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UNIVERSITY OF ALBERTA

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# CRYSTAL STRUCTURES OF SOME ALICYCLIC COMPOUNDS AND AN IRON COMPLEX

by

ⓒ JAMES THOMAS PURDHAM

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
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## ABSTRACT

A brief summary of the crystallographic method is given, with the emphasis upon the methods used for phase determination.

The crystal structure of bis-nitrosyl - tris-1,2-diphenyl dithiolene diiron was determined. An unusual asymmetric bridging mode of the dithiolene ligand, was found to be responsible for the observation of two iron sites in the Mössbauer spectrum of the compound. There was no evidence of coordination with solvent, as had been suggested by one author. It is suggested that this type of bridging may be present in several other transition metal dithiolene complexes.

The conformation of cyclohexa-1,4-diene has been a controversial topic. The crystal structure of 1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene was determined to provide additional evidence concerning the planarity of the ring system. This molecule was found to be almost planar, but with significant deviations from planarity leading to a slight chair conformation. It appears that repulsive interaction between the bulky substituents is responsible for this chair conformation.

The crystal structure of 1,2,4,5-tetraphenyl-3,6-dicarbomethoxytricyclo[3.1.0.0$^{2,4}$]hexane was carried out to determine the exact stereochemistry of the molecule and to obtain precise structural information on the cyclopropane and cyclobutane rings in highly strained fused systems. The molecule was found to be the *anti* configuration with the carbomethoxy groups in the *exo* position. The molecule exhibits an unusual feature in that all the bond lengths within the tricyclic framework are equal. The bond lengths in the cyclopropane rings are longer than in cyclopropane itself and those in the cyclobutane ring are shorter than in cyclobutane. A discussion of the geometry of cyclopropane and cyclobutane rings in fused systems is given.

In the preparation of exo-tricyclo[3.1.1.$0^{2,4}$]hept-6-yl-acetate by addition of carbene to exo-bicyclo[2.1.1]-hex-2-ene-5-yl acetate only one isomer is formed. The X-ray crystal structure of the p-bromobenzoate derivative revealed that this is the isomer in which the cyclopropane ring is *anti* with respect to the bridgehead carbon bearing the p-bromobenzoate group. Structural evidence is provided to support the view that the hydrogen on C5 of the bicyclohexene derivative sterically interferes with the formation of the syn isomer.

An appendix gives a critisism of the structure determination of $WOF_4$ and describes an attempt to refine it in terms of a disordered model.

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# CRYSTALLOGRAPHIC INTRODUCTION

## Crystal Lattice

A crystal may be regarded as a body consisting of a regular repetition in space of identical units. The repetition is along three axes x, y, z, which can be arbitrary, but for convenience are chosen to coincide with symmetry elements within the crystal. The repeat distances, a along x, b along y, and c along z, and the angles between the axes, $\alpha$ between y and z, $\beta$ between x and z, and $\gamma$ between x and y, define a parallelopiped which is the repeating unit in space and is termed the unit cell. Each unit cell contains the same number of molecules arranged in the same way.

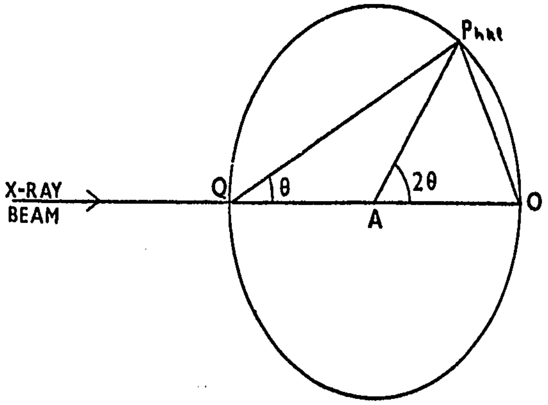
The dimensions of the unit cells of most crystals are of the same order of magnitude as the wavelength of X-rays and therefore crystals can act as three dimensional diffraction gratings for X-rays.

## The Reciprocal Lattice

Interaction of X-rays with crystals is accounted for by Bragg's Law, $n\lambda = 2d \sin \theta$, in which sets of parallel planes in the crystal, separated by a distance d, reflect X-rays of wavelength $\lambda$ when their angle to the beam satisfies the expression. Therefore the specification and identification of the planes is important in interpreting the X-ray diffraction process.

The planes are usually described by the indices hkℓ which are the reciprocals of the intercepts of the planes on the unit cell axes. Indexing of the diffraction pattern in terms of these indices is readily done when the planes are considered in terms of a reciprocal space lattice.

The reciprocal lattice may be constructed from the direct lattice by taking a lattice point as origin and constructing normals to all possible direct lattice planes. These normals are terminated a distance $1/d_{hk\ell} = d^*_{hk\ell}$ from the origin, where $d_{hk\ell}$ is the spacing between the sets of planes (hkℓ). In this way a set of points, each labelled according to the (hkℓ) family of planes it represents, are produced, and these constitute the reciprocal lattice. An important property of the reciprocal lattice is that if a sphere is constructed of radius $1/\lambda$, with the reciprocal lattice origin O on its circumference, then every time a reciprocal lattice point hkℓ coincides with the sphere, then the real set of planes, parallel to PQ, are in the correct orientation to satisfy the condition for Bragg reflection.



## Scattering of X-rays by Matter

An electron located in the path of an X-ray beam will be forced into oscillation by the electromagnetic field of the X-ray impinging upon it and so becomes a source of radiation itself. In this way the electron is said to scatter the X-rays.

The scattering from an atom then will be directly related to the number of electrons it possesses. The efficiency of scattering in a particular direction is known as its atomic scattering factor, fo, and is expressed by the ratio $fo = A_A/A_e$, where $A_A$ is the amplitude of the wave from the whole atom and $A_e$ the amplitude from a free electron, scattering under the same conditions. Some of the factors which affect fo will be discussed later.

The amplitude of a wave in a given direction, scattered by N atoms, is the sum of the scattering power of each of the atoms for that particular diffraction angle. If the phase of the jth atom with respect to the origin is $\delta_j$ then the amplitude can be written as $F_\Theta = \sum_{j=1}^{N} f_j e^{i\delta_j}$, where $f_j$ is the scattering factor of the jth atom. The phase $\delta$ can be obtained from the positions of the atoms in the unit cell. If the coordinates of the jth atom are $x_j$, $y_j$, $z_j$, then $\delta_j$ will be given by:

$$\delta_j = 2\pi(hx_j + ky_j + \ell z_j). \qquad (1)$$

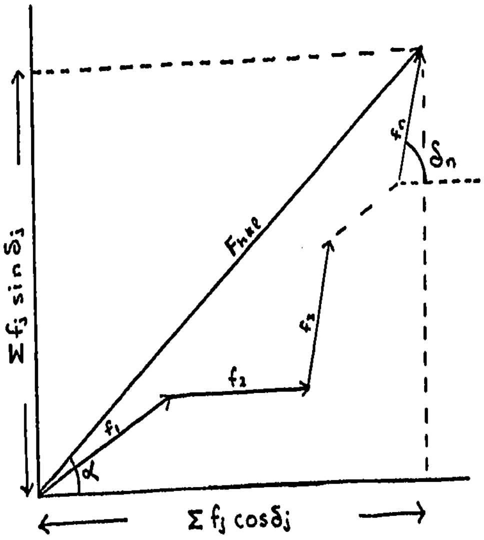
so that the structure factor for a wave diffracted from the set of planes (hkℓ) is

$$F_{hk\ell} = \sum_{j=1}^{N} f_j \exp\,[2\pi i(hx_j + ky_j + \ell z_j)] \qquad (2)$$

This can be rewritten as:

$$F_{hk\ell} = \sum_{j=1}^{N} f_j \cos 2\pi(hx_j + ky_j + \ell z_j) + \sum_{j=1}^{N} f_j i \sin 2\pi(hx_j + ky_j + \ell z_j) \qquad (3)$$

which can be represented in diagramatic form on the Argand diagram.



From this we see that:

$$|F_{hk\ell}| = \sqrt{(\Sigma_j f_j \cos\delta_j)^2 + (\Sigma_j f_j \sin\delta_j)^2} \qquad (4)$$

and $$\alpha = \tan^{-1}\left(\frac{\Sigma_j f_j \cos \delta_j}{\Sigma_j f_j \sin \delta_j}\right) \qquad (5)$$

or $$|F_{hk\ell}| = \sqrt{A^2_{hk\ell} + B^2_{hk\ell}} \text{ and } \alpha = \tan^{-1}\left(\frac{B_{hk\ell}}{A_{hk\ell}}\right)$$

With the above formulas structure factor amplitudes and phases can be calculated once the positions of the atoms are known. The expression for the structure factor is a general expression which is modified by the presence of symmetry elements. For example the presence of a centre of symmetry reduces it to

$$F_{hk\ell} = 2 \sum_{j=1}^{N/2} f_j \cos 2\pi(hx_j + ky_j + \ell z_j) \qquad (6)$$

## The Scattering Factor

The scattering factor used in the above calculations has been defined as the scattering power of the atom relative to the scattering power of one electron. The maximum value it can attain then, is Z, the atomic number of the atom and this occurs in the direction of the incident beam, i.e. at $\theta = 0$, since in this direction all the electrons will be scattering in phase. However because of the finite size of the atom, as $\sin\theta/\lambda$ increases, the scattering factor decreases, since the X-rays scattered from an electron in one part of the atom will be, to an increasing extent, out of phase with those in other parts of the atom, the resulting interference reducing the scattering efficiency.

The scattering power is also subject to thermal effects, since, in general, the higher the temperature, the greater the vibration of the atom. The effect of the vibration or thermal motion is to cause the electrons to sweep out a larger volume than they would occupy if the atom were at rest, thus causing the scattering power to fall off even more rapidly with increasing sin $\theta/\lambda$. These effects are illustrated in fig. 1.

It has been shown that the required correction to the scattering factor for isotropic vibration is given by:

$$f = fo \exp \left(-B \sin^2\theta/\lambda^2\right) \qquad (7)$$

where B, known as the isotropic temperature factor, is related to the mean square amplitude of vibration.

When anisotropic vibration is being considered, the exponential term in (7) takes the form $\exp-(h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})$, which describes the magnitude and orientation of a vibrational ellipsoid with respect to the crystallographic axes.

The scattering factor has also to be corrected for the effect of anomalous dispersion, which arises when the wavelength of the incident beam lies near an absorption edge of any of the atomic species present in the crystal. Under

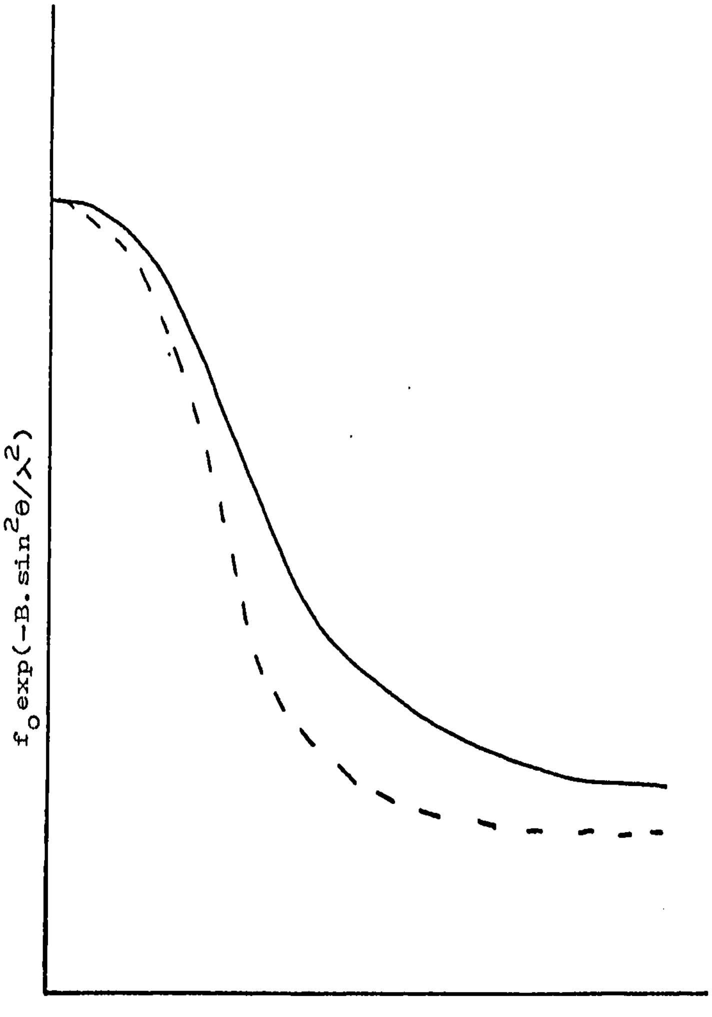


Fig. 1. The variation of fo with sin θ/λ — no temperature correction ---- B = 4.0 applied.

these circumstances, the wave scattered by an atom undergoes an anomalous phase shift. The resultant scattering factor can be expressed by addition of two correction terms, one real and one imaginary, to the normal scattering factor.

$$f = fo + \Delta f' + i\Delta f''$$

$$= f' + i\Delta f'' \qquad (8)$$

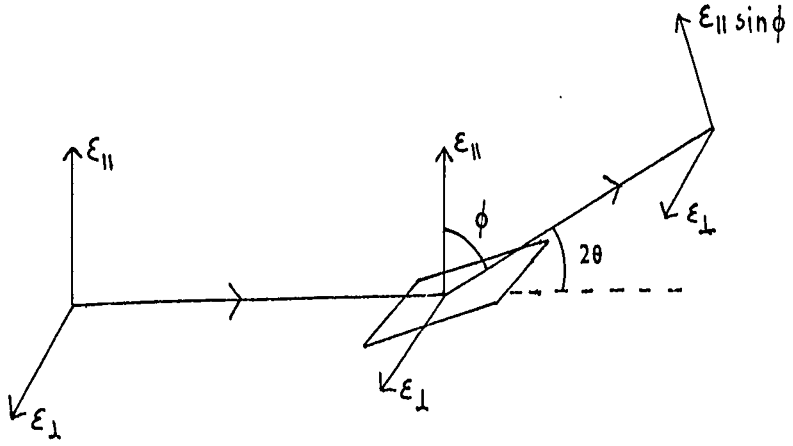
## Data Reduction

Structure factor amplitudes may be obtained from the experimentally observed intensities after correction has been made for several geometric and physical factors which affect these intensities. The relationship is expressed by the equation:

$$F_{hk\ell} = \sqrt{\frac{K\ I_{hk\ell}}{Lp}} \qquad (9)$$

where K is a constant, L is the Lorentz factor and p the polarisation factor. $I_{hk\ell}$ is the measured intensity.

The polarisation factor arises because the incident beam is unpolarised whereas the reflected beam is partially polarised, which has the effect of decreasing the intensity. The electric vectors in the unpolarised beam may all be considered in terms of their components in two directions, perpendicular and parallel to the plane of the incident and reflected beam. ($\varepsilon_{\perp}$ and $\varepsilon_{||}$). Since the electric vectors in the unpolarised beam are randomly oriented, these two components will occur with equal frequency and the intensities associated with each are therefore equal. ie. $I_{\perp} = I_{||} = 1/2\ I_{incident}$



Since the intensity is proportional to the square of the electronic vector, after reflection, $I_{\perp}' = k\varepsilon^2_{\perp} = I_{\perp}$

and $I'_{||} = k\varepsilon^2_{||} \sin^2\phi = I_{||} \sin^2\phi$

$$= I_{||} \cos^2 2\Theta$$

$$\therefore I_{reflected} = I_{\perp} + I_{||} \cos^2 2\Theta$$

$$= 1/2\ I_{incident} + 1/2\ I_{incident} \cos^2 2\Theta$$

$$= pI_{incident}$$

where $p = 1/2 + 1/2 \cos^2 2\Theta$ (10)

The Lorenz factor L arises because the time required for a reciprocal lattice point to pass through the sphere of reflection varies with the direction in which it approaches the sphere. The correction term has been shown to be

$$L = \frac{\sin \Theta}{\sin 2\Theta \sqrt{\sin^2\Theta - \sin^2\mu}} \qquad (11)$$

for equi-inclination geometry, in which $\mu$ is the equi-inclination angle. This however reduces to

$$I = \frac{1}{\sin 2\Theta} \qquad (12)$$

for diffractometer data collected by the $2\Theta$ scan method.

The term K is a scale factor for putting the $|F|$'s on an absolute scale. Usually scaling is done at a later stage of the analysis.

Other physical effects upon the intensity are primary extinction, secondary extinction and absorption. Primary extinction is an interference process, caused by multiple reflection at a set of planes, which reduces the intensity of the beam as it passes through the crystal. This problem is not important, except in crystals which contain little or no mosaic character where the effect is to make I

$\propto F_{hk\ell}$ rather than $F^2_{hk\ell}$.

Secondary extinction is a more serious problem, which arises when an appreciable amount of the incident radiation is reflected at a given instant by the first planes it encounters, so that deeper planes receive less incident intensity and therefore reflect with reduced power. This effect can be corrected for by a method proposed by Zachariesen which is described later in the thesis.

The effect of absorption is to attenuate the X-ray beam as it passes through the crystal. The effect can be corrected for if the precise geometry of the crystal is known, since then, the exact path length can be determined for a beam reflecting from each infinitesimal portion of the crystal. Integration over the entire volume of the crystal gives the correction factor[1]

$$A = \int \frac{1}{V} \exp\left[-\mu(\ell_1 + \ell_2)\right] dV \qquad (13)$$

where V is the volume of the crystal, $\mu$ is the linear absorption coefficient and $\ell_1$ and $\ell_2$ are the path lengths along the direction of the primary and diffracted beam directions.

When the intensities have been corrected for these effects, structure amplitudes may be determined. The object of the crystal structure analysis then becomes one of finding the structural model which gives the closest agreement between the observed and calculated structure amplitudes.

## The Phase Problem

Since a crystal is periodic, its electron density distribution can be represented by a Fourier series

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_\ell F_{hk\ell} \exp\,[-2\pi i(hx + ky + \ell z)] \tag{14}$$

or

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_\ell |F_{hk\ell}| \exp[-2\pi i(hx + ky + \ell z - \alpha_{hk\ell})] \tag{15}$$

V is the volume of the unit cell, $|F_{hk\ell}|$ is the structure factor amplitude and $2\pi\alpha_{hk\ell}$ is its phase. From the measured intensity data, the structure factor amplitudes can be obtained, but the phases cannot. The solution of the crystal structure then, reduces essentially to determining the phases of the structure amplitudes, since when these are known, the electron density within the unit cell can be determined from (15).

The problem of determining the phases is simplified to some extent, in that it is not necessary to arrive at a solution for all the reflections at the outset of the analysis, but only for a large enough number of the stronger intensities to provide an approximation to the structure, which can then be used for calculating the phases of the remaining reflections.

Several methods have been used to obtain a solution to the phase problem. The two that were used in this thesis will now be described.

## The Patterson Method

The electron density in a unit cell may be represented by equation (14). The relationship between that and the function

$$P_{(u,v,w)} = \frac{1}{V^2} \sum_h \sum_k \sum_\ell |F_{hk\ell}|^2 \exp[-2\pi i(hu + kv + \ell w)] \tag{16}$$

was demonstrated by A.L. Patterson[2,3]. If $\rho(x,y,z)$ has peaks corresponding to atomic locations in the unit cell, then, $P_{(u,v,w)}$ will have peaks corresponding to the ends of vectors between all pairs of atoms in $\rho(x,y,z)$, radiating from the origin.

This is most easily seen for the one dimensional case. Consider the electron density at the points $x$ and $x + u$ along a line of period $a$,

$$\rho(x) = \frac{1}{a} \sum_h F_h \exp(-2\pi ihx)$$

$$\rho(x + u) = \frac{1}{a} \sum_h F_h \exp[-2\pi ih(x + u)]$$

The product of these is:

$$\rho(x)\rho(x + u) = \left(\frac{1}{a} \sum_h F_h \exp(-2\pi ihx)\right)\left(\frac{1}{a} \sum_h F_h \exp[-2\pi ih(x + u)]\right)$$

This is the product of the electron densities at a chosen separation u for a location x which may take all values from 0 to 1. If we work in absolute coordinates, then this is a separation U (= ua) for a location X (= xa) which may vary from 0 to a. The average value of this product when we allow X to assume all values within the period is given by the integral

$$A(U) = \frac{1}{a}\int_{0}^{a} \rho(X)\rho(X + U)\ dX$$

$$= \frac{1}{a}\int_{0}^{a} \left(\frac{1}{a}\sum_{h} F_h \exp(-2\pi ihX/a)\right)\left(\frac{1}{a}\sum_{h} F_h \exp[-2\pi ih(X + U)/a]\right) dX$$

$$= \frac{1}{a}\sum_{h}\sum_{h}\int_{0}^{a} \left(\frac{1}{a} F_h \exp(-2\pi ihX/a)\right)\left(\frac{1}{a} F_h \exp[-2\pi ih(X + U)/a]\right) dX$$

This is the sum of integrals of terms which are products of $F_h$ with $F_h$, the value of h in the two F's being, in general, different, and for clarity can be written as m and q. Using this notation and taking terms which do not involve X outside the integral, the equation can be rewritten as

$$A(U) = \frac{1}{a} \sum_{m} \sum_{q} \frac{1}{a^2} F_m F_q \exp(-2\pi iqU/a)$$

$$\int_0^a \exp(-2\pi imX/q) \exp(-2\pi iqX/a) dX$$

$$= \frac{1}{a} \sum_{m} \sum_{q} \frac{1}{a^2} F_m F_q \exp(-2\pi iqU/a)$$

$$\int_0^a \exp[-2\pi i(m + q)X/a] \, dX$$

This integral vanishes for all values of m and q except when q = -m in which case it simply reduces to:

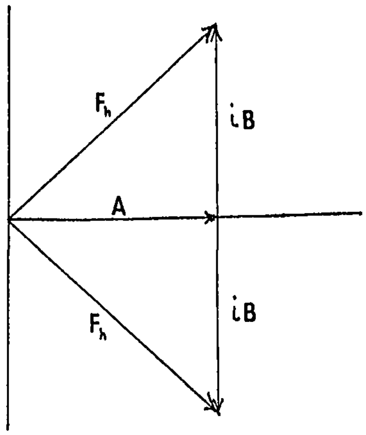
$$A(U) = \frac{1}{a} \sum_{m} \sum_{-m} \frac{1}{a^2} F_m F_{-m} \exp(-2\pi imU/a) \int_0^a e^0 \, dX$$

$$= \frac{1}{a} \sum_{m} \sum_{-m} \frac{1}{a} F_m F_{-m} \exp(-2\pi imU/a)$$

The double summation depends only on m and so can be written as a single summation

$$A(U) = \frac{1}{a^2} \sum_{h} F_h F_{-h} \exp(-2\pi ihU/a)$$

According to Friedel's Law $F_h$ and $F_{-h}$ have identical magnitudes but opposite phases.



$$F_hF_{-h} = (A + iB)(A - iB) = A^2 + B^2$$

$$= |F_h|^2$$

Substituting this in the equation, we obtain,

$$A(U) = \frac{1}{a^2} \sum_h |F_h|^2 \exp(-2\pi ihU/a) \qquad (17)$$

The function will have large values if somewhere in the period a, there are large values of electron density separated by the selected distance u.

Extending this to three dimensions, a peak at (u, v, w) in the Patterson function is related to the peaks of the ath and bth atoms in the electron density function by $u = x_a - x_b$, $v = y_a - y_b$, $z = z_a - z_b$. If there are n atoms in $\rho(x,y,z)$ then there will be $n^2$ peaks in the Patterson function, n of which occur at the origin.

When n is small, it is often possible to deduce the correct atomic arrangement from the distribution of peaks in P(u,v,w), especially if the structure or some part of it is known in advance in broad detail. However as the complexity of the molecule increases so does that of its vector pattern. This together with the increased possibility of overlapping peaks can make the interpretation of a Patterson map a difficult task.

To make the identification of single atom-single atom interactions easier, the so called Harker sections may be used. Harker showed that certain sections or lines of the Patterson contained vectors related only by certain of the space group elements[4]. For example if the space group contains a two-fold axis, coincident with the b axis, then if there is an atom at (x,y,z) there will be a crystallographically equivalent atom at $(\bar{x}, y, \bar{z})$. The vector between these atoms has the components (2x, 0, 2z) and consequently there will be a maximum in P(u,v,w) at the point (2x, 0, 2z). There will be such a maximum in the plane y = 0 for each different kind of atom in the crystal, and the x and z coordinates for all the atoms in the crystal can consequently be found by evaluating P(u,v,w) for y = 0 only. Harker summarized the forms of P(u,v,w) best suited to the various symmetry elements in the manner shown in Table 1.

The problem is further simplified if the molecule

## TABLE 1

Forms of P(x,y,z) best suited to the determination of atomic coordinates in crystals having various symmetry elements.

| Symmetry Element | Form of P(x,y,z) |
|---|---|
| (a) Axes parallel to b axis | |
| (i) $2, 4, 4_2, \bar{4}, 6, 6_2, 3, \bar{3}, 6_3$ | P(x,0,z) |
| (ii) $2_1, 4_1, 4_3, 6_1, 6_5$ | P(x,1/2,z) |
| (iii) $3_1, 6_2, 6_4$ | P(x,1/3,z) |
| (b) Planes perpendicular to b-axis | |
| (i) reflection plane m | P(0,y,0) |
| (ii) glide plane, glide = 1/2 a | P(1/2,y,0) |
| (iii) glide plane, glide = 1/2 c | P(0,y,1/2) |
| (iv) glide plane, glide = 1/2 (a + c) | P(1/2,y,1/2) |
| (v) glide plane, glide = 1/4 (a + c) | P(1/4,y,1/4) |

contains at least one atom which is substantially heavier than the others. The height of a Patterson peak is directly proportional to the products of the atomic numbers of the atoms between which a vector occurs. Therefore vectors between heavy atoms stand out strongly against the background of heavy-light and light-light atom vectors, and the coordinates of the heavy atoms can therefore be found very often without too much difficulty. The significance of this is that the X-ray scattering will be largely dominated by the heavy atoms and so the approximation may be made that the phases of the structure amplitudes are those which would be required for the heavy atoms alone. The coordinates of the heavy atoms may be used to calculate structure factors and phases and the calculated phases are then combined with the observed structure amplitudes in a Fourier synthesis, which should give an approximation to the electron density distribution in the cell. From this the positions of the lighter atoms may be obtained which can be added to the structure factor and phase calculations and the process repeated until all atom positions are known.

## Direct Methods of Phase Determination

In discussing direct methods of phase determination, various forms of the structure factor other than $F_{hk\ell}$ will be used and are best defined at the outset. The unitary structure factor $U_{hk\ell}$ is given by

$$U_{hk\ell} = \frac{F_{hk\ell}}{\sum_{j=1}^{N} f_j} \qquad (18)$$

where N is the number of atoms in the unit cell. This is a factor with the same phase as $F_{hk\ell}$, but whose values range from -1 to +1. As N increases, the average value of $|U|$ decreases, and since the inequality and probability relationships to be discussed later require large $|U|$'s, their use is somewhat limited.

A much more useful term is the normalised structure factor $E_{hk\ell}$ given by:

$$E^2_{hk\ell} = \frac{U^2_{hk\ell}}{\bar{U}^2} \qquad (19)$$

or

$$E^2_{hk\ell} = \frac{|F_{hk\ell}|^2}{\varepsilon \sum_{j=1}^{N} f_j^2} \qquad (20)$$

where ε is an integer which corrects for space group extinctions. The advantage of using $E_{hk\ell}$'s is that the average value of $E^2_{hk\ell}$ is always 1 and is therefore independent of the complexity of the structure.

The origin of direct methods can probably be traced back to the work of Harker and Kasper on inequality relationships[5]. By application of the classical Schwarz and Cauchy inequalities to the structure factor expressions, they were able to derive the seemingly trivial result:

$$|F_{hk\ell}|^2 \leqslant F_{000}{}^2 \quad \text{or} \quad |U_{hk\ell}|^2 \leqslant 1$$

However on addition of the requirement of centrosymmetry, decidedly non-trivial results were obtained , e.g.

$$U^2_{hk\ell} \leqslant 1/2(1 + U_{2h,2k,2\ell})$$

which, if both U's are large, would require that $U_{2h,2k,2\ell}$ be positive for the inequality to hold. Other inequality relationships can be derived for this symmetry element and for the addition of other symmetry requirements.

Sayre used the self convolution theorem to arrive at an equation interrelating structure factors for crystals containing equal resolved atoms[6]. The self convolution theorem states that if a function is represented as a Fourier series, then the coefficients of the Fourier series of the squared function may be found from:

$$F^{sq}_{(hk\ell)} = \frac{1}{V} \sum_p \sum_q \sum_r F_{(pqr)} F_{(h-p,k-q,\ell-r)} \quad \text{for all } hk\ell.$$

The $F_{hk\ell}$ and the $F^{sq}_{hk\ell}$ are related to each other by a simple scaling term and so the equation can be rewritten as:

$$F_{hk\ell} = \frac{\theta_{hk\ell}}{V} \sum_{p} \sum_{q} \sum_{r} F_{pqr} F_{(h-p)(k-q)(\ell-r)} \qquad (19)$$

Thus an array of phases can only be correct if it causes this relationship to be satisfied. Although this relationship is valid whether or not the crystal possesses a centre of symmetry, Sayre only used it for the centrosymmetric case. It would appear from the equation that in order to determine the sign of $F_{hk\ell}$ it would be necessary to know the magnitude and phases of all others. However, Sayre pointed out that in the centrosymmetric case, if $F_{hk\ell}$ is large, the series must tend strongly in one direction (+ or -). The products which contribute most to this direction in the summation will be those between large $|F|$ and so for the case of large reflections, we have

$$S(F_{hk\ell}) \sim \left(S \sum_{p_r} \sum_{q_r} \sum_{r_r} F_{h-p,k-q,1-r} F_{pqr}\right) \qquad (20)$$

where S is 'the sign of', and ~ means probably equal to, and the suffix r means that the summation is carried out only for large $|F|$.

This work paralleled the work of Karle and Hauptmann, who using the criterion that the electron density distribution had to be a non-negative function, derived a complete set of inequalities, which are valid for all space groups and embraced the Harker-Kasper inequalities[7]. The inequalities could be written as a series of relationships which increased in complexity. The first three were:

$$F_{000} \geqslant 0 \tag{21}$$

$$|F_{hk\ell}| \leqslant F_{000} \tag{22}$$

$$\left| F_{(h_1+h_2,k_1+k_2,\ell_1+\ell_2)} - \frac{F_{h_1k_1\ell_1} \cdot F_{h_2k_2\ell_2}}{F_{000}} \right|$$

$$\leqslant \frac{\begin{vmatrix} F_{000} & F_{\bar{h}_1\bar{k}_1\bar{\ell}_1} \\ F_{h_1k_1\ell_1} & F_{000} \end{vmatrix}^{1/2} \begin{vmatrix} F_{000} & F_{\bar{h}_2\bar{k}_2\bar{\ell}_2} \\ F_{h_2k_2\ell_2} & F_{000} \end{vmatrix}^{1/2}}{F_{000}} \tag{23}$$

It is this third inequality which parallels the Sayre relationship. If we let $h = h_1 + h_2, k_1 + k_2, \ell_1 + \ell_2$ and $k = h_2, k_2, \ell_2$, then (23) can be rewritten.

$$F_h - \frac{F_{h-k}F_k}{F_{000}} \leqslant \frac{\begin{vmatrix} F_{000} & F^*_{h-k} \\ F_{h-k} & F_{000} \end{vmatrix}^{1/2} \begin{vmatrix} F_{000} & F^*_k \\ F_k & F_{000} \end{vmatrix}^{1/2}}{F_{000}}$$

$$\leqslant r \tag{24}$$

The larger the values of $|F_{h-k}|$ and $|F_k|$ the smaller will be r and the closer will be $F_h$ to $F_{h-k}F_k/F_{ooo}$. Since k can be varied arbitrarily there will be many such relationships and it would be expected that $F_h$ would be proportional to the average $F_{h-k}.F_k/F_{ooo}$, involving the larger $|F|$s, as k is varied. i.e.

$$F_h \propto \langle F_k.F_{h-k} \rangle_k \tag{25}$$

which gives the same result as the Sayre relationship for centrosymmetric crystals if large structure factor magnitudes are involved.

Since $F_h = |F_h| \exp(i\phi_h)$ then

$\phi_h \simeq \langle \phi_k + \phi_{h-k} \rangle_k$ follows from this.

The Sayre relationship (20) can be expressed in terms of normalised structure factors, when it becomes the $\Sigma_2$ relationship of Hauptmann and Karle[8].

$$S(E_h) \sim S(\Sigma_k E_k E_{h-k}) \tag{26}$$

This relationship is a probability relationship. The probability that the sign of $E_h$ be positive was given by Woolfson[9] and Woolfson and Cochran[10], which when expressed in terms of normalised structure factors is,

$$P_{+(h)} = \frac{1}{2} + \frac{1}{2} \tanh\left\{\frac{\sigma_3}{\sigma_2^{3/2}} |E_h| \sum_k E_k E_{h-k}\right\} \qquad (27)$$

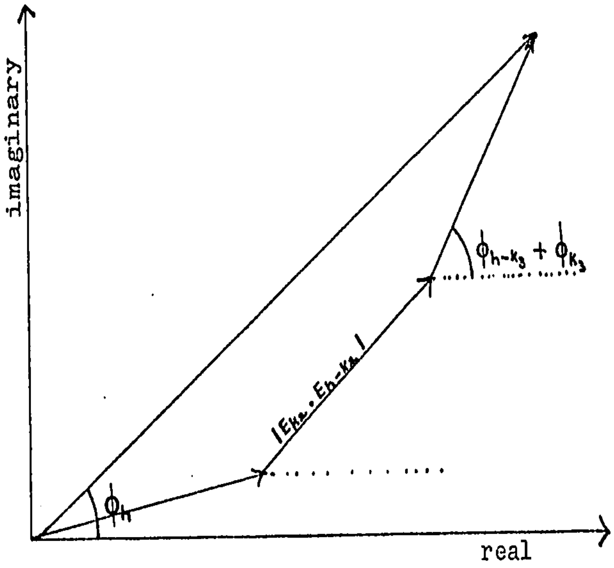
where $\sigma_3 = \sum_i^N n_i^3$ , $\sigma_2 = \sum_i^N n_i^2$ and

$$n_i = \frac{f_i}{\sum_{j=1}^{N} fj} .$$

The $\Sigma_2$ relationship can be used in conjunction with this probability formula to give a set of phases, for centrosymmetric space groups, which have a high probability of being correct.

For non centrosymmetric cases, the sum of the angles formula $\phi_h \simeq < \phi_{h-k} + \phi_k >_k$ may be used but it presents difficulties when the phase indications are very different.

It has been found better, to regard each phase indication as a vector of length $|E_{h-k}.E_k|$ and direction $(\phi_{h-k} + \phi_k)$ and to add them vectorially.



From this we obtain

$$\tan \phi_h = \frac{\Sigma_k |E_k E_{h-k}| \sin(\phi_k + \phi_{h-k})}{\Sigma_k |E_k E_{h-k}| \cos(\phi_k + \phi_{h-k})} \qquad (28)$$

which is the tangent formula of Karle and Hauptmann[11].

The $\Sigma_2$ relationship for centrosymmetric crystals and the sum of the angles and tangent formulas for non-centrosymmetric crystals all need a basic set of phases in order to use them for obtaining additional phases. The Karles have generalised the procedure for obtaining the basic set and extending them in both the centrosymmetric and non-centrosymmetric cases, using what they have termed 'the symbolic addition procedure'[12].

The basic set used is composed of those phases necessary to fix the origin and some additional phases denoted by symbols corresponding to the large $|E|$.

Three or less phases, depending on the space group, may be assigned arbitrarily, subject to certain restrictions, to specify the origin[8]. Consider the space group $P\bar{1}$. Here there are eight possible centres which could be used as the origin of the cell. Changing the origin affects the phases of many of the structure factors. For a structure of N atoms with coordinates $x_j$, $y_j$, $z_j$, etc., with respect to the origin (0,0,0) the structure factor expression is

$$F_{hk\ell}\,(0,0,0) = \sum_{j=1}^{N} f_j \cos 2\pi(hx_j + ky_j + \ell z_j)$$

Changing the origin to the point (1/2, 0,0) say, the equation becomes

$$F_{hk\ell}(1/2,0,0) = \sum_{j=1}^{N} f_j \cos 2\pi\,(h(x_j + 1/2) + ky_j + \ell z_j)$$

$$= (-1)^h F_{hk\ell}(0,0,0)$$

which is + $F_{hk\ell}$ (0,0,0) for h even (e) or $-F_{hk\ell}$ for h odd (o). By considering the other alternative origins in the same way, it is found that the structure factors may be divided into eight groups that behave differently, according to the parities of h,k and $\ell$. This is summarized in Table 2, for the eight possible origins.

Reflections for which h, k and $\ell$ are all even (eee) are unaffected by the origin shifts. These are known as structure invariants. They are determined solely by the structure and are independent of the origin choice, and therefore can not be given values at will. All other classes are positive for four origins and negative for the other four. One member from one of these sets may be assigned a phase arbitrarily since this merely corresponds to selecting one origin set (+ or -) from the two possibilities, reducing the possible number of origins to four. The phases of all the reflections of this class are now fixed and no further choices

## TABLE 2

Variation of Structure Factor Sign with Origin and Parity of the Reflection

| | Origin | eee | eeo | eoe | eoo | oee | oeo | ooe | ooo |
|---|---|---|---|---|---|---|---|---|---|
| 1. | 0,0,0 | + | + | + | + | + | + | + | + |
| 2. | 0,0,1/2 | + | - | + | - | + | - | + | - |
| 3. | 0,1/2,0 | + | + | - | - | + | + | - | - |
| 4. | 0,1/2,1/2 | + | - | - | + | + | - | - | + |
| 5. | 1/2,0,0 | + | + | + | + | - | - | - | - |
| 6. | 1/2,0,1/2 | + | - | + | - | - | + | - | + |
| 7. | 1/2,1/2,0 | + | + | - | - | - | - | + | + |
| 8. | 1/2,1/2,1/2 | + | - | - | + | - | + | + | - |

can be made from this set. All the remaining classes however (except eee) are positive for two of these origins and negative for the other two. Thus a reflection from one of these classes can be assigned a phase, which reduces the choice of origin to two possibilities. A third reflection can now be chosen from another class and assigned a phase and this will assign the origin uniquely. However there are restrictions on this choice, in that it must be linearly independent of the other two, i.e. the parity sum of the three classes must not equal eee. For example, if a reflection from the parity group (eeo) had been assigned a phase of +, inspection of Table 2 shows that the origin choices has been restricted to origins 1,3,5 and 7. Now assigning a phase of + to a reflection from the parity group (eoe), further restricts the origin choice to 1 or 5. Now the assignment of a third phase is restricted to a reflection from one of the parity groups oee, oeo, ooe or ooo, since if eoo is taken the parity sum of eeo + eoe + eoo = eee, which is not allowed.

The above applies to all primitive space groups for the classes triclinic through orthorhombic. Addition of centreing merely places a restriction on the origin, e.g. in the space group $C_{2/c}$ there are only four possible origin centres. Therefore only two reflections need be assigned phases to fix the origin, but these must be chosen from a class for which $\ell$ is odd.

For the non-centrosymmetric case a further phase must be assigned to fix the enantiomorph[13]. This is assigned to an invariant and it must not be 0 or $\pi$.

Along with the origin-defining phases, other reflections with large $|E|$ are given symbols as phases. These are used in the $\Sigma_2$ or tangent formula to produce a set of phases in terms of these symbols. Usually relationships between the symbols appear during the process, so that at the end of the phase determining procedure you may be left with only a few symbolic signs unknown. In any case relatively few E maps (Fourier maps in which the $E_{hk\ell}$ are the coefficients) need be produced, from which if the phasing has been successful a chemically reasonable structure or part of a structure can be found.

If only part of the structure is found it can be used to produce a Fourier from which the positions of other atoms may be found, as described at the end of the section dealing with the Patterson method. Another powerful tool in the location of missing atoms in the model is the difference fourier. This is a Fourier in which $\Delta F$'s ($= |F_o| - |F_c|$) are used as coefficients. Obviously this will be sensitive to errors in the model and so, if the model is incomplete, peaks will appear in positions where there are missing atoms.

## Least Squares Refinement

The positions of the atoms in the unit cell obtained by the above methods give a rather crude model. In order to determine the accurate structure it is necessary to refine the atom parameters. A powerful method for doing this involves the principle of least squares. The principle of least squares says that, for a linear function with n variables $(x_1, x_2 \ldots . x_n)$, whose value is determined by these variables and a set of independent parameters $p_1 \ldots . p_n$, such that:

$$f = p_1 x_1 + p_2 x_2 + \ldots . + p_n x_n, \tag{29}$$

then, if the value of the function is measured at m different points, the best values for the parameters $p_1 \ldots . p_n$ are those which minimise the sums of the squares of the properly weighted differences between the observed and calculated values of the function for all m points. Thus the quantity to be minimised is given by:

$$D = \sum_{r=1}^{m} W_r \, (f_{o_r} - f_{c_r})^2 \tag{30}$$

In order for this function to be a minimum, the derivative of the right hand side must be zero. That is,

$$\sum_{r=1}^{m} W_r \, (f_{o_r} - f_{c_r}) \frac{\partial f_{c_r}}{\partial p_j} = 0 \quad (j = 1,2, \ldots . n) \tag{31}$$

Substituting for $f_{c_r}$ and $\partial f_{c_r} / \partial p_j$, we obtain n equations known as the normal equations.

$$\sum_{r=1}^{m} W_r(f_{o_r} - x_{r_1}p_1 - x_{r_2}p_2 - \dots - x_{r_n}p_n)x_{r_1} = 0$$

$$\sum_{r=1}^{m} W_r(f_{o_r} - x_{r_1}p_1 - x_{r_2}p_2 - \dots - x_{r_n}p_n)x_{r_2} = 0$$

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

$$\sum_{r=1}^{m} W_r(f_{o_r} - x_{r_1}p_1 - x_{r_2}p_2 - \dots - x_{r_n}p_n)x_{r_n} = 0$$

which on rearranging gives,

$$\sum_{r=1}^{m} W_r x_{r_1}^{2} p_1 + \sum_{r=1}^{m} W_r x_{r_1} x_{r_2} p_2 + \dots + \sum_{r=1}^{m} W_r x_{r_1} x_{r_n} p_n = \sum_{r=1}^{m} W_r f_{o_r} x_{r_1}$$

$$\sum_{r=1}^{m} W_r x_{r_2} x_{r_1} p_1 + \sum_{r=1}^{m} W_r x_{r_2}^{2} p_2 + \dots + \sum_{r=1}^{m} W_r x_{r_2} x_{r_n} p_n = \sum_{r=1}^{m} W_r f_{o_r} x_{r_2}$$

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

$$\sum_{r=1}^{m} W_r x_{r_n} x_{r_1} p_1 + \sum_{r=1}^{m} W_r x_{r_n} x_{r_2} p_2 + \dots + \sum_{r=1}^{m} W_r x_{r_n}^{2} p_n = \sum_{r=1}^{m} W_r f_{o_r} x_{r_n}$$

from which the best values of the p's may be obtained.

If the function is nonlinear, then it can be approximated as a Taylor series

$$f(p_1p_2\ldots p_n) = f(a_1a_2\ldots a_n) + \frac{\partial f(a_1a_2\ldots a_n)}{\partial p_1}(p_1-a_1) + \ldots \frac{\partial f(a_1a_2\ldots a_n)}{\partial p_2}(p_n-a_n) \qquad (32)$$

in which the $a_1 \ldots a_n$ are approximations of the $p_1 \ldots p_n$. If $(p_1 - a_1)$ to $(p_n - a_n)$ are given the symbols $\Delta p_1 \ldots \Delta p_n$, then if the $a_j$ are a good approximation, the $a'_j$ given by

$$a'_j = a_j + \Delta p_j$$

will be a closer approximation to $p_j$. The process is iterative and eventually converges at the best values for the various p's.

In a crystallographic least squares refinement, the function being minimised is

$$D = \sum_{hk\ell} W_{hk\ell} (|Fo| - |kF_c|)^2 \qquad (33)$$

The weighting function $W_{hk\ell}$ can be obtained from the standard deviation of the $|Fo|$ since,

$$W_{hk\ell} = \frac{1}{\sigma^2_{hk\ell}} \quad \text{and} \quad \sigma_{hk\ell} = \frac{k}{\sqrt{Lp}} \cdot \frac{\sqrt{\sigma}}{2|Fo|}$$

$\sigma$ is defined on page 42

The scale factor is applied to Fc since if it is applied to Fo the least squares process minimises D by reducing |kFo| and |Fc| to zero. This it does by reducing k to zero to remove |kFo| and by increasing the thermal parameters to reduce |Fc|.

Taking the derivative of the right hand side of (33) and setting it to zero we obtain

$$\sum_{hk\ell} W_{hk\ell} \left(|Fo| - |kFc|\right) \frac{\partial|kFc|}{\partial p_j} = 0 \quad j = 1,2,\ldots n \tag{34}$$

Substituting for kFc and $\partial kFc/\partial p_j$ with Fc in the form of a Taylor series we obtain the n normal equations:

$$\sum_{hk\ell} W_{hk\ell} \frac{\partial|kFc|}{\partial p_1}^2 \Delta p_1 + \sum_{hk\ell} W_{hk\ell} \frac{\partial|kFc|}{\partial p_1} \frac{\partial|kFc|}{\partial p_2} \Delta p_2 + \ldots + \Sigma W_{hk\ell} \frac{\partial|kFc|}{\partial p_1} \frac{\partial|kFc|}{\partial p_n} \Delta p_n = \sum_{hk\ell} W_{hk\ell} \Delta F \frac{\partial|kFc|}{\partial p_1}$$

$$\sum_{hk\ell} W_{hk\ell} \frac{\partial|kFc|}{\partial p_2} \frac{\partial|kFc|}{\partial p_2} \Delta p_1 + \sum_{hk\ell} W_{hk\ell} \frac{\partial|kFc|}{\partial p_2}^2 \Delta p_2 + \ldots$$

$$\vdots$$

$$+ \sum_{hk\ell} W_{hk\ell} \frac{\partial|kFc|}{\partial p_2} \frac{\partial|kFc|}{\partial p_n} \Delta p_n = \sum_{hk\ell} W_{hk\ell} \Delta F \frac{\partial|kFc|}{\partial p_2}$$

$$\vdots$$

$$\sum_{hk\ell} W_{hk\ell} \frac{\partial|kFc|}{\partial p_n} \frac{\partial|kFc|}{\partial p_1} \Delta p_1 + \sum_{hk\ell} W_{hk\ell} \frac{\partial|kFc|}{\partial p_n} \frac{\partial|kFc|}{\partial p_2} \Delta p_2 +$$

$$\ldots . + \sum_{hk\ell} W_{hk\ell} \frac{\partial |kFc|}{\partial p_n}^2 \Delta p_n = \sum_{hk\ell} W_{hk\ell} \Delta F \frac{\partial |kFc|}{\partial p_n}$$

The various Δp's can be found from these equations. These, when added to the initial a's will give a better approximation which can be used in the above process to obtain a still better approximation. The process is repeated until it converges.

The above equations can be written in matrix notation with

$$a_{ij} = \sum_{hk\ell} W_{hk\ell} \frac{\partial |kFc|}{\partial p_i} \frac{\partial |kFc|}{\partial p_j}, \quad x_j = \Delta p_j,$$

$$v_i = \sum_{hk\ell} W_{hk\ell} \; F\frac{\partial |kFc|}{\partial p_i}$$

$$\begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix} = \begin{pmatrix} v_1 \\ v_2 \\ \\ v_n \end{pmatrix}$$

or

$$Ax = v \text{ so that } x = A^{-1}v.$$

If the elements of $A^{-1}$ are $b_{ij}$, then, the standard deviations of the variables are given by

$$\sigma p_j = \sqrt{b_{jj}(\Sigma W_{hk\ell}\, \Delta F^2)/(m-n)}$$

where m is the total number of observations and should exceed n.

For a more detailed treatment of the material in this chapter, the reader is referred to the following texts:

G.H. Stout and L.H. Jensen, 'X-Ray Structure Determination', MacMillan Co., New York, 1968.

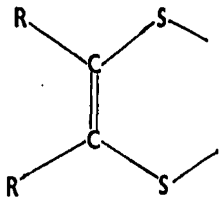
M.J. Buerger, 'Crystal Structure Analysis', Wiley and Sons Ltd., New York, 1967.

# CHAPTER ONE

## The Crystal and Molecular Structures of $[Fe_2(NO)_2(S_2C_2Ph_2)_3]CHCl_3$

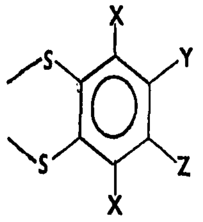
## INTRODUCTION

Transition metal complexes containing the 1,2-dithiolene ligands (1 and 2)



1

R = H, $CH_3$, $CF_3$, CN, $C_6H_5$



2

X = Y = Z = H, $CH_3$, F, Cl

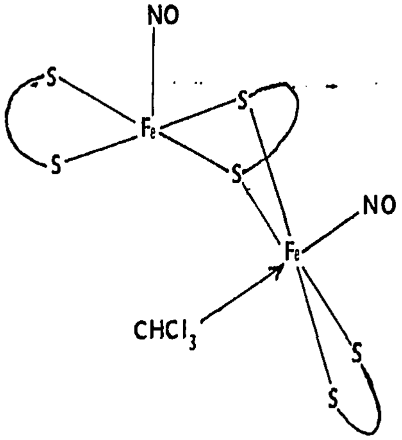
X = Y = H, Z = $CH_3$

X = H, Y = Z = $CH_3$

have been extensively studied over the last decade,[14,15] since the almost simultaneous appearance in 1962 of two short communications [16,17] concerning the synthesis of the neutral and dianionic bisdithiolene complexes of nickel $[Ni\{S_2C_2(CN)_2\}_2]^{0,-2}$. The interest in these compounds arose primarily from the chemical and structural properties of the "pure" dithiolene complexes. The bis complexes have been found to possess square planar geometry for a large range of metals [18-26], and for any given metal and ligand the complex is capable of stable existence in more than one oxidation state. These are often readily interconverted by reversible one-electron transfer reactions [27]. These ligands have also been found to stabilise the unusual trigonal prismatic geometry in the neutral tris complexes[28-32]. Again these compounds undergo facile one-electron transfer reactions[33,34] although it would appear that the reduced complexes are no longer trigonal prismatic but distorted towards octahedral coordination[15,35].

In their investigations into the synthesis and characterisation of these and related complexes, McCleverty and co-workers isolated the complexes $[Fe_2(NO)_2(S_2C_2Ph_2)_3]^{0,-1}$ which were found to possess several interesting properties[36-38]. The neutral complex displayed two terminal nitrosyl stretching frequencies in the solid state and in solution. The Mössbauer spectrum revealed the presence of two distinct iron sites[39,40]. The monoanion exhibited an E.S.R. spectrum in solution which consisted of a three line multiplet due to hyperfine interactions with only one $^{14}N$ whereas a quintet would have been expected if both N's coupled.

From the Mössbauer data, a structure 3 has been tentatively put forward for the neutral complex which involves interaction with the solvent of crystallisation at one of the iron sites[40]. However, it was by no means certain that this was in fact the true structure, and so, in order to unambiguously determine the structure of the molecule and to try to explain some of the properties of both it and the monoanion, a full X-ray crystal structure determination of the neutral complex $[Fe_2(NO)_2(S_2C_2Ph_2)_3]$ $CHCl_3$ was undertaken.



3

## EXPERIMENTAL

Very deep purple, almost black, irregularly shaped crystals of $[Fe_2(NO)_2(S_2C_2Ph_2)_3]CHCl_3$ were prepared by McCleverty and co-workers, by the action of nitrous oxide on $[Fe(S_2C_2Ph_2)_2]_2$ in cold chloroform[36,37]. Attempts at re-crystallisation from chloroform, led to what appeared to be triclinic crystals, but which on subsequent examination by Laue photographs, proved to be powders. Consequently, several small crystals from the irregularly shaped batch were mounted on glass fibres and examined by Laue photographs until one was found which was considered suitable for data collection and photographic work. The dimensions of the crystal were 0.32 mm x 0.14 mm x 0.09 mm.

Weissenberg photographs for the hk0, hk1, and hk2 layers and precession photographs for the $h0\ell$ and $0k\ell$ layers were obtained. These showed the Laue symmetry to be mmm and the crystals to be orthorhombic. The following systematic absences:

(i) $0k\ell$ $k + \ell = 2n + 1$ -- implying an n glide perpendicular to a

(ii) $h0\ell$ $h + \ell = 2n + 1$ -- implying an n glide perpendicular to b

defined the space group as either Pnn2 or Pnnm.

The lattice parameters were obtained from the two zero layer precession photographs and the errors in these parameters were calculated by the method of Patterson and Love[41]. These results were: a = 21.82(2), b = 21.20(2), c = 9.50(1). (The figure in parentheses gives the error in the last figure quoted).

The experimental determination of density by flotation in an aqueous solution of potassium iodide gave a range of values from 1.366 to 1.454 gms. cm.$^{-3}$ with an average value of 1.42 gms. cm.$^{-3}$.

The calculated densities for a unit cell of volume 4394.5 Å$^3$ containing four molecules of complex and 0, 0.5, and 1 molecule of chloroform per molecule of complex were 1.358, 1.448, and 1.538 gms. cm.$^{-3}$ respectively. The observed density then corresponded most closely to one half a molecule of $CHCl_3$ per molecule of complex, but was obviously variable.

The requirement of four molecules of complex in the unit cell places no restrictions on the position of the molecule in the unit cell for the space group Pnn2, but does dictate that the molecule sit either in the mirror plane or on the two-fold axis if the space group is Pnnm, since there are eight general positions in this space group.

Intensity data were collected on a PAILRED automatic diffractometer using graphite crystal monochromated Mo Kα radiation and included the layers $hk\ell$ for $\ell = 0$ to 8. Because of the small size of the crystal, the intensities were generally low, and a slow scan rate of 0.25°/min. was used throughout the data collection. The scan width, however, varied, increasing as the layer number increased. For $\ell = 0$

the scan width was 1.8° while for $\ell = 8$ it was 2.2°. A stationary background count for 100 seconds was taken on each side of the scan.

Since the PAILRED diffractometer necessarily gives both the $hk\ell$ and $\bar{h}k\ell$ data, which are equal for the case of either of the two possible space groups, the two data sets were averaged before data reduction.

In the data reduction process, reflections were rejected on the basis of two criteria:

(i) $I \leqslant 0$

(ii) $I \leqslant 2\sigma$

where $I = T - tB$ and $\sigma = [T + tB + (pI)^2]^{1/2}$

T is the total integrated peak count obtained in time $t_1$, B is the total background count obtained in time $t_2$, t is the ratio $t_1/t_2$ and the p term accounts for machine errors. Of the 2023 reflections measured, 638 were rejected in this way giving 1385 observed reflections.

Measurement of three standard reflections at the end of each layer showed that no significant decomposition took place during the data collection.

Absorption was kept at a minimum by use of Mo$k\alpha$ radiation. Because of this, together with the irregular shape of the crystal, no absorption correction was applied. The linear absorption coefficient for this compound was 10.67 $\text{cm.}^{-1}$.

Corrections for Lorentz and polarisation effects were applied and structure amplitudes and standard deviations calculated.

At this stage of the study, it was quite clear that the data set would allow the determination of the gross structure, but that any detailed discussion of bond lengths would be precluded.

## SOLUTION OF STRUCTURE AND REFINEMENT

A Patterson map was computed, and inspection of the Harker plane at z = 0 and the Harker line at x = 0, y = 0, confirmed the space group as Pnn2. The Harker plane at z = 0 contained peaks corresponding to vectors between atoms related by a two-fold axis, these being of the general type (2x, 2y, 0). Both space groups would have given this type of vector. However, if the space group were Pnnm, then additional peaks would have appeared on the Harker line, corresponding to vectors between atoms related by the mirror plane, except for the case where both atoms sit in the mirror plane and have a z coordinate of zero. These vectors have the form (0,0,2z).

The three possible situations that could have existed for the space group Pnnm were:

(i) The molecule sits on the two-fold axis. -- The Harker plane would contain the intramolecular iron-iron vector and the Harker line a peak corresponding to the intermolecular iron-iron vector between the mirror related iron atoms.

(ii) The molecule sits in the mirror plane and the two iron atoms are mirror related. -- The Harker line would contain the intramolecular iron-iron vector.

(iii) The molecule sits in the mirror plane, the two iron atoms having z = 0 but different x and/or y coordinates. -- No iron-iron vectors would appear on the Harker line, but the Harker plane would contain four peaks corresponding to

7

an iron-iron intramolecular vector and three iron-iron intermolecular vectors, and these peaks would be arranged in a definite pattern. The iron-iron intramolecular vector would be about 2.5 - 3.5 Å from the origin. The other three peaks would be in a straight line which would be parallel to the line between the intramolecular vector and the origin, and would be separated from each other by the intramolecular iron-iron distance.

The Harker line contained only one medium-sized peak 1.67 Å from the origin. This clearly eliminated the first two possibilities since this peak was too small and too close to the origin to be either an inter- or an intramolecular iron-iron vector. None of the peaks in the Harker plane conformed to the pattern described in the third possibility. The space group was therefore taken to be Pnn2.

Four of the peaks in the Harker plane were interpreted as being due to the two iron-iron intermolecular vectors of the type (2x, 2y, 0) and two iron-sulphur "image vectors", these appearing in the Harker plane, because the plane formed by the two sulphur atoms and the iron to which they were attached, lay parallel to the Harker plane. This S - Fe - S pattern is repeated at the origin as normal intramolecular vectors.

This interpretation gave the x and y coordinates of the two iron atoms and two sulphur atoms, and the z coordinate of the sulphur atoms relative to the iron atom to which they were attached. With the x and y coordinates of the two iron atoms known, the intramolecular iron-iron vector was easily found and from this, the difference in z coordinate between the two iron atoms was determined. Since there is no unique origin along the two-fold axis of the space group Pnn2, the z coordinate of one of the iron atoms was fixed arbitrarily at 0.1 and was not refined. The z coordinates of the other three atoms were determined relative to this atom.

These four atoms positions were used as input to a structure factor calculation, which gave a residual R factor of 0.472. The calculated phases were used to compute an electron density map, which revealed the positions of the other four sulphur atoms.

Two cycles of refinement, using the positions of all eight atoms in the structure factor calculation, reduced the R factor to 0.318 at which point an electron density difference map was computed, from which the positions of all the light atoms in the molecule were found.

In order to reduce the number of variables in the remaining full matrix least squares refinement, and hence computer storage, the phenyl rings were refined as rigid bodies with a C-C distance of 1.397 Å and a C-C-C bond angle of 120°.

In four cycles of refinement, with all these atoms included, the R factor fell to 0.153. An electron density difference Fourier gave evidence of anisotropic thermal motion on the part of the eight heavy atoms. Consequently, these were allowed to refine anisotropically and the R factor reduced to 0.123. Inclusion of the hydrogen rigid bodies on the phenyl rings, in which the C-H distance was 1.0 Å and the temperature factors of the hydrogen atoms were fixed at a value 10% greater than that of the carbon atom to which they were attached, further reduced the R factor to 0.114.

An electron density difference map was calculated and showed no features consistent with an ordered chloroform molecule. Two relatively small peaks (1.56e $A^3$) were located in a pocket between molecules, having a separation of the order found between chlorine atoms in a chloroform molecule. These two were included in the refinement as chlorine atoms and, in accordance with the density experiment, were given half weight. The R factor converged to 0.098. The weighted R factor, defined as $R_2 = [\Sigma w (|Fo| - |Fc|)^2 \ / \ \Sigma w|Fo|^2]^{1/2}$ where w is a weighting factor, was 0.124. An electron density difference map did not yield the positions of the remaining carbon and chlorine atom of the chloroform molecule, the residual density being mainly associated with one of the rigid bodies (0.94 electrons/$\mathring{A}^3$). This was assumed to be due to the variable occupancy and possible disorder of the molecule and the relatively poor quality of the data.

The scattering factors for all atoms other than hydrogen in the above calculations were calculated from

Cromer's coefficients[42]. The scattering factors for hydrogen were those of Mason and Robertson[43].

Since the space group is polar in the z direction, the solution corresponding to the structure of opposite hand was refined. This solution was obtained simply by changing the sign of the z coordinate of each atom. The R factor converged to 0.099 with $R_2 = 0.125$. A Hamilton test[44] showed that the hypothesis that this solution best described the correct structure could be rejected at the 0.005 confidence level. This statistical test cannot be accepted at face value in view of the poor quality data set. However, the dispersion effects are small in this structure and since only the gross features are to be discussed, an error in choice of handedness is not considered important.

## RESULTS

Table 3 gives the observed ($|Fo|$) and calculated ($|Fc|$) structure amplitudes (electrons X 10). The final atomic coordinates for all atoms and isotropic temperature factors for the light atoms are listed in Table 4, the anisotropic temperature factors for iron and sulphur atoms in Table 5. In these tables and all those which appear later, standard deviations in the least significant figures are given in parentheses. Interatomic distances and angles are listed in Tables 6 and 7. Table 11 gives the iron-sulphur distances found in dithiolene complexes while the geometry of the cis-1, 2-diphenyl dithiolene ligand is summarised in Table 12.

A diagram of the whole molecule is shown in Fig. 2. A packing diagram of the contents of the unit cell projected into the [a][b] plane is shown in Fig. 3.

In Table 5 and all other tables of anisotropic temperature factors, the $U_{ij}$ are related to the $\beta_{ij}$ (page 6) by:

$$U_{ij} = \frac{\beta_{ij}}{2\pi^2 x_i x_j} \qquad \text{where for } i = 1 \quad x_i = a^*$$

$$i = 2 \quad x_i = b^*$$

$$i = 3 \quad x_i = c^*$$

## TABLE 3

Observed and Calculated Structure Amplitudes. (Electrons x 10)

```
  H  K FOBS  FCAL     H  K FOBS  FCAL     H  K FOBS  FCAL     H  K FOBS  FCAL     H  K FOBS  FCAL
 **L =    0****       2  6 -490  -446     1 14  200   267     4  3  640   573    10  9  318   313
  4  0 1220  1649     3  6  248    24     2 14  333   297     5  3 1131  1064    11  9 -414  -390
  6  0  788   664     4  6  580   385     4 14  757   720     7  3  351   284    12  9  358   369
  8  0 1621  1319     5  6  618   385     5 14 -275  -321     8  3 -600  -469    13  9 -274  -291
 10  0 2145  2222     8  6  268   423     6 14  719   734     9  3  244   263    15  9 -114  -123
 12  0 1135  1376     9  6 -418  -469     7 14 -268  -343    10  3 -495  -502    17  9 -200  -177
 14  0  993  1006    10  6  653   587     8 14  682   761    11  3 -160  -141     4 10-1023 -1018
 16  0  605   620    11  6-1100 -1080    10 14  343   322    12  3 -486  -536     2 10 -170  -209
 18  0  391   335    12  6  173    97    14 14  283   224    13  3 -232  -254     3 10 -929  -885
 20  0  423   394    15  6  273   229    16 14  297   396    14  3 -339  -349     4 10 -112  -135
  4  1  174    72    16  6  223   159    17 14 -276  -339    15  3  -92   -76     5 10 -735  -748
  5  1  417   456    19  6 -348  -385     1 15  620   711    16  3   88    90     7 10 -626  -701
  6  1 1587  1254    21  6 -450  -393     3 15  197   103    18  3 -119  -106     8 10   70    69
  7  1 1658  1374     1  7 -693  -663     8 15 -252  -343    19  3  198   150     9 10 -810  -843
  8  1  828   645     2  7  704   409     9 15  359   377     1  4-1205 -1154    10 10  -79   -76
  9  1 1469  1403     7  7  254   319    11 15  208   262     2  4 -452  -272    11 10 -401  -375
 10  1-1892 -1684     8  7  347   332    16 15 -232  -260     3  4  -41   -44    12 10  -69   -75
 11  1 1318  1376     9  7 -296  -215     0 16  740   671     4  4  778   646    17 10 -368  -352
 12  1-1531 -1551    10  7 -505  -487     1 16 -273  -169     5  4  319   292     0 11 -768  -939
 13  1  416   447    12  7 -648  -653     2 16  233   297     6  4  489   447     2 11-1088 -1020
 14  1-1071 -1028    15  7  252   249     3 16  266   204     7  4 -170  -146     4 11 -882  -973
 15  1  197   138    16  7  365   280     4 16 -253  -293     8  4  122   146     6 11-1069 -1095
 18  1 -354  -323    17  7 -247  -240     5 16  454   391     9  4 -632  -590     8 11 -810  -854
 20  1 -407  -473    20  7 -270  -238     6 16 -521  -490    10  4   -4    -3     9 11  468   437
 22  1 -357  -375     0  8-1861 -1870     7 16  344   340    11  4 -298  -349    10 11 -796  -858
  4  2-2099 -2107     1  8 -335  -259     9 16 -335  -339    13  4 -204  -235    11 11  439   429
  5  2-1115  -853     2  8 -936  -953    11 16 -325  -308    14  4  -31   -28    12 11 -417  -406
  6  2-1256 -1145     3  8  504   541    12 16  242   254    16  4  -76   -75    13 11  178   147
  7  2  315   402     5  8  309    83     1 17 -540  -537    18  4 -147  -129    14 11 -329  -356
  8  2-1274 -1295     6  8 -360  -353     3 17 -382  -371    19  4 -140  -134    16 11 -449  -431
  9  2 -206  -142     8  8  324   231    10 17 -452  -390     0  5 -994  -967     1 12 -169  -172
 10  2-1073 -1021     9  8  423   450     0 18 -529  -570     1  5 -311  -334     2 12  315   213
 11  2 -237  -310    11  8  260   365     2 18 -580  -570     2  5-1287 -1227     3 12 -164  -111
 12  2 -658  -490    13  8  469   475     4 18 -463  -464     3  5 1164  1093     5 12 -194  -190
 14  2 -392  -457    15  8  529   560     6 18 -587  -582     4  5  458   417     7 12  -35   -29
 15  2  352   318    19  8  338   418     8 18 -705  -612     5  5  767   560     8 12  291   252
 16  2 -318  -410    20  8  453   498    10 18 -370  -399     6  5  228   208     9 12  -63   -87
 18  2 -208  -123     2  9  277   227    12 18 -342  -331     7  5 -441  -369    10 12  206   210
 21  2 -310  -273     3  9  707   506     1 19 -464  -405     8  5 -366  -378    11 12 -265  -294
  1  3-1105 -1315     4  9  392   271     3 19 -399  -442     9  5 -395  -365    12 12   65    71
  2  3 -574  -736     5  9  457   140     5 19 -349  -353    10  5 -351  -402    13 12 -356  -285
  3  3-3029 -2724     6  9  380   353     6 19  294   187    14  5  240   251     0 13  617   676
  5  3-1288 -1193     7  9 -249   -27     7 19 -317  -220    17  5 -177  -181     2 13  339   340
  6  3  843   837     8  9  292   428     8 19  430   440    19  5 -212  -245     3 13  -16   -16
  7  3-1289 -1341     9  9  451   510    10 19  387   358     1  6 -895 -1060     4 13  448   492
  8  3 1223  1089    10  9 1277  1305     0 20  362   411     2  6  269   283     5 13  -50   -34
  9  3-1008 -1143    11  9  458   457     3 20 -250  -220     3  6 -509  -385     6 13  641   631
 10  3  934   896    12  9  908  1040     6 20  230   107     4  6  688   724     8 13  544   516
 11  3-1419 -1360    14  9  594   607     1 21  505   519     5  6  417   421     9 13 -103   -98
 12  3 -255   -90    16  9  483   485     3 21  414   390     6  6 -592  -643    10 13  300   290
 13  3 -783  -876    18  9  567   573     5 21  304   300     8  6 -799  -775    11 13 -187  -114
 14  3 -296  -294    19  9  252   234     **L =    1****     9  6 -301  -256    14 13  218   187
 15  3 -563  -531    20  9  570   666     5  0  511   365    10  6 -121  -198     1 14  225   251
 17  3 -282  -405     0 10 1305  1243     7  0 -798  -811    11  6  -43   -43     2 14  -40   -43
 18  3  230   270     2 10 1234  1389     9  0 -699  -672    12  6  220   199     3 14  519   565
 19  3 -200  -180     3 10 -508  -464    11  0  259   269    15  6  261   254     4 14 -165  -163
 20  3  396   379     5 10 -585  -626    13  0  436   418    16  6 -263  -220     5 14  460   472
 22  3  274   237     6 10  485   463    15  0  500   513     0  7 1039  1011     6 14   32    31

  0  4  351   454     7 10  439   514    17  0  258   275     1  7  532   311     7 14  667   671
  1  4 -930  -717     8 10  541   609    19  0  373   370     2  7  100    91     9 14  468   405
  2  4-1224 -1172     9 10  532   695     4  1  802   778     3  7  655   698     0 15  142   118
  4  4-1292 -1247    10 10  483   528     5  1 1169   929     4  7  371   441     1 15   63    40
  5  4-1273 -1265    11 10  300   304     6  1 -427  -392     5  7  265   354     2 15  118   133
  6  4  285    82    17 10  287   255     7  1  263   257     6  7  328   358     4 15  206   116
  7  4  198   246    19 10  217   253     8  1 -271  -133     7  7 -666  -672     8 15  -67   -81
  9  4  919   871    20 10 -245  -246     9  1  259   282     8  7  365   403    10 15  -99   -89
 11  4 -542  -449     2 11 -678  -503    10  1  750   692     9  7 -308  -305     1 16 -197  -187
 12  4 -484  -401     4 11 -297  -373    11  1  388   401    10  7  550   619     2 16  410   424
 13  4 -185  -142     6 11 -196  -170    12  1  292   256    11  7  183   216     3 16 -276  -250
 15  4 -371  -450     7 11 -305  -264    13  1   97   104    12  7  287   286     5 16 -290  -302
 17  4 -218  -240     9 11 -343  -399    14  1  235   209    13  7  460   424     6 16  106    75
 18  4 -237  -248    10 11 -553  -517    16  1   86    84    14  7  124   138     7 16 -210  -256
 20  4 -262  -243    11 11 -351  -383    17  1  365   317     1  8 1572  1607     9 16 -146  -145
 21  4  290   320    12 11 -891  -928    18  1  -68   -57     2  8  378   203    10 16   90   104
 22  4 -204  -204    13 11 -331  -320    19  1  439   445     3  8 1089  1211     0 17  168   135
  2  5 -168   -81    14 11 -351  -383     4  2 -499  -399     4  8   47    66     2 17 -117  -117
  3  5  851   757     0 12 -846  -906     5  2  314   167     5  8  496   458     3 17  230   218
  4  5  272    39     2 12 -874  -796     6  2  112   131     7  8  966   924     4 17 -293  -333
  5  5 -437  -479     5 12  462   269     8  2  256   389     8  8 -363  -319     6 17 -253  -234
  6  5 -550  -575     6 12 -622  -604     9  2   86    92     9  8 1023  1033     8 17  157   178
  7  5  374   411     8 12 -515  -501    10  2  507   479    10  8 -166  -168    10 17  191   160
  8  5 -238  -236    10 12 -583  -618    11  2 -150  -158    11  8  770   846     1 18  390   379
 10  5 -403  -407    11 12 -567  -590    12  2  267   240    12  8   72    85     2 18 -246  -252
 11  5  233   246    12 12 -445  -460    13  2 -423  -418    13  8  528   480     3 18  205   208
 12  5 -275  -279    18 12 -242  -195    14  2  129   100     0  9  865   909     4 18 -185  -187
 13  5  191    38     1 13 -497  -514    15  2  -81   -92     1  9 -549  -505     5 18  -45   -41
 15  5  266   192     3 13  226   226    16  2  261   228     2  9  481   415     7 18   62    65
 16  5 -269  -308     5 13  760   695    18  2  267   301     3  9 -201  -224     0 19   77    97
 17  5  497   433     7 13  420   509    20  2  419   372     4  9  343   445     2 19  -25   -20
 18  5 -549  -492    11 13 -276  -287     0  3 -502  -406     6  9  255   285     3 19 -277  -222
 21  5 -337  -338    12 13  293   192     1  3 -917  -930     7  9 -317  -368     4 19   38    21
  0  6 1373  1647    14 13 -232  -244     2  3 -322  -340     8  9  368   301     5 19 -179   -87
  1  6 -210  -130     0 14  237    58     3  3  -19   -18     9  9 -120  -123     **L =    2****
```

```
  H   K FOBS   FCAL    H   K FOBS   FCAL    H   K FOBS   FCAL    H   K FOBS   FCAL    H   K FOBS   FCAL
  4   0  969    858    8   6  383    405    5  14  276    248    0   5  -41    -35   15  11 -189   -196
  6   0  370    378   12   6 -152   -119    6  14  187    179    1   5   92    100    1  12 -351   -334
  8   0 -421   -387   13   6  -56    -43    8  14   86     85    2   5 -161    -48    2  12 -654   -579
 10   0  181    222   16   6   23     23   14  14  213    162    3   5  284    335    3  12 -117   -149
 12   0   74     83   17   6 -379   -360    2  15  237    158    4   5  251    310    4  12  -62    -62
 18   0  375    375    1   7  252    254    3  15  184    217    5   5 -120   -121    5  12   15     14
 20   0  410    417    3   7 -169   -153    4  15  234    225    6   5  240    237    7  12  -97    -91
  4   1   -8    -10    4   7 -157   -108    5  15  287    266    7   5 -181   -168    9  12 -371   -392
  5   1 -421   -308    5   7 -351   -383    7  15  333    231    8   5  875   -748   12  12 -118    -91
  6   1  350    330    7   7 -370   -344   11  15  -38    -37   12   5 -202   -183    0  13 -112   -110
  7   1  -42    -47    8   7 -246   -273   13  15  -37    -35   14   5  -26    -22    2  13    2      2
  8   1  442    384    9   7  202    206    0  16 -293   -303   16   5  363    374    4  13  347    355
  9   1   86     57   10   7    6      7    1  16  142     93   18   5  470    478    8  13 -178   -177
 10   1  797    764   11   7  251    237    3  16  253    245    1   6 -191   -199    9  13  253    212
 11   1  167    160   12   7  489    506    6  16  242    230    2   6  279    234   10  13 -133   -171
 12   1  430    431   13   7   39     41    7  16 -151   -133    3   6 -625   -655   11  13  183    129
 13   1  -34    -33   14   7  209    195    9  16  213     91    4   6  128    104    1  14   49     42
 14   1  -26    -25   17   7    4      4   11  16   58     61    5   6 -438   -450    2  14  247    298
 15   1  -23    -23   18   7 -175   -148    1  17  155    124    6   6   -7     -9    3  14   65     54
 16   1  -80    -80    0   8 1266   1306    2  17 -176   -163    7   6  106    116    4  14  288    289
 18   1  122    117    1   8  407    345    4  17  -22    -19    8   6  -66    -56    5  14  194    202
 19   1  323    205    2   8  647    693    5  17 -153   -151    9   6  115    104   12  14   10     12
 20   1  225    244    3   8    4      6    0  18  468    453   10   6 -123   -148    0  15 -188   -197
  4   2 -557   -395    4   8  -81    -80    4  18  225    177   11   6   98     89    2  15 -168   -154
  5   2  488    309    6   8 -271   -270    2  19   51     41   12   6 -104   -113    3  15  270    318
  6   2 -779   -705    7   8  -97    -71    4  19  -37    -46   13   6 -340   -346    4  15 -262   -267
  7   2  623    593    8   8   -9     -8       **L =  3****     16   6  138    137    6  15 -223   -213
  8   2 -440   -484   10   8  378    410    5   0   75     82   17   6 -105   -106    7  15 -213   -295
  9   2  904    960   11   8 -154   -127    7   0  400    409   18   6 -154   -177    8  15   81     89
 10   2 -246   -249   12   8  380    379    9   0 1121   1040    0   7 -301   -293    9  15 -264   -274
 11   2  247    255   14   8  300    258   11   0  621    576    1   7  -88   -102   10  15   -2     -2
 13   2  -85    -88   18   8  -61    -60   13   0 -213   -193    2   7 -964   -988    1  16  -83    -68
 14   2 -219    -94    1   9  427    438   17   0 -139   -145    3   7 -346   -381    3  16 -184   -189
 15   2  -90   -107    2   9 -263   -259   19   0  181    185    4   7 -626   -630    5  16 -368   -333
 17   2   78     92    4   9  100     82    4   1  180    189    5   7 -557   -516    6  16  179     87
 18   2 -254   -294    5   9 -101   -117    5   1 -246   -233    6   7 -537   -583    7  16  -51    -51
 19   2  201    204    6   9 -224   -277    6   1  249    255    7   7 -173   -116    9  16  -10    -11
  1   3 -644   -558    7   9  245    191    7   1  280    255    8   7 -649   -669    0  17 -209   -271
  2   3  376    345    8   9 -150   -145    8   1  545    559    9   7 -193   -249    3  17 -238   -271
  3   3 -464   -488    9   9  335    352    9   1 -284   -300   10   7 -457   -448    4  17  121     92
  5   3 -448   -463   10   9 -752   -651   10   1  -74    -83   12   7 -301   -335    7  17 -196   -112
  6   3  229    229   11   9  246    347   11   1 -940   -991   14   7 -197   -210    1  18   17     17
  7   3 -744   -720   12   9 -614   -665   13   1-1124  -1089   16   7 -130   -147    3  18 -117    -97
  8   3  493    499   13   9  205    124   15   1 -745   -800   17   7 -102   -105    5  18 -180   -252
  9   3 -803   -798   14   9 -177   -179   16   1 -265   -299    1   8 -443   -455       **L =  4****
 12   3    0      0   16   9  -93    -86   17   1 -603   -642    3   8 -835   -795    4   0 -158   -167
 13   3 -135   -112   17   9 -147   -113   19   1 -472   -502    4   8  533    486    6   0-1417  -1346
 15   3  198    177    0  10 -475   -464    4   2 -105   -110    5   8 -602   -569    8   0 -923   -972
 16   3  202    193    1  10 -457   -317    5   2 -702   -705    6   8  -95    -89   10   0 -747   -718
 18   3  237    266    2  10 -743   -789    6   2 -387   -321    7   8 -801   -795   12   0 -208   -203
  0   4 -451   -482    3  10 -300   -306    7   2-1038  -1047    8   8  114     64   16   0 -340   -277
  1   4  909    745    4  10  139    135    8   2 -118   -110    9   8 -645   -750    4   1  347    384
  2   4  112    109    6  10 -399   -409    9   2 -726   -682   11   8 -231   -211    5   1 -190   -236
  3   4  600    614    7  10 -157   -171   10   2 -127   -110   13   8 -175   -195    6   1  303    287
  4   4  566    520    8  10 -190   -192   11   2 -181   -192   14   8  283    271    7   1 -777   -716
  5   4  735    679   10  10 -228   -210   12   2 -297   -337   15   8    5      4    8   1  173    152
  6   4  205    230   11  10 -383   -370   13   2  151    147    0   9  389    376    9   1 -372   -364
  7   4  423    369   12  10 -192   -169   14   2 -474   -487    1   9  395    441   10   1  178    191
  8   4  307    295   14  10 -238   -301   16   2 -319   -339    2   9  236    219   11   1  132     87
  9   4 -290   -283   16  10  -77    -84   17   2 -284   -273    3   9  400    494   12   1   79     78
 10   4 -175   -195    1  11 -495   -506   18   2 -246   -249    4   9 -180   -210   13   1   44     39
 11   4  160    154    2  11 -460   -468   19   2 -232   -127    5   9  278    274   14   1  -92    -86
 12   4   33     32    3  11 -391   -410    1   3  582    605    6   9   32     33   16   1  142    118
 14   4    3      4    4  11 -174   -191    2   3 -289   -293    7   9  401    358   17   1 -368   -370
 15   4  256    237    5  11 -431   -416    3   3  434    448    8   9  352    358   18   1  257    270
 16   4  176    166    6  11  148    142    4   3 -220   -223    9   9  240    249    4   2  416    432
 17   4  310    345    7  11 -203   -211    5   3 -239   -264   10   9  459    507    5   2 -350   -315
 18   4  173    153    8  11  382    437    6   3   11     10   11   9  421    425    6   2  177    160
 19   4  186    204    9  11 -413   -406    8   3 -199   -209   12   9  337    369    7   2  -27    -28
  1   5  236    268   10  11  279    278    9   3  442    452   13   9  542    531    8   2  545    617
  2   5  312    262   11  11 -411   -383   10   3 -364   -335   15   9  362    359    9   2   20     16
  3   5  581    515   12  11  123    117   11   3  273    225    1  10 1265   1371   10   2  482    413
  4   5  463    413   13  11 -430   -367   12   3   25     23    3  10  768    770   11   2  193    189
  5   5 1071   1017   14  11 -199   -173   14   3  173    208    4  10 -380   -390   12   2  -93    -97
  6   5   12     27   15  11 -242   -249   15   3  -50    -47    5  10  526    517   13   2   45     39
  7   5 1028   1041    0  12 -137   -146   18   3  -69    -58    7  10  503    557   15   2 -183   -214
  8   5  -44    -44    1  12 -373   -456   19   3  132    151    8  10  162    176    1   3  594    640
  9   5  639    573    2  12 -341   -333    1   4  308    292    9  10  935    832    2   3 -317   -283
 10   5 -243   -145    3  12 -254   -253    2   4  530    488   10  10  207    224    3   3  938    869
 11   5   -3     -3    7  12  318    358    3   4  152    181   11  10  567    591    4   3 -277   -260
 12   5 -376   -288    8  12 -220   -183    4   4  188    169   13  10  -67    -73    5   3  572    622
 16   5  246    241    9  12  537    522    5   4  767    791   16  10  287    247    6   3   41     43
 17   5   41     36   10  12 -243   -273    6   4  -32    -41    0  11  489    501    7   3  684    690
 18   5   76     61   14  12  -32    -39    7   4  690    675    1  11 -360   -366    8   3  123    116
 19   5  125    126    1  13  -39    -39    9   4  420    415    2  11  207    225    9   3  397    405
  0   6  -84    -62    5  13  106     79   11   4   98    120    3  11 -322   -348   10   3 -336   -297
  1   6  124     77    7  13  -32    -28   12   4  103    116    4  11  495    498   11   3  344    356
  2   6 -853   -808    8  13  136    164   13   4  134    130    6  11  336    372   12   3 -364   -371
  3   6  215    219    9  13 -111   -169   14   4 -107   -114    7  11   34     36   14   3 -304   -310
  4   6  790    756   10  13  118    105   15   4  447    448    8  11  356    303   16   3 -307   -300
  5   6 -392   -416   15  13  338    290   16   4  -25    -22   11  11 -702   -655   17   3  342    316
  6   6  597    569    3  14  284    291   17   4  222    201   12  11 -180   -169    0   4   69     53
  7   6 -486   -464    4  14  156    176   18   4  337    318   13  11 -352   -390    1   4 -492   -474
```

```
 H  K  FOBS  FCAL     H  K  FOBS  FCAL     H  K  FOBS  FCAL     H  K  FOBS  FCAL     H  K  FOBS  FCAL
 2  4   -73   -80     2 12   272   364    10  4   594   583     2 14   -13   -12     5 11   301   290
 3  4  -575  -647     3 12   323   372    11  4   336   341     3 14  -257  -243     7 11   272   251
 4  4  1001  1096     4 12   315   334    12  4   552   496     5 14  -220  -260     9 11   242   201
 5  4  -167  -171     5 12   215   281    13  4   318   255     8 14   235   223     0 12  -225  -209
 6  4   465   454     6 12   585   610    14  4   343   364     0 15    98    81     1 12   -58   -35
 7  4   285   285     8 12   453   450    15  4   330   337       **L =   6****       2 12    67    59
 8  4   327   349     9 12   241   204    16  4   318   283     4  0  -294  -313     7 12   155   143
 9  4    32    26    11 12   303   256     0  5  1078  1108     6  0   381   354     1 13   -89   -84
10  4   173   168    13 12   233   230     1  5   127   128     8  0   239   260     3 13    28    27
11  4  -174  -132     1 13   320   321     2  5   733   689    12  0   -78   -65       **L =   7****
12  4   189   187     2 13  -126   -94     4  5   438   477     3  1  -108  -108     3  0  -200  -313
13  4  -295  -330     3 13   175   165     5  5    67   114     4  1  -201  -212     5  0  -113  -116
14  4   418   414     5 13   390   349     6  5   518   503     5  1    37    29     7  0  -214  -187
15  4  -390  -420     7 13   353   371     8  5   402   371     6  1  -154  -187     9  0  -137  -143
16  4   317   343     9 13   251   289     9  5   303   288     7  1   -37   -38    11  0  -117  -136
17  4  -243  -278     0 14  -319  -373    10  5   432   421    10  1  -190  -202     3  1     0     0
 1  5  -411  -418     2 14  -330  -301    12  5   500   442    12  1  -488  -440     4  1   -40   -46
 2  5   215   172     3 14  -214  -216    13  5   223    87    13  1  -314  -341     6  1   -60   -54
 3  5  -155  -156     4 14   -96   -78    14  5   274   337    14  1  -140  -161     8  1  -153  -147
 5  5   215   217     7 14   -99   -88     2  6    -4    -4     3  2   -50   -53     9  1   272   281
 7  5  -325  -295     9 14  -191  -185     3  6  -112  -114     6  2  -205  -257    11  1   144   134
 9  5  -314  -282    10 14  -293  -221     4  6    92    82     8  2  -329  -317     3  2   240   261
11  5    62    63     1 15  -520  -509     6  6  -178  -122    10  2  -165  -118     4  2   -73   -77
12  5   190   184     3 15  -370  -324     8  6  -301  -284    11  2  -137  -143     5  2   181   175
13  5   281   285     4 15    31    31    10  6  -418  -385    13  2  -103   -84     7  2   160   195
15  5   425   356     5 15  -380  -393    12  6  -227  -232     1  3   131   138     9  2   260   268
 0  6 -1192 -1218     6 15  -340  -265    14  6    36    31     5  3   233   230    10  2   208   146
 1  6    67    65     7 15  -506  -512    15  6    -9    -6     7  3   153   122    11  2   235   235
 2  6  -380  -331     8 15  -154  -165     0  7  -616  -596    10  3   162   172     0  3   518   789
 3  6   532   556     9 15  -538  -540     1  7    52    63    12  3   122   158     1  3  -147  -247
 4  6  -685  -744     0 16  -243  -169     2  7  -553  -547    13  3   265   141     2  3   253   285
 5  6   188   157     1 16   205   180     3  7   273   248     0  4   381   371     3  3  -178  -192
 6  6  -486  -535     2 16  -393  -399     4  7  -441  -437     2  4   263   279     4  3   263   246
 8  6  -434  -398     3 16   296   279     6  7  -598  -625     4  4   316   335     6  3   -74   -78
 9  6   -42   -29     4 16  -293  -229     7  7  -216  -244     6  4   384   395     8  3   295   312
10  6  -383  -386     6 16  -395  -373     8  7  -357  -325     7  4  -162  -172    10  3   272   280
11  6   315   394     1 17   239   226     9  7  -288  -291     8  4   317   315    11  3  -270  -270
13  6   515   469     2 17   320   179    10  7  -504  -468     9  4   148    99    12  3   218   171
15  6   199   142     4 17   294   221    11  7  -304  -281    10  4   196   217     1  4  -121  -156
17  6   309   271       **L =   5****    13  7    71    66    11  4   -95   -92     2  4  -255  -271
 1  7  -468  -489     3  0  -531  -620    14  7  -329  -328    12  4   190   160     3  4   -41   -35
 2  7   427   405     5  0  -696  -691     1  8  -262  -261    13  4   -26   -24     5  4    30    32
 3  7  -491  -555     7  0  -506  -492     3  8  -291  -325     1  5     3     4     7  4   -60   -50
 4  7   468   455     9  0  -668  -626     4  8  -132   -36     3  5   219   192    10  4  -277  -226
 5  7  -320  -314    11  0  -483  -465     6  8  -100   -94     5  5   238   267     0  5  -511  -561
 7  7  -300  -247    15  0  -127  -132     7  8  -235  -206     7  5   206   192     2  5  -457  -463
 8  7  -266  -247     3  1   403   397     8  8  -159  -111     8  5  -119  -117     4  5  -145  -163
 9  7  -189  -207     4  1  -475  -517     9  8  -241  -231     9  5   109    67     5  5    68    57
11  7  -223  -192     6  1  -672  -636    11  8  -194  -176    10  5     2     2     8  5  -336  -265
12  7   403   477     7  1   130   128    12  8  -133  -133    11  5    66    61    10  5  -237  -264
13  7  -488  -522     8  1  -231  -224    13  8  -281  -292     0  6  -171  -187     1  6  -579  -561
14  7   547   560     9  1  -180  -164     0  9   203   299     2  6  -197  -182     3  6  -314  -292
15  7  -282  -270    10  1  -106  -190     1  9   -97  -150     3  6     1     1     4  6    -6    -7
16  7   316   264    11  1  -132  -133     2  9   -40   -34     6  6  -173  -148     5  6  -150  -151
 0  8   573   627    12  1  -230  -193     3  9  -200  -171     9  6   -43   -39     9  6  -129  -135
 3  8   -81   -93    13  1  -192  -185     4  9   123   118    10  6     1     1    10  6   274   256
 5  8    56    23    14  1  -371  -314     5  9  -408  -431    11  6    50    45     0  7    -1    -1
 6  8    -8    -8    16  1  -161  -172     6  9  -163  -139     1  7  -302  -313     1  7  -239  -268
 8  8   226   203     3  2  -396  -422    10  9   195   225     2  7  -223  -221     2  7    87    80
 9  8  -203  -119     5  2    11    11    11  9  -105  -104     3  7  -355  -324     9  7   226   240
12  8  -214  -235     6  2   165   156    13  9  -275  -265     5  7  -329  -333     1  8   434   506
14  8  -330  -316     7  2   145   148     1 10   389   391     6  7  -233  -291     3  8   257   279
 2  9  -586  -520     8  2    96   156     2 10  -293  -308     7  7  -316  -312     5  8   -84   -75
 4  9  -545  -531     9  2    27    29     3 10   122   115     8  7    31    30     7  8   -69   -74
 5  9   183   161    10  2  -181  -180     4 10  -175  -144     9  7  -306  -311     4  9   138   130
 6  9  -137  -163    11  2   -46   -39     5 10   -50   -52    10  7    70    72     5  9   168   200
 7  9   211   228    12  2  -407  -421     6 10  -219  -208    11  7  -268  -266     6  9   141   143
 8  9    32    34    13  2  -300  -254     7 10   -10   -11    12  7   -53   -43     8  9   183   190
 9  9    30    32    15  2    35    19     9 10    77    83     0  8  -385  -413     1 10  -234  -207
10  9  -343  -292     0  3  -290  -355    11 10   217   222     2  8  -278  -253     7 10   -36   -20
11  9   270   197     1  3  -151  -147     0 11   341   360     3  8   217   276     0 11   -94   -85
12  9  -455  -411     2  3   -42   -55     1 11   124   138     4  8  -256  -225     2 11   -67   -74
14  9  -387  -407     3  3   -56   -50     2 11   372   420     6  8  -607  -609     4 11    79    99
16  9  -337  -336     4  3   496   479     7 11   119   100     7  8  -107  -115       **L =   8****
 0 10    44    44     5  3    76    79     8 11   -20   -18     8  8  -596  -542     4  0   253   231
 3 10  -306  -282     6  3   403   416     9 11    -3    -3    10  8  -317  -351     6  0     8     8
 4 10   -16   -18     7  3   169   102    11 11   -93   -87    12  8  -126  -156     3  1    35    43
 7 10  -129  -133     8  3   325   288    12 11   211   231     3  9    37    41     5  1    29    37
 8 10  -331  -299    10  3    56    59     1 12   -97   -90     4  9   313   280     3  2    33    33
 9 10  -115  -160    11  3   234   247     2 12    37    25     5  9  -108  -122     4  2   -86   -73
10 10  -114  -116    13  3   208   204     3 12    61    74     6  9    16    14     6  2    42    52
15 10  -171  -148    14  3   206   227     4 12   -50   -51     7  9    -4    -3     1  3  -309  -414
 2 11   194   188    15  3   113    89     5 12   210   211     8  9  -126  -114     2  3    58    70
 3 11   187   149    16  3   210   127     6 12   201   150     9  9   204   181     3  3  -168  -170
 4 11   153   291     1  4   567   601     7 12    56    61     0 10   779   854     4  3     9     7
 5 11   246   227     2  4    81    75     8 12   234   200     2 10   458   440     5  3  -104  -148
 7 11   -74   -86     3  4   620   545     9 12   -28   -28     3 10  -114  -124     1  4    99   116
10 11   355   333     4  4   221   210     0 13  -599  -576     4 10   373   420     3  4   130   184
12 11   171   192     5  4   680   652     2 13  -335  -331     6 10   311   259     1  5   361   387
13 11   168   181     6  4   196   203     4 13  -108   -79     8 10   430   406     3  5   182   180
14 11   202   216     7  4   664   667     6 13  -131  -102    10 10   267   240     0  6    79    97
 0 12   431   390     8  4   353   376     8 13   -45   -54     1 11   371   350     2  6   115   112
 1 12   142   122     9  4   487   503     1 14  -290  -270     3 11   274   287
```

TABLE 4

Atomic Coordinates and Isotropic Temperature Factors

| Atom | x | y | z | B |
|---|---|---|---|---|
| Fe1 | -0.0043(2) | 0.1380(2) | 0.1000 | 3.9* |
| Fe2 | 0.0128(2) | 0.1956(2) | 0.3600(6) | 3.9* |
| S1 | 0.1119(3) | 0.1983(4) | 0.3581(11) | 4.3* |
| S2 | 0.0169(3) | 0.2971(4) | 0.3246(10) | 4.9* |
| S3 | 0.0923(4) | 0.1154(4) | 0.0325(10) | 4.7* |
| S4 | 0.0049(4) | 0.2226(4) | -0.0341(10) | 5.2* |
| S5 | -0.0757(3) | 0.1910(3) | 0.2210(10) | 4.1* |
| S6 | 0.0148(3) | 0.0889(3) | 0.2987(10) | 4.0* |
| N1 | -0.0415(11) | 0.0923(13) | 0.0138(30) | 5.5(6) |
| O1 | -0.0653(13) | 0.0553(14) | -0.0695(33) | 9.9(8) |
| N2 | -0.0132(12) | 0.1831(12) | 0.5169(28) | 5.2(6) |
| O2 | -0.0318(13) | 0.1766(14) | 0.6346(34) | 9.4(8) |
| C1 | 0.1355(12) | 0.2725(13) | 0.3337(30) | 3.9(6) |
| C2 | 0.0930(12) | 0.3221(12) | 0.3229(27) | 3.6(6) |
| C3 | 0.1198(13) | 0.0674(13) | 0.1690(29) | 3.8(6) |
| C4 | -0.0551(13) | 0.2702(13) | 0.0209(33) | 4.0(6) |
| C5 | -0.0892(12) | 0.2569(12) | 0.1254(27) | 3.2(6) |
| C6 | 0.0910(13) | 0.0565(13) | 0.2812(31) | 3.6(7) |
| CL1 | -0.2854(14) | 0.1730(14) | 0.3436(38) | 14.0(10) |
| Cl2 | -0.3945(13) | 0.1782(14) | 0.1966(30) | 12.4(8) |

*These values are equivalent isotropic temperature factors corresponding to the anisotropic thermal parameters shown in Table 5.

(Continued on next page)

Table 4 continued

## Rigid Bodies

(a) Phenyl Carbon Atoms

| Atom | x | y | z | B |
|---|---|---|---|---|
| C11 | 0.2007(7) | 0.2856(7) | 0.3191(16) | 3.3(6) |
| C12 | 0.2390(7) | 0.2483(7) | 0.2359(16) | 6.3(8) |
| C13 | 0.3025(7) | 0.2561(7) | 0.2425(16) | 7.2(9) |
| C14 | 0.3277(7) | 0.3013(7) | 0.3325(16) | 6.2(8) |
| C15 | 0.2894(7) | 0.3387(7) | 0.4157(16) | 5.8(8) |
| C16 | 0.2259(7) | 0.3309(7) | 0.4090(16) | 5.2(8) |
| D | 0.7473(1) | | | |
| E | 0.0654(1) | | | |
| F | 3.3044(1) | | | |
| | | | | |
| C21 | 0.1079(6) | 0.3868(7) | 0.2876(16) | 5.2(7) |
| C22 | 0.1504(6) | 0.4025(7) | 0.1833(16) | 5.3(7) |
| C23 | 0.1610(6) | 0.4657(7) | 0.1498(16) | 6.0(8) |
| C24 | 0.1292(6) | 0.5133(7) | 0.2207(16) | 8.1(10) |
| C25 | 0.0867(6) | 0.4976(7) | 0.3251(16) | 6.6(8) |
| C26 | 0.0761(6) | 0.4343(7) | 0.3585(16) | 4.3(6) |
| D | 6.2448(2) | | | |
| E | 0.8101(2) | | | |
| F | 4.4296(1) | | | |

(Continued on next page)

Table 4 continued

| Atom | x | y | z | B |
|---|---|---|---|---|
| C31 | 0.1857(7) | 0.0499(6) | 0.1548(17) | 3.0(6) |
| C32 | 0.2282(7) | 0.0596(6) | 0.2626(17) | 6.4(8) |
| C33 | 0.2891(7) | 0.0411(6) | 0.2444(17) | 8.6(10) |
| C34 | 0.3076(7) | 0.0129(6) | 0.1184(17) | 6.6(8) |
| C35 | 0.2651(7) | 0.0032(6) | 0.0106(17) | 6.7(8) |
| C36 | 0.2041(7) | 0.0217(6) | 0.0288(17) | 6.0(8) |
| D | 5.1617(1) | | | |
| E | 2.6209(3) | | | |
| F | 0.7011(3) | | | |
| | | | | |
| C41 | -0.0556(5) | 0.3291(6) | -0.0780(19) | 4.3(7) |
| C42 | -0.0538(5) | 0.3290(6) | -0.2250(19) | 4.9(8) |
| C43 | -0.0529(5) | 0.3860(6) | -0.2986(19) | 7.2(9) |
| C44 | -0.0537(5) | 0.4431(6) | -0.2254(19) | 8.5(11) |
| C45 | -0.0555(5) | 0.4432(6) | -0.0784(19) | 6.4(9) |
| C46 | -0.0564(5) | 0.3862(6) | -0.0047(19) | 4.2(7) |
| D | 0.0610(1) | | | |
| E | 1.5435(1) | | | |
| F | 4.1872(1) | | | |

(Continued on next page)

Table 4 continued

| Atom | x | y | z | B |
|---|---|---|---|---|
| C51 | -0.1431(6) | 0.2964(6) | 0.1740(16) | 4.9(7) |
| C52 | -0.1455(6) | 0.3107(6) | 0.3174(16) | 5.2(7) |
| C53 | -0.1959(6) | 0.3432(6) | 0.3721(16) | 8.7(10) |
| C54 | -0.2437(6) | 0.3615(6) | 0.2833(16) | 5.1(7) |
| C55 | -0.2413(6) | 0.3471(6) | 0.1399(16) | 5.3(8) |
| C56 | -0.1910(6) | 0.3146(6) | 0.0852(16) | 6.2(7) |
| D | 2.0886(2) | | | |
| E | 1.9325(3) | | | |
| F | 1.5011(3) | | | |
| | | | | |
| C61 | 0.1081(7) | 0.0252(8) | 0.4091(20) | 5.4(8) |
| C62 | 0.0899(7) | 0.0389(8) | 0.5467(20) | 7.4(9) |
| C63 | 0.1111(7) | 0.0019(8) | 0.6583(20) | 9.7(11) |
| C64 | 0.1506(7) | -0.0486(8) | 0.6323(20) | 6.6(8) |
| C65 | 0.1688(7) | -0.0622(8) | 0.4947(20) | 13.3(16) |
| C66 | 0.1476(7) | -0.0253(8) | 0.3831(20) | 9.1(12) |
| D | 5.6295(1) | | | |
| E | 1.4374(2) | | | |
| F | 0.7840(1) | | | |

(Continued on next page)

Table 4 continued

(b) Phenyl Hydrogen Atoms

| Atom | x | y | z | B |
|---|---|---|---|---|
| H12 | 0.2194 | 0.2163 | 0.1730 | 6.6 |
| H13 | 0.3285 | 0.2283 | 0.1815 | 8.0 |
| H14 | 0.3735 | 0.3055 | 0.3343 | 6.7 |
| H15 | 0.3093 | 0.3706 | 0.4786 | 5.7 |
| H16 | 0.2001 | 0.3585 | 0.4701 | 5.2 |
| D | 0.7464 | | | |
| E | 0.0653 | | | |
| F | 4.3346 | | | |
| | | | | |
| H22 | 0.1719 | 0.3673 | 0.1360 | 5.8 |
| H23 | 0.1913 | 0.4753 | 0.0755 | 6.1 |
| H24 | 0.1376 | 0.5581 | 0.1948 | 8.4 |
| H25 | 0.0644 | 0.5331 | 0.3745 | 6.7 |
| H26 | 0.0450 | 0.4251 | 0.4349 | 4.1 |
| D | 6.2444 | | | |
| E | 0.8100 | | | |
| F | 5.4597 | | | |

(Continued on next page)

Table 4 continued

| Atom | x | y | z | B |
|---|---|---|---|---|
| H32 | 0.2130 | 0.0797 | 0.3514 | 7.0 |
| H33 | 0.3180 | 0.0487 | 0.3241 | 8.9 |
| H34 | 0.3513 | 0.0002 | 0.1095 | 6.4 |
| H35 | 0.2798 | -0.0172 | -0.0779 | 7.1 |
| H36 | 0.1748 | 0.0138 | -0.0507 | 6.7 |
| D | 5.1618 | | | |
| E | 2.6205 | | | |
| F | 1.7313 | | | |
| H42 | -0.0535 | 0.2869 | -0.2741 | 5.4 |
| H43 | -0.0518 | 0.3837 | -0.4042 | 7.1 |
| H44 | -0.0531 | 0.4827 | -0.2822 | 9.0 |
| H45 | -0.0561 | 0.4848 | -0.0300 | 7.0 |
| H46 | -0.0577 | 0.3879 | 0.1001 | 4.5 |
| D | 0.0013 | | | |
| E | 1.5440 | | | |
| F | 5.2173 | | | |
| H52 | -0.1103 | 0.2968 | 0.3743 | 5.6 |
| H53 | -0.1958 | 0.3526 | 0.4720 | 9.5 |

(Continued on next page)

Table 4 continued

| Atom | x | y | z | B |
|---|---|---|---|---|
| H54 | -0.2789 | 0.3847 | 0.3232 | 5.3 |
| H55 | -0.2764 | 0.3610 | 0.0765 | 5.8 |
| H56 | -0.1908 | 0.3052 | -0.0213 | 6.2 |
| D | 2.0890 | | | |
| E | 1.9330 | | | |
| F | 2.5315 | | | |
| | | | | |
| H62 | 0.0611 | 0.0755 | 0.5608 | 7.6 |
| H63 | 0.0965 | 0.0132 | 0.7551 | 10.0 |
| H64 | 0.1643 | -0.0739 | 0.7148 | 6.9 |
| H65 | 0.1967 | -0.0987 | 0.4801 | 13.5 |
| H66 | 0.1613 | -0.0364 | 0.2859 | 9.1 |
| D | 5.6294 | | | |
| E | 1.4369 | | | |
| F | 1.8141 | | | |

D, E and F are the angles by which the coordinates of the individual atoms of the rigid body are rotated with respect to a set of axes X, Y, Z. The origin of these axes is placed at the centre of the ring with the X axis parallel to a*, the Z axis parallel to c, and the Y axis parallel to the line defined by the intersection of the plane containing a* and b* with the plane containing b and c.

Table 5

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

| Atom | $U_{11}$ | $U_{22}$ | $U_{23}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Fe1 | 0.036(2) | 0.046(2) | 0.065(2) | −0.003(2) | −0.005(3) | −0.004(3) |
| Fe2 | 0.034(2) | 0.047(3) | 0.067(3) | −0.002(2) | 0.000(3) | −0.006(3) |
| S1 | 0.042(4) | 0.039(4) | 0.082(5) | −0.003(4) | −0.007(5) | 0.006(5) |
| S2 | 0.044(4) | 0.049(5) | 0.092(7) | −0.001(4) | −0.006(5) | −0.012(5) |
| S3 | 0.046(5) | 0.060(5) | 0.072(5) | 0.014(4) | −0.004(4) | 0.004(5) |
| S4 | 0.056(5) | 0.055(5) | 0.085(6) | 0.013(5) | 0.015(5) | 0.000(5) |
| S5 | 0.032(4) | 0.042(4) | 0.082(6) | −0.002(4) | −0.011(4) | 0.001(5) |
| S6 | 0.030(4) | 0.042(4) | 0.079(5) | −0.004(4) | −0.005(4) | 0.005(4) |

## Table 6

## Interatomic Distances

| Atoms | Distance Å | Atoms | Distance Å |
|---|---|---|---|
| Fe1 - Fe2 | 2.780(6) | S4 - C4 | 1.73(3) |
| Fe1 - S3 | 2.253(9) | S5 - C5 | 1.69(3) |
| Fe1 - S4 | 2.208(9) | S6 - C6 | 1.81(3) |
| Fe1 - S5 | 2.238(9) | N1 - O1 | 1.23(3) |
| Fe1 - S6 | 2.195(9) | N2 - O2 | 1.20(3) |
| Fe2 - S1 | 2.163(8) | C1 - C2 | 1.40(3) |
| Fe2 - S2 | 2.181(9) | C3 - C6 | 1.26(3) |
| Fe2 - S5 | 2.340(8) | C4 - C5 | 1.27(3) |
| Fe2 - S6 | 2.335(8) | C1 - C11 | 1.46(3) |
| Fe1 - N1 | 1.51(3) | C2 - C21 | 1.45(3) |
| Fe2 - N2 | 1.62(3) | C3 - C31 | 1.49(3) |
| S1 - C1 | 1.67(3) | C4 - C41 | 1.56(3) |
| S2 - C2 | 1.74(3) | C5 - C51 | 1.51(3) |
| S3 - C3 | 1.76(3) | C6 - C61 | 1.43(3) |

## Table 7

## Intramolecular Angles

| Atoms | Angles | Atoms | Angles |
|---|---|---|---|
| S6 - Fe1 - S5 | 85.9(4) | N1 - Fe1 - S4 | 105(1) |
| S6 - Fe1 - S3 | 88.1(3) | N1 - Fe1 - S5 | 103(1) |
| S4 - Fe1 - S3 | 85.6(3) | N1 - Fe1 - S6 | 105(1) |
| S4 - Fe1 - S5 | 87.2(3) | N2 - Fe2 - S1 | 111(1) |
| S5 - Fe2 - S6 | 80.5(3) | N2 - Fe2 - S2 | 108(1) |
| S5 - Fe2 - S2 | 89.3(3) | N2 - Fe2 - S5 | 103(1) |
| S2 - Fe2 - S1 | 86.0(3) | N2 - Fe2 - S6 | 95(1) |
| S1 - Fe2 - S6 | 90.3(3) | | |
| Fe1 - S5 - Fe2 | 74.7(3) | Fe2 - S1 - C1 | 110(1) |
| Fe1 - S6 - Fe2 | 75.6(3) | Fe2 - S2 - C2 | 110(1) |
| Fe1 - Fe2 - S1 | 97.9(3) | S1 - C1 - C2 | 121(2) |
| Fe1 - Fe2 - S2 | 107.6(3) | S2 - C2 - C1 | 114(2) |
| Fe1 - Fe2 - S5 | 51.0(2) | S1 - C1 - C11 | 120(2) |
| Fe1 - Fe2 - S6 | 49.9(2) | S2 - C2 - C21 | 120(2) |
| Fe2 - Fe1 - S4 | 98.3(3) | Fe2 - S5 - C5 | 114(1) |
| Fe2 - Fe1 - S3 | 102.8(3) | Fe1 - S5 - C5 | 105(1) |
| Fe2 - Fe1 - S5 | 54.3(2) | Fe1 - S4 - C4 | 103(1) |
| Fe2 - Fe1 - S6 | 54.5(2) | S4 - C4 - C5 | 123(2) |
| Fe1 - N1 - O1 | 171(3) | S5 - C5 - C4 | 120(2) |
| Fe2 - N2 - O2 | 177(3) | S4 - C4 - C41 | 107(2) |
| N1 - Fe1 - Fe2 | 147(1) | S5 - C5 - C51 | 115(2) |
| N2 - Fe2 - Fe1 | 135(1) | Fe2 - S6 - C6 | 114(1) |
| N1 - Fe1 - S3 | 102(1) | Fe1 - S3 - C3 | 103(1) |

(continued on next page)

Table 7 continued

| Atoms | Angles | Atoms | Angles |
|---|---|---|---|
| Fe1 - S6 - C6 | 106(1) | S2 - S5 - S6 | 90.9(3) |
| S3 - C3 - C6 | 124(2) | S2 - S4 - S3 | 94.7(3) |
| S6 - C6 - C3 | 118(2) | S2 - S1 - S6 | 91.8(3) |
| S3 - C3 - C31 | 114(2) | S2 - S1 - S3 | 99.8(3) |
| S6 - C6 - C61 | 110(2) | S4 - S2 - S1 | 81.3(3) |
| | | S4 - S3 - S1 | 83.5(3) |
| S2 - S5 - S4 | 74.1(3) | S4 - S3 - S6 | 87.9(3) |
| S2 - S4 - S5 | 54.3(2) | S5 - S6 - S1 | 87.5(3) |
| S5 - S2 - S4 | 51.6(2) | S5 - S6 - S3 | 91.6(3) |
| S1 - S6 - S3 | 69.5(3) | S5 - S2 - S1 | 88.7(3) |
| S1 - S3 - S6 | 56.5(2) | S5 - S4 - S3 | 91.8(3) |
| S6 - S1 - S3 | 54.0(2) | S6 - S5 - S4 | 88.6(3) |

## Table 8

## Selected Intramolecular Non Bonded Contacts

| Atom 1 | Atom 2 | Distance |
|---|---|---|
| S1 | S2 | 2.96(1) |
| S3 | S6 | 3.09(1) |
| S4 | S5 | 3.07(1) |
| S1 | S6 | 3.19(1) |
| S1 | S3 | 3.58(1) |
| S2 | S5 | 3.18(1) |
| S2 | S4 | 3.77(1) |
| S3 | S4 | 3.03(1) |
| S5 | S6 | 3.02(1) |
| CL1 | CL2 | 2.76 |
| CL1 | Fe1 | 6.60(3) |
| CL1 | Fe2 | 6.52(3) |
| O1 | Fe1 | 2.73(3) |
| O2 | Fe2 | 2.81(3) |
| N2 | H62 | 2.83(3) |
| O2 | H62 | 3.03(3) |
| S2 | H52 | 2.82(1) |
| H26 | H46 | 3.97 |
| H12 | H32 | 3.36 |
| H12 | C32 | 3.43 |

## Table 9

## Intermolecular Contacts

| Atom 1 | Atom 2 | Symmetry Operation on2 | Distance |
|---|---|---|---|
| O1 | H63 | $\bar{x},\bar{y},z-1$ | 2.31(3) |
| O1 | H36 | $\bar{x},\bar{y},z$ | 2.81(3) |
| O2 | H42 | x,y,z+1 | 2.54(3) |
| O2 | H14 | 1/2+x-1, 1/2-y, 1/2+z | 2.83(3) |
| O2 | S4 | x,y,z+1 | 3.39(3) |
| CL1 | H65 | $\bar{x},\bar{y},z$ | 2.81(3) |
| CL1 | H22 | 1/2+x-1, 1/2-y, 1/2+z | 3.05(4) |
| CL2 | H16 | 1/2+x-1, 1/2-y, 1/2+z-1 | 3.08(4) |
| H13 | H42 | 1/2+x, 1/2-y, 1/2+z | 2.63 |
| H13 | H53 | 1/2+x, 1/2-y, 1/2+z-1 | 2.68 |
| H14 | H42 | 1/2+x, 1/2-y, 1/2+z | 2.73 |
| H16 | H35 | 1/2-x, 1/2+y, 1/2+z | 2.71 |
| H24 | H46 | $\bar{x},\bar{y}+1, z$ | 2.27 |
| H25 | H26 | $\bar{x},\bar{y}+1, z$ | 2.61 |
| H25 | H43 | x,y+1,z+1 | 2.76 |
| H26 | H43 | x,y,z+1 | 2.75 |
| H32 | H55 | 1/2+x, 1/2-y, 1/2+z | 2.49 |
| H34 | H44 | 1/2+x, 1/2-y, 1/2+z | 2.35 |
| H36 | H63 | x,y,z-1 | 2.51 |
| H36 | H54 | 1/2+x, 1/2-y, 1/2+z-1 | 2.66 |
| H44 | H44 | $\bar{x},\bar{y}+1,z$ | 2.43 |
| H45 | H45 | $\bar{x},\bar{y}+1,z$ | 2.53 |
| H56 | C13 | 1/2+x-1, 1/2-y, 1/2+z-1 | 2.60 |
| H56 | C14 | 1/2+x-1, 1/2-y, 1/2+z-1 | 2.68 |

## Table 10

## Least Squares Planes

(1) Atoms defining plane: S3, S4, S5, S6

Equation of plane $0.5431X + 0.6446Y + 0.5380Z - 2.8810 = 0$

| Atom | Deviation from Least Squares Plane (Å) |
|---|---|
| S3 | -0.044 |
| S4 | 0.045 |
| S5 | -0.037 |
| S6 | 0.037 |
| Fe1 | -0.534 |

(ii) Atoms defining plane: S1, S2, S5, S6

Equation of plane $-0.3039X - 0.0461Y + 0.9561Z - 2.4151 = 0$

| Atom | Deviation from Least Squares Plane (Å) |
|---|---|
| S1 | -0.114 |
| S2 | 0.117 |
| S5 | -0.103 |
| S6 | 0.100 |
| Fe2 | 0.563 |

## Table 11

## Some Fe-S Distances in Dithiolene Complexes of Iron

| Compound | Fe-S | $Fe-S_{bridge}$ | S-Fe-S | Reference |
|---|---|---|---|---|
| $[Fe(NO)S_4C_4(CN)_4]^{2-}$ | 2.28 | ----- | | 48 |
| $\{Ph_3POFe[S_2C_2(CF_3)_2]_2\}^{-}$ | 2.23 | ----- | | 49 |
| $[FeS_4C_4(CN)_4]_2^{2-}$ | 2.22 | 2.28 | 90.0 | 47 |
| $\{Fe[S_2C_2(CN)_2]_3\}^{2-}$ | 2.26 | ----- | 88.0 | 15 |
| $[Fe(NO)_2(S_2C_2Ph_2)]_3$ | 2.21 | 2.23<br>2.34 | 87.1 | This work |

## Table 12

## The 1, 2-Diphenyl - Dithiolene Ligand Geometry

| $S - C$ | $C - C$ | $C - C_{phen}$ | $M - S - C$ | $S - C - C$ | $S - C - C_{phen}$ | $C_{phen} - C - C$ | References |
|---|---|---|---|---|---|---|---|
| 1.69 | 1.34 | 1.53 | 109 | 120 | 115 | 125 | 28,29 |
| 1.69 | 1.42 | 1.48 | 110 | 119 | 117 | 124 | 31,32 |
| 1.73 | 1.31 | 1.48 | 106 | 120 | 115 | 125 | This work |

Bond distances are in Angstroms, bond angles in degrees.

7

Fig. 2

A Perspective View of $Fe_2(NO)_2(S_2C_2Ph_2)_3$

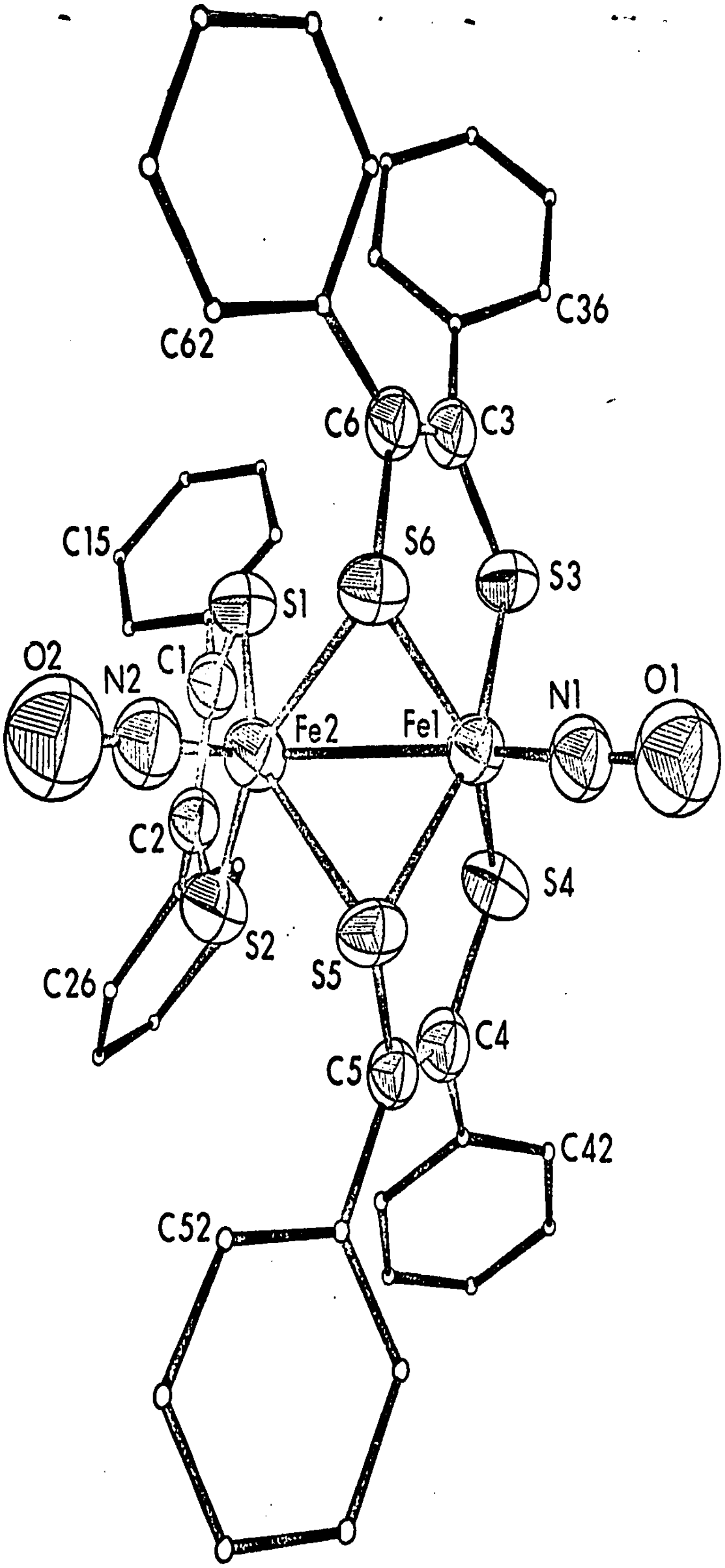
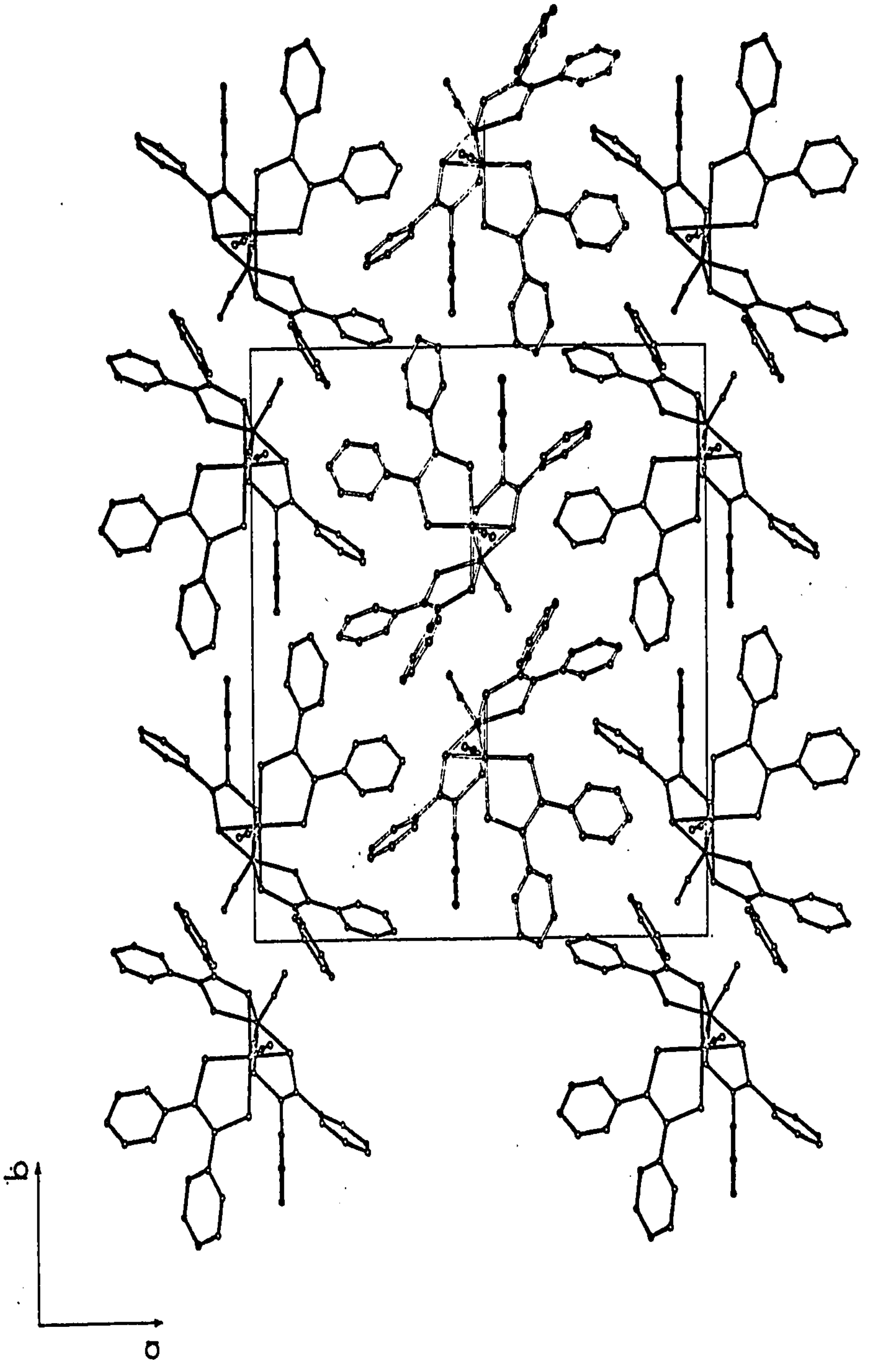

C62
C36
C6
C3
C15
S6
S3
S1
O2
N2
C1
Fe2
Fe1
N1
O1
C2
S4
S2
S5
C26
C4
C5
C42
C52

Fig. 3

Unit Cell Contents Projected on to [a][b] Plane


b
a

7

# DISCUSSION

The geometry of the complex is shown in Fig. 2. The six sulphur atoms form a distorted trigonal prism. The distortion takes the form of the elongation of two sulphur-sulphur distances to 3.77 and 3.58 Å from the average distance of 3.08 Å found between the other sulphur atoms. Thus the prism has only two square faces, near the centre of which, sit iron atoms. Each iron atom is pentacoordinated, neglecting any iron-iron interaction, the coordination polyhedron being a square based pyramid in which the four sulphur atoms of the square face form the base and a nitrosyl group the apex. Both iron atoms are displaced 0.56 Å out of the plane containing the four sulphur atoms toward the apical nitrosyl group. An alternative description is to consider the two basal planes of the two square based pyramids as being joined along the S5-S6 line at a dihedral angle of 71.5°.

Despite the fact that both iron atoms have the same coordination polyhedron, the environment of each iron atom is distinctly different. One of the dithiolene ligands is coordinated only to Fe2, while the other two are formally attached to Fe1. However, one sulphur atom from each of these two ligands also forms a bond to Fe2, making these two ligands bridging. The bond to Fe2, however, is weaker than to Fe1, and this is reflected in the different iron-sulphur bond lengths in the bridging system. The average Fe1-S bridge bond length is 2.22 Å while the Fe2-S bridge bond length is 2.34 Å, significantly longer.

Although both metal ions are formally electron deficient, and this would be relieved to some extent by the formation of an iron-iron bond, the internuclear distance of 2.780 Å in this compound is toward the long end of the range of iron-iron bond distances that have been observed in various complexes, ranging from 2.43 Å in $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$[45] to 3.05 Å in $[Fe(NO)_2I]_2$.[46] It remains, therefore, a valid question as to whether or not an iron-iron bond exists in this complex.

Dithiolene ligands acting as sulphur bridges between iron ions have also been observed in the anion $[Fe_2S_4C_4(CN)_4]_2^{2-}$ whose structure was determined by Hamilton and Bernal.[47] In this anion it was postulated that there was no iron-iron bond, interaction between unpaired electrons in the Fe(III) ions taking place via the sulphur bridges. The iron-iron separation was 3.08 Å and Fe - S bridge - Fe angle was 81°.

Dahl et al have pointed out, that the Metal - Bridge - Metal angle is sensitive to the presence or absence of a metal-metal bond.[46] In complexes containing a metal-metal bond the angle tends to be quite acute, ranging from 68° - 74°, whereas in the absence of a bond they are much larger, usually close to 90°. In this compound, the two Fe1 - S bridge - Fe2 angles average 75.1° which is very close to that of compounds in which there is a metal-metal bond.

It is concluded then, that the shortening of the iron-iron distance from the nonbonded contact of 3.08 Å in

$[FeS_4C_4(CN)_4]_2^{2-}$ to 2.780 Å, together with the contraction of the Fe - S bridge - Fe angle, is indicative of the presence of an iron-iron bond in this compound, albeit a weak one.

The two long sulphur-sulphur contacts between S2 and S4, and S1 and S3 must be considered as being due to repulsive interaction between these pairs of atoms. In the monomeric tris dithiolene complexes which have trigonal prismatic geometry, it has been suggested that interligand sulphur-sulphur bonding is a significant factor in stabilising the geometry[28,29,31,35]. If the sulphur-sulphur interactions are attractive, then this compound could gain extra stability by formation of a trigonal prism of S atoms. If the S2 - S4 and S1 - S3 distances shortened to 3.1 Å, the Fe - Fe distance would become 2.55 Å which would not be too short for an iron-iron bond. Also, there are no steric interactions between phenyl rings attached to C3 and C4 with those attached to C1 and C2, preventing the sulphur atoms from moving closer together. The closest approach of two atoms in the above entities is 3.43 Å between H12 and H32. It would appear, therefore, that interligand S - S bonding assumes its maximum importance only if there is a single metal cation at the centre of the trigonal prism.

There are two iron-sulphur bond distances in the complex. The iron-sulphur distances within the five-membered rings formed by the metal ion and the dithiolene ligands average 2.21 Å which is similar to that found in other dithiolene complexes of iron[15, 47-49]. This information is summarised in Table 11.. The iron-sulphur bonds in the chelate ring attached to Fe2 may be slightly shorter than in those attached to Fe1, indicating more Fe - Sπ-bonding in the Fe2 - S1 - S2 system,but differences of this magnitude cannot be distinguished with this data set. The other iron-sulphur distance is the Fe2 - $S_{bridge}$ bond length, which is 2.34 Å and definitely longer than any of the other iron-sulphur bond lengths in the complex. This situation is similar to that found by Bernal and Hamilton[47] in $[FeS_4C_4(CN)_4]_2^{2-}$, in which the Fe - $S_{bridge}$ bond length is long to the sulphur atom which is part of the chelate ring attached to the other metal ion.

Thus the iron ions are not symmetrically bridged by the sulphur atoms, giving rise to two iron environments which agrees with the observation of two iron sites in the Mössbauer spectrum. The coordination of solvent is definitely not responsible for the difference between the two iron environments, as has been suggested elsewhere[40], since the closest approach of either of the two chlorine atoms to an iron atom is 6.52 Å.

If this structure were maintained in solution after reduction to the monoanion, it could explain the observation of the triplet signal in the E.S.R. spectrum since it is possible to envisage that the extra electron could be localised on one half of the dimer, probably on Fe1 since it is formally the most electron deficient. If this were the case, then the electron could only interact with one $^{14}N$ nucleus, giving rise to a triplet signal. However, this would not explain the observation of one iron site in the Mössbauer spectrum of the monoanion[14] and probably a separate crystal structure of the monoanion will be necessary to resolve this problem.

The average geometry of the 1,2-diphenyldithiolene ligand is similar to that which has been found in two other compounds in which it is present[28,29,31,32]. This geometry is summarised in Table 12.

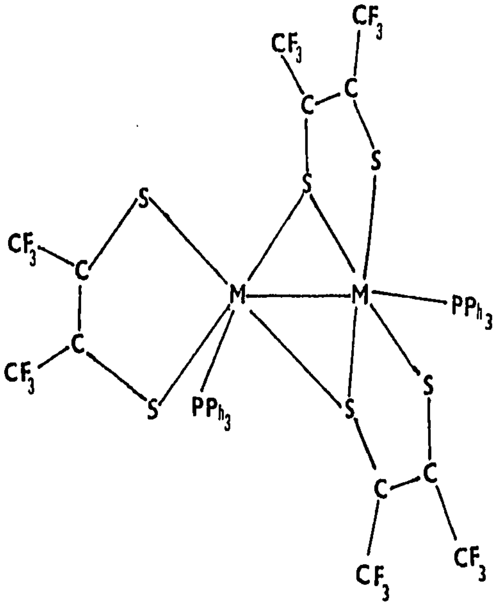
Also of interest is the mode of attachment of the nitrosyl group. The nitrosyl group has been found to coordinate in both linear and bent manner. These two different types of bonding have been regarded as being due to the amphoteric nature of $NO^+$ [50]. Compounds in which the $NO^+$ acts as a Lewis base, donating a pair of $\sigma$ electrons to the metal using an sp hybrid on nitrogen, are characterised by M - N - O angles of 180° and short metal-nitrogen bond lengths due to extensive $\pi$ back-bonding from the metal to the NO moiety. Compounds in which the $NO^+$ acts as a Lewis acid, accepting electrons from the metal using an $sp^2$ hybrid orbital, have M - N - O angles close to 120° and longer M - N bond lengths.

In $[Fe_2(NO)_2(S_2C_2Ph_2)_3]$, neither Fe - N - O angle differs significantly from 180°. The Fe - N distances average 1.56 Å and the N - O distance is 1.22 Å. These distances are similar to others found for iron-nitrosyl bonds where the nitrosyl is attached in an essentially linear fashion[48,51,52].

Clearly in this compound there is significant $\pi$-bonding between the iron and the nitrosyl group.

At the time this structure was determined, no other compounds were known which possesed this type of bridging, in which two dithiolene ligands chelating the same metal ion form sulphur bridges to a second metal ion. Recently however, the structure of dicarbonyl bis (triphenyl phosphine) tris (toluene-3,4-dithiolate) diiridium(III) was published[53]. This compound contains the same type of dithiolene bridging and the variation of bond lengths in the bridging unit is the same as in the iron dithiolene complex. The Ir - S distances from one iridium to the bridging sulphur atoms, which form part of the chelate systems attached to the other iridium atom , are longer than all other Ir - S bond lengths. There is no Ir - Ir bond in the compound and the Ir - $S_{bridge}$ - Ir angle is 98.4°.

This type of bridging has also been postulated to explain the n.m.r. spectrum of $Mo_2(tdt)_5$ which indicates four distinct ligand environments[54]. This type of bridging may also be present in the two compounds $[M_2(PPh_3)_2(S_2C_2(CF_3)_2)_3]$ (M = Rh, Ir), prepared by McCleverty *et al*[55], since it would readily explain the $^{19}F$ n.m.r. spectrum of these complexes. The spectrum consisted of two quartets (1 : 3 : 3 : 1) and a singlet. The relative areas of these signals are 1 : 1 : 1 which have been postulated as having arisen from three different pairs of $CF_3$ groups, two of which were mutually coupled. Two possibilities exist: either there are three chemically distinct sulphur ligands in the compounds or the $CF_3$ groups are nonequivalent in two of them. If the latter were the case, then the structure 4 could be postulated, with bridging dithiolene ligands of the type found in $[Fe_2(NO)_2(S_2C_2Ph_2)_3]$, making the $CF_3$ groups in these ligands nonequivalent. It is possible, therefore, that $[Fe_2(NO)_2(S_2C_2Ph_2)_3]$ is only one of a family of compounds having this type of bridging system.



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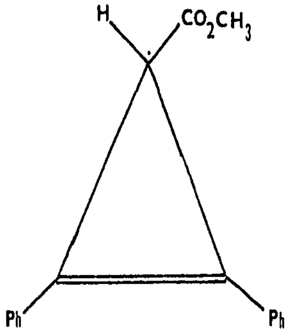
# Chapter Two

## The Crystal and Molecular Structures of 1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene.

## INTRODUCTION

The photodimerisation of 3 carbomethoxy-1,2-diphenylcyclopropane 5 was carried out in this department by Dr. S. Masamune and S. Takada[56]. Two products were obtained which were tentatively assigned *cis*- and *trans*- tricyclic structures 6 and 7 on the basis of their n.m.r. and u.v. spectra. However, these physical data are not sufficient to distinguish between the four symmetrical tricyclo[3.1.0.0$^{2,4}$]hexane and two cyclohexa-1,4-diene structures which are possible for the two photodimers. The X-ray crystal structure determinations of both compounds were undertaken to establish the stereochemistry of these compounds and to determine the exact geometry of the novel tricyclic systems. The crystal structure of the



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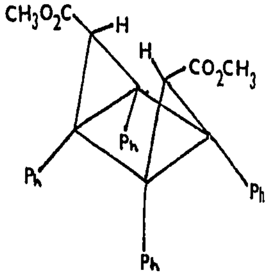

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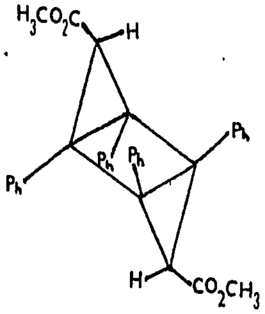

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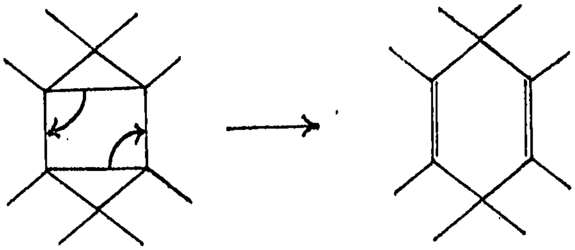
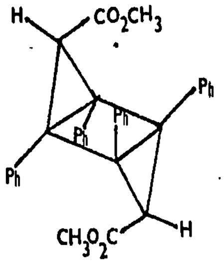
tricyclic compound 7 will be discussed in the next chapter.

Raman spectra of the two compounds in the region 1600 - 1700 $cm^{-1}$ indicated that the assignment of the tricyclic structures to 6 was incorrect. Both spectra exhibited intense peaks at 1600 $cm^{-1}$ which could be attributed to the carbonyl group, while 6 showed an additional strong band at 1680 $cm^{-1}$, a value consistent with the C = C ring stretching frequency of a cyclohexa-1,4-diene structure[57]. The X-ray analysis of this compound was continued because the stereochemistry of the compound was still unestablished and also because the conformation of cyclohexa-1,4-diene itself has been the subject of some controversy.

The photodimer may be either *syn*- or *anti*- 1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene, if it is considered as being formed by the rearrangement of a tricyclic compound.



In addition to 6 and 7, two other compounds 8 and 9 could be formed in the photo dimerisation.



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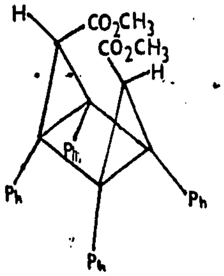

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It can be seen then that 6 and 9 would rearrange to give the *syn* product while 7 and 8 would give the *anti*- cyclohexadiene derivative, assuming a photochemical mechanism.

The conformation of cyclohexa-1,4-diene has been studied by various methods. Gerding and Haak assigned the molecule a planar structure with $D_{2h}$ symmetry on the basis of its vibrational Raman and infrared spectrum[58]. Monsotori and Weber came to the same conclusion from rotational Raman data[59]. The conclusions of Gerding and Haak were later confirmed by Stidham[57]. A more recent study by R.C. Lord and J. Laane in the far infrared region also favored a planar structure[60]. Although the results of these investigations indicate that the planar conformation may be the most stable, they are not conclusive and cannot rule out the possibility that small amounts of a boat form with $C_{2v}$ symmetry is present, nor a form rapidly interconverting between $C_{2v}$ and $C_{2h}$ (chair form) symmetry through the planar $D_{2h}$ symmetry[57].

1,4-Dichlorocyclohexa-1,4-diene has been found to have a measurable dipole moment of 0.3 D.U., indicating that in this compound at least the cyclohexa-1,4-diene ring is non-planar[61]. Dipole moment measurements on cyclohexadiene itself suggested a small dipole moment, but the experimental error was too large to distinguish between the planar and boat conformations[62].

Herbstein concluded, from calculations in which the angle strain and steric interaction between hydrogens was minimised, that the boat form was the most stable conformation, and that the dihedral angle between the two halves was approximately 140°[63]. However, Favini *et al*, taking a similar approach, but introducing an extra factor, due to torsional strain from rotation around single bonds, found that the planar conformation was the most stable[64].

Two electron diffraction studies of cyclohexa-1,4-diene have been carried out[65,66]. Dallinga and Toneman[65] considered chair, boat, planar and skew conformations in the initial stages of their refinement, but since the refinement of the boat, skew and chair models did not converge, only the planar model was pursued to completion. The conclusion they drew from their calculations was that the molecule was essentially planar but that other conformations, especially the chair form, could not be precluded with certainty. However, the suggested deviations from the plane were $\leqslant$ 0.05 Å.

On the other hand, Oberhammer and Bauer[66], obtained a structure with a boat conformation. The dihedral angle between the two halves of the molecule was 159.3° corresponding to a deviation of 0.23 Å from the diene plane for the methylene

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type carbon atoms.

Crystal structure determinations to date have not been very helpful in resolving the problem. The crystal structures of 1,4-dicarbomethoxycyclohexa-1,4-diene has been determined in two forms[67,68]. The molecule was found to be planar, but due to the poor quality of the data, small deviations from planarity would not have been detected. However, since the molecule occupies an inversion centre in the unit cell, it is definitely not in the boat conformation, unless disordered. The structure of 1,4-cyclohexadiene-1-glycine was also found to be planar within experimental error[69], but again, small deviations from planarity to either the boat or chair form could not be detected.

In view of the contradictory conclusions arrived at regarding the structure of the cyclohexa-1,4-diene ring, the X-ray crystal structure determination of 1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene was undertaken in order to provide additional evidence concerning the planarity of this ring system.

## EXPERIMENTAL

1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene crystallises as transparent needles. A suitable crystal was chosen and examined by photographic methods (dimensions 0.15 mm x 0.07 mm x 0.07 mm). Weissenberg photographs for the $h0\ell$, $h1\ell$ and $h2\ell$ layers were obtained together with precession photographs for the $0k\ell$ and $hk0$ layers. The Laue symmetry was found to be 2/m and the crystals to be monoclinic. The following systematic absences:

(i) $hk\ell$ $h + k + \ell = 2n + 1$ implying a body centered cell

(ii) $h0\ell$ $h = 2n + 1$ implying an a glide perpendicular to b.

defined the space group as either I2/a which is centrosymmetric or Ia which is non-centrosymmetric.

The lattice parameters were obtained by the least squares refinement of the $2\Theta$ values for several high angle reflections, these having been accurately measured using a PICKER manual four circle diffractometer. The results obtained were: a = 20.052(1); b = 5.756(1); c = 22.782(2); and $\beta$ = 95.73°(1).

The density obtained experimentally by flotation in aqueous potassium iodide solution was 1.26 gm $cm^{-3}$, while the calculated density for four molecules of molecular weight 400 in a cell of volume 2616.24 $\mathring{A}^3$ was 1.27 gms $cm^{-3}$. The density therefore requires that the molecule occupies a special position, either on the two-fold axis or on a centre of symmetry, if the space group is I2/a, while there are no restrictions if the space group is Ia.

Intensity data were collected on a PICKER manual diffractometer using graphite crystal monochromated CuKα radiation, the crystal being mounted with the b axis along the $\phi$ axis of the diffractometer. The intensity data were collected using the coupled $\omega/2\Theta$ scanning technique. The scan width was 2° with a scan rate of 2°/min. and a $2\Theta$ maximum of 120°. A stationary background count was taken for 30 seconds on each side of the scan.

Before the data collection was complete, the crystal was inadvertently lost, and it was necessary to complete the intensity measurements with a second crystal. The intensities of six reflections were measured periodically throughout the data collection and with neither crystal was there any evidence of decomposition taking place.

During the data reduction process, reflections were rejected if $I \leqslant 0$ or if $I \leqslant 3\sigma$. Of the 1940 reflections collected 875 were rejected in this way, giving 1065 observed reflections.

An absorption correction was not applied, the linear absorption coefficient for this compound being only 6.67 $cm^{-1}$. The data were corrected for Lorentz and polarisation effects and structure factor amplitudes and standard deviations calculated, using an uncertainty factor[70] p of 0.03.

## SOLUTION OF STRUCTURE AND REFINEMENT

The structure was solved by direct methods using the programmes FAME and MAGIC, to produce E statistics and to carry out the symbolic addition procedure, respectively. Since MAGIC was not programmed to carry out the symbolic addition procedure for a body centred cell, it was necessary first of all to transform the indices of the reflections to those of an A centred cell which had common [a] and [b] axes. This was accomplished by means of the following transformation matrix:

$$\begin{bmatrix} h \\ k \\ \ell \end{bmatrix}_A = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{bmatrix} \begin{bmatrix} h \\ k \\ \ell \end{bmatrix}_I$$

The cell parameters for the A centred cell were $a = 20.052$; $b = 5.756$; $c = 31.818$; $\beta = 134.568$. This cell was not used in the subsequent refinement because of the very large $\beta$ angle.

Normalised structure factors were calculated, using the method described on page 20. The distribution of the normalised structure factors is dependent upon whether or not the space group is centrosymmetric. The distribution obtained is shown below and compared with the theoretical values.

The distribution for this structure is in very close agreement with the theoretical distribution for a centrosymmetric space group and from this point on the space group I2/a (A2/a for FAME and MAGIC) was assumed to be the correct

| | This Structure | Centro-symmetric | Non-centro-symmetric |
|---|---|---|---|
| $<\|E\|>$ | 0.820 | 0.798 | 0.886 |
| $<\|E\|^2>$ | 0.988 | 1.000 | 1.000 |
| $<\|\|E\|^2 - 1\|>$ | 0.958 | 0.968 | 0.736 |
| Percentage $\|E\|>1$ | 28.45 | 32.00 | 37.00 |
| Percentage $\|E\|>2$ | 4.77 | 5.00 | 1.80 |
| Percentage $\|E\|>3$ | 0.39 | 0.30 | 0.01 |

one.

Woolfson has pointed out that the greatest weakness of the symbolic addition method is in the early stages of its application, when single sign relationships must be relied upon to determine new signs[71]. For this reason, the initial input to the symbolic addition programme MAGIC consisted only of those reflections with very high E values (greater than 2.0), since any relationships between these will lead to new signs which have a high probability of being correct.

The following seven reflections which were of large $|E|$ were assigned symbols and used to initiate the symbolic addition procedure:

| I2/a | | | A2/a | | | E | Symbol |
|---|---|---|---|---|---|---|---|
| -9 | 2 | 13 | -9 | 2 | 22 | 3.127 | A |
| 4 | 1 | 19 | 4 | 1 | 15 | 2.709 | B |
| -9 | 3 | 12 | -9 | 3 | 21 | 4.046 | C |
| 14 | 2 | 6 | 14 | 2 | -8 | 3.014 | D |
| 17 | 2 | 5 | 17 | 2 | -12 | 2.668 | E |
| 2 | 1 | 19 | 2 | 1 | 17 | 3.700 | F |
| -3 | 5 | 2 | -3 | 5 | 5 | 3.244 | G |

A new phase was not accepted if the probability of it being correct was below 0.990. After several new phases had been determined, this criterion was relaxed slightly but the acceptance level was not allowed to drop below 0.987. Twenty-two new signs were determined bringing the total to 29. These were used as input to MAGIC using the full set of data with $|E| \geqslant 1.500$. The probability acceptance level was set initially at 0.990 and allowed to fall slowly as the sign determination proceeded to 0.982. 133 more signs were determined giving a total of 162 phases determined in terms of the seven starting symbols.

Throughout the determination, relationships between the symbols became apparent. For example, if a sign was determined as +A with a probability of 0.9 and also as +B with a probability of 0.8, then there is an indication that AB is positive with a probability of 0.72. These relation-

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ships, are summarised below:

| Symbol | Number of indications of + with probability ≥ 0.90 | Number of indications of - with probability ≥ 0.90 |
|---|---|---|
| 1. CEF | 3 | 0 |
| 2. CDG | 1 | 0 |
| 3. BF | 2 | 2 |
| 4. BCDFG | 0 | 3 |
| 5. ADFG | 1 | 87 |
| 6. ACF | 0 | 2 |
| 7. ACDEG | 0 | 17 |
| 8. ABDG | 4 | 2 |

It was obvious that only relationships 5, ADFG = -, and 7, ACDEG = -, could be used with any confidence to reduce the number of possible solutions to a manageable number. Reflections -9 2 22 and -9 3 21 (A2/a) were used to determine the origin, both being given + signs. This, of course, made symbols A and C both positive, so that relationships 5. and 7. reduced to DFG = - and DEG = -. Therefore, F and E were of the same sign. B remained unknown. Using the above relationships between D, F and G and placing no restrictions on B, a total of eight possible solutions was obtained. These are given in the table below:

| Solution Number | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| 1. | + | + | + | - | + | + | + |
| 2. | + | + | + | + | + | + | - |
| 3. | + | - | + | - | + | + | + |
| 4. | + | - | + | + | + | + | - |
| 5. | + | + | + | + | - | - | + |
| 6. | + | + | + | - | - | - | - |
| 7. | + | - | + | + | - | - | + |
| 8. | + | - | + | - | - | - | - |

From the less certain relationship BCDFG = -, B = + was obtained, and so the three dimensional E maps (Fourier maps in which the E's whose phases had been determined were used as coefficients) for solutions 1, 2, 5 and 6 were computed first.

In the E map corresponding to solution 2. i.e. A = B = C = D = F = +, G = -, a six-membered ring occupying a centre of symmetry at the cell origin was easily detected.

Further inspection of this map revealed the positions of all the nineteen carbon and oxygen atoms in the asymmetric unit. The coordinates of these atoms were used to compute structure factors using scattering factors for carbon and oxygen calculated from Cromer's coefficients. A residual R factor of 0.273 was obtained which reduced to 0.097 after three cycles of full matrix least squares refinement.

An electron density difference map computed at this point in the refinement revealed the positions of all the hydrogen atoms in the asymmetric unit apart from the three methyl hydrogens.

These eleven hydrogen atoms were now included in the structure factor calculations and least squares refinement, their contribution to the overall scattering being calculated from the scattering factors of Mason and Robertson[43]. Two cycles of refinement reduced the R factor to 0.082, but the positions of the hydrogen atoms of the methyl group were not resolved in a difference Fourier calculated from this data. The difference Fourier was recalculated using only the data with sin $\theta/\lambda \leqslant 0.35$, since this data is more sensitive to the light atom positions than the high order reflections because the scattering power of the light atoms falls off more rapidly than that of heavier atoms as sin $\theta/\lambda$ increases and the high angle data are particularly sensitive to errors in thermal parameters. From the resulting difference map the positions of the three hydrogens were located and included in all remaining structure factor calculations and least squares refinement cycles.

In two more cycles of full matrix least squares refinement the R factor fell to 0.070 and an electron density difference map calculated at this point gave evidence of anisotropic thermal motion for many of the carbon and oxygen atoms. Consequently, the carbon and oxygen atoms were allowed to refine anisotropically and in four more cycles the R factor converged at 0.043.

Inspection was then made of the observed and calculated structure amplitudes, where it was seen that the observed structure amplitudes with low sin $\theta/\lambda$ and relatively large magnitude were consistently smaller than the calculated structure factors, indicating that the crystals suffered from secondary extinction and that a correction was necessary. The calculated structure factors were modified by the term 1/ (1 + $\beta$ (2$\theta$). C.I.) suggested by Zachariasen[72]. I was the raw intensity, C was the secondary extinction parameter, which became a variable parameter in the subsequent refinement, and $\beta(2\theta)$ accounts for the angular variation of the extinction correction. This latter term could be split into two components, a polarisation term and an absorption term.

$$\beta(2\theta) = \frac{(1 + \cos^2 2\theta m)(\cos^2 2\theta m + \cos^4 2\theta)}{(\cos^2 2\theta m - \cos^2 2\theta)^2} \times \frac{A^{*\prime}(2\theta)}{A^{*}(0)}$$

where $2\theta m$ was the monchromator angle. The second term was a ratio of absorption factors at $2\theta$ and at $2\theta = 0$. Since absorption was negligible in this crystal, this ratio was assumed to be 1 and the calculated structure factors were corrected for the polarisation part of the extinction correction only.

When this correction was applied, the refinement converged in two cycles to $R_1 = 0.040$ and $R_2 = 0.042$. The largest peak in an electron density difference map, computed at the end of the refinement, was 0.17 electrons per $\mathring{A}^3$.

Of the 162 phases determined with the $\Sigma_2$ relationship, only four were incorrect, and these all occurred in the later stages of the sign determination.

## RESULTS

The observed (|Fo|) and calculated (|Fc|) structure amplitudes (electrons x 10) are listed in Table 13. The final atomic coordinates for all atoms and isotropic temperature factors for the hydrogen atoms are given in Table 14, the anisotropic temperature factors for the carbon and oxygen atoms are listed in Table 15. Interatomic distances and angles are listed in Tables 16 and 17.

A diagram of the molecule is shown in Fig. 4, and a packing diagram with the molecules projected on to the [a][c] plane is shown in Fig. 5. Some selected views of the molecule along certain bonds are given in Fig. 6.

# Table 13

## Observed and Calculated Structure Amplitudes (electrons x 10)

```
   H   L  FOBS  FCAL      H   L  FOBS  FCAL      H   L  FOBS  FCAL      H   L  FOBS  FCAL      H   L  FOBS  FCAL
   **K =    0****         4  22   182   171    -11   2   140   151      0  21   157   141     13  16   148   127
 -22   4   340   313      4  24   280   249    -11   4   256   247      0  25   171   195     14   3   442   430
 -22   6   349   341      6   0   775   784    -11   6   124   114      1   0   101   124     14   5   571   571
 -20   4   421   411      6   2  1196  1149    -11   8   714   714      1   2  1101  1119     14   7   191   155
 -20   6   531   529      6   4   139   154    -11  10   154   163      1   4    95    79     14   9   210   191
 -20   8   129   124      6   6  1164  1113    -11  14   171   131      1   6   349   353     15   0   503   492
 -20  10   173   173      6   8  1753  1671    -11  18   177   196      1   8   473   491     15   2   161   146
 -18   6   113    76      6  10   457   461    -11  22   106   117      1  10    79    75     15   6   137   149
 -18   8   350   359      6  12   479   481    -10   1   209   194      1  14   389   381     16   1   355   391
 -18  12   182   189      6  14   324   303    -10   3   302   282      1  16   127   113     16   5   172   200
 -16   4   155   148      6  20   384   369    -10   5   110    98      1  18   265   259     16  11   133   135
 -16   6   237   232      6  22   302   326    -10   9   104    93      1  20   449   441     16  13   123   120
 -16   8   359   345      8   0   490   482    -10  11   324   316      1  24   111   132     17   0   178   167
 -16  10   129   131      8   2   730   722    -10  17   149   155      2   1   784   824     17   6   224   277
 -16  14   293   302      8   4   209   208    -10  19   293   277      2   3   249   240     17  14   129   126
 -16  16   114    85      8   6   543   509     -9   2   311   313      2   5   439   455     18   1   215   222
 -16  18   106   190      8   8   468   474     -9   6   536   537      2   9   665   649     18   3   140   176
 -14   2   401   395      8  14   299   284     -9   8   449   450      2  11   469   472     18   5   160   214
 -14   4   176   194      8  16   264   279     -9  10   244   230      2  15   215   202     18   9   115   125
 -14   6   319   341      8  18   382   375     -9  12   288   286      2  19   612   604     19   0   382   373
 -14   8   348   335      8  22   234   267     -9  14   360   358      2  21   203   206     19   4   125    93
 -14  10   141   137     10   0   581   591     -9  16   235   228      2  23   158   165     20   1   250   256
 -14  12   624   620     10   2   136   118     -9  18   153   166      3   0   254   264     20   3    99    42
 -14  14   541   539     10   4    55    89     -9  24   104   105      3   2   778   816     21   4   145   131
 -14  16   271   285     10   6   463   449     -8   1   928   951      3   4  1745  1740        **K =    2****
 -12   2   232   218     10  10   249   236     -8   3   870   879      3   6   723   733    -21   1   120   133
 -12   4   116   121     10  12   524   493     -8   5   531   513      3   8   341   358    -21   5   113   111
 -12   6   672   652     10  14   217   219     -8   7   131   138      3  12   180   168    -20   6   189   203
 -12   8   450   458     10  18   177   161     -8  13   118   115      3  14   213   215    -19   1   247   249
 -12  10   216   209     10  20   206   208     -8  15   116    92      3  16   233   231    -19   3   112   105
 -12  12   206   221     12   0   288   293     -8  17   155   170      3  20   171   154    -19   7   106    85
 -12  16   337   355     12   2   129   115     -8  19   114   125      4   1  1141  1153    -19  11   130   135
 -12  22   130   134     12   4   565   523     -8  21   148   178      4   3   899   914    -19  13   162   143
 -10   2   147   171     12   6   201   212     -8  23   133   116      4   5   189   190    -18   4   151   200
 -10   4    57   106     12  10   142   120     -7   2   816   829      4   7   192   172    -18   6   437   438
 -10   6   299   298     12  12   140   141     -7   4   237   234      4   9   480   466    -18  10   194   193
 -10  10   592   576     12  14   143   137     -7   6   417   428      4  11   292   288    -18  12   104   107
 -10  12   137   155     12  16   171   134     -7   8   838   856      4  13   171   170    -17   5   292   320
 -10  18   516   529     12  18   169   185     -7  10   375   376      4  15   486   479    -17   9   230   235
 -10  20   336   348     14   0   413   400     -7  12   292   287      4  17   493   501    -17  11   174   187
 -10  22   182   200     14   2   207   197     -7  14   210   200      4  19   418   407    -17  13   116   130
  -8   4   105   111     14   8   225   250     -7  16   132   138      4  21   166   175    -16   6   117   141
  -8   6   636   639     14  12   308   334     -7  18   180   195      5   0   498   517    -16   8   174   156
  -8   8    96    82     14  18    97    97     -7  22   185   189      5   2  1439  1460    -16  10   132   113
  -8  10   400   395     16   0   247   240     -7  24   127   108      5   4   382   380    -15   5   198   210
  -8  12   812   805     16   2   325   305     -6   1   132   131      5   6   203   208    -15  11   413   405
  -8  14   210   219     16   4   150   314     -6   3   285   298      5   8   360   354    -15  17   168   192
  -8  18   222   223     16   8   142   110     -6   5   265   260      5  10   349   342    -14   2   173   157
  -8  24   126   140     16  10   273   268     -6   7   412   441      5  12   825   802    -14   8   139   150
  -6   2   695   700     16  12   240   246     -6   9   996   993      5  14   136   131    -14  10   204   222
  -6   4  1186  1181     16  14   144   177     -6  11   298   289      5  16   363   352    -14  12   208   220
  -6   6   668   668     18   0   371   368     -6  13   306   357      5  18   222   223    -14  14   121   122
  -6   8   342   341     18   2   335   326     -6  15   124   110      5  20   339   331    -14  16   275   277
  -6  10   720   690     18   4   467   440     -6  17   237   242      5  22   190   181    -13   7   150   150
  -6  12   355   349     18   6   134   137     -5   2   982   907      6   1   757   777    -13   9   397   408
  -6  14   430   422     20   2   213   213     -5   4   642   674      6   3   403   401    -13  11   231   224
  -6  16   185   169     20   4   267   247     -5   6   950  1000      6   5   458   461    -13  13   417   409
  -6  18   341   340     22   0   237   223     -5  12   318   318      6   7   529   524    -13  17   162   177

  -4   2  2107  2149        **K =    1****      -5  14   276   254      6   9   583   550    -12   2   233   247
  -4   4  1703  1707    -22   3   168   190     -5  16   279   265      6  13   257   242    -12   4   163   152
  -4   6   253   266    -21   6   230   247     -5  18   155   145      6  15   329   330    -12   8   223   241
  -4   8   909   919    -21  10   111   105     -5  20   179   176      6  19   176   185    -12  12   720   708
  -4  10  1511  1472    -20   5   399   421     -4   1   751   785      6  23    97   112    -12  14   558   554
  -4  12   555   543    -20   7   250   298     -4   3   741   756      7   0   192   199    -11   1   430   431
  -4  14   123   112    -19   2   156   143     -4   5   933   956      7   2   957   562    -11   3   231   206
  -4  16   123   141    -19   4   149   129     -4   9   197   184      7   8   681   675    -11   5   204   169
  -4  18   252   227    -19  10   119   114     -4  11   183   193      7  10   292   287    -11   7   224   211
  -4  22   292   302    -19  12   108   132     -4  13   160   177      7  12   231   251    -11  15   376   366
  -4  24   219   197    -18   1   129   138     -4  19   287   296      7  14   297   302    -11  17   169   155
  -2   2   280   287    -18   3   202   184     -4  25   201   213      7  16   157   144    -11  19   248   216
  -2   6  1530  1546    -18   5   290   290     -3   2   359   370      7  22   109    76    -10   2   138   141
  -2   8   206   205    -18   7   449   457     -3   4   950   963      8   1   157   155    -10   6   149   154
  -2  10  1064  1060    -18  13   268   252     -3   6  1012  1024      8   3   387   410    -10  10   229   209
  -2  12   215   208    -17   2   344   350     -3   8   409   408      8   5   880   857    -10  12   422   428
  -2  16   203   193    -17   4   112    71     -3  10   528   502      8   7   167   183    -10  16   115   129
  -2  20   381   309    -17   6   214   220     -3  14   170   161      8   9   180   174    -10  20   130   119
  -2  24   113   101    -17  10   363   368     -3  16   339   346      8  15   204   221     -9   3   214   220
   0   2   875   889    -17  14   135   155     -3  22   255   261      8  17   183   179     -9   7   215   220
   0   4   337   341    -17  18    96    66     -2   1  1020  1061      9   0   421   408     -9   9   332   337
   0   6   814   826    -16   3   143   152     -2   3   666   668      9   2   453   463     -9  13   771   768
   0  12   269   262    -16  15   107    85     -2   5  1080  1107      9   6   560   539     -9  15   310   305
   0  14   201   175    -16  17   157   166     -2   7   114   121      9  10   306   290     -9  17   167   152
   0  16   315   302    -15   4   318   310     -2   9   398   387      9  12   185   207     -8   2  1125  1064
   0  18   210   212    -15   6   116   113     -2  11   351   387      9  16   213   220     -8   4   657   652
   0  22   262   273    -15   8   413   408     -2  13   569   561      9  18   311   334     -8   6   292   254
   0  24   389   390    -15  10   157   185     -2  15   109   124     10   1   334   336     -8   9   322   322
   2   0  1150  1183    -15  12   183   174     -2  17   323   335     10   3   119   156     -8  12   300   309
   2   2   146   147    -15  18   108   137     -2  21   157   159     10   5   481   491     -8  14   300   292
   2   4   660   653    -15  20   120   101     -2  23   169   183     10   7   146   141     -8  18   236   246
   2   6  1585  1623    -14   1   303   299     -1   2   723   747     10   9   136   116     -7   1   103   101
   2   8  1306  1313    -14   5   145   167     -1   4  1477  1509     10  15   167   165     -7   3   292   308
   2  10   744   742    -14   7   116    95     -1   6   494   510     11   0   365   374     -7   5   963   956
   2  12   148   140    -14  11   605   602     -1   9   227   224     11   2   807   793     -7   7   283   280
   2  14   435   426    -14  13   459   467     -1  10   180   178     11   4   314   319     -7  11   160   168
   2  16   263   274    -14  15   355   371     -1  12   250   236     11   6   303   294     -7  13   373   348
   2  18   970   952    -13   6   151   162     -1  14   604   607     11   8   230   240     -7  19   311   305
   2  20   274   251    -13   8   162   154     -1  18   286   292     11  12   196   207     -7  21   119   113
   2  22   276   259    -13  10   263   276     -1  20   152   183     11  14   174   159     -7  23   117   119
   4   0  1381  1411    -13  14   140   332      0   1  2405  2657     12   3   502   487     -6   6   244   234
   4   2   966   975    -13  16   165   139      0   3   717   725     12   5   205   246     -6   8   375   372
   4   4  2915  2835    -13  18   125   115      0   5   309   309     12  11   220   219     -6  10   759   764
   4   6   595   624    -12   3   321   324      0   7   652   667     12  15   237   233     -6  12   437   430
   4   8   958   945    -12   7   454   431      0   9   197   203     13   0   146   118     -6  14   121    99
   4  10   261   247    -12  11   335   332      0  11   482   474     13   2   178   184     -6  16   253   243
   4  12   352   340    -12  13   157   373      0  13   218   217     13   4   159   205     -6  18   150   160
   4  14   502   490    -12  15   295   305      0  17   332   325     13   6   373   401     -6  20   262   280
   4  16   489   492    -12  17   221   216      0  19   202   211     13   8   304   290     -5   1   158   158
   4  18   685   691    -12  21   120   136
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  H   L  FOBS  FCAL     H   L  FOBS  FCAL     H   L  FOBS  FCAL     H   L  FOBS  FCAL     H   L  FOBS  FCAL
 -5   3   364   357     8   4   141   161    -4  19   211   217   -16   4   241   254     9   7   113   117
 -5   9   709   710     8   6   149   155    -3   4   501   481   -16  10   203   204    10   2   271   277
 -5  13   249   250     8   8   316   319    -3   8   358   171   -15   5   244   245    10   8   100   303
 -5  17   242   245     8  10   290   291    -3  14   353   154   -13   7   172   188    10  12   166   187
 -5  19   251   241     8  12   393   385    -3  16   158   142   -12   8   287   312    11   5   161   151
 -5  23   174   166     8  16   124   106    -3  18   245   265   -12  10   155   182    11   7   212   265
 -4   2   454   466     9   1   270   276    -2   1   350   332   -12  12   115   116    12   6   255   240
 -4   4   129   122     9   5   654   649    -2   3   184   183   -12  14   365   374    13   3   161   198
 -4   6   115   130     9   7   119    89    -2   5   289   265   -11   1   217   204    14   0   326   345
 -4   8   196   104     9   9   234   234    -2   9   134   117   -11   3   272   277    14   2   174   165
 -4  12   342   332     9  11   152   170    -2  15   147   133   -11   5   122   122    14   6   332   340
 -4  14   266   258     9  17   252   267    -2  21   111   105   -11  11   183   177    14   8   109   153
 -4  16   152   142    10   0   334   335    -1   2   285   287   -11  13   250   262    15   7   249   231
 -4  18   294   294    10   4   200   189    -1   4   373   357   -10   2   136   106    16   4   320   303
 -4  20   291   288    10   6   698   706    -1   6   552   542   -10   4   402   307    16   6   181   187
 -3   3  1424  1415    10  10   297   310    -1   8   228   231   -10  12   292   317    17   1   165   175
 -3   5   433   451    10  14   386   412    -1  10   267   254    -9   7   270   285    17   3   221   235
 -3   9   552   555    10  16   147   103    -1  10   195   188    -9  11   332   341      **K =    5****
 -3  11   341   345    11   3   400   403     0   1   526   515    -9  13   165   145   -14   3   130   147
 -3  15   254   277    11   7   340   370     0   3   597   582    -9  17   117    84   -13   6   135   127
 -3  17   233   223    11  13   233   235     0   7   278   250    -8   6   291   305   -12   5   137   157
 -3  21   156   148    11  17   120   157     0  11   200   171    -8   8   157   167   -11   6   129   125
 -2   2   739   747    12   2   294   280     0  15   243   239    -8  14   284   293   -10   5   160   169
 -2   4   111   125    12   4   172   237     0  17   347   343    -7   3   142   117    -9   6   151   147
 -2   6   303   302    12   8   297   318     0  19   188   187    -7   9   167   166    -8   9   187   196
 -2  10   392   397    12  10   189   185     0  21   128   124    -6   4   164   134    -7   2   158   156
 -2  12   267   275    12  12   230   248     1   0   355   364    -6   8   348   341    -7   8   135   150
 -2  14   146   111    12  16   117   123     1   4   130   123    -6  10   128   124    -7  10   239   254
 -2  18   366   361    13   3   316   317     1   8   167   163    -6  12   245   251    -6   3   157   135
 -2  22   107    84    13   5   157   151     1  10   129   130    -6  16   215   200    -6   9   228   227
 -1   1   208   223    13   7   238   246     1  12   173   182    -5   1   200   261    -5   6   154   165
 -1   3   273   257    13   9   364   370     1  18   151   127    -5   3   277   274    -5   8   149   150
 -1   7   172   166    14   0   205   205     1  20   189   197    -5   5   241   241    -5  12   276   266
 -1   9   828   818    14   4   790   777     1  22   132   152    -5   7   276   209    -4   3   145   135
 -1  11   313   321    14   6   586   583     2   1   676   651    -5   9   133   125    -4   7   132   137
 -1  13   154   150    15   7   183   182     2   3   299   298    -5  13   308   284    -4   9   266   263
 -1  17   441   449    16   2   158   172     2   5   584   538    -5  15   121   140    -4  11   139   158
 -1  19   249   234    16   4   312   313     2  17   415   431    -4   2   242   256    -3   2   663   647
 -1  23   120   103    16  14   120   134     2  21   135   107    -4   4   314   326    -3   8   255   262
  0   0   104    99    17   5   421   417     3   0   297   279    -4   6   346   362    -2   1   393   396
  0   2   537   534    17   7   130   156     3   2   211   218    -4  10   292   290    -2   3   431   433
  0   4   784   700    18   0   123   136     3   4   333   323    -4  14   332   336    -2   7   168   197
  0   6   451   446    18   2   134    94     3   6   595   571    -3   1   391   411    -2   9   205   198
  0   8   465   461    18   6   150   215     3   8   133   116    -3   3   213   201    -1   6   311   302
  0  12   205   205    18  10   205   193     3  10   210   192    -3   7   251   292    -1   8   273   269
  0  14   216   209      **K =    3****     4   3   174   191    -3  11   134   118    -1  10   230   245
  0  18   515   510   -18   7   108    94     4   5   142   155    -3  13   154   166    -1  16   186   186
  0  20   129   145   -18  11   118   122     4   7   118   127    -3  15   150   153     0   1   220   217
  1   3   252   231   -17  10   165   165     4  11   192   168    -3  17   128   154     0   3   250   266
  1   5   140   131   -17  12   161   175     4  15   159   146    -2   2   394   304     0   5   224   213
  1   7   417   427   -16   3   196   181     4  17   309   312    -2   4   346   327     0   7   129   101
  1   9   250   250   -16   5   234   244     5   0   483   465    -2   8   176   157     1   0   457   437
  1  11   163   173   -16  13   158   152     6   1   475   441    -2  14   191   181     1   4   151   152
  1  13   294   287   -15   4   351   366     6   3   220   207    -2  18   168   164     1   6   219   216
  1  17   268   250   -15   6   164   154     6   7   309   383    -2  20   232   250     2   1   201   200
  1  23   147   180   -15  10   158   189     6  11   240   249    -1   5   140   153     2   3   165   178
  2   0   914   921   -15  14   262   248     6  13   217   217    -1   9   131   126     2  15   166   179
  2   2   603   571   -14   7   142   143     6  15   189   189    -1  11   253   246     3   0   492   483
  2   4   158   156   -14  11   125   106     7   0   215   200    -1  17   157   208     3   6   225   232
  2   6   628   605   -14  15   259   270     7   4   164   160     0   2   157   170     3   8   230   218
  2  12   225   218   -13   2   276   247     7   6   152   131     0   4   438   445     3  10   144   132
  2  14   310   305   -13   8   187   190     7   8   275   300     0   6   376   343     3  14   168   177
  2  18   226   232   -13  14   394   429     7  10   212   179     0  12   161   109     4   1   225   227
  2  20   237   229   -13  16   290   283     7  12   175   160     0  16   214   196     4   3   129   134
  2  22   132    96   -12  13   412   430     7  14   218   219     1   3   279   268     4   7   148   155
  3   1   428   432   -12  15   164   173     7  16   277   287     1   5   138   163     4  11   172   171
  3   3   211   210   -12  17   340   346     8   7   419   431     1   7   135   120     4  15   175   175
  3   5   551   557   -11   4   425   439     8   9   259   247     1  13   125   125     5   0   127   116
  3   7   199   196   -11   6   224   248     8  11   323   307     1  15   117   107     5   4   157   139
  3   9   374   366   -11   8   238   249     8  13   161   137     1  19   301   315     5   6   160   165
  3  13   156   194   -11  12   455   455     8  15   163   148     2   2   164   165     5   8   210   203
  3  15   158   189   -11  14   118    99     9   4   345   360     2   4   257   249     5  12   110   103
  3  17   301   302   -10   1   196   198     9  10   226   213     2   6   320   311     6   1   187   175
  3  19   114   101   -10  11   571   566     9  12   252   252     2  10   283   270     6   3   173   184
  4   0   656   712   -10  13   307   308     9  14   143   145     2  12   240   234     6   7   246   264
  4   2   452   451    -9   2   150   136     9  16   100   179     2  14   258   311     7   4   154   168
  4   4   117   125    -9   6   258   279    10   7   330   332     2  16   402   416     7   6   201   206
  4   6   407   404    -9  12   850   891    10   9   146   167     2  18   154   203     8   3   161   157
  4   8   433   425    -9  16   210   199    10  11   221   222     3   1   196   185     8   7   135   142
  4  16   399   388    -9  18   292   291    10  13   369   365     3   3   175   192     9   2   136   136
  4  18   305   315    -8   1   284   272    11   0   231   198     3  13   142   137     9   4   138   122
  4  20   130   135    -8   3   160   146    11   2   143   130     3  15   217   232     9   6   308   396
  4  22   118   119    -8   9   227   236    11   6   542   522     4   0   303   315     9   8   113   198
  5   1   735   720    -7   2   390   371    11   8   141   146     4   2   259   255    10   5   176   173
  5   3   101    96    -7   4   261   241    11  14   197   201     4   4   297   303    11   0   220   240
  5   5    98    97    -7  10   218   226    12   7   416   441     4   6   165   183      **K =    6****
  5   7   105   115    -7  14   206   207    12  11   186   201     4   8   165   138    -7   1   226   230
  5   9   239   237    -7  16   290   310    13   0   195   148     4  12   113    92    -7   5   130   122
  5  11   305   297    -7  19   163   163    13   4   138   133     4  16   291   304    -6   2   115    94
  5  13   300   304    -7  20   143   145    13   6   427   437     5   1   360   341    -5   1   150   194
  5  15   354   357    -6   1   220   194    13   8   313   308     5   7   252   249    -5   3   151   151
  5  19   155   197    -6   5   343   338    13  12   172   190     5  17   259   249    -5   5   137   155
  5  21   124   105    -6   9   166   145    14   5   428   431     6   4   408   449    -4   6   190   174
  6   2   129   127    -6  11   527   521    14   7   257   255     6   6   167   176    -4   8   147   158
  6   4   223   229    -6  19   148   159    14   9   276   226     6  12   251   257    -3   1   295   312
  6   8   207   204    -6  21   157   175    15   0   146   152     6  14   246   262    -3   3   139   165
  6  10   127   124    -5   2   823   796    15   2   150   128     6  10   208   213    -3   5   205   215
  6  14   304   294    -5   4   141   124    15   8   316   316     7   5   165   195    -2   2   345   346
  6  16   351   358    -5   6   408   406    16   3   256   269     7   9   212   217    -2   8   166   152
  7   1   443   438    -5  14   299   315    16   5   182   215     7  15   165   200     0   2   181   214
  7   5   311   301    -5  16   479   461    17   2   222   203     7  17   224   228     1   1   174   187
  7   7   122   113    -5  18   162   160    17   4   399   380     8   0   178   199     1   3   147   157
  7   9   241   252    -4   1   383   367    17   8   211   221     8   2   316   298     3   1   138   142
  7  15   256   249    -4   7   116   142    18   1   130   100     8   6   221   219     4   0   117   115
  7  17   181   148    -4   9   282   269      **K =    4****     8   8   369   372     4   2   194   183
  8   0   209   215    -4  11   523   525   -17   1   105    92     8  10   214   215     6   2   180   164
  8   2   476   457    -4  17   213   255   -17   7   102   107     9   5   294   353     8   0   205   186
```

Table 14

Atomic Coordinates and Isotropic Temperature Factors

| Atom | x | y | z | B |
|---|---|---|---|---|
| C1 | 0.0489(2) | -0.0090(6) | 0.0510(1) | 2.22* |
| C2 | -0.0143(2) | 0.0307(6) | 0.0604(1) | 2.29* |
| C3 | -0.0706(2) | 0.0377(7) | 0.0104(1) | 2.31* |
| C4 | -0.1180(2) | -0.1633(8) | 0.0220(1) | 2.78* |
| C5 | -0.2113(3) | -0.2643(13) | 0.0726(3) | 5.83* |
| C11 | 0.1057(2) | -0.0239(6) | 0.0990(1) | 2.31* |
| C12 | 0.1169(2) | 0.1543(7) | 0.1403(2) | 2.89* |
| C13 | 0.1707(2) | 0.1402(8) | 0.1845(2) | 3.57* |
| C14 | 0.2132(2) | -0.0475(8) | 0.1871(2) | 3.77* |
| C15 | 0.2022(2) | -0.2249(8) | 0.1461(2) | 3.81* |
| C16 | 0.1488(2) | -0.2129(7) | 0.1021(2) | 3.28* |
| C21 | -0.0383(2) | 0.0590(7) | 0.1204(1) | 2.35* |
| C22 | -0.0731(2) | 0.2576(7) | 0.1334(2) | 3.18* |
| C23 | -0.0985(2) | 0.2832(8) | 0.1876(2) | 3.52* |
| C24 | -0.0900(2) | 0.1078(8) | 0.2288(2) | 3.54* |
| C25 | -0.0558(2) | -0.0923(8) | 0.2164(2) | 3.50* |
| C26 | -0.0301(2) | -0.1163(7) | 0.1624(1) | 2.83* |
| O1 | -0.1080(1) | -0.3626(5) | 0.0113(1) | 4.21* |
| O2 | -0.1704(1) | -0.0852(5) | 0.0481(1) | 3.96* |
| H12 | 0.090(2) | 0.290(7) | 0.139(2) | 4.9(10) |
| H13 | 0.179(2) | 0.272(7) | 0.213(2) | 5.0(9) |
| H14 | 0.253(2) | -0.053(6) | 0.219(1) | 4.4(8) |
| H15 | 0.232(2) | -0.363(7) | 0.146(2) | 5.3(10) |

(continued on next page)

| Atom | x | y | z | B |
|---|---|---|---|---|
| H16 | 0.142(2) | -0.355(7) | 0.072(1) | 4.8(8) |
| H22 | -0.080(2) | 0.376(6) | 0.104(1) | 4.1(8) |
| H23 | -0.121(2) | 0.429(7) | 0.194(2) | 5.2(10) |
| H24 | -0.106(2) | 0.125(6) | 0.267(2) | 4.7(9) |
| H25 | -0.050(2) | -0.225(8) | 0.247(2) | 7.1(12) |
| H26 | -0.006(2) | -0.247(7) | 0.152(1) | 4.0(9) |
| H51 | -0.257(3) | -0.184(9) | 0.074(2) | 8.0(13) |
| H52 | -0.194(2) | -0.282(10) | 0.111(2) | 8.9(16) |
| H53 | -0.214(3) | -0.404(10) | 0.043(2) | 10.8(20) |
| H3 | -0.097(1) | 0.182(5) | 0.012(1) | 1.8(6) |

*These are equivalent isotropic temperature factors corresponding to the anisotropic parameters listed in Table 15.

## Table 15

## Anisotropic Temperature Factors (Å$^2$)

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.035(2) | 0.025(2) | 0.024(2) | 0.002(2) | 0.004(1) | -0.001(2) |
| C2 | 0.037(2) | 0.028(2) | 0.022(2) | -0.002(2) | 0.004(2) | 0.001(2) |
| C3 | 0.028(2) | 0.034(2) | 0.025(2) | 0.005(2) | 0.004(1) | 0.001(2) |
| C4 | 0.028(2) | 0.050(3) | 0.026(2) | 0.002(2) | 0.002(2) | 0.004(2) |
| C5 | 0.047(3) | 0.108(5) | 0.070(3) | -0.020(4) | 0.024(3) | 0.016(4) |
| C11 | 0.029(2) | 0.034(2) | 0.025(2) | -0.004(2) | 0.005(1) | 0.000(2) |
| C12 | 0.036(2) | 0.040(3) | 0.034(2) | 0.005(2) | 0.007(2) | -0.002(2) |
| C13 | 0.042(2) | 0.056(3) | 0.038(2) | -0.009(2) | 0.003(2) | -0.008(2) |
| C14 | 0.038(2) | 0.063(3) | 0.041(2) | -0.002(3) | -0.004(2) | 0.000(2) |
| C15 | 0.046(2) | 0.046(3) | 0.051(2) | 0.012(2) | -0.002(2) | 0.003(2) |
| C16 | 0.049(2) | 0.038(3) | 0.037(2) | 0.012(2) | 0.000(2) | -0.003(2) |
| C21 | 0.027(2) | 0.038(2) | 0.024(2) | -0.003(2) | 0.004(2) | -0.002(2) |
| C22 | 0.049(2) | 0.040(3) | 0.033(2) | 0.004(2) | 0.010(2) | 0.000(2) |

(Continued on next page)

Table 15 continued

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| C23 | 0.047(2) | 0.048(3) | 0.040(2) | 0.007(2) | 0.009(2) | −0.006(2) |
| C24 | 0.046(2) | 0.059(3) | 0.031(2) | −0.009(2) | 0.013(2) | −0.007(2) |
| C25 | 0.047(2) | 0.055(3) | 0.032(2) | −0.002(2) | 0.011(2) | 0.007(2) |
| C26 | 0.036(2) | 0.040(3) | 0.032(2) | 0.005(2) | 0.007(2) | 0.005(2) |
| O1 | 0.062(2) | 0.036(2) | 0.065(2) | −0.004(2) | 0.021(1) | −0.003(2) |
| O2 | 0.035(1) | 0.062(2) | 0.057(2) | −0.001(2) | 0.019(1) | 0.000(2) |

## Table 16

## Interatomic Distances (Å)

| | | | |
|---|---|---|---|
| C1 - C2 | 1.326(4) | C4 - O1 | 1.194(4) |
| C1 - C3' | 1.513(4) | C4 - O2 | 1.336(4) |
| C2 - C3 | 1.523(4) | C5 - O2 | 1.462(5) |
| C1 - C11 | 1.501(4) | | |
| C2 - C21 | 1.502(4) | C12 - H12 | 0.95(4) |
| C3 - C4 | 1.537(5) | C13 - H13 | 1.01(4) |
| C3 - H3 | 0.98(3) | C14 - H14 | 1.02(3) |
| | | C15 - H15 | 1.00(4) |
| C11 - C12 | 1.395(5) | C16 - H16 | 1.06(4) |
| C12 - C13 | 1.402(5) | C22 - H22 | 0.95(4) |
| C13 - C14 | 1.374(5) | C23 - H23 | 0.98(4) |
| C14 - C15 | 1.386(5) | C24 - H24 | 0.95(3) |
| C15 - C16 | 1.395(5) | C25 - H25 | 1.03(4) |
| C16 - C11 | 1.387(5) | C26 - H26 | 0.93(4) |
| C21 - C22 | 1.387(5) | | |
| C22 - C23 | 1.390(5) | C5 - H51 | 1.03(5) |
| C23 - C24 | 1.378(5) | C5 - H52 | 0.92(5) |
| C24 - C25 | 1.384(5) | C5 - H53 | 1.04(5) |
| C25 - C26 | 1.387(5) | | |
| C26 - C21 | 1.390(5) | | |

## Table 17

### Intramolecular Angles

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| C3' - C1 - C2 | 122.4(3) | C22 - C21 - C26 | 118.6(3) |
| C3' - C1 - C11 | 113.7(3) | C21 - C22 - C23 | 120.9(4) |
| C11 - C1 - C2 | 124.4(3) | C22 - C23 - C24 | 119.8(4) |
| C1 - C2 - C3 | 122.1(3) | C23 - C24 - C25 | 120.0(4) |
| C1 - C2 - C21 | 124.4(3) | C24 - C25 - C26 | 120.0(4) |
| C21 - C2 - C3 | 113.4(3) | C25 - C26 - C21 | 120.7(4) |
| C2 - C3 - C1' | 115.4(3) | | |
| C2 - C3 - C4 | 106.1(3) | C3 - C4 - O1 | 124.7(4) |
| C2 - C3 - H3 | 110(2) | C3 - C4 - O2 | 110.6(3) |
| C1' - C3 - C4 | 108.4(3) | O1 - C4 - O2 | 124.7(4) |
| C1' - C3 - H3 | 110(2) | C4 - O2 - C5 | 115.4(4) |
| C4 - C3 - H3 | 107(2) | | |
| | | H12 - C12 - C11 | 122(2) |
| C1 - C11 - C12 | 120.6(3) | H12 - C12 - C13 | 118(2) |
| C1 - C11 - C16 | 120.3(3) | H13 - C13 - C12 | 119(2) |
| C12 - C11 - C16 | 119.0(3) | H13 - C13 - C14 | 120(2) |
| C11 - C12 - C13 | 120.1(4) | H14 - C14 - C13 | 119(2) |
| C12 - C13 - C14 | 120.4(4) | H14 - C14 - C15 | 121(2) |
| C13 - C14 - C15 | 119.6(4) | H15 - C15 - C14 | 123(2) |
| C14 - C15 - C16 | 120.5(4) | H15 - C15 - C16 | 117(2) |
| C15 - C16 - C11 | 120.3(4) | H16 - C16 - C15 | 118(2) |
| C2 - C21 - C22 | 119.8(3) | H16 - C16 - C11 | 122(2) |
| C2 - C21 - C26 | 121.4(3) | H22 - C22 - C21 | 119(2) |

(Continued on next page)

Table 17 continued

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| H22 - C22 - C23 | 120(2) | H26 - C26 - C21 | 117(2) |
| H23 - C23 - C22 | 117(2) | 02 - C5 - H51 | 103(3) |
| H23 - C23 - C24 | 123(2) | 02 - C5 - H52 | 105(3) |
| H24 - C24 - C23 | 121(2) | 02 - C5 - H53 | 107(3) |
| H24 - C24 - C25 | 119(2) | H51 - C5 - H52 | 106(4) |
| H25 - C25 - C24 | 120(2) | H52 - C5 - H53 | 121(5) |
| H25 - C25 - C26 | 120(2) | H53 - C5 - H51 | 112(4) |
| H26 - C26 - C25 | 123(2) | | |

## Table 18

## Intramolecular Non Bonded Contacts

| Atoms | Distance |
|---|---|
| C1' - C4 | 2.474(5) |
| C2 - C4 | 2.445(5) |
| C1 - C1' | 2.888(6) |
| C2 - C2' | 2.888(6) |
| C3 - C3' | 2.947(7) |
| C1 - C3 | 2.496(5) |
| C2 - C3' | 2.489(5) |
| C1 - C2' | 2.566(4) |
| C11 - C21 | 3.013(5) |
| C11 - C26 | 3.251(5) |
| C21 - C12 | 3.148(5) |
| C12 - C26 | 3.416(5) |
| C11 - O1' | 3.360(4) |
| C21 - O2 | 3.090(4) |
| C22 - O2 | 3.273(5) |
| O1 - O2 | 2.242(4) |
| C4 - C11 | 2.993(5) |
| C4 - C21 | 2.916(5) |
| H12 - O1' | 3.49(4) |
| H22 - O2 | 3.39(3) |
| H3 - H16' | 2.27(4) |
| H3 - H22 | 2.37(4) |

Table 19

Intermolecular Contacts

| Atom 1 | Atom 2 | Symmetry Operation | Distance |
|---|---|---|---|
| C22 | C26 | x,1+y,z | 3.750(5) |
| C23 | C25 | x,1+y,z | 3.740(5) |
| C23 | C26 | x,1+y,z | 3.785(5) |
| C12 | C16 | x,1+y,z | 3.811(5) |
| C13 | C15 | x,1+y,z | 3.823(5) |
| O1 | C3 | x,1-y,z | 3.534(5) |
| C5 | H15 | x-1/2,-y-1,z | 3.01(4) |
| C5 | H53 | -1/2-x,y,-z | 3.01(5) |
| C13 | H51 | 1/2+x,-y,z | 3.04(5) |
| C14 | H51 | 1/2+x,-y,z | 3.01(5) |
| C15 | H51 | 1/2+x,-y,z | 3.03(5) |
| C15 | H24 | -x,y-1/2,1/2-z | 3.03(4) |
| C24 | H25 | -x,1/2+y,1/2-z | 2.96(4) |
| O1' | H16 | x,y-1,z | 2.54(4) |
| O1 | H22 | x,y-1,z | 2.61(4) |
| O1 | H3 | x,y-1,z | 2.63(3) |
| H13 | H14 | 1/2-x,1/2-y,1/2-z | 2.54(5) |
| H13 | H24 | -x,1/2+y,1/2-z | 2.57(5) |
| H24 | H13 | -x,y-1/2,1/2-z | 2.57(5) |
| H53 | H53 | -1/2-x,y,-z | 2.3(1) |

## Table 20

## Least Squares Planes

(1) Atoms defining plane. C1 C2 C3 C1' C2' C3'

Equation of plane. $0.1449X + 0.9867Y - 0.0741Z = 0$

Distances of atoms from plane in Å

| | |
|---|---|
| C1 | -0.012(3) |
| C2 | 0.011(4) |
| C3 | -0.012(4) |
| C1' | 0.012(3) |
| C2' | -0.011(4) |
| C3' | 0.012(4) |

$\chi^2 = 62.46$ - Hypothesis that these atoms lie in the least squares plane can be rejected at the 99.9% confidence level.

(2) Atoms defining plane. C1 C2 C1' C2'

Equation of plane. $0.1617X + 0.9838Y - 0.0768Z = 0$

Distances of atoms from plane in Å

C1, C2, C1', C2' 0.0

Distances of other atoms from plane in Å

| | |
|---|---|
| C3 | -0.037(4) |
| C3' | 0.037(4) |
| C11 | -0.001(4) |
| C21 | -0.044(4) |

(Continued on next page)

Table 20 continued

(3) Atoms defining plane. C3 C4 O1 O2 C5

Equation of plane. $-0.4428X + 0.1145Y - 0.8893Z - 0.4970 = 0$

Distances of atoms from plane in Å

| | |
|---|---|
| C3 | -0.044(3) |
| C4 | 0.023(3) |
| O1 | 0.007(3) |
| O2 | 0.039(2) |
| C5 | -0.186(6) |

(4) Atoms defining plane. C11 C12 C13 C14 C15 C16

Equation of plane. $0.6475X + 0.4693Y - 0.6005Z + 0.1848 = 0$

Distance of atoms from plane in Å

| | |
|---|---|
| C11 | -0.002(3) |
| C12 | 0.003(4) |
| C13 | -0.004(4) |
| C14 | 0.003(4) |
| C15 | -0.001(4) |
| C16 | 0.001(4) |

(Continued on next page)

Table 20 continued

Distances of other atoms from plane in Å.

| | |
|---|---|
| H12 | 0.05(4) |
| H13 | 0.02(4) |
| H14 | 0.03(3) |
| H15 | 0.02(4) |
| H16 | -0.02(3) |

(5) Atoms defining plane. C21 C22 C23 C24 C25 C26

Equation of plane. $-0.8239X - 0.4139Y - 0.3812Z + 0.3213 = 0$

Distances of atoms from planes in Å

| | |
|---|---|
| C21 | -0.003(3) |
| C22 | 0.005(4) |
| C23 | -0.004(4) |
| C24 | 0.000(4) |
| C25 | 0.002(4) |
| C26 | 0.001(4) |

Distances of other atoms from plane in Å

| | |
|---|---|
| H22 | 0.04(3) |
| H23 | -0.03(4) |
| H24 | -0.03(3) |
| H25 | 0.02(4) |
| H26 | -0.01(3) |

(Continued on next page)

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Table 20 continued

(6) Atoms defining plane. C3, C2, C21, C1, C11, C3'

Equation of plane. $0.1462X + 0.9871Y - 0.0651Z - 0.0041 = 0$

Distances of atoms from plane in Å

| | |
|---|---|
| C3 | -0.016(4) |
| C2 | 0.019(4) |
| C21 | 0.001(4) |
| C1 | -0.004(3) |
| C11 | -0.010(4) |
| C3' | 0.007(4) |

Table 21

A Survey of Literature Values for

C = C and $C_{(sp^3)}$ - $C_{(sp^2)}$ Bond Lengths

| Compound | C = C | $C_{(sp^3)}$ - $C_{(sp^2)}$ | Reference |
|---|---|---|---|
| 4-Diethyl carbamoyl-1-cyclohexene-5-carboxylic acid | 1.322 | 1.503 | 73 |
| Cyclohexene | 1.335 | 1.504 | 74 |
| Bicyclohexylidene | 1.332 | 1.518 | 75 |
| Cyclooctatetraene carboxylic acid | 1.322 | - | 76 |
| Octaphenyl cyclooctatetraene | 1.343 | - | 77 |
| cis,cis,cis-1,4,7-cyclononatriene | 1.34 | 1.52 | 78 |
| Hydrobromide of 1-p-(2-Dimethylamino-ethoxy-phenyl)-1,2-cis-diphenylbut-1-ene | 1.33 | 1.52 | 79 |
| 8,12-Diethyl-2,3,7,13,17,18-hexamethylcorrole | - | 1.507 | 80 |
| Tazettine Methiodide | 1.33 | 1.52 | 81 |
| 1,1-Di-(p-nitrophenyl) ethylene | 1.326 | - | 82 |
| Cyclohexa-1,4-diene | 1.330 | 1.498 | 65 |
| Cyclohexa-1,4-diene | 1.347 | 1.511 | 66 |
| 1,3-Cyclohexadiene | - | 1.523 | 66 |
| 1,4-Cyclohexadiene-1-glycine | 1.347 | 1.485 | 69 |
| Weighted Average | 1.333 | 1.509 | |

## Table 22

## A Selection of Carboxylic Acid and Ester Group Geometries

| Compound Name | C=O | C-O | $O-C_{est}$ | $C\alpha-\hat{C}=O$ | $C\alpha-\hat{C}-O$ | $C_{est}-\hat{O}-C$ | $O=\hat{C}-O$ | Reference |
|---|---|---|---|---|---|---|---|---|
| 1,1,2,2-tetracarbomethoxyethane | 1.192<br>1.188 | 1.324<br>1.317 | 1.453<br>1.461 | 125.0<br>123.6 | 109.6<br>110.9 | 114.6<br>116.4 | 125.4<br>125.5 | 88 |
| Salicylic Acid | 1.234 | 1.307 | - | 122.9 | 116.0 | - | 121.2 | 89 |
| Acetyl Salicyclic Acid | 1.183 | 1.364 | 1.402 | 126.4 | 110.7 | 115.7 | 122.9 | 90 |
| Trans-1,3-cyclobutane dicarboxylic acid | 1.238 | 1.345 | - | 124.1 | 113.0 | - | 122.9 | 91 |
| (±)-trans-1,2-cyclohexane dicarboxylic acid | 1.209 | 1.314 | - | 123.5 | 113.1 | - | 123.3 | 92 |
| trans-bicyclo[4.2.0]octyl-1-3,5-dinitrobenzoate | 1.200 | 1.323 | 1.486 | 122.0 | 111.1 | 117.2 | 126.9 | 93 |
| 3'-O-acetyladenosine | 1.200 | 1.358 | 1.445 | 125.7 | 110.6 | 116.6 | 123.7 | 94 |

(Continued on next page)

Table 22 continued

| Compound Name | C=O | C-O | $O-C_{est}$ | $C\alpha-\hat{C}=O$ | $C\alpha-\hat{C}-O$ | $C_{est}-O-C$ | O=C-O | Reference |
|---|---|---|---|---|---|---|---|---|
| 1,2,4,5-tetraphenyl-3,6-dicarbomethoxy-tricyclo[3.1.0.0$^{2,4}$]hexane | 1.200 | 1.329 | 1.449 | 126.2 | 110.0 | 116.2 | 123.8 | This work (Chapter 3) |
| 1,2,4,5-tetraphenyl-3,6-dicarbomethoxy-cyclohexa-1,4-diene | 1.194 | 1.336 | 1.462 | 124.7 | 110.6 | 115.4 | 124.7 | This work |

Fig. 4

A Perspective View of the 1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene molecule

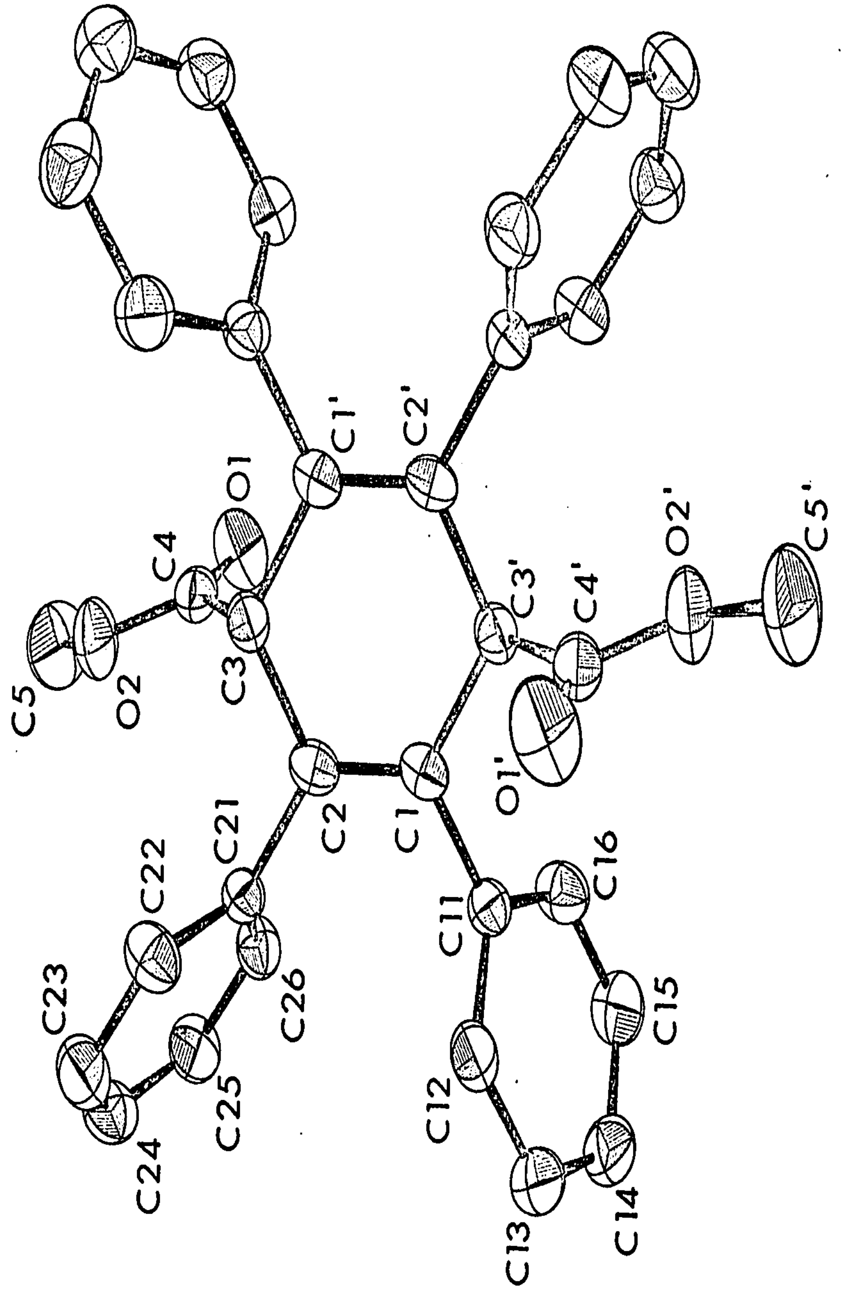

C1'
C2'
O1
C4
O2'
C5'
C3'
C4'
C5
O2
C3
O1'
C2
C1
C21
C22
C16
C11
C23
C26
C15
C12
C25
C24
C13
C14

Fig. 5

Contents of the Unit Cell Projected onto the [a][b] Plane

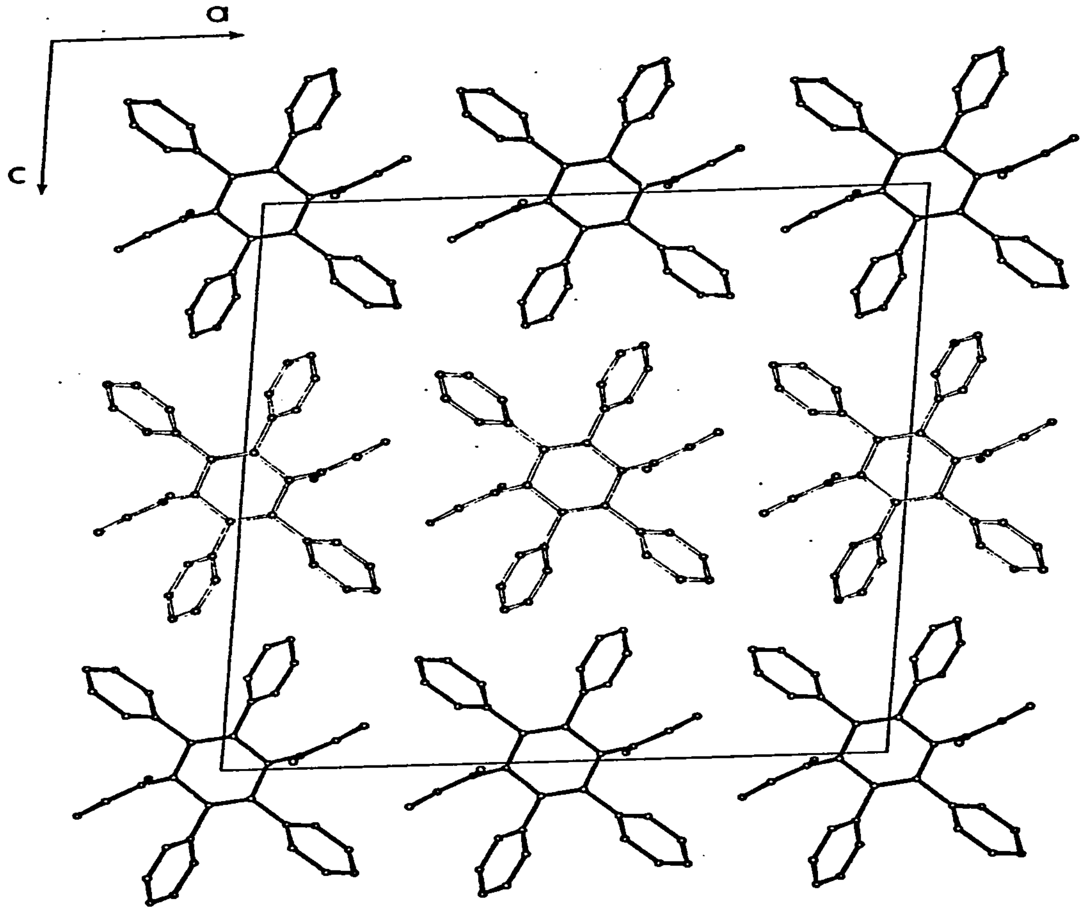

a
c

Fig. 6

A Selection of Newman Projections:

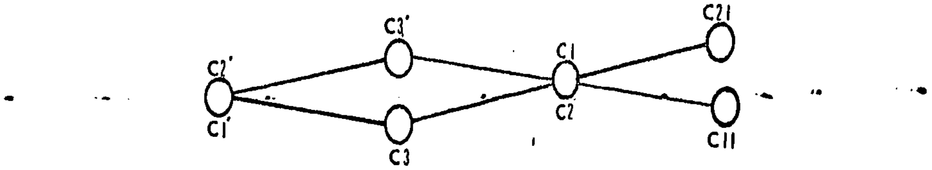
(a) theoretical view down C2-C1 for slight chair conformation

(b) actual view down C2-C1 (exaggerated)

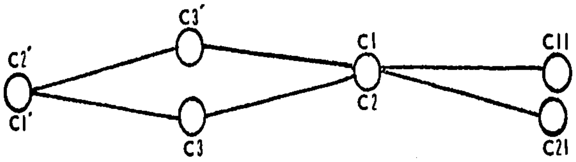
(c) down C3-C4

(d) down O2-C4

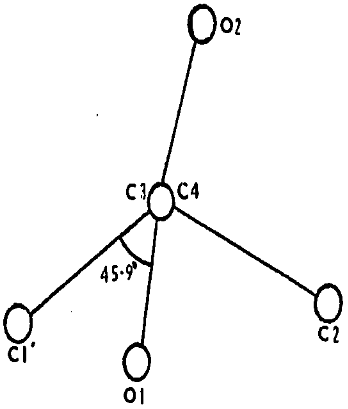
(e) down C5-C4 virtual bond showing partial staggering of hydrogen atoms with respect to carbonyl oxygen


C2'
C1'
C3'
C3
C1
C2
C21
C11

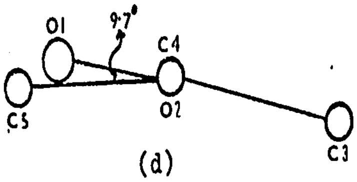
(a)


C2'
C1'
C3'
C3
C1
C2
C11
C21

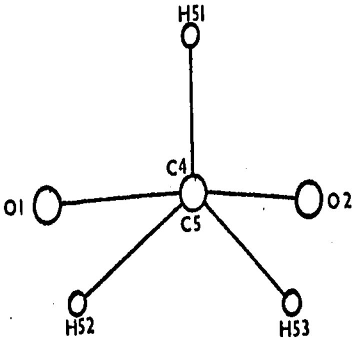
(b)


O2
C3
C4
45·9°
C1'
O1
C2

(c)


O1
9·7°
C4
C5
O2
C3

(d)


H51
C4
O1
C5
O2
H52
H53

(e)

## DISCUSSION

The molecule is shown in Fig. 4. It crystallises with the cyclohexadiene ring occupying a crystallographic inversion centre, with the plane of the ring almost perpendicular to the b axis. Because it occupies an inversion centre, the compound is necessarily *anti*-1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene and any deviations from planarity of the cyclohexadiene ring lead to a chair not a boat form.

The double bonds in the cyclohexadiene ring have a length of 1.326 Å, while the single bonds average 1.518 Å. This is not in particularly good agreement with the geometry found by Jandaceck and Simonsen, who obtained average bond lengths of 1.347 Å and 1.485 Å for the double and single bonds respectively in the cyclohexadiene ring of 1,4-cyclohexadiene-1-glycine[69]. However, the large standard deviations on the bond lengths in their structure render the differences insignificant. The results are, however, in good agreement with values commonly found in the literature. A survey of twelve structures containing unconjugated carbon-carbon double bonds and ten containing $C(sp^3) - C(sp^2)$ single bonds, gave a range of values from 1.312 Å to 1.347 Å with an average of 1.333 Å for the double bond, and 1.485 Å to 1.523 Å with an average of 1.509 Å for the single bond (Table 21). The double and single bond lengths in the cyclohexadiene ring can therefore be taken as normal. The bond angles within the cyclohexadiene ring are essentially the same as those found by

Jandaceck and Simonsen.

The exocyclic bonds to the phenyl rings have lengths 1.501 and 1.502 Å which is similar to that found in two independent structure determinations of octaphenyl cyclooctatetraene[77,83] and in hexaphenyl benzene[84], where the exocyclic bond lengths to phenyl rings average 1.50 Å. The angles that these bonds make with the double bond of the cyclohexadiene ring of 124.4° are slightly larger than those normally found around $sp^2$ hybridised carbon atoms. The widening of this bond angle serves to decrease the intramolecular repulsion between the phenyl rings. A similar situation is again observed in octaphenyl cyclooctatetraene.

Both the phenyl rings are planar within experimental error and the hydrogen atoms associated with them all lie in these planes. The average C - C bond length in these rings is 1.388 Å and the C - H bond length is 0.99 Å. The average C - C - C angle is 120.0° and the average H - C - C angle is 120°, all of which are very close to accepted values. The phenyl rings are rotated by angles of 52.2° and 58.7° respectively from a position which would be coplanar with the plane containing the two ethylenic bonds.

The preferred conformation of the ester group with the C = O, synplanar with respect to the $C_\alpha - C_\beta$ bond, i.e. with the torsion angle $C_\beta - C_\alpha - C = O$ equal to or close to zero[85-87], cannot be attained in this compound because of steric interference by the phenyl rings. This steric interference causes the carbomethoxy group to rotate about the $C_4 - C_3$ bond, giving a torsion angle of 45.9° for $C_1' - C_3 - C_4 = O_1$, to what is perhaps an optimum position, minimising intramolecular interaction between the two oxygen atoms and the phenyl rings and intermolecular contacts between $O_1$ and the phenyl ring attached to $C_1'$ one unit cell beneath it. At the same time these forces affect the geometry at $C_3$ slightly. Angle $C_2 - C_3 - C_4$ is 106.1°, significantly smaller than the 108.4° angle of $C_1' - C_3 - C_4$. This reduces intramolecular contact between $O_1$ and the phenyl ring attached to $C_1'$ but increases that between $O_2$ and the phenyl ring attached to $C_2$. This may account for the greater rotation of this phenyl group with respect to the plane containing the ethylenic linkages. The bond length $C_3 - C_4$ is 1.537 Å which is 0.02 - 0.03 Å longer than that commonly observed in the literature for this type of bond. No satisfactory explanation can be provided for this, other than that once again, the lengthening of this bond reduces intramolecular non-bonded interaction between the phenyl rings and the carbomethoxy group. The position thus taken up by the carbomethoxy group is such that the minimum intramolecular contact between $O_2$ and phenyl ring 2 is 3.090 Å between $O_2$ and $C_{21}$, and that between $O_1$ and phenyl 1' is 3.360 between $O_1$ and $C_{11}'$. The closest $O_1$-phenyl intermolecular contact is $O_1 - H_{16}'$ of 2.54 Å.

The bond lengths and angles within the ester group are similar to those found in the literature (Table 22). The group is close to being planar, but the deviations from the best plane through the five atoms $C_3$, $C_4$, $O_1$, $O_2$, $C_5$, although small, are significant (Table 8), with $C_5$ lying 0.186 Å out of this plane. The carbonyl group does not eclipse the methyl group, the torsional angle $O = C - O - CH_3$ being 9.7°, and the hydrogens of the methyl group are only partially staggered with respect to the $C = O$ bond. Thus the carbomethoxy group does not take up the accepted conformation for primary esters[87,95], probably due to the intra- and intermolecular forces acting upon it.

The cyclohexa-1,4-diene ring has small but significant deviations from planarity (Table 20), each of the six atoms lying 0.011 to 0.012 Å out of the least squares plane. If we define the reference plane as the one containing the four olefinic ($C_{sp^2}$) carbon atoms, then the deviation of the methylenic ($C_{sp^3}$) carbon atom from this plane is 0.037 Å. The dihedral angle between the plane formed by $C_2\ C_3\ C_1'$ and that by $C_1\ C_2\ C_1'\ C_2'$ is 177.4°. This agrees well with the electron diffraction work of Dallinga and Toneman[65], who refined a planar form of the molecule to completion but could not rule out the possibility that other nearly planar conformations, especially the chair form, were present, with a maximum deviation from the plane of 0.05 Å. The results are, however, in disagreement with the electron diffraction study of Oberhammer and Bauer[66], who concluded that the molecule had a pronounced boat conformation.

However, one must always be cautious when extrapolating results obtained from solid state studies to molecules in the liquid or gaseous phase. While the cyclohexa-1,4-diene ring in this structure is not severely constrained, as it would be in a fused ring system, the question remains as to whether the slight chair conformation is a preferred conformation, or whether it is imposed upon the ring as a result of either intermolecular forces in the condensed phase or intramolecular forces due to the bulky substituents.

The intermolecular forces would appear not to be responsible. The closest C---C contacts occur between phenyl rings and are all greater than 3.74 Å. The closest carbon-hydrogen contacts are about 3.0 Å or more, and hydrogen - hydrogen contacts are 2.54 Å or greater. All these distances are greater than the sum of the Van der Waals radii of the atoms concerned. The intermolecular interaction between the carbonyl oxygen and the methylenic carbon atom and its hydrogen atom in the molecule one unit cell away in the b direction also is not important. The $O_1$---$H_3$ distance of 2.63 Å and the $O_1$---$C_3$ distance of 3.533 Å are both greater than the sum of the Van der Waals radii of the atoms involved, 2.6 Å and 3.1 Å respectively.

Intramolecular forces, on the other hand, are very important in this sterically overcrowded molecule. The phenyl-phenyl repulsions are reduced to some extent by the widening of the $C_{phen}$ - C = C angle. Of course, they would be further reduced by the adoption of a slight chair conformation by the molecule, since, normally, this would lead to a slightly staggered conformation of $C_{11}$ and $C_{21}$ with respect to the olefinic bond. It should be noted that this distortion would be expected to lead to a slight reduction in the $\pi$-bond overlap. However, an examination of the olefinic plane (Table 20) indicates that this is not the case in this structure. The deviations from the least squares plane are not what would be expected for the normal chair structure. The situation is shown, much exaggerated, in Fig. 6(a) and (b). If we again use the plane defined by the four ethylenic carbon atoms as the reference plane, then $C_3$ and $C_3'$ lie 0.037 Å below and above this plane respectively. For the chair structure, one would expect deviations opposite in sign for $C_{21}$ and $C_{11}$ and of more or less the same magnitude as for $C_3$ and $C_3'$. Also, $C_{21}$ should lie on the opposite side of the plane to $C_3$, and $C_{11}$ should lie on the opposite side of the plane to $C_3'$ (Fig. 6a). However, the deviations of these atoms from the plane (Table 20) are 0.0015 Å for $C_{11}$ which is smaller than expected, but in the right direction and 0.044 Å for $C_{21}$ which is slightly larger than expected, and in the wrong direction (Fig. 6b). The atoms $C_{11}$ and $C_{21}$, therefore, have assumed positions closer to what one would expect for a completely planar or even boat form of the molecule. This situation lends itself to two possible interpretations:

(a) The inter- and intramolecular forces are attempting to constrain the molecule in a planar or boat conformation and despite this, the ring retains a slight chair conformation; or,

(b) The preferred conformation is that assumed by the substituents and the inter- and intramolecular repulsive interactions are forcing the ring to take up a chair conformation.

Examination of the intramolecular contacts between the phenyl rings and the carbomethoxy group greatly favour the latter interpretation. The $C_4$---$C_{21}$ and $C_4$---$C_{11}'$ distances are 2.916 and 2.993 Å respectively, significantly shorter than the Van der Waals contact of 3.4 Å and are, therefore, repulsive in nature. Since $C_4$ lies further below the plane of the four ethylenic carbon atoms than do $C_{11}'$ and $C_{21}$, the effect of this repulsive interaction would be to force it even further below the plane, which in turn will cause $C_3$ to move below this plane. The centrosymmetrically related $C_3'$ will be correspondingly raised above the plane, thus leading to a chair conformation.

Because of the possibility that the conformation of the cyclohexa-1,4-diene ring may be forced upon it by intramolecular forces between the bulky substituents, this molecule is particularly unsuitable for conformational studies concerning the planarity of the cyclohexa-1,4-diene ring.

The packing of the molecule in the [a.c.] plane is shown in Fig. 5. The phenyl rings of molecules related by a two-fold axis are in the 'herring bone' arrangement commonly found for aromatic groups. There are very few close contacts between molecules in either the a or c direction, the closest packing being in the b direction where the cyclohexadiene rings are parallel to each other and with the normal to the plane of the ring almost coincident with the b axis. There are no intermolecular contacts between molecules smaller than one would expect assuming all intermolecular forces are of the Van der Waals type. The closer intermolecular contacts are shown in Table 7 together with the symmetry relationship between the two molecules involved.

# Chapter Three

# The Crystal and Molecular Structures of 1,2,4,5-tetraphenyl-3,6-dicarbomethoxy-tricyclo[3.1.0.0$^{2,4}$]hexane

7

# INTRODUCTION

The 1,2,4,5-tetraphenyl-3,6-dicarbomethoxy-$[3.1.0.0^{2,4}]$ tricyclohexane was prepared as described on page 76 by Dr. S. Masamune and co-workers. Similar compounds have been prepared by other workers[96-102]. The stereochemistry of the products, however, was either undetermined or assigned only on the basis of mechanistic considerations or n.m.r. studies which left the assigned stereochemistry, at least, uncertain. The X-ray crystal structure of the $[3.1.0.0^{2,4}]$-tricyclohexane derivative was undertaken in order to unambiguously determine its stereochemistry and also to determine the precise geometry of the novel strained tricyclo system, since it affords the opportunity of observing the effect of ring fusion upon the geometry of the cyclopropane and cyclobutane rings. In cyclobutane it has been observed that the geometry is in general dependent upon the environment in which it is found, the effect of fusion with other rings varying, depending upon the nature of the fusing rings[103]. The effect of ring fusion upon the geometry of the cyclopropane ring does not appear to have received much attention up to this time.

## EXPERIMENTAL

The crystals, which approximated hexagonal needles, were supplied by Dr. S. Masamune. One, which was regarded as suitable for photographic work and data collection, was mounted on glass fibre (maximum dimensions 0.17 mm x 0.12 mm x 0.07 mm). Weissenberg photographs were obtained for the $0k\ell$, $1k\ell$ and $2k\ell$ layers and precession photographs for the $hk0$, $hk\ell$, and $h1\ell$ layers. These showed the Laue symmetry to be 2/m and the crystals to be monoclinic. The following systematic absences:

(1) $h0\ell$ $h + \ell = 2n + 1$ implying an n glide perpendicular to b

(2) $0k0$ $k = 2n + 1$ implying a $2_1$ axis parallel to b

defined the space group uniquely as $P_{2_1/n}$ (non standard setting of $P_{2_1/c}$).

The lattice parameters were obtained by the least squares refinement of the $2\theta$ values for several high angle reflections. The $2\theta$ values were measured on a PICKER manual four circle diffractometer. The dimensions obtained were:

$a = 10.044(4)$; $b = 9.500(2)$; $c = 14.172(4)$; $\beta = 104.38(2)$.

The experimentally observed density of 1.28 obtained by flotation in aqueous potassium iodide solution agrees well with the calculated density of 1.27 assuming two molecules of molecular weight 500 in a cell of volume 1309.90 $\mathring{A}^3$. The density therefore required that the molecule occupied a crystallographic inversion centre, which eliminated $\underset{\sim}{9}$ (Chapter 3 p 78) as a possible structure.

Intensity data were collected on a PAILRED automatic diffractometer using crystal monochromated $CuK_\alpha$ radiation and included the layers $nk\ell$ for n = 0 to 8. A constant scan rate of 2.5°/min was used throughout the data collection, but the scan width varied from 1.4° at h = 0 to 2.7° at h = 8. A stationary background count was taken for 20 secs on each side of the scan.

In the data reduction process, reflections were rejected if, (i) I = 0 (ii) $I \leqslant 3\sigma$. Of the 1316 reflections measured, 478 were rejected in this way giving 838 observed reflections. Measurement of five standard reflections at the end of each layer indicated no significant decomposition took place during the data collection.

An absorption correction was not applied, the linear absorption coefficient for this compound was quite small, being only 6.67 $cm^{-1}$.

Lorentz and polarisation corrections were applied and structure factor amplitudes and standard deviations were calculated.

During the course of the subsequent structure determination and refinement, it became clear that the data for several layers were very poor. Consequently the data were recollected using a PICKER manual four circle diffractometer.

Crystal monochromatised $CuK_\alpha$ radiation was used and the intensity data collected using the coupled $\omega/2\theta$ scanning technique. The scan width was 3° with a scan rate of 2°/min and a $2\theta$ maximum of 120°. A stationary background count was taken for 20 secs on each side of the scan.

Reflections were again rejected if $I \leqslant 0$ or if $I \leqslant 3\sigma$. 932 of the 1958 reflections collected were rejected in this manner giving 1032 observed reflections.

Lorentz and polarisation corrections were applied, but no correction for absorption was made. Structure factor amplitudes and standard deviations were then calculated.

## SOLUTION OF STRUCTURE AND REFINEMENT

The structure was solved, using the PAILRED data, by direct methods. The symbolic addition was performed using the N.R.C. system of programmes SAP1 - 4(b).

Normalised structure factors were calculated (page 20) and their distribution shown below, was clearly in agreement with the known centrosymmetric space group.

| | This Structure | Centrosymmetric | Non Centrosymmetric |
|---|---|---|---|
| $<\|E\|>$ | 0.825 | 0.798 | 0.886 |
| $<\|E\|^2>$ | 0.969 | 1.000 | 1.000 |
| $<\|E\|^2 - 1>$ | 1.058 | 0.968 | 0.736 |
| Percentage $\|E\| > 3$ | 0.84 | 0.30 | 0.01 |
| Percentage $\|E\| > 2$ | 5.55 | 5.00 | 1.80 |
| Percentage $\|E\| > 1$ | 28.57 | 32.00 | 37.00 |

Three reflections were arbitrarily given positive signs and used to define the origin, and to initiate the symbolic addition procedure. These were:

| Reflection | $\|E\|$ |
|---|---|
| 1 3 -1 | 3.238 |
| 2 1 1 | 3.816 |
| 1 0 -3 | 2.919 |

The acceptance level for a sign determination was set initially at $\sum_k \sigma_3 \sigma_2^{-3/2} |E_h| E_k E_{h-k} = 7.9$ and was allowed to fall slowly during the sign determination to a minimum acceptable value of 1.9 which corresponds to a probability of 0.978.

When the acceptance level had fallen to 6.4 and no new signs had been determined, symbol A was assigned to reflection 2 5 -3 ($|E| = 3.587$). At 4.9 B was assigned to 1 8 2 ($|E| = 3.263$) and at 3.4 C was assigned to 2 1 0 ($|E| = 3.851$).

118 reflections were assigned phases in terms of these three symbols. During the phase determining procedure, several relationships between symbols occured. Such relationships were accepted if both contributors had $\sum_k \sigma_3 \sigma_2^{-3/2} |E_h| E_k E_{h-k}$ greater than 1.9. These relationships are summarised in the table below.

| Symbol | No. of Indications +ve | No. of Indications -ve |
|---|---|---|
| A | 1 | 2 |
| B | 0 | 7 |
| AB | 0 | 0 |
| C | 0 | 3 |
| AC | 0 | 1 |
| BC | 4 | 2 |
| ABC | 5 | 0 |

From these relationships, it was possible to say confidently that B = - and ABC = +, which meant that A and C were opposite in sign. The indication seemed to be that C was negative and therefore A positive, but $E_{maps}$ corresponding to both possible solutions, (i) A = +, B = -, C = - and (ii) A = -, B = +, C = +, were computed. In the first of these maps, the structure was eventually recognised, but not without difficulty due to the presence of several quite large but meaningless peaks. All the atoms were located in this E map apart from four carbon atoms from one of the phenyl rings.

These fifteen atom positions were used as input to a structure factor calculation, which gave a residual R factor of 0.511. The calculated phases were used to compute an electron density map which revealed the positions of the remaining four carbon atoms. At this early stage of the structure determination, the two phenyl rings in the asymmetric unit were refined as rigid bodies with a C - C distance of 1.397 Å and a C - C - C angle of 120°.

In three cycles of refinement the R factor dropped to 0.259, but analysis of the R factor for each level collected showed that the data was suspect. The R factors are shown in tabulated form below:

| Level | $R_1$ | $R_2$ |
|---|---|---|
| hkℓ (all data) | 0.259 | 0.489 |
| hk0 | 0.199 | 0.923 |
| h0ℓ | 0.246 | 0.872 |
| 0kℓ | 0.218 | 0.359 |

(Continued on next page)

| Level | $R_1$ | $R_2$ |
|---|---|---|
| 1kℓ | 0.227 | 0.321 |
| 2kℓ | 0.238 | 0.327 |
| 3kℓ | 0.253 | 0.314 |
| 4kℓ | 0.437 | 1.273 |
| 5kℓ | 0.296 | 0.342 |
| 6kℓ | 0.284 | 0.393 |
| 7kℓ | 0.259 | 0.289 |
| 8kℓ | 0.264 | 0.312 |

Clearly the data for the 4kℓ level contained some very large errors. This data was omitted from the subsequent refinement cycles, and the complete data set was recollected using a PICKER four circle manual diffractometer (see page 122). While the data recollection was in process, the refinement was continued with the PAILRED data minus the 4kℓ reflections.

In two more cycles, the R factor reduced to 0.153, at which point, the atoms of the phenyl rings were allowed to refine as free atoms. The R factor fell in one cycle to 0.136. There were indications here that even more of the upper level data was suspect, since the R factors for 5kℓ and 6kℓ were 0.213 and 0.205 respectively.

An electron density difference map was now calculated, and from it, all the hydrogen atom positions in the molecule were obtained without difficulty. Inclusion of these atoms in the least squares refinement caused the R factor to drop in two more cycles to 0.111.

Two further refinement cycles in which all atoms other than the hydrogen atoms were allowed to refine anisotropically, further reduced the R factor to 0.073.

The data collected on the PICKER diffractometer was now substituted for the faulty PAILRED data. In four cycles the refinement converged with $R_1 = 0.040$, $R_2 = 0.048$.

Inspection of the observed and calculated structure amplitudes of low $\sin \theta/\lambda$ and large magnitude revealed that the crystal was suffering secondary extinction. Since absorption was negligible in this crystal, a correction was made for the polarisation part of the secondary extinction correction only. (See page 89).

After this correction had been applied, the refinement reconverged in two cycles to a final $R_1$ of 0.038 and $R_2 =$ 0.038. The largest peak in an electron density difference map computed at the end of the refinement was only 0.13 electrons per $\mathring{A}^3$ and was situated close to the methyl hydrogens.

Of the 118 signs determined in the symbolic addition procedure, 14 were incorrectly determined, which may account for some of the meaningless peaks in the E map.

# RESULTS

The observed and calculated structure amplitudes are listed in Table 23. Atomic coordinates and isotropic temperature factors are given in Table 24 and anisotropic temperature factors for the carbon and oxygen atoms are in Table 25. Bond lengths and angles are given in Tables 26 and 27. A selection of intramolecular and intermolecular non bonded contacts is given in Tables 28 and 29. The geometries of the cyclopropane and cyclobutane rings in various systems are summarised in Tables 30 and 31.

A perspective view of the molecule is given in Fig. 7. The contents of the unit cell projected onto the [a][c] plane is shown in Fig. 8. A selection of Newman projections is shown in Fig. 9.

## Table 23

Observed and Calculated Structure Amplitudes (electrons x 10)

```
  K   L FOBS  FCAL     K   L FOBS  FCAL     K   L FOBS  FCAL     K   L FOBS  FCAL     K   L FOBS  FCAL
  **H = -2****         8   0  160   156     5   2   89    93     1   7  137   127    -3  -8   54    50
  0  12   55    38     8   1  116   126     5   4  204   191     1   9  147   140    -3  -7  160   150
  1  12   84    91     8   5  127   126     5   6   99    96     1  11   68    79    -3  -6   93    90
  1  13   56    60     8   7  148   145     5   7   77    72     2   0  332   329    -3  -5  208   209
  3  12   86    92     8   9   82    79     5   8   89    87     2   1  324   332    -3  -4   68   109
  4  12  122   127     9   1  154   162     5  10  103   104     2   2  319   328    -3  -3  475   468
  5  12   69    68     9   3   75    75     5  12   82    91     2   3   97    96    -3  -2  141   144
  6  13   64    70     9   4   87    91     6   0   95    92     2   4   45    32    -3  -1  384   380
  **H = -1****         9   5   58    48     6   4   77    71     2   5  100   100    -2  -9   62    70
  0   7  196   199     **H =  1****         6   5  104    91     2   6  122   121    -2  -7   70    77
  0  11   95    93   -10  -5   58    66     6   9   82    79     2   7   56    44    -2  -6  241   236
  1   6  226   223   -10  -2   80    80     7   1  107   111     2   8  176   168    -2  -5  109   100
  1   7  130   125    -9  -5   56    57     7   3  114   110     2   9   86    83    -2  -4  304   310
  1   8  181   176    -9  -4   86    88     7   4   91    85     2  11   61    57    -2  -3  288   289
  1   9   73    70    -9  -3   59    58     7   5   83    82     2  12   54    59    -2  -1  136   135
  1  10   48    30    -9  -2  157   163     7   7   54    45     3   0  415   429    -1 -13  103   106
  1  13   65    76    -9  -1   98   100     8   0   73    67     3   1  110   115    -1 -12   80    78
  1  14   74    78    -8  -4   94    87     8   1   61    52     3   2  129   127    -1 -11   57    60
  2   7   42    32    -8  -3  141   138     8   2  276   276     3   3  142   139    -1  -9  104   103
  2   8   75    79    -8  -1  131   132     8   4  119   128     3   5  108   108    -1  -7  165   155
  2   9  155   151    -7  -4   94    97     8   5   70    81     3   9   90    86    -1  -6  126   130
  2  11  107   102    -7  -2  107   110     8   6  112   112     3  10  134   136    -1  -4  332   325
  3   7  162   163    -7  -1  229   230     8   8   95    92     3  12   97   100    -1  -2  346   341
  3   8  203   205    -6  -5   63    51     9   2  109   105     4   0  502   512    -1  -1  177   178
  3  11  216   216    -6  -3  174   175     9   3   75    77     4   1  145   144     0  -9  357   360
  3  15   43    37    -6  -2  164   164     9   7   91    88     4   2  241   241     0  -5  694   678
  4   8  225   222    -6  -1   62    61    10   2   63    67     4   3  116   114     0  -3   57    44
  4   9   59    43    -5  -5   98   103     **H =  2****         4   4   86    86     0  -1  724   730
  4  10   97   107    -5  -4  303   291   -10  -4   53    40     4   6  169   166     0   1  616   601
  4  13   67    69    -5  -3  266   251    -9  -7   67    70     4   9  138   150     0   3  284   282
  5   7  208   209    -5  -2   60    58    -9  -6   56    52     4  10   68    66     0   5  228   225
  5   8  152   154    -5  -1  175   165    -9  -2   74    76     4  12   65    75     0   7   95    94
  5  10   57    51    -4  -5   66    64    -8  -6   66    52     5   2  112   109     0   9  192   199
  5  12  133   131    -4  -4  149   150    -8  -4   82    89     5   3   50    51     1   0  237   242
  6   9  106   110    -4  -3   89    81    -8  -3  164   163     5   8   78    84     1   1  188   190
  6  10  132   124    -4  -2  264   256    -7  -9   88    94     5   9  101    95     1   2  502   496
  6  11   60    55    -4  -1  166   168    -7  -7   71    70     5  10   85    75     1   3   46    57
  6  12   64    69    -3  -5  505   505    -7  -5   94    92     5  11   63    59     1   5  192   199
  7   8  110    95    -3  -4   42    43    -7  -3   87    94     6   1  164   163     1   7  115   121
  7  11   93    91    -3  -3   70    65    -6 -10   88    87     6   2  127   124     1   8   77    65
  8   6   64    56    -3  -1  858   856    -6  -9   76    78     6   3   51    58     1   9   95    95
  8   8   54    51    -2  -5  135   136    -6  -8  137   134     6   4  118   116     1  10  155   149
  8  10   77    73    -2  -4   61    54    -6  -6  161   153     6   6   62    62     1  11   85    84
  **H =  0****        -2  -3  318   321    -6  -5   65    59     6   9   85   102     2   0  197   196
  0   2  516   527    -2  -2  422   431    -6  -4   94    93     7   0  138   142     2   1  262   256
  0   4  831   840    -2  -1  403   409    -6  -3   87    81     7   2  144   141     2   2   79    71
  0   6  413   411    -1  -5  126   123    -6  -2  212   223     7   5   90    86     2   3   55    42
  0   8  494   474    -1  -4  274   281    -5 -11  137   140     7   6   51    33     2   4   48    40
  0  12   95    86    -1  -3  185   190    -5  -9  187   189     7   7   64    61     2   6  209   208
  1   1  669   683    -1  -2  126   130    -5  -8   86    86     7   9   77    80     2   9   77    78
  1   2  191   195    -1  -1  552   562    -5  -7  137   133     8   0   71    73     3   0   53    44
  1   3  224   224     0  -5  677   688    -5  -5  249   242     8   1  205   212     3   1  443   440
  1   4  157   154     0  -3 1515  1446    -5  -4   97    97     8   2  178   177     3   2  116   111
  1   5  157   158     0  -1  526   541    -5  -3  483   466     8   3   88    93     3   4  215   214
  1   6   63    70     0   1  354   367    -5  -2  124   127     8   4   62    54     3   5   49    37
  1   7  181   169     0   3  110   115    -5  -1  110   117     8   6   61    54     3   8   75    80
  1   8  112   119     0   5  606   608    -4 -11   91    94     8   8   61    48     3   9   96    95
  1   9   64    56     0   7   91    91    -4 -10  106   105     8   9   62    71     3  10   82    73
  1  10  112   110     0   9  216   212    -4  -9  154   151     9   0   66    69     3  11   56    56
  1  12   54    54     0  11  102   111    -4  -8   61    75     9   1   87    86     3  12   76    85
  2   0  653   681     0  13  125   131    -4  -7   75    79     9   2   59    60     4   0   92    92
  2   1  958   956     1   0  324   330    -4  -5  117   125     9   5   52    36     4   1  274   271
  2   2  110   112     1   1  226   232    -4  -3   81    75     9   7   45    46     4   2   94    97
  2   3  305   310     1   2  321   331    -4  -2  323   314    10   3   45    46     4   3  182   179
  2   4  192   194     1   3  809   801    -3 -11  214   210    10   4   49    38     4   4  283   277
  2   5  114   110     1   4   74    71    -3 -10  195   201     **H =  3****         4   5  172   171
  2   6  308   308     1   5  523   524    -3  -9   51    47   -10  -3   49    44     4   6  108   113
  2   7  224   222     1   6   61    73    -3  -7   48    31    -9  -7   76    77     4   7   80    90
  2   8  311   299     1   7  229   229    -3  -3  439   431    -9  -5   75    80     4   8  133   142
  2  10  137   136     1   9  165   162    -3  -2  318   326    -8  -9   65    67     4   9  141   148
  2  11  129   120     1  12   96    99    -3  -1  294   301    -8  -4   56    80     4  11  108   108
  2  12   55    50     1  13   64    62    -2 -11  149   150    -8  -2  110   115     5   1  156   153
  3   2  324   328     2   0  376   376    -2 -10  146   149    -8  -1  155   158     5   2  163   159
  3   5   83    77     2   1   39    29    -2  -8  205   208    -7  -8  194   202     5   3  181   178
  3   6  112   114     2   2   60    58    -2  -6   90    96    -7  -2  106   107     5   4  125   133
  3  14   56    53     2   3  309   309    -2  -4  338   332    -7  -1  169   173     5   5  199   196
  4   0  288   288     2   4  305   317    -2  -3  100   100    -6  -9  125   131     5   7  192   196
  4   1  111   112     2   5  291   285    -2  -2  233   233    -6  -8   87    89     5   8  112   111
  4   2   38    32     2   6  170   165    -2  -1  481   491    -6  -3   70    67     5   9  101   105
  4   3  289   282     2   7  117   113    -1 -11  153   151    -6  -2  224   228     6   0  136   133
  4   4  370   363     2   8   51    48    -1 -10  148   146    -6  -1   88    85     6   3   64    62
  4   5  145   144     2   9   74    66    -1  -8  109   103    -5 -14   43    34     6   5   72    58
  4   7   62    61     2  12   71    68    -1  -7  297   300    -5 -10  136   134     6   6  137   139
  4   9  104   106     2  14   64    69    -1  -6   70    72    -5  -9  181   179     6   7   78    79
  4  10  219   221     3   0  315   325    -1  -5   50    35    -5  -8  195   192     6   8   52    41
  4  11   77    91     3   1   73    71    -1  -4  114   116    -5  -7   98   105     6  10   78    67
  4  12  100   101     3   2   83    82    -1  -3  270   274    -5  -6  176   180     7   0  284   288
  5   2  140   133     3   3  447   447    -1  -2  364   380    -5  -5  149   146     7   1  128   131
  5   4   82    89     3   5   42    46    -1  -1  411   417    -5  -4  179   182     7   2  138   140
  5   7   61    62     3   6  144   146     0  -6  276   273    -5  -1  288   286     7   3  110   116
  5   8   77    78     3   7   51    43     0  -4  142   145    -4 -13   69    68     7   4  107    98
  5   9   53    39     3   8   72    71     0  -2  599   604    -4 -12  104   101     7   5   81    83
  6   0  142   143     3   9  208   207     0   0  435   461    -4 -11   73    67     7   6   94    96
  6   2  100   103     3  12   58    53     0   2  900   898    -4  -9  152   154     7   9   58    65
  6   3   61    66     4   0  270   278     0   4  445   453    -4  -8  104   103     8   1   55    56
  6   4   76    73     4   1  160   162     0   6  181   179    -4  -7  101    95     8   2   76    72
  6   6   63    59     4   2   91    83     0   8  344   337    -4  -6   80    71     8   3   82    76
  6   7   68    73     4   3  248   243     0  10  146   148    -4  -5  240   233     8   6   95    98
  6   8   56    57     4   4  202   202     0  12   76    83    -4  -4  175   172     9   3   70    72
  6   9   67    69     4   5  100    94     1   0  896   905    -4  -3   61    65     9   5   57    53
  6  10   59    64     4   9   90    86     1   1 1293  1255    -4  -2  207   207     **H =  4****
  7   2   73    75     4  11   76    69     1   4  276   232    -4  -1  178   183    -9  -5   72    74
  7   3  100    95     5   0  301   360     1   5  123   124    -3 -14   81    87    -9  -2  139   139
  7   7   49    30     5   1   54    52     1   6   78    78    -3 -11   69    67    -8  -3  160   158
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  K   L FOBS  FCAL     K   L FCBS  FCAL     K   L FOBS  FCAL     K   L FOBS  FCAL     K   L FOBS  FCAL
 -8  -2   71    67     8   1   66    63     5   1   83    88     5   1  108   101    -2  -8  209   212
 -8  -1   57    44     8   5   94    92     5   2   71    73     5   2  115   112    -2  -6  138   144
 -7 -10   51    59     9   3   63    65     5   4   98    97     6   0   77    76    -2  -4  160   165
 -7  -8   77    77      **H = 5****         5   5   59    40     6   2  159   164    -2  -3   66    51
 -7  -7   72    73    -9  -5   66    58     5   6   59    57     6   4   76    75    -1 -13   52    49
 -7  -3  129   130    -9  -1   67    72     6   1  116   115     7   0   69    61    -1 -11  105   105
 -7  -2  181   181    -8  -8   72    71     6   2   65    61     7   1   97    98    -1 -10  128   135
 -6  -9  110   105    -8  -4   86    86     6   3   83    82     8   1   55    52    -1  -7   61    63
 -6  -8  111   121    -7  -8  121   123     6   5   74    76      **H = 7****        -1  -6   78    92
 -6  -7   87    98    -7  -5   83    78     6   7   57    64    -8  -3   56    55    -1  -5  256   248
 -6  -5   66    72    -7  -3   87    86     7   0  172   178    -8  -1   49    56    -1  -4  119   114
 -6  -3   80    75    -6 -11   83    78     7   1   55    56    -7  -3   78    85    -1  -3  157   160
 -6  -2  138   131    -6 -10   52    55     7   7   48    55    -7  -2   73    65    -1  -2  137   132
 -6  -1  150   149    -6  -9   67    79     8   0  126   130    -7  -1  125   125     0 -12   65    69
 -5 -13   59    48    -6  -7  196   207     8   1   65    72    -6  -9   78    92     0 -10   83    69
 -5  -9  291   295    -6  -6  141   145     8   3   60    55    -6  -8   61    69     0  -8  214   212
 -5  -7   57    62    -6  -5  141   140     9   0   60    55    -6  -5  132   140     0  -6  125   116
 -5  -6   70    72    -6  -4  140   144      **H = 6****        -6  -4   98    96     0  -4  206   216
 -5  -4  151   145    -6  -3  185   162    -8  -4   54    60    -6  -3  137   147     0   0   65    52
 -5  -1  123   121    -6  -1  150   146    -7 -10   90    91    -5 -12   63    61     0   2   99   108
 -4 -13   88    90    -5 -12  151   140    -7  -7  109   109    -5 -10   93    89     0   4   88    95
 -4 -11   84    91    -5  -9   84    76    -7  -6  120   122    -5  -9   68    74     1   0  172   167
 -4 -10   76    80    -5  -8  143   139    -7  -4   60    56    -5  -8   81    82     1   1   68    64
 -4  -9  102   104    -5  -7   87    96    -7  -3  121   128    -5  -7  100   107     1   2   94    96
 -4  -8   71    66    -5  -4  149   141    -7  -1   92    94    -5  -6   80    71     1   3  128   130
 -4  -5  149   143    -5  -3   73    79    -6 -11   84    75    -5  -5  153   150     1   4   77    71
 -4  -3   48    35    -5  -1  113   113    -6  -9   89    80    -5  -4  158   170     2   0   92    89
 -4  -2  241   232    -4 -12   80    79    -6  -7   72    86    -5  -3   81    83     2   4  133   140
 -4  -1   66    64    -4 -11   92    96    -6  -6   69    72    -4 -11  132   135     3   2  105   105
 -3 -10  320   320    -4 -10  168   171    -6  -5  105   109    -4 -10   70    75     3   3  119   119
 -3  -8   83    82    -4  -8   95   100    -6  -3   70    72    -4  -9   70    69     3   4   58    62
 -3  -5  169   164    -4  -4   69    59    -5 -12   67    67    -4  -8   60    66     4   1   86    88
 -3  -3   70    61    -4  -3  122   113    -5  -8  151   151    -4  -7  130   120     5   0  112   111
 -3  -2  345   331    -4  -2   77    77    -5  -7   95    97    -4  -3  117   120     5   1   81    75
 -3  -1  122   115    -3 -13   59    69    -5  -5   93    91    -3 -13   97    80     6   2   81    83
 -2 -12  205   220    -3 -12  136   139    -5  -4   70    77    -3  11   82    85     6   3   48    52
 -2 -11   63    68    -3 -10  162   164    -5  -3  111   114    -3  -9   59    62     7   1   46    46
 -2 -10  110   110    -3  -7   84    84    -5  -2  273   272    -3  -6   73    61      **H = 9****
 -2  -9  159   161    -3  -6  149   155    -5  -1  120   109    -3  -4  133   136    -6  -6   55    35
 -2  -8   93    91    -3  -5  308   295    -4 -13   65    63    -3  -3  232   237    -5  -7   71    56
 -2  -7   83    89    -3  -4  290   290    -4 -12   52    33    -2 -13   97   101    -5  -6   55    52
 -2  -6  220   218    -3  -1  100   105    -4 -10   64    54    -2 -11   75    86    -5  -5   52    57
 -2  -5  155   153    -2 -15   50    57    -4  -9  125   125    -2 -10   62    58    -4  -9   83    78
 -2  -4  240   231    -2 -13   92    94    -4  -8  100    90    -2  -9  248   241    -4  -7   96    99
 -2  -2   66    72    -2 -12  105   110    -4  -5   70    64    -2  -6  156   155    -4  -4   67    66
 -2  -1  265   267    -2 -11  132   137    -3 -13   72    71    -2  -5  253   252    -4  -3  114   111
 -1 -14   52    76    -2 -10   71    86    -3 -12  154   151    -2  -4  116   118    -3 -11   52    64
 -1 -13  114   124    -2  -9   80    78    -3  -9  133   125    -2  -3  330   332    -3  -9  103   107
 -1 -11  201   204    -2  -8   98    95    -3  -8  229   233    -2  -1   60    49    -3  -8   75    63
 -1  -8   82    82    -2  -7   77    79    -3  -7   71    59    -1 -10  128   131    -3  -7   77    86
 -1  -7   53    52    -2  -6  217   213    -3  -6  165   172    -1  -5   75    80    -3  -5  104    55
 -1  -6  217   220    -2  -2  166   163    -3  -4   55    69    -1  -3  151   150    -2 -10  101   103
 -1  -5   69    67    -2  -1  182   181    -3  -2   67    66    -1  -2  210   207    -2  -6   83    88
 -1  -4  121   113    -1 -14   92    92    -2  -9   88   100     0 -13  122   117    -2  -5   90    91
 -1  -3   96    99    -1 -13   82    85    -2  -7  110   103     0 -11  122   122    -2  -4  179   181
 -1  -2  247   245    -1 -12   75    80    -2  -6   69    70     0  -9   72    82    -2  -3  213   218
 -1  -1   62    67    -1 -11   66    72    -2  -5  216   211     0   1   60    74    -2  -2  119   120
  0 -12  275   282    -1 -10   68    69    -2  -4   67    51     0   3  107   106    -2  -1  160   164
  0 -10  145   144    -1  -7  164   160    -2  -3  120   119     0   7   71    75    -1  -8  150   147
  0  -8  116   120    -1  -6  273   266    -2  -1  289   283     1   4   65    71    -1  -6  157   172
  0  -4  226   226    -1  -5  289   287    -1 -15   53    44     1   6   56    60    -1  -5  165   166
  0  -2   65    33    -1  -4  150   152    -1 -12   56    59     2   1  136   131     0 -11  183   190
  0   0  191   186    -1  -2   65    76    -1 -11   94    97     2   3  141   146     0  -7  317   314
  0   2  197   204    -1  -1   61    58    -1  -9  113   111     2   4   66    58     0  -5  135   141
  0   8   99    98     0 -13  154   161    -1  -8   91    85     2   5   56    46     0  -3  155   153
  1   0  422   420     0 -11   84    69    -1  -7   61    62     2   6   69    76     0  -1  103    90
  1   1  421   412     0  -9  104    95    -1  -4  131   129     3   0  155   159     1   1   66    68
  1   2  380   380     0  -7  370   358    -1  -3   78    60     3   2   61    61     2   1  132   134
  1   3  244   250     0  -5  150   147    -1  -2  100    99     3   4  148   153     2   3  107   105
  1   5  130   122     0  -3  170   162    -1  -1   80    66     3   5   65    53     2   4   53    60
  1   6   91    88     0  -1  270   269     0 -10   82    86     3   6   58    82     3   0   66    70
  1   7  176   174     0   1  153   149     0  -8  142   130     4   3   70    69     3   1   54    54
  1   8   84    87     0   5  134   125     0  -6  121   123     4   5   89    94     5   0   57    53
  1   9   87    92     0   7  110   110     0  -4   82    81     4   7   49    51      **H = 10****
  2   0  277   282     0   9  125   125     0  -2  218   221     5   0   67    67    -4  -7   55    54
  2   2  119   128     1   0  390   395     0   0  164   161     5   6   59    65    -4  -5   57    50
  2   3   67    77     1   3   89    91     0   2  276   270     5   7   51    49    -4  -4   55    31
  2   4  229   223     1   4  111   112     0   6  114   117     6   0   79    78    -3  -9   46    30
  2   6  117   127     1   6  155   154     0  10   55    59     6   1  170   168    -3  -2   75    71
  2   9  108    98     1   7  129   136     1   0  124   115     6   2   74    69    -2 -10   86    57
  3   0   65    50     1   8  157   167     1   2  165   175     6   3   52    31    -2  -6  131   130
  3   1  273   269     1  11   46    11     1   3   90    54     6   6   57    62    -2  -5   68    68
  3   2  237   237     2   0  246   257     1   7   79    82      **H = 8****        -2  -4   97    55
  3   3   47    38     2   1  217   216     1   8   61    69    -7  -1   62    53    -2  -3   56    52
  3   4  199   190     2   2  149   151     2   0  132   134    -6  -7  126   119    -1  -8   93    98
  3   6  104   114     2   3  181   184     2   1  267   275    -6  -4   62    58    -1  -7  127   120
  3   9  122   123     2   4   86    83     2   2  160   160    -6  -2   96   101    -1  -4   55    89
  3  11   54    60     2   5  112   106     2   6  105   105    -6  -1   67    63    -1  -3   64    47
  3  12   69    76     2   6  122   120     2   7  120   120    -5  -9   52    51     0  -8   60    55
  4   0  133   135     2   9   91    93     2   8   64    61    -5  -8   85    75     0  -6   59    50
  4   1  155   153     2  10   63    76     2   9   65    62    -5  -6   59    56     0  -2   85    80
  4   2  115   117     3   0  122   117     3   0   55    62    -5  -4  130   136     0   2   65    76
  4   3  175   169     3   2  109   107     3   1   61    61    -5  -3   71    68     1   0   54    59
  4   5  114   116     3   3  122   121     3   3  194   193    -5  -2   61    53     2   0   65    65
  4   8   95    97     3   5  142   141     3   7   87    92    -5  -1   55    51     3   2  113   121
  5   1  225   225     3   6  124   120     3   8   67    77    -4  -9   76    70      **H = 11****
  5   2  114   109     3   7   94    86     3   9   67    76    -4  -3  122   122    -2  -3   47    46
  5   3  143   137     3   8  112   110     4   0  136   138    -4  -2   67    72    -2  -2   46    46
  5   4  107   105     3   9   57    64     4   1  109   109    -3 -10  173   180    -1  -7   85    75
  5   6  112   112     4   2   81    72     4   2  133   129    -3  -9  166   102    -1  -6   70    69
  6   0   54    35     4   3   55    45     4   3   59    73    -3  -8  103   185    -1  -4   53    48
  6   1   80    84     4   4   81    81     4   4   70    81    -3  -6  251   245     0  -5   50    52
  7   1  124   128     4  10   49    54     4   7   54    39    -3  -3   62    70     0  -3   50    39
  7   2  117   121     5   0  122   119     4   8   55    43    -3  -1  131   130     0  -1   50    52
```

## Table 24

Atomic Coordinates and Isotropic Temperature Factors

| Atom | x | y | z | B |
|---|---|---|---|---|
| C1 | -0.1037(3) | -0.0163(3) | -0.0442(2) | 2.95* |
| C2 | 0.0235(3) | 0.0630(3) | -0.0575(2) | 2.80* |
| C3 | 0.0600(3) | 0.1703(3) | 0.0250(2) | 3.11* |
| C4 | 0.1672(3) | 0.2756(4) | 0.0210(2) | 3.46* |
| C5 | 0.2256(6) | 0.5160(5) | 0.0455(5) | 6.33* |
| O1 | 0.2699(2) | 0.2549(3) | -0.0057(2) | 4.90* |
| O2 | 0.1317(2) | 0.4010(2) | 0.0486(2) | 4.51* |
| C11 | -0.2453(3) | 0.0339(3) | -0.0862(2) | 3.15* |
| C12 | -0.2938(4) | 0.0369(5) | -0.1865(3) | 4.86* |
| C13 | -0.4242(4) | 0.0872(5) | -0.2292(3) | 5.51* |
| C14 | -0.5063(4) | 0.1349(4) | -0.1722(4) | 4.96* |
| C15 | -0.4609(4) | 0.1337(5) | -0.0744(4) | 5.51* |
| C16 | -0.3300(4) | 0.0844(4) | -0.0313(3) | 5.09* |
| C21 | 0.0556(3) | 0.0841(4) | -0.1540(2) | 3.04* |
| C22 | 0.0286(4) | 0.2130(4) | -0.2008(3) | 4.26* |
| C23 | 0.0496(4) | 0.2329(5) | -0.2930(3) | 5.03* |
| C24 | 0.0977(4) | 0.1249(4) | -0.3388(3) | 4.64* |
| C25 | 0.1237(4) | -0.0034(4) | -0.2946(3) | 4.56* |
| C26 | -0.0241(4) | -0.0241(4) | -0.2030(3) | 3.91* |
| H51 | 0.223(5) | 0.533(5) | -0.018(3) | 8.2(16) |
| H52 | 0.319(4) | 0.490(5) | 0.080(3) | 7.4(13) |

(Continued on next page)

Table 24 continued

| Atom | x | y | z | B |
|---|---|---|---|---|
| H53 | 0.190(5) | 0.596(6) | 0.074(3) | 10.5(17) |
| HB | -0.012(3) | 0.209(3) | 0.051(2) | 3.6(7) |
| H12 | -0.238(4) | -0.001(4) | -0.228(2) | 6.0(9) |
| H13 | -0.454(4) | 0.091(4) | -0.299(3) | 6.4(10) |
| H14 | -0.596(4) | 0.166(4) | -0.203(2) | 5.3(8) |
| H15 | -0.518(4) | 0.156(4) | -0.030(3) | 6.5(10) |
| H16 | -0.303(3) | 0.073(3) | 0.032(2) | 4.0(8) |
| H22 | -0.004(3) | 0.289(4) | 0.165(2) | 5.4(8) |
| H23 | 0.020(4) | 0.325(4) | -0.323(3) | 7.2(10) |
| H24 | 0.114(3) | 0.144(4) | -0.399(3) | 5.7(10) |
| H25 | 0.159(3) | -0.080(4) | -0.323(2) | 5.0(8) |
| H26 | 0.119(3) | -0.110(3) | -0.176(2) | 3.6(7) |

---

*These are equivalent isotropic temperature factors corresponding to the anisotropic parameters given in Table 25.

## Table 25

### Anisotropic Temperature Factors

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.033(2) | 0.038(2) | 0.045(2) | 0.005(2) | 0.018(2) | 0.005(2) |
| C2 | 0.034(2) | 0.033(2) | 0.043(2) | 0.006(1) | 0.017(1) | 0.004(2) |
| C3 | 0.038(2) | 0.038(2) | 0.048(2) | 0.004(2) | 0.021(2) | 0.001(1) |
| C4 | 0.043(2) | 0.044(2) | 0.049(2) | 0.006(2) | 0.020(2) | 0.003(2) |
| C5 | 0.081(4) | 0.045(3) | 0.126(5) | -0.013(3) | 0.049(4) | -0.002(3) |
| O1 | 0.045(1) | 0.057(2) | 0.095(2) | -0.001(1) | 0.038(1) | -0.008(1) |
| O2 | 0.062(2) | 0.035(2) | 0.088(2) | 0.000(1) | 0.044(1) | -0.002(2) |
| C11 | 0.037(2) | 0.039(2) | 0.049(2) | 0.003(1) | 0.020(2) | 0.006(2) |
| C12 | 0.045(2) | 0.089(3) | 0.054(3) | 0.008(2) | 0.017(2) | 0.007(2) |
| C13 | 0.051(3) | 0.098(3) | 0.058(3) | 0.011(3) | 0.009(2) | 0.020(3) |
| C14 | 0.040(2) | 0.055(3) | 0.088(4) | 0.009(2) | 0.007(3) | 0.010(3) |
| C15 | 0.050(3) | 0.083(3) | 0.078(3) | 0.024(2) | 0.019(3) | -0.010(3) |
| C16 | 0.050(3) | 0.091(3) | 0.053(3) | 0.021(2) | 0.014(2) | 0.006(3) |

(Continued on next page)

Table 25 continued

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| C21 | 0.033(2) | 0.045(2) | 0.042(2) | 0.002(2) | 0.019(2) | 0.003(2) |
| C22 | 0.064(3) | 0.049(3) | 0.057(3) | 0.011(2) | 0.031(2) | 0.007(2) |
| C23 | 0.086(3) | 0.057(3) | 0.056(3) | 0.014(2) | 0.032(2) | 0.013(2) |
| C24 | 0.076(3) | 0.063(3) | 0.047(3) | 0.002(2) | 0.033(2) | 0.009(2) |
| C25 | 0.075(3) | 0.051(3) | 0.057(3) | 0.002(2) | 0.034(2) | −0.001(2) |
| C26 | 0.060(2) | 0.044(2) | 0.050(2) | 0.004(2) | 0.025(2) | 0.002(2) |

## Table 26

Interatomic Distances (Å)

| Atoms | Distance | Atoms | Distance |
|---|---|---|---|
| C1 - C2 | 1.535(4) | C23 - C24 | 1.366(5) |
| C2 - C1' | 1.532(4) | C24 - C25 | 1.366(5) |
| C2 - C3 | 1.526(4) | C25 - C26 | 1.385(5) |
| C3 - C1' | 1.532(4) | C26 - C21 | 1.382(4) |
| C3 - C4 | 1.481(4) | C3 - HB | 0.97(3) |
| C4 - O1 | 1.199(3) | C12 - H12 | 0.97(3) |
| C4 - O2 | 1.330(4) | C13 - H13 | 0.97(3) |
| O2 - C5 | 1.450(5) | C14 - H14 | 0.95(3) |
| C1 - C11 | 1.478(4) | C15 - H15 | 0.98(4) |
| C2 - C21 | 1.495(4) | C16 - H16 | 0.87(3) |
| C11 - C12 | 1.384(4) | C22 - H22 | 0.98(3) |
| C12 - C13 | 1.384(5) | C23 - H23 | 0.99(3) |
| C13 - C14 | 1.368(5) | C24 - H24 | 0.93(4) |
| C14 - C15 | 1.347(6) | C25 - H25 | 0.95(3) |
| C15 - C16 | 1.386(6) | C26 - H26 | 0.90(3) |
| C16 - C11 | 1.374(4) | C5 - H51 | 0.91(4) |
| C21 - C22 | 1.387(4) | C5 - H52 | 0.97(4) |
| C22 - C23 | 1.386(5) | C5 - H53 | 0.97(5) |

## Table 27

### Intramolecular Angles

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| C3' - C1 - C2' | 59.7(2) | C2 - C3 - C1' | 60.1(2) |
| C2' - C1 - C2 | 89.9(2) | C2 - C3 - C4 | 117.4(3) |
| C3' - C1 - C11 | 125.8(3) | C2 - C3 - HB | 119(2) |
| C2' - C1 - C11 | 134.5(3) | C1' - C3 - HB | 120(2) |
| C11 - C1 - C2 | 122.6(3) | C4 - C3 - HB | 112(2) |
| C3' - C1 - C2 | 106.3(2) | C1' - C3 - C4 | 118.2(3) |
| C1 - C2 - C1' | 90.1(2) | C3 - C4 - O1 | 126.3(3) |
| C1 - C2 - C21 | 123.6(3) | C3 - C4 - O2 | 110.1(3) |
| C1 - C2 - C3 | 106.4(2) | O1 - C4 - O2 | 123.6(3) |
| C21 - C2 - C3 | 123.1(3) | O2 - C5 - H51 | 108(3) |
| C21 - C2 - C1' | 135.8(3) | O2 - C5 - H52 | 110(3) |
| C3 - C2 - C1' | 60.1(2) | O2 - C5 - H53 | 105(3) |
| H51 - C5 - H53 | 110(4) | H15 - C15 - C14 | 124(2) |
| H51 - C5 - H52 | 110(4) | H15 - C15 - C16 | 116(2) |
| H52 - C5 - H53 | 113(4) | C14 - C15 - C16 | 119.9(4) |
| C1 - C11 - C12 | 118.6(3) | H16 - C16 - C15 | 121(2) |
| C1 - C11 - C16 | 123.7(3) | H16 - C16 - C11 | 118(2) |
| C12 - C11 - C16 | 117.7(3) | C15 - C16 - C11 | 121.3(4) |
| H12 - C12 - C11 | 120(2) | C2 - C21 - C22 | 119.6(3) |
| H12 - C12 - C13 | 119(2) | C2 - C21 - C26 | 122.3(3) |
| C11 - C12 - C13 | 120.6(3) | C22 - C21 - C26 | 117.8(3) |
| H13 - C13 - C12 | 119(2) | H22 - C22 - C21 | 117(2) |

(Continued on next page)

Table 27 continued

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| H13 - C13 - C14 | 121(2) | H22 - C22 - C23 | 122(2) |
| C12 - C13 - C14 | 120.0(4) | C21 - C22 - C23 | 120.9(4) |
| H14 - C14 - C13 | 118(2) | H23 - C23 - C22 | 116(2) |
| H14 - C14 - C15 | 121(2) | H23 - C23 - C24 | 124(2) |
| C13 - C14 - C15 | 120.3(4) | C22 - C23 - C24 | 120.0(4) |
| H24 - C24 - C23 | 117(2) | C24 - C25 - C26 | 120.0(4) |
| H24 - C24 - C25 | 123(2) | H26 - C26 - C25 | 118(2) |
| C23 - C24 - C25 | 120.2(4) | H26 - C26 - C21 | 121(2) |
| H25 - C25 - C24 | 123(2) | C25 - C26 - C21 | 121.1(4) |
| H25 - C25 - C26 | 117(2) | | |

## Table 28

### Intramolecular Non-bonded Contacts

| Atoms | Distance | Atoms | Distance |
|---|---|---|---|
| C3 - C1 | 2.451(5) | O1 - O2 | 2.230(3) |
| C3 - C2' | 2.454(5) | O1 - C21 | 3.073(4) |
| C1 - C1' | 2.170(6) | O1 - C11' | 3.073(4) |
| C2 - C2' | 2.168(6) | O1 - C22 | 3.218(5) |
| C4 - C11' | 3.123(5) | O1 - C16 | 3.298(5) |
| C4 - C21 | 3.056(5) | C11 - C21 | 3.425(4) |
| C3 - C11 | 3.342(5) | C11' - C21 | 3.641(5) |
| C3 - C21' | 3.404(5) | C1' - HB | 2.18(3) |
| C3 - C11' | 2.679(5) | C2 - HB | 2.17(3) |
| C3 - C21 | 2.656(5) | C1 - HB | 2.58(3) |
| C3 - O1 | 2.394(4) | C2 - HB' | 2.59(3) |
| C3 - O2 | 2.306(4) | C4 - HB | 2.05(3) |

## Table 29

### Selected Intermolecular Contacts Less than 4.0 Å

| Atom 1 | Atom 2 | Distance | Symmetry Operation |
|---|---|---|---|
| C5 | C12 | 3.884(8) | 1/2+x, 1/2-y, 1/2+2 |
| O1 | C15 | 3.302(5) | 1+x, y, z |
| O1 | C23 | 3.576(5) | 1/2+x, 1/2-y, 1/2+z |
| O2 | O2' | 3.260(5) | x, 1+y, z |
| O2 | C13 | 3.335(5) | 1/2+x, 1/2-y, 1/2+2 |
| O2 | C12 | 3.689(5) | 1/2+x, 1/2-y, 1/2+2 |
| C12 | C13 | 3.828(6) | -1/2-x, -1/2+y, -1/2-z |
| C13 | C23 | 3.635(6) | -1/2-x, -1/2+y, -1/2-2 |
| C14 | C25 | 3.625(6) | -1/2-x, 1/2+y, -1/2-z |
| C14 | C26 | 3.701(6) | -1/2-x, 1/2+y, -1/2-z |
| C15 | C15' | 3.514(10) | x-1, y, z |
| C15 | C16' | 3.537(7) | x-1, y, z |
| C22 | C13 | 3.769(6) | -1/2-x, 1/2+y, -1/2-z |
| C3 | H53' | 3.39(5) | x, 1+y, z |
| C5 | H24 | 3.16(4) | 1/2-x, 1/2+y, -1/2-z |
| O1 | H15 | 2.43(4) | 1+x, y, z |
| O2 | H13 | 2.51(4) | 1/2+x, 1/2-y, 1/2+z |
| C12 | H23 | 3.06(4) | -1/2-x, y-1/2, -1/2-z |
| C13 | H23 | 2.83(4) | -1/2-x, y-1/2, -1/2-z |
| C14 | H23 | 2.94(4) | -1/2-x, y-1/2, -1/2-z |
| C16 | H15' | 2.99(4) | x-1, y, z |
| C24 | H52 | 2.96(4) | x-1/2, 1/2-y, z-1/2 |

(Continued on next page)

Table 29 continued

| Atom 1 | Atom 2 | Distance | Symmetry Operation |
|---|---|---|---|
| C25 | H14 | 3.14(4) | x-1/2, 1/2-y, z-1/2 |
| H51 | H24 | 2.47(6) | 1/2-x, 1/2+y, -1/2-z |
| H14 | H25 | 2.54(5) | -1/2-x, 1/2+y, -1/2-z |

## Table 30

### Geometry of the Cyclopropane Ring

(a) Unfused Systems

| Compound Name | C - C | Method | Reference |
|---|---|---|---|
| Cyclopropane | 1.510 | E.D. | 104 |
| Cyclopropyl carbinol | 1.514 | M.W. | 105 |
| Cyclopropane Carboxamide | 1.500 | X.R. | 106 |
| Cis-1,2,3-tricyanocyclopropane | 1.518 | X.R. | 107 |
| Cyclopropyl chloride | 1.514 | M.W. | 108 |
| Bicyclopropyl | 1.504 | X.R. | 109 |
| 1,1'-Dimethylbicyclopropyl-2,2'-dicarboxylate | 1.51 | X.R. | 110 |
| Cis-1,2-diacetonyl-1,2,3,3-tetrachlorocyclopropane | 1.50 | X.R. | 111 |
| Cyclopropane | 1.514 | R | 112 |
| Cyclopropane carboxaldehyde | 1.507 | E.D. | 113 |

(Continued on next page)

Table 30 continued

(b) Fused Systems

| Compound Name | C - C | Method | Reference |
|---|---|---|---|
| 2,5-dimethyl-7,7-dicyanonorcaradiene | 1.501 (ring junction)<br>1.557 | X.R. | 114 |
| 6,6-diphenyl-3,3-diethyl-3-azabicyclo[3.1.0]hexane bromide monohydrate | 1.517 | X.R. | 115 |
| 1,5-diphenyltricyclo-[2.1.0.0$^{2,5}$]pent-3-yl p-bromobenzoate | 1.44 (junction of cyclopropane rings)<br>1.53 | X.R. | 116, 117 |
| Bicyclo[2.1.0]pentane | 1.536 (ring junction)<br>1.507 | M.W. | 118 |
| Bicyclo[1.1.0]butane | 1.498 | M.W. | 143 |
| 1-2,4,5-tetraphenyl-3,6-dicarbomethoxytricyclo [3.1.0.0$^{2,4}$]hexane | 1.531 | X.R. | This work |

X.R. = X-ray

E.D. = Electron Diffraction

M.W. = Microwave

R = Raman

## Table 31

## Geometry of the Cyclobutane Ring

(a) Unfused Systems

| Compound | C - C | Method | Reference |
|---|---|---|---|
| Cyclobutane | 1.548 | E.D. | 119 |
| Cyclobutane | 1.558 | R. | 120 |
| Trans-1,3-cyclobutane-dicarboxylic acid | 1.560 | | 91 |
| Trans-1,2-cyclobutane-dicarboxylic acid | 1.553<br>1.517 (between trans substituents) | X.R. | 121 |
| Cis-1,2-cyclobutane-dicarboxylic acid | 1.554 | X.R. | 122 |
| Trans-1,2-dyclobutane-dicarboxylic acid-sodium salt (and free acid as solvent of crystallisation) | 1.563 (dianion)<br>1.552 (acid) | X.R. | 123 |
| Cis-1,2-dibromo-1,2-dicarbomethoxycyclobutane | 1.55 | X.R. | 124 |
| Trans-1,2-dibromo-1,2-dicarbomethoxycyclobutane | 1.56 | X.R. | 124 |
| Cis-trans-cis-1,2,3,4-tetracyanocyclobutane | 1.561 (between cis substituted carbons<br>1.547 (between trans substituted carbons) | X.R. | 125 |
| Octahydroxycyclobutane | 1.563 | X.R. | 126 |
| Cis-trans-cis-1,2,3,4-cyclobutanetetracarboxylic acid tetramethyl ester | 1.572 (between cis substituted carbons)<br>1.541 (between trans substituted carbons) | X.R. | 127 |

(Continued on next page)

Table 31 continued

| Compound | C - C | Method | Reference |
|---|---|---|---|
| 2,2,4,4-tetramethylcyclobutane-trans-1,3-diol | 1.545 | X.R. | 128 |
| 1,1,3,3-tetrafluorocyclobutane | 1.566 | E.D. | 129 |
| Cyclobutane carboxylic acid chloride | 1.540 | E.D. | 130 |
| 1,2,3,4-tetraphenylcyclobutane | 1.585 (between cis substituted carbons)<br>1.555 (between trans substituted carbons) | X.R. | 131 |

(b) Fused Systems

| Compound | C - C | Method | Reference |
|---|---|---|---|
| Cubane | 1.551 | X.R. | 132 |
| dℓ-Photodimer C of 1,3-dimethyl thymine | 1.531 (ring junction)<br>1.574 (inter thymine ring) | X.R. | 133 |
| Photodimer E of Thymine | 1.547 (ring junction)<br>1.587 (inter thymine ring) | X.R. | 134 |
| Photodimer of cyclopentanone | 1.54 (ring junction)<br>1.59 (inter cyclopentane ring) | X.R. | 135 |
| Tricyclo [2.1.0.0$^{2,5}$]-pentane | 1.53 | X.R. | 116, 117 |

(Continued on next page)

Table 31 continued

| Compound | C - C | Method | Reference |
|---|---|---|---|
| Thymine Photodimer | 1.540 (ring junction)<br>1.568 (inter thymine ring) | X.R. | 136 |
| Photodimer of 1-methylthymine | 1.543 (ring junction)<br>1.571 (inter thymine ring) | X.R. | 137 |
| Bicyclo-[2.1.0]pentane | 1.536 (ring junction)<br>1.565, 1.528, 1.528<br>average 1.534 | M.W. | 118 |
| 7-endo-chlorobicyclo-[3.2.0]hept-2-ene-6-endo-ol-p-bromobenzoate | 1.540 (ring junction)<br>1.507, 1.537, 1.542<br>average 1.532 | X.R. | 138 |
| Trans-Bicyclo[4.2.0] octyl-1-3,5-dinitrobenzoate | 1.532 (ring junction)<br>1.540, 1.547<br>average 1.544 | X.R. | 93 |
| 3,4:7,8-dibenzo-tricyclo[4.2.0.0$^{2,5}$]-octa-3,7-diene | 1.593 (ring junction)<br>1.559 (inter cyclobutane rings) | X.R. | 139 |
| 1,2,4,5-tetraphenyl-3,6-dicarbomethoxy-tricyclo[3.1.0.0$^{2,4}$]-hexane | 1.534 | X.R. | This Work |
| Bicyclo[1.1.1]pentane | 1.545 | E.D. | 143 |
| Chlorobicyclo[1.1.1]-pentane | 1.536, 1.556 | M.W. | 144 |

X.R. = R-Ray, R = Raman, E.D. = Electron Diffraction,

M.W. = Microwave.

## Table 32

## Least Squares Planes for 1,2,4,5-Tetraphenyl-3,6-Dicarbomethoxytricyclo[3.1.0.0$^{2,4}$]hexane

A. Phenyl Rings

(i) Atoms defining the plane: C11 C12 C13 C14 C15 C16

Equation of Plane: $-0.3925X - 0.9194Y + 0.0247Z - 0.5177 = 0$

Distance of atoms from plane in Å

| | | | |
|---|---|---|---|
| C11 | 0.005 | C14 | 0.003 |
| C12 | -0.003 | C15 | 0.003 |
| C13 | -0.002 | C16 | -0.007 |

(ii) Atoms defining the plane. C21 C22 C23 C24 C25 C26

Equation of the plane: $0.8671X + 0.2823Y + 0.4108Z - 0.3045 = 0$

Distance of atoms from plane in Å

| | | | |
|---|---|---|---|
| C21 | 0.008 | C24 | 0.006 |
| C22 | -0.003 | C25 | 0.003 |
| C23 | -0.005 | C26 | -0.009 |

(iii) Atoms defining plane: H12 H13 H14 H15 H16

Equation of plane: $-0.3913X - 0.9293Y - 0.0010Z - 0.6105 = 0$

(Continued on next page)

Table 32 continued

Distance of atoms from plane in Å

|  |  |  |  |
|---|---|---|---|
| H12 | -0.020 | H15 | -0.018 |
| H13 | 0.026 | H16 | 0.016 |
| H14 | -0.004 |  |  |

(iv) Atoms defining the plane: H22 H23 H24 H25 H26

Equation of plane: $0.8623X + 0.2892Y + 0.4156Z - 0.2793 = 0$

Distance of atoms from plane in Å

|  |  |  |  |
|---|---|---|---|
| H22 | 0.040 | H25 | 0.010 |
| H23 | -0.071 | H26 | -0.016 |
| H24 | 0.038 |  |  |

B. Tricyclic System

(i) Atoms defining the plane: C2 C3 C1'

Equation of plane: $-0.9500X - 0.1976Y + 0.2420Z + 0.7257 = 0$

(ii) Atoms defining the plane: C1 C2 C1' C2'

Equation of plane: $-0.4132X + 0.8212Y + 0.3935Z = 0$

C. Carbomethoxy Group

Atoms defining plane: C4 C5 O1 O2

(Continued on next page)

Table 32 continued

Equation of plane: $0.2706X - 0.1980Y + 0.9421Z -$

$0.1867 = 0$

Distance of atoms from plane in Å

| | | | |
|---|---|---|---|
| C4 | 0.001 | O1 | -0.0006 |
| C5 | 0.0008 | O2 | -0.0009 |
| | | C3 | -0.0442 |

Fig. 7

A Perspective View of 1,2,4,5-Tetraphenyl-
3,6-dicarbomethoxytricyclo[3.1.0.0$^{2,4}$]hexane

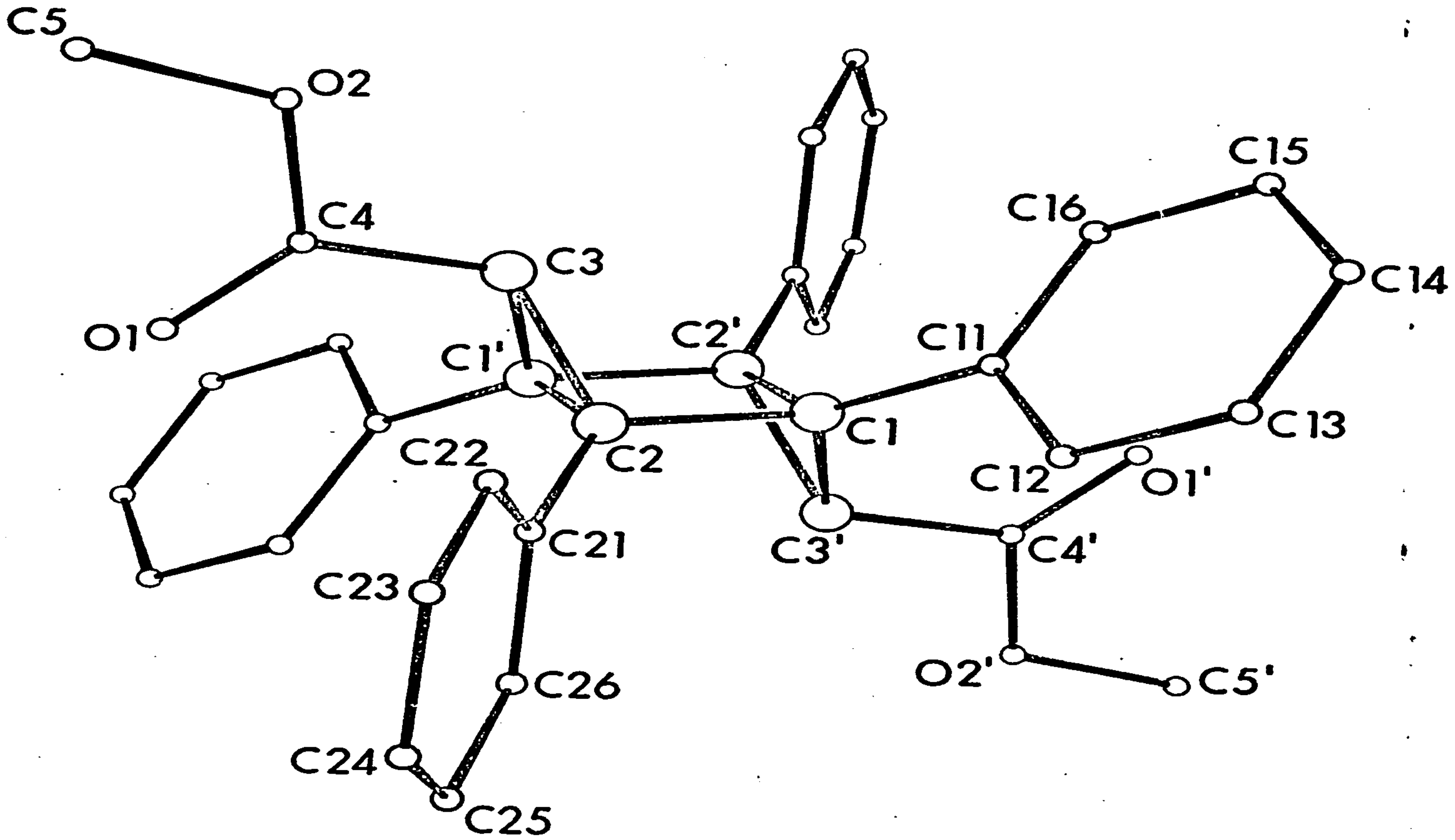

C5
O2
C4
C3
O1
C1'
C2'
C11
C16
C15
C14
C2
C1
C13
C22
C12
O1'
C21
C3'
C4'
C23
C26
O2'
C5'
C24
C25

Fig. 8

Contents of the Unit Cell Projected onto the [a][c] Plane.

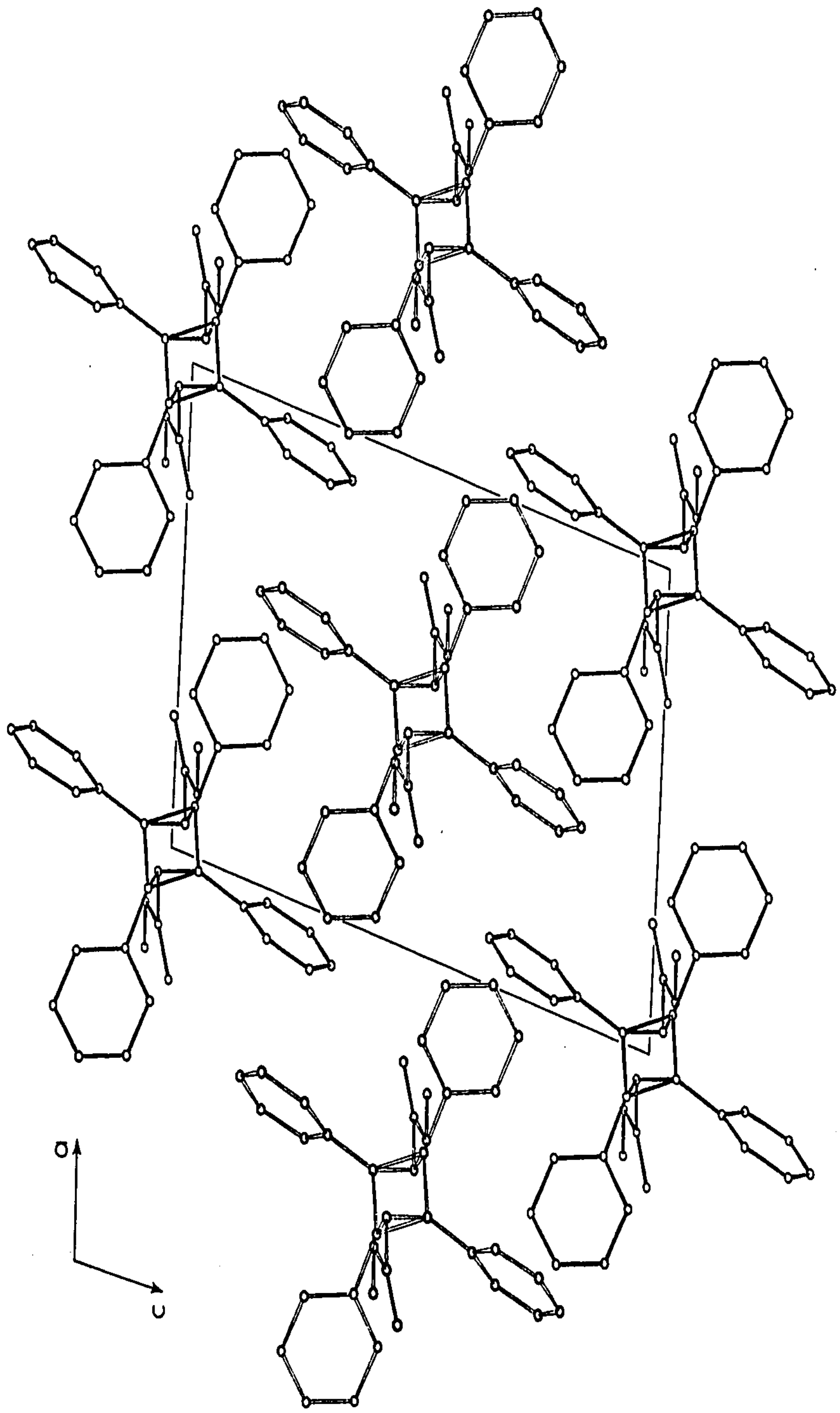

a
c

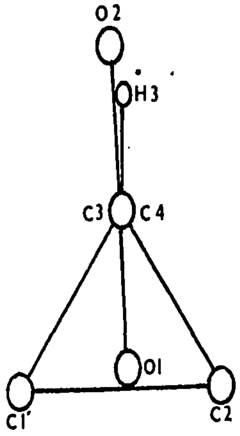
Fig. 9

A Selection of Newman Projections:

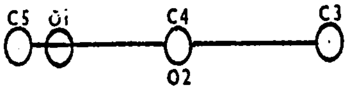
(a) down C4-C3 bond

(b) down O2-C4 bond

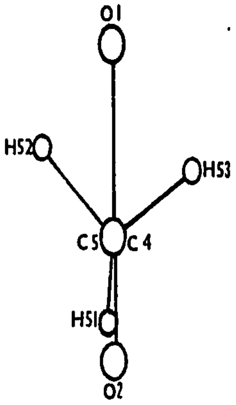
(c) down C5....C4 virtual bond



(a)



(b)



(c)

## DISCUSSION

1,2,4,5-tetraphenyl-3,6-dicarbomethoxy-tricyclo-[3.1.0.0$^{2,4}$]hexane crystallises on a crystallographic inversion centre and consequently is in the anti-configuration and has a planar cyclobutane ring. The carbomethoxy groups are in the *exo*-position. A diagram of the molecule is shown in Fig. 8.

The most outstanding detailed structural feature of the molecule is that all bond lengths within the tricyclohexane framework are equal within experimental error and average 1.531Å. The bond distances in the cyclopropane ring average 1.530 Å and the bond angles within the ring average 60°. The bond lengths are longer than the 1.510 Å bond lengths found in cyclopropane itself[104], and that found in various substituted unfused cyclopropanes (Table 30).

The bond lengths in the cyclobutane ring average 1.534 Å and the ring is planar and square, the bond angles within the ring averaging 90.0°. The bond lengths are shorter than the 1.548 found in cyclobutane itself[119] and in substituted unfused cyclobutanes,(Table 31.) The cyclopropane and cyclobutane rings meet at an angle of 109.0°.

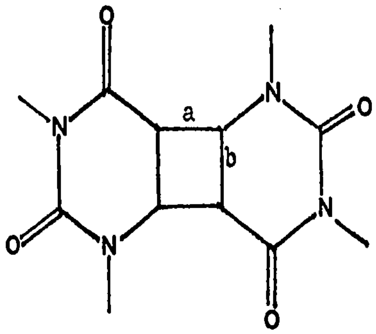
The bond distances from the tricyclic system to the substituent phenyl and carbomethoxy groups are all about 0.02 Å shorter than is normally found in unstrained systems. This bond shortening to substituent groups is characteristic of highly strained systems[114, 140,141] and has been observed in many of the compounds listed in Tables 30 and 31.

The angles within the phenyl rings are normal. The angle at the attached carbon atom averages 117.8° and all other angles cluster closely around 120°, with an average value of 120.2°. However, the bond lengths in the phenyl rings range from 1.347 Å to 1.389 Å with an average value of 1.376 Å. The variation of bond lengths is systematic. In both rings it is the bonds which are furthest from the tricyclic system which have shortened significantly from accepted values. This bond shortening is undoubtedly due to the effect of thermal motion, probably a libration of the molecule as a whole, which would have the observed effect. The carbon hydrogen distances in the phenyl rings average 0.95 Å. Both rings are planar within experimental error and the associated hydrogen rings are coplanar with them (Table 32). The plane containing the phenyl ring attached to C2 is perpendicular to the plane of the cyclobutane ring while that attached to C1 is skewed. A similar situation is found in tetraphenyl cyclobutane[131].

The bond distances and angles within the carbomethoxy group are similar to those found in other compounds (Table 22, Chapter 2). The carbomethoxy group in this compound does not experience such great intramolecular forces as the carbomethoxy group in 1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene, as can be seen by the longer C4---C11 and C4---C21 contacts, 3.123 Å and 3.056 Å respectively, compared with 2.993 Å and 2.916 Å in the cyclohexadiene derivative. However, these contacts are still much shorter than the normal Van der Waals contact between two non-bonded carbon atoms. The oxygen contacts with the phenyl groups are all close to or greater than the sum of the Van der Waals radii for carbon and oxygen, the shortest (3.073 Å) are the contacts between O1 and the first atom of each phenyl group C21 and C11'. The external angles around C3 are also normal, C4 -C3 - C2 is 117.4° and C4 - C3 - C1' is 118.2°, both of which are close to the values found in other substituted cyclopropane rings[106-108], although the C4 - C3 - HB bond angle of 112° is slightly smaller than the 116° average found in these compounds. However the large standard deviation on this angle, makes the difference insignificant. The carbomethoxy group is planar within experimental error. Despite the above, the intramolecular forces would seem to be still great enough to prevent the carbomethoxy group from taking up its preferred orientation with the C=O syn-planar with the $C_\alpha$ - $C_\beta$ bond[85-87], in this case the C3 - C2 bond. The torsion angle C2 - C3 - C4 = O1 is 38.3°, which, being smaller than the 45.9° found in the cyclohexa-1,4-diene derivative, may reflect the lessening of intramolecular nonbonded repulsions in this compound. However Hoffmann and Davidson[146] have pointed out that for a carbomethoxy group attached to a cyclopropane ring the syn-planar arrangement may not be the preferred conformation. They showed that the low lying $\pi^*$ orbital of the carbonyl can interact with the pseudo-$\pi$ ring orbital and this interaction is greatest if the plane containing carbomethoxy group is perpendicular to the plane of the ring and the C=O is anti-planar with respect to the ring C - H bond, that is if the torsion angle O = C - C - H is 180°. This they termed the bisected conformation. This is exactly the conformation found in this compound. The plane of the carbomethoxy group is perpendicular to the plane of the cyclopropane ring and the torsional angle O1 - C4 - C3 - HB is 178°. The carbonyl group is also in the preferred syn-planar orientation with respect to the ester methylcarbon[87,95], the torsion angle O1 = C - O2 - C5 being 0°. Two other molecules which have this conformation, which Hoffmann and Davidson called the bisected configuration are cyclopropane carboxaldehyde[113] and cyclopropane carboxamide[106]. On the other hand, 1,1'-dimethylbicyclopropyl-2,2'-dicarboxylate[110], takes up the 'normal' orientation, the $O = C - C_\alpha - C_\beta$ torsion angle being 4°.

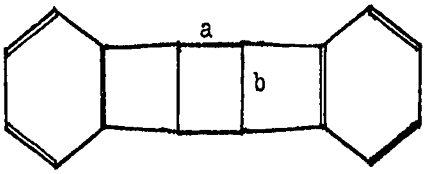
The cyclobutane ring has equal bond lengths within experimental error which average 1.534 Å. This is unexpected since in cyclobutane itself the bond length is 1.548 Å which is longer than that found in normal paraffins. If the cyclobutane ring is substituted then the bond between cis substituted carbons is even longer[125,127,131]. In tetraphenylcyclobutane the bond lengths are 1.585 Å between the cis substituted carbons, and 1.555 Å between the trans substituted carbons[131]. Thus the fusion with two cyclopropane rings has drastically affected the geometry of the cyclobutane ring.

In other fused systems containing the cyclobutane ring, the tendency towards longer than normal bond lengths is continued, but the situation is slightly different (Table 31). If the cyclobutane ring is formed by a dimerisation of two unsaturated rings such as two thymine rings 10, then the bridgehead carbon-carbon bond is usually close to normal values, which means that the ring fusion has little effect upon the geometry of the other ring, but the unshared bonds of the cyclobutane ring are elongated, averaging about 1.575 Å in various thymine photodimers[133,134,136,137] and 1.59 in the photodimer of cyclopentanone[135]. However one structure has been reported in which the bridgehead bonds are significantly longer than the unshared bonds[139]. In 3,4:7,8-dibenzotricyclo$[4.2.0.0^{2,5}]$octa-3,7-diene 11, the bridgehead carbon-carbon bond is 1.593 Å while the unshared carbon-carbon bond is 1.559 Å. This was rationalised in the following way. In photodimers of thymine, the cyclobutane ring



a > b

10



a < b

11

is fused to two essentially strain free rings, whereas in

3,4:7,8-dibenzotricyclo[4.2.0.0]octa-3,7-diene, the fusing rings are highly strained four membered rings, probably even more strained than the central cyclobutane ring. In this type of system the ring strain and non bonded interactions are relieved by the lengthening of the bridgehead bonds.

If this argument were correct, then one would expect the bridgehead bond in 1,2,4,5-tetraphenyl-3,6-dicarbomethoxytricyclo[3.1.0.$0^{2,4}$]hexane to be longer than its unshared cyclobutane bonds, since in this compound, the cyclobutane ring is again fused to two rings which are more strained than it is. However, as has been pointed out all the bonds in this tricyclic system are shorter than are found in other cyclobutane systems. A survey of the literature shows that this shortening of, at least the average, bond length of the cyclobutane ring has been observed in a few other compounds in which the cyclobutane ring exists in a highly strained environment and these will be discussed later.

The cyclopropane ring has bond lengths which are longer than those found in cyclopropane itself, which have been determined by electron diffraction studies to be 1.510 Å. This geometry seems to be little affected by substitution (Table 30). Fusion with other rings, be it with a strained system or a more flexible system, usually results in at least one bond being longer than that found in unfused cyclopropanes, and the average bond length within the ring system tends also to be longer, except in bicyclo[1.1.0]butane in which all bonds are equal within experimental error and have a value of 1.498 Å (Table 30).

In highly strained fused systems, for which structural information is available in the literature, there seems to be a tendency towards shortening of cyclobutane bonds and lengthening of cyclopropane bonds. Thus in one tricyclo[2.1.0.0$^{2,5}$]-pentane derivative[116,117] all the bond lengths except one average 1.53 Å. In a bicyclo[2.1.0]pentane[118], the cyclopropane bonds average 1.517 Å, and the cyclobutane bonds 1.534 Å. In a bicyclo[3,2.0]heptene derivative, the cyclobutane ring has an average bond length of 1.532 Å[138].

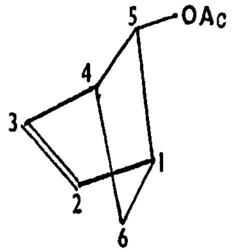
The microwave structure of bicyclo[2,1.0]pentane is interesting from the point of view of comparison with the structure of 1,2,4,5-tetraphenyl-3,6-dicarbomethoxytricyclo-[3.1.0.0$^{2,4}$]hexane, since it consists of one cyclopropane ring fused to a planar cyclobutane ring at a dihedral angle of 112.7° while our compound has an extra cyclopropane ring. Here the average bond length in the cyclopropane ring, 1.517 Å is slightly longer than that in cyclopropane and the average bond length in the cyclobutane ring is 1.534, somewhat shorter than the 1.548 Å of cyclobutane. Suenram and Harmony argue that since the rings have three and four centre $\pi$-like orbitals it is possible for them to relocate the total available electron density around the ring as needed to satisfy geometrical strain or other factors. The observed changes in bond length would correspond to a small shift of electron density from the cyclopropyl ring to the cyclobutyl ring. The geometry observed in 1,2,4,5-tetraphenyl-3,6-dicarbomethoxytricyclo[3.1.0.$0^{2,4}$]-hexane would certainly support this delocalisation argument, however as Suenram and Harmony pointed out, such a conclusion must be considered highly speculative, and detailed molecular orbital calculations would be required to see if the predicted electron density provided any supporting evidence for this view. Also arguments of this type neglect the effect of the substituents, which as Hoffman pointed out[145], can greatly affect the geometry of the cyclopropane ring, depending upon whether they have electron donating or electron accepting groups. In a norcardiene derivative[114] the lengthening of two bonds in the ring is rationalised on the basis of a delocalisation of electrons from a pseudo π-orbital on the cyclopropane ring into the π* orbitals of two geminally substituted cyanide groups[145]. Since the carbomethoxy group is in the correct position to maximise this type of pseudo π - π* interaction, the effect of this substituent at least may be important in determining the geometry of the system.

# CHAPTER FOUR

## Crystal and Molecular Structures of *exo*-Tricyclo[3.1.1.$0^{2,4}$]hept-6-yl p-bromobenzoate.

# INTRODUCTION

*Exo*-tricyclo[3.1.1.$0^{2,4}$]hept-6-yl acetate were prepared by R. Vukov of this department by the addition of carbene to exo-bicyclo[2.1.1]-hex-2-en-5-yl acetate 12. Both *syn* and *anti* isomers were expected since both sides of the double bond



12

appear equally accessible to the approach of the carbene. However only one major product was obtained from the reaction. Assignment of a *syn* or *anti* configuration to this isomer could not be made on the basis of its n.m.r. spectrum. Consequently the X-ray crystal structure of the p-bromobenzoate derivative was undertaken in order to determine the configuration and also to see if the geometry of the product could provide an explanation of the stereospecificity of the carbene addition. Furthermore this structure determination would provide more information on the geometry of the cyclopropane and cyclobutane rings in highly strained fused systems.

## EXPERIMENTAL

A crystal was chosen which was regarded as suitable for photographic work after examination of a Laue photograph. This was used to produce Weissenberg photographs for the 0kℓ, 1kℓ and 2kℓ layers and precession photographs for the hk0, hk1, and h0ℓ, h1ℓ layers. The Laue symmetry was found to be 2/m, and the photographs exhibited the same systematic absences as the tricyclohexane derivative, establishing the space group as P21/n.

The lattice parameters were obtained by carefully measuring the 2θ values for several reflections, using a PICKER manual four circle diffractometer. A least squares refinement of the cell parameters to give the best fit to the 2θ values yielded the following results: a = 6.704(1); b = 12.087(1); c = 15.577(2); β = 94.12(1).

The experimentally observed density of 1.52 gms $cm^{-3}$, obtained by flotation in aqueous potassium iodide solution, agreed reasonably well with the calculated density of 1.545 gms $cm^{-3}$, obtained by assuming four molecules of molecular weight 292.9 occupying a cell of volume 1258.96 $Å^3$. The density therefore did not require that the molecule occupy a special position within the cell.

Intensity data were collected on a PICKER four circle manual diffractometer. The scan width was 3° with a scan rate of 2°/min. The 2θ limit was placed at 90°. A stationary background count was taken on each side of the scan.

In the data reduction process, reflections were rejected if $I \leqslant 0$ or if $I \leqslant 2\sigma$. 534 of the 1061 measured reflections were rejected in this fashion giving a total of 527 observed reflections.

Six standard reflections were measured at five hour intervals and indicated extensive decomposition. By the end of the data collection the standards had lost some 40% of their original intensity. The decomposition was found to be approximately linear with time, and independent of $2\theta$. A correction was made by application of a linear scale factor between standards.

The bounding faces of the crystal were tentatively identified as $011$, $0\bar{1}1$, $0\bar{1}\bar{1}$, $01\bar{1}$, $1\bar{1}\bar{1}$ and $\bar{1}00$. The identification of the faces was made difficult because the extensive decomposition obscured the defining edges of the faces. The absorption coefficient was 48.03 $cm^{-1}$ and the maximum dimensions of the crystal were 0.25 mm x 0.07 mm x 0.05 mm.

The data was corrected for absorption and for Lorentz and polarisation effects, and structure amplitudes and standard deviations were calculated.

## SOLUTION OF STRUCTURE AND REFINEMENT

The position of the bromine atom in the unit cell was located from a Patterson map and used as input to a structure factor calculation, from which an electron density difference fourier was calculated. The electron density difference fourier gave the positions of the six carbon atoms of the phenyl ring and the carbon and one oxygen of the carboxyl group. A structure factor calculation based on these atoms gave a residual R factor of 0.343 which reduced in one cycle of refinement to 0.323. In these calculations the phenyl ring was included as a rigid body, with C - C bond length of 1.397 Å and a C - C - C angle of 120°.

Another electron density difference fourier was calculated from which five of the atoms of the tricycloheptane system were located. These atoms were included in a structure factor calculation which gave a residual R factor of 0.291 which reduced in one cycle of refinement to 0.259. The temperature factors of two of the atoms in the tricycloheptane system had become quite large and these were removed from subsequent calculations. An electron density difference fourier calculated at this point gave the positions of one more carbon atom of the tricyclic system and the other oxygen of the carboxyl group.

One more cycle of refinement, with what now amounted to fourteen of the seventeen non-hydrogen atoms of the asymmetric unit included in the calculations, reduced R to 0.255. One of these fourteen atoms was again found to have a very high temperature factor. This atom was removed from the calculations and the R factor fell in two cycles to 0.231. An electron density difference fourier was calculated and this gave the position of the remaining four atoms, which when included in the structure factor calculation caused the refinement to converge in three cycles at R = 0.140. Refinement of the bromine atom anisotropically further reduced R to 0.092. On changing from the rigid body to a free atom model, the R factor remained unchanged, but $R_2$ changed from 0.075 to 0.072. A Hamilton R factor statistical test[44] showed that the hypothesis that the rigid body model best described the structure could be rejected at the 99.5% confidence level.

The rejection criterion, preventing structure factors for which there was poor agreement between observed and calculated structure amplitude from being used in the least squares refinement, was made more stringent and the R factor fell to 0.089.

Up to this point data which had only been corrected for decomposition and Lorentz and polarisation corrections had been used in the calculations. Now data which had also been corrected for absorption effects was substituted. This had little effect upon the refinement, the R factor falling only slightly to 0.088.

The positions of the hydrogen atoms were calculated assuming a C - H bond length of 1.0 Å and, as closely as possible, $sp^3$ hybridisation at the carbon atoms. These atoms were included in the refinement, with temperature factors one unit greater than the carbon atom to which they were attached, however, neither their coordinates nor their temperature factors were refined. The refinement then converged in two cycles to $R_1 = 0.080$ and $R_2 = 0.063$.

An electron density difference fourier was computed. This showed rather large peaks around the two oxygen atoms which evidently required anisotropic refinement. Consequently, the hydrogen atoms were removed from the calculations and the refinement repeated with the oxygens anisotropic. The refinement converged at $R_1 = 0.082$ and $R_2 = 0.076$. The positions of the hydrogen atoms were recalculated and when these were included in the calculations the refinement converged to a final $R_1 = 0.072$, $R_2 = 0.055$.

An electron density difference fourier was computed at the end of the refinement and this showed only moderate peaks, the largest, (0.47 electrons $\mathring{A}^{-3}$) occurring near the bromine atom.

## RESULTS

The observed and calculated structure amplitudes are listed in Table 33. Table 34 gives the atomic coordinates and thermal parameters of the atoms. Interatomic distances and bond angles are listed in Tables 35 and 36 while nonbonded contacts are shown in Tables 37 and 38. Least squares planes data is presented in Table 40.

A perspective view of the molecule is shown in Fig. 10. A packing diagram in which the contents of the unit cell are projected onto the [b][c] plane is shown in Fig. 11.

## TABLE 33

Observed and Calculated Structure Amplitudes (electrons x 10)

```
  K   L  FOBS  FCAL      K   L  FOBS  FCAL      K   L  FOBS  FCAL      K   L  FOBS  FCAL      K   L  FOBS  FCAL
  **H =  0****          -3  -7   160   200     -7  -3   152   156     -7  -7   198   159     -4  -2   397   415
  0   2   602   621     -3  -6   144   151     -7  -1   331   256     -7  -6   200   275     -3  -7   373   382
  0   4  1126  1130     -3  -5   215   220     -6 -11   204   146     -7  -5   200   203     -3  -4   156   154
  0   6   966   931     -3  -4   322   306     -6  -9   172   189     -7  -2   259   233     -3  -3   417   455
  0   8   207   184     -3  -3  1005   983     -6  -6   180   170     -7  -1   391   388     -3  -2   335   342
  0  10   289   285     -3  -2   269   257     -6  -5   197   213     -6 -10   195   144     -3  -1   195   187
  1   1   379   379     -3  -1   478   473     -6  -4   222   203     -6  -7   199    32     -2 -10   182   172
  1   3   590   575     -2 -14   186   154     -6  -3   397   413     -6  -6   218   222     -2  -9   182    45
  1   4   431   432     -2 -12   258   246     -5 -12   179   125     -6  -4   460   441     -2  -7   427   437
  1   5   599   601     -2  -8   701   688     -5  -8   301   329     -5  -9   353   336     -2  -5   393   416
  1   6   150   167     -2  -4   883   856     -5  -7   228   178     -5  -8   230   245     -2  -3   270   256
  1   7   176   165     -2  -2   707   777     -5  -4   372   367     -5  -5   282   288     -2  -1   663   671
  1   8   177   195     -2  -1   507   480     -5  -3   420   410     -5  -3   300   290     -1 -10   245   270
  1  10   154   138     -1 -10   260   275     -5  -2   145    38     -5  -2   275   275     -1  -7   312   275
  1  11   200   217     -1  -9   210   238     -5  -1   437   411     -5  -1   230   200     -1  -6   208   175
  1  12   153   177     -1  -7   423   436     -4  -8   223   263     -4 -11   217   217     -1  -4   330   316
  1  13   155   158     -1  -6   353   351     -4  -6   465   488     -4  -3   546   534     -1  -3   390   418
  2   0   223   222     -1  -5   197   226     -4  -2   609   609     -4  -2   200   164     -1  -2   266   256
  2   1   815   830     -1  -4   323   292     -3 -11   190   228     -4  -1   385   366      0  -8   324   352
  2   2   941   906     -1  -3   398   389     -3 -10   279   303     -3  -9   204   208      0  -4   638   639
  2   3  1007   972     -1  -2   910   825     -3  -7   348   322     -3  -8   193   185      0   0   324   295
  2   4   137   134      0 -11   328   330     -3  -6   305   320     -3  -6   348   350      0   2   556   578
  2   7   817   819      0  -9   171   179     -3  -5   863   833     -3  -5   400   416      0   4   194   186
  2   8   194   165      0  -7   245   243     -3  -4   713   699     -3  -2   562   513      0   6   344   332
  2   9   253   221      0  -5  1110  1060     -3  -1   560   585     -3  -1   401   417      0   8   233   236
  2  11   228   225      0  -3   160   107     -2 -12   260   234     -2 -12   175   102      1   0   564   574
  2  13   170   140      0  -1   795   804     -2  -9   391   427     -2 -10   301   431      1   1   282   302
  3   1  1092  1102      0   1   478   525     -2  -6   369   357     -2  -6   547   510      1   4   240   253
  3   2   405   401      0   3  2075  2064     -2  -5   727   713     -2  -4   379   391      1   5   180    83
  3   3   530   532      0   5   698   706     -2  -3   529   548     -2  -3   546   521      1   7   212   161
  3   5   406   368      0   7   144   179     -1 -11   301   340     -1  -9   330   378      1   8   220   234
  3   6   407   393      0   9   735   763     -1 -10   214   208     -1  -8   237   249      2   0   140   101
  3   7   148   132      0  11   163   103     -1  -8   450   454     -1  -6   528   455      2   1   342   346
  3   8   355   340      1   0    92    88     -1  -7   565   564     -1  -5   555   509      2   3   381   391
  3   9   144   168      1   1   235   250     -1  -5   467   467     -1  -4   394   370      2   5   210   208
  3  11   143    88      1   2   605   653     -1  -4   353   359     -1  -3   685   637      2   9   220   220
  4   0   594   605      1   3   632   628     -1  -3   612   605     -1  -2   848   834      3   0   217   226
  4   1   176   181      1   4   156   179     -1  -2   313   317      0 -11   270   221      3   1   210   198
  4   2   253   242      1   5   383   376     -1  -1   399   408      0  -9   349   367      3   4   258   279
  4   3   284   302      1   7   336   350      0 -12   308   358      0  -7   492   504      3   7   238   238
  4   4   503   511      1   8   319   302      0 -10   240   271      0  -5   598   515      4   2   380   358
  4   6   480   475      1   9   167    82      0  -8   276   295      0  -3   833   850      4   6   227   187
  4   8   166   145      2   0   626   646      0  -6   646   655      0  -1   623   633      5   0   420   420
  4  10   307   287      2   1  1194  1201      0  -4   557   541      0   1   417   426      5   1   303   323
  5   1   532   537      2   2  1923  1908      0  -2  1309  1280      0   3   622   624      5   4   225   199
  5   2   381   403      2   3   514   510      0   0   471   479      0   7   492   499      5   5   152   110
  5   4   140   134      2   4   618   624      0   2   693   677      0   9   185   175      5   6   188    94
  5   5   483   480      2   5   240   257      0   4   719   787      0  11   171   156      6   3   156    94
  5   6   146   182      2   6   634   649      0   8   367   358      1   0   159   165      6   4   163   134
  5   8   243   256      2   8   509   537      0  10   172   122      1   1   576   597      6   5   190   218
  5   9   147   183      2  10   220   211      0  12   180   185      1   2   174   159      7   1   145   171
  6   1   376   368      2  12   162   148      1   0   350   364      1   3   312   298      7   3   212   205
  6   3   430   431      3   0   298   403      1   2   586   580      1   5   501   540      7   4   158   121
  6   4   321   330      3   1  1064  1079      1   3   594   582      1   6   168    99      9   0   164   136
  6   7   222   217      3   2   328   328      1   4   135    95      1   8   197   175      9   2   128    13
  6  11   167   126      3   3   740   736      1   5   331   331      1  11   177   115       **H =  5****
  7   1   213   228      3   4   418   451      1   6   349   377      2   0   736   758     -6  -3   178    21
  7   2   277   301      3   5   328   332      1   7   203   166      2   2   269   251     -5  -5   320   296
  7   3   121    27      3   7   174   170      1   9   293   284      2   4   540   514     -5  -4   229   200
  7   4   140   122      3   8   153   155      1  10   191   151      2   5   233   207     -4  -5   346   344
  7   8   207   103      3  12   158    73      1  12   158    92      2   6   447   469     -4  -2   204    90
  7   9   237   246      4   1   475   485      2   1   784   790      2  10   260   230     -4  -1   388   411
  8   0   278   274      4   2   429   442      2   2   193   165      3   0   165   169     -3  -8   197   250
  8   1   175   171      4   3   380   392      2   5   806   795      3   1   329   353     -3  -7   193   198
  8   2   299   294      4   4   155   265      2   7   369   369      3   2   334   338     -3  -2   200   178
  8   3   245   266      4   5   418   412      2  11   314   331      3   5   147   146     -3  -1   195   175
  8   4   318   324      4   6   334   331      3   0   536   569      3   6   264   255     -2  -6   297   331
  8   5   135    78      4   7   130    87      3   1   304   290      3   7   179    90     -2  -2   456   451
  8   6   234   185      4   9   264   269      3   3   296   286      3   9   195   120     -1  -7   193   207
  8   8   152    88      5   0   242   250      3   4   297   290      4   1   261   261     -1  -5   224   261
  9   1   224   188      5   1   540   517      3   6   525   534      4   2   189   255     -1  -4   302   285
  9   2   165   173      5   2   186   221      3   7   151   171      4   3   322   301     -1  -1   375   399
  9   7   186   192      5   3   324   342      3   9   147   128      4   4   203    88      0  -9   328   266
 10   0   139   190      5   4   383   369      3  10   183   171      4   7   314   303      0  -5   424   414
 10   5   145   108      5   5   187   143      4   0   458   472      4   9   190   151      0  -3   313   308
 11   5   163   139      5   6   126    65      4   1   321   318      5   1   268   257      0   1   394   373
  **H =  1****.          5   7   300   285      4   2   615   638      5   2   386   386      0   3   242   202
 -9  -3   206   178      5   8   202   229      4   3   202   177      5   6   219   282      0   5   297   264
 -8  -5   211   172      5   9   144    39      4   4   970   970      6   0   285   310      1   0   327   335
 -7 -10   163   148      6   0   569   583      4   5   354   372      6   2   233   189      1   2   173   163
 -7  -6   346   335      6   1   227   257      4   7   304   313      6   4   149   187      1   3   252   203
 -7  -5   154   164      6   2   614   668      4   8   443   442      6   6   299   269      1   5   185   142
 -7  -3   202   206      6   4   119    57      4  10   263   290      7   2   236   250      2   0   263   197
 -6  -8   170   155      6   5   280   281      5   0   122   104      7   3   189   133      2   2   240   248
 -6  -6   191   204      6   6   452   473      5   3   537   552      7   5   250   264      2   4   342   316
 -6  -4   410   419      6   8   156   159      5   4   429   458      7   6   173   172      3   0   163   131
 -6  -2   458   466      7   0   181   189      5   5   307   288      7   7   149   122      3   2   321   347
 -6  -1   422   405      7   1   235   212      5  10   200    87      7   8   143   119      3   3   194   158
 -5 -11   187   204      7   3   154   161      6   1   415   401      8   3   173   166      3   6   174   177
 -5  -9   340   383      7   4   167   204      6   4   176   187      9   1   267   245      4   1   372   411
 -5  -8   239   247      7   7   216   214      6   5   280   292      9   2   136   153      5   0   247   277
 -5  -7   344   373      7   9   182   141      6   7   217   197       **H =  4****          5   1   162   179
 -5  -6   557   576      8   3   201   176      6   8   151   183     -7  -6   206   267      5   2   170   141
 -5  -5   302   295      8   5   216   223      6   9   286   307     -7  -3   335   306      5   3   221   221
 -5  -4   236   206      8   7   241   261      7   0   209   192     -7  -2   278   326      6   1   162   116
 -5  -3   220   278      8   8   162   186      7   2   139    91     -7  -1   270   237      7   2   201   191
 -5  -2   146   151      9   1   275   263      7   3   335   315     -6  -8   193    73       **H =  6****
 -4 -11   186   170     11   1   138   141      7   5   163   178     -6  -2   334   254     -2  -3   259   296
 -4  -9   175   157       **H =  2****          8   0   220   210     -6  -1   323   296      0  -4   204   216
 -4  -8   533   517     -9  -7   179   125      8   4   213   213     -5  -9   225   293      0   0   257   219
 -4  -4   261   258     -9  -4   193   195      9   0   150   112     -5  -6   391   375      1   1   169   185
 -4  -3   131    93     -9  -3   163   124      9   2   183   161     -5  -4   227   212      1   2   294   246
 -4  -1   852   873     -8  -6   286   205     10   0   138    63     -5  -3   183   259      2   0   178   165
 -3 -13   219   239     -8  -2   176   196       **H =  3****         -4 -10   172   145      2   1   256   247
 -3 -10   283   313     -7  -9   166   122     -9  -5   324   280     -4  -8   391   402      4   0   158   179
 -3  -9   247   224     -7  -7   237   262     -9  -4   232   231     -4  -4   462   434      5   0   139   111
 -3  -8   284   282     -7  -4   352   349     -9  -3   255   200     -4  -3   226   264
```

## Table 34

### Atomic Coordinates and Temperature Factors

| Atom | x | y | z | B |
|---|---|---|---|---|
| Br | 0.0798(3) | 0.1298(2) | 0.1017(2) | 7.3* |
| O1 | 0.816(2) | 0.193(1) | -0.178(1) | 7.8* |
| O2 | 0.891(2) | 0.330(1) | -0.083(1) | 6.4* |
| C1 | 1.005(3) | 0.433(1) | -0.209(1) | 5.7(5) |
| C2 | 1.219(3) | 0.443(2) | -0.242(1) | 7.0(6) |
| C3 | 1.325(3) | 0.551(2) | -0.226(1) | 6.5(5) |
| C4 | 1.338(3) | 0.470(2) | -0.157(2) | 6.9(5) |
| C5 | 1.158(3) | 0.466(1) | -0.096(1) | 5.5(5) |
| C6 | 1.058(2) | 0.358(2) | -0.132(1) | 4.8(4) |
| C7 | 0.989(3) | 0.527(1) | -0.145(1) | 4.9(5) |
| C8 | 0.785(3) | 0.244(2) | -0.112(2) | 5.0(5) |
| C9 | 0.617(2) | 0.216(1) | -0.056(1) | 4.0(4) |
| C10 | 0.485(2) | 0.132(2) | -0.086(1) | 5.5(4) |
| C11 | 0.326(2) | 0.105(2) | -0.037(1) | 4.9(5) |
| C12 | 0.298(2) | 0.163(1) | 0.037(1) | 4.8(5) |
| C13 | 0.426(3) | 0.247(1) | 0.067(1) | 4.3(4) |
| C14 | 0.591(3) | 0.272(1) | 0.017(1) | 4.4(4) |

*These are equivalent B's corresponding to the following anisotropic parameters:

(Continued on next page)

Table 34 continued

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Br | 0.061(1) | 0.121(2) | 0.099(2) | −0.036(2) | 0.018(1) | 0.021(3) |
| O1 | 0.088(11) | 0.087(11) | 0.129(14) | −0.031(8) | 0.061(10) | −0.050(10) |
| O2 | 0.073(10) | 0.080(11) | 0.096(12) | −0.042(9) | 0.035(9) | 0.001(7) |

Table 34 continued

Calculated Hydrogen Positions

| Atom | x | y | z | B |
|---|---|---|---|---|
| H1 | 0.881 | 0.413 | -0.249 | 7.4 |
| H2 | 1.271 | 0.385 | -0.282 | 8.5 |
| H31 | 1.241 | 0.623 | -0.220 | 7.6 |
| H32 | 1.442 | 0.575 | -0.260 | 7.6 |
| H4 | 1.471 | 0.429 | -0.140 | 7.7 |
| H5 | 1.186 | 0.477 | -0.032 | 6.4 |
| H6 | 1.159 | 0.296 | -0.143 | 6.0 |
| H71 | 0.861 | 0.536 | -0.113 | 6.2 |
| H72 | 1.022 | 0.605 | -0.166 | 6.2 |
| H10 | 0.512 | 0.092 | -0.142 | 7.0 |
| H11 | 0.232 | 0.043 | -0.055 | 5.4 |
| H13 | 0.401 | 0.289 | 0.121 | 5.8 |
| H14 | 0.687 | 0.337 | 0.036 | 6.0 |

7

## Table 35

## Interatomic Distances

| Atoms | Distance |
|---|---|
| BR - C12 | 1.88(2) |
| | |
| C9 - C10 | 1.40(2) |
| C10 - C11 | 1.39(2) |
| C11 - C12 | 1.37(2) |
| C12 - C13 | 1.39(2) |
| C13 - C14 | 1.42(2) |
| C14 - C9 | 1.36(2) |
| | |
| C8 - C9 | 1.51(2) |
| C8 - O1 | 1.23(2) |
| C8 - O2 | 1.32(2) |
| O2 - C6 | 1.44(2) |
| | |
| C1 - C2 | 1.56(2) |
| C1 - C6 | 1.52(2) |
| C1 - C7 | 1.52(2) |
| C2 - C3 | 1.50(2) |
| C2 - C4 | 1.53(3) |
| C3 - C4 | 1.46(2) |
| C4 - C5 | 1.59(2) |
| C5 - C6 | 1.54(2) |
| C5 - C7 | 1.52(2) |

## Table 36

Intramolecular Angles

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| C1 - C6 - C5 | 82.0(14) | C1 - C6 - O2 | 114.1(15) |
| C6 - C5 - C7 | 86.5(13) | C5 - C6 - O2 | 110.4(15) |
| C5 - C7 - C1 | 82.9(13) | O2 - C8 - O1 | 123.6(21) |
| C7 - C1 - C6 | 87.2(14) | O2 - C8 - C9 | 113.0(21) |
| | | O1 - C8 - C9 | 123.4(22) |
| C7 - C1 - C2 | 105.3(15) | | |
| C6 - C1 - C2 | 98.0(15) | C8 - C9 - C10 | 116.8(19) |
| C7 - C5 - C4 | 104.8(15) | C8 - C9 - C14 | 121.5(19) |
| C6 - C5 - C4 | 98.1(15) | C14 - C9 - C10 | 121.7(18) |
| C1 - C2 - C3 | 117.1(17) | C9 - C10 - C11 | 118.1(19) |
| C5 - C4 - C3 | 117.1(17) | C10 - C11 - C12 | 120.3(18) |
| C1 - C2 - C4 | 99.9(16) | C11 - C12 - C13 | 122.1(17) |
| C5 - C4 - C2 | 97.7(15) | C12 - C13 - C14 | 117.5(16) |
| | | C13 - C14 - C9 | 120.3(17) |
| C4 - C2 - C3 | 57.5(12) | | |
| C2 - C3 - C4 | 62.3(12) | C13 - C12 - Br | 117.6(15) |
| C3 - C4 - C2 | 60.2(12) | C11 - C12 - Br | 120.3(14) |

## Table 37

### Intramolecular Non-Bonded Contacts

| Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance |
|---|---|---|---|---|---|
| C1 | C5 | 2.01(3) | BR | C11 | 2.83(2) |
| C6 | C7 | 2.10(2) | BR | C13 | 2.81(2) |
| C6 | C2 | 2.33(3) | O1 | O2 | 2.25(2) |
| C6 | C4 | 2.37(3) | O1 | C6 | 2.64(2) |
| C7 | C2 | 2.45(3) | O1 | C1 | 3.21(2) |
| C7 | C4 | 2.46(3) | O1 | C10 | 2.83(3) |
| C1 | C4 | 2.36(3) | O2 | C5 | 2.45(2) |
| C5 | C2 | 2.35(3) | O2 | C1 | 2.48(2) |
| C6 | C3 | 3.34(3) | O2 | C7 | 2.70(2) |
| C7 | C3 | 2.68(3) | O2 | C14 | 2.73(2) |
| C5 | C3 | 2.60(3) | C6 | C8 | 2.33(3) |
| C1 | C3 | 2.61(3) | H31 | H72 | 1.76 |

(from calculated positions)

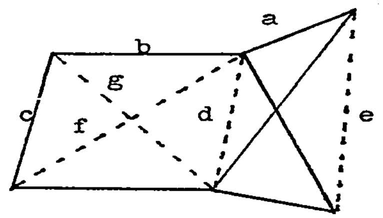
## Table 38

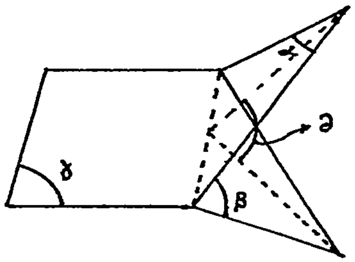
Intermolecular Contacts

| Atom 1 | Atom 2 | Distance | Symmetry Operation |
|---|---|---|---|
| BR | C2 | 3.67(2) | x-1 1/2, 1/2-y, 1/2+z |
| BR | C14 | 3.85(2) | x-1, y, z |
| BR | O2 | 3.91(2) | x-1, y, z |
| BR | C3 | 3.94(2) | x-1 1/2, 1/2-y, 1/2+z |
| O1 | C3 | 3.39(2) | x+1 1/2, 1/2+y, 1/2-z |
| O1 | C7 | 3.87(2) | x+1, y, z |
| O2 | C5 | 3.76(2) | 2-x, 1-y, -z |
| O2 | C12 | 3.78(2) | 1+x, y, z |
| C2 | C10 | 3.71(2) | 1 1/2-x, 1/2+y, -z-1/2 |
| C3 | C10 | 3.60(2) | 1 1/2-x, 1/2+y, -z-1/2 |
| C5 | C14 | 3.76(2) | 2-x, 1-y, -z |
| C6 | C11 | 3.79(2) | 1+x, y, z |
| C6 | C12 | 3.80(2) | 1+x, y, z |
| C10 | C11 | 3.62(2) | 1-x, -y, -z |
| C11 | C11 | 3.59(2) | 1-x, -y, -z |

## Table 39

## Comparison of Bicyclo[2.1.1]hexane Geometries





| Ref. | a | b | c | d | e | f | g | α | β | γ | ∂ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 147 | 1.544 | 1.565 | 1.513 | 2.172 | 1.946 | 2.381 | 2.395 | 89.4 | 78.2 | 102.1 | 125.0 |
| 148 | 1.547 | 1.537 | 1.537 | 2.098 | 2.057 | 2.374 | 2.364 | 85.4 | 83.3 | 100.5 | 129.5 |
| This Work (average values) | 1.53 | 1.575 | 1.53 | 2.01 | 2.10 | 2.40 | 2.36 | 82.1 | 86.8 | 98.8 | 132.1 |

## Table 40

### Least Squares Planes and Dihedral Angles

(i) Phenyl Ring

Atoms defining plane: C9, C10, C11, C12, C13, C14

Equation of Plane:

$$0.5286X - 0.6702Y + 0.5210Z - 0.0151 = 0$$

Distance of atoms from plane (Å):

| | |
|---|---|
| C9 | -0.001 |
| C10 | -0.007 |
| C11 | 0.011 |
| C12 | -0.006 |
| C13 | -0.002 |
| C14 | 0.005 |
| BR | -0.020 |
| C8 | -0.047 |
| O1 | -0.027 |
| O2 | -0.158 |

(ii) Plane A

Atoms defining plane: C5, C6, C1

Equation of plane:

$$-0.8818X + 0.2619Y + 0.3921Z + 6.0507 = 0$$

(Continued on next page)

Table 40 continued

(iii) Plane B

Atoms defining plane: C5, C1, C7

Equation of plane:

$$-0.7030X - 0.5251Y + 0.4796Z + 9.2034 = 0$$

(iv) Plane C

Atoms defining plane: C5, C1, C2, C4

Equation of plane:

$$0.1428X - 0.9777Y + 0.1537Z + 4.6116 = 0$$

Distance of atoms from plane (Å)

| | |
|---|---|
| C5 | 0.004 |
| C1 | -0.004 |
| C2 | 0.006 |
| C4 | -0.006 |

(v) Plane D

Atoms defining plane: C2, C3, C4

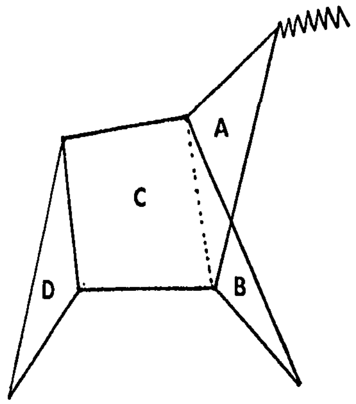
Equation of plane:

$$-0.8483X + 0.3878Y + 0.3605Z + 6.4368 = 0$$

(Continued on next page)

7

Table 40 continued



| Plane 1 | Plane 2 | Dihedral Angle |
|---|---|---|
| A | B | 132.1° |
| A | C | 108.8° |
| B | C | 119.1° |
| C | D | 116.4° |

Fig. 10

A Perspective View of

exo-Tricyclo[3.1.1.$0^{2,4}$]-6-yl-p-bromobenzoate.

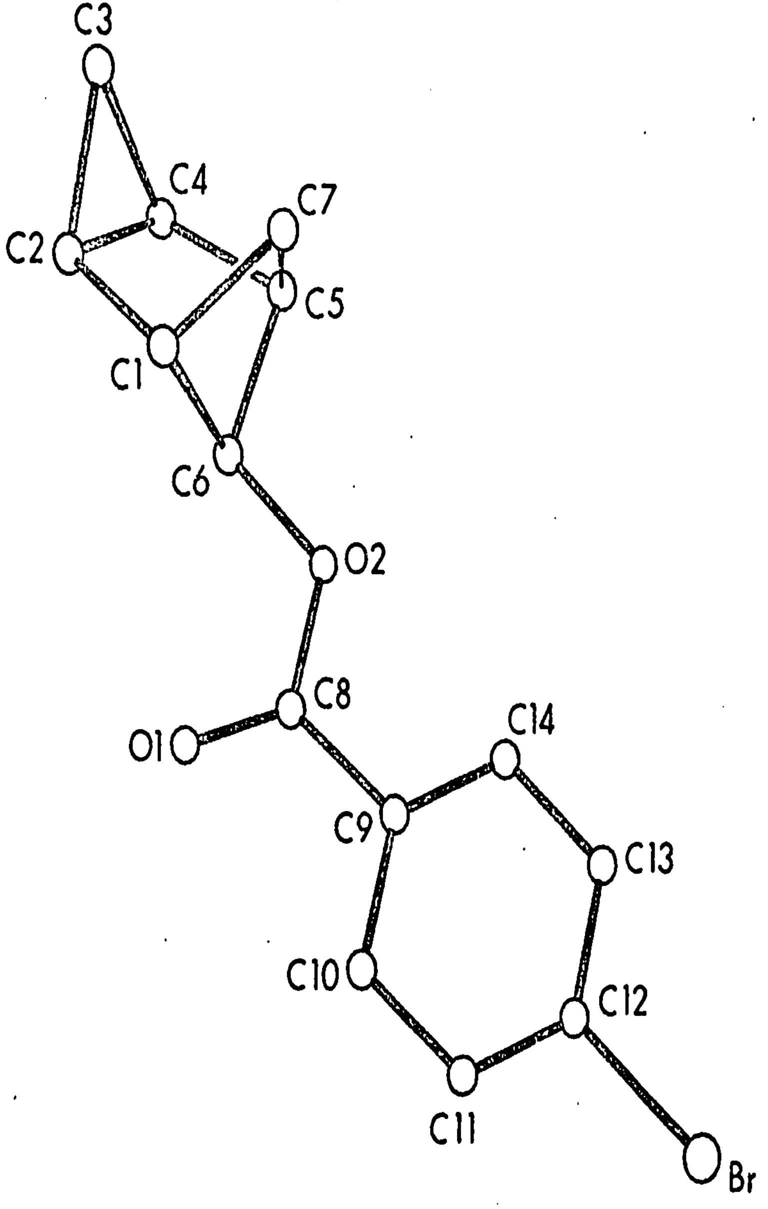
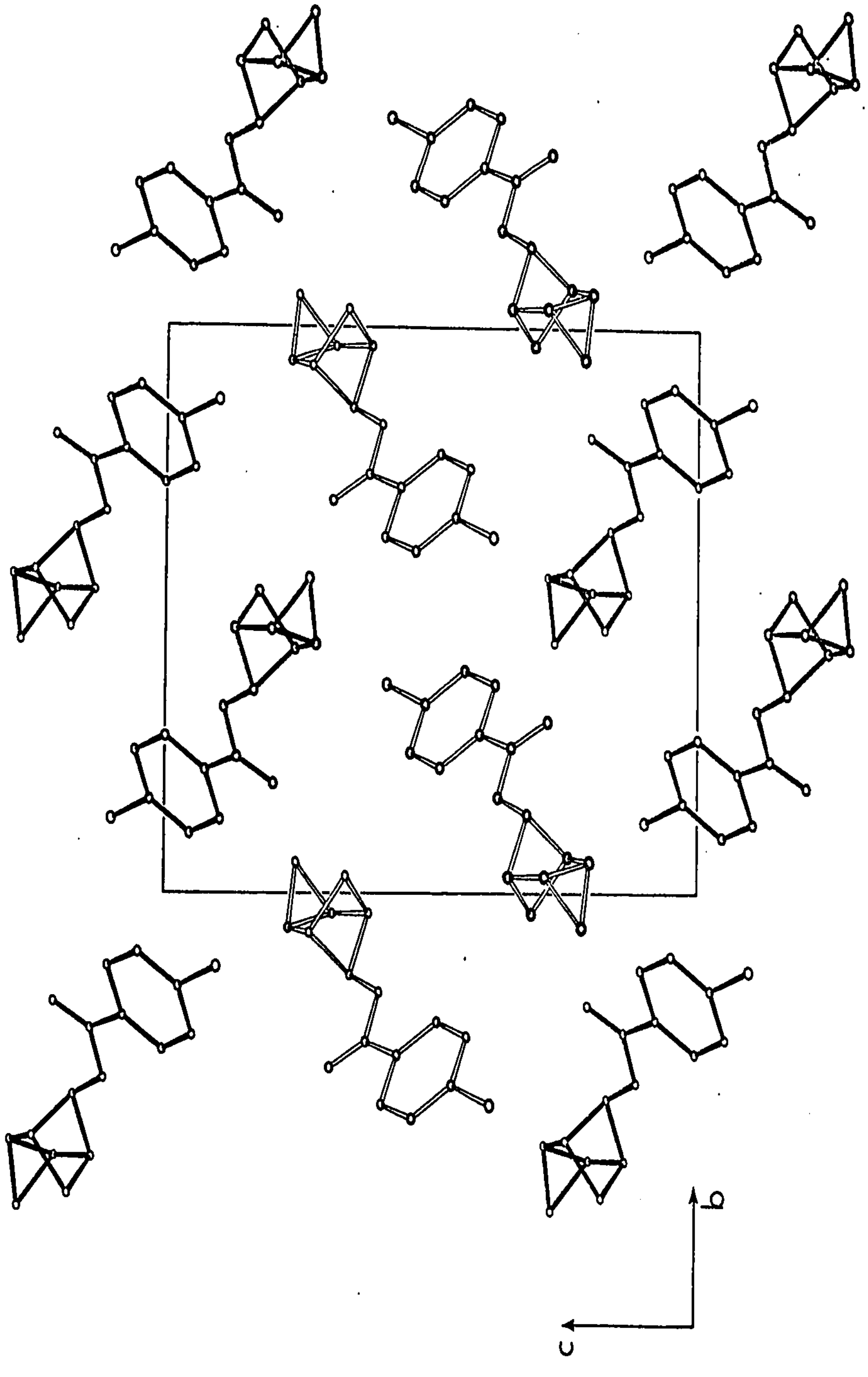

C3
C4
C7
C2
C5
C1
C6
O2
C8
O1
C14
C9
C13
C10
C12
C11
Br

Fig. 11

Contents of the Unit Cell Projected onto the [b][c] Plane


b
c

# DISCUSSION

Tricyclo[3.1.1.0$^{2,4}$]hept-6-yl-p-bromobenzoate crystallises with the cyclopropane ring *anti* relative to the bridgehead bearing the exo-p-bromobenzoate group. A diagram of the molecule is shown in Fig. 10.

The rather large standard deviations for the bond lengths and angles does not allow discussion of the geometry of the molecule beyond that of the gross structural features. The cyclopropane ring has an average bond length of 1.50 Å, the bridgehead bond being longest at 1.53 Å. The average bond angle is 60°. These values are similar to those found in cyclopropane itself.

The cyclobutane ring is puckered with a dihedral angle of 132.1°. The average bond length within the ring is 1.53 Å which would agree with the observation that cyclobutane bond lengths are shortened in highly strained systems. However, because of the large standard deviations in the bond lengths, this value is not significantly different from that found in cyclobutane itself. The angles within the cyclobutane ring are 87° at C1 and C5 and 82.5° at C6 and C7.

Part of the molecule consists of a bicyclo[2.1.1]-hexane entity, and it is interesting to compare the geometry found in this structure with that found for bicyclo[2.1.1]-hexane itself, which has been determined by two independent electron diffraction studies[147,148]. This comparison is summarised in Table 39. As can be seen from the table this structure does not differ significantly from either of the other two structures, but most of the dimensions and angles are closer to Dallinga and Toneman's structure[148]. Apart from the sizeable errors in the geometry of the system, the presence of the cyclopropane ring undoubtedly has an effect upon the system, especially upon the bond lengths and angles around C2 and C4. Thus it would be meaningless to use this structure to try to resolve the conflict between the two electron diffraction results.

The phenyl ring of the p-bromobenzoate group is planar within experimental error and the bromine atom lies in this plane (Table 40). The C - Br bond length is 1.88 Å and the average C - C bond length in the ring is 1.39 Å. The average bond angle is 120°. The carboxyl group has a normal geometry (see Table 22 p 107). The overall geometry of the p-bromobenzoate group is similar to that found in other structures[138,149].

The anti isomer was the only product in the addition of carbene to exo-bicyclo[2.1.1]hex-2-ene-5-yl acetate. It has been suggested that the hydrogen at C5 may exert some steric control on the reaction, if intramolecular forces between the acetate group and the hydrogens on C6 of the bicyclohexene derivative forced C5 closer to the double bond than C6[150]. The hydrogen on C5 would then sit further over the double bond than the hydrogen on C6, hindering the approach of the carbene from that side. There is some structural evidence to support this view.

The plane formed by C1, C5, C2 and C4 (plane C) makes a dihedral angle of 108.8° with the plane defined by

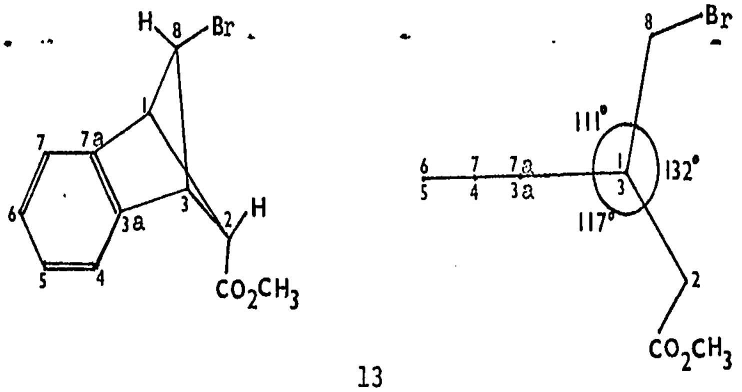
C1, C5 and C6 (plane A) but a much greater angle 119.1° with the plane defined by C1, C5 and C7 (plane B). It also is inclined at 116.4° to the cyclopropane ring (plane D). Because of the difference in dihedral angle, C6 sits closer to the C2 - C4 bond (which would be the C2 - C3 double bond in bicyclo[2.1.1]hexene) than C7. This is further evidenced by the difference in C2---C6, C4---C6 and C2---7 and C4---C7 nonbonded contacts. Those between C2, C4 and C6 average 2.35 Å shorter than the corresponding contacts with C7 which average 2.45 Å. Also angles C7 - C1 - C2 and C7 - C5 - C4 are greater than angles C6 - C1 - C2 and C6 - C5 - C4. Those angles involving C7 average 105° while those involving C6 average 98°.

The question remains as to whether the difference in dihedral angle is a result of intramolecular forces between the p-bromobenzoate substituent at C6, and C7, forcing C6 closer to the C2 - C4 bond, or whether it is the result of intramolecular forces between the hydrogens attached to C3, and those on C7, forcing C7 away from the C2 - C4 bond. If it is the former, then the same situation would exist in the parent olefin and this could explain the formation of only one product in the reaction with carbene. The intramolecular forces in question are those between C7 and O2 between which there is the very short distance of 2.70 Å, and those between H31 and H72 which have been calculated to be only 1.76 Å apart. C3 and C7 are only 2.68 Å apart too, an extremely short nonbonded contact.

There is some evidence, although most of it indirect, to support the proposition that C6 is being forced closer to C2 - C4 bond, which in turn means that C5 in the bicycloolefine is being forced closer to the double bond.

To reduce the repulsive interaction between C3 and C7, either plane D can move back, widening the dihedral angle between D and C from its preferred value, or plane B can widen its dihedral angle with C, or both can occur. Plane D makes a dihedral angle with plane C of 116.4° which is wider than the 109.0° found in anti-1,2,4,5-tetraphenyl-3,6-dicarbomethoxytricyclo[3.1.0.0$^{2,4}$]hexane. The dihedral angle between B and C is 119.1°. In bicyclohexane itself, the average value for this angle obtained from the two electron diffraction studies is 116.25°. In bicyclohexene[147], this angle is 118.25°. Thus it would seem that the repulsive forces are reduced by widening the dihedral angle between D and C to 116.4° from a preferred 109.0° and possibly by lengthening the bonds between C1 and C2, and C4 and C5 (1.575 Å average). Also the dihedral angle between plane A and plane C is reduced to 108.8° from a preferred angle of 117°. Plane B is relatively unaffected.

The structure of a related compound, 8-exo-bromo-1,3-methanoindane-2-endo-carboxylate 13 has been determined[151]. In this compound there are no repulsions of the type encountered between C3 and C7 in the tricyclo[3.1.1.0$^{2,4}$]heptane derivative. The dihedral angles then depend upon the substituents at the bridgehead. The bromine in the exo compound is only



13

3.15 Å from C2 while the sum of the Van der Waals radii for bromine and carbon is 3.65 Å. This is similar to the type of interaction between O2 and C7 in the tricycloheptane derivative. The dihedral angle between the planes which correspond to A and C in the tricycloheptane compound is 111° while that which would correspond to the angle between B and C is 117°. Thus the same pattern is observed with or without the presence of the cyclopropane ring, so that these angles are influenced mainly by the substituents at the bridgehead positions.

By extrapolation then it would appear that C5 in exo-bicyclo[2.1.1]hex-2-en-5-yl acetate will be closer to the C2 - C4 bond and the hydrogen attached to it may sterically interfere with the formation of a syn isomer of tricyclo-[3.1.1.$0^{2,4}$]hept-6-yl acetate.

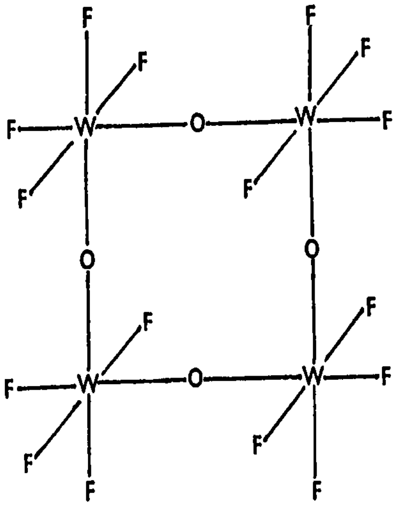
A packing diagram of the molecule is shown in Fig. 11, in which the contents of the unit cell have been projected on to the [b][c] plane. Intermolecular contacts are listed in Table 38. None of these are less than the sum of the

Van der Waals radii of the two atoms concerned. The closest packing occurs in the direction of the a axis. Other close contacts occur between molecules related by the n glide and separated by two unit cells in the a direction.

# APPENDIX

## The Structure of Tungsten Oxide Tetrafluoride.

As part of a general structural investigation of fluorides and oxide tetrafluorides, the solid state structure of tungsten oxide tetrafluoride was carried out by Edwards and Jones[152]. The reported structure consisted of a tetrameric unit with idealised symmetry $D_{4h}$ 14.



14

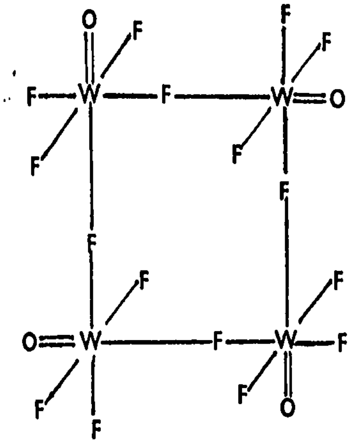
The assignment of the oxygen atoms to the bridging positions was based on the symmetry requirements of the space group and the stoichiometry of the compound. This assignment assumed an ordered structure, and no disordered structures with fluorine atoms in the bridging positions were tested.

The oxygen bridged structure has been criticized on the basis of the infrared and Raman spectra of the tetramer in the solid state[153,154]. On the basis of their structure determination, Edwards and Jones had assigned a band at 1050 $cm^{-1}$ to a terminal W - F stretching frequency. Beattie and coworkers found this untenable, since in $NbF_5$ and $TaF_5$, which are structurally similar to $WOF_4$, no fundamental higher than

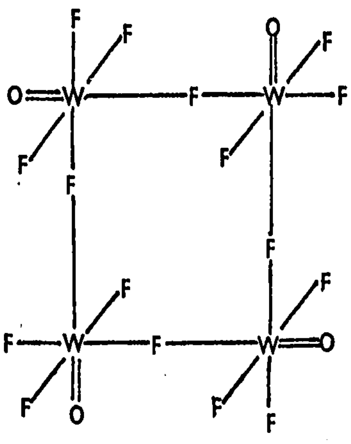
766 $cm^{-1}$ is observed, and so assigned the band at 1050 $cm^{-1}$ to either a terminal or bridging oxygen mode, but pointed out that 1050 $cm^{-1}$ for a bridging oxygen mode would be uniquely high. The Raman spectrum showed a very strong band at 1058 $cm^{-1}$. Since the band from a bridging linear M - O - M species, would be expected to be at most weak, they concluded that the structure contained terminal oxygens and was therefore disordered.

The disorder of oxygen and fluorine atoms is not without precedent in oxymetal fluoride systems. In the cesium salt of $CrO_3F^-$, the anion occupies a position with site symmetry $S_4$ and only one bond length of 1.53 Å is observed for the weighted average of Cr = O and Cr - F distances.

All the data can be interpreted by a disorder of two orientations of an asymmetrically fluorine-bridged structure, 15 and 16. The idealized symmetry of the tetrameric unit is



15



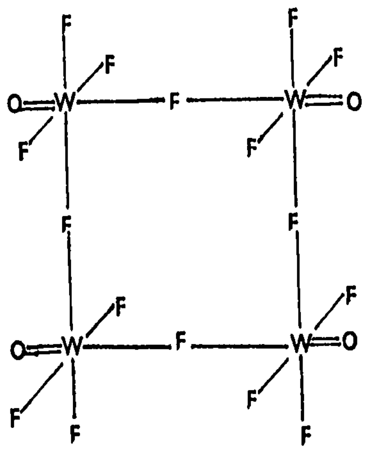
16

then $C_{4h}$.

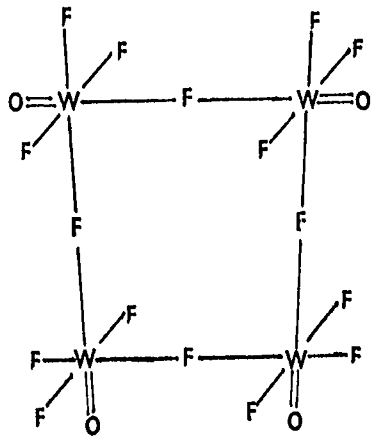
The relative merits of oxygen and fluorine bridged structures can be evaluated on the basis of expected bond lengths. A simple symmetry-based molecular orbital treatment of the oxygen-bridged structure shows that one might expect significant π bonding and hence a short tungsten-oxygen distance. The molecular orbitals, after construction of the σ framework can be briefly described as follows for the $D_{4h}$ oxygen-bridge model. Along each edge of the square array perpendicular to the plane of the four metal atoms, a three centre W - O - W π-bonding system, consisting of a dπ orbital from each metal and the corresponding oxygen pπ orbital, would result in bonding, nonbonding and antibonding orbitals. Two electrons, those on the oxygen, are available to populate the bonding levels, thus giving an out of plane π-bond order of 0.5. In the plane, a more extensively delocalisation system results. The metal dπ orbitals transform as $A_{1g} + B_{2g} + Eu$ and the oxygen pπ orbitals as $A_{1g} + B_{1g} + Eu$. The metal and oxygen $A_{1g}$ and Eu orbitals give rise to bonding and antibonding combinations of each symmetry. The eight available electrons are housed in the $A_{1g}$ and Eu bonding orbitals and the $B_{1g}$ non bonding orbital (which remains localised on the oxygen atoms). Thus a total in plane π-bond order of 3 is distributed among the eight equivalent W - O linkages. The total σ + π bond order is therefore 1.875 for each metal-oxygen bond. The approximate bond order vs. bond length curve of

Cotton and Wing[155] would suggest a W - O bond length of 1.8 Å, assuming that W - O distances parallel Mo - O distances. However the observed W - 'O' distances are 2.10 and 2.12 Å which correspond to a bond order of 1.0.

Simple electron counting for a fluorine bridged structure suggest one oxygen per tungsten atom, and the pattern of in-plane and out-of-plane tungsten-ligand bond lengths[152] suggest that the oxygen atoms lie in the plane of the four tungsten atoms, since it is in the plane that the rather short W - 'F' distances of 1.65 Å occur. These requirements allow three structures **15**, **17** and **18**.



**17**



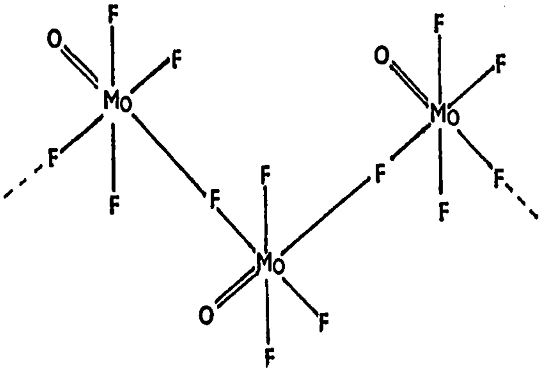
**18**

The particular arrangement of the tungsten atoms in this structure requires either or both of the diagonals to be coincident with symmetry elements, depending upon the choice of space group C2, Cm or C2/m. Since none of these structures has a mirror plane that contains the diagonal tungsten atoms, a disorder and hence the presence of a pseudo symmetry element

7

has to be postulated in each case. Structure **15** is preferred over **17** and **18** because the disorder is based on a square, while **17** and **18** would probably contain a rectangle or trapezoid of tungsten atoms respectively.

The apparent W - F bridge distance, where the fluorine atom is placed at a position corresponding to the average of structures **15** and **16**, can be readily assessed from the structure of MoOF$_4$[156]. This structure forms infinite chains rather than the discrete tetrameric units found in WOF$_4$. However, the essential heavy atom environments are the same as shown in **19**.



**19**

The average of the two independent Mo - F distances (1.96 and 2.27) in this asymmetrically bridged structure is 2.11 Å, the same as is found for bridge bonds in the tungsten compound.

The hypothesis of the disordered structure was then tested using the published structure factor amplitudes. Two models were refined: (a) the ordered oxygen bridged structure **14** and (b) an average of structure **15** and **16** with two independent half weight fluorine atoms in each bridge, the terminal in plane atoms each being treated as a single atom comprising half oxygen and half fluorine. Both models were refined isotropically in the space group C2/m using scattering factors that contained the real and imaginary components of anomalous dispersion and the weighting scheme of Edwards and Jones. In model (b), only one half weight fluorine was refined in each cycle because of the resolution limits of the data set.

Both models refined to R factors of 0.126. The refinement of the disordered model produced asymmetric bridges with individual tungsten-fluorine distances 2.04 (7) and 2.19 (7). The other values were not significantly different from those observed by Edwards and Jones.

The X-ray data do not allow the rejection of the ordered model **14**[44]. This is not surprising in view of the quality of the data used and the relative insensitivity of the structure factors to small changes in the light atoms when a third row transition metal is present. Therefore the choice between the ordered and disordered models has to be made on the basis of other evidence. In this case the spectroscopic and structural arguments favour a fluorine bridged structure of which **15** is the most attractive.

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