X - Ray Crystallographic Studies of Some Organic Compounds.

THESIS

PRESENTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN THE

UNIVERSITY OF GLASGOW

BY

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December, 1959.

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Preface.

This thesis is based on a three year period of research performed in the laboratories of Professor J. M. Robertson under the supervision of Dr. J.C. Speakman.

In putting forward this work it is very appropriate that acknowledgement should be made by the author of the stimulus provided, the encouragement given and the interest taken in its various aspects by Dr. Speakman.

I have to thank Dr.'s G. Buchanan and H. Sutherland, and also Dr.'s G. Eglinton and A.R. Galbraith and Mr. O.M. Behr for the supplies of crystals kindly provided for the x-ray analysis.

I should like to thank Mr. J.B. Findlay of the Chemistry Department for invaluable assistance in the preparation of diagrams.

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INTRODUCTION

Crystals differ from amorphous, liquid and gaseous systems in that they possess the properties both of homogeneity and anisotropy. Early workers engaged in the geometric study of crystals found them to exhibit a definite number of microscopic symmetry elements. On the basis of these observations they attributed to the crystal a regular lattice structure in which identical aggregations of lattice points comprised the microscopic building units of the crystal structure. By 1893, the total possible number of varieties of these aggregations had been evolved - the 230 spacegroups.[1]

It was not until 1912 that quantitative proof of the lattice structure was achieved through the discovery that the wavelength of the recently discovered x-rays and interatomic distances were of the same order of magnitude. From analogy with the diffraction of light by a grating, Von Laue concluded that if the crystal was indeed composed of a three dimensional atomic lattice then the passage of an x-ray beam through it should be accompanied by diffraction of the x-rays in discrete directions. The experimental realisation of this hypothesis was effected by Friedrich and Kipping and the diffraction pattern recorded on a photographic plate.

The correlation of this effect to the structure of the crystal is termed x-ray crystallographic structural analysis.

Methods of Structural Analysis

Unfortunately the complete structure of the crystals or molecules cannot be calculated directly from the positions and intensities of the reflections from the crystal lattice planes appearing on the diffraction photograph. These relate to the amplitudes $|F|$ of the composite

waves/

waves diffracted by the atoms of the unit cell in given directions, and contain no information as to the phases of those waves. Hence the resolution of crystal structures has had to follow indirect routes; these endeavour to find a structural arrangement of atomic parameters which will afford a set of calculated F, or structure factor, values with amplitudes |F| similar to those obtained from the observed data.

The nature of these techniques can be exemplified by a brief review of some of those methods which found useful application in the present work.

Trial and Error Methods

When all the data relating to any particular crystal structure has been assessed, it is sometimes possible, especially in more simple structures, to detect one or more factors which can be exploited to reveal the specific dispositions of the molecules within the unit cells.

Whilst consideration of the spatial requirements of the molecules as deduced from conventional inter- and intra-molecular contact distances can provide a general impression of the molecular distribution, it is only in very favourable cases that these aspects in themselves can provide a complete solution. In general, the presence of an additional factor or factors is necessary and this can take a number of forms.

It may be the case that the symmetry elements of the unit cell can infer one or more of the co-ordinates of the atoms by requiring the molecule to assume a particular orientation. Significant information can often be extracted from strongly reflecting planes; the intersections of/

of the tracings of these planes often coincide with an atomic site and the presence of a single outstandingly strong reflection in a particular zone implies its close proximity to many or all of the atoms of the structure. Again the distribution of the strong reflections may be made to conform to an alternative reciprocal lattice network from the original one: the contents of a sub-cell of this nature incorporated within the real cell are often simple to resolve and may preclude the solution of the main structure. An overall survey of the entire intensity data can yield further clues. Weak intermediate layer lines corresponding to virtual axial halving serve to indicate the close similarity of adjacent rows of molecules, whilst a study of the form of the diffuse reflections may reveal certain molecular features.

In addition to the evidence from x-ray data, useful information as to the positions of the atoms, especially in the case of simpler molecular structures, can be obtained purely from their physical properties. Of these the most relevant data has been provided by crystal morphology and cleavage, optical, magnetic and infra-red absorption data.

Patterson Synthesis

In order to avoid use of the phase-determined coefficients necessary for the direct representation of the electron density by Fourier Series, Patterson^2 considers only the directly measureable quantity $\{F^2\}$ as provided by the intensities of the reflections.

Patterson thus derives the expression

$$P(u\,v\,w) = \int_0^a\int_0^b\int_0^c \rho(xyz)\,\rho(x+u,\,y+v,\,z+w)\,dx\,dy\,dz = \frac{1}{V}\sum_{-\infty}^{+\infty}\sum\sum F^2_{hkl}\cos 2\pi\left(\frac{hu}{a}+\frac{kv}{b}+\frac{l}{}\right)$$

It is clear that the foregoing integral can only become large when ρ (x, y, z) and ρ (x + u, y + v, z + w) are both large, i.e. whenever there are atoms at both the points (x,y,z) and (x + u, y + v, z + w) separated by the vector distance (uvw). Hence for a molecule containing N atoms, a vector distribution of $\frac{N}{2}$ (N + 1) essentially distinct interatomic vector peaks of magnitudes proportional to the weights of their component atoms is afforded; thus it should be possible to derive the actual atomic co-ordinates provided these latter peaks are well resolved. In practice this is usually only true in the case of very simple structures containing only a few atoms, or where the nature of the structure provides a large number of interatomic bonds of similar lengths and orientation. An instance of the latter case is presented later in this thesis.

In general, the degree of overlap prevailing can vary with the complexity of the structure to an extent such as to make its interpretation comparable to that of a trial and error analysis. Several methods of "sharpening" the degree of resolutions have been devised;[3,4] these all serve to reduce the atoms to point scattering sources and contain modifications designed to offset the divergent nature of the series introduced by this process.

Direct Approaches

The methods previously described have attempted to establish the phases of the structure factors by solution of atomic co-ordinates. It is however possible in certain cases to derive these phases directly by the use of inequality and identity relationships. These all assume that/

that in direct space the electron density in crystals is always positive and that the diffracting atoms are spherically symmetrical. Under these conditions the reciprocal lattice of the crystal can be weighted in terms of the unitary structure factor values for point atoms rather than actual atoms. This increases the strength of the inequality relationships since the unitary structure factor expression for point atoms viz. $U = \frac{1}{N} \sum \cos 2\pi H r$ does not decrease with increase of θ. Harker and Kasper[5] have applied these concepts to both Schwarz's Inequality and Cauchy's Inequality for practical sign determination. Unfortunately Harker Kasper Inequalities can only produce a complete structural solution in the case of very simple molecules containing only a few atoms. For more complex systems the attendant decrease in $\overline{U}$ (Hughes and Wilson[6] – $\hat{U} = \frac{1}{\sqrt{N}}$, where N = the number of atoms in the unit cell) suppresses the large number of high U values necessary to solve the structure.

Attempts to overcome this problem have been made by Karle and Hauptmann[7], Sayre[8], Cochrane[9], and Zacharaisen[10]. The expression given by Sayre is confined to structures in which the atoms are identical and fully resolved from one another. In its general form R Sayre's equation states that if U_{hkl}, $U_{h'k'l'}$ and $U_{h+h',k+k',l+l'}$ are all sufficiently large, then s(hkl) = s(h'k'l') s(h + h',k+k',l+l') will be true to a reasonably high degree of probability when the crystal is centro-symmetric. In actuality, Sayre's Equation is often found to hold when the equivalent inequality conditions are not realised, and the individual atoms are not fully resolved from one another. This observation has permitted further extensions to the scope of these relationships/

relationships to be made by Cochran and Zacharaisen.

Zacharaisen's approach constitutes a development of the Harker Kasper Inequalities, and in its final form employs the statistical equivalent of Sayre's Equation, viz.

$$s\,(H) = s\left\{\overline{s\,(H')\quad s(H + H')}\right\}$$

Zacharaisen considers this expression to be reliable at least for $\overline{U} > 0.07$, and presupposes that a sufficient number of related, large structure factors are available to provide a self-consistent set with respect to this equation.

Numerous developments of these earlier concepts have subsequently been made and amongst these the utilisation of a method due to Woolfson[11] is described later in this thesis. However the dependence of these methods upon the derivation of a few basic signs from the Harker Kasper Inequalities and upon the somewhat precarious reliability of Sayre's Equation has restricted their practical application to only a relatively small number of favourable cases.

REFINEMENT PROCEDURES

The rather premature nature of the structure inferred by the previous methods makes it necessary to devise methods for confirming and improving the degree of accuracy of the atomic parameters.

Method of Successive Fourier Syntheses

The periodic repetition of the unit cell within the crystal enables it to be represented by a Fourier Series[12] in which the signs of the calculated structure factors are attributed to the coefficients of the terms of this Series

$$\rho(xyz) = \sum\sum\sum \frac{|F_{hkl}|}{V} \cos\left\{2\pi \frac{hx}{a} + 2\pi \frac{ky}{b} + 2\pi \frac{lz}{c} - \alpha(hkl)\right\}$$

where the phase associated with the amplitude $|F\ hkl|$ is provided by the value of α (hkl).

The graphical representation of this summation initiates refinement of the atomic co-ordinates by the method of successive Fourier Syntheses, in which the calculation of structure factors from the atomic positions implied by the previous Fourier map continues until no further changes of phase are obtained. The course of the refinement may be traced at each Fourier stage by reference to the discrepancy factor,

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

However the form of this type of Fourier Series introduces errors owing to the replacement of a theoretically infinite summation series by one which is finite[13]; nor does it make any allowance for temperature factor effects caused by the thermal motion of the atoms at temperatures other than Absolute Zero. Provision can be made for these factors by employing the back-shift method of correction but in practice it is more convenient to use either the method of Least Squares[14] or that of Difference Synthesis[15,16] in the later stages of the refinement.

DIFFERENCE SYNTHESES

In this synthesis, the values $F_o - F_c$ constitute the coefficients of the Fourier Series and are inserted only for those terms for which F_c is actually observed. The criterion for refinement by Difference Synthesis is then to adjust the atomic co-ordinates (from which the F_cs. are evaluated) until the gradients at these atomic sites are zero, i.e. until

$$\left(\frac{\partial D}{\partial x_n}\right) = \left(\frac{\partial D}{\partial y_n}\right) = \left(\frac{\partial D}{\partial z_n}\right) = 0$$

The extent of the shift is given by $\Delta r = \dfrac{\left(\frac{\partial D}{\partial r}\right)_n}{\left(\frac{\partial^2 \rho_c}{\partial r^2}\right)}$ where r represents a distance measured in the direction in which D increases most rapidly. The completion of this process equalises the gradients of the F_o and F_c Syntheses and hence affords co-ordinates free from series-termination errors, provided that the correct values of the temperature factor have been chosen. This latter requirement can easily be fulfilled by adjustments inferred directly from the Difference map; thus the situation of an atom in a negative electron density trough indicates an increase in the temperature factor and vice versa. For an atom exhibiting anisotropic thermal vibration^{17}, positive and negative peaks are found along the directions of maximum and minimum vibration respectively. Refinement of these thermal parameters can be carried out simultaneously with the co-ordinate refinement.

In addition to its refinement application, the Difference Synthesis may be employed to reveal the presence of significant, low electron density regions (e.g. hydrogen atoms, bonding electrons,etc.) which are inaccessible to the Fourier Synthesis method owing to the distortion of the electron density by termination of series and thermal motion errors.

Least Squares/

Least Squares

The application of this method is directed towards the determination of the atomic parameters which result in minimization of the function

$$R = \sum_{hkl} w_{hkl} \left\{ |F_o| - |F_c| \right\}^2$$

Each plane provides one observational equation from which the linear equations necessary for a Least Squares solution can be developed. Refinement of parameters then proceeds by successive solution of the n simultaneous linear equations, or normal equations, in the n unknown parameters. In ganeral, the number of equations will considerably exceed the number of unknowns, and to achieve the greatest accuracy it is necessary to employ all the available data.

The use of the Least Squares method is not confined to refinement of the atomic co-ordinates alone; it is suitable also for thermal motion analysis and it has proved possible to construct punched card programmes capable of performing these two latter parameter refinements simultaneously on an electronic computer.

Assessment of Crystal Structure Accuracy

The errors introduced in the course of a crystal structure analysis can be classified as either systematic or random. Correction procedures have been used to eliminate the systematic errors, or errors due to termination of series or thermal vibrations; for the estimation of random errors, or errors due to experimental and computational inaccuracies and to the method for correction for systematic errors, a general quantitative method has been developed by Cruickshank.[18,19]. f?

Cruickshank considers that, for orthorhombic or monoclinic cells, the standard deviations of the co-ordinates of a peak position are given by

$$6(x) = \frac{6\left(\frac{\partial\rho}{\partial x}\right)}{\frac{\partial^2\rho}{\partial x^2}} \; ; \; 6(y) = \frac{6\left(\frac{\partial\rho}{\partial y}\right)}{\frac{\partial^2\rho}{\partial y^2}} \; ; \; 6(z) = \frac{6\left(\frac{\partial\rho}{\partial z}\right)}{\frac{\partial^2\rho}{\partial z^2}}$$

where $6\left(\frac{\partial\rho}{\partial x}\right) = \frac{2\pi}{aV}\left\{\sum_h h^2 \Delta F^2\right\}^{\frac{1}{2}}$ as deduced from the theory of errors; and $\frac{\partial^2\rho}{\partial x^2}$ is the curvature of the electron density function in the neighbourhood of the relevant atom.

For a completely refined structure the following result should hold (assuming symmetrical thermal motion) - $6(x) = 6(y) = 6(z)$. [illegible] From this the standard deviation of a bond length between two atoms is given by

$$6(\ell) = \left\{ 6^2(A) + 6^2(B) \right\}^{\frac{1}{2}}$$

or when the atoms are identical by $6(\ell) = \sqrt{2}\; 6(A)$

For atoms related by symmetry elements or in special positions, a more general formula is required. The presence of a mirror plane or centre of symmetry requires for the bonds concerned $6(\ell) = 2\; 6(A)$

A/

A formula has also been deduced for the standard deviation 6(θ) of an angle θ between three independent atoms A, B, and C with positional standard deviations 6 (A), 6 (B) and 6 (C).

Cruickshank has also studied the statistical significance of these values; thus for a Gaussian distribution of errors, it is suggested that the difference in the lengths of two bonds is significant to a probability of 99.9% when it is greater than 36. In fact subsequent work has indicated these calculations probably to represent minimum estimates of atomic accuracy.

Comparison of the X-Ray Method with Related Physical Methods

Much lower standard deviations in bond measurements can be achieved by the spectroscopic method when this is rigorously applied to a substance in the gaseous state. The scope of this method is, however, limited to simple substances containing only a few atoms; it therefore finds little application in the field of organic chemistry although its use has been extended in recent years to more complex organic compounds by the development of microwave spectroscopic analysis,

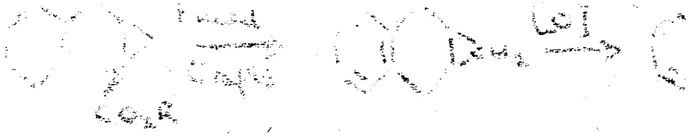
In recent years advances have also been made in the use of electron diffraction, neutron diffraction and nuclear magnetic resonance methods, but at present the only significant advantage afforded by these techniques is their ability to detect hydrogen atoms.

2:3-Dihydro-2:3-Methylene-1:4-Naphthaquinone.

Summary of the Work of A. Vos (and J.C. Speakman). - Pre-October, 1956.

The intensity data for the hk0 - zone was collected and "processed", and the space group tentatively proposed as $P2_1/m$. Analysis of the (001) projection was commenced and proceeded as far as the postulation of the trial structures (a) and (b) - vide page 16.

[illegible]



The formulation of the structure as (I) furnish points of stereochemical interest:-

[illegible] conformation adopted by the quasi-quinon[illegible] [illegible] of its environment.

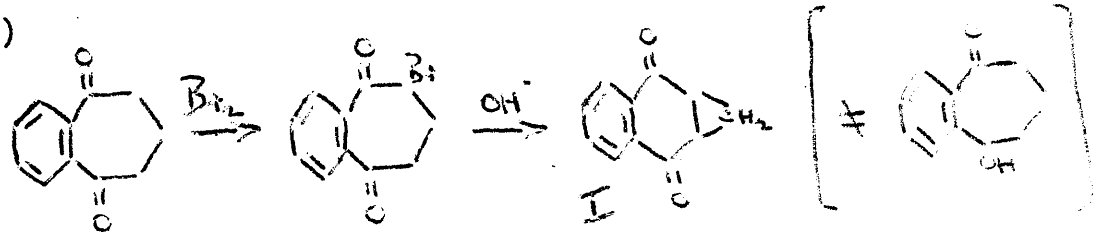
(2) The bond distributions around the heavily strained [illegible] at the junctures of the quinonoidal and cyclopropane [illegible]

(3) The cyclopropane ring and the influence [illegible]

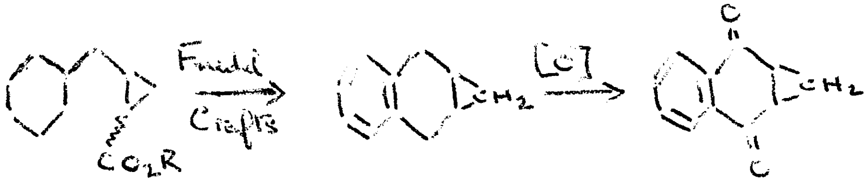
It was mainly with a view to elucidating these [illegible]

INTRODUCTION

In the course of studies on tropolone compounds by Buchanan and Sutherland,[21] attempts to synthesise an isomer of $\alpha\beta$ - benzotropolone viz. 4-hydroxy-2:3-benzotropone, produced instead the tricyclic isomer (I)



The rather novel rearrangement mechanism implied by the product (I) requires definite confirmation of its structure. Buchanan and Sutherland[22] have achieved the structural proof of this compound by chemical analysis and infra red spectroscopy, and have demonstrated a synthetic route to its preparation from allyl benzene viz.



The formulation of the structure as (I) furnishes a number of points of stereochemical interest:-

(1) The conformation adopted by the quasi-quinonoid ring under the influence of its environment.

(2) The bond distributions around the heavily strained carbon atoms at the junctures of the quinonoidal and cyclopropane rings.

(3) The cyclopropane ring and the influence exerted by it.

It was mainly with a view to elucidating these points and comparing the results with the stereochemistry and electronic distributions/

distributions of related compounds, that the present x-ray analysis of this substance was undertaken.

[illegible]

[illegible] of the b axis. The (100) pinacoid [illegible] 011 and/or 110 were usually present; [illegible] recognizable. The crystal morphology [illegible] as monoclinic prismatic.

The following dimensions were obtained from [illegible] oscillation and moving film photographs [illegible] using copper K_α radiation:

a = [illegible].98Å, b = 10.55Å, c = 9.4[illegible]Å (each [illegible]

Volume of unit cell = 400.9Å^3. Density measured b[illegible] chloride solution = 1.40 gms/cc. Density cal[illegible] two molecules per unit cell = 1.420 gms/c[illegible] coefficient for x rays = 9.2 cms.$^{-1}$ F(000) = 190

Absent spectra — 0k0 when k is odd

Space group is either $P2_1$ (C_2^2) or $P2_1/m$

Choice of Space Group

The results of the Wilson test[22], N(z)[23], and [illegible] the hk0 zone intensity data each independently [illegible] symmetry. In addition comparison of the average hk[illegible]

Crystallographic Data

The crystals, which possessed a reddish colouration, were prepared by Buchanan and Sutherland, and afforded, after re-crystallisation from toluene, a melting point of 128° - 130°. Those used for photographic work were shown to exhibit complete extinction in polarised light, and had the form of laths with pointed or wedge-shaped ends, elongated in the direction of the b axis. The (100) pinacoids were most prominent and the domes {011} and/or {110} were usually present; {001} pinacoids were sometimes recognizable. The crystal morphology could be classified as monoclinic prismatic.

The following dimensions were obtained from single crystal rotation, oscillation and moving film photographs about the a, b and c axes using copper K_α radiation.

$a = 6.98Å$, $b = 10.55Å$, $c = 5.46Å$ (each $\pm 0.02Å$) $\beta = 94\frac{1}{2}°$

Volume of unit cell = $400.9Å^3$. Density measured by flotation in zinc chloride solution = 1.40 grms/cc. Density calculated on the basis of two molecules per unit cell = 1.426 grms/cc. Absorption coefficient for x rays = 9.2 cms.$^{-1}$ F(000) = 180

Absent spectra - 0 k0 when k is odd

The space group is either $P2_1$ (C^2_2) or $P2_1/m$(C^2_{2h})

Choice of Space Group

The results of the Wilson test[23], N(z)[24], and variance test[25] on the hk0 zone intensity data each independently indicated centrosymmetry. In addition comparison of the average hk0 zone intensities with those of the hol zone showed considerable enhancement of the latter. When the intensities from the two zones were placed on the same scale, and/

and sub-divided into a number of 2 sin Θ regions, the following results were obtained -

ξ	0.3-1.0	1.0-1.5	1.5-2.0
$\frac{\langle F_{h0l}\rangle}{\langle F_{hk0}\rangle}$	1.22	1.34	1.51

Wilson[26] considers that for a mirror place perpendicular to the y axis $\frac{\langle F_{h0l}\rangle}{\langle F_{hk0}\rangle} = \sqrt{2}$.

Hence the space group was selected as P $2_1/m$.

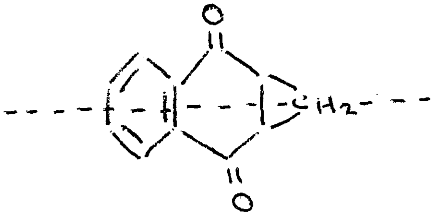
Intensity data was collected for the zero layer lines by Weisenberg moving film photographs about each of the three principal axes. Each series contained five films for intensity estimation by visual integration using the Robertson multiple film technique.[27] The film factor between adjacent films was estimated as 3.3 and for the 189 reflections observed out of 234 accessible to copper K radiation, the range of intensities measured was about 5,500 to 1. The crystals used had cross-sectional dimensions, normal to the a, b and c rotation axes of 0.320 x 0.292 mllms., 0.189 x 0.162 mms., and 0.36 x 0.24 mms. respectively so that absorption corrections were negligible and were neglected. Conversion of the measured intensity data to an absolute scale was effected by means of the Wilson relationship[28] $c \langle F_{h0l}^2 \rangle = \Sigma f_n^2$ c being evaluated by graphical interpolation. Lorentz and polarization[illegible] factor corrections completed the "processment" of the intensity data.

STRUCTURE ANALYSIS

Space Group Consideration

Since the general position of the space group P $2_1/m$ is fourfold, the/

the presence of two molecules in the unit cell implies the symmetric unit to be half a molecule. It is possible that this provision may be fulfilled for each whole molecule by coincidence of its plane of bisection with a mirror plane of the unit cell in the manner shown.



(001)Projection

Approximate temperature factors were calculated graphically for the carbon and oxygen atoms using the expressions, $I_o = I_c\, e^{-\frac{2B\sin^2\theta}{\lambda^2}}$ where $I_o = {F_o}_{hkl}^{\,2}$; $I_c = \sum f_n^{\,2}$; B = temperature factor.

The gradients inferred gave B = 2.5Å^2 and 3.0Å^2 for carbon and oxygen atoms respectively; these temperature factor values were used to adjust the atomic scattering factor curves constructed by Hoerni and Ibers[29] for zero thermal motion.

The situation of the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$ defined assuming standard interatomic distances, the approximate y co-ordinates of all the atoms of the molecule. Correlation of these values to the intersections of the cosine maxima of the strongest reflections suggested two possible structures:-

(a) with the oxygen atoms at $x \approx \frac{a}{3}$

(b) with the oxygen atoms at $x \approx \frac{a}{4}$

Structure factors were calculated for both structures and discrepancy factors of 0.46 and 0.56 obtained for (a) and (b) respectively. The better agreement given by (a) favoured the initial choice of this structure for attempted refinement.

Two successive syntheses performed on this structure lowered the discrepancy to $R = 0.26$, from which stage refinement was continued by difference synthesis. This process subsequently revealed anisotropic thermal vibration of the oxygen atoms; the component parameters of this vibration varied from a maximum of $B = 3.5\text{Å}^2$ in the direction normal to the carbonyl bond, to a minimum of $B = 2.5\text{Å}^2$ at right angles to the latter direction, and were corrected for by the use of a nomogram. In addition adjustments of an isotropic nature were made to the temperature factors of the carbon atoms to relieve the situations of these atoms in negative electron density troughs. Very little evidence for libration of the molecule as a whole about its centre of mass was detected at any stage of the analysis. A sequence of gradually diminishing gradients in the neighbourhood of atoms was presented in successive difference maps before the sixth such map indicated the need for only negligible atomic shifts. At this stage the discrepancy was $R = 0.13$.

A final Fourier Synthesis, based on the last set of calculated structure factors, was performed on the digital computer designed by Robertson.[30] This map is illustrated on figure 1.

(010) Projection

The mirror planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$ are now parallel to the plane of projection; hence the molecule, as viewed down this axis, should appear to consist of five carbon atoms and one oxygen atom, each of double weight, plus one carbon atom of normal weight.

Furthermore, the resolution of the c axis projection leaves only the z co-ordinates of the atoms to be determined. A survey of the

hol/

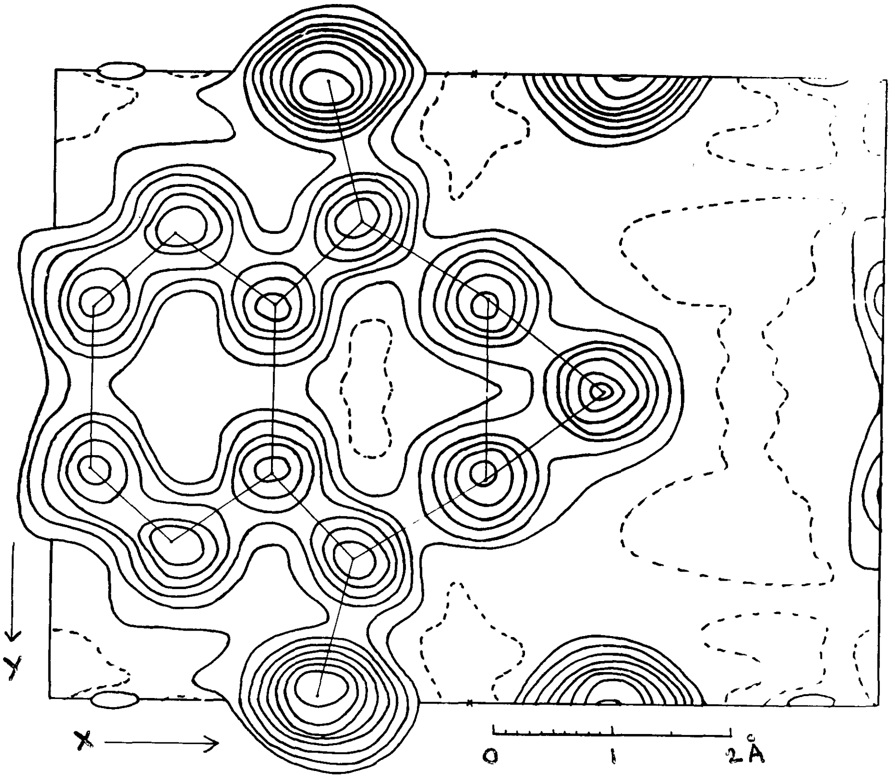


Figure 1.

Final Fourier synthesis of the hk0 - zone. The contour line interval is 1 electron per square Å with the zero electron level marked with a broken line.

hol zone intensity data suggested that it was possible to affix the average tilt of the molecule to the x and z axes from that of the outstandingly strong (201) reflection, along which plane it was assumed the greater part of the molecule must lie. An experimental structure was deduced from a review of the intersections of the strongest planes with the (201) plane; this proposed unambiguous sites for the oxygen atom and carbon atoms $C_1 - C_5$, and even at this stage indicated a slight tendency of the conformation of the central ring towards that of a boat. For the C_6 atom the picture was not quite so clear; there were two possible directions in which the cyclopropane ring could be orientated with respect to the $C_4 - C_5$ bond depending upon whether the quasi-axial or quasi-equatorial bonds were used for ring fusion. Unfortunately reference to the hk0 projection showed the projected lengths of the $C_4 - C_5$ and $C_5 - C_6$ bonds to be consistent with either type of ring juncture. Anal~~a~~ogous stereochemical alternatives have generally indicated the di-equatorially fused isomer to constitute the preferred conformation, and since the intersections of the strongest planes appeared to substantiate this latter conformation, it was adopted as the first trial structure for analysis.

An initial discrepancy of R = 0.41 was obtained, which three successive Fourier syntheses reduced to R = 0.30. Further refinement was continued by difference syntheses but proceeded slowly, the discrepancy following to only R = 0.25 after four such syntheses had been performed.

Since this value appeared close to the limit of refinement, it was/

was concluded that the supposition of the di-equatorial isomer was wrong and that the next step should be the investigation of the diaxial form.

The analysis of this projection had been hindered throughout by the almost complete overlap of the electronic peaks arising from the oxygen atom and carbon attached to it. To obtain a detailed refinement with respect to these atoms would be a lengthy process so that it appeared more convenient at this stage to suspend work on this projection, and start on the (100) projection using the z parameters last indicated for the atoms C_1,C_2,C_3,C_4 and C_5 by the b axis projection analysis.

(100) Projection

The y and z co-ordinates were chosen as far as possible from the c and b axis projections and suitable modifications made to accommodate the intersections of the strongest planes. A preliminary Fourier synthesis computed on the basis of this structure led to a discrepancy of $R = 0.36$ which on the application of two further Fourier syntheses fell to $R = 0.29$. The introduction of difference syntheses methods produced a gradual fall in the discrepancy, but possibly at a slower rate than might have been expected owing to the failure of one or two of the larger reflections to calculate to an appreciable value. For these a process of trial and error had to be employed so that, in all, five difference syntheses were carried out before the discrepancy fell to an ultimate value of $R = 0.12$. In the course of this refinement correction was made for anisotropic thermal vibration of the oxygen atoms, the component parameters of this/

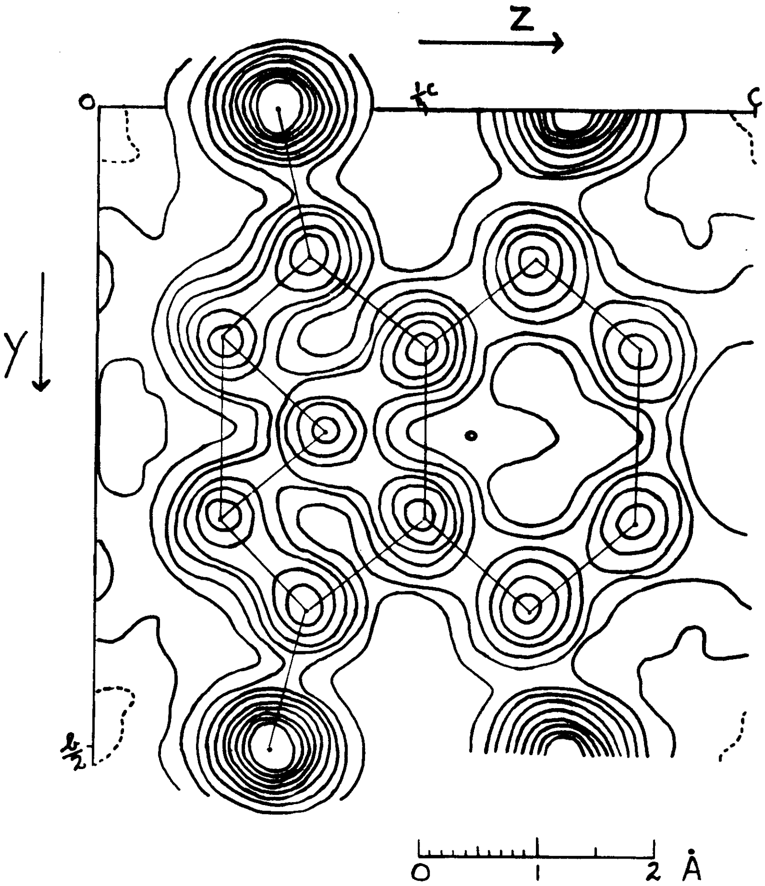


Figure 2.

Final electron density projection along the a - axis. The contour line interval is 1 electron per square Å with the zero electron level marked with a dotted line.

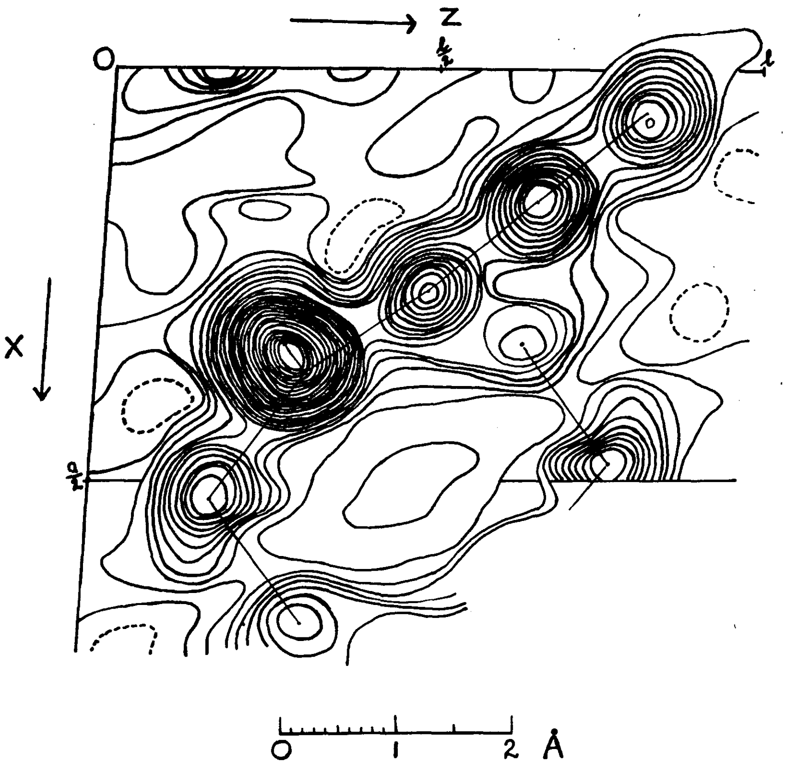


Figure 3.

Final Fourier synthesis of the h0l - zone in which the molecular conformation is revealed. The contour line interval is 1 electron per square Å with the zero electron level marked with a broken line.

this vibration being similar to those found to apply in the hko projection. A map of the final Fourier synthesis was constructed and this has been reproduced in figure 2.

(010)Projection (contd.)

Co-ordinates of the latest x and z parameters gave an initial discrepancy of R = 0.15. Adjustment of the temperature factors from their assigned values (i.e. those afforded by the c axis projection) to 2.8Å^2 and 3.3Å^2 for carbon and oxygen atoms respectively lowered this figure to R = 0.11. The final Fourier synthesis corresponding to this value is graphically depicted in figure 3; in it the cis relationship of the cyclopropane ring to the benzenoid system about the $C_4 - C_5$ bond is clearly illustrated.

Hydrogen Atoms

At suitable stages in the refinement of each projection, plausible positions were assigned to the hydrogen atoms, and their contributions incorporated into the calculated structure~~s~~ factors. In each instance the improvement in the discrepancy afforded by this process was approximately 1 - 3%. Final difference maps on TWO each of the three projections, in which the donations from the hydrogen atoms have been removed from the calculated structure factors, revealed electron density peaks of from 0.6 - 1.0 e.d.u/Å^2 arising at or near to their theoretical positions. Reproductions of these maps are shown on figures 4(a), 4(b) and can be compared with the corresponding unaltered final difference maps depicted on figures 5(a), 5(b), 5(c).

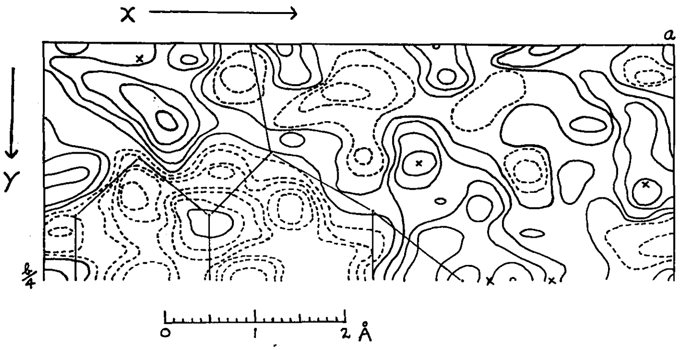


Figure 4(a)

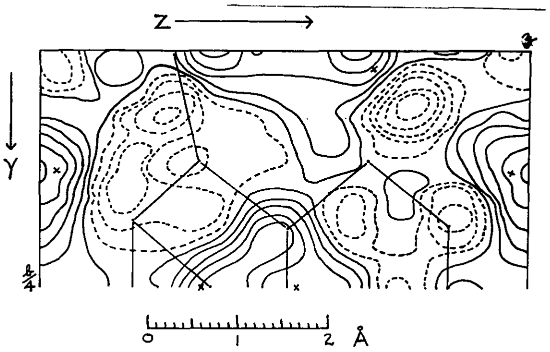


Figure 4(b)

$(F_o - F_c)$- Syntheses of the hk0 and 0kl zones. The contour interval is one electron per square Å and the negative electron density regions are marked by a broken line. The positions of the hydrogen atoms are denoted by crosses.

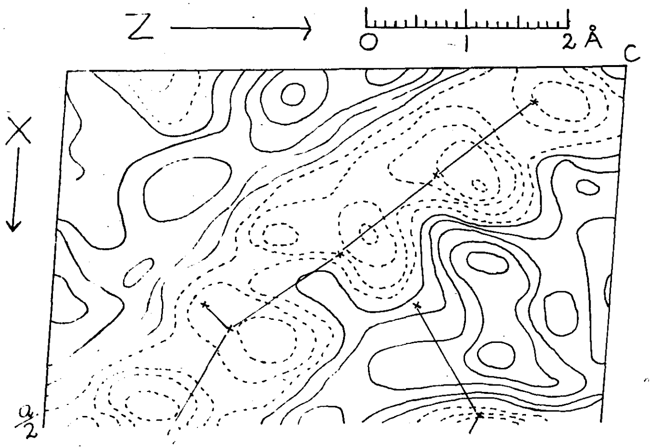


Figure 5([illegible])

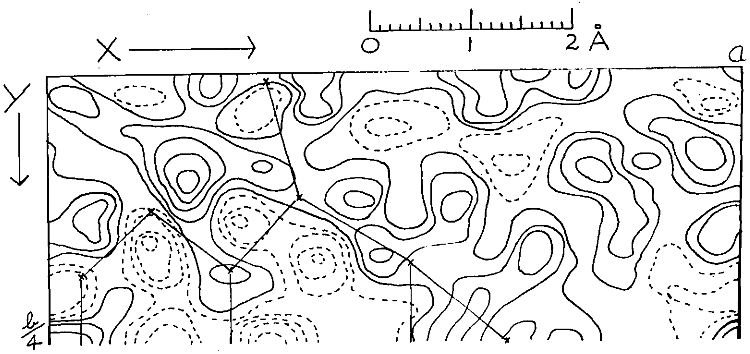


Figure 5(a)

Final $(F_o - F_c)$ Syntheses of the $h0l$ and $hk0$ zones. The contour interval is one electron per square Å and the negative electron density regions are marked by a broken line.
Figure 5(c) shows the position immediately prior to an over-all reduction in the temperature factor of the atoms of the molecule. which improved the discrepancy by 4%.

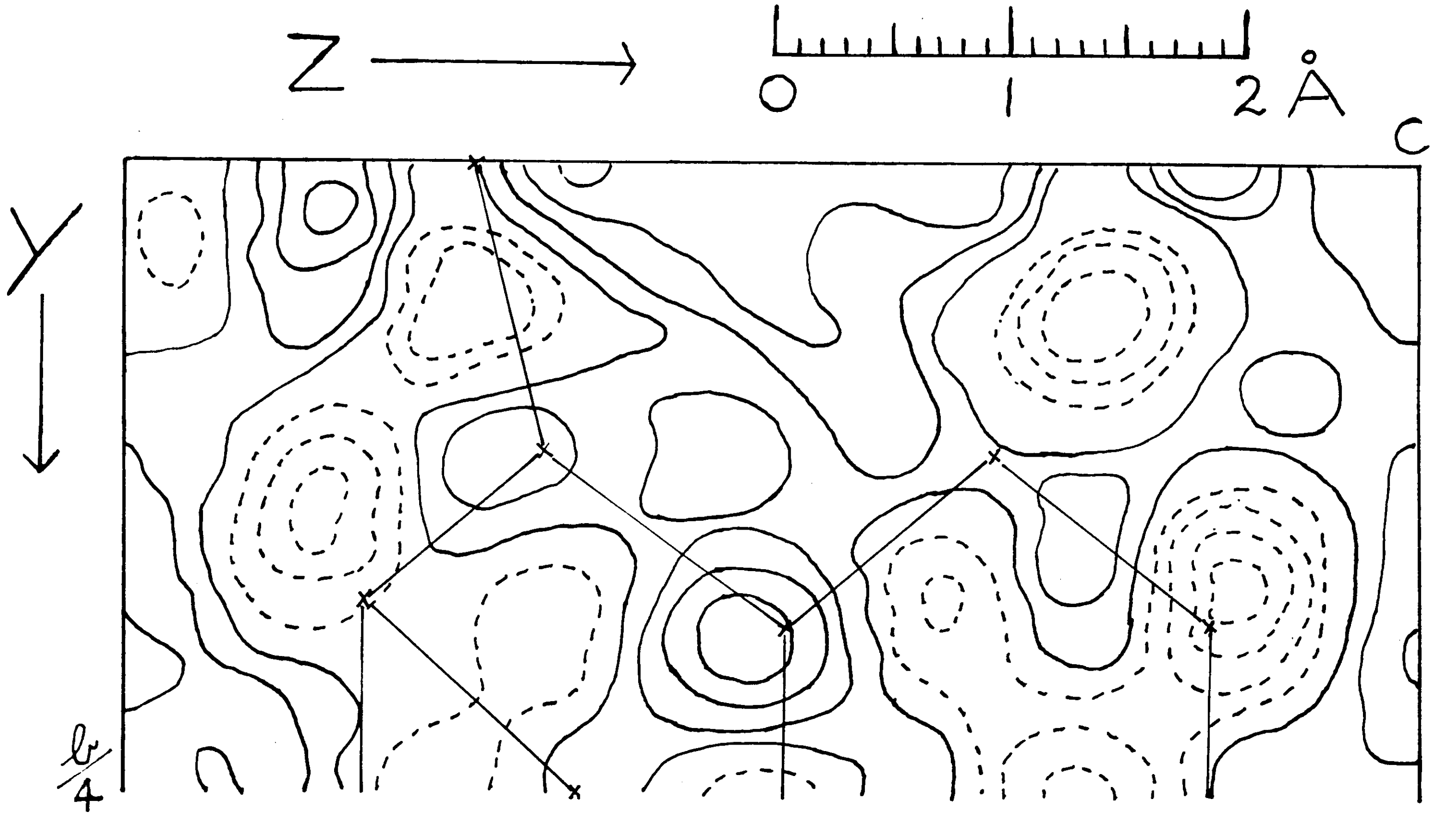


Figure 5(b)

Final $(F_o - F_c)$ Synthesis of the Okl zone. The contour interval is one electron per square Å and the negative density areas are denoted by a broken line. Note the positions of the atoms in regions of approximately zero gradient.

Final Atomic Parameters and Assessment of Crystal Structure Accuracy

The final atomic co-ordinates x,y,z listed as fractions of axial lengths and the Debye temperature factors B in Å ^{2} (for the three independent zones are presented in Table 1. ———— P 20

To obtain the most probable set of interatomic distances and bond angles, the co-ordinates contained in Table 1 were coalesced into the mean values listed in Table 2; in this table also appear the co-ordinates of hydrogen atoms, the numbering of these atoms being directly related to the carbon atom to which any one hydrogen atom is attached. The averaged fractional atomic co-ordinates were converted into Å (X,Y,Z) and hence to X^1, Y^1, Z^1 which are referred to orthogonal axes by the relationships

$$X^1 = X \sin\beta \quad ; \quad Y^1 = Y \quad ; \quad Z^1 = Z + X\cos\beta$$

The interatomic distances and bond angles subsequently calculated are portrayed in figure 6, on which all intermolecular atomic contacts greater than 3.4Å in length have been omitted. A perspective representation of the adopted molecular conformation is shown in figure 7; the viewer is presumed to be looking down at an angle of about 45° on to the equatorial plane of molecular symmetry. A schematic diagram portraying the over-all stereochemical picture pertaining in the neighbourhood of the heavily strained C_5 atom was also constructed and is reproduced in figure 8. The dihedral angles shown were calculated by reduction of the positional co-ordinates of the relevant atoms to two separate planes/

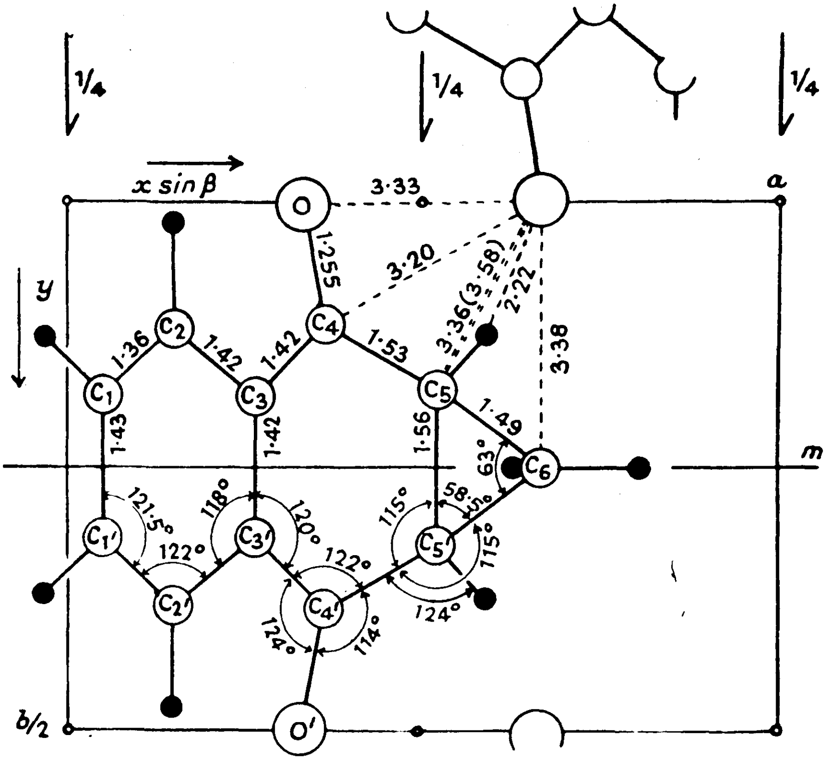


Figure 6.

The molecule as seen in its c - axis projection showing the numbering of the atoms, and intramolecular bond lengths (Å) and angles along with some significant intermolecular contact distances (Å).

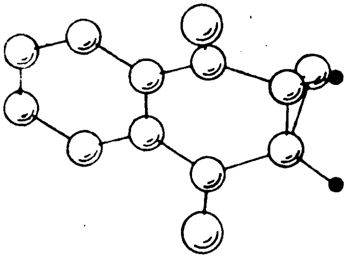


Figure 7

Perspective View of the Molecular Conformation

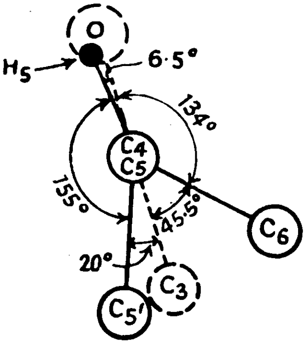


Figure 8

Bond Distribution around the C_5 atom

planes (each defined by three atoms), inclined to one another at the angle (dihedral) ψ, where

$$\cos\psi = \frac{AA' + BB' + CC'}{\sqrt{(A^2+B^2+C^2)(A'^2+B'^2+C'^2)}}$$

where A, B anc C are the co-efficients of the three equations used to project three atoms on to the same plane.

Estimates of crystal structure accuracy were carried out using the final values of the observed and calculated structure factors denoted in Table 4. Unobserved reflections have been omitted from this table, but it should be noted that only ten of the forty-five "missing" reflections afforded calculated structure factors consistent with their being just detectable. The remarkably favourable crystallographic conditions facilitating the structural refinement of this compound enable the crystal structure accuracy to be assessed by two different methods:-

(1) The availability of co-ordinates, each of which was determined in two independent projections, permits comparisons of their consistency to be made. The standard deviations (σ) of the co-ordinates from their means are listed in Table 3(a), and represent the estimates provided by the six carbon atoms and one oxygen atom taken together. This coalescence was performed for convenience since the inclusion of the deviation due to the oxygen atom has little effect upon the averaged value for the six carbon atoms.

(2) The clear resolution presented in all three projections allows a reliable application of Cruickshank's method[18,19] for which the

resultant/

resultant standard deviations are given in Table 3(b). This shows the σ-values to be largest for the zone giving the most favourable projection of the molecule, although the R value is hardly inferior; it is probable that the larger number of reflections in the hko zone is responsible for this effect. The root mean square deviation of the σ-values derived for each of the three independent zones were calculated (Table 3(c)) and used to assess the σ-values for inter-atomic bond lengths and angles.

For the purposes of assigning bond length standard deviations, there are three distinct types of bond present.

(a) $\sigma(C - O) = \sqrt{\sigma(C)^2 + \sigma(O)^2} = \pm 0.015$Å

(b) $\sigma(C - C)$ for bonds lying across the mirror plane = $2\sigma(C) = \pm 0.030$Å and this value applies only to the y co-ordinates of the atoms terminal to these bonds.

(c) $\sigma(C - C)$ for other bonds = $\sqrt{2}\,\sigma(C) = \pm 0.008$Å and this figure, deduced from $\sigma(r)$, concerns the x, y and z co-ordinates of the relevant atoms.

For bond angles near to 120°, $\sigma(\Theta) = \pm 1.1^\circ$

The calculation of standard deviations for the hydrogen atoms awaits a more detailed knowledge of their atomic co-ordinates. At this stage it is possible that they are located within ± 0.2Å of their true position.

Structural Refinement in Three Dimensions

The two dimensional refinement has revealed the stereochemical requirements of the heavier carbon and oxygen atoms of the structure but has been unable to provide any concise information as to the part played by the hydrogen atoms. In particular, knowledge of the positions of the H_5, H_6 and H_6^1 atoms could facilitate a more detailed assessment of the degree of strain associated with the cyclopropane ring system and its juncture to the rest of the molecule. To achieve an accurate refinement of the positions of the hydrogen atoms, a very large number of observational equations are necessary and, in fact, necessitate the collection of three dimensional data.

Furthermore, the advantages arising from the presence of the mirror planes in the unit cell to the structural analysis of I do not extend to its structural refinement (other than facility of computation). In fact the mirror plane serves to increase the standard deviations for these bonds lying across it. Thus the rather interesting bond length distributions obtained in the two dimensional analysis perhaps require the more severe limitations imposed by a three dimensional analysis before a high degree of validity can be attributed to them.

Accumulation of Three Dimensional Data

Three dimensional intensity data were collected by moving film photographs, using copper K_α radiation, about all three axes for the following zones (Table 5).

In all cases, intensity estimations were carried out by visual integration using the Robertson multiple film technique[27] in conjunction with/

with a step wedge. The attendant increase in the film factor with successive layer lines was calculated using a method due to Grenville-Wells[31] for upper layer lines which had been collected by normal beam Weisenberg photographs, and a method due to Rossmann[32] for those obtained from equi-inclination Weisenberg photographs viz. the higher layer lines of the b axis. These values are shown in Table 5. In addition to the usual Lorentz and polarisation corrections to the observed reflections, allowance had to be made for the fact that when the reflecting plane does not lie on the equatorial layer (and hence does not contain the axis of rotation of the crystal) the resultant decrease in the angular velocity of the planes causes them to reflect for different intervals of time. The methods of Cox and Shaw[33], and Tunnel[34] for normal beam and equi-inclination Weisenberg photographs respectively were applied for this correction in combination with those for the Lorentz and polarisation factors.

Crystal Dimensions

The three crystals used for the upper layer lines photographs had the following dimensions:-

Crystal	Rotation axis	Cross-Sectional Edges Normal to Rotation Axis
1	a	1.325 mms. x 0.50 mms.
2	b	0.20 mms. x 0.25 mms.
3	c	1.00 mms. x 0.40 mms.

The relative absorption of x rays by the principal planes of each crystal were calculated and showed that the degree of absorption by/

by crystals 1 and 3 could not be ignored. Correction for absorption was made by Albrecht's method[35] using a Deuce T.I.P. programme due to Speakman[36]. The crystal grid over which the x ray absorption was averaged was selected in proportion to the crystal cross-sectional area normal to the rotation axis, and the absorption further plotted on a chart in terms of Weisenberg space for a suitable array of ϕ and ψ values where ϕ and ψ represent the co-ordinates of any point in Weisenberg space. The superimposition of this chart on a Weisenberg film enabled the appropriate modification to be made to the intensity value of every observed plane. The square roots of these "processed" intensity values then represented the relative structure amplitudes. The observed structure factors were subsequently placed on an appropriate absolute scale by correlation with the averaged reflections of the zero layer projections. Of the 1,057 planes detected and estimated on the individual layer lines only some 619 (or 70% of the total number contained in the hemisphere of reflection) proved to be effectively independent, thus permitting a considerable number of cross-checks to be made on the absolute structure factor values.

Refinement

The atomic parameters submitted for Least Squares analysis using Deuce were the mean values listed in Table 2. The composition of the refinement programme[37] permits its application in three forms with respect to the hydrogen atoms:-

(a)/

(a) With the hydrogen atoms excluded from both the calculated structure factors and the Least Squares analysis.

(b) With the hydrogen atoms contributing to the calculated structure factors but not in the Least Squares analysis.

(c) With the hydrogen atoms presented both for structure factor calculations and Least Squares refinement.

The use of programme (a) produced an initial discrepancy of R = 0.222 which four further cycles lowered to R = 0.170. At this stage programme (c) was adopted and its application lowered the R factor, after five cycles, to an ultimate value of R = 0.136. The course of this latter refinement had been traced and it was noted that two of the hydrogens, viz. H_1 and H_6^1, had failed to refine. In view of this effect an attempt was made to reduce the discrepancy by use of programme (b), but this did not prove possible owing to a programme failure.

The final values of all atomic parameters are given in Tables 6 and 7, and the calculated and observed structure factors in Table 11.

Accuracy

Since the effects of the off-diagonal terms in the matrix of the Least Squares normal equations had not been included in the programme used, the form of the standard deviation expression had to be modified[38] to -

? incorrect

$$6\,(x)^2 = \frac{\Sigma\omega\Delta^2}{(n-s)\left[\Sigma\omega\left(\frac{\partial F}{\partial x}\right)^2\right]}$$

where (n-s) is the number of degrees of freedom =

$$\frac{\text{Number of planes observed} - \text{Number of atomic parameters}}{\cancel{\text{Unit cell}}\ \text{volume}}$$

Both/

Both $\Sigma w \Delta^2$ and $\Sigma w \left(\frac{\partial F}{\partial x}\right)^2$ could be obtained from the least squares programme optional output production.

The results of these calculations for all positional co-ordinates of oxygen, carbon and hydrogen atoms are contained in Table 8. Tables 9 and 10 use the figures afforded by Table 8 to show the standard deviations of bond lengths and bond angles respectively, their method of calculation following a scheme previously outlined.[18,19]

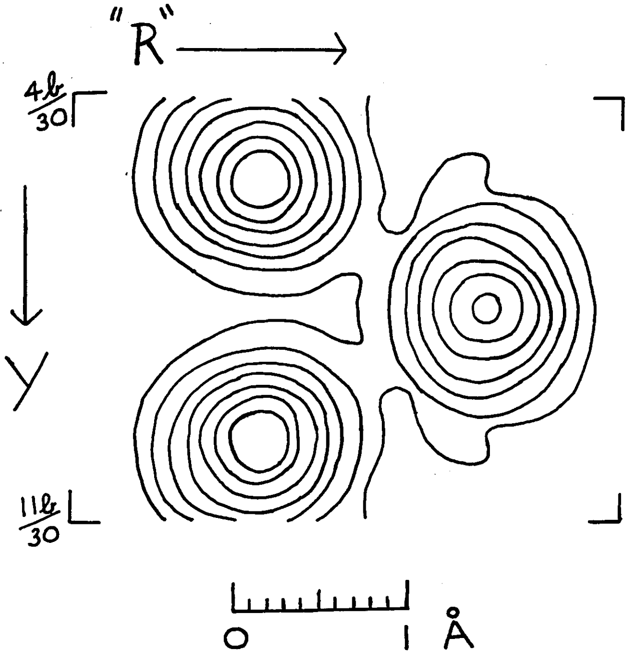


Figure 9(a)

3D. Section through the plane of the cyclopropane ring.

DISCUSSION

In proceeding from the two dimensional to the three dimensional refinement of this structure, certain alterations in the bond lengths of the molecule have taken place; all of these changes, although in themselves within the limits permitted by the standard deviations, serve collectively to afford two molecules with significantly different trends of electronic distributions without, however, in any way affecting the general conformation of the molecular structure. In view of the much larger number of observational equations included in the three-dimensional refinement, it is certain that greater importance should be attached to this latter refinement rather than to the initial two dimensional analysis.

Of the stereochemical aspects of this structure previously enumerated viz. the napthaquinone residue; the cyclopropane; and the bond distribution at their juncture, the greatest scope for comparison with related structures is provided by the bicyclic ring system.

X ray analysis by Robertson and Trotter[39] of p - benzoquinone and electron diffraction of the vapour form By Swingle[40] have separately shown this compound to be a planar structure with conventional bond lengths and angles. Subsequent work on polycyclic ring structures containing a quinonoid ring have, however, revealed this theoretically planar, conjugated system to be capable of undergoing buckling, the extent and direction of which would appear to be dependant upon the steric or polar requirements of substituents.

In anthraquinone, Sen[41] has found the structure still to be planar with/

with bond lengths and angles similar to those found for p - benzoquinone, but in this case there are no operative steric or polar factors.

Such however is not the case in indanthrone and 1:5 - dichloroanthraquinone both of which have been investigated by Bailey.[42,43] In the latter compound the quinonoid ring assumes a shallow chair conformation owing to the dipolar repulsion of the oxygen and chlorine substituents, whilst in the former the situation of the nitrogen atoms with respect to the oxygens leads to slight staggering of the three central rings. The sensitivity of the quinonoid structure to steric influences has been illustrated by Harnik and Schmidt[44] in their work on dianthronylidene. Here the overcrowded arrangement of the atoms is relieved by the distortion of the carbon-carbon bonds of the quinonoid ring out of the planes of the benzene rings to which they are exocyclic.

In the present compound there is also distortion of the quasi-quinonoid system; the ring assumes a half-boat conformation in which the atoms attached to the C_5 and C_5^1 atoms lie in eclipsed positions, and the oxygen atoms are directed towards the "bowsprit" of the boat. Since the molecule is not overcrowded and it possesses no polar substituent, the causes of this deformation must differ from those already mentioned. An explanation of this effect in terms of the influence of the cyclopropane ring is discussed later.

Another unusual feature of the ring is the non-collinearity of the carbonyl bonds. This is in distinct contrast to the previous quinonoid ring structures analysed; the deviation of the carbonyl groups/

groups from the normal to the mirror plane of the molecule is quite considerable, the dihedral angle between the $C_4 - O$ and $C_2 - C_3$ bonds about the $C_3 - C_4$ being 14°. There are several possible factors to which this deviation can be attributed:-

(1) The shortness of the $C_3 - C_3^{1}$ bond on the left side of the ring compared with the $C_5 - C_5^{1}$ bond on the right side might serve to draw the oxygen atoms towards the former side of the ring.

(2) The opportunity presented for intermolecular hydrogen bonding by virtue of the nature of the packing of the molecules. Measurement of non-bonded distances show the hydrogen atom attached to the C_5 atom of one molecule to be only 2.25Å distant from the oxygen atom of a neighbouring molecule - vide figure 6. This distance could permit hydrogen bonding which would help to pull the carbonyl bond from its normal orientation. The degree of hydrogen bonding present is probably small since the infra red spectrum shows no trace of C - OH, and the melting point, 128°, is not appreciably different from that of the non hydrogen bonded p-benzoquinone.

Although preference must be given to the results of the three dimensional work, the extent of the differences in the atomic sites found in the two and three dimensional refinements suggests that, for the respective sets of bond lengths and standard deviations to be mutually consistent, the most probable actual bond length values may be partially intermediate between the earlier and later figures. Acceptance of this argument does permit inference of a slight degree of resonance between the benzene ring and the carbonyl groups. No essentially reliable correlation of the benzene ring bond lengths

can/

can be made to the analogous ring systems of the aromatic hydrocarbons, e.g. naphthalene[45], anthracene[46], acridine[47],etc., although the two dimensional refinement did show the short, reactive $C_1 - C_2$, $C_1{}^1 - C_2{}^1$ bonds also existing in the latter compounds.

The most significant feature of the rather limited number of cyclopropane compounds so far investigated has been the shortness of the carbon-carbon bond compared with the generally accepted value of 1.54Å. In spiropentane, electron diffraction analysis by Donohue, Humphrey and Schomaker[48] showed the inner carbon-carbon bond lengths to be 1.48Å, whilst those of the less strained peripheral bonds were 1.51Å. Similar techniques by O'Gorman and Schomaker[49] on monochloro - and 1 : 2 - dichloro-cyclopropane gave 1.52Å whilst that on cyclopropane itself by Bastiensen and Hassell[50] indicated the bond length to be 1.54Å. The use of microwave spectra analysis on ethylene oxide and ethylene sulphide by Cunningham et al.[51] gave the carbon-carbon bonds as 1.49Å and 1.47Å and on cyclopropyl chloride by Friend, Schneider and Dailey[52] gave 1.47Å.

No explanation of these apparent anomalies was forthcoming until wave mechanical calculations by Coulson and Moffitt[53] evolved the theory of "bent" single bonds; the basis of this work postulates that the great angular strain of the three-ring system is best relieved by bending (rehybridizing) the endo ring orbitals to only 106° and not to the angle between the carbons - 60°. This entails the use of sp 4.12 orbitals [54] instead of the usual longer tetrahedral sp^3 orbitals formed at 109° 18'. When these former orbitals/

orbitals are used and the distance along the arc tangent is measured, the value of the single carbon-carbon bond length is raised to approximately 1.54Å. This decrease in the endo ring orbitals produces a corresponding increase in the angle of the exo orbitals (sp.$^{2.28}$)[54] to 116° which agrees with the HCH angles measured on the previous compounds.

An apparent anomaly with respect to this theory would appear to be presented in the case of Feist's acid[55] - Figure 9.

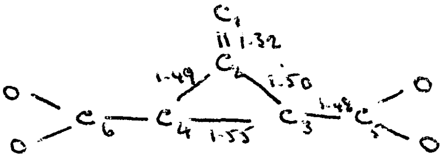


Figure 9.

In this compound which, by virtue of its carboxyl group substituents, may be regarded as approximating the most closely of all the cyclopropane compounds analysed to the present one, the carboxyl groups, as might be expected from steric considerations, have adopted a trans-configuration. However in the cyclopropane ring of this compound, the predicted bond contraction is found with only two of the bonds; in marked contrast to these is the length of the third bond viz. 1.55Å. The two dimensional refinement did appear to support this bond length distribution, but the amended bond lengths afforded by the three dimensional refinement now indicate the difference to be exaggerated. It is possible a more detailed refinement of Feist's acid might produce a similar alteration. Nevertheless this bond still remains longer than the other bonds of the three dimensional ring, and probably serves to reflect in part a measure of the strain associated with its delimiting atoms.

In/

In agreement with the ultra violet data of Buchanan and Sutherland, the degree of conjugation of the $sp^{4.12}$ orbitals of cyclopropane ring with the p orbitals of the carbonyl groups is seen from the bond length values to be hardly significant, the length of the formal single bond $C_4 - C_5$ being only slightly reduced from 1.54Å; that these $sp^{4.12}$ orbitals are indeed used is substantiated by the bond angles around the cyclopropane ring viz. endo angle $C_5^1 - C_5 - C_6 = 58.5^\circ$, exo ring angle $C_4 - C_5 - C_5^1 = 116^\circ$.

As already stated the configuration of the carbonyl groups linkage, in contrast to that found in Feist's acid, is cis not trans. This can be ascribed to their incorporation into the quasi-quinonoid ring structure. Cis fusion of a three-membered ring to a cyclohexane ring in the stable chair conformation involves the utilisation of an equatorial and an axial bond as compared with two equatorial bonds in the trans juncture. On the basis of previously developed concepts, the isomer with two equatorial bonds would be expected to be more stable, since this form leads to fewer skew butane interactions. This theory has been realised experimentally but has only so far been tested for the fusion of two six-membered rings, or a six-membered ring and a five-membered ring.

It can easily be seen from models that in order to fuse a six-membered ring and a three-membered ring, it is necessary to distort the six-membered ring so as to bring the bonds used in the attachment of the three-membered ring closer together. In the cis form the main distortion is a deformation of the chair conformation of the six-membered ring to that of a boat, a motion readily possible through/

through the planar form of the molecule, and one which only raises the energy content of the molecule by an amount equal to the replacement of two skew butane interactions by two eclipsed ones. (For the cyclohexene ring system, Beckett, Freeman and Pitzer[56] have calculated the energy increase in passing from the chair to the boat conformation to be about 2.7 k.cal./mole.) In the trans form, however, the requisite distortion leads to a much more severe chair form of the six-membered ring. This introduces additional angle strain into both rings which results in bond shortening with consequent non-bonded interaction of axial hydrogen atoms. Such stresses in the trans form should lead to a much higher energy content for the molecule than is the case for a strainless structure fused with two equatorial bonds. Hence the preferential assumption of a quasi-boat conformation with cis fusion in which the substituents on the carbon atoms of the ring juncture lie in eclipsed positions as is presented in the structure of I can possibly be explained in terms of the greater energy increase which strong angular strain promotes over that of eclipsed interaction. Furthermore, the distortion of the ring into the non-planar half-boat form would tend to suggest that the angular strain requirements of the cis ring juncture must be accommodated before those of pure sp^2 hybridization. Therefore the cis fusion of the cyclopropane ring, by its destruction of the planar trigonal hybridization of the C_4 and $C_4{}^1$ atoms may also be a contributary factor to the tilting of the oxygen atoms towards the benzene ring.

However/

However these arguments would appear to supply no answer as to why, in this instance, the cis ring juncture should employ the two axial rather than the two equatorial bonds, a circumstance which causes the orientation of the methylene group to the benzenoid residue about the $C_4 - C_5$ bond to be cis rather than the more usual trans. Only a tentative explanation of this feature can be proposed from consideration of the overall stereochemical picture pertaining in this region. This is illustrated in Figure 8 which provides a view along the $C_4 - C_5$ bond of the bond distribution from these two atoms as given by calculations of the relevant dihedral angles. From this diagram it can be seen that the cis, or diaxially fused, configuration allows the bond $C_4 - C_3$ to take up an azimuthal position between the bonds $C_5 - C_5^{1}$ and $C_5 - C_6$, and the polar bond $C_4 - O$ to lie nearly in a plane with $C_5 - H$. It is possible that this effect in conjunction with the requirements of intermolecular contact distances may help to settle the molecule in its conformation.

examined.

wing unit cell dimensions were obtained fr

llation and moving film photographs taken

K radiation.

Unit Cell Dimensions of Some Derivatives of 2:3-Dihydro-2:3-Methylene 1:4-Naphthaquinone.

Crystals of 2:3-Dibromo-2:3-methylene-1:4-naphthaquinone and 2:3-dimethyl-2:3-methylene-1:4-naphthaquinone were prepared and supplied for the x-ray investigation by Buchanan and Sutherland.

(1) 2:3-Dibromo-2:3-Methylene-1:4-Naphthaquinone.

The crystal form was similar to, but less clearly defined, than that of the parent compound.

The following unit cell dimensions were obtained from single crystal rotation, oscillation and moving film photographs about the a, b and c axes using copper K_α radiation.

$a = 12.13Å$, $b = 8.44Å$, $c = 10.33Å$ (each ± 0.02Å) $\beta = 90^\circ$.

Volume of unit cell = 1066.8A. Density measured by flotation in zinc chloride solution = 1.94 grms. / cc. Density calculated on the basis of 4 molecules per unit bell = 1.98 grms. / cc. Absorption coefficient for x-rays = 13.9 cm.$^{-1}$ F(000) = 624.

Absent spectra:- h00 when h is odd, 0k0 when k is odd, 00l when l is odd.

The space group is $P2_12_12_1$.

(2) 2:3-Dimethyl-2:3-Methylene-1:4-Naphthaquinone.

The crystal morphology was here much more indeterminate, and classification of the individual crystal faces proved rather difficult in the crystals examined.

The following unit cell dimensions were obtained from single crystal rotation, oscillation and moving film photographs taken about the b axis using copper K_α radiation.

$a = 14.30Å$, $b = 9.06Å$, $c = 8.42Å$ $\beta = 90^\circ$

Volume of unit cell = 1098.5A. Density measured by flotation in zinc chloride solution = 1.15 grms/cc. Density calculated for 4 molecules per unit cell = 1.18 grms/cc. Absorption c0efficient for x-rays = 5.1 $cm.^{-1}$ F(000) = 424.

Absent spectra:h00 when h is odd, 00l when l is odd.

The space group is very probably orthorhombic (either $P2_12_12_1$ of $P2_12\ 2_1$.

It is hoped to make a more definite assessment of the space group of this latter compound in the near future.

Nevertheless it can be stated that , on the basis of their symmetry elements, neither of these two compounds would appear as favourable for x-ray analysis as the parent structure.

TABLE I

Zone	hk0		h0l		0kl	
	x	y	x	z	y	z
O	0.327	0.005	0.330	0.270	0.000	0.270
C(1)	.050	.182	.047	.830	.182	.833
C(2)	.150	.120	.150	.667	$.117_5$	.670
C(3)	.263	.182	.267	.503	.183	.507
C(4)	.363	.115	.363	.327	.115	.327
C(5)	.523	.177	.523	.190	.175	.190
C(6)	.667	.250	.667	.347	.250	.347
B_O	Ranging from 3.5 parallel to x to 2.5 parallel to y		3.5		Ranging from 3.5 parallel to z to 2.5 parallel to y	
B_C	2.8		3.3		2.8	

TABLE 2

Atom	x	y	z	X^1	Y	Z^1
O	0.328_5	0.001_5	0.270	2.177	0.016	1.470
C(1)	$.048_5$	.182	$.831_5$	-0.018	1.920	4.526
C(2)	.150	$.118_8$	$.668_5$	0.761	1.253	3.639
C(3)	.265	$.182_5$	.505	1.633	1.925	2.749
C(4)	.363	.115	.327	2.394	1.213	1.780
C(5)	.523	.176	.190	3.569	1.857	1.034
C(6)	.667	.250	.347	4.507	2.638	1.889
H(1)	-0.03	0.13	0.97	-0.64	1.40	5.26
H(2)	.15	.02	.67	0.76	0.18	3.64
H(5)	.59	$.12_5$	.03	4.13	1.32	0.18
H(6)	.63	.25	.53	4.26	2.64	2.89
$H(6^1)$	.81	.25	.33	5.40	2.64	1.80

TABLE 3

		$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(l)$
(a) C and O atoms		0.0080	0.0101	0.0063	-
(b) C atoms	hk0	.020	.022	—	-
	h0l	.008	-	.008	-
	0kl	-	.009	.012	-
	hk0	.009	.010	-	-
O atom	0kl	-	.004	.005	-
(c) R.M.S. values	C	0.0133	0.0149	0.0090	0.0126
	O	.0085	.0085	.0057	.0082

Table 4.

Observed structure amplitudes and calculated structure factors.

hk0 - zone.

h k	F_c	F_o	h k	F_c	F_o
0 2	-14.1	12.5	2 2	-16.5	18.1
0 4	-2.1	3.8	2 3	+6.7	9.2
0 6	+24.6	25.0	2 4	-12.0	12.3
0 8	+6.9	8.1	2 5	+0.8	0.9
0 10	+10.4	11.5	2 6	-1.0	1.5
0 12	+3.4	4.0	2 7	-1.4	2.3
1 0	-17.1	17.1	2 8	-10.8	9.1
1 1	-29.6	28.4	2 9	-0.3	1.6
1 2	-5.9	6.4	2 10	-2.4	3.3
1 3	-23.0	23.9	2 11	+1.5	2.1
1 4	-8.2	8.2	3 0	+22.6	23.2
1 5	+15.0	15.0	3 1	+0.6	1.3
1 6	-3.3	4.6	3 2	+10.5	10.5
1 7	-4.1	2.7	3 3	-6.2	5.8
1 8	-3.8	4 2	3 4	+17.4	18.7
1 9	+2.3	3.3	3 5	+1.6	1.0
1 10	-1.0	2.8	3 6	+2.7	2.7
1 11	-6.0	6.8	3 7	+7.0	7.2
1 12	-2.8	3.5	3 8	+7.5	7.6
1 13	+0.2	1.1	3 9	-0.8	2.2
2 0	-11.9	12.2	3 10	+2.2	3.7
2 1	-19.8	21.7	3 11	+2.0	1.4

h k	F_c	F_o
3 12	+2.9	2.9
4 0	-4.4	3.1
4 1	-7.9	8.2
4 2	-12.9	14.3
4 3	+2.0	2.8
4 4	-1.6	2.9
4 5	+5.6	4.8
4 6	+8.7	9.7
4 7	-10.5	9.9
4 8	-13.4	14.3
4 9	+4.6	4.6
4 12	+4.7	1.9
5 0	-11.3	8.5
5 1	-1.9	3.0
5 2	+0.9	1.9
5 3	+13.5	14.2
5 4	-6.9	7.0
5 5	-3.2	3.4
5 6	-7.0	8.2
5 7	-7.8	8.2
5 8	+1.7	2.7
5 9	+2.8	3.0
5 11	+3.5	2.3
6 0	+9.5	8.0
6 1	-3.8	4.5
6 2	+4.7	4.6
6 4	+1.6	0.9
6 5	+2.5	1.9
6 6	-0.2	1.1
6 8	+6.8	6.6
6 9	+2.3	1.4
7 0	-3.0	3.5
7 1	+3.6	3.5
7 2	+2.2	1.2
7 3	-1.7	2.2
7 7	-1.3	0.7
8 0	+1.8	0.9
8 1	-6.6	4.6
8 2	-0.9	0.7
8 3	+1.4	1.0
8 4	-4.0	2.5
8 5	+2.8	0.9

H01 - zone.

h l	F_c	F_o	h l	F_c	F_o
0 1	-32.1	32.3	2 1	+76.3	66.0
0 2	-36.6	35.2	2 2	-25.7	20.3
0 3	+4.3	4.6	2 3	-19.9	19.9
0 4	+4.4	5.5	2 5	+8.1	6.7
0 5	-6.4	6.3	2 6	-2.3	2.3
0 6	+10.4	10.4	3 $\bar{5}$	-2.5	3.3
1 $\bar{6}$	-1.7	1.9	3 $\bar{4}$	+8.3	9.2
1 $\bar{5}$	+6.2	6.3	3 $\bar{3}$	+6.0	6.2
1 $\bar{4}$	-1.4	3.1	3 $\bar{2}$	-14.8	16.5
1 $\bar{3}$	-14.6	15.6	3 $\bar{1}$	-14.8	14.7
1 $\bar{2}$	+11.1	11.8	3 0	+24.7	26.1
1 $\bar{1}$	+14.5	10.5	3 1	-1.1	2.1
1 0	-22.5	24.2	3 2	+6.4	8.2
1 1	+4.9	3.4	3 3	+3.2	3.5
1 2	+11.6	11.8	3 4	-1.0	2.5
1 3	+7.7	8.0	3 5	-6.8	6.2
1 4	-10.5	10.9	4 $\bar{5}$	+5.7	5.5
1 5	-5.2	5.3	4 $\bar{4}$	+9.3	10.2
1 6	+3.2	2.9	4 $\bar{3}$	-25.3	21.2
2 $\bar{6}$	+2.9	2.7	4 $\bar{2}$	+4.0	2.9
2 $\bar{5}$	+11.2	11.6	4 $\bar{1}$	+15.1	16.1
2 $\bar{4}$	-14.6	18.8	4 0	-4.4	2.8
2 $\bar{2}$	+6.5	8.1	4 1	-6.5	6.6
2 $\bar{1}$	-8.4	6.9	4 2	+19.0	19.1
2 0	-13.2	14.5	4 3	-12.8	18.1

h l	F_c	F_o	h l	F_c	F_o
5 $\bar{3}$	+8.9	9.2	6 1	-4.2	3.1
5 $\bar{2}$	-3.7	3.8	6 2	-6.2	6.2
5 $\bar{1}$	-9.6	10.5	6 3	+11.1	12.4
5 0	-10.7	9.9	6 4	-4.8	7.8
5 1	+14.5	15.5	7 $\bar{2}$	+2.7	3.3
5 2	+10.4	11.4	7 $\bar{1}$	-5.0	3.2
5 4	-5.7	5.5	7 0	3.1	3.2
6 $\bar{3}$	+5.9	6.0	8 $\bar{2}$	3.4	2.2
6 $\bar{2}$	-14.6	12.8	8 $\bar{1}$	4.6	2.5
6 0	+11.0	10.7			

0kl - zone.

k l	F_c	F_o	k l	F_c	F_o
2 0	-17.3	15.8	5 1	-2.9	3.3
4 0	-5.0	3.5	6 1	+3.0	1.8
6 0	+25.4	25.8	7 1	+1.6	1.6
8 0	+8.2	9.5	8 1	-5.0	4.7
10 0	+9.3	11.6	10 1	-2.9	2.3
12 0	+3.1	3.3	0 2	-36.1	33.7
0 1	-30.5	32.6	1 2	+7.7	7.4
1 1	-7.8	8.9	2 2	-17.5	17.6
2 1	+2.7	1.9	3 2	-8.4	8.0
3 1	+5.4	5.5	4 2	-7.3	6.3
4 1	-1.4	1.0	5 2	+5.8	4.5

k l	F_c	F_o	k l	F_c	F_o
6 2	-8.3	8.6	7 5	-1.5	1.2
7 2	-2.0	2.6	8 5	-2.6	2.6
8 2	-10.5	12.5	0 6	+8.7	9.0
10 2	-3.8	4.4	2 6	-4.1	3.2
12 2	-1.1	1.2	3 6	+1.1	1.1
0 3	+3.6	3.6	4 6	-4.1	3.1
1 3	+4.2	3.8			
2 3	+17.7	16.9			
3 3	+0.6	1.7			
4 3	-2.2	4.1			
5 3	-3.1	1.9			
6 3	-14.1	14.1			
7 3	+2.8	1.9			
8 3	+17.0	18.1			
0 4	+3.8	4.0			
2 4	+5.8	3.4			
4 4	+6.1	3.5			
5 4	-2.0	1.3			
6 4	+6.9	9.3			
7 4	+1.3	2.6			
8 4	-0.9	1.5			
10 4	+1.1	1.2			
0 5	-5.3	5.2			
2 5	-3.2	3.2			
5 5	+1.3	1.4			

[illegible]	[illegible]	2kl
[illegible]	[illegible]	83
[illegible]	[illegible]	138
3.30	3.33	3.46
0°	12°48'	25°12'

h0l	h1l	h2l	h3l
70	71	62	58
95	[illegible]	90	89
3.30	3.31	3.34	3.3
0°	[illegible]	8°24'	12°4

[illegible]	hkl
86	127
96	182
3.30	3.36
0°	16°30'

TABLE 5

a axis	okl	1kl	2kl	3kl			
b axis	hol	h1l	h2l	h3l	h4l	h5l	h6l
c axis	hko	hk1	hk2				

a axis	okl	1kl	2kl	3kl
No. of observed planes	55	124	83	55
No.of accessible planes	72	145	132	105
Film Factor	3.30	3.33	3.46	3.66
	0°	12°48'	25°12'	41°30'

b axis	hol	h1l	h2l	h3l	h4l	h5l	h6l
No. of observed planes	70	71	61	50	59	48	49
No. of access. planes	95	92	90	85	76	65	55
Film Factor	3.30	3.31	3.34	3.39	3.47	3.58	3.72
	0°	4°10'	8°24'	12°42'	17°	21°27'	26°

c axis	hko	hk1	hk2
No. of observed planes	86	127	119
No. of access. planes	96	182	160
Film Factor	3.30	3.36	3.51
	0°	16°30'	34°30'

TABLE 6

Atomic coordinates x, y and z expressed as fractions of the unit cell edges, and referred to

Table 6

Atomic co-ordinates x, y and z expressed as fractions of the unit cell axes (b-axis two-fold).

Atom	x	y	z
O	0.3284	0.0015	0.2733
C_1	0.0512	0.1837	0.8321
C_2	0.1563	0.1196	0.6682
C_3	0.2651	0.1836	0.50184
C_4	0.36745	0.1112	0.3190
C_5	0.5191	0.1779	0.1933
C_6	0.6650	0.2560	0.3531
H_1	-0.1425	0.1357	0.9687
H_2	0.1584	0.0225	0.6722
H_5	0.5822	0.1269	0.0434
H_6	0.6171	0.2500	0.5220
H_6^1	0.7701	0.2500	0.2965

Fractional atomic co-ordinates referred to orthogonal axes (vide page 21).

O	0.3274	0.0015	0.2991
C_1	0.0511	0.1837	0.8361
C_2	0.1558	0.1196	0.6805
C_3	0.2643	0.1836	0.5226
C_4	0.3664	0.1112	0.3478
C_5	0.5175	0.1779	0.2340
C_6	0.6630	0.2500	0.4023
H_1	-0.1421	0.1357	0.9575
H_2	0.1579	0.0225	0.6843
H_5	0.5806	0.1269	0.0891
H_6	0.6153	0.2500	0.5704
H_6^1	0.7678	0.2500	0.3569

Table 7

Vibrational components of the Debye temperature factor B, for each atom in the direction of the three principal axes, as expressed by the relationship:- $T = e^{-\left(B_\theta \frac{\sin^2\theta}{\lambda^2}\right)} \times 2^{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{31}lh + B_{12}hk)}$

Atom	a	b	c
O	3.643	1.238	6.056
	-0.821	0.728	-0.144
C_1	2.400	1.764	4.451
	-0.072	-0.241	0.098
C_2	2.982	1.295	4.626
	0.546	0.590	0.082
C_3	2.761	1.158	4.010
	0.411	-0.016	0.171
C_4	3.392	1.241	4.220
	0.022	0.444	-0.216
C_5	2.442	1.262	4.722
	-0.302	0.107	-0.240
C_6	3.346	1.511	5.804
	-	-0.692	-
H_1	2.981	1.296	4.869
	-	0.592	-
H_2	2.981	1.296	4.869
	-	0.592	-
H_5	2.981	1.296	4.869

These are coefficients by the [illegible] program [illegible] 2 [illegible]

N.B. Each of the above b_{ij} values should be multiplied by a factor of 10^{-2}.

TABLE 8

Estimates of standard deviations (6) in the final atomic co-ordinates (Å)

Table 8

Estimates of standard deviations (σ) in the final atomic co-ordinates.

	σ (x)	σ (y)	σ (z)
0	0.00384	0.00338	0.00344
C_1	0.00558	0.00506	0.00508
C_2	0.00509	0.00559	0.00470
C_3	0.00500	0.00422	0.00426
C_4	0.00558	0.00517	0.00448
C_5	0.00468	0.00485	0.00497
C_6	0.00775	-	0.00792

Estimated standard deviations in the positions of the hydrogen atoms were of the order 0.055-0.070 Å.

TABLE 9

Bond Lengths (Å) and their estimated standard deviations, 6(l) Å

Bond	Bond Lengths (Å)	6(1) Å
$C_1 - C_2$	1.40	0.0210
$C_2 - C_3$	1.38	0.0198
$C_3 - C_4$	1.48	0.0196
$C_4 - C_5$	1.48	0.0204
$C_5 - C_6$	1.496	0.0285
$C_1{}^{1} - C_1{}^{L}$	1.40	0.0192
$C_3 - C_3{}^{1}$	1.40	0.0158
$C_5 - C_5{}^{1}$	1.524	0.0184
$C_4 - O$	1.21	0.0179

TABLE 10

Bond Angles and their estimated standard deviations

Table 10

Interbond Angles

$C_1{}^{1}C_1C_2$	119°25'	$C_4C_5C_5{}^{1}$	118°16'
$C_1C_2C_3$	121°52'	$C_5{}^{1}C_5C_6$	59°24'
$C_2C_3C_3{}^{1}$	118°45'	$C_5C_6C_5{}^{1}$	61°11'
$C_3{}^{1}C_3C_4$	120°59'	C_3C_4O	121°18'
$C_3C_4C_5$	117°47'	OC_4C_5	121° 2'

Table 11.

Observed structure factor, F_o, and structure factors, F_c, calculated from the final atomic co-ordinates x, y and z.

h k l	F_c	F_o	h k l	F_c	F_o
0 0 1	-29.58	30.50	0 4 0	-4.40	3.56
0 0 2	-37.86	31.94	0 4 1	-0.50	0.92
0 0 3	+3.22	3.84	0 4 2	-5.10	5.90
0 0 4	+4.72	4.40	0 4 3	-3.24	3.66
0 0 5	-5.74	5.44	0 4 4	+4.62	3.46
0 0 6	+8.98	9.10	0 4 5	+1.12	1.40
0 1 1	-9.58	8.34	0 4 6	-4.26	3.18
0 1 2	+7.02	6.94	0 5 1	-3.82	3.08
0 1 3	+3.94	4.68	0 5 2	+4.02	4.22
0 1 4	-1.52	1.50	0 5 3	-1.76	1.78
0 1 5	-1.08	1.40	0 5 4	-2.06	1.68
0 1 6	-1.46	1.12	0 5 5	+1.86	1.40
0 2 0	-17.30	13.78	0 6 0	+22.58	23.82
0 2 1	+1.94	1.78	0 6 1	+2.08	2.06
0 2 2	-17.06	16.50	0 6 2	-6.84	8.06
0 2 3	+18.38	16.22	0 6 3	-12.12	13.32
0 2 4	+3.94	4.02	0 6 4	+7.16	8.54
0 2 5	-3.52	3.08	0 7 1	+1.74	2.62
0 2 6	-4.74	3.84	0 7 2	-2.56	1.50
0 3 1	+3.46	5.06	0 7 3	+1.76	1.80
0 3 2	-7.94	8.50	0 7 4	+2.06	2.04
0 3 3	+1.98	1.50	0 7 5	-1.66	1.12
0 3 6	+1.68	1.02	0 8 0	+6.00	8.06

h k l	F_c	F_o	h k l	F_c	F_o
0 8 1	-3.98	3.46	1 1 $\bar{6}$	-5.56	6.20
0 8 2	-9.22	11.06	1 1 $\bar{5}$	+10.54	8.90
0 8 3	+16.50	16.98	1 1 $\bar{3}$	+7.36	7.02
0 8 4	-1.52	1.40	1 1 $\bar{2}$	-10.16	12.20
0 8 5	-3.26	2.44	1 1 $\bar{1}$	-27.56	26.64
0 10 0	+9.24	10.78	1 1 0	-31.62	25.64
0 10 1	-2.20	1.74	1 1 1	+63.62	55.70
0 10 2	-3.90	2.68	1 1 2	+2.98	2.90
0 10 4	+1.80	1.12	1 1 3	+0.92	1.50
0 12 0	+2.60	3.36	1 1 4	-7.98	7.28
0 12 2	-1.20	1.12	1 1 6	-2.60	2.34
0 13 1	-2.22	1.40	1 2 $\bar{5}$	+2.74	2.62
1 0 $\bar{6}$	-1.64	1.94	1 2 $\bar{4}$	+1.60	1.68
1 0 $\bar{5}$	+7.10	7.10	1 2 $\bar{3}$	-9.36	7.88
1 0 $\bar{4}$	-1.96	2.78	1 2 $\bar{2}$	+0.74	1.02
1 0 $\bar{3}$	-15.54	14.36	1 2 $\bar{1}$	+26.30	26.18
1 0 $\bar{2}$	+11.80	11.26	1 2 0	-6.30	6.00
1 0 $\bar{1}$	+14.10	10.22	1 2 1	-34.68	32.08
1 0 0	-23.86	20.16	1 2 2	+12.98	12.00
1 0 1	+4.90	4.50	1 2 3	+6.98	6.94
1 0 2	+12.90	11.34	1 2 4	-3.90	4.02
1 0 3	+6.96	7.50	1 2 5	+1.10	1.12
1 0 4	-9.52	10.22	1 2 6	+1.14	1.12
1 0 5	-3.98	4.96	1 3 $\bar{4}$	-1.84	2.80
1 0 6	+3.26	2.80	1 3 $\bar{3}$	-12.68	11.34

h k l	F_c	F_o	h k l	F_c	F_o
1 3 $\bar{2}$	+22.16	17.72	1 5 $\bar{1}$	+0.80	1.22
1 3 $\bar{1}$	+4.66	4.96	1 5 0	+15.24	14.82
1 3 0	-22.18	22.42	1 5 1	-20.86	23.46
1 3 1	+13.98	12.56	1 5 2	-4.08	3.74
1 3 2	+3.12	3.18	1 5 3	+4.32	4.40
1 3 3	-13.54	14.34	1 5 5	-1.22	1.50
1 3 4	+9.80	8.54	1 5 6	+2.32	1.84
1 3 5	+1.26	1.40	1 6 $\bar{4}$	-0.96	1.50
1 3 6	-2.78	3.18	1 6 $\bar{3}$	-1.98	2.34
1 4 $\bar{5}$	+2.62	2.52	1 6 $\bar{1}$	+8.18	7.96
1 4 $\bar{4}$	+1.06	1.22	1 6 0	-3.76	4.32
1 4 $\bar{3}$	-9.50	7.02	1 6 1	-8.48	8.44
1 4 $\bar{2}$	+3.36	3.00	1 6 2	+9.10	8.62
1 4 $\bar{1}$	+14.80	15.20	1 6 3	+4.64	4.68
1 4 0	-8.94	7.88	1 6 4	-6.02	6.28
1 4 1	-8.04	8.24	1 6 5	-2.02	2.06
1 4 2	+3.28	3.46	1 6 6	+1.30	1.22
1 4 3	+3.52	3.36	1 7 $\bar{4}$	+4.30	3.66
1 4 4	-1.70	1.78	1 7 $\bar{3}$	+10.10	7.60
1 4 5	-1.28	1.40	1 7 $\bar{2}$	-18.50	17.92
1 4 6	+0.88	1.30	1 7 0	-2.14	2.62
1 5 $\bar{6}$	+3.10	2.44	1 7 1	+5.32	6.28
1 5 $\bar{5}$	-4.34	3.00	1 7 2	+4.00	3.94
1 5 $\bar{4}$	-2.32	2.06	1 7 3	+6.40	6.56
1 5 $\bar{2}$	+4.26	4.02	1 7 4	-11.00	10.98

h k l	F_c	F_o	h k l	F_c	F_o
1 8 $\bar{5}$	+3.02	3.28	1 11 0	-5.02	6.38
1 8 $\bar{3}$	-5.46	7.12	1 11 1	+3.78	4.96
1 8 $\bar{2}$	+3.88	3.46	1 11 3	-2.54	2.24
1 8 $\bar{1}$	+5.18	6.18	1 12 $\bar{3}$	-1.28	1.68
1 8 0	-3.30	3.94	1 12 $\bar{2}$	+0.88	1.02
1 8 1	-4.52	5.62	1 12 $\bar{1}$	+2.14	2.34
1 8 3	+2.12	2.44	1 12 0	-2.64	3.18
1 9 $\bar{5}$	-1.50	2.34	1 12 1	-1.42	1.68
1 9 $\bar{4}$	-1.74	1.78	1 12 2	+2.36	2.06
1 9 $\bar{3}$	-3.08	8.06	1 12 3	+0.80	0.74
1 9 $\bar{2}$	+7.26	7.29	1 13 $\bar{1}$	-1.28	1.12
1 9 $\bar{1}$	-1.00	1.03	1 13 0	-0.74	1.02
1 9 0	+3.28	3.26	1 13 1	+2.48	1.98
1 9 1	-4.96	4.68	2. 0 $\bar{6}$	+3.00	2.80
1 9 3	-1.84	1.78	2 0 $\bar{5}$	+12.34	11.26
1 9 4	+3.56	3.94	2 0 $\bar{4}$	-15.66	14.16
1 10 $\bar{3}$	-3.50	3.84	2 0 $\bar{3}$	-0.70	0.48
1 10 $\bar{1}$	+5.16	7.02	2 0 $\bar{2}$	+6.26	8.68
1 10 0	-2.02	2.44	2 0 $\bar{1}$	-7.90	6.46
1 10 1	-4.02	5.24	2 0 0	-10.32	12.28
1 10 2	+3.84	5.34	2 0 1	+76.22	72.62
1 10 3	+1.32	1.02	2 0 2	-21.24	19.88
1 10 4	-3.32	4.22	2 0 3	-20.56	18.76
1 11 $\bar{3}$	-2.10	2.14	2 0 5	+6.54	6.10
1 11 $\bar{2}$	+3.54	3.74	2 0 6	-2.98	2.80

h k l	F_c	F_o	h k l	F_c	F_o
2 1 $\bar{5}$	-1.26	1.40	2 3 $\bar{4}$	+0.96	1.02
2 1 $\bar{4}$	+3.06	2.44	2 3 $\bar{3}$	+2.02	2.24
2 1 $\bar{3}$	-1.36	0.76	2 3 $\bar{2}$	-7.50	7.88
2 1 $\bar{2}$	+5.52	5.16	2 3 $\bar{1}$	+3.32	3.64
2 1 $\bar{1}$	-0.92	1.02	2 3 0	+8.80	8.44
2 1 0	-17.86	19.80	2. 3 1	-6.06	7.60
2 1 1	-3.80	4.02	2 3 2	-0.86	1.50
2 1 2	+5.74	3.84	2 4 $\bar{6}$	+1.14	0.92
2 1 3	+3.96	4.30	2 4 $\bar{5}$	-6.68	7.40
2 1 4	+4.90	5.24	2 4 $\bar{4}$	+2.56	2.52
2 1 5	-4.12	5.06	2 4 $\bar{3}$	+4.66	3.66
2 1 6	-2.34	2.24	2.4 $\bar{2}$	-4.44	4.58
2 2 $\bar{6}$	+1.20	0.92	2 4 $\bar{1}$	+2.12	2.24
2 2 $\bar{5}$	-4.62	5.04	2 4 0	-10.98	11.62
2 2 $\bar{4}$	-4.98	6.18	2 4 1	-7.40	8.62
2 2 $\bar{3}$	+8.20	8.06	2 4 2	+16.52	20.44
2 2 $\bar{2}$	+32.76	33.68	2 4 3	-5.54	5.68
2 2 $\bar{1}$	-36.46	33.58	2 4 4	-6.32	6.94
2 2 0	-15.98	16.50	2 4 5	+4.80	3.36
2 2 1	+6.10	5.16	2 5 $\bar{6}$	-0.82	0.92
2 2 2	+7.58	9.76	2 5 $\bar{5}$	+1.00	1.50
2 2 3	-4.60	5.62	2 5 $\bar{4}$	+0.30	1.50
2 2 4	+5.96	6.84	2 5 $\bar{3}$	-0.72	1.40
2 2 5	-2.26	1.96	2 5 $\bar{2}$	-0.96	1.04
2 3 $\bar{5}$	-2.04	2.52	2 5 $\bar{1}$	-1.06	1.40

<u>h</u> <u>k</u> <u>l</u>	F_c	F_o	<u>h</u> <u>k</u> <u>l</u>	F_c	F_o
2 5 0	+0.76	1.02	2 8 $\bar{3}$	+2.48	4.58
2 5 1	+9.02	10.78	2 8 $\bar{2}$	+16.70	20.26
2 5 2	-3.86	4.12	2 8 $\bar{1}$	-12.86	12.94
2 5 3	-4.16	3.84	2 8 0	-8.06	8.54
2 6 $\bar{6}$	+1.32	0.84	2 8 1	+4.02	4.54
2 6 $\bar{5}$	+3.82	3.84	2 8 2	+4.06	4.62
2 6 $\bar{4}$	-4.98	5.06	2 9 $\bar{4}$	+0.94	1.30
2 6 $\bar{3}$	+0.94	2.14	2 9 $\bar{3}$	-2.26	3.28
2 6 $\bar{2}$	-5.68	5.70	2 9 $\bar{1}$	+2.02	2.52
2 6 $\bar{1}$	+1.18	1.50	2 9 0	-1.52	1.50
2 6 0	+1.04	1.58	2 9 1	+3.66	3.94
2 6 1	+15.34	15.88	2 10 $\bar{4}$	-4.06	4.12
2 6 2	-5.62	5.90	2 10 $\bar{3}$	+1.38	1.58
2 6 3	-4.46	3.56	2 10 $\bar{2}$	+2.74	3.94
2 6 4	-4.98	4.78	2 10 $\bar{1}$	-4.40	5.16
2 6 5	+5.40	5.34	2 10 0	-2.14	3.08
2 7 $\bar{4}$	-0.92	1.68	2 10 1	+8.48	10.50
2 7 $\bar{3}$	+0.62	1.40	2 10 2	-3.32	5.44
2 7 $\bar{2}$	+3.18	3.94	2 11 $\bar{3}$	+1.06	1.02
2 7 $\bar{1}$	-1.84	2.06	2 11 $\bar{2}$	-2.10	2.90
2 7 0	-1.40	2.14	2 11 $\bar{1}$	-0.44	1.02
2 7 1	-4.80	4.68	2 11 0	+1.40	1.96
2 7 2	+3.34	3.94	2 12 $\bar{2}$	-2.18	1.86
2 8 $\bar{5}$	-2.42	2.80	2 12 $\bar{1}$	+1.70	2.44
2 8 $\bar{4}$	-2.24	3.00	3 0 $\bar{6}$	-1.60	1.30

h k l	F_c	F_o	h k l	F_c	F_o
3 0 $\bar{5}$	-3.00	3.08	3 2 $\bar{4}$	+3.16	3.18
3 0 $\bar{4}$	+9.46	8.84	3 2 $\bar{3}$	+1.26	1.40
3 0 $\bar{3}$	+4.80	5.80	3 2 $\bar{2}$	-8.90	7.02
3 0 $\bar{2}$	-15.92	15.28	3 2 $\bar{1}$	+8.46	7.96
3 0 $\bar{1}$	-15.72	14.70	3 2 0	+9.92	9.84
3 0 0	+18.98	24.20	3 2 1	-2.08	1.86
3 0 1	+2.46	2.24	3 2 2	-16.80	16.70
3 0 2	+4.74	7.96	3 2 3	+1.38	1.50
3 0 3	+2.82	3.36	3 2 4	+7.22	7.40
3 0 4	-2.30	2.44	3 3 $\bar{6}$	-1.96	0.92
3 0 5	-5.68	6.28	3 3 $\bar{4}$	+1.90	1.86
3 1 $\bar{6}$	-1.54	1.40	3 3 $\bar{3}$	-4.82	4.88
3 1 $\bar{5}$	-3.30	4.02	3 3 $\bar{2}$	-3.24	2.80
3 1 $\bar{4}$	+16.12	15.10	3 3 $\bar{1}$	+18.60	16.70
3 1 $\bar{3}$	-3.16	2.72	3 3 0	-5.80	5.72
3 1 $\bar{2}$	-6.92	6.38	3 3 1	-3.70	5.64
3 1 $\bar{1}$	-7.04	5.80	3 3 2	+2.68	4.50
3 1 0	+1.12	1.22	3 3 3	+0.26	1.78
3 1 1	-9.46	10.50	3 3 4	-2.90	4.02
3 1 2	+29.48	26.74	3 4 $\bar{3}$	+5.44	4.78
3 1 3	-6.56	7.22	3 4 $\bar{2}$	-7.72	6.74
3 1 4	-3.96	3.30	3 4 $\bar{1}$	-6.68	6.18
3 1 6	+1.08	0.92	3 4 0	+17.24	16.98
3 2 $\bar{6}$	-1.26	0.92	3 4 1	-2.86	2.14
3 2 $\bar{5}$	-2.54	2.80	3 4 2	-11.52	11.62

h k l	F_c	F_o
3 4 3	+3.14	3.00
3 5 $\bar{5}$	+0.62	1.40
3 5 $\bar{4}$	-6.68	4.78
3 5 $\bar{3}$	+1.60	1.02
3 5 $\bar{2}$	+1.08	1.22
3 5 $\bar{1}$	+5.12	4.40
3 5 0	-1.10	0.92
3 5 1	-1.28	1.40
3 5 2	-7.98	8.44
3 5 3	+2.34	2.90
3 5 4	+1.54	2.06
3 6 $\bar{4}$	+4.02	3.94
3 6 $\bar{3}$	+1.84	2.44
3 6 $\bar{2}$	-3.70	3.00
3 6 $\bar{1}$	-7.10	6.56
3 6 0	+3.14	2.72
3 6 1	+5.42	6.18
3 6 5	-3.10	2.72
3 7 $\bar{4}$	+1.74	1.68
3 7 $\bar{3}$	+1.42	1.50
3 7 $\bar{2}$	+4.34	3.36
3 7 $\bar{1}$	-18.62	12.94
3 7 0	+5.90	6.74
3 7 1	+5.56	6.00
3 7 2	-0.62	1.36
3 8 $\bar{2}$	-3.94	3.00
3 8 $\bar{1}$	+3.74	2.44
3 8 0	+5.88	6.94
3 8 1	-2.86	4.12
3 8 2	-7.48	8.06
3 9 $\bar{4}$	-2.20	1.30
3 9 $\bar{2}$	-2.28	1.86
3 9 $\bar{1}$	+7.96	5.16
3 9 0	-1.18	2.06
3 9 1	-1.82	1.40
3 9 2	-2.22	2.90
3 10 $\bar{2}$	-3.66	2.90
3 10 0	+3.14	3.46
3 10 2	-1.00	1.40
3 11 $\bar{1}$	+3.04	2.34
3 11 0	-1.50	1.30
3 11 1	-2.36	2.52
3 11 2	+2.32	1.96
3 12 $\bar{1}$	-2.06	1.68
3 12 0	+2.26	2.72
4 0 $\bar{5}$	+5.74	5.24
4 0 $\bar{4}$	+10.10	9.86
4 0 $\bar{3}$	-25.48	20.16
4 0 $\bar{2}$	+2.06	2.80
4 0 $\bar{1}$	+15.40	14.82

h k l	F_c	F_o	h k l	F_c	F_o
4 0 0	-2.82	2.80	4 3 0	+3.28	2.62
4 0 1	-6.06	6.18	4 3 1	+1.40	1.86
4 0 2	+15.80	17.92	4 3 2	+0.40	1.86
4 0 3	-11.28	15.94	4 3 3	-3.26	2.90
4 1 $\bar{5}$	-1.22	1.40	4 4 $\bar{4}$	-3.18	2.90
4 1 $\bar{4}$	-4.30	6.28	4 4 $\bar{3}$	+1.20	1.68
4 1 $\bar{3}$	+8.72	7.78	4 4 1	-1.06	1.58
4 1 $\bar{2}$	+4.38	5.06	4 4 0	+1.98	2.80
4 1 $\bar{1}$	-2.90	3.66	4 4 1	-3.04	3.46
4 1 0	-7.33	7.68	4 4 2	-4.18	2.90
4 1 1	-6.28	6.66	4 4 3	+8.32	9.18
4 1 2	-2.02	2.62	4 4 5	-4.22	3.66
4 1 3	+11.70	11.44	4 5 $\bar{5}$	+1.24	0.74
4 2 $\bar{5}$	+0.80	1.22	4 5 $\bar{1}$	-2.58	2.62
4 2 $\bar{4}$	-1.78	1.68	4 5 0	+4.62	4.58
4 2 $\bar{2}$	+0.62	1.22	4 5 1	+3.04	2.62
4 2 $\bar{1}$	+16.30	15.38	4 5 2	-0.90	1.50
4 2 0	-14.14	13.22	4 5 3	-3.08	2.72
4 2 1	-10.88	11.62	4 5 4	-1.52	1.86
4 2 2	+5.04	4.88	4 6 $\bar{5}$	+1.54	1.40
4 2 3	+7.20	7.96	4 6 $\bar{3}$	-6.60	5.24
4 2 4	-4.38	4.96	4 6 $\bar{2}$	-2.26	2.24
4 2 5	+1.62	1.96	4 6 0	+8.90	9.18
4 3 $\bar{2}$	-1.72	2.40	4 6 1	-7.58	7.78
4 3 $\bar{1}$	-1.18	1.40	4 6 2	+3.48	3.74

h k l	F_c	F_o	h k l	F_c	F_o
4 6 5	-1.54	1.68	5 1 2	-3.46	5.44
4 7 $\bar{2}$	+2.30	1.50	5 1 3	+6.18	7.12
4 7 $\bar{1}$	+4.58	3.28	5 1 4	-2.68	4.12
4 7 0	-8.74	9.28	5 2 $\bar{5}$	-0.62	1.22
4 7 1	-3.22	4.12	5 2 $\bar{4}$	-5.14	4.88
4 7 2	+2.40	3.56	5 2 $\bar{2}$	+8.18	8.62
4 8 $\bar{1}$	+9.72	4.90	5 2 $\bar{1}$	-2.36	2.14
4 8 0	-12.20	13.42	5 2 0	+1.60	1.86
4 8 2	+3.04	4.46	5 2 2	-3.92	4.96
4 9 0	+4.20	4.30	5 2 3	-4.04	3.28
4 10 $\bar{1}$	+2.50	2.62	5 2 4	+3.26	2.72
4 10 1	-2.42	3.56	5 3 $\bar{5}$	-2.56	2.24
4 10 2	+4.06	1.22	5 3 $\bar{3}$	+3.72	3.46
4 12 0	+1.74	2.06	5 3 $\bar{2}$	-3.60	3.28
5 0 $\bar{3}$	+10.42	8.62	5 3 $\bar{1}$	-2.10	2.80
5 0 $\bar{2}$	-3.84	3.94	5 3 0	+11.08	13.04
5 0 $\bar{1}$	-9.98	9.56	5 3 1	-6.54	7.60
5 0 0	-8.62	8.90	5 3 2	-1.50	1.86
5 0 1	+10.60	14.54	5 3 3	+3.58	4.02
5 0 2	+9.64	10.68	5 4 $\bar{4}$	-1.70	1.58
5 0 4	-6.08	5.74	5 4 $\bar{3}$	-1.90	2.34
5 1 $\bar{3}$	+8.72	8.34	5 4 $\bar{2}$	+4.98	3.28
5 1 $\bar{2}$	-7.50	7.40	5 4 $\bar{1}$	-0.74	1.40
5 1 0	-2.14	2.80	5 4 0	-6.08	6.28
5 1 1	+5.06	5.90	5 4 1	+3.84	3.36

h k l	F_c	F_o	h k l	F_c	F_o
5 4 2	+2.24	2.90	5 11 0	+2.08	2.14
5 4 3	-4.98	5.72	6 0 $\bar{3}$	+5.72	5.80
5 5 $\bar{3}$	-5.34	3.94	6 0 $\bar{2}$	-14.38	12.38
5 5 $\bar{2}$	+4.64	3.64	6 0 $\bar{1}$	+2.00	1.40
5 5 0	-2.56	3.00	6 0 0	+8.54	9.56
5 5 2	+1.48	1.86	6 0 1	-2.36	3.00
5 5 3	-3.88	4.78	6 0 2	-5.30	5.80
5 5 4	+2.58	2.52	6 0 3	+6.80	11.62
5 6 $\bar{3}$	+3.30	2.34	6 0 4	-3.78	7.22
5 6 $\bar{2}$	+1.64	2.06	6 1 $\bar{4}$	-0.96	1.22
5 6 $\bar{1}$	-6.16	4.78	6 1 $\bar{3}$	+1.24	1.40
5 6 0	-6.68	7.50	6 1 $\bar{2}$	+7.90	6.18
5 6 1	+7.46	6.56	6 1 $\bar{1}$	-0.58	1.50
5 6 2	+4.14	3.94	6 1 0	-5.56	5.32
5 6 4	-3.30	2.90	6 1 1	-7.24	7.02
5 7 $\bar{2}$	-1.66	1.30	6 1 2	+3.02	3.74
5 7 0	-6.52	6.68	6 2 0	+4.32	4.30
5 7 1	+5.82	6.00	6 2 1	-2.64	3.18
5 8 $\bar{2}$	+2.00	1.12	6 2 3	-1.42	2.52
5 8 0	+2.28	2.52	6 2 4	+2.58	2.72
5 8 1	-2.30	2.44	6 3 $\bar{3}$	-2.04	2.34
5 9 $\bar{2}$	+1.70	1.68	6 3 $\bar{2}$	+1.48	1.96
5 9 0	+2.64	2.80	6 3 $\bar{1}$	+5.20	5.44
5 10 $\bar{1}$	-2.74	2.90	6 3 2	-2.12	2.24
5 10 1	+2.70	2.44	6 4 $\bar{3}$	+0.50	2.06

h k l	F_c	F_o	h K l	F_c	F_o
6 4 $\bar{2}$	+1.72	1.86	7 0 2	+5.54	4.30
6 4 $\bar{1}$	-4.06	3.74	7 1 $\bar{2}$	+3.94	4.40
6 4 1	+3.86	4.02	7 1 $\bar{1}$	-5.34	6.10
6 4 2	-2.84	3.18	7 1 0	+2.20	3.36
6 4 3	-1.44	2.06	7 1 $\bar{2}$	-1.34	1.68
6 5 $\bar{4}$	+1.10	0.74	7 1 3	-1.22	1.30
6 5 $\bar{2}$	-4.98	5.16	7 2 $\bar{2}$	-0.82	1.40
6 5 $\bar{1}$	+1.68	1.68	7 2 $\bar{1}$	+6.90	6.18
6.5 0	+2.42	1.68	7 2 0	+1.12	1.12
6 5 1	+1.18	1.40	7 2 1	+3.16	2.72
6 6 $\bar{2}$	-3.62	2.90	7 2 2	-2.52	1.96
6 6 0	+0.58	1.02	7 3 $\bar{2}$	+1.34	1.30
6 6 1	+3.86	5.06	7 3 0	-1.30	1.86
6 6 2	-4.24	4.02	7 3 1	+3.28	4.22
6 7 $\bar{2}$	+3.28	3.28	7 3 2	-1.58	1.86
6 7 $\bar{1}$	-5.20	5.24	7 3 3	-0.78	1.78
6 8 $\bar{2}$	-1.38	0.98	7.4 $\bar{3}$	-2.72	1.86
6 8 0	+5.18	6.18	7 4 $\bar{2}$	-0.80	1.12
6 8 1	-4.64	4.88	7 4 $\bar{1}$	+4.52	3.36
6 9 0	+1.20	1.40	7 4 0	-1.04	1.40
6 9 1	+2.28	3.28	7 4 1	-2.74	1.96
7 0 $\bar{2}$	+3.40	3.56	7 5 $\bar{2}$	-1.28	1.22
7 0 $\bar{1}$	-6.92	4.88	7 5 $\bar{1}$	+1.44	1.30
7 0 0	-3.48	3.08	7 5 1	-0.86	1.02
7 0 1	+1.40	2.14	7 6 1	-2.04	3.08

h k l	F_c	F_o
7 6 2	+4.74	3.36
7 7 0	+0.94	0.64
7 7 1	-2.96	2.62
8 0 $\bar{2}$	+3.10	3.46
8 0 $\bar{1}$	-4.08	3.18
8 1 $\bar{2}$	+2.52	1.68
8 1 $\bar{1}$	+3.84	3.74
8 1 0	-5.16	4.68
8 2 0	-1.02	0.74
8 2 1	+2.94	2.90
8 4 0	-2.36	2.34
8 4 1	+0.08	1.30
8 4 2	+2.78	0.88
8 6 $\bar{1}$	-0.98	0.92

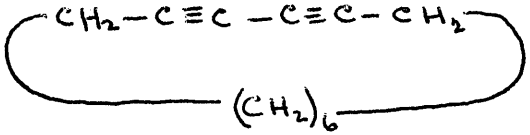
1:2:7:8:13:14-Tribenzcycloctadecahexyne.

INTRODUCTION

Carbocyclic compounds of alicyclic and aromatic nature have been investigated structurally for many years with a view to correlating the variations in the physical and chemical properties of these compounds from those of their open chain isomers to their inherent stereochemical features. With the formulation of Baeyer's strain ring theory[57] and the development of modern wave mechanical concepts the existence of these rings has been rationalised and an explanation given of the modifications in their properties resulting from their cyclic nature.

In more recent years successful attempts have been made to prepare ring systems incorporating an acetylenic linkage. Greater difficulty has been encountered in forming small rings containing a triple bond linkage than with their alicyclic and aromatic analogues, since the quantum mechanical requirements of the two carbon atoms of the linkage produces a linear four carbon atom chain. So far the smallest ring of this type prepared has been cyclo-octyne.

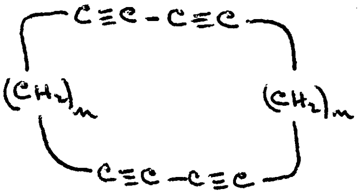
From this beginning subsequent work in this field has led to the construction of cyclic systems containing α -diacetylenic units. The first compounds of this type were prepared by Eglinton and Galbraith[58] who found the smallest ring structure obtainable under the methods employed to be the twelve-membered ring system



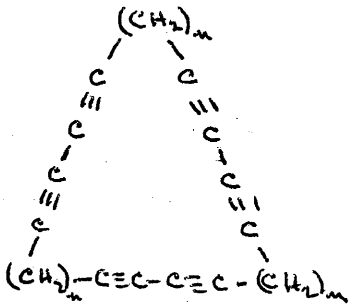
This result is in accord with the stability demands imposed by the rigidity of the six carbon α - diacetylenic chain.

Synthesis of similar nature have also been carried out by Söndheimer et al.[59] who prepared the series of poly-ynic compounds II,III,IV starting from I

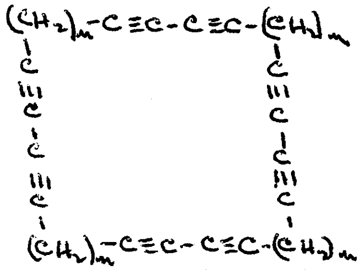
I $HC\equiv C-(CH_2)_n-C\equiv CH$



II



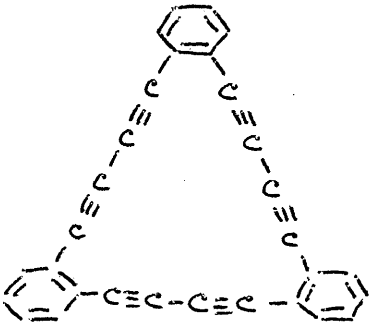
III



IV

Once more, as in prior instances, the authors found the feasibility of the cyclic structure to be a function of n. Hence it was found impossible to obtain II, III or IV with n = 1, whilst for n = 2 the compounds obtained tended to be rather unstable and to decompose on heating. In each case the cyclic polymer obtained in highest yield was that for which the smallest, strainless molecular model could be built.

As a natural consequence of his sequence of preparations, Eglington and Galbraith[60] attempted the synthesis of the novel cohjugated cyclic systen A



A

From analogy with III, n = 2, the proximity of the α - diyne rods could have interesting effects on its light absorption bands, whilst its chemical reactions might involve an appreciable amount of transannular activity.

The high degree of unsaturation possessed by this system also makes it of interest from the quantum mechanical viewpoint. Catalin models have shown it to be a rigid, planar, strainless structure in which all the valency angles conform to the type of hybridization present. The orientation of the p_y orbitals of the acetylenic carbon atoms of the arms of the triangle should permit overlap with those of the aromatic carbon atoms to form effectively a completely conjugated double bonded system round the thirty carbon atoms constituting the ring. The p_z orbitals of the carbon atoms of the α - diyne unit cannot overlap with the p_z orbitals of the aromatic nuclei so that these are localised within the diyne rods.

If this is indeed the case these effects and the degree to which they are present should show in the bond lengths of the molecule, and it was partly towards this determination that the present X -ray investigation was undertaken. In addition comparisons could be made between the bond lengths obtained from this cyclic structure and similar types of bonds previously measured in open chain structures, e.g. diphenyl diacetylene and other substituted diacetylenic compounds.

Formulation/

Formulation of the Structure as a Triangle

Chemical Evidence

The synthetic route followed is reported by Eglinton and Galbraith[60]. The essential features of the reaction entail oxidative coupling of o-di-ethynylbenzene by the cupric acetate: pyridine methanol reagent under high dilution conditions.

The substance obtained was believed by the authors to have the structure A on account of "its mode of preparation, its light absorption, analytical and molecular weight measurements, and its properties in general":-

(1) A well tested coupling reaction was used. Previous reactions of similar nature, vide Sondheimer et al., indicated the cyclic structure obtained in greatest yield to be the smallest strainless system permissible by Catalin models. In no case had any product been formed which analysed as a structure too strained to be built by Catalin models.

(2) The extremely unstable nature of the crystals made calculation of the molecular weight by the usual methods a task of great difficulty. Eventually it seemed that the only practical approach was through co~~r~~relation of the density of the crystal to X-ray measurements of its unit cell dimensions - vide page 72. Accordingly crystals were grown from benzene, ether and dioxane, and the densities determined for each type of crystal by flotation in an aqueous medium as given in Table 12.

These values, when compared with measurements of the unit cell dimensions of similar crystals, performed by the X-ray section, indicated the presence in the unit cell of amounts of matter consistent/

consistent with two molecules of trimer. The molecular weights calculated from these experimentally determined densities are also given in Table 12, P, P where $C_{30}H_{18}$ requires M = 372.4. The apparently anomalous value found with the crystals grown from benzene was explained by postulation of one molecule of benzene solvent of crystallisation included per unit cell. Subsequent detection and quantitative estimation of this benzene was performed by co-distillation with dioxane, followed by calculation of the benzene content of the distillate from ultra violet intensity measurements.

(3) Analytical data were in agreement with the formulation $2C_{30}H_{12} \cdot C_6H_6$ per unit cell for crystals grown from benzene. (Found C 96,4, H 3.85, $C_{30}H_{12}\frac{1}{2}C_6H_6$ requires C 96.35, H 3.50)

(4) The cyclic nature of the structure was indicated by the absence of any trace of infra red absorption bands attributable to a terminal acetylenic residue. The characteristic di-substituted $-C \equiv C-$ bands were obtained at 2215 cm.$^{-1}$ and 2135 cm.$^{-1}$, and a series of bands located at 3056, 1961, 1927, 1894, 1850, 1816, and 746 cm.$^{-1}$ almost identical to those of o - diethynylbenzene and attributable to the aromatic nuclei of the system were detected. Further the ultra violet spectrum in benzene whilst of a more complex nature did contain features characteristic of those of the diphenylpoly - ynes.

(5) Nuclear magnetic resonance spectrum run on a very dilute solution provided further support for cyclisation in that it showed the presence of only one type of aromatic hydrogen atom.

(6) The substance gave a stable, crystalline complex with trinitrofluorenone. This supports the attachment of the

α - diyne units to terminal aromatic nuclei, since it is only in compounds of the latter type that this adduct process has previously proceeded viz. diphenyldiactylene, tolane.

No complexes were obtained with the di-alkyl substituted diacetylenes

$$CH_3(CH_2)_3C\equiv C-C\equiv C(CH_2)_3CH_3\ ;\ AcO(CH_2)C\equiv C-C\equiv C(CH_2)OAc.$$

The complex formed was unusual in that the analysis indicated a rate of 1.5 moles of T.N.F.: 1 mole A, the first such ratio reported. However it was found that the rigid triangular structure of A permitted a satisfactory geometrical explanation of this allocation.

(7) Hydrogenation of A produced a mixture of two hydrocarbons, one of which gave a melting point of 230 - 231, and the other 120 - 122. Analysis of these compounds implied a transannular reaction to give ca. two new riggs, since light absorption results denied the presence of any double bonds. Mass spectrographic analysis of both these compounds gave molecular weight values of 398 ± 5, closely agreeing with the theoretical value of 390 - 396 based on a hydrogenated triangle.

This represented the chemical evidence for the proposed triangular structure at the commencement of the X-ray structural investigations of the substance.

Since then the original hydrogenation experiments have been repeated on several occasions with a view to ultimately dehydrogenating/

dehydrogenating the hydroaromatic product, and obtaining a typically stable, easily characterised, aromatic system. On every occasion various postulated, transannularised products were obtained each analysing on the mass spectrometer for a molecular weight of 400 ± 5, but which resisted all attempts at dehydrogenation to the desired structure.

Eventually crystals of the pure, unsaturated triangle were sent to Cambridge where the molecular weight was calculated employing the thermistor method[60]. This produced a value of 370 ± 5 in complete accord with that of the proposed trimeric structure.

Crystallographic Data

Crystals of this compound were provided by Eglinton and Galbraith. Those used for photographic work had the form of fine yellow needles, and were re-crystallised from benzene, since it was not found possible to obtain sufficiently large samples from other solvents, e.g. ether and dioxane. In addition, the general properties of the crystals imposed strict limitations on their feasible exposure times. They were found to be rapidly oxidised in light or air to a black powdery solid, although they could be stored at -10° for about ten days or a fortnight, without appreciable decomposition. Since the decomposition appeared always to be restricted to the surface of the crystal the acquisition of satisfactorily/

satisfactorily complete X-ray photographs obviously depended upon the employment of as large a crystal as possible. The crystal used by Dr. Speakman to take the initial photographs had the dimensions 0.1 mms. X 0.2 mms, and had a life-time of six days, which enabled the following photographic data to be collected, Cu K_α radiation being used throughout:-

Rotation photographs about each of the three axes gave:-

a = 28.42Å, b = 3.87Å, c = 11.55Å each ± 0.02Å

Weissenberg series of the h01 and hI1 zones, of adequate exposure time, were also taken. not a zone!

Absent Spectra h00 present only for h = 2n

001 present only for l = 2n

From this evidence, the h01 plane group appeared to be pgg. No direct inference of the space group could be made but correlation of the hI1 net, and h01 zone, symmetries suggested it to be a non-centred orthorhombic type, probably $P2_12_12_1$ or $P2_1\ 2\ 2_1$

Unfortunately no subsequent crystal of comparable size was prepared. The crystals used have had dimensions of the order 0.06 x .03 mms. in the directions normal to the needle axis, and consequently the longer requisite exposure times coupled with the time needed to set the crystal about other than the needle axis has made the collection of data about the a and c - axes a very difficult task using Weissenberg cameras at room temperature.

The intensities of the reflexions on the h01 Weissenberg series were measured using the Robertson multiple film technique in conjunction with a suitable step wedge. After the estimated intensities/

intensities had been converted to the corresponding structure amplitudes with the appropriate Lorentz and polarization corrections, the Wilson Relationship was used to place the "processed" data on an approximate absolute scale. Initial temperature factor values for the carbon atoms were also calculated using the formula

$$\Sigma I_e = \Sigma I_c e^{-\frac{2B\sin^2\theta}{\lambda^2}} \quad \text{where } I_c = \Sigma f_n^2$$

the mean value was obtained as B = 2.2

Choice of Plane Group

As already stated, the systematic absences implied the hol plane group to be pgg. However the density measurements require two molecules of triangle per unit cell, a value incompatible with the four-fold symmetry of pgg. Hence it appeared that these two seemingly contradictory facts could only be reconciled if the plane group was modified from pgg to pmg. For this alteration to be justified, it has to be assumed that the axial halving of the a-axis is accidental, and brought about by the inherent symmetry of the molecule. The general position of pmg is also four-fold, but it is now possible to distribute the two molecules in the unit cell in such a way that each half of one molecule constitutes one asymmetric unit. This is achieved by coincidence of the mirror plane of the plane group with that of the molecule in the matter represented - figure 10.

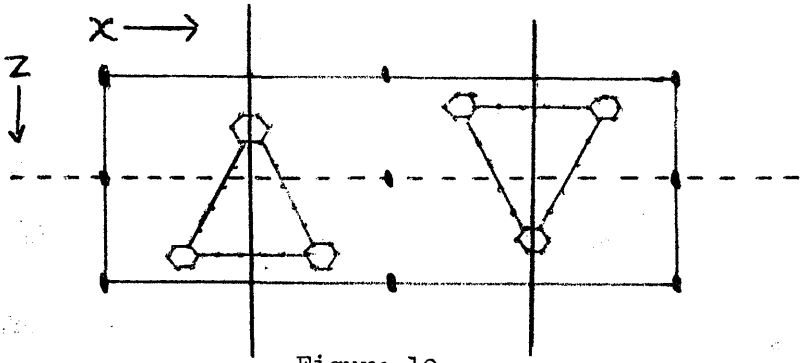


Figure 10.

In this orientation it is obvious that, subject to the tilting of the molecule about the axis of the bisector of the triangle, the x co-ordinates of the atoms are fixed, whilst the z co-ordinates may alter according ~~to~~ as the molecule slides up or down the mirror plane.

Although in the suggested modification of the plane group it would appear optional whether pmg or pgm were chosen, this does not prove to be the case. Molecular packing considerations restrict the two possible alignments of the side AB of the triangle to the one parallel to the x axis even allowing maximum tilt of the molecule to the b axis, viz. 25°, as shown in figure 11.

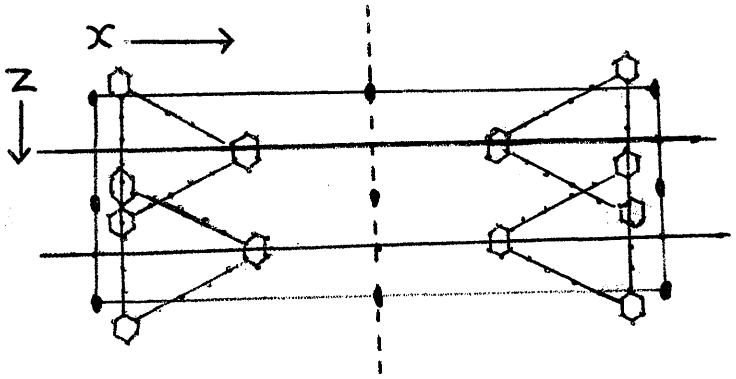


Figure 11.

Hence the extremely limited dispositions of the molecule within the unit cells should render the structural analysis a straightforward process.

Influence of Benzene Present as Solvent Molecule of Crystallisation

The effect of benzene solvent present in as high a ratio as one molecule benzene to two molecules of A could quite conceivably bring about disruption of the aggregations of triangle molecules and possibly of the triangular system itself. However, geometric considerations permit random distribution of benzene molecules throughout the unit cells. Furthermore x-ray powder photographs ? powder of crystals grown from benzene, ether and dioxane showed that the unit cell was essentially the same in each case. A table of the data obtained is given - Table 13.

The results provide strong evidence that the influence of the benzene structure is negligible.

Table 13

Nature of Ring		Diameter of Ring (mm)		
	Crystal Ex.	Benzene	Ether	Dioxane
Weak		40.95	-	-
Weak		32.25	32.95	32.50
Weak		29.00	29.00	28.80
Strong		26.60	26.30	26.25
Weak		21.00	21.20	21.00
Strong		16.00	15.85	15.85
Weak		13.40	13.85	13.50

STRUCTURE ANALYSIS

(010) Projection

Patterson Synthesis - Calculated

The large number of parallel bonds comprising each side of the molecule coupled with its molecular orientation, viz. one side parallel to , and the other two at 60^0, to the x - axis, suggest that a Patterson synthesis would provide a simple confirmation of the triangular form of the structure. The shortness of the projected axis, viz. 3.87Å , should exclude any overlap of peaks and the salient features of the intramolecular vector electron density distribution should be quite clearly resolved. The preferred alignment of the molecule with respect to the axes was used to calculate an intramolecular Patterson vector set and this is represented in Figure 12.

x?

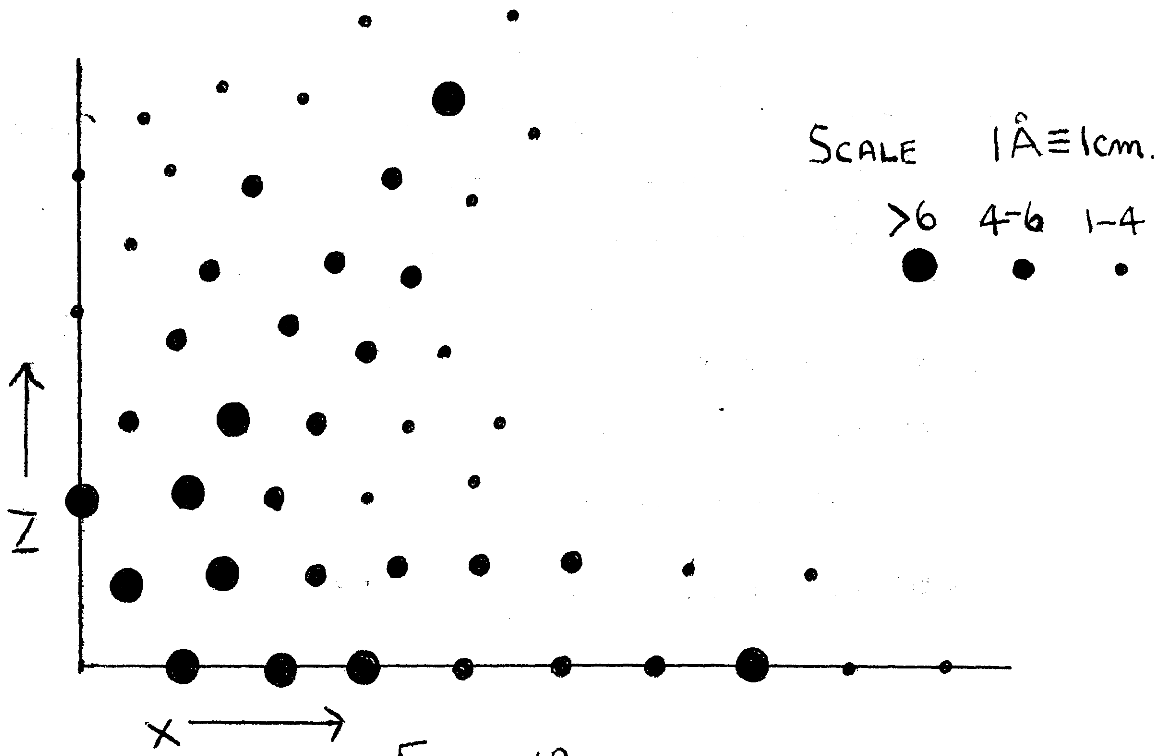


Figure 12

It can be seen that there are two main distributions of the electron density, the first consisting of a row of slightly elongated vector peaks of successively diminishing weight parallel to the x axis, and the second line of peaks at 60° to the x axis and similar to the first subject to the molecular tilt to the b axis. The second set of peaks is attributable to sides AB and BC of the triangle whilst the first arises from side AC. The double weight of the latter is a consequence of their coincidence with the mirror plane of the plane group of the Patterson. The distances of these peaks from the origin increases by multiples of 1.2 - 1.4Å.

Patterson Synthesis - Observed

All the available intensity data was employed in the computed Patterson Synthesis. For the purposes of computation it was first necessary to convert the fundamental space symmetry elements into their vector space analagues. It should be noted that the modification of the direct space plane group symmetry from pgg to pmg does not affect this conversion process since both these latter symmetries become pmm invector space.

On this basis, the expression for the Patterson Synthesis of the hol zone intensity data is unequivocally defined as

$$P(U\ W) = \frac{1}{A}\sum_h\sum_l |F_{hl}^2| \left\{ 2\cos 2\pi hx + 2\cos 2\pi ly + 4\cos 2\pi hx \cos 2\pi ly \right\}$$

Computation was effected using 3° Beever Lipson strips and a desk calculating machine, the sub-division of the axes being

$\frac{1}{120}^{\text{ths}}$ along the x axis and $\frac{1}{60}^{\text{ths}}$ along the z axis. A diagrammatic representation of the electron density pattern obtained is shown in Figure 13.

Interpretation

The electron density distribution depicted on figure 13 did not reveal any simple correlation to the postulated structure. No strong line of peaks at 60° to the x axis can be detected, and, although the requisite row of peaks along the x axis is present, they are elongated in the opposite direction to that anticipated. In addition, the order of the peak height values is not in accord with that expected; rather are they consistent with two parallel molecules of length ca. 9 Å and separated by ca 3Å .

However, before any definite conclusion is drawn from this method, it would be preferable both to bring the existing peaks into greater relief and also to eliminate the screening effect of the origin peak on the vital neighbouring peaks.

The latter process was effected employing the series

$$P\,(U\,W) = \frac{1}{A}\left\{|F_{hl}^2| - \Sigma f_{hl}^2\right\}\left\{2\cos 2\pi hx + 2\cos 2\pi lz + 4\cos 2\pi hx \cos 2\pi lz\right\}$$

where the origin peak contribution is given by

$$\Sigma f_{hl}^2\left\{2\cos 2\pi hx + 2\cos 2\pi lz + 4\cos 2\pi hx \cos 2\pi lz\right\} = \langle F_{hl}^2\rangle\left\{2\cos 2\pi hx + 2\cos 2\pi lz + 4\cos 2\pi hx \cos 2\pi lz\right\}$$

To achieve a greater resolution of the individual peaks it is necessary to modify the coefficients of the Patterson Series by a suitable function which will sharpen the central maxima of each peak but does not introduce subsidiary maxima of minima capable of affecting neighbouring peaks. The modification/

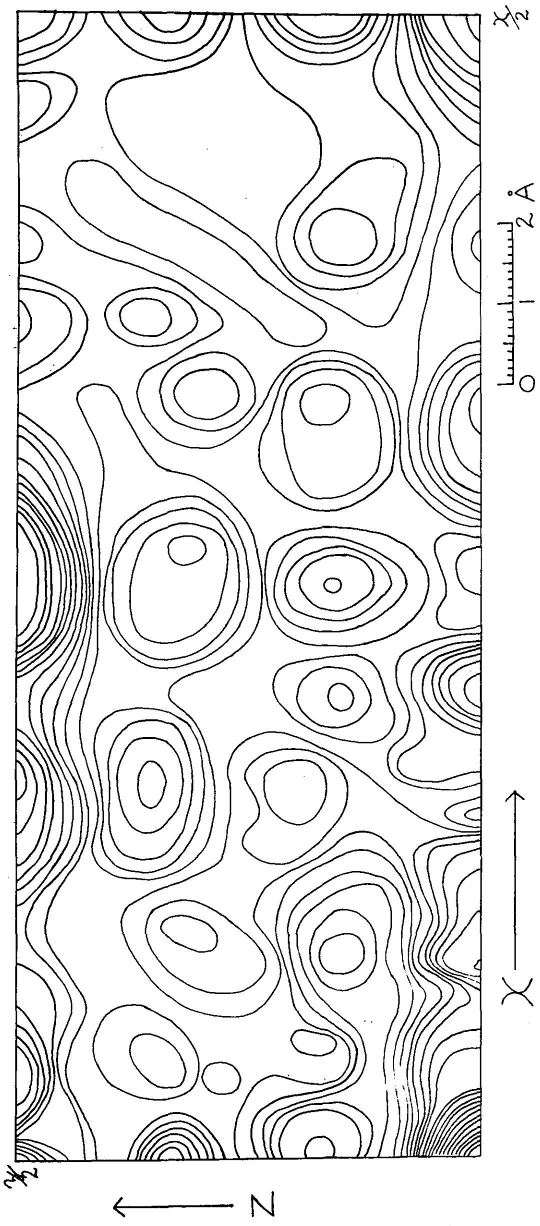


Figure 13.

Patterson synthesis (unsharpened) of h01 - zone.

modification factor chosen entailed the use of the Lorentz Polarization nomogram, the general form of this expression being consistent with the above requirements. The Patterson map, re-drawn on the basis of these modified coefficients, is illustrated in Figure 14.

This shows the general vector distribution to have remained as before. The most striking feature of the map is the lines of parallel peaks separated by $\frac{z}{2}$ Å . These suggest parallel rows of atoms approximately $\frac{z}{2}$ Å apart. The peak distributions are therefore reminiscent of those obtained with layer type structures. Attempts were also made to detect the benzene rings but these proved unsuccessful.

Patterson Synthesis of Diphenyldiacetylene

The similarity of electronic distribution in diphenyldiacetylene to that presumably existing in a single side of triangle affords an opportunity of ascertaining the degree of clarity of observation of the theoretically predicted vector peak arrangements from triangle by comparison with that of the Patterson of diphenyldiacetylene. The x-ray structure analysis of the latter compound has already been reported by Wiebenga[62] and its structure portrayed by a Fourier Synthesis. Patterson methods had, however, not been utilised at any stage in this analysis so that the structure factors of Wiebenga had first to be processed for Patterson computation. The axis of projection most favourable to atomic resolution was the b axis; hence the Patterson was constructed for the hol zone data and its illustration given in Figure 15.

In/

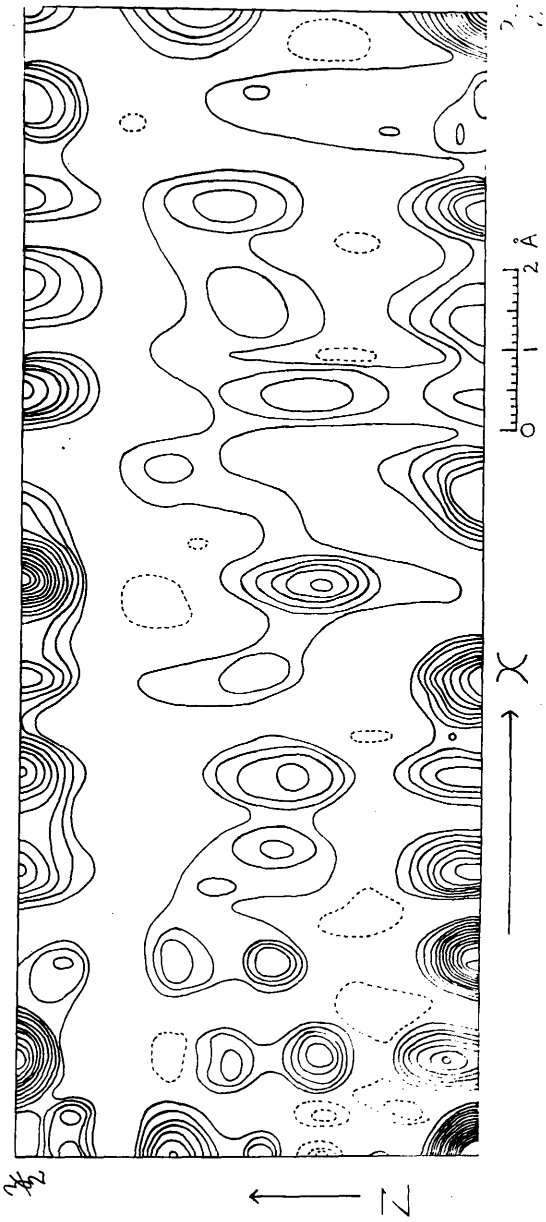


Figure 14.

Patterson synthesis - sharpened - of the h0l - zone.

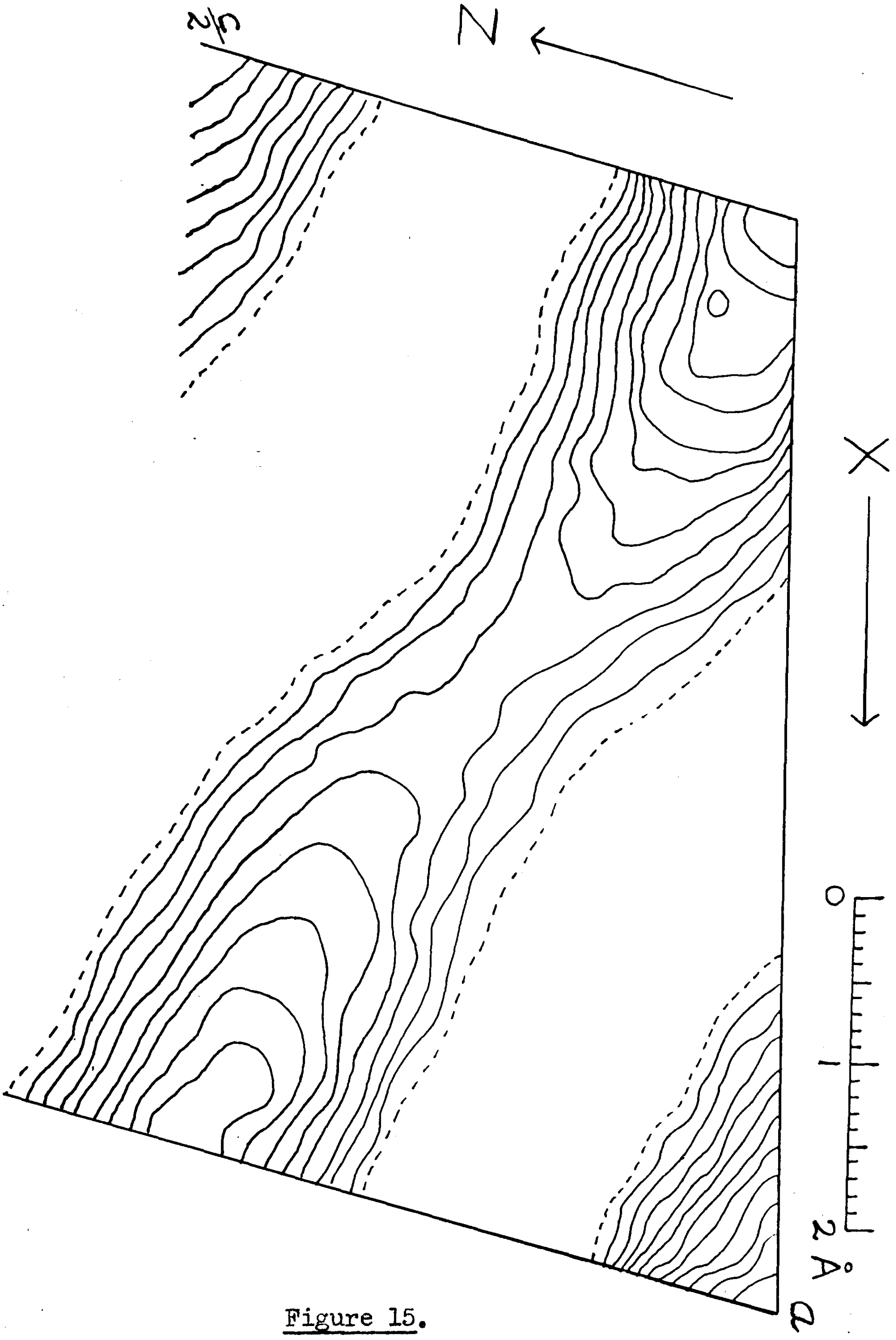


Figure 15.

Patterson synthesis (unsharpened) of the h0l - zone of diphenyldiacetylene.

In the Fourier depicted by Wiebenga for this zone, the four carbon atoms of the diacetylene chains lay on a straight line with the p carbon atoms of the benzene rings, the angle of inclination of this line to the x axis being 75°. These features are in complete accord with the derived Patterson which shows a linear line of vector peaks of magnitudes decreasing proportionate to the number of vectors possible between successive and alternate carbon atoms. The angle between this line and the x axis is again 75°.

With the exception of the sequence of the magnitudes of the peak heights and the presence of some randomly distributed portions of vector matter between the two major peak regions in triangle, the Patterson maps of the intensity data of two compounds are not dissimilar.

Trial and Error Methods

Despite the failure of the Patterson Synthesis to produce any positive information concerning the structure it was decided to attempt a solution from correlation of structure factors calculated from trial structures to those obtained from the observed intensity data. This rather laborious task was much simplified by the approximate fixation of x co-ordinates of the atoms by the mirror plane, and the subjection of the variation of the central z co-ordinate of the molecule, z_m, to the limits $z_m = 0 - \frac{z}{2}$ Å. The first stage was to obtain a measure of agreement between the observed and calculated structure factors for the axial reflexions.

Z Axis Terms/

Z Axis Terms

Plausible values were assigned to the bonds of the molecule and the z atomic co-ordinates calculated for $z_m = 0$. Allowance was made for the fact that packing considerations required the molecule to assume almost maximum possible tilt to the b axis. Structure factors were calculated for the observed z axis reflections viz. (002), (004), (006), and (008), and their values compared with the observed ones. No agreement was obtained. The process was repeated at intervals of 0.5 A up the z axis until the value $z_m = 5.5Å$ was reached. In no instance was any reasonably comparable sets of values obtained. Further, it was noted that the maximum values calculated for the (006) reflection never approached more than one-third of the unitary structure factor value for this plane. Slight alterations in the bond lengths and degree of tilt of the molecule did not appreciably affect the situation. Presumably this anomaly can be related to the similarity of the intercarbon bond lengths to the distance between the positive and negative maxima of the cosine curve for the (006) plane. This factor causes the waves diffracted by successive rows of carbon atoms to cancel out thus preventing the total diffracted matter from the (006) plane, one of the strongest planes, from attaining an appreciable value regardless of the value of z_M.

Thus it would appear impossible to reconcile the position of the triangle, as proposed astride the mirror plane, with the magnitude of the (006) term.

The Method of Sign Relationship

In view of the inability of the previous techniques to provide any indication of the triangular structure being disposed in the unit cell in the simple manner predicted, an attempt was made to synthesise a Fourier Series using coefficients phase-determined by the method of sign relationships. This method enables the signs of the structure factors to be inferred directly without presuming any knowledge of the atomic co-ordinates, and hence was felt to possess possibly a better opportunity of revealing the triangle if it were present in other than the orientation postulated.

Preliminary considerations indicated the presence of several of the favourable features necessary for an analysis of this type. The atoms of the structure are all identical and the shortness of the projection axis implies that they should be well resolved from one another. In addition the root mean square of the unitary structure factor values for point atoms, $\overline{U}$, had been calculated where

$$U_{HKL} = \frac{F_{HKL}}{N f} \quad , N = \text{number of atoms in unit cell}$$

With allowance for the missing reflections, $\overline{U} = 0.073$, reasonably fulfilling the statistical requirements in this respect of a successful analysis (subject to the reliability of the scaling factor), based on a variation of Zacharaisen's "chain process" method of sign determination due to Woolfson. Details of subsequent calculations using this method - by which signs were attributed to forty of the strongest reflexions - are contained in Appendix 1.

Sign Relationship Fourier Synthesis

A Fourier map was constructed from these phase-determined coefficients and is shown in Figure 16. Four regions of significant electron density, each of length comparable to one side of triangle, stand out. However, the distribution of these regions could not be accommodated with an aggregation of triangle molecules. Once more, as in the case of the Patterson Syntheses, chains of atoms 2½Å apart were indicated. Furthermore, the lengths of the chains appeared better defined and to infer the presence of complete molecular entities of length ca. 10Å. This measure is consistent with a dimer structure, but requires molecular weight and density values different from those previously found in the organic analysis of the compound.

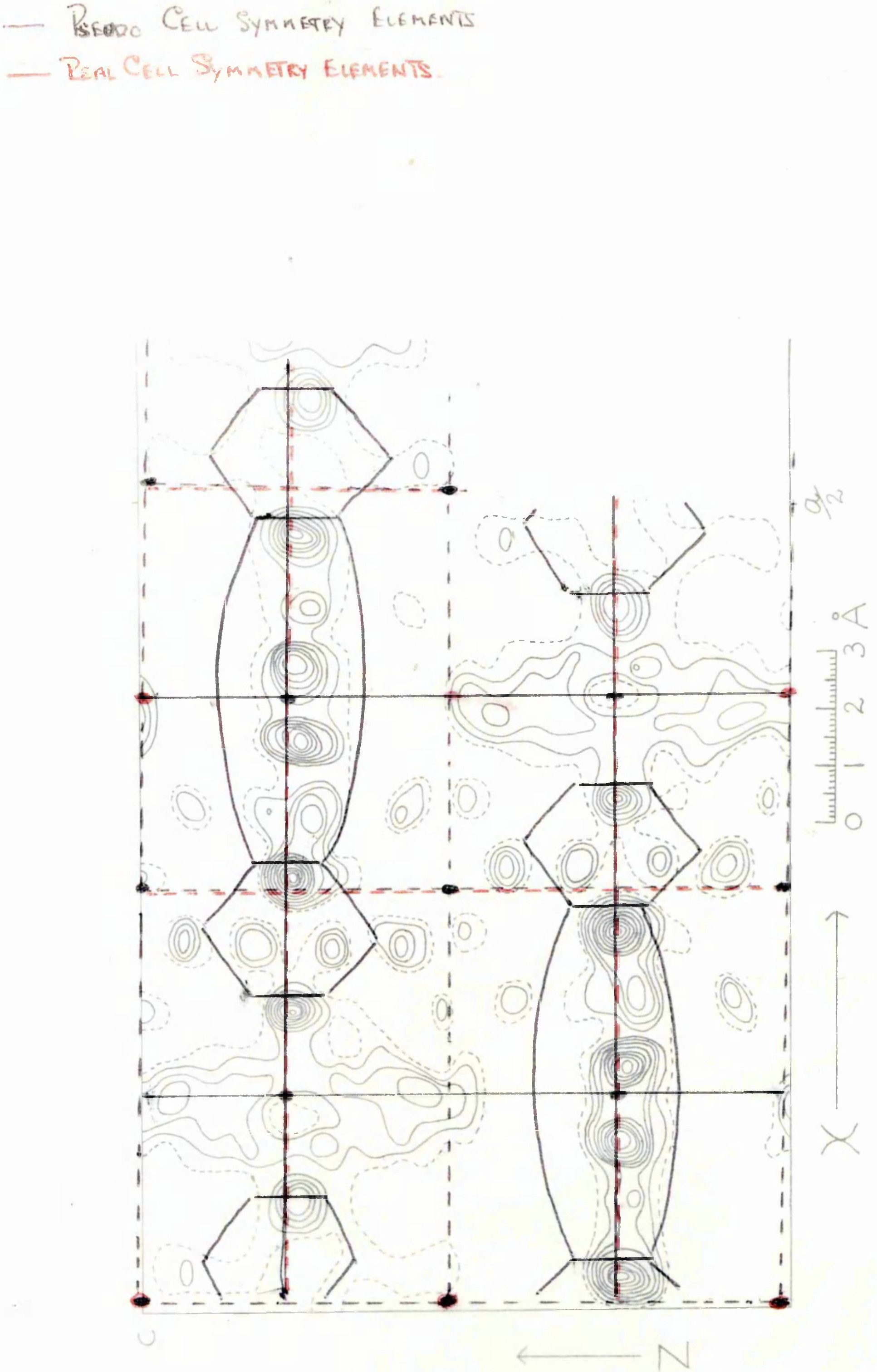


Figure 16.

Fourier synthesis based on 40 terms phase-determined by the method of sign relationships.

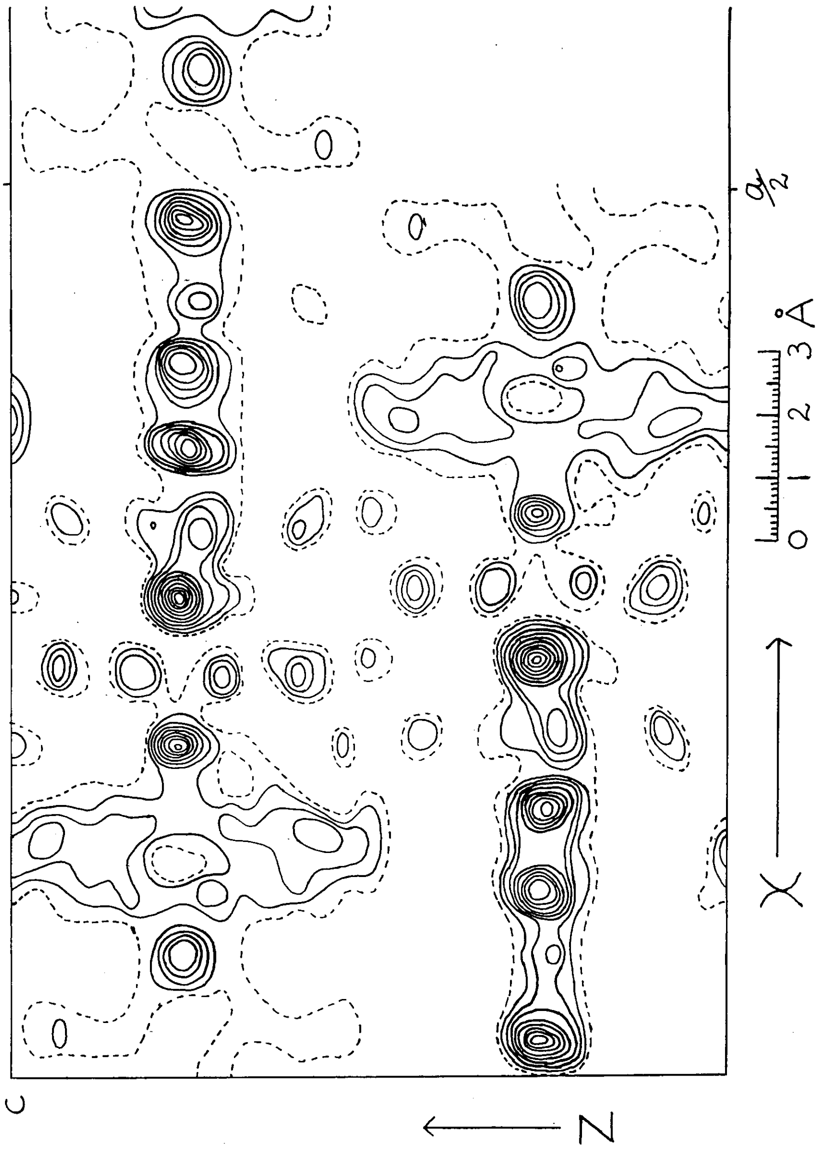


Figure 16.

Fourier synthesis based on 40 terms phase-determined by the method of sign relationships.

Weighted Reciprocal Lattice

The reciprocal lattice of the hol projection, weighted as in figure 17, was drawn up for a single quadrant and an attempt made to relate its principal features to those which might be produced by triangle. The macrocyclic nature of the molecules coupled with their relatively close-packing should produce a fine-textured transform, but one which ought to show quite clearly the predominant trigonal symmetry of the structural material of the unit cell. Thus a hexagonal array of individual strong reflections should be obtained at the orientations to and distances from the origin outlined. No such distribution can be observed and indeed the only symmetry present appears to be the four-fold symmetry of the plane group. The presence of chains of carbon atoms 1.2 - 1.4Å apart and parallel to the x axis is indicated once again by the strong peak at $x = 1.4Å$, $z = 0$. An attempt was also made to pick out the benzene rings. These account for approximately one tenth of the area of the projection and should thus give rise to a relatively coarse-textured transform each region of which will contain several of the reciprocal lattice points. However, it was not found possible to detect these rings on the lattice and it can only be concluded that their transform, not altogether surprisingly. has become obscured by interference from the other constituents of the unit cell.

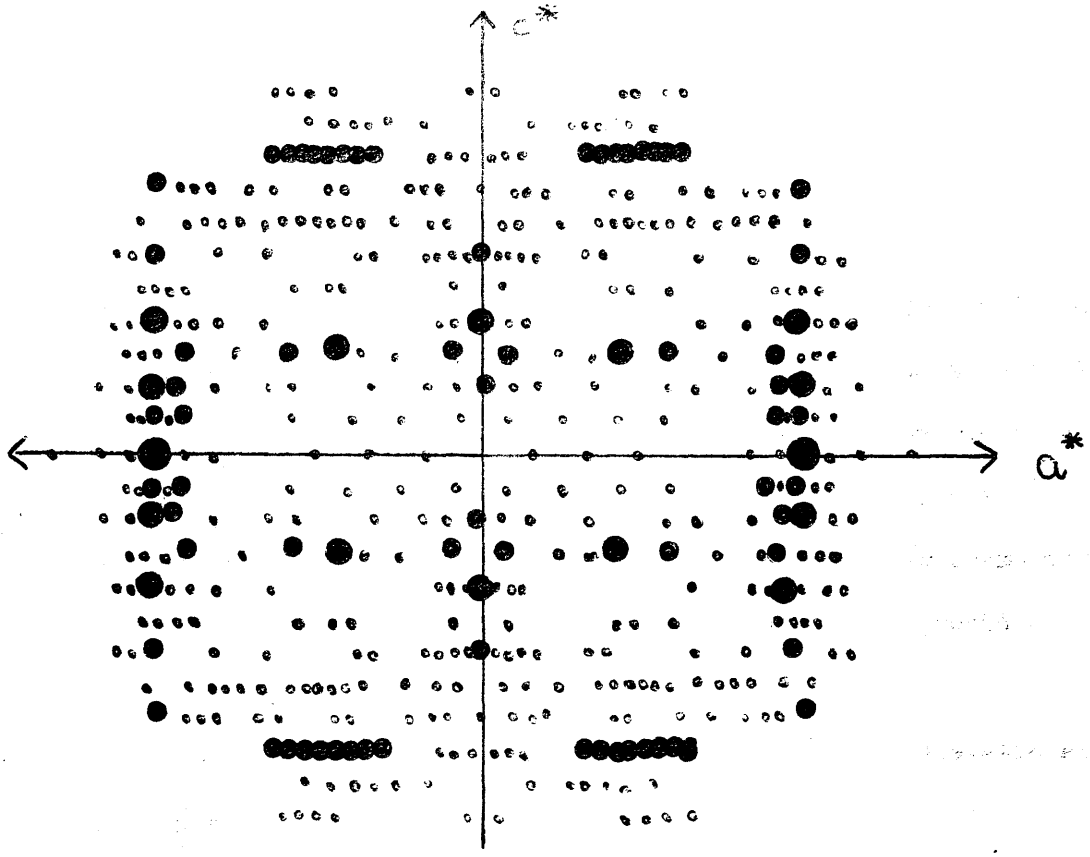


Figure 17 (a).

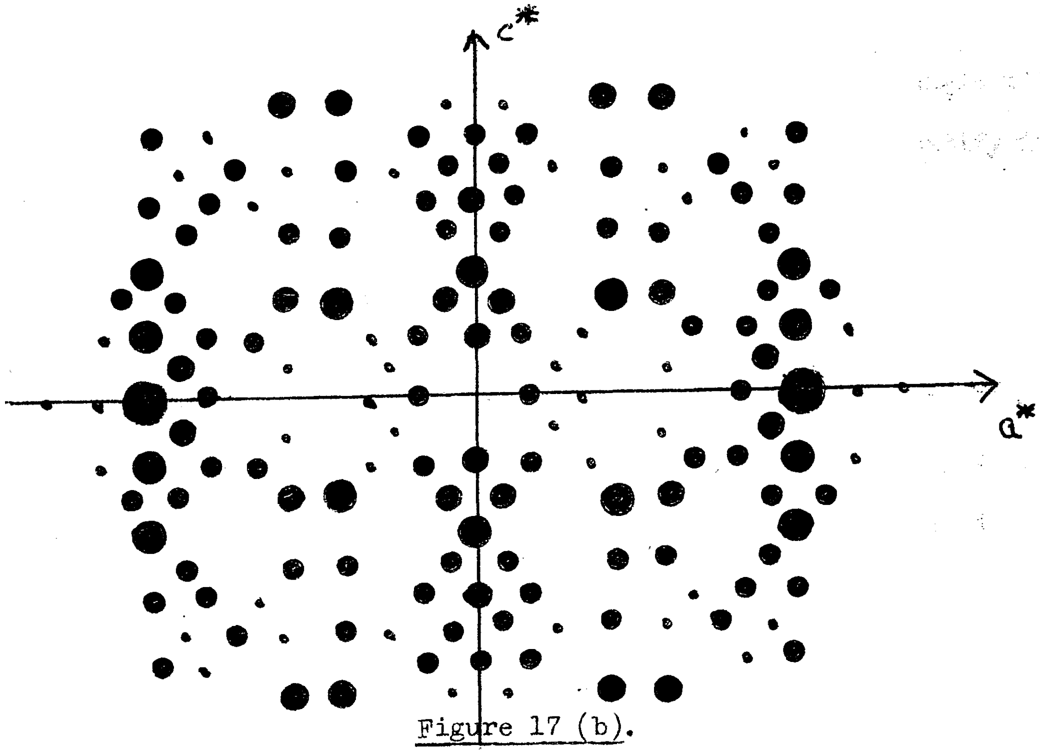


Figure 17 (b).

Alternative weighed reciprocal lattice afforded by many of the strongest reflections and indicative of a sub-cell.

Further Considerations of the Plane Group pgg

(a) Sub-Cell

It was soon realised that the weighted reciprocal lattice, in which only the largest unitary structure factors were displayed, could, to a fair approximation, be made to furnish an alternative lattice network. This is superimposed on the original lattice in figure 17 and shows the parent cell to incorporate a sub cell. Several choices of sub-cell can be made from this new frame work, but it is most convenient to consider the one which provides orthogonal axes.

The latter gave the following dimensions and systematic absences:-

$$a^1 = \frac{a}{2} = 14.21\text{Å} \qquad c^1 = c = 11.54\text{Å} \qquad \beta = 90^\circ$$

$$\left.\begin{array}{l} hoo \text{ present only for } h = 2n \\ ool \text{ present only for } l = 2n \\ hol \text{ present only for } h + l = 2n \end{array}\right\} \text{These define the plane group as CMM.}$$

Efforts were made to reconcile portions of triangle with the dimensions of the sub-cell in such a manner as to justify its presence but these proved unsuccessful.

(b) Disordered Structures

Although the composition of the spots obtained on the Weisenberg Series was perfectly uniform, and no traces of alternation of weak and strong layer lines could be detected on the rotation photographs, the possibility of layers of molecules alternately stacked in the manner shown in figure 18 was considered.

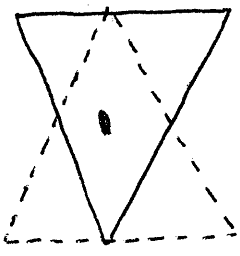


Figure 18.

This arrangement permits a re-appraisal of the plane group as pgg. Now each molecular contributes half-weight to the asymmetric unit so that the four-fold symmetry generates four "half" molecules in strict accord with the presence of two molecules per unit cell. Further the two fold axes perpendicular to the plane of projection now permit~~s~~ free rotation of the molecules about them, thus dispensing with the rigidly defined dispositions of the molecules previously required. The effectively centro-symmetrical relationship of the two "half" molecules in figure 18 to one another should also facilitate a simple application of the Fourier Transform method.

However, further consideration revealed several drawbacks in addition to those already mentioned. In effect, it was found that molecular packing requirements restricted the supposedly free rotation of the "half" molecules with respect to the two-fold axes, to some 4.5°. Hence, to a close approximation, this arrangement could be classified along with the original one.

DISCUSSION

In none of the techniques employed had any trace of triangle been detected despite the unusually favourable crystallographic conditions pertaining in this instance. Consequently, during the course of the analysis, the conclusion became unescapable that this compound could not have the triangular structure proposed.

Attention was now directed towards the consideration of possible alternatives. Of these the most favourable in order of ease of chemical formation were:-

Y
(a) A polymer composed of zig-zag chains of polymerised o-diethynlbenzene. This system is subject to exactly the same symmetry requirements as the closed triangle itself and thus can readily be discounted.

(b) Dimer or Tetramer.

A dimeric structure seemed highly unlikely since the proposed molecular weight of the compound required three molecules of dimer per unit cell. Hence the four-fold symmetry of the plane group necessitates three-quarters of a molecule to be the asymmetric unit, a most unugual measure and one which cannot be reconciled with the inherent molecular symmetry in any obvious manner.

Nevertheless the dimer could be accommodated with all the analytical procedures employed. Both the Patterson and sign relationship maps could be satisfactorily explained on the basis of such a structure. Unfortunately all these explanations depended upon the presence of four molecules of dimer per unit cell.

The tetramer appears equally unlikely, a consideration of its disadvantages showing them to be essentially the same as those of the dimer.

(c)/

(c) Higher Order Cyclic Polymers

The larger cyclic polymers could be excluded by the results of both crystallographic and chemical analyses, the theoretically strain-free hexamer providing the same vector set as triangle itself by virtue of its hexagonal symmetry.

(d) Linear Polymer

A discrete linear polymer is probably the system most amenable to the crystallographic data but the nature of which is at variance with the course of the chemical synthesis.

latter formula has begun to place the previous molecular weight determination in some doubt. Consequently a sufficient quantity of triangle was prepared to enable Bernhardt[63] to perform a [illegible] analysis in camphor. This provided a value in close agreement with dimerisation. Almost simultaneously the spectrum of one of the hydrogenation products was found to be identical with that of the known [illegible] II, a compound which could only have arisen from hydro

1:2-7:8-Dibenzocyclododeca-1:7-diene-3:5:9:11-tetrayne.

These findings led to a complete recapitulation of the chemical analysis, and the results of this are reported by Behr, Eglinton and Raphael[64] on the basis of the dimer formulation as 1:2-7:8-dibenzocyclododeca-1:7-diene-3:5:9:11-tetrayne - Figure 19.

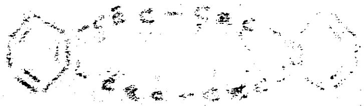
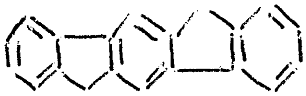


Figure 19.

Part II of this thesis has presented an investigation of the compound formulated as 1:2:7:8:13:14-tribenzcycloctadecahexyne. By April, 1959 the failure of the x-ray evidence to substantiate this latter formula had begun to place the previous molecular weight determination in some doubt. Consequently a sufficient quantity of triangle was prepared to enable Bernhardt[63] to perform a micro-Rast analysis in camphor. This provided a value in close agreement with dimerisation. Almost simultaneously the spectrum of one of the hydrogenation products was found to be identical with that of the known fluorenacene II, a compound which could only have arisen from hydrogenation of the dimer.



II

These findings led to a complete recapitulation of the chemical analysis, and the results of this are reported by Behr, Eglinton and Raphael[64] on the basis of the dimer formulated as 1:2-7:8-dibenzocyclododeca-1:7-diene-3:5:9:11-tetrayne - figure 19.

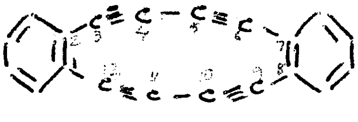


Figure 19.

Re-determination of Crystal Density

The crystals used were the product of several re-crystallisations from benzene. A batch of these crystals was taken and evacuated using an oil pump. Two or three crystals were selected and placed in a dilute solution of zinc chloride which had previously been pumped free of dissolved air on a water pump. Saturated zinc chloride solution was added, with thorough stirring, until the crystals tended to float on the surface of the solution. Water was now added until the crystals partially sank and remained in equilibrium in the solution.

A pyknometer (ca. one ml. capacity) had previously been standardised with distilled water.

Weight of pyknometer empty = 4.5967 grms.
Weight of pyknometer + water = 5.6726 grms.

Weight of water = 1.0759 grms.
Weight of pyknometer + zinc chloride solution = 6.0026 grms.

Weight of zinc chloride solution = 1.4061 grms.

$$D_4^{19} = 1.306 \text{ grms./cc.}$$

This value is consistent with FOUR molecules of dimer per unit cell.

Sign Relationships Fourier Synthesis

The four portions of significant electron density contained in this map could now be readily attributed to the four dimer molecules. These portions possess no intramolecular resolution, but their length and intermolecular distribution exemplifies the very regular molecular packing arrangements which might be expected from the compact symmetrical character of the dimer. In addition, for the molecules situated as depicted in the Fourier Synthesis, their intermolecular vector set is clearly illustrated in the Patterson map, in which the two outstanding peaks along the line $x = 0$, $z = \frac{1}{2}$, correspond to the vectors between the centroids of adjacent benzene rings, and between the centroids of the molecules respectively, as indicated in figure .

A most striking feature of this arrangement emerges when the symmetry of the sub-cell, cmm, is superimposed upon that of the real cell by coincidence of the centres of symmetry common to both, i.e. $(\frac{1}{2},0,\frac{1}{2})$ in the real cell with $(\frac{1}{4},0,\frac{1}{4})$ in the sub-cell. It can clearly be seen from figure 16 that the molecular arrangements as suggested by the sign relationship map is amenable to both sets of symmetry elements. In effect this compound has used its inherent molecular symmetry in attempting to create a smaller cell of higher symmetry than that of the parent cell, and the sub-cell here actually constitutes a pseudo cell. Obviously this modification could never have been fully effected otherwise the pseudo cell would have been obtained as the real cell.

Patterson Synthesis

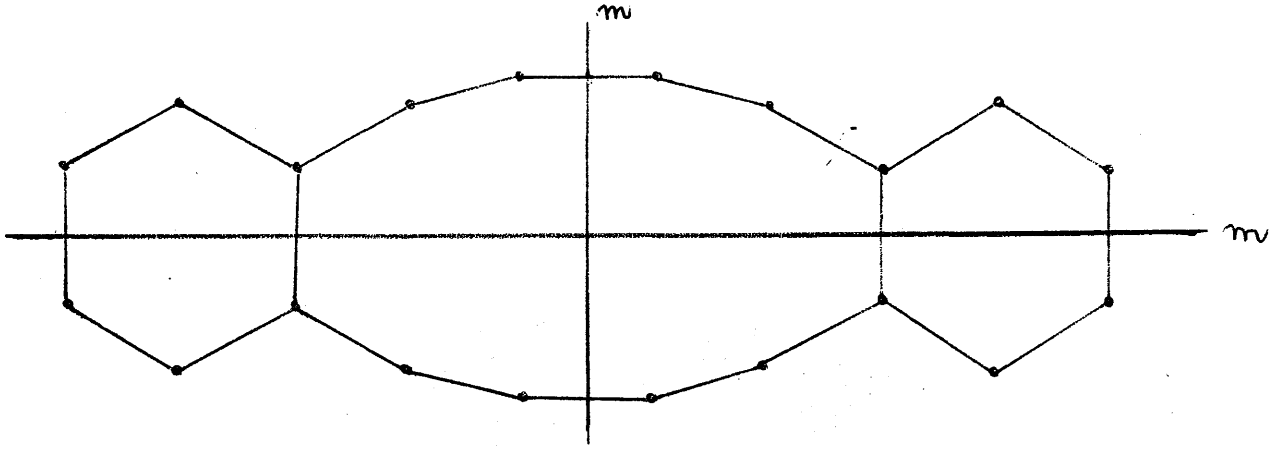
The correlation of the intermolecular vector set of the dimer molecules has been discussed in the previous section.

The dimer model depicted in figure 19 was used to provide an approximate intramolecular vector set and this is represented in figure 20. In its orientation the molecule was made to conform to the cmm symmetry of the pseudo cell. Again comparison shows a close similarity to the peak distribution in the Patterson.

Transform of "Idealized" Dimer

A weighted reciprocal lattice was drawn up to include only the pseudo cell reflections. A mask was punched out of several adjoining unit cell projections (two along x by four along z) containing the molecules in the positions defined by their pseudo cell symmetry. Comparison of the lattice with the optical transform of the mask can be made from figures 17 and 21. A clear agreement is shown and offers further confirmation of the dimeric structure. Comparison is poorest for the high sin Θ regions but this might be expected since these are the most affected by deviations from the pseudo cell symmetry.

The photographs shown in figures 17 and 21 were taken by Taylor, and followed an attempt by him to relate essentially the same weighted reciprocal lattice to the atomic distribution within the unit cell. In this process no preconceived molecular structures were assumed and no consideration was given to the chemical feasibility of the structure indicated. The preliminary results of these calculations, which were communicated at the same time as the alteration of the triangle structure to that of the/



For the construction of the intramolecular vector set the molecule is positioned astride the mirror planes of the plane group cmm as shown. Excluding the origin peak the number of essentially distinct peaks (with allowance for the centrosymmetry of the atomic distribution here) $= \frac{N(N-1)}{4} = 95$.

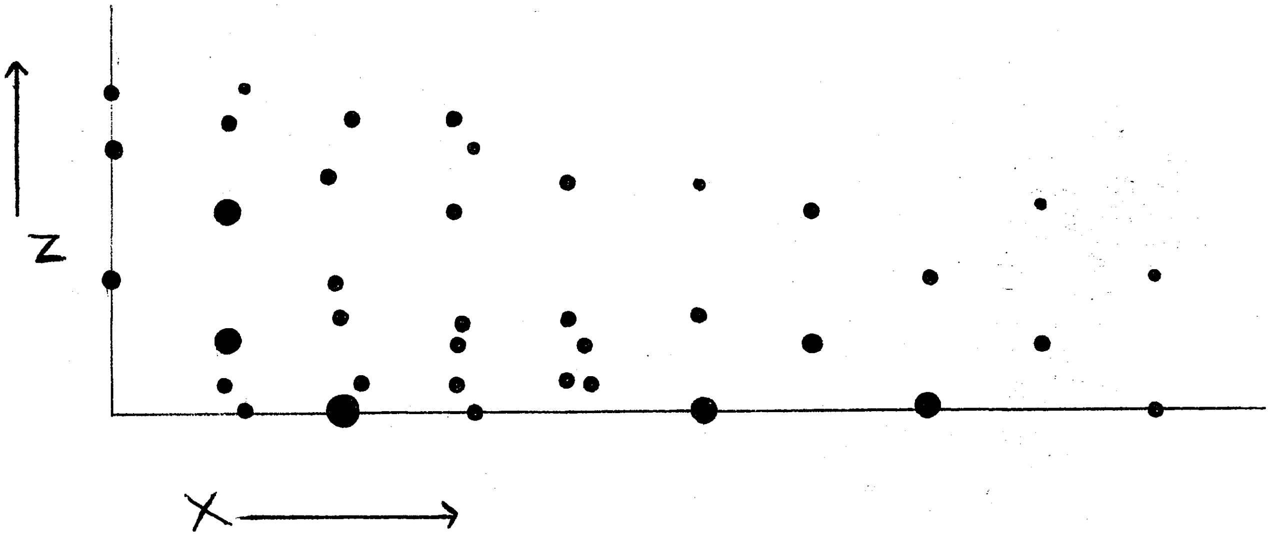


Figure 20.

Intramolecular vector set of the dimer showing ca. 90% of the possible vector peaks.

Weighting system	8	6	4	2	1
	●	●	●	●	●

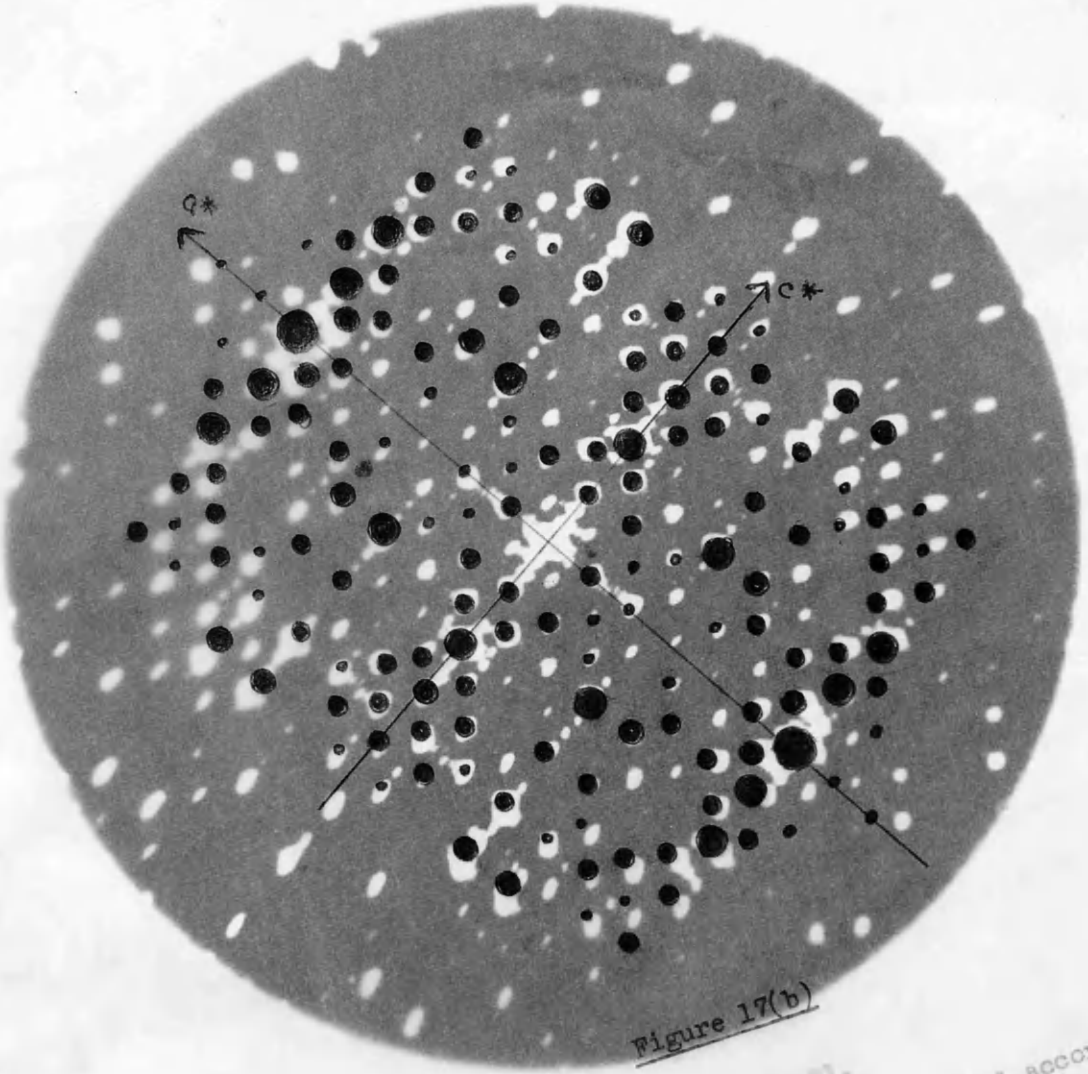


Figure 17(b)

Figure 21.

Optical transform for the dimer molecules packed according to cmm symmetry.

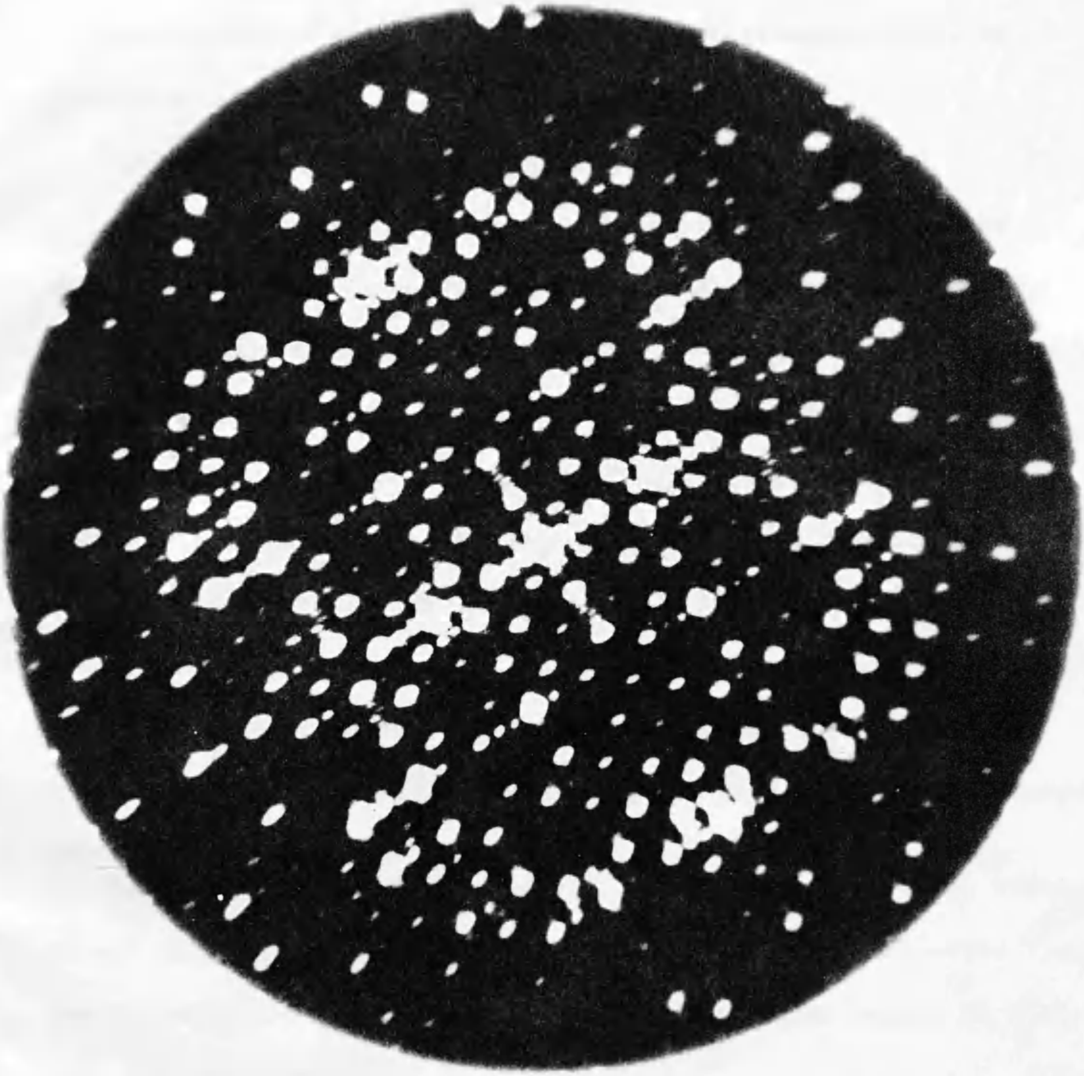


Figure 21.

Optical transform for the dimer molecules packed according to cmm symmetry.

the dimer, suggested the molecule shown in figure 22.

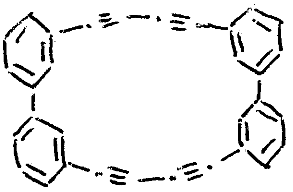


Figure 22.

No reconciliation of the observed data with triangle could be obtained.

Pseudo Cell Analysis

The pseudo cell offers a more convenient approach to the structure analysis than does the parent cell since its symmetry elements affix the molecule in a special position and provide much simplification of complication. Further it was found that for pseudo cell reflections , $\Sigma U = 7.121$ (U = unitary structure factor of any plane), whilst for non pseudo cell terms $\Sigma U = 7.158$, so that approximately one half of the diffracted matter comes from the planes of the pseudo cell, although these only comprise one-third of the total possessed by the parent unit cell. Hence it should be quite possible to observe the "idealized" dimer molecule presented by the pseudo cell reflections. This ought to take the form of an "averaged" structure, as shown in figure 23, since, except at high $\sin\Theta$ values, the distortions of the molecules from cmm symmetry are virtually excluded from the terms common to both real and pseudo cells.

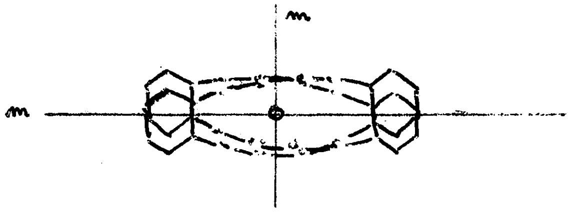


Figure 23.

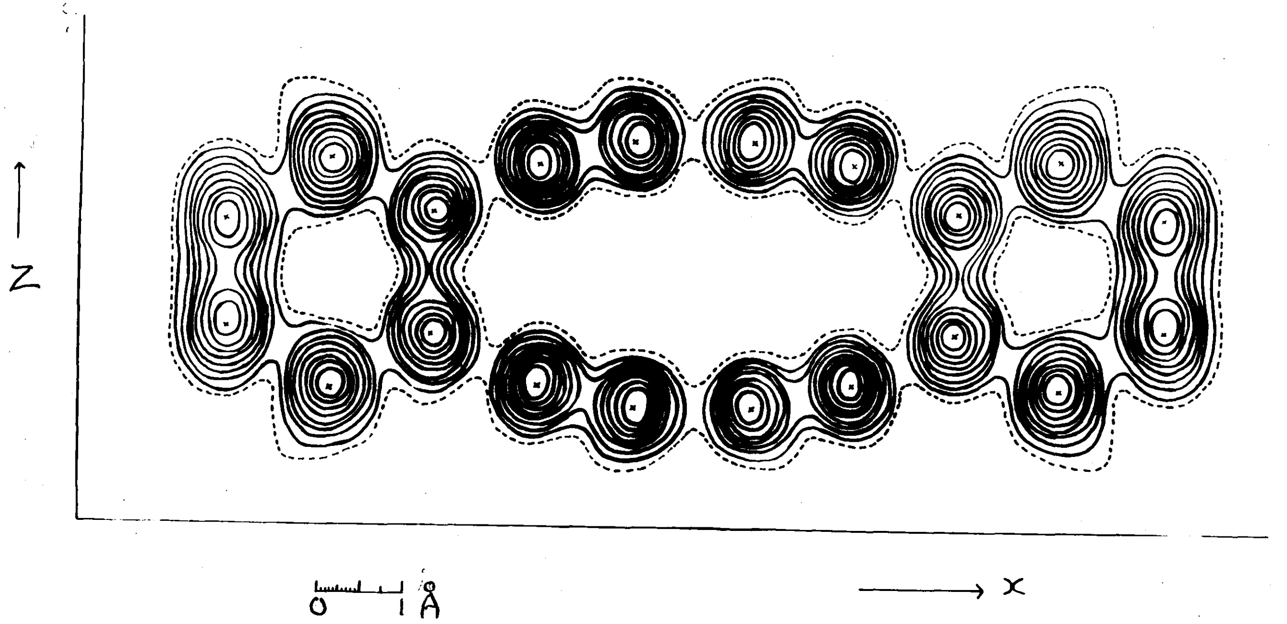


Figure 24.

Final Fourier synthesis of the h01 - zone based on the pseudo cell reflections only. The contour interval is 1 electron per square Å and the zero electron level is denoted by a broken line.

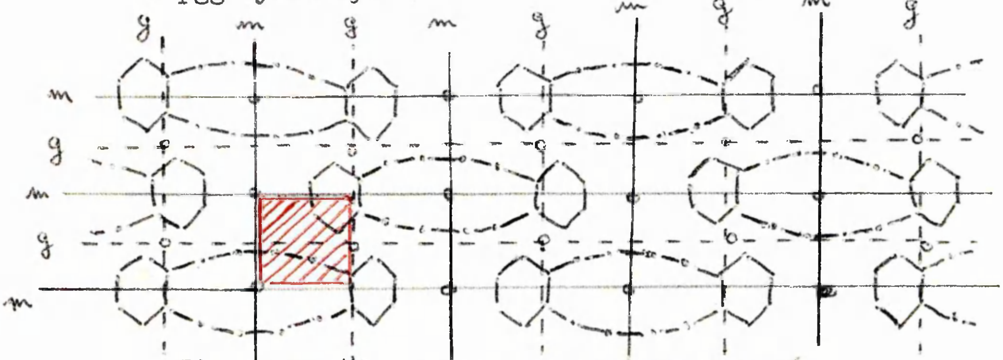
As a preliminary to this process the more concentrated nature of the scattering matter contained in the pseudo cell necessitated an adjustment in the scaling factor K. Plausible co-ordinates were assigned to the carbon atoms and analysis then proceeded by trial and error correlations of these co-ordinates to the x^1 and z^1 axial terms. Eventually extension of this process produced a discrepancy factor, for the sixty-two observed planes of the pseudo cell, of $R = 0.24$. No spurious peaks were obtained on the resultant Fourier map, and the atomic co-ordinates implied by this map gave $R = 0.19$. A second Fourier map was synthesised from the data and is illustrated in figure 24.

Transformation to Parent Cell

All plane indices were revised by the transformation, $h = 2h^1$, $l = l^1$ and atomic co-ordinates by $\frac{x}{a} = \frac{x^1}{a} - \frac{\pi}{4}$; $\frac{z}{c} = \frac{z^1}{c} + \frac{\pi}{2}$

Before trial structures could be erected it was necessary to destroy the mutual coincidence of the centres of symmetry of the real and pseudo cells.

The schematic diagrams of figures 25(a), 25(b) and 25(c) show the component stages of the conversion from cmm symmetry to pgg symmetry.



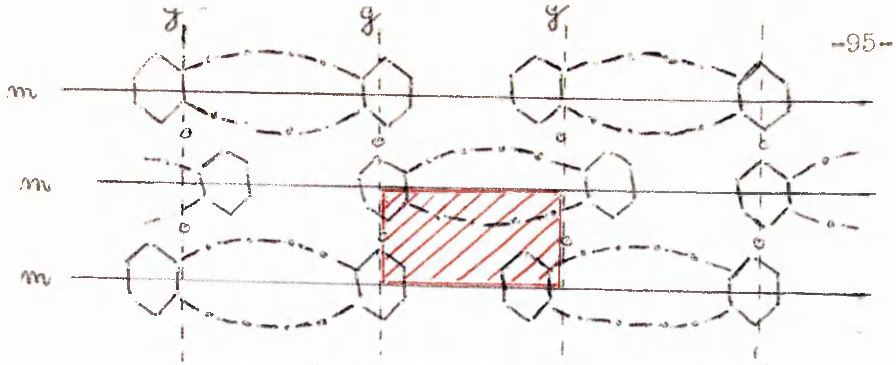
Plane group cmm

Asymmetric unit

= $\frac{1}{4}$ molecule

($\frac{1}{2}$ x $\frac{1}{4}$) unit cell.

Figure 25 (a) Structure idealised 100%.



Plane group pmg.

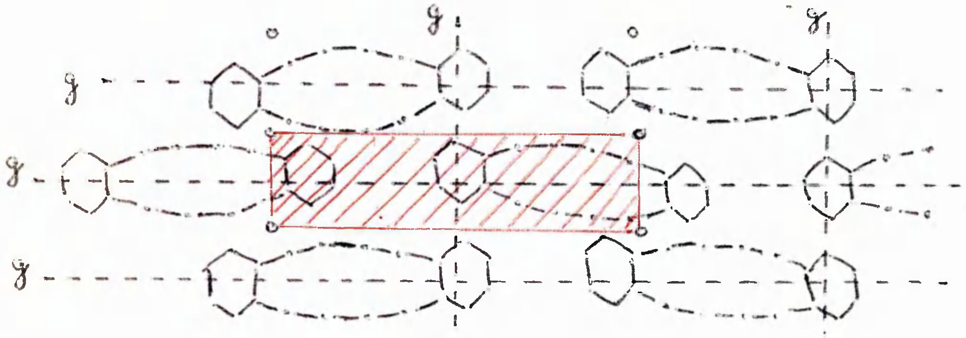
Asymmetric unit

= $\frac{1}{2}$ molecule

($\frac{1}{2}$ x $\frac{1}{2}$) unit cell.

Figure 25 (b). Structure idealised 50%

(introduces lateral translation per e.g. 22,00).



Real Cell.

Plane group pgg.

Asymmetric unit

= whole molecule

($\frac{1}{2}$ x 1) unit cell.

Figure 25 (c). Structure idealised 0%

(entails translation + tilt).

In this, it was fortunate that the inherent four-fold symmetry of the molecule greatly limited the number of effectively different ways in which this could be done. This factor causes each of the eight possible combinations of molecular translations and tilts in the plane of projection to become equivalent merely by change of origin. Hence the x axis translation was obtained simply from consideration of those x axis terms not common to the pseudo cell. Both the z co-ordinates and the tilt of the molecule were found in conjunction mainly from the strong ninth z order bank of reflections - planes (909), (11,09), (13,09), and (15,09) providing the z co-ordinates, and plane (12,09) the degree of tilt.

The final /

The final displacements of the molecule from its pseudo cell alignment were 0.075Å along the z axis, 0.085Å along the x axis, and a tilt of 3° to the x axis.

The structure factors calculated from these co-ordinates gave an agreement factor of $R = 0.268$ for the 183 observed reflections of the parent cell. Refinement of the structure was continued by successive Fourier Syntheses, After temperature factor adjustments, the practical limits of this approach seemed to be attained at a discrepancy factor of $R = 0.240$,and the final Fourier map corresponding to this value is shown in figure 26. Subsequent refinement proceeded by the method of least squares, five cycles of which lowered the discrepancy to $R = 0.166$.

The atomic co-ordinates giving rise to the latter discrepancy are given in Table 14, and the corresponding calculated structure factors compared with the observed structure factors in Table 15.

Crystal Structure Accuracy

The standard deviations in the final atomic co-ordinates x and z of Table 14 were estimated as in a previous method and are shown in Table 16. Subsequent estimated standard deviations in bond lengths are given in Table 17(a) along with the bond lengths Table 17(b) lists the bond angles and their estimated standard deviations.

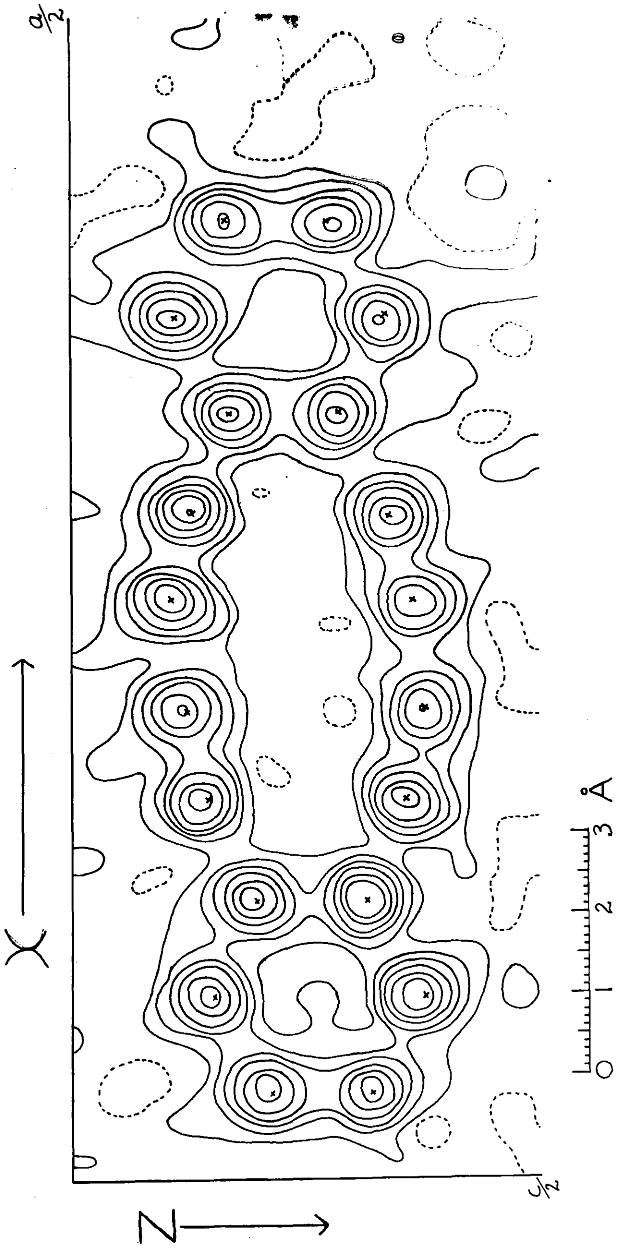


Figure 26.

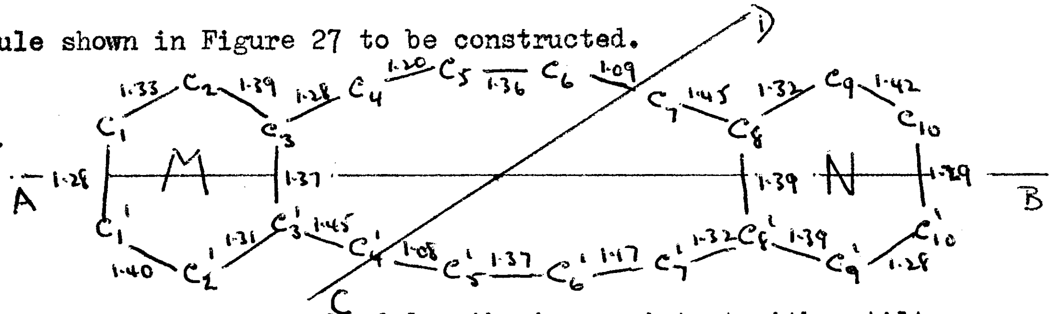
Final Fourier synthesis of the h0l - zone of the real cell. The contour interval is 1 electron per square Å with the zero contour marked with a broken line. "

Y Co-ordinate - hil Zone

In view of the difficulties connected with the collection of intensity data about the zero layer lines of the a and c axes, estimation of intensities was carried out upon a Weisenberg Series taken about the first layer line of the b axis of the crystal. Ideally an approach of this type presupposes the observation of a sufficiency of comparable planes in the hol and hil zones.to permit an attempted solution by the method of generalized projections. In this instance, however, the hol zone and hil zone photographs could only show about one-third and one-sixth respectively of the planes detectable to Cu K_α radiation. Consequently, in the light of these figures no practical application of the method of generalized projections could be envisaged without a more complete picture of the hol and hil zones.

Nevertheless, an analysis of the strongest planes of the hil zone could conceivably afford a general impression of the molecular conformation, and perhaps indicate the areas of the molecule most affected by torsional distortions if this were present to a significant degree. Calculation of bond lengths from the results of the two dimensional analysis of the hol zone enabled the projected molecule shown in Figure 27 to be constructed.

Figure 27



The pattern of these bond lengths is consistent with a tilt of the molecule about the axis CD. This axis is parallel to the sides/

sides $c_1 - c_2$, $c_1^1 - c_2^1$, etc. of the benzene rings and hence is inclined at 30° to the principal axis AB of the molecule. Comparison of the cross-sectional dimensions of the benzene rings in the ~~elevation~~ ~~direction~~ at right angles to CD with those of a regular benzene hexagon indicate the former to be foreshortened in accord with the tilts of 23° and 19° about CD for M and N respectively. For the central twelve-membered ring, however, this effect would seem to exist only for the four bonds immediately exocyclic to the benzene rings. In the case of the four acetylenic bonds, the angle of tilt in fact appears to be reversed in seeming indication that these bonds lie appreciably out of the mean molecular plane.

However, rather than make possibly premature assertions as to the nature of the molecular buckling at this stage in the analysis, the atomic co-ordinates were evaluated for a planer molecule rotated around the axis CD by 21° from the plane of projection. Since the space group had not been uniquely determined structure factors, based on th~~e~~is model, had to be calculated for both the space groups $P2_122_1$ and $P2_12_12_1$

For the computation of structure factors the appropriate transformations of the atomic co-ordinates used in the two-dimensional calculations listed in Table 14 were

(a) $\underline{P2_122_1}$ $\quad \frac{X}{a} = \frac{x}{a} ; \frac{Y}{b} = \frac{y}{b} ; \frac{Z}{c} = \frac{z}{c}.$

(b) $\underline{P2_12_12_1}$ $\quad \frac{X}{a} = \frac{x}{a} ; \frac{Y}{b} = \frac{y}{b} ; \frac{Z}{c} = \frac{1}{4} + \frac{z}{c}.$

For both $P2_122_1$ and $P2_12_12_1$ the combination of symmetry elements/

elements present produced reduces the effective variation of Y_M, the central Y co-ordinate of the molecule, to a range of $\frac{Y}{4}$ of 0.968Å for translations of the molecule parallel to the b axis.

Accordingly structure factor calculations, performed only for the twelve strongest planes, were carried out only over the range $Ym = 0.00$Å to $Ym = 0.96$Å, the interval of sub-division of the molecular translation up the b axis being 0.2Å. No apparent agreement could be obtained between the structure factors evaluated from the formulae of either $P2_122_1$ or $P\,2_12_12_1$ and the observed structure amplitudes. Since the structure factor expressions[65] consisted of triple products of various combinations of sine and cosine functions, and since two of the three definitive co-ordinates were known for each atom, it was possible to conclude from certain of the structure factors with a fair measure of certainty that the structure does not closely approximate to planority, and that some of the atoms may be as much as 10° out of the mean molecular plane.

The failure of the structure to refine in an obvious manner in three dimensions starting from a simple planar model now makes the solution of the Y co-ordinates much more complex. Various non-planar alternatives can be proposed, each capable of a wide range of inclination to the plane of projection. Hence it may be that the solution of the Y co-ordinates requires the employment in the analysis of a much larger number of reflexions than those which it has so far been possible to obtain by the photographic apparatus available.

DISCUSSION

Owing to the rather limited proportion of the accessible planes (approximately 40° of the possible total) detected on the Weisenberg Series of the hol zone, too much reliance cannot be placed at this stage upon the magnitudes of the standard deviations evaluated for the bond lengths and angles of the molecule. Nevertheless, from examination of figure 27, it can be stated with a fair degree of certainty that the molecular structure is not completely planar. The lengths of the bonds $C_4 - C_5$, $C_4^1 - C_5^1$, $C_6 - C_7$ and $C_6^1 - C_7^1$ show that at least the atoms C_5, C_5^1, C_6 and C_6^1 are not co-planar with the remaining atoms of the molecule. However this aspect cannot be considered altogether surprising; the "bowed" conformation of the α-diacetylene chains, clearly illustrated in figure 26, shows the pure digonal sp hybridisation of the orbitals of the four central carbon atoms in each chain to have been destroyed with consequent disappearance of the criteria of linear and planarity associated with this type of chain system. For the rest of the molecule the situation is still indefinite; preliminary considerations indicate this latter portion of the molecule to be approximately planar and tilted through an angle of roughly 20° about the axis CD, although the lengths of the bonds $c_1 - c^1$, $c_3 - c_3^1$, $c_8 - c_8^1$ and $c_{10} - c_{10}^{10}$ may infer slight buckling of the terminal benzene rings - possibly towards partial chair or boat conformations. It should be noted, however, that there are several alternative non-planar conformations of the molecule, each of which would give rise to the same projected

bond/

bond length distribution found in figure 27 . In each of these the inherent molecular strain is relieved by plausible staggering of the bonds of the molecule.

There is no evidence contained in figure 27 to suggest that the molecule attempts to accommodate its internal strain by assuming a propellor shape.

Whatever conformation the solution of the y co-ordinates show the molecule to have adopted, there can be little doubt that the quantum mechanical aspects of the structure will be of much interest, since a rigid application of these concepts would not permit the existence of the molecule in its present form. The dimer, in fact, represents the first structure in which it has been shown possible to appreciably distort the strongly bonded diacetylenic unit, and the central twelve-membered ring possesses the highest degree of unsaturation so far incorporated into any synthetic cyclic structure.

APPENDIX I

Essentially the application of this method depends upon the symmetry elements present. Thus, for the plane group pgg, Woolfson uses a systematic process of sign determination initiated by knowledge of the phases of the structure invariants from the symmetry of this plane group. The structure invariants, or structure factors, of even indices whose signs do not vary with choice of origin of the unit cell, can be phase-determined from combination of the probabilities of the following equations holding when the corresponding structure factors are large.

$$s(h+h^1,k) \approx s(h,k-k^1) \; s(h^1k^1) = ab \quad \ldots\ldots\ldots\ldots (1)$$

$$s(h-h^1,k) \approx (-1)^{h^1+k^1} ab \quad \ldots\ldots\ldots\ldots (2)$$

$$s(2h,2k) \approx (-1)^{h^1+k^1} \quad \ldots\ldots\ldots\ldots (3)$$

Hence it is possible to deduce the sign of $U_{2h,2k}$ is probably the sign of $\sum_{h'}\sum_{k'} W(-1)^{h^1k^1}$ where

$$(4)\ldots\ldots \quad \begin{array}{ll} W_{h'k'} = \tanh(N|U_{2h,2k}, U_{h+h',k}, U_{h-h',k}|) & \tanh(N|U_{2h2k} U_{hk+k'} U_{hk-k'}|) \\ \times \tanh(N|U_{h+h',k} U_{h,k+k'} U_{h'k'}|) + & \times \tanh(N|U_{h,k+k'} U_{h+h',k} U_{hk}|) \\ \times \tanh(N|U_{h-h',k} U_{h,k+k'} U_{h'k'}|) & \times \tanh(N|U_{h,k-k'} U_{h-h',k} U_{hk}|) \end{array}$$

In the present analysis certain preliminary simplifications of the computation were performed. Thus to render them in a more convenient form all U values were multiplied by $\frac{100}{3}$ and expressed to the nearest whole number. Two reciprocal lattice charts, one of which was transparent, were now constructed on each of which the modified U values were plotted. By a convolution of origin through the point (2h,2k) all the related pairs $U_{h+h^1,k}$, $U_{h-h^1,k}$ were revealed and the triple product computed in two parts corresponding to $(-1)^{h^1+k^1}$ being positive or negative. By similar procedures with respect to the lattice points $(h + h^1,k)$, $(h - h^1,k)$ and $(h, k+ k^1)$, $(h\ k-k^1)$ it was possible

possible to evaluate all the components products of (4).

This process was carried out for some eight of the largest invariant structure factors and the final summation values with the inferred signs listed in Table 1.

Table 1

2h	21	U	$\sum_{h'}\sum_{k'} W_{h'k'}(-1)^{h'+k'}$	2h	21	U	$\sum_{h'}\sum_{k'} W_{h'k'}(-1)^{h'+k'}$
4	0	0.126	-	20	2	0.130	-
4	8	.113	- ~~+~~	24	4	.270	-
16	2	.100	+	24	6	.140	+
20	0	.121	-	24	2	.236	+

Probable phases had actually been assigned to the largest of the axial invariant structure factors prior to this by their proven self-consistency with respect fo a special case of Sayre's Equation, viz.

$$s(2h,0) \approx s(hk)\,s(h\bar{k}) \text{ where in this case } \begin{cases} F(hl) = F(h\bar{l}) & h+l = 2n \\ F(hl) = -F(h\bar{l}) & h+l = 2n+1 \end{cases}$$

Exs

$$\overset{-}{s}(24,00) = \overset{+}{s}(12,\bar{0}9)\,\overset{+}{s}(\bar{12},\bar{0}9) \qquad \overset{+}{s}(004) = \overset{+}{s}(\bar{0}02)\,\overset{+}{s}(\bar{0}0\bar{2})$$

$$\overset{+}{s}(22,00) = \overset{+}{s}(\bar{11},09)\,\overset{+}{s}(\bar{11},0\bar{9}) \qquad \overset{+}{s}(008) = \overset{+}{s}(004)\,\overset{+}{s}(00\bar{4})$$

$$\overset{-}{s}(20,00) = \overset{+}{s}(10,\bar{0}9)\,\overset{+}{s}(\bar{10},0\bar{9})$$

Also more generally,

$$\overset{-}{s}(24,00) = \overset{-}{s}(24,04)\,\overset{+}{s}(004) \qquad \overset{-}{s}(002) = \overset{+}{s}(004)\,\overset{-}{s}(006)$$

$$\overset{-}{s}(24,00) = \overset{+}{s}(24,02)\,\overset{-}{s}(002) \qquad \overset{-}{s}(002) = \overset{-}{s}(006)\,\overset{+}{s}(008)$$

$$\overset{-}{s}(24,00) = \overset{+}{s}(14,\bar{0}3)\,\overset{+}{s}(10,0\bar{3})$$

ETC.

By this method it was possible to infer the following signs for the large axial terms.

2h	2l	U_{2h2l}	Sign	2h	2l	U_{2h2l}	Sign
24	0	0.470	−	0	8	0.100	+
0	4	0.293	+	22	0	0.130	+
0	2	0.213	−	8	0	0.100	+
0	6	0.193	−				

These signs were now used to provide a reliable background for the next stage of the analysis. This commences with sub-division of the largest unitary structure factors into four groups as shown:-

(a) <u>h even, l even</u>

$a_1 = S(24.00)$
$a_2 = S(004)$
$a_3 = S(24,04)$
$a_4 = S(24,02)$
$a_5 = S(002)$
$a_6 = S(006)$
$a_7 = S(24,06)$
$a_8 = S(24,08)$
$a_9 = S(20,02)$
$a_{10} = S(22,00)$
$a_{11} = S(400)$
$a_{12} = S(204)$
U > 0·10 • $a_{13} = S(20,00)$

(b) <u>h odd, l odd</u>

$b_1 = S(11,09)$
$b_2 = S(13,09)$
$b_3 = S(15,09)$
$b_4 = S(909)$
$b_5 = S(23,05)$
$b_6 = S(907)$
.$b_7 = S(25,03)$
$b_8 = S(25,01)$
U>0·10. $b_9 = S(15,0,11)$

(c) <u>h odd, l even</u>

$c_1 = S(23,02)$
$c_2 = S(23,04)$
U > 0·10.

(d) <u>h even, l odd</u>

$d_e = S(24,01)$
$d_1 = S(10,03)$
$d_2 = S(10,09)$
$d_3 = S(12,09)$
$d_4 = S(14,09)$
$d_5 = S(22,01)$
$d_6 = S(14,03)$
$d_7 = S(203)$
$d_8 = S(22,03)$
$d_9 = S(809)$
$d_{10} = S(22,05)$
$d_{11} = S(10,07)$
$d_{12} = S(\cancel{14,05}\ 207)$
$d_{13} = S(14,05)$
$d_{14} = S(24,05)$
$d_{15} = S(205)$
U > 0·10 $d_{16} = S(10,05)$

All possible sign relationships of the type $a_r\ d_s\ d_t$ were noted and then tabulated in the form shown in Table 2 following substitution of the appropriate sign for a.

TABLE 2.

	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}
d_0									+		-					
d_1			-		-		+ +	+				+		- -		
d_2		-		-	+		-					=		+		
d_3			-							+				-		
d_4		-	+							-		-		+		
d_5								= = +	-		+ +		=		-	++
d_6		+ +	-		-				+					-		-
d_7	+					- - $\frac{1}{2}$-			+ + +		= +		+			-
d_8	+						+	+ + =			-		+			= +
d_9				+	-											
d_{10}	-					+ +		= +	-				=			+ -
d_{11}		+	=		-								+	-		
d_{12}						=		+ +			=	+	-		-	-
d_{13}		=	+	-	+		-					-				
d_{14}	+					-										=
d_{15}						+	-	-	= = -		+		-		=	

From Table 2 it is clear that the following results probably hold with a high degree of probability.

$d_1 \approx -d_2 \approx -d_4$ and $-d_7 \approx +d_{10}$ etc.

The lines d_1, d_2, d_4 and d_7, d_{10}, d_{12}, can then be combined to give the revised Table 3. From this table further relationships emerge and continuation of this process produces Table 4.

TABLE 3.

	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}
d_0									+		−					
$d_1-d_2-d_4$		‡	=		=		‡ ‡	+				‡+		= =		
d_3			−	+						+				−		
d_5								≡	−		‡		=		−	‡
d_6		‡	−		−				+							−
$-d_7+d_{10}-d_{12}$	=					‡‡‡		== +	● =		‡‡ −	−	=	+		‡+ −
d_8	+						+	‡			−		+			= +
d_9				+	−											
d_{11}		+	=		−							+/	+	−		
d_{13}		=	+	−	+		−					−				
d_{14}	+					−										=
d_{15}						+	−	−	= =		+		−		=	

TABLE 4.

	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}
$d_1-d_2+d_3-d_8$ $+d_6+d_{11}-d_{13}$		++ ++ ++ +	== == == −	‡	= = = −		‡+	+	+	‡		++ ‡+	+	● − ==		
d_0									+		−				+	
$d_5-d_7-d_8+d_{12}$ $+d_{14}+d_{15}$	= =					‡‡ +		== == ==	=	= ==	‡‡ ‡‡	−	≡ = ≡		≡	‡‡ ‡‡ ++ +
d_9				+	−											

The same procedure was repeated for all terms of the form $a_r\ b_s\ b_t$ providing the initial Table 5 and final Table 6 as shown.

Table 5.

	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	b_9
b_1		−	+	−					
b_2	−		−	+					
b_3	+	−		−		+			−
b_4	−	+	−			−			+
b_5								−	
b_6			+	−					−
b_7								−	
b_8						−,		−	
b_9			−	+		−			

Table 6.

$b_1-b_2+b_3-b_4$ $+b_6-b_9$	+ + +	− − −	+ + + +	= =		+ +			
b_5								−	
b_7								−	
b_8					−	−	−		

Only one correlation of the form $a_r\ c_s\ c_t$ could be found, viz.

$a_5\ c_1\ c_2 \approx +$ i.e. $-\ c_1\ c_2 \approx +$

On the basis of arbitrary sign assignation to sections (b), (c), (d) the four groups can be re-written as in Table 7.

Table 7/

Table 7

(a)	(b)	(c)	(d)
a_1 + a_9 −	LET b_1 = +	Let c_1 = +	Let d_1 = +
a_2 + a_{10} +	b_1 + b_8 ?	c_1 +	d_0 + d_6 +
a_3 − a_{11} ?	b_2 − b_9 −	c_2 −	d_1 + d_9 +
a_4 + a_{12} −	b_3 +		d_2 − d_{10} −
a_5 − a_{13} −	b_4 −		d_3 + d_{11} +
a_6 −	b_5 ?		d_4 − d_{12} +
a_7 +	b_6 +		d_5 − d_{13} −
a_8 −	b_7 ?		d_6 + d_{14} +
			d_7 + d_{15} −
			d_{16} ?

Reversing the signs of all the members of one of the groups (b), (c), (d), is merely equivalent to a change of origin but since there are four alternative origin sites in pgg. arbitrary signs can only be reliably attributed to two of the groups. Hence to fix the non-arbitrary group, self-consistent sign relationships of the type b_r, c_s, d_t were sought and recorded viz.

$$- c_1 b_2 d_{11} \approx + \qquad - c_1 b_4 d_9 \approx + \qquad - c_1 b_6 d_4 \approx +$$

$$- c_2 b_4 d_{13} \approx + \qquad - c_1 b_6 d_{13} \approx + \qquad - c_2 b_6 d_6 \approx +$$

It was found that every one of these six relationships was satisfied on substituting the signs given to the members of the groups in Table 7.

Table 14 (a)

Final atomic co-ordinates x, z for the (010) projection, listed as fractures of the unit cell edges.

Atom	x	z	Atom	x	z
C_1	0.93762	0.31684	C_1'	0.93835	0.20837
C_2	0.97926	0.36940	C_2'	0.97969	0.14351
C_3	0.02213	0.30875	C_3'	0.02030	0.19148
C_4	0.06307	0.35709	C_4'	0.06604	0.15422
C_5	0.10421	0.37866	C_5'	0.10341	0.11070
C_6	0.15128	0.36443	C_6'	0.15134	0.11037
C_7	0.18888	0.34394	C_7'	0.19176	0.12824
C_8	0.23326	0.28533	C_8'	0.23532	0.16700
C_9	0.27520	0.33495	C_9'	0.27754	0.10798
C_{10}	0.31919	0.27628	C_{10}'	0.31901	0.16423

Table 14 (b)

Vibrational components of the Debye temperature factor B , for each atom in the direction of the three principal axes, as expressed by the relationship:- $T = e^{-(B_0 \sin^2\theta/\lambda^2)} \times 2^{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{31}lh + B_{12}hk)}$

Atom	a	c	Atom	a	c
C_1	0.103	1.040	C_1'	0.158	1.496
C_2	0.080	0.998	C_2'	0.161	0.449
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C_6	0.177	1.562	C_6'	0.066	0.578
C_7	0.117	1.360	C_7'	0.086	1.020

<u>N.B.</u> Each of the above b_{ij} values should be multiplied by a factor of 10^{-2}.

Table 14 (b) contd.

Atom	a	c	Atom	a	b
C_8	0.091	0.918	C_8'	0.093	0.757
C_9	0.130	1.215	C_9'	0.048	1.962
C_{10}	0.125	$0\overset{1}{.}676$	C_{10}'	0.088	1.318

Table 12

	Density	Molecular Weight
Crystal from benzene	1.076 grm./cc.	403
ether	0,988 grm/cc.	370
dioxane	0.995 grm./cc.	375

Molecular weight of pure triangle = 372.4

Table 15.

Observed and calculated structure factors - real cell.

h0l - zone.

h l	F_c	F_o	h l	F_c	F_o
0 2	-143.48	120.76	3 5	+7.20	8.14
0 4	-139.92	133.00	3 6	-13.12	14.36
0 6	+50.54	50.18	3 7	+11.82	15.78
0 8	+22.46	17.54	3 8	+7.30	9.38
1 2	-25.08	20.74	3 9	-12.44	10.10
1 3	+12.38	15.06	4 0	+73.32	71.82
1 4	-31.24	38.82	4 1	-3.30	11.34
1 5	-5.52	7.26	4 2	-59.24	50.18
1 6	+29.50	24.46	4 4	+8.52	12.58
1 7	-7.86	4.96	4 6	+31.66	26.44
1 8	-4.28	6.90	4 7	+3.78	4.42
1 9	+10.50	10.28	4 8	-19.86	19.50
1 11	-6.98	5.66	4 10	-5.16	6.20
2 1	-45.94	40.24	5 1	-6.38	8.86
2 2	-2.72	4.42	5 3	-4.50	5.68
2 3	-80.40	74.12	5 4	-4.18	4.96
2 4	-6.64	4.96	5 6	+9.82	8.14
2.5	+41.72	32.62	5 7	+6.32	4.42
2 6	+9.26	13.46	5 8	-7.34	10.10
2 7	+27.18	25.70	6 0	+7.92	10.10
2 9	-16.00	12.94	6 1	+32.30	40.24
3 2	+9.30	6.90	6 3	+30.62	27.66
3 3	-11.22	12.94	6 5	-6.18	4.42
3 4	+7.00	3.72	6 7	-17.20	16.66

h l	F_c	F_o	h l	F_c	F_o
7 1	+3.84	5.26	10 2	+13.80	15.06
7 2	-4.66	8.50	10.3	+69.76	77.14
7 3	+6.08	8.86	10 4	-12.18	10.64
7 4	-5.36	5.06	10 6	-5.84	6.88
7 5	-5.42	4.76	10.5	-17.92	8.46
7 6	+10.90	8.86	10 7	-22.60	21.28
7 7	-8.32	8.86	10 8	+1.04	0.74
7 10	-5.56	7.26	10 9	+28.54	24.46
8 0	-42.32	43.26	11 3	+12.42	17.54
8 1	+5.78	6.20	11 4	-7.30	6.90
8 2	+26.24	30.68	11 5	-5.74	15.78
8 4	+5.52	7.44	11 7	-17.06	11.34
8 5	-6.12	4.96	11 8	-9.64	7.80
8 6	-12.18	11.88	11 9	+18.84	23.22
8 7	-9.30	8.86	11 10	-7.72	7.44
8 9	+15.36	18.80	11 11	-7.20	6.20
8 10	+9.00	7.44	12 0	+19.02	20.74
9 1	+5.08	7.40	12 1	-4.72	4.96
9 2	+7.64	6.90	12 2	-12.18	13.82
9 3	-22.94	23.94	12 3	+5.50	6.20
9 4	-4.86	4.42	12 7	-11.42	11.34
9 5	+13.40	10.28	12 9	+23.38	23.22
9 6	-4.60	9.06	12 11	-8.04	6.20
9 7	+22.08	21.28	13 1	+5.46	6.20
9 9	-31.20	21.98	13 3	-13.40	13.06
9 10	-0.84	6.56			
10 1	-22.60	24.46	13 4	+4.34	5.00

h l	F_c	F_o	h l	F_c	F_o
13 7	+14.34	11.88	17 4	+10.62	8.88
13 9	-14.12	21.98	17 5	+3.66	5.66
13 10	+6.62	6.90	17 8	-7.76	6.90
14 1	-20.34	21.28	18 0	+8.28	7.44
14 2	+9.08	15.06	18 1	+11.16	8.14
14 3	+34.94	40.78	18 3	+14.24	11.34
14 4	-7.62	8.84	18 6	-5.54	5.66
14 5	-19.12	21.28	18 7	-14.48	12.22
14 7	-12.14	12.58	19 6	+5.38	6.20
14 9	+22.72	21.26	19 7	-6.06	6.90
14 11	-8.30	6.90	20 0	-25.82	20.74
15 3	+5.80	6.56	20 1	+10.44	8.86
15 4	-9.78	8.86	20 2	+22.24	21.28
15 5	-8.20	7.44	20 3	-5.34	6.20
15 8	+16.02	10.64	20 4	-5.58	8.86
15 9	+17.50	20.02	20 5	-4.32	4.96
15 11	-8.80	8.86	20 6	-14.06	13.12
16 0	+5.58	4.60	20 7	+8.60	6.90
16 1	-6.06	4.96	20 8	+10.00	8.86
16 2	-19.58	20.74	21 4	+4.40	5.66
16 3	+9.78	9.04	21 8	+7.98	8.86
16 4	+12.62	11.34	22 0	-13.80	19.50
16 6	+12.78	11.88	22 1	-32.74	26.94
16 7	-7.90	10.10	22 3	-20.10	19.50
17 1	-4.66	4.96	22 4	+12.64	13.12

h l	F_c	F_o	h l	F_c	F_o
22 5	+19.78	14.36	26 4	-4.40	5.32
22 7	+9.10	7.44	26 6	-6.30	5.66
22 8	-4.20	4.96	27 6	+5.16	4.96
23 1	-6.68	7.26	27 4	-3.58	6.20
23 2	-4.08	20.74	28 0	-10.96	9.56
23 4	-7.78	12.58	28 2	+8.82	6.90
23 5	+8.64	11.34	32 0	+7.60	6.20
24 0	-82.98	60.06			
24 1	+30.24	28.18			
24 2	+27.10	28.90			
24 3	+6.98	6.20			
24 4	+35.16	30.14			
24 5	-13.42	11.34			
24 6	-16.96	14.18			
24 8	-9.28	11.36			
25 1	+8.74	11.88			
25 2	+5.46	5.48			
25 3	-8.10	3.60			
25 4	+8.86	10.10			
25 5	-6.88	9.38			
25 7	+9.76	8.86			
26 0	-5.36	6.20			
26 1	-7.14	7.44			
26 2	+8.26	6.90			
26 3	+12.52	10.64			

TABLE 16

Estimated standard deviations (6) in Å in the final atomic co-ordinates

	6(x)	6(z)		6(x)	6(z)
C_1	0.0130	0.0372	C_1^1	0.0151	0.0420
C_2	0.0124	0.0341	C_2^1	0.0137	0.0290
C_3	0.0130	0.0325	C_3^1	0.0110	0.0400
C_4	0.0139	0.0340	C_4^1	0.0138	0.0302
C_5	0.0125	0.0309	C_5^1	0.0130	0.0368
C	0.0163	0.0420	C^1	0.0119	[illegible]

Table 16

Estimated standard deviations (σ) in Å in the final atomic co-ordinates.

	σ(x)	σ(z)		σ(x)	σ(z)
C_1	0.0204	0.0237	C_1^1	0.0237	0.0268
C_2	0.0195	0.0217	C_2^1	0.0215	0.0185
C_3	0.0204	0.0207	C_3^1	0.0173	0.0255
C_4	0.0218	0.0217	C_4^1	0.0217	0.0192
C_5	0.0196	0.0197	C_5^1	0.0204	0.0234
C_6	0.0256	0.0268	C_6^1	0.0187	0.0208
C_7	0.0226	0.0269	C_7^1	0.0213	0.0220
C_8	0.0209	0.0232	C_8^1	0.0173	0.0214
C_9	0.0206	0.0255	C_9^1	0.0177	0.0267
C_{10}	0.0204	0.0239	C_{10}^1	0.0185	0.0261

TABLE 17(a)

Bond Lengths (Å) and their Estimated Standard Deviations 6(1) Å

The numbering of the atoms is as in figure 27.

Bond	Bond Length (Å)	6(1)	Bond	Bond Length (Å)	6(1
C_1-C_2	1.33	0.029	$C_{10}-C_{10}{}^1$	1.29	0.055
C_2-C_3	1.39	·027	$C_1{}^1-C_2{}^1$	1.40	·032
C_3-C_4	1.28	·027	$C_2{}^1-C_3{}^1$	1.31	·029
C_4-C_5	1.20	·021	$C_3{}^1-C_4{}^1$	1.45	·029
C_5-C_6	1.36	·023	$C_4{}^1-C_5{}^1$	1.08	·022
C_6-C_7	1.09	·025	$C_5{}^1-C_6{}^1$	1.37	·021
C_7-C_8	1.45	·031	$C_6{}^1-C_7{}^1$	1.17	·022
C_8-C_9	1.32	·030	$C_7{}^1-C_8{}^1$	1.32	·026
C_9-C_{10}	1.42	·031	$C_8{}^1-C_9{}^1$	1.39	·026
$C_1-C_1{}^1$	1.28	·055	$C_9{}^1-C_{10}{}^1$	1.28	·027
$C_3{}^1-C_3{}^1$	1.37	·050			
$-{}^1$	1.39	·049			

Table 17 (b)

Interbond Angles

The numbering of the atoms is in accordance with the system outlined on figure 27.

$C_1C_2C_2$	115°53'	$C_7C_8C_8{}^1$	119°50'	$C_8{}^1C_7{}^1C_6{}^1$	9°8'
$C_1C_2C_3$	123°8'	$C_8{}^1C_8C_9$	112°40'	$C_7{}^1C_6{}^1C_5{}^1$	8°37'
$C_2C_3C_3{}^1$	117°31'	$C_8C_9C_{10}$	125°51'	$C_6{}^1C_5{}^1C_4{}^1$	14°45'
$C_3{}^1C_3C_4$	117°53'	$C_9C_{10}C_{10}{}^1$	118°5'	$C_5{}^1C_4{}^1C_3{}^1$	12°18'
$C_3C_4C_5$	13°5'	$C_{10}C_{10}{}^1C_9{}^1$	119°22'	$C_4{}^1C_3{}^1C_3$	114°45'
$C_4C_5C_6$	15°44'	$C_{10}{}^1C_9{}^1C_8{}^1$	122°0'	$C_3C_3{}^1C_2{}^1$	117°50'
$C_5C_6C_7$	6°2'	$C_9{}^1C_8{}^1C_8$	121°14'	$C_3{}^1C_2{}^1C_1{}^1$	121°42'
$C_6C_7C_8$	15°88'	$C_8C_8{}^1C_7{}^1$	106°54'	$C_2{}^1C_1{}^1C_1$	123°6'

REFERENCES

1. ROBERTSON, J.M. - Organic Crystals and Molecules
2. PATTERSON - Z. Krist, 90, 517, 1935
3. PATTERSON - Ibid
4. YU - Nature 1942, 638
5. HARKER and KASPER - Acta 1, 70, 1948
6. HUGHES - Acta 2, 258, 1949
7. KARLA AND HAUPTMANN - Acta 3, 181, 1950
8. SAYRE - Acta 5, 60, 1952
9. COCHRAN~~E~~ - Acta 5, 65, 1952
10. ZACHARAISEN - Acta 5, 68, 1952
11. WOOLFSON - Acta 10, 116, 1957
12. ROBERTSON, J.M. - Organic Crystals and Molecules
13. COCHRAN~~E~~ - Acta 1951, 4, 408
14. HUGHES - J.A.C.S. 63, 1737, 1941
15. COCHRAN~~E~~ - Acta 4, 408, 1951
16. COCHRAN~~E~~ - Acta 4, 81, 1951
17. COCHRAN~~E~~ - Acta 7, 503, 1954
18. CRUICKSHANK - Acta 2, 65, 1949
19. CRUICKSHANK - Acta 2, 154, 1949
20. CRUICKSHANK - and ROBERTSON A.P. - Acta 6, 698, 1953
21. BUCHANAN and SUTHERLAND - JCS. 1060, 1954
22. IDEM, - JCS. 1060, 1954
23. WILSON - Acta 2, 318, 1949
24. HOWELLS, PHILLIPS and ROGERS - Acta 3, 210, 1950
25. ROGERS and WILSON - Acta 6, 439
26. WILSON - Acta 3, 258, 1950
27. ROBERTSON, J.M. - J.Sci.Instr. , 20, 175, 1943

28/

28. WILSON - Nature 150, 152, 1942

29. HOERNI and IBERS - Acta 7, 744, 1954

30. ROBERTSON, J. M. - Acta 7,817, 1954; 8, 286, 1955

31. GRENVILLE WELLS - Acta 8, 512, 1955

32. ROSSMANN - Acta 9, 819, 1956

33. COX and SHAW - Prac.Roy.Soc. 127, 71, 1930

34. TUNNELL - Amer.Min. 24, 448m 1939

35. ALBRECHT - Rev.Sci.Instr. 10, 221, 1939

36. SPEAKMAN - person~~ne~~al communication

37. ROLLETT - person~~nel~~al communication Chemistry Dept.

38. ROLLET - Acta 8, 487, 1955

39. ROBERTSON, J.M. and TROTTER - Trotter Thesis, 1957

40. SWINGLE - J.A.C.S. 1409, 1954

41. SEN - Indian J. Phys. 1948, 22, 347

42. BAILEY

43. BAILEY - Acta 8, 182, 1955

44. HARNIK and SCHMIDT - J.C.S. 3295, 1954

45. CRUICKSHANK - J. 9, 757, 1956

46. CRUICKSHANK - 9, 915, 1956

47. PHILLIPS - 9, 236, 1956

48. CONOHUE, HUMPHREY and SCHOMAKER - J.A.C.S. 67,332,1945

49. O'GORMAN and SCHOMAKER - Ibid, 68,1138,1946

50. BASTIENSEN and HASSELL - Acta Chem.Scand. I,156,1947

51. CUNNINGHAM, BOYD, MYERS, GWINN and LE VAL - J.Chem.Phys.19,676,1953

52. FRIEND, SCHNEIDER and DAILEY - Ibid - 23, 1557, 1955

53. COULSON and MOFFATT - Phil. Mag. 40, 1,1949

54. Idem, Ibid.

55. /

55. LLOYD, DOWNIE and SPEAKMAN - Chem. and Ind. 222,492,1951

56. BECKETT, FREEMAN and PITZER - JACS. 70,4227,1948

57. GILMAN - Organic Chemistry Vol. 1

58. EGLINTON and GALBRAITH - Chem. and Ind., 656, 1959

59. SONDHEIMER, AMIEL and WALOVSKY - J.A.C.S. 79, 6263, 1957

60. EGLINTON and GALBRAITH - Prac. Chem.Soc. 350, 1957

61. CLARK (CAMBRIDGE) person~~ne~~al communication Chemistry Dept.

62. WIEBENGA - Z. fur Chemic. 514, 1939

63. BERNHARDT - Microrast in Camphor (Mex.Planck-Institut)

64. BEHR, EGLINTON and RAPHAEL - Chem. and Ind. 669, 1959

65. INTERNATIONAL TABLES - Vol. 1, Kynoch Press, Birmingham