X' - 0.2584Y - 0.8620Z' = -0.8788$

PLANE 4 $-0.9935X' + 0.0419Y - 0.1058Z' = -5.7691$

PLANE 5 $0.5267X' - 0.3438Y - 0.7774Z' = 4.9101$

TABLE 3.11 (contd.)

Distances of Atoms (in Å) from the Planes

PLANE 1	C(13)	-0.0033	C(16)	-0.0045
	C(14)	0.0152	C(17)	0.0159
	C(15)	-0.0111	C(18)	-0.0122
	Br	0.0388	C(12)	-0.0373
PLANE 2	C(2)	0.0019	C(13)	0.0020
	C(12)	-0.0063	O(3)	0.0024
PLANE 3	C(1)	0.0158	C(3)	0.0266
	C(2)	-0.0269	C(4)	-0.0155
PLANE 4	C(1)	-0.0258	C(5)	-0.0435
	C(4)	0.0254	C(6)	0.0438
	O(2)	0.1230		
PLANE 5	C(1)	-0.0078	C(7)	0.0139
	C(4)	0.0080	C(8)	-0.0141
	O(3)	-0.0561		

Dihedral Angles Between Planes

PLANE 1 - PLANE 2	18.20°
PLANE 3 - PLANE 4	59.09°
PLANE 3 - PLANE 5	58.04°
PLANE 4 - PLANE 5	62.91°

Dihedral Angles Between Bonds About the C(1),C(4) Axis

[C(1)-C(2)] - [C(3)-C(4)]	2.78°
[C(1)-C(6)] - [C(4)-C(5)]	4.92°
[C(1)-C(7)] - [C(4)-C(8)]	1.47°

Torsional Angles About Bridge Bonds

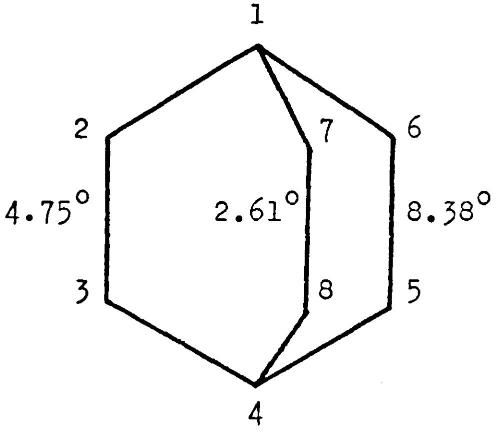


FIGURE 3.1

The Harker section at v = 1/2 of the Patterson function P(uvw). The bromine vector is marked with a cross. Contours are at arbitrary levels.

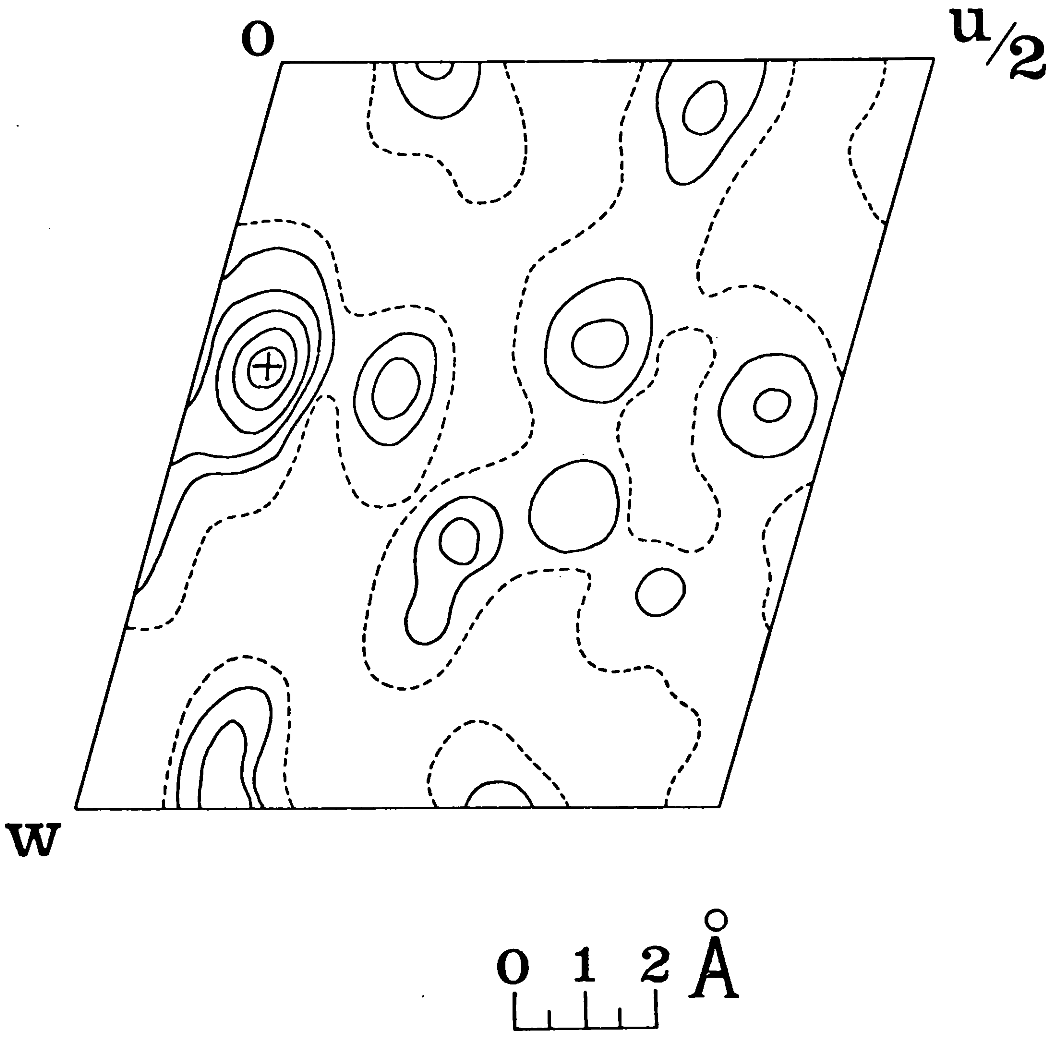

0
u/2
w
0 1 2 Å

FIGURE 3.2

Superimposed sections of the final electron-density distribution viewed down the b-axis. Contour-levels are at intervals of 1e/Å^3 except around the bromine atom where they are at intervals of 5e/Å^3.

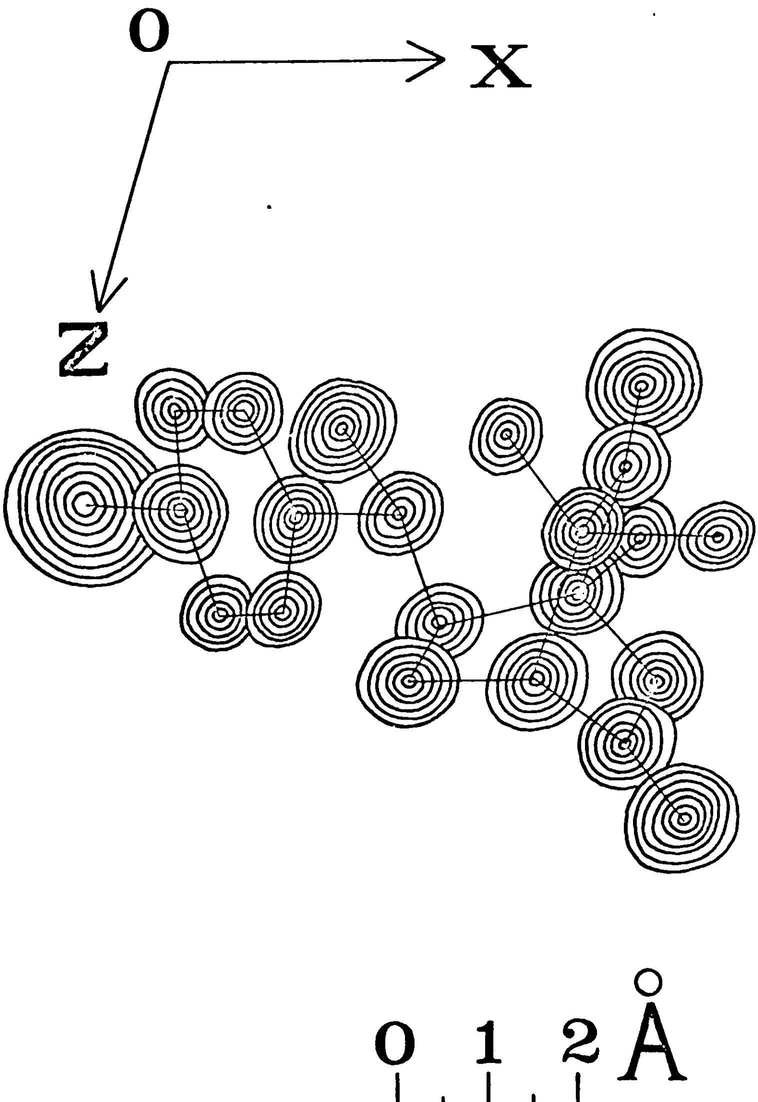

O
X
Z
0 1 2 Å

FIGURE 3.3

Atomic numbering scheme. Hydrogen atoms are numbered as the carbon atoms to which they are bonded.

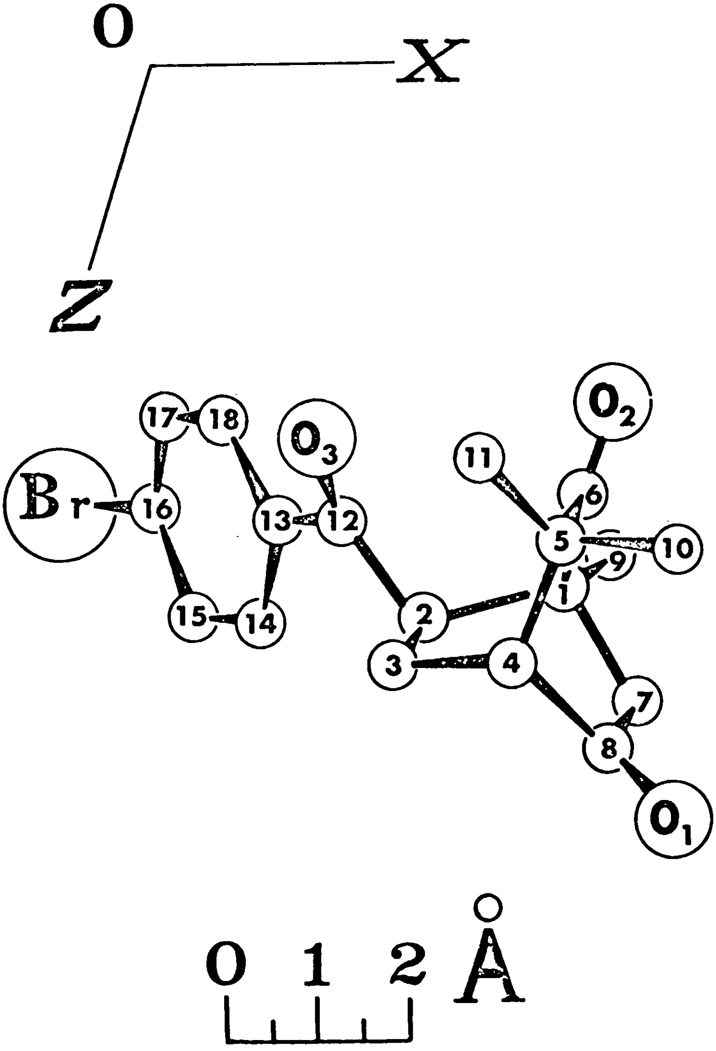

O
X
Z
Br
16
17
18
15
14
13
12
O3
2
3
4
11
6
O2
5
10
9
1
7
8
O1
0 1 2 Å

FIGURE 3.4

Molecular packing viewed down the b-axis.

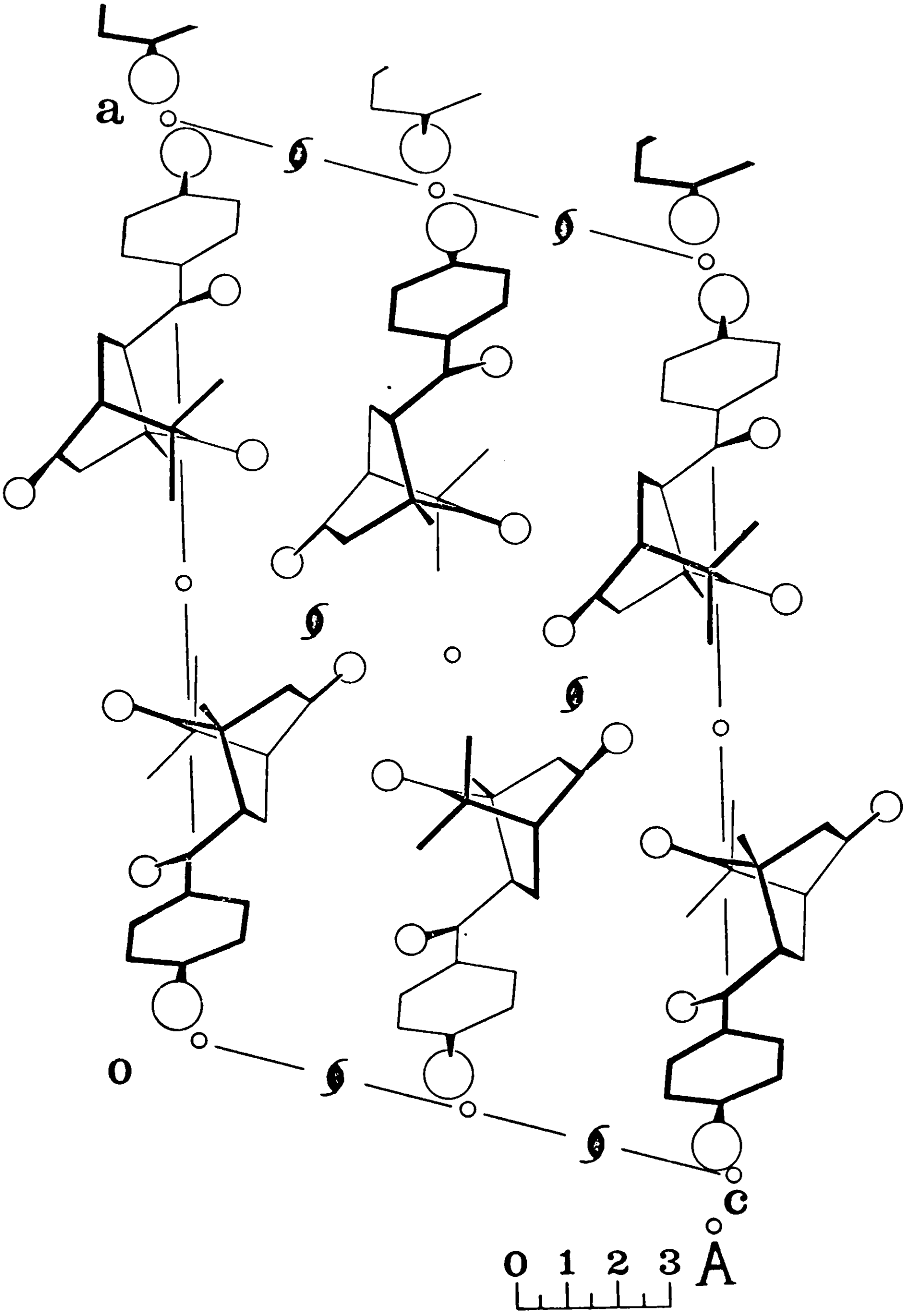
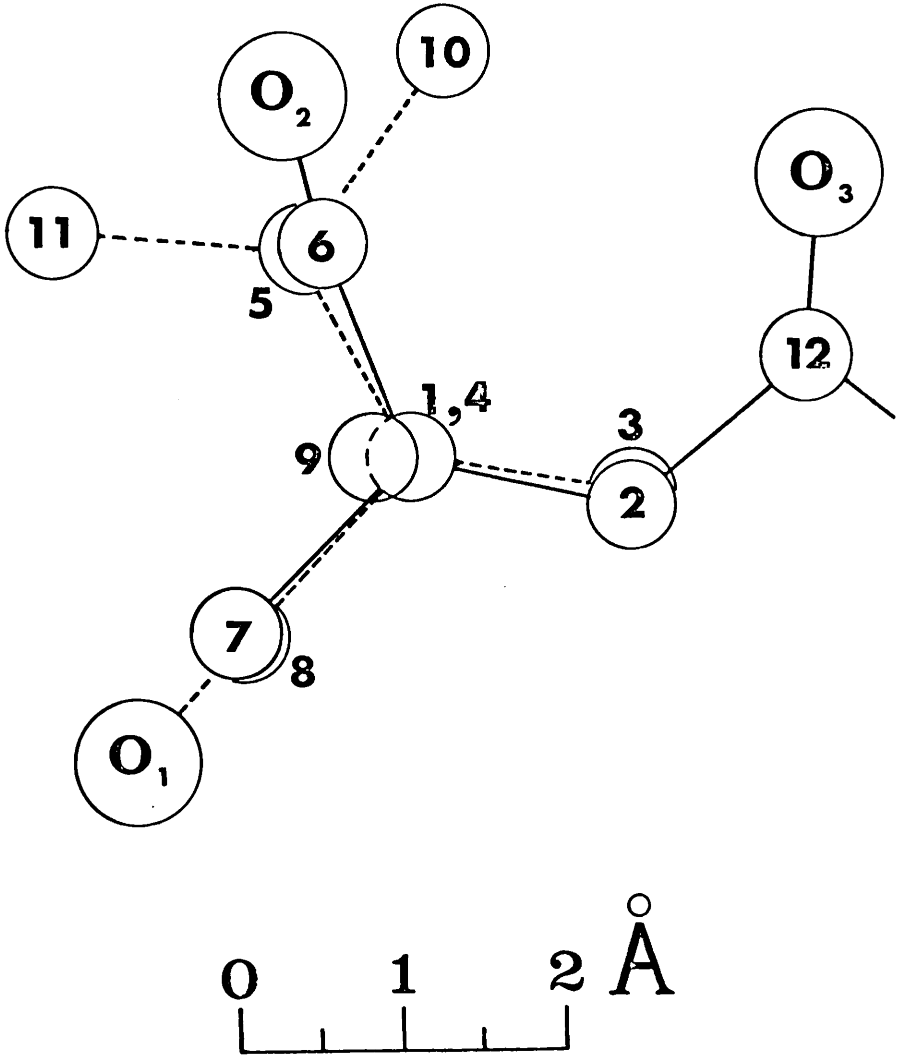

a
o
c
0 1 2 3 Å

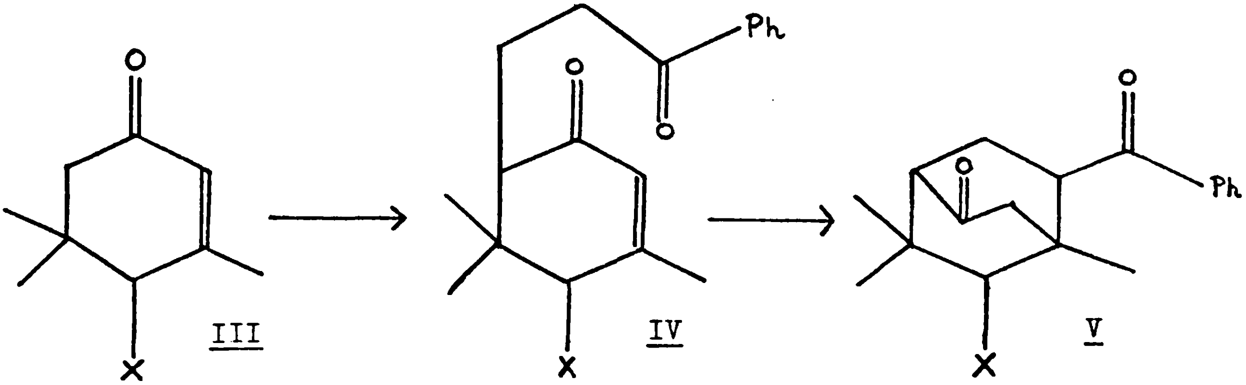
FIGURE 3.5

View of the bicyclic ring system along the axis through atoms C(1) and C(4).


10
O2
O3
11
6
5
12
1,4
3
9
2
7
8
O1
0
1
2
Å

3.3 DISCUSSION

The elucidation of the structure of this compound has rationalised the mechanism of its formation which has proved to be an abnormally oriented thermal Michael condensation. The additional carbonyl group has been postulated as arising from peroxide or hydroperoxide present in the original sample of isophorone used for the preparation, since freshly purified isophorone yields products of the expected molecular weight (Brown and Buchanan, unpublished) and the base-catalysed conversion of hydroperoxides into ketones is well authenticated (Davies, 1961). Aside from this, the reaction is remarkable as a double Michael reaction in which the isophorone functions both as donor and acceptor molecule (viz. $\mathrm{III}\longrightarrow\mathrm{IV}\longrightarrow\mathrm{V}$; X = O_2H or O) , decomposition of the hydroperoxide occurring at some point in the sequence.



The participation of $\alpha\beta$-enones as donors is well known (Beereboom, 1966; Woodward, Sondheimer, Taub, Heusler and McLamore, 1952; Engel and Lessard, 1963) , but in the present instance the orientation of the product IV is strikingly abnormal and appears to be equally abnormal in peroxide-free reactions on $\alpha\beta$- unsaturated ketones (Brown and Buchanan, unpublished) under thermal Michael conditions.

Assignation of the low-field triplet in the n.m.r. spectrum was made possible by the structure determination. It was observed (Brown, Buchanan, Cameron and Ferguson, 1967) that after deuterium exchange (D_2O - OD^-) the signal disappeared. The low-field triplet can therefore be assigned to the C(2) proton (see Figure 3.3 for numbering) , strongly deshielded by a conformationally frozen aroyl group. A study of the molecular model confirms that non-bonded interactions severely limit rotation about the C(2) - C(12) bond, and although the aromatic ring is free to rotate about the C(12) - C(13) bond (the aromatic proton signal in II (R = Br) is a symmetrical A_2B_2 quartet) , the C(2) proton is permanently in the deshielding zones of the carbonyl C(12) - O(3) and of the aromatic ring.

For the most part the bond distances within the molecule do not differ significantly from literature values (Sutton et al., 1965) . However, the values of 1.43 Å and 1.12 Å for the C(4) - C(5) and C(6) - O(2) bonds respectively are unusual. It is felt that these abnormal values are indicative of slight errors in atomic positioning rather than of a feature of the molecular geometry. The crystals were of rather poor quality and the diffraction data were correspondingly poor. Under such circumstances slight errors would not be unexpected.

The valency angles are all acceptably similar to literature values, any slight deviations being explicable in terms of the constraints placed on the atoms by the bicyclic system, and in terms of non-bonded interactions. The C(4) - C(8) - C(7) value of 114° and the C(1) - C(6) - C(5) value of 118° are both consistent with sp^2 hybridised centres constrained to exist in a bicyclic system, and the C(6) - C(1) - C(9) value of 116° is explained by steric interaction between C(9) and O(2) which are separated by 2.81 Å .

The best-plane (Table 3.11) calculated through the six atoms C(13),....,C(18) of the benzene ring shows that within experimental error the ring is planar and that the deviations of C(12) and the bromine atom from this plane are not significant. The four atoms C(2), C(12), C(13) and O(3) are also planar and the angle between this plane and the plane of the benzene ring is 18° .

Best-plane calculations (Table 3.11) involving the atoms of the bicyclo[2,2,2]octane skeleton reveal that the atoms C(1), C(2), C(3) and C(4), which form the only bridge without an sp^2 hybridised centre, are distorted from planarity. The bond C(1) - C(2) is twisted by approximately 3° about the C(1),C(4) axis relative to the C(3) - C(4) bond (Table 3.11) . This corresponds to 5° dihedral angles between substituents on this bridge. As would be expected, the bridge formed by atoms C(1), C(4), C(7) and C(8) is within experimental error planar as a result of the

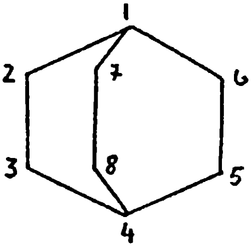
sp^2 hybridised carbon atom C(8). Rather unexpectedly, however, the bridge formed by atoms C(1), C(4), C(5) and C(6) is distinctly non-planar, the bond C(1) - C(6) being rotated by approximately 5° about the C(1),C(4) axis relative to the C(4) - C(5) bond. The twisting of this bridge may be presumably attributed to the steric interaction between the methyl group C(9) and the adjacent carbonyl oxygen O(2) , the C(9)...O(2) distance being 2.81 Å . Without bridge-twisting the C(9)...O(2) interaction would be fully eclipsed. The C(6) - C(1) - C(9) valency angle is also increased to 116° . Figure 3.5 is a view of the bicyclic moiety down the C(1),C(4) axis and shows the relative twisting of the three bridges. The implications of the above molecular-geometry calculations are discussed more fully in Chapter 5 in relation to the strain effects operative in bicyclic systems. In addition, Halford (1956) has shown that the stretching frequencies of carbonyls in bicyclic systems are increased to about 1731 cm^{-1}, and that this increase is indicative of molecular strain. In the case of the present molecule the stretching frequency of the bicyclic carbonyls is 1733 cm^{-1}, this being further proof that the bicyclic system is strained.

CHAPTER 4 THE CRYSTAL STRUCTURE OF 1-BROSYLOXYMETHYL-BICYCLO[2,2,2]OCTANE

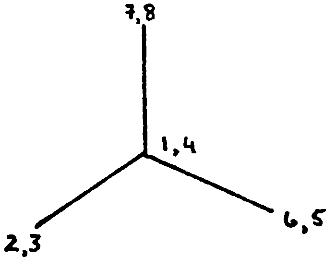
4.1 INTRODUCTION

This analysis was undertaken specifically to study the conformation of the bicyclo[2,2,2]octane system (I) about which there has been considerable controversy in the literature. All previous attempts to determine the conformation using either the parent hydrocarbon or a suitable derivative have proved inconclusive. The conformational possibilities for this system are either the fully eclipsed conformation with D_{3h} symmetry (II - viewed along the C(1),C(4) axis) , or a slightly staggered conformation with D_3 symmetry (III - viewed along the C(1),C(4) axis) . The factors which might be expected to bias the conformation are the 1:3 and 1:2 non-bonded hydrogen interactions and torsional interactions around the bonds of the bicyclic system. A full analysis of the effects of the two conformations on these strain-producing mechanisms is given in Table 5.1 (Chapter 5) .

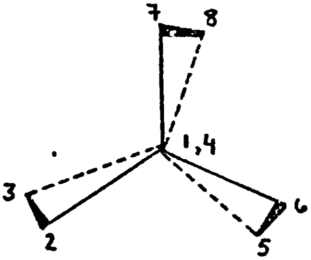
The heat of hydrogenation of bicyclo[2,2,2]octene (IV) to bicyclo[2,2,2]octane (I) was found to be 28.25 k.cals/mole, 1.15 k.cals/mole greater than the corresponding value for the cyclohexene-cyclohexane hydrogenation (Turner, Meador and Winkler, 1957) . To explain this unexpected result it was considered that



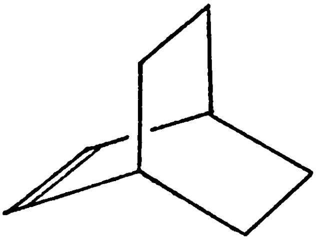
I



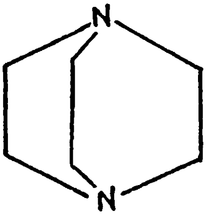
II



III



IV



V

the hydrogenation value of 28.25 k.cals/mole represented the enthalpy change for the conversion of bicyclo[2,2,2]octene into a staggered conformation of bicyclo[2,2,2]octane, with this staggered form representing an energy minimum. Turner and his co-workers pointed out that up to 10° of twist could be accommodated without distortion of bond angles, and also that a relatively large total energy change may be brought about by a small reduction in each of the opposed H...H interactions. Alternatively, the high heat of hydrogenation was explained by allowing for twisting in the bicyclo[2,2,2]octene molecule, which would have the effect of introducing torsional strain of the double bond.

Macfarlane and Ross (1960) have studied the infra-red and polarised Raman spectra of bicyclo[2,2,2]octane, and conclude that the spectra were consistent with those predicted on the assumption that the molecule is eclipsed (i.e. has D_{3h} symmetry) although a structure in which the molecule is slightly twisted about its three-fold axis could not be excluded. Similar results have been obtained with the infra-red and Raman spectra of 1,4-diazabicyclo[2,2,2]octane (V) (Marzocchi, Sbrana and Zerbi, 1965) .

Nethercot and Javan (1953) have reported the microwave spectra of both 1-bromo and 1-chlorobicyclo[2,2,2]octane and found neither bond-length nor valency-angle strain. They report that the angle of twist about the three-fold symmetry axis is $0 \pm 4^{\circ}$. The solution infra-red spectra of bicyclo[2,2,2]octane, quinuclidine, and

1,4-diazabicyclo[2,2,2]octane have been studied, but again an unequivocal choice between the eclipsed and staggered conformations is impossible (Bruesch and Gunthard, 1966) . However, Gleicher and Schleyer (1967) have recently predicted, on the basis of theoretical strain-energy calculations, that the eclipsed D_{3h} conformation should be energetically more favoured than the staggered D_3 conformation; the empirical nature of their strain-energy calculations is admitted.

Our interest in the above controversy was primarily aroused by the molecular-geometry calculations described in Chapter 3, and in collaboration with Dr.D.G.Morris a new compound, 1-brosyloxymethylbicyclo[2,2,2]octane was prepared to study this problem. A single-crystal structure analysis using 1715 three-dimensional data has been completed, and the results of the molecular-geometry calculations have proved unambiguously that in this case at least, the bicyclo[2,2,2]octane skeleton adopts the staggered D_3 conformation, the presence of the 1-brosyloxymethyl group appearing to have had little or no effect on the conformation.

4.2 EXPERIMENTAL

Diels Alder condensation of 1-carboethoxycyclohexa-1,3-diene (Sayigh, 1952) with maleic anhydride gave an adduct which was converted (Grob, Ohta, Renk and Weiss, 1958) into the experimental material 1-brosyloxymethylbicyclo[2,2,2]octane for which satisfactory analysis figures were obtained. This synthesis was executed by Dr.D.G.Morris.

4.2.1 Crystal Data

1-brosyloxymethylbicyclo[2,2,2]octane, $C_{15}H_{19}SO_3Br$, M = 359.3 ,

Monoclinic, a = 18.99±0.05, b = 6.65±0.02, c = 12.56±0.03 Å ,

β = 96.0±0.2° , U = 1577 Å^3, D_m = 1.50 g.cm.$^{-3}$ (by flotation in

KI/H_2O) , z = 4, D_x = 1.53 g.cm.$^{-3}$,

F(000) = 736,

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

Linear absorption coefficient for X-rays (λ =1.5418 Å), μ = 51.4 cm^{-1}

4.2.2 Crystallographic Measurements

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

Exposing a small crystal rotating about b to Cu-Kα radiation, 1715 independent reflexions from the reciprocal lattice nets h0ℓ - h5ℓ were recorded on equatorial and equi-inclination Weissenberg photographs using the multiple-film technique with six films in each pack. The intensities were measured using a Joyce-Loebl flying-spot integrating microdensitometer which was also used to measure the background adjacent to each reflexion. The intensities thus obtained were the integrated intensities and a background reading was subtracted in each case. After correction for Lorentz and polarisation factors the amplitudes were subsequently placed on an approximately absolute scale by making $k\Sigma|F_o| = \Sigma|F_c|$ for each layer. No allowance was made for absorption and unobserved reflexions were not considered.

4.2.3 Structure Determination

The value of 1.22 for the ratio $f^2_{Br} / \sum_R f^2_R$ indicated a reasonable chance of success for the heavy-atom method of phase determination (Lipson and Cochran, 1966) and the analysis subsequently proceeded on this basis.

After sharpening to point bromine atom at rest, the data were used to compute the three-dimensional Patterson function from which the bromine coordinates (0.0375, 0.4246, 0.6765) were unambiguously determined (c.f. Chapter 2, 2.3.2) . The sulphur coordinates were not determined directly from the Patterson function, but after locating the sulphur atom in the first (bromine-phased) electron-density distribution, it proved possible to identify most of the peaks in the Patterson function which were attributable to sulphur-sulphur and to bromine-sulphur vectors. The Harker section at $v = 1/2$ of the Patterson function is shown in Figure 4.1 .

The first electron-density distribution, evaluated with the observed amplitudes and the signs appropriate to the bromine atom, revealed the complete structure. One further round of structure-factor and electron-density calculations yielded an improved set of atomic positional parameters. In both structure-factor calculations an overall isotropic temperature factor $U_{iso} = 0.05\ \text{Å}^2$ was assumed, and after each calculation the layers $h0\ell$ - $h5\ell$ were put on an approximately absolute scale by making $k\sum|F_o| = \sum|F_c|$ for each layer. In the calculation of the first electron-density distribution an appropriate modification function (Sim, 1961) was applied to the Fourier coefficients to improve the resolution.

4.2.4 Structure Refinement

The refinement of positional, vibrational (isotropic and anisotropic) and scale parameters by three-dimensional least-squares methods converged after 14 cycles with R = 0.107 and R' = 0.0189 . Details of the refinement are given in Table 4.1 .

After cycle 4 the data were converted to an overall absolute scale using the refined values of the layer-scale factors, and in all subsequent cycles the overall-scale factor was refined. A weighting scheme of the form

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

was applied in all cycles. Initially the parameters $p_1, \ldots, p_3$ were chosen to give unit weights to all reflexions, but were subsequently varied according to the dictates of the weighting analysis (c.f. Chapter 2, 2.2.4 , page 77) , the final values being

$$p_1 = 50, \quad p_2 = 0.01, \quad p_3 = 0.001$$

Coordinates were calculated from geometrical considerations for all the hydrogen atoms and their contributions were included in the structure-factor calculations, with an overall assumed isotropic temperature factor $U_{iso} = 0.05$ Å^2, after cycle 8 . The hydrogen parameters were not refined. Also after cycle 8 , anisotropic thermal parameters were refined and because of computer-store limitations this necessitated the use of a block-diagonal approximation to the normal-equation matrix in all subsequent cycles. The strategy employed in refining anisotropic vibrational parameters was similar to that used in the refinement of laurencin (Part II , Chapter 1 , 1.2.4 , page 49) .

The least-squares refinement was terminated when the calculated shifts were less than one-third of the estimated standard deviations. Structure factors were calculated with the final parameters excluding contributions from the hydrogen atoms, and a final electron-density distribution and a three-dimensional difference synthesis were evaluated. Superimposed sections of the final electron-density distribution viewed down the b - axis are shown in Figure 4.2 . The difference synthesis revealed no errors in the structure, and although there were a number of diffuse peaks in positions stereochemically acceptable for hydrogen atoms, it was not possible to determine their coordinates with any accuracy. The refinement of the structure was therefore considered complete.

In all the structure-factor calculations the atomic scattering factors used were those given in "International Tables for Crystallography", Vol. III . Values of $|F_o|$ and the final values of F_c are given in Table 4.2 . The final fractional coordinates are given in Table 4.3 and the anisotropic thermal parameters given in Table 4.4 are the values of U_{ii} and $2U_{ij}$ in the expression

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

The appropriate estimated standard deviations estimated from the inverse of the least-squares matrix are included in Tables 4.3 and 4.4 . Orthogonal coordinates are listed in Table 4.5 , and Table 4.6 contains the calculated hydrogen coordinates.

Table 4.7 contains bond distances and Table 4.8 contains valency angles. The average estimated standard deviations for C - C, C - S, C - Br and S - O bonds are respectively 0.014 Å , 0.009 Å , 0.010 Å , and 0.007 Å , and for valency angles is 0.7° . These should be regarded as minimum values. Some intramolecular non-bonded distances are listed in Table 4.9 , and all intermolecular distances < 4 Å are given in Table 4.10 . Details of all best-plane calculations and of torsional angles are given in Table 4.11 .

The atomic numbering scheme is shown in Figure 4.3 , the hydrogen atoms being numbered as the carbon atoms to which they are bonded. The molecular packing viewed down the b - axis is shown in Figure 4.4 .

TABLE 4.1

COURSE OF REFINEMENT

Cycles	Parameters refined	Final R	Final R'	$\Sigma w\Delta^2$
1 - 4	x, y, z, U_{iso} for Br, O, C, S, Layer scale factors, Unit weights, full matrix.	0.172	0.0340	41,001
5 - 8	x, y, z, U_{iso} for Br, O, C, S, Overall scale factor, Full matrix, weighting scheme adjusted.	0.166	0.0295	19,821
9 - 14	x, y, z, U_{ij} for Br, O, C, S, Overall scale factor, Block diagonal, weighting scheme applied, hydrogen atoms included	0.107	0.0189	7,038

TABLE 4.2

Observed amplitudes and calculated (final) structure factors.

H	K	L	Fo	Fc
10	0	14	7.3	8.3
9	0	14	5.4	9.6
5	0	14	13.8	-12.7
4	0	14	11.1	-14.9
3	0	14	19.0	18.4
1	0	14	18.3	-20.4
-3	0	14	19.5	-18.1
-4	0	14	23.3	-23.0
-5	0	14	11.1	-10.5
-6	0	14	11.0	11.4
-7	0	14	16.3	16.5
-11	0	14	6.3	7.0
-12	0	14	5.8	7.6
11	0	12	7.6	-9.2
7	0	12	15.4	-11.6
6	0	12	14.6	-13.5
4	0	12	13.0	-8.9
3	0	12	21.1	21.5
1	0	12	29.1	-23.2
-1	0	12	31.7	28.7
-2	0	12	32.3	31.6
-5	0	12	31.3	30.9
-6	0	12	42.0	42.6
-7	0	12	16.5	15.9
-13	0	12	14.8	-12.1
-14	0	12	19.3	-15.1
-15	0	12	5.6	-7.8
12	0	10	15.3	-12.5
11	0	10	19.4	-13.7
10	0	10	14.1	12.7
9	0	10	39.7	40.9
8	0	10	46.0	44.2
4	0	10	21.3	15.5
3	0	10	38.2	34.5
2	0	10	11.9	11.8
1	0	10	14.5	-12.9
0	0	10	19.2	14.9
-1	0	10	23.1	14.0
-2	0	10	9.1	6.3
-3	0	10	26.5	-21.6
-4	0	10	32.7	-26.0
-5	0	10	21.3	-15.5
-7	0	10	34.8	-32.9
-8	0	10	65.7	-69.0
-9	0	10	13.4	-10.0
-11	0	10	21.3	-21.8
-12	0	10	15.3	-14.4
-13	0	10	21.4	-22.0
-14	0	10	13.7	-11.8
15	0	10	5.6	-2.5
-16	0	10	30.2	28.1
-17	0	10	19.3	17.9
14	0	8	14.7	12.8
13	0	8	19.8	18.5
10	0	8	35.7	28.1
9	0	8	55.1	50.4
8	0	8	13.9	9.2
7	0	8	56.1	-59.6
6	0	8	67.1	-72.9
5	0	8	32.9	-34.7
3	0	8	43.5	-36.0
2	0	8	42.8	-41.1
1	0	8	61.9	-57.1
0	0	8	40.7	-32.1
-1	0	8	26.2	-24.9
-2	0	8	28.0	-27.1
-3	0	8	11.6	-7.8
-4	0	8	11.2	-8.0
-7	0	8	33.9	29.5
-8	0	8	23.1	-14.5
-9	0	8	17.5	13.3
-10	0	8	73.6	76.0
-11	0	8	33.1	29.2
-12	0	8	23.7	20.8
-13	0	8	15.5	15.4
-14	0	8	15.5	16.9
-15	0	8	36.5	34.7
-16	0	8	23.7	22.5
-18	0	8	18.4	-16.0
-19	0	8	14.7	-12.0
16	0	6	8.3	-10.0
15	0	6	12.1	-9.4
14	0	6	22.9	-20.3
13	0	6	27.4	23.6
12	0	6	47.3	-48.1
11	0	6	58.5	-59.1
10	0	6	7.2	7.8
9	0	6	10.9	-12.9
8	0	6	20.6	-16.5
5	0	6	22.2	15.4
4	0	6	21.3	14.4
3	0	6	34.5	25.4
1	0	6	86.2	91.8
0	0	6	96.7	97.2
-1	0	6	82.1	75.0
-2	0	6	82.3	89.1
-3	0	6	64.7	59.5
-4	0	6	30.0	34.1
-5	0	6	44.5	37.8
-6	0	6	50.6	46.5
-7	0	6	34.0	32.8
-8	0	6	24.5	-21.1
-9	0	6	28.9	-20.6
-10	0	6	37.6	40.1
-11	0	6	16.9	13.9
-12	0	6	44.5	-46.7
-13	0	6	57.9	-59.7
-14	0	6	42.9	-36.1
-15	0	6	12.2	-7.6
-16	0	6	9.5	-9.6
-17	0	6	34.0	-29.0
-18	0	6	17.6	-15.3
22	0	4	10.2	-11.0
21	0	4	19.6	-19.4
19	0	4	11.4	11.4
17	0	4	20.5	-16.7
16	0	4	18.7	-17.1
15	0	4	27.9	25.5
12	0	4	32.2	32.6
11	0	4	27.0	-25.9
10	0	4	69.0	74.0
9	0	4	95.0	100.3
8	0	4	53.5	54.5
7	0	4	50.5	52.3
6	0	4	30.6	27.3
5	0	4	76.0	74.7
4	0	4	10.7	19.3
3	0	4	32.4	23.1
2	0	4	53.4	34.5
1	0	4	12.2	12.4
0	0	4	57.2	39.2
-1	0	4	87.0	-41.0
-2	0	4	105.7	-102.3
-3	0	4	104.0	-107.4
-5	0	4	52.5	-43.6
-6	0	4	28.4	-31.2
-10	0	4	20.8	18.5
-11	0	4	16.0	-12.2
-12	0	4	50.4	-47.2
-13	0	4	28.5	-25.2
-14	0	4	15.7	14.0
-15	0	4	49.4	47.3
-16	0	4	35.8	30.9
-17	0	4	12.9	10.9
-19	0	4	31.2	27.0
-20	0	4	17.2	13.8
-22	0	4	12.7	14.1
20	0	2	17.3	15.6
19	0	2	32.7	27.4
18	0	2	23.1	17.4
16	0	2	15.9	13.6
15	0	2	30.8	27.3
14	0	2	22.6	21.7
12	0	2	21.4	20.0
11	0	2	26.6	27.2
10	0	2	16.2	-11.7
9	0	2	18.5	-14.3
8	0	2	32.6	-32.8
7	0	2	88.3	-92.2
6	0	2	90.7	-94.6
5	0	2	76.7	-95.2
4	0	2	64.8	-63.3
1	0	2	25.2	-32.7
0	0	2	56.8	49.0
-1	0	2	24.9	-12.7
-3	0	2	69.5	-72.7
-4	0	2	53.1	42.5
-5	0	2	57.8	68.3
-6	0	2	77.4	82.0
-7	0	2	27.3	27.5
-8	0	2	19.2	16.3
-9	0	2	71.6	88.5
-10	0	2	64.1	70.7
-11	0	2	62.7	64.6
-12	0	2	32.5	28.9
-13	0	2	29.8	30.2
-14	0	2	52.7	46.0
-15	0	2	34.4	28.5
-17	0	2	17.9	-14.4
-18	0	2	12.2	-13.7
-21	0	2	23.9	-20.8
-22	0	2	23.6	-19.9
-23	0	2	18.8	-9.6
22	0	0	10.2	-10.2
21	0	0	14.7	-12.9
18	0	0	23.5	-13.7
17	0	0	26.3	-30.4
16	0	0	28.7	-35.0
15	0	0	15.7	-13.5
14	0	0	41.8	-34.4
13	0	0	42.3	-34.9
12	0	0	34.5	-21.8
11	0	0	55.6	-59.0
10	0	0	23.7	-20.8
9	0	0	38.6	-41.6
8	0	0	36.4	-35.8
7	0	0	31.3	17.6
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-10	3	1	19.9	-17.1
-11	3	1	21.3	-22.7
-12	3	1	15.9	16.1
-13	3	1	29.8	31.1
-14	3	1	24.3	-22.6
-15	3	1	26.5	-23.7
-16	3	1	10.9	-7.8
-19	3	1	10.6	-10.2
-20	3	1	7.9	-8.0
22	3	0	5.5	6.4
21	3	0	11.7	14.2
20	3	0	8.5	10.0
19	3	0	10.9	11.1
16	3	0	9.3	8.7
14	3	0	27.8	26.9
12	3	0	35.7	-37.4
11	3	0	23.7	-25.4
10	3	0	33.1	-35.8
9	3	0	42.2	-47.2
8	3	0	40.0	-45.2
7	3	0	34.7	-39.4
6	3	0	37.4	-43.2
5	3	0	61.1	-80.4
3	4	13	3.7	5.6
0	4	13	7.7	-11.0
-4	4	13	9.9	-8.2
-5	4	13	6.5	-10.4
-7	4	13	8.0	-5.1
2	4	12	6.6	6.7
-4	4	12	8.7	-2.0
-5	4	12	8.2	-11.5
-6	4	12	7.1	-8.7
-8	4	12	9.8	8.0
-10	4	12	11.9	-6.7
10	4	11	8.3	-12.7
9	4	11	6.5	-10.3
6	4	11	6.7	-9.3
5	4	11	6.9	-7.2
-1	4	11	7.5	6.7
-2	4	11	14.5	14.7
-3	4	11	11.1	9.4
-6	4	11	8.4	7.7
-7	4	11	19.0	22.6
-8	4	11	21.6	25.6
-10	4	11	6.6	-7.6
11	4	10	6.2	6.2
9	4	10	8.1	-10.1
8	4	10	8.0	-7.9
6	4	10	8.0	4.5
4	4	10	12.1	-14.2
3	4	10	7.1	-6.8
2	4	10	12.3	11.6
-1	4	10	10.2	-10.8
-8	4	10	15.2	16.7
-9	4	10	11.5	12.6
-13	4	10	11.8	13.6
-14	4	10	6.7	9.2
12	4	9	5.6	1.7
8	4	9	11.9	10.8
7	4	9	15.4	15.5
6	4	9	11.5	9.8
5	4	9	10.7	9.1
4	4	9	10.2	5.2
3	4	9	30.3	27.4
2	4	9	16.3	16.1
-1	4	9	9.1	-7.6
-2	4	9	15.9	14.8
-3	4	9	13.8	13.3
-4	4	9	14.1	-10.9
-5	4	9	22.4	-19.2
-6	4	9	10.2	-9.7
-8	4	9	10.7	-10.7
-9	4	9	23.4	-20.3
-10	4	9	23.6	-25.9
-11	4	9	11.1	-11.6
-14	4	9	8.1	-12.0
7	4	8	15.1	15.7
6	4	8	15.1	14.6
5	4	8	8.5	9.3
4	4	8	15.8	-10.4
3	4	8	23.4	-19.3
2	4	8	37.3	37.2
1	4	8	27.5	25.8
0	4	8	11.7	-8.2
-3	4	8	10.4	11.9
-5	4	8	8.4	-6.8
-8	4	8	15.1	15.9
-10	4	8	6.4	-7.2
-11	4	8	6.4	-7.0
-12	4	8	6.2	-8.2
-15	4	8	14.8	-15.5
-16	4	8	8.8	-10.8
12	4	7	11.3	12.8
9	4	7	16.5	15.6
8	4	7	12.1	9.8
7	4	7	12.9	9.9
6	4	7	14.7	-12.7
5	4	7	10.9	-8.5
4	4	7	24.4	-20.7
3	4	7	15.3	-15.1
1	4	7	65.1	-62.6
0	4	7	45.6	-44.1
-1	4	7	5.9	-5.9
-2	4	7	8.4	5.4
-3	4	7	9.4	5.4
-4	4	7	34.8	-35.2
-5	4	7	27.1	-27.7
-6	4	7	8.7	-9.5
-7	4	7	19.1	14.6
-8	4	7	17.8	16.1
-10	4	7	16.7	16.2
-11	4	7	21.9	22.9
-12	4	7	18.3	17.1
-13	4	7	11.4	13.1
-14	4	7	8.6	10.0
-15	4	7	10.5	12.4
-16	4	7	12.6	13.8
-17	4	7	6.2	9.4
16	4	6	8.6	10.7
9	4	6	11.2	-8.1
8	4	6	10.6	11.2
7	4	6	12.1	11.3
5	4	6	15.5	-15.7
4	4	6	16.4	-14.8
3	4	6	21.5	-18.8
2	4	6	20.0	16.9
1	4	6	36.3	35.0
0	4	6	36.6	-33.6
-1	4	6	36.7	-33.7
-2	4	6	8.6	-7.2
-3	4	6	14.2	-12.8
-4	4	6	14.0	-12.2
-5	4	6	24.4	-22.9
-6	4	6	17.6	-13.5
-7	4	6	8.5	7.2
-9	4	6	8.3	-7.7
-10	4	6	9.0	-9.3
-11	4	6	8.5	-9.0
-15	4	6	6.8	-9.1
-17	4	6	12.7	11.6
-18	4	6	7.7	10.7
15	4	5	8.2	-8.6
14	4	5	9.7	-9.3
12	4	5	11.2	-11.1
11	4	5	12.1	-10.5
10	4	5	25.8	-22.6
9	4	5	20.3	-21.0
8	4	5	11.5	-10.7
7	4	5	18.5	-15.0
6	4	5	35.2	-35.2
5	4	5	34.9	-37.9
4	4	5	7.7	9.4
3	4	5	16.5	13.0
2	4	5	21.4	17.8
-1	4	5	55.8	54.0
-2	4	5	58.5	56.2
-3	4	5	29.7	25.3
-4	4	5	6.8	5.3
-5	4	5	27.0	21.5
-6	4	5	42.3	45.6
-7	4	5	26.4	28.8
-8	4	5	11.0	12.2
-10	4	5	7.6	-4.7
-13	4	5	16.6	-12.8
-14	4	5	20.3	-18.7
-15	4	5	18.5	-18.1
-16	4	5	11.6	-12.5
-17	4	5	9.8	-10.8
-18	4	5	12.4	-11.6
15	4	4	6.8	-8.2
14	4	4	15.0	-14.1
13	4	4	12.0	-13.0
11	4	4	11.1	-12.8
10	4	4	25.2	-26.3
9	4	4	19.9	-19.9
7	4	4	20.8	20.5
5	4	4	18.5	-16.7
4	4	4	11.3	-9.6
3	4	4	10.3	-8.4
2	4	4	14.4	11.0
1	4	4	26.1	23.3
0	4	4	7.2	-7.5
-1	4	4	28.5	-27.4
-3	4	4	27.5	24.0
-4	4	4	9.4	4.8
-7	4	4	32.2	29.3
-8	4	4	39.4	38.0
-9	4	4	10.5	-7.5
-10	4	4	14.9	17.1
-11	4	4	26.3	25.0
-13	4	4	13.7	11.3
-15	4	4	7.8	-7.6
-17	4	4	13.5	12.0
-18	4	4	11.8	12.0
17	4	3	5.6	-6.7
16	4	3	16.6	-16.4
13	4	3	7.2	9.9
12	4	3	7.2	6.2
11	4	3	17.8	-17.8
10	4	3	9.2	-5.3
9	4	3	24.8	23.4
8	4	3	44.1	47.8
7	4	3	36.3	38.9
6	4	3	13.5	13.7
5	4	3	27.2	24.5
4	4	3	51.0	54.0
3	4	3	54.4	60.1
2	4	3	22.9	23.7
1	4	3	17.7	-13.9
-2	4	3	13.7	-13.5
-3	4	3	17.4	-15.5
-4	4	3	31.3	-31.6
-5	4	3	27.9	-25.3
-6	4	3	33.2	-33.1
-7	4	3	32.2	-30.3
-8	4	3	40.9	-43.2
-9	4	3	42.4	-46.4
-11	4	3	10.6	-9.0
-12	4	3	8.9	-5.4
-14	4	3	26.3	-27.1
-16	4	3	18.5	15.5
-17	4	3	23.0	21.3
-18	4	3	6.8	8.6
-20	4	3	10.2	10.8
20	4	2	6.5	-2.1
16	4	2	10.6	9.2
12	4	2	12.7	12.6
11	4	2	12.8	11.1
10	4	2	11.9	-10.8
9	4	2	17.9	17.1
8	4	2	35.9	38.0
7	4	2	32.8	34.3
6	4	2	15.9	15.5
5	4	2	13.8	-14.0
3	4	2	18.2	15.5
2	4	2	27.1	23.4
1	4	2	34.5	34.2
-1	4	2	10.2	-9.0
-3	4	2	13.5	11.7
-4	4	2	14.1	13.1
-5	4	2	16.1	-13.8
-8	4	2	20.5	20.4
-9	4	2	20.7	-19.0
-10	4	2	34.6	-34.3
-11	4	2	17.6	14.3
-12	4	2	13.7	-13.1
-13	4	2	29.0	-27.2
-14	4	2	14.5	-15.6
-15	4	2	20.9	-20.5
-19	4	2	6.8	-5.6
18	4	1	10.3	12.7
17	4	1	15.0	15.0
15	4	1	12.8	10.5
14	4	1	23.7	23.1
13	4	1	30.1	28.0
11	4	1	15.1	-15.5
10	4	1	13.9	12.5
9	4	1	31.6	30.8
8	4	1	27.6	29.1
7	4	1	13.5	-11.5
6	4	1	39.1	-48.6
5	4	1	35.2	-39.0
4	4	1	23.9	-23.9
3	4	1	39.1	-43.8
2	4	1	50.6	-59.6
-2	4	1	20.9	-23.4
-3	4	1	15.8	-16.4
-4	4	1	8.4	-3.0
-6	4	1	26.1	25.9
-7	4	1	21.4	21.2
-8	4	1	32.1	34.5
-10	4	1	21.1	21.1
-11	4	1	53.8	57.0
-12	4	1	14.3	12.1
-13	4	1	9.0	9.6
-14	4	1	9.1	7.0
-15	4	1	12.9	16.1
-16	4	1	25.4	24.8
-17	4	1	8.5	6.9
-19	4	1	8.9	-11.7
20	4	0	5.4	6.4
18	4	0	9.7	10.8
17	4	0	17.0	19.0
16	4	0	8.3	8.7
14	4	0	8.6	-7.3
13	4	0	7.8	-7.2
12	4	0	17.1	17.5
11	4	0	10.0	9.9
10	4	0	21.1	-20.1
9	4	0	6.7	-5.0
8	4	0	11.7	11.5
6	4	0	21.6	-23.0
5	4	0	25.2	-24.4
4	4	0	14.0	-15.0
5	5	12	7.6	-11.6
4	5	12	4.1	-7.7
-7	5	12	9.4	14.5
-8	5	12	6.8	8.7
-11	5	11	9.3	12.9
10	5	10	4.9	-8.9
9	5	10	6.3	-9.2
5	5	10	7.6	-6.5
3	5	10	12.3	11.0
2	5	10	15.6	15.1
-1	5	10	13.1	11.7
-2	5	10	19.0	17.6
-3	5	10	7.7	7.5
-7	5	10	6.2	8.1
-9	5	10	10.4	-12.2
-10	5	10	14.1	-17.3
11	5	9	8.5	-12.6
9	5	9	7.2	[illegible]
5	5	9	8.8	-8.4
3	5	9	11.3	[illegible]
2	5	9	8.6	8.0
-3	5	9	12.7	11.3
-4	5	9	10.6	8.8
-5	5	9	6.3	8.2
-6	5	9	12.4	12.7
-7	5	9	12.3	11.3
-13	5	9	7.7	-5.5
12	5	8	6.5	5.3
8	5	8	10.9	9.4
7	5	8	6.0	7.1
6	5	8	15.2	6.8
5	5	8	10.2	-11.0
4	5	8	9.2	5.4
3	5	8	16.4	17.1
1	5	8	15.2	12.1
0	5	8	27.3	-23.1
-2	5	8	9.8	9.2
-3	5	8	12.4	-11.9
-4	5	8	27.3	-25.3
-5	5	8	24.3	-24.6
-7	5	8	8.7	6.6
-9	5	8	8.5	-10.7
-11	5	8	7.6	7.3
-12	5	8	13.5	14.8
-13	5	8	12.7	15.9
11	5	7	8.7	11.0
9	5	7	6.7	6.9
8	5	7	7.5	3.9
6	5	7	16.1	15.6
5	5	7	9.3	8.9
4	5	7	17.8	15.4
3	5	7	14.8	14.8
2	5	7	9.7	-6.9
1	5	7	12.2	-10.1
-4	5	7	9.7	-8.7
-6	5	7	9.3	-6.1
-7	5	7	19.3	-18.5
-8	5	7	18.1	-19.4
-9	5	7	17.5	-17.9
-10	5	7	10.1	-11.0
-13	5	7	5.6	-8.3
7	5	6	9.3	-7.0
6	5	6	25.2	-22.2
5	5	6	35.2	-29.6
4	5	6	15.6	-13.9
3	5	6	26.7	25.3
1	5	6	26.2	-24.7
0	5	6	27.8	-27.6
-2	5	6	23.8	29.9
-3	5	6	11.2	6.4
-5	5	6	9.4	9.4
-6	5	6	23.5	21.3
-7	5	6	26.6	24.0
-10	5	6	16.7	17.8
-11	5	6	14.1	16.5
-15	5	6	11.4	-10.6
11	5	5	8.6	-7.2
9	5	5	7.6	-7.2
7	5	5	8.1	-8.1
6	5	5	12.7	-11.9
5	5	5	18.0	-15.8
4	5	5	23.0	-21.0
3	5	5	15.0	-12.2
2	5	5	27.2	-24.9
1	5	5	29.2	-28.1
0	5	5	7.5	5.1
-2	5	5	22.3	-18.8
-6	5	5	18.2	16.0
-7	5	5	8.9	-8.0
-9	5	5	15.9	12.5
-10	5	5	15.2	13.8
-11	5	5	12.4	13.2
-12	5	5	15.1	14.1
-13	5	5	13.1	12.9
-15	5	5	12.9	14.6
-16	5	5	13.5	15.0
12	5	4	11.4	-10.2
11	5	4	22.1	-22.1
10	5	4	20.8	-19.7
9	5	4	11.9	13.4
7	5	4	14.5	-11.5
6	5	4	16.7	-14.1
5	5	4	16.3	-15.0
4	5	4	27.4	25.8
3	5	4	48.5	51.4
2	5	4	34.4	30.5
1	5	4	10.5	-8.4
-1	5	4	35.8	33.0
-2	5	4	29.4	28.9
-3	5	4	10.7	11.0
-4	5	4	17.8	-13.6
-5	5	4	15.1	-13.5
-7	5	4	17.5	-12.7
-8	5	4	19.4	-15.6
-9	5	4	22.5	-17.9
-10	5	4	11.1	-9.8
-12	5	4	16.7	-17.1
-13	5	4	18.2	-17.9
-14	5	4	12.6	-14.0
-16	5	4	7.5	7.2
-17	5	4	6.9	6.8
18	5	3	7.1	-10.5
16	5	3	8.3	-9.7
15	5	3	10.3	-11.7
13	5	3	10.5	-9.2
8	5	3	14.1	-11.7
7	5	3	13.9	-13.7
5	5	3	16.3	15.5
4	5	3	23.2	22.8
3	5	3	18.8	15.0
2	5	3	22.9	18.5
1	5	3	22.9	18.6
0	5	3	17.4	14.7
-1	5	3	35.7	35.1
-2	5	3	12.9	9.3
-3	5	3	13.2	11.8
-4	5	3	36.8	35.9
-5	5	3	8.1	5.8
-6	5	3	19.2	18.7
-7	5	3	9.4	8.1
-8	5	3	10.2	-11.1
-13	5	3	8.7	-7.1
-14	5	3	5.2	-6.2
-15	5	3	6.5	-6.3
-16	5	3	8.2	-9.9
-17	5	3	13.1	-14.3
-18	5	3	13.4	-15.7
13	5	2	23.0	21.4
12	5	2	12.8	12.3
9	5	2	31.3	32.1
8	5	2	37.2	40.2
7	5	2	14.3	-18.1
6	5	2	13.5	-11.0
5	5	2	15.9	15.9
4	5	2	16.9	16.2
3	5	2	25.3	26.9
2	5	2	6.0	-6.9
1	5	2	21.9	-25.0
0	5	2	27.0	-29.4
-1	5	2	16.4	-16.7
-2	5	2	6.0	-3.5
-3	5	2	35.6	-37.0
-4	5	2	31.2	-31.1
-5	5	2	21.7	-21.9
-7	5	2	[illegible]	9.7
-8	5	2	18.3	-19.1
-10	5	2	11.6	3.0
-11	5	2	25.6	23.0
-12	5	2	25.4	22.0
-14	5	2	15.2	6.6
-15	5	2	12.5	12.1
-16	5	2	19.0	17.6
-17	5	2	7.7	9.2
-18	5	2	5.0	-5.9
16	5	1	12.2	[illegible]
14	5	1	16.0	15.0
13	5	1	22.3	21.1
12	5	1	8.2	6.9
11	5	1	12.7	13.3
10	5	1	19.5	13.1
7	5	1	15.2	14.2
6	5	1	26.1	25.2
5	5	1	26.6	27.6
4	5	1	11.1	11.7
2	5	1	18.1	-21.9
-2	5	1	8.0	-8.2
-3	5	1	31.9	-30.6
-4	5	1	22.7	-24.7
-5	5	1	18.2	-18.1
-6	5	1	18.1	-16.3
-7	5	1	12.8	-11.5
-8	5	1	30.0	-31.2
-9	5	1	13.4	-13.0
-10	5	1	5.9	-4.0
-11	5	1	16.5	-13.4
-12	5	1	7.6	-7.9
-18	5	1	9.7	3.9
-19	5	1	5.7	3.7
19	5	0	9.9	11.2
18	5	0	13.7	12.8
17	5	0	5.8	9.1
14	5	0	19.7	19.0
13	5	0	20.3	13.2
11	5	0	19.1	-19.2
10	5	0	23.1	-22.5
7	5	0	35.0	-35.5
6	5	0	39.5	-43.7
5	5	0	11.9	-10.3

TABLE 4.3

FRACTIONAL COORDINATES AND E.S.D.S

ATOM	x/a	y/b	z/c
C(1)	0.34686 ± 38	0.01901 ± 136	0.42457 ± 62
C(2)	0.40271 ± 55	0.16295 ± 185	0.48581 ± 69
C(3)	0.43661 ± 64	0.30059 ± 220	0.40833 ± 86
C(4)	0.40069 ± 50	0.26699 ± 165	0.29445 ± 73
C(5)	0.31999 ± 57	0.30711 ± 174	0.29488 ± 86
C(6)	0.29003 ± 48	0.15142 ± 173	0.36762 ± 81
C(7)	0.38446 ± 52	-0.08863 ± 150	0.34049 ± 77
C(8)	0.41254 ± 54	0.05247 ± 205	0.26040 ± 86
C(9)	0.31642 ± 49	-0.11731 ± 171	0.50641 ± 72
C(10)	0.15671 ± 41	-0.13420 ± 133	0.56596 ± 59
C(11)	0.16380 ± 46	-0.07728 ± 166	0.67202 ± 67
C(12)	0.12695 ± 46	0.08489 ± 153	0.70746 ± 67
C(13)	0.08525 ± 45	0.19767 ± 165	0.63088 ± 71
C(14)	0.07881 ± 48	0.13798 ± 171	0.52190 ± 72
C(15)	0.11445 ± 50	-0.01650 ± 161	0.49046 ± 69
O(1)	0.26121 ± 31	-0.24504 ± 102	0.45149 ± 42
O(2)	0.24268 ± 37	-0.43691 ± 115	0.61347 ± 50
O(3)	0.16164 ± 40	-0.45874 ± 121	0.44905 ± 56
S	0.20533 ± 12	-0.34109 ± 36	0.52219 ± 16
Br	0.03622 ± 7	0.42479 ± 24	0.67814 ± 11

TABLE 4.4

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S (in $\AA^2$)

ATOM	U11	U22	U33	2U23	2U31	2U12
C(1)	0.0267	0.0327	0.0375	0.0041	-0.0008	-0.0074
	37	56	41	68	63	65
C(2)	0.0631	0.0732	0.0323	0.0049	-0.0216	-0.0405
	60	83	43	95	81	109
C(3)	0.0742	0.0996	0.0491	0.0310	-0.0603	-0.0905
	72	107	55	121	105	142
C(4)	0.0548	0.0499	0.0445	0.0225	-0.0065	-0.0168
	55	73	50	89	84	92
C(5)	0.0665	0.0410	0.0629	0.0010	-0.0186	0.0107
	65	73	60	99	98	101
C(6)	0.0411	0.0555	0.0622	0.0036	0.0074	0.0217
	48	76	58	101	85	88
C(7)	0.0565	0.0378	0.0527	0.0137	0.0329	0.0235
	54	65	52	88	86	90
C(8)	0.0487	0.0850	0.0597	0.0163	0.0342	0.0246
	55	99	63	116	96	108
C(9)	0.0471	0.0660	0.0406	0.0232	0.0051	-0.0256
	50	78	45	91	77	94
C(10)	0.0379	0.0308	0.0313	0.0039	0.0006	-0.0159
	41	57	37	68	62	69
C(11)	0.0405	0.0625	0.0341	0.0113	-0.0012	0.0019
	45	74	42	85	70	86
C(12)	0.0443	0.0473	0.0364	0.0076	0.0078	-0.0025
	47	67	42	78	71	84
C(13)	0.0364	0.0594	0.0456	0.0085	0.0265	-0.0083
	44	72	47	88	73	82
C(14)	0.0442	0.0636	0.0428	0.0169	-0.0020	0.0007
	50	78	47	92	78	90
C(15)	0.0523	0.0511	0.0359	0.0261	-0.0063	0.0047
	52	70	45	83	75	90

TABLE 4.4 (contd.)

ATOM	U11	U22	U33	2U23	2U31	2U12
O(1)	0.0478	0.0506	0.0298	0.0025	0.0113	-0.0279
	33	45	28	52	50	57
O(2)	0.0663	0.0636	0.0396	0.0423	0.0068	0.0339
	42	54	33	64	60	71
O(3)	0.0727	0.0594	0.0528	-0.0360	0.0102	-0.0535
	46	55	39	71	69	77
S	0.0480	0.0317	0.0354	0.0128	0.0110	-0.0077
	12	15	10	19	17	19
Br	0.0808	0.0860	0.0829	-0.0061	0.0328	0.0631
	8	11	9	14	13	14

ORTHOGONAL COORDINATES

The orthogonal axes X', Y and Z' are defined as follows:-

X' is parallel to a*

Z' is parallel to c

Y is normal to X' and Z' so as to
complete a right-handed set.

TABLE 4.5

ORTHOGONALISED COORDINATES AND E.S.D.S (in Å)

ATOM	X'	Y	Z'
C(1)	6.5508 ± 71	0.1264 ± 90	4.6441 ± 78
C(2)	7.6056 ±104	1.0836 ±123	5.3024 ± 88
C(3)	8.2458 ±121	1.9989 ±146	4.2620 ±112
C(4)	7.5674 ± 94	1.7755 ±110	2.9029 ± 92
C(5)	6.0433 ±108	2.0423 ±116	3.0685 ±109
C(6)	5.4775 ± 91	1.0069 ±115	4.0416 ±101
C(7)	7.2609 ± 98	-0.5894 ±100	3.5134 ± 95
C(8)	7.7912 ±102	0.3489 ±136	2.4517 ±106
C(9)	5.9759 ± 93	-0.7801 ±114	5.7324 ± 90
C(10)	2.9596 ± 77	-0.8924 ± 88	6.7974 ± 74
C(11)	3.0935 ± 87	-0.5139 ±110	8.1154 ± 84
C(12)	2.3976 ± 87	0.5645 ±102	8.6337 ± 84
C(13)	1.6100 ± 85	1.3145 ±110	7.7546 ± 88
C(14)	1.4884 ± 91	0.9176 ±114	6.3986 ± 90
C(15)	2.1615 ± 94	-0.1097 ±107	5.9330 ± 87
O(1)	4.9332 ± 59	-1.6295 ± 68	5.1522 ± 52
O(2)	4.5832 ± 70	-2.9055 ± 76	7.2235 ± 63
O(3)	3.0527 ± 76	-3.0506 ± 80	5.3192 ± 70
S	3.8779 ± 23	-2.2682 ± 24	6.1511 ± 20
Br	0.6840 ± 13	2.8249 ± 16	8.4455 ± 14

TABLE 4.6

CALCULATED HYDROGEN FRACTIONAL COORDINATES

ATOM	x/a	y/b	z/c
H(2)	0.44283	0.07256	0.52793
H(2')	0.37643	0.25092	0.54041
H(3)	0.49194	0.27308	0.41132
H(3')	0.43030	0.45552	0.43092
H(4)	0.42298	0.36194	0.23792
H(5)	0.31209	0.45411	0.32510
H(5')	0.29430	0.29892	0.21609
H(6)	0.26331	0.22549	0.42491
H(6')	0.25554	0.05434	0.31719
H(7)	0.34756	-0.18836	0.29806
H(7')	0.42847	-0.16824	0.38035
H(8)	0.38554	0.02709	0.18257
H(8')	0.46751	0.02715	0.25639
H(9)	0.35681	-0.20604	0.54661
H(9')	0.29369	-0.02588	0.56445
H(11)	0.19914	-0.15914	0.72799
H(12)	0.13024	0.12210	0.79060
H(14)	0.04474	0.22246	0.46522
H(15)	0.11173	-0.05398	0.40754

TABLE 4.7

INTRAMOLECULAR BONDED DISTANCES AND E.S.D.S (in Å)

ATOM A	ATOM B	A - B	ATOM A	ATOM B	A - B
C(1)	- C(2)	1.569 ± 14Å	C(10)	- C(11)	1.378 ± 11Å
C(1)	- C(6)	1.513 ± 13	C(10)	- C(15)	1.413 ± 13
C(1)	- C(7)	1.515 ± 13	C(11)	- C(12)	1.384 ± 14
C(1)	- C(9)	1.529 ± 13	C(12)	- C(13)	1.398 ± 13
C(2)	- C(3)	1.527 ± 16	C(13)	- C(14)	1.418 ± 13
C(3)	- C(4)	1.535 ± 15	C(14)	- C(15)	1.314 ± 15
C(4)	- C(5)	1.556 ± 14	S	- C(10)	1.776 ± 9
C(4)	- C(8)	1.513 ± 17	S	- O(1)	1.587 ± 6
C(5)	- C(6)	1.529 ± 16	S	- O(2)	1.433 ± 7
C(7)	- C(8)	1.513 ± 15	S	- O(3)	1.409 ± 8
C(9)	- O(1)	1.465 ± 12	Br	- C(13)	1.902 ± 10

TABLE 4.8

VALENCY ANGLES AND E.S.D.S (in degrees)

ATOM A	ATOM B	ATOM C	A-B-C	ATOM A	ATOM B	ATOM C	A-B-C
C(2)	-C(1)	-C(7)	106.6±7 °	C(11)	-C(10)-	S	120.7±7 °
C(2)	-C(1)	-C(6)	106.8±8	C(15)	-C(10)-	S	119.9±6
C(2)	-C(1)	-C(9)	108.4±7	C(10)	-C(11)	-C(12)	121.6±8
C(6)	-C(1)	-C(9)	111.2±7	C(11)	-C(12)	-C(13)	117.8±8
C(6)	-C(1)	-C(7)	108.1±7	C(12)	-C(13)	-C(14)	120.0±9
C(7)	-C(1)	-C(9)	115.3±8	C(12)	-C(13)-	Br	118.2±7
C(1)	-C(2)	-C(3)	111.2±8	C(14)	-C(13)-	Br	121.9±7
C(2)	-C(3)	-C(4)	109.3±9	C(13)	-C(14)	-C(15)	120.9±9
C(3)	-C(4)	-C(5)	108.3±8	C(10)	-C(15)	-C(14)	120.4±8
C(3)	-C(4)	-C(8)	109.6±9	C(9)	-O(1)	- S	117.2±5
C(5)	-C(4)	-C(8)	109.8±9	C(10)-	S	- O(1)	105.1±4
C(4)	-C(5)	-C(6)	108.3±9	C(10)-	S	- O(2)	109.1±4
C(1)	-C(6)	-C(5)	112.6±8	C(10)-	S	- O(3)	110.0±4
C(1)	-C(7)	-C(8)	113.3±9	O(1) -	S	- O(2)	108.8±4
C(4)	-C(8)	-C(7)	108.9±8	O(1) -	S	- O(3)	103.9±4
C(1)	-C(9)	-O(1)	109.2±7	O(2) -	S	- O(3)	118.9±5
C(11)	-C(10)	-C(15)	119.2±8				

TABLE 4.9

INTRAMOLECULAR NON-BONDED DISTANCES (in Å)

ATOM A	ATOM B	A-B	ATOM A	ATOM B	A-B
C(1)...	C(4)	2.605Å	C(6)...	O(1)	2.912Å
C(1)...	S	3.892	C(9)...	O(2)	2.945
C(2)...	C(5)	2.890	C(9)...	O(3)	3.725
C(2)...	C(8)	2.950	C(10)...	C(13)	2.757
C(2)...	O(1)	3.812	C(11)...	C(14)	2.752
C(3)...	C(6)	2.949	C(11)...	O(2)	2.956
C(3)...	C(7)	2.869	C(12)...	C(15)	2.793
C(5)...	C(7)	2.934	C(15)...	O(3)	3.134
C(6)...	C(8)	2.883			
C(7)...	O(1)	3.031			

TABLE 4.10

INTERMOLECULAR DISTANCES (in Å) < 4 Å

Transformations should be applied to the coordinates of the second atom.

ATOM A ATOM B	e.p.	DISTANCE Å
C(5)...O(1)	iii	3.801 A
C(5)...O(2)	i	3.565
C(5)...C(11)	ii	3.667
C(5)...C(12)	ii	3.784
C(6)...C(12)	ii	3.926
C(6)...O(2)	i	3.526
C(6)...O(3)	iii	3.737
C(7)...O(2)	i	3.715
C(8)...O(2)	i	3.627
C(11)...O(3)	iv	3.492
C(12)...O(3)	iv	3.151
C(13)...O(2)	iii	3.877
C(13)...O(3)	iii	3.638
C(14)...C(15)	v	3.745
C(14)...O(3)	iii	3.287

Equivalent positions are :-

i)	x	, -1/2 - y	, -1/2 + z
ii)	x	, 1/2 - y	, -1/2 + z
iii)	x	, 1 + y	, z
iv)	x	, -1/2 - y	, 1/2 + z
v)	-x	, -y	, 1 - z

TABLE 4.11

Best-planes calculated through various atoms of the molecule and dihedral angles between the bonds of the bicyclic system.

(Schomaker et al., 1959)

Atoms Defining the Planes

PLANE 1	C(10), C(11), C(12), C(13), C(14), C(15), Br, S
PLANE 2	C(1), C(2), C(3), C(4)
PLANE 3	C(1), C(4), C(5), C(6)
PLANE 4	C(1), C(4), C(7), C(8)

Plane Equations

PLANE 1 $0.7778X' + 0.5874Y - 0.2235Z' = 0.2848$

PLANE 2 $0.7060X' - 0.6762Y - 0.2106Z' = 3.5457$

PLANE 3 $-0.1663X' - 0.6554Y - 0.7367Z' = -4.5768$

PLANE 4 $-0.8675X' - 0.0106Y - 0.4973Z' = -8.0107$

Distances of Atoms (in Å) from the Planes

PLANE 1	C(10)	-0.0162	C(13)	0.0067
	C(11)	0.0058	C(14)	-0.0181
	C(12)	-0.0178	C(15)	0.0060
	S	0.0142	Br	0.0093

TABLE 4.11 (contd.)

PLANE 2	C(1)	0.0152	C(3)	0.0262
	C(2)	-0.0260	C(4)	-0.0156
PLANE 3	C(1)	-0.0168	C(5)	-0.0275
	C(4)	0.0159	C(6)	0.0284
PLANE 4	C(1)	0.0170	C(7)	-0.0292
	C(4)	-0.0166	C(8)	0.0287

Dihedral Angles Between Planes

PLANE 2 - PLANE 3	61.25°
PLANE 2 - PLANE 4	59.96°
PLANE 3 - PLANE 4	58.83°

Dihedral Angles Between Bonds About the C(1),C(4) Axis

[C(1)-C(2)] - [C(3)-C(4)]	2.76°
[C(1)-C(6)] - [C(4)-C(5)]	3.00°
[C(1)-C(7)] - [C(4)-C(8)]	3.14°

TABLE 4.11 (contd.)

Torsional Angles About the Bridge Bonds

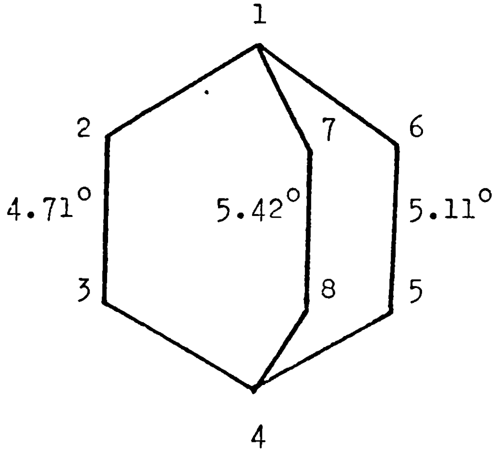


FIGURE 4.1

The Harker section at $v = 1/2$ of the Patterson function $P(uvw)$. The bromine vector is marked with an asterisk and the sulphur vector is marked with a cross.

Contours are at arbitrary levels.

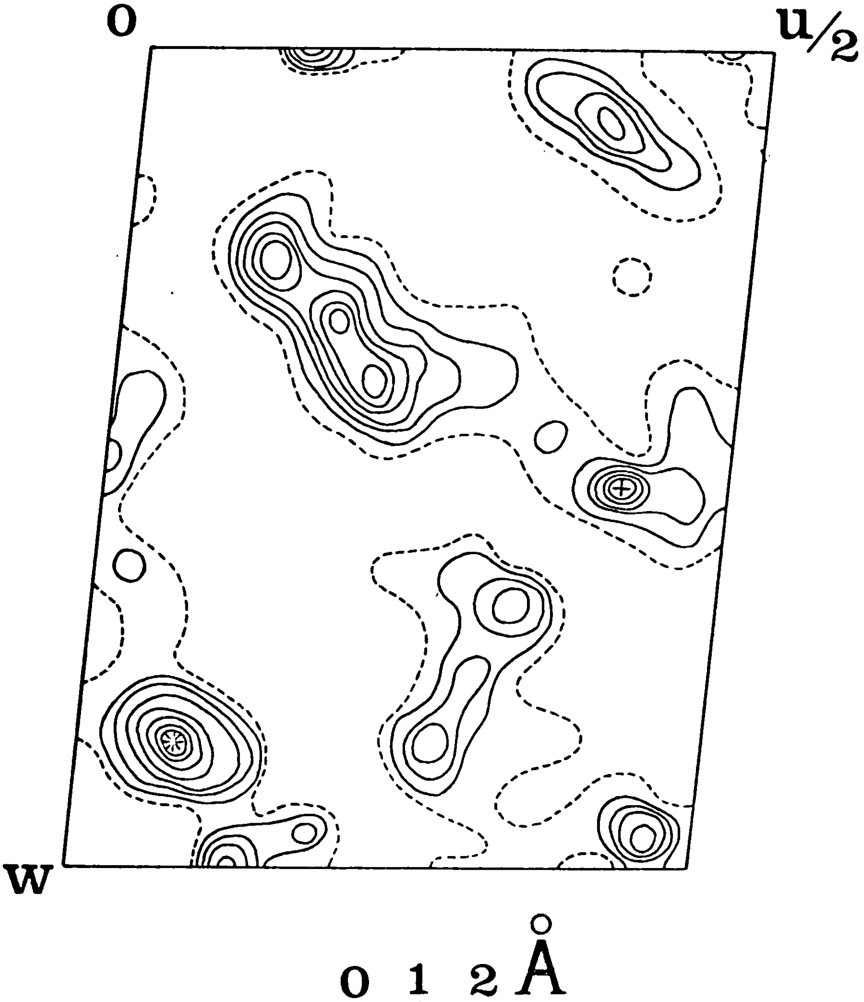

0
u/2
w
0 1 2 Å

FIGURE 4.2

Superimposed sections of the final electron-density distribution viewed down the b-axis. Contour-levels are at intervals of 1e/Å^3 except around the bromine and sulphur atoms where they are at intervals of 5e/Å^3.

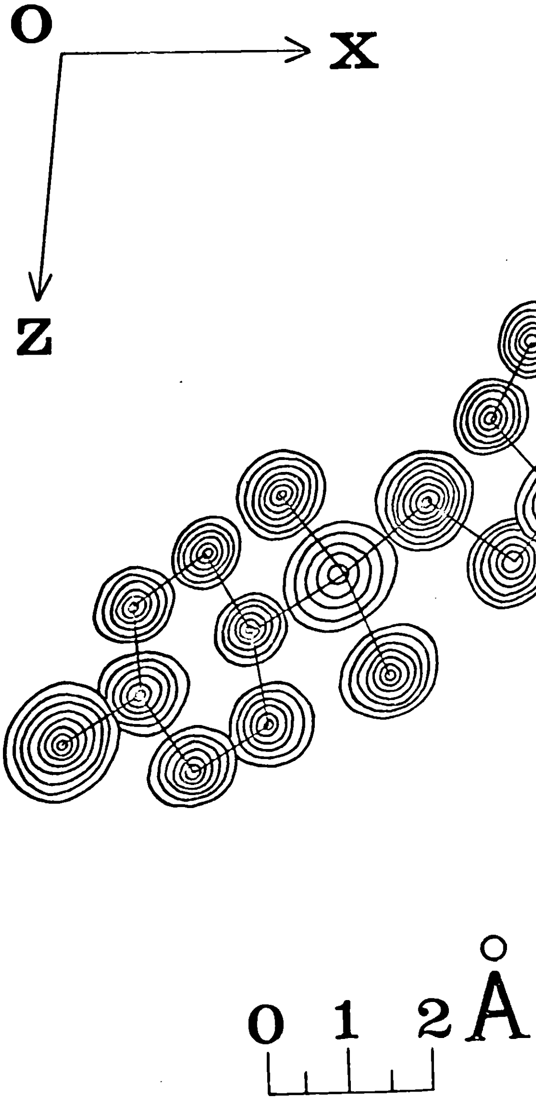

O
X
Z
0 1 2 Å

FIGURE 4.3

Atomic numbering scheme. Hydrogen atoms are numbered as the carbon atoms to which they are bonded.

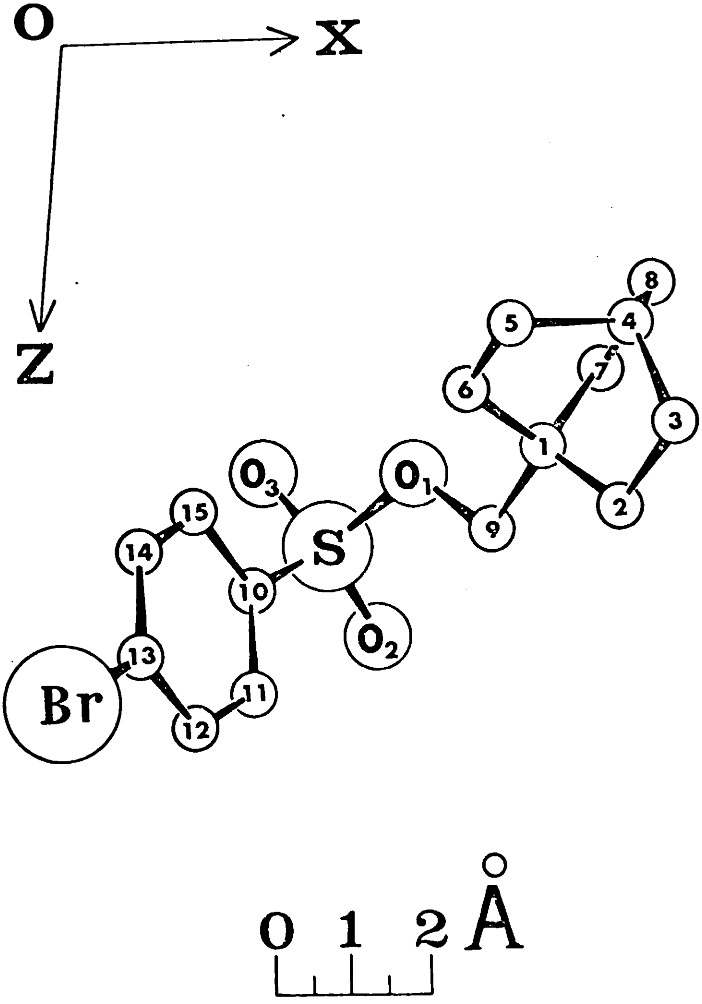

O
X
Z
Br
13
14
15
12
11
10
S
O3
O2
O1
9
1
2
3
4
5
6
7
8
0 1 2 Å

FIGURE 4.4

Molecular packing viewed down the b-axis.

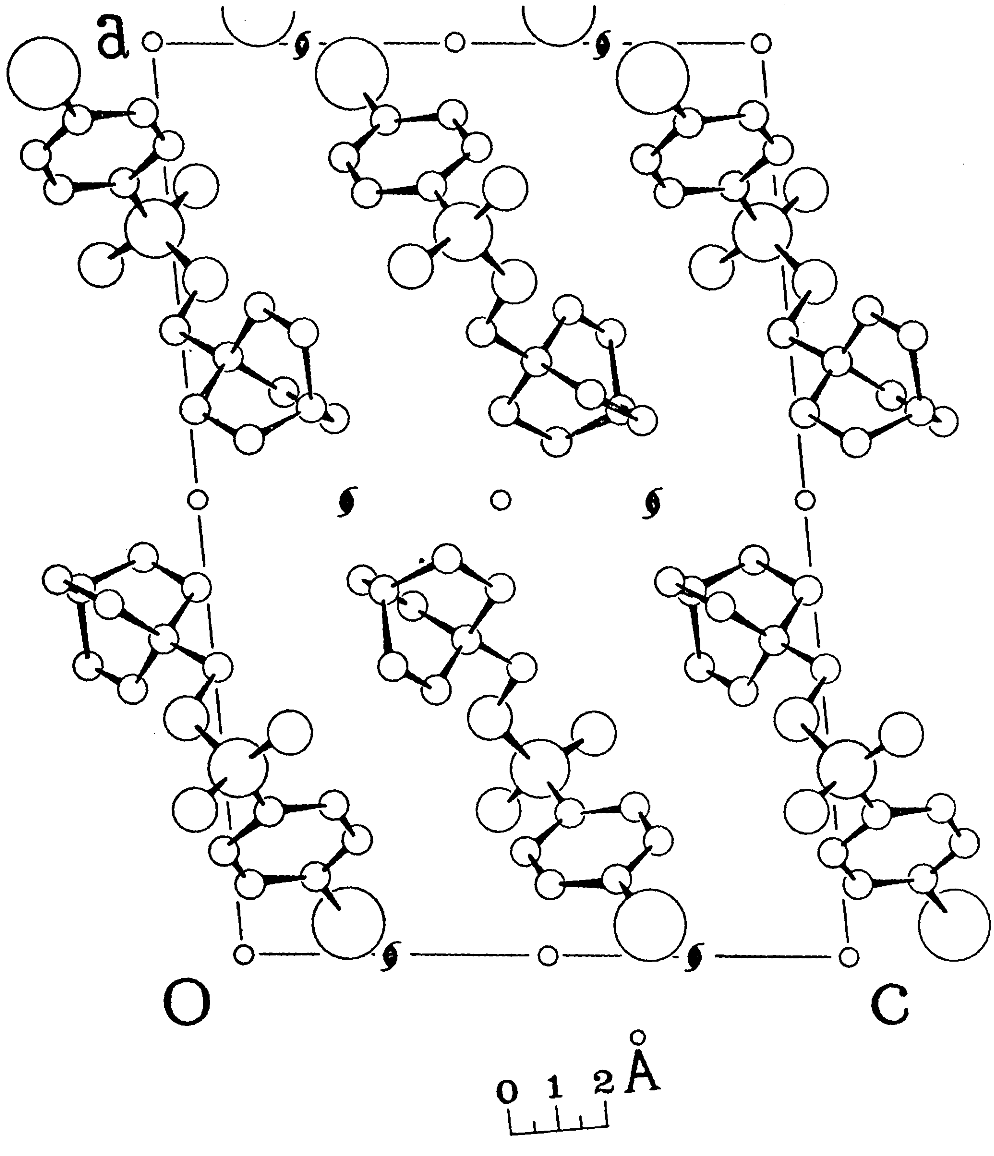
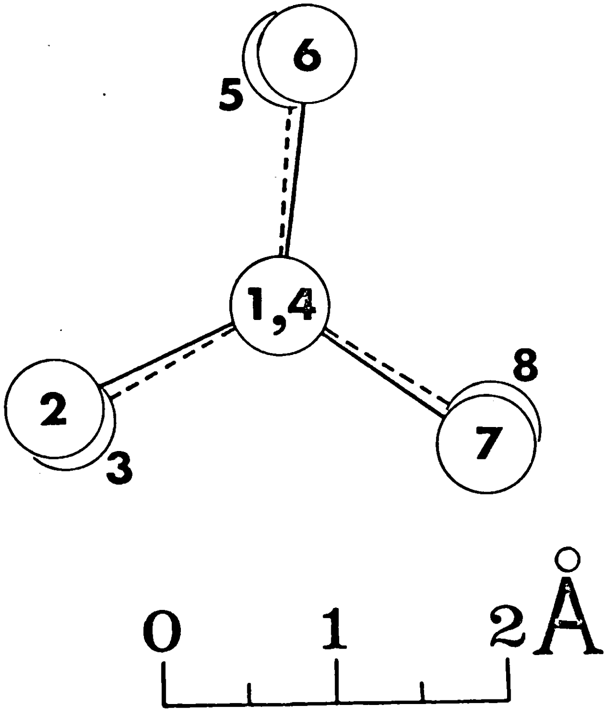

a
O
c
0 1 2 Å

FIGURE 4.5

View of the bicyclic ring system along the axis through atoms C(1) and C(4).


6
5
1,4
8
2
3
7
0
1
2
Å

4.3 DISCUSSION

The structure analysis of 1-brosyloxymethylbicyclo[2,2,2]-octane has proved unambiguously that in this instance the preferred conformation of the bicyclo[2,2,2]octane moiety corresponds closely to the staggered D_3 conformation. Calculation of the best-planes (Table 4.11) through the atoms of each bridge shows that all three bridges are significantly non-planar and that the distortions from planarity are within experimental error the same for each bridge. The symmetry of the results adds significance to the overall observation of staggering. It is found (Table 4.11) that the group of atoms C(2), C(6), C(7) is rotated 3° about the C(1),C(4) axis relative to the group of atoms C(3), C(5), C(8) (see Figure 4.3 for numbering). The 3° twist represents a staggering of 5° for substituents on the bridges. The probable error for these angles is 0.5°. Figure 4.5 shows the bicyclic part of the molecule viewed along the C(1),C(4) axis and demonstrates the staggering clearly. The distortion of the bicyclic system is also apparent in the intramolecular non-bonded distances (Table 4.9). For example, the mean value of the C(2)...C(5), C(6)...C(8) and C(3)...C(7) distances is 2.88 Å, whereas the mean value of the C(3)...C(6), C(5)...C(7) and C(2)...C(8) distances is 2.94 Å.

There are no unusual carbon-carbon bond distances in the bicyclo[2,2,2]octane part of this molecule, and the mean value of

1.530 Å compares well with the value of 1.533 Å suggested by Hendrickson (1961) and the value of 1.545 Å obtained by Nethercot and Javan (1953) . It may be concluded therefore that the molecule is free from bond strain. The mean values of 112.4° for the valency angle C(1) - C(2) - C(3) and its counterparts on the other two bridges, and 108.8° for the angle C(2) - C(3) - C(4) and its counterparts, indicate that there is very little angle-strain present in the molecule. These relative values of 112.4° and 108.8° are consistent with the presence of the methyl substituent on C(1) as opposed to the hydrogen sited on C(4) . Apart from the slight influence on valency angles, the assumption that the 1-brosyloxymethyl group would not grossly bias the conformation appears to have been fully justified, since there are no close intramolecular contacts (Table 4.9) involving this group and the bicyclic part of the molecule.

It has also been assumed that the conformation is a property of the molecule and not of the solid state. That there are no close intermolecular contacts (Table 4.10) involving atoms of the bicyclic system would appear to vindicate this assumption. However, the dangers of extrapolating from solution to solid-state chemistry must be borne in mind when considering this analysis. The conformation of this bicyclo[2,2,2]octane system is further discussed in Chapter 5 in relation to the steric effects operative in the molecule.

The bond distances and valency angles of the 1-brosyloxymethyl group do not vary significantly from values obtained for this grouping in previous analyses of similar molecules (Brown, Martin and Sim, 1965) . Within experimental error the benzene ring and the bromine and sulphur substituents may be considered to be planar (Table 4.11) .

CHAPTER 5 MOLECULAR STRAIN AND CONFORMATIONS IN BICYCLIC SYSTEMS

The classical treatment for the quantitative determination of steric effects in molecules was developed by Westheimer (1956). Steric effects are considered to be the sum of various independent strain-producing mechanisms, expressed in energy terms by the equation

$$E_{\text{total strain}} = E_{\text{bond length strain}} + E_{\text{bond angle strain}} + E_{\text{torsional strain}} + E_{\text{non-bonded interactions}}$$

.

Application of equations such as this in conformational analyses has been made possible by iterative processes of minimising the total strain energy with respect to the atomic parameters. Hendrickson (1961), Wiberg (1965), and more recently Gleicher and Schleyer (1967) are among those who have computerised the techniques of minimisation to calculate optimum geometries in terms of total strain energies for various alicyclic compounds, and have compared their results with those geometries inferred from other experimental sources. For example, strain effects have been correlated with both equilibria and rates of reactions for series of compounds (Gleicher and Schleyer, 1967).

Considering each of the terms on the right-hand side of the above equation, it might be expected that minimisation of strain energy via bond deformation should be relatively unimportant because of the large amounts of energy involved in distorting a bond. Rough calculations show, for example, that it requires about 70 times more energy to remove the unfavourable hydrogen-hydrogen interaction in phenanthrene via bond deformation than via angle deformation (Gleicher and Schleyer, 1967) . Molecules should therefore prefer to distort angles rather than bonds.

The exact nature of torsional strain in molecules is not understood although several hypotheses have been suggested (Gleicher and Schleyer, 1967 and references therein). Despite this, a simple relationship exists which allows for calculation of this quantity :-

$$E_{\substack{\text{torsional}\\\text{strain}}} = (V_o/2)(1 + \cos 3\theta)$$

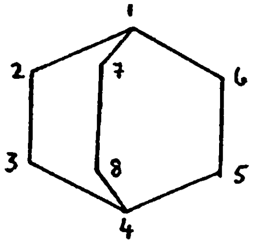
where V_o is the height of the barrier to rotation and θ is the dihedral angle. For any substituted ethane V_o will have a value of about 3 k.cals/mole. Wiberg (1965) has pointed out the importance of avoiding a zero dihedral angle and has emphasised the energy-lowering effect of even a small increase in angle.

The non-bonded interaction term will be composed of both a repulsive and an attractive component. The attractive component arising from London dispersion forces, is usually taken as a function of the inverse sixth power of the internuclear separation, the values determined by Pitzer and Catalano generally being used.

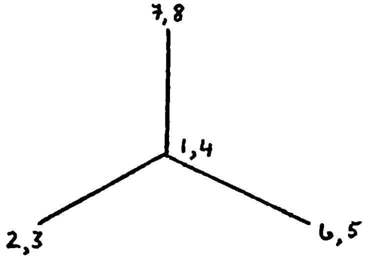
More controversial are the functions to be used for the repulsive potential. These are functions of either the inverse twelfth power of the internuclear distance, or of an exponential function, different workers using and modifying different functions.

In the particular case of bicyclo[2,2,2]octane (I) , for which the two conformational possibilities are the eclipsed D_{3h} conformation (II) or the staggered D_3 conformation (III), there are four types of non-bonded hydrogen interactions. Firstly there are the 1:4 interactions involving, for example, hydrogens on C(2) and C(8); secondly there are the 1:3 interactions involving hydrogens on C(2) and C(6); thirdly there are the 1:2 interactions between hydrogens on C(1) and C(2) and lastly there are those 1:2 interactions involving hydrogens on C(2) and C(3) . The torsional interactions degenerate into those interactions about the C(1) - C(2) type bonds and those interactions about the C(2) - C(3) type bonds. The effects of the two conformational possibilities on these different interactions are summarised in Table 5.1 . Without a prior and detailed knowledge of the relative magnitudes of the strain-producing interactions, choice of preferred conformation is difficult. However, Gleicher and Schleyer (1967) predict, on the basis of energy-minimising calculations, that the eclipsed D_{3h} conformation should be energetically more favourable than the staggered D_3 conformation.

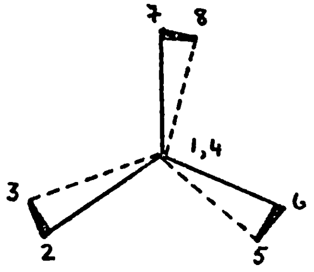
The structure analysis of 1-brosyloxymethylbicyclo[2,2,2]-octane has proved that in this case the preferred conformation of



I



II



III

TABLE 5.1

An analysis of the effects of the staggered D_3 and eclipsed D_{3h} conformations of bicyclo(2,2,2)octane on the strain effects present in the molecule.

MOLECULAR STRAIN	D_3 CONFORMATION	D_{3h} CONFORMATION
1:3 non-bonded hydrogen interactions	relieved	maximum
1:2 non-bonded hydrogen interactions C(1)-C(2) type	slightly increased	minimum
1:2 non-bonded hydrogen interactions C(2)-C(3) type	relieved	maximum
C(1)-C(2) type torsional interactions	slightly increased	minimum
C(2)-C(3) type torsional interactions	relieved	maximum

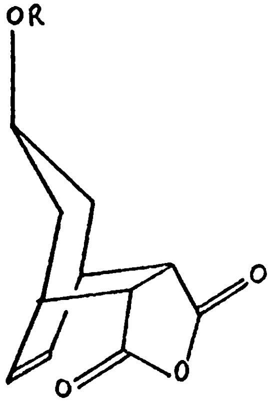
the bicyclo[2,2,2]octane moiety corresponds closely to the staggered D_3 conformation. The group of atoms C(2), C(6), C(7) is rotated 3° about the C(1),C(4) axis relative to the group of atoms C(3), C(5), C(8) (see Figure 4.3 for atomic numbering) . This twisting, which is shown in Figure 4.5, corresponds to 5° staggering of substituents on the bridges. In addition, there was no evidence of bond-length strain, and little or no evidence of valency-angle strain. The presence of a substituent at C(1) has had a slight effect on valency angles in the bicyclic skeleton, but does not appear to have had any gross effect on the overall conformation.

In view of the effects of the staggered D_3 conformation on the strain-producing interactions (Table 5.1) , that the bicyclic skeleton of 1-brosyloxymethylbicyco[2,2,2]octane is found to adopt this conformation would suggest that the 1:3 (C(2),C(6) type) and the 1:2 (C(2),C(3) type) non-bonded hydrogen interactions, and the C(2) - C(3) type torsional interactions have been the dominant conformation-determining factors. Also, the theoretical effect of the staggered conformation is to worsen the non-bonded and torsional interactions of substituents on C(1) . Therefore, to have found the staggered conformation in the presence of the substituent at C(1) adds further weight to the conclusion that in this instance the staggered D_3 conformation is the more stable of the two conformational possibilities. It must again be stressed, however, that although the absence of close intermolecular contacts would suggest that the conformation is a property of the molecule and not of the solid state, the dangers of extrapolating from solid-state to solution chemistry must be borne in mind when considering the results. Also, it should be stressed that these results are valid for this particular molecule and that different conformations may be found in other cases, since Dunitz (1968, personal communication) has examined a bicyclo[2,2,2]octane system where there is little or no evidence of twisting.

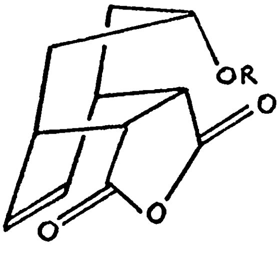
Further strain-energy calculations on our part based on the staggered D_3 conformation would at best be speculative in view of the lack of knowledge of hydrogen positions and the empirical nature of such calculations. It is also known that the bicyclo-[2,2,2]octane skeleton can exist in a non-eclipsed conformation, for example in twistane (Whitlock, 1962) , although it is anticipated that in such cases some angle strain is present.

Comparison of the bicyclo[2,2,2]octane skeletons of 1-brosyloxymethylbicyclo[2,2,2]octane (Chapter 4) and of 1,5,5-trimethyl-2(3'-p-bromophenyl-3'-oxopropyl)-bicyclo[2,2,2]-octan-6,8-dione (Chapter 3) is limited both by the large number of substituents and sp^2 hybridised centres on the latter molecule and the evident inaccuracies in its structure analysis. However, within these limitations it may be said that the bicyclo[2,2,2]-octane skeleton described in Chapter 3 reflects the conformational trends found in the relatively unsubstituted bicyclic skeleton described in Chapter 4 . Only one bridge, that formed by atoms C(1), C(2), C(3), C(4) (see Figure 3.3 for numbering) is directly comparable with the three unsubstituted bridges of 1-brosyloxymethylbicyclo[2,2,2]octane, and this bridge exhibits approximately 3° twisting with 5° dihedral angles between substituents on the bridge. It was also found for the molecule described in Chapter 3 that one of the bridges containing an sp^2 hybridised centre was considerably more distorted than any of the unsubstituted sp^3 bridges on both molecules, and that considerable steric relief resulted from this particular distortion. It may be concluded, therefore, that the presence of one sp^2 hybridised centre on a bridge does not inhibit twisting of that bridge where considerable steric relief is obtained as a result of the twisting.

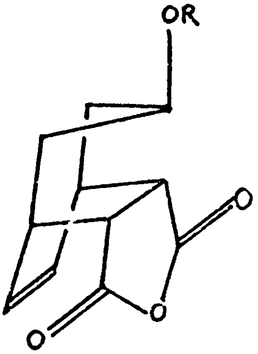
The conformation of the bicyclo[3,2,2]non-6-ene system of anti-3-exo-p-bromobenzoyloxybicyclo[3,2,2]non-6-ene-8,9-endo-dicarboxylic acid anhydride (IV) which is described in Chapter 2, provides an interesting contrast to the conformations of the bicyclo(2,2,2)octane skeletons described in Chapters 3 and 4. In the first place with the bicyclo[3,2,2]non-6-ene system there is the possibility of "flipping" of the three-carbon bridge to produce the syn-3-endo conformer (V). The analysis described in Chapter 2 has proved that the anti-3-exo epimer (IV) is more stable than the syn-3-exo epimer (VI), and it follows that the anti-3-exo conformation (IV) must be more stable than the syn-3-endo conformation (V) because of the highly unfavourable environment of the p-bromobenzoyloxy substituent in the latter conformation. Bridge "flipping" is therefore highly unlikely in the molecule IV.



IV (anti-3-exo)



V (syn-3-endo)



VI (syn-3-exo)

It was also noted (Chapter 2) that the bicyclo[3,2,2]non-6-ene system relieved the steric strain of non-bonded hydrogen and torsional interactions by valency-angle increases accompanied by flattening of the three-carbon bridge. Ring-flattening and valency-angle increases are well documented methods of relieving steric strain. Flattening of three-carbon bridges has been reported in 1-p-bromobenzene-sulphonyloxy-methyl-5-methylbicyclo-[3,3,1]nonan-9-ol (Brown, Martin and Sim, 1965), and in a tricyclo[5,3,1,$1^{2,6}$]dodecane derivative (Macrossan and Ferguson, 1968). General ring-flattening has been reported in certain steroids (Pucket, Sim, Cross and Siddall, 1967),(Tamura and Sim, 1968), and in cyclooctane derivatives (Dobler,Dunitz and Mugnoli, 1966; Ferguson, MacNicol, Oberhänsli, Raphael and Zabkiewicz, 1968) . Complete lack of twisting in the bicyclo[3,2,2]non-6-ene system is evidenced by the molecular geometry calculations described in Chapter 2, and sufficient relief from steric strain appears to be derived from the valency-angle increases.

In conclusion, there has been evidence of molecular strain in the three bicyclic systems described in Chapters 2, 3 and 4, bicyclo[2,2,2]octane skeletons apparently being capable of relieving the molecular strain by adopting staggered or twisted conformations although a slight effect on valency angles was noted. On the other hand, the bicyclo[3,2,2]non-6-ene system is not twisted and sufficient relief from steric strain is obtained by valency-angle increases with accompanying ring-flattening. It must be noted, however, that the bicyclo[2,2,2]octane skeleton does not have the same facility for relieving steric strain purely by valency-angle increases as exists in the bicyclo[3,2,2]non-6-ene system. No evidence of bond-length strain was found in any of the bicyclic systems studied.

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