THE CRYSTAL STRUCTURES OF SOME ORGANIC MOLECULES.

THESIS

presented for the Degree

of

Doctor of Philosophy

in the

University of Glasgow

by

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Chemistry Department. April, 1957.

PREFACE.

This thesis describes the results of research work carried out under the supervision of Professor J.M. Robertson during the years 1954 - 57, when I was an Assistant in the Chemistry Department of the University of Glasgow. I wish to express my sincerest thanks to Professor Robertson for his constant guidance, advice and encouragement throughout the course of the work.

I am indebted also to many others in the X-ray analysis group in the Chemistry Department for much helpful discussion, to Dr. E. Clar for crystals of dinaphthoperopyrene, and to Dr. P.L. Pauson and Dr. E.O. Fischer for samples of the "sandwich" compounds. Finally, may I thank Mr. J.B. Findlay for assistance with many of the diagrams.

SUMMARY.

This thesis deals with the elucidation of the crystal and molecular structures of some organic molecules using X-ray diffraction methods. The thesis is divided into four parts. In Part I the process of X-ray crystal analysis is described briefly, and some methods of overcoming the fundamental difficulty in crystal analysis - the phase problem - and obtaining an approximate structure are outlined.

Many investigations however are undertaken with the object of obtaining accurate molecular dimensions, and methods of refining a structure are described in Part II. The use of $(F_o - F_c)$ syntheses is illustrated by the refinements of the crystal structures of p-benzoquinone and coronene. More accurate values of the bond lengths and valency angles in benzoquinone have been obtained, and these agree reasonably well with those obtained in an electron-diffraction investigation of the vapour, and with those in related molecules. In the coronene refinement, the discrepancies between measured and calculated bond lengths have been reduced, and the hydrogen atoms have been resolved.

Part III describes the analysis of the structure of dinaphthoperopyrene, an "overcrowded" polynuclear aromatic hydrocarbon. An interesting series of regions of diffuse

scattering indicates the presence of a stacking disorder, but in spite of this the molecular dimensions have been determined with considerable precision. The molecule is distorted so that the distance between the overcrowded carbon atoms is 2.95 A, but this separation is achieved with little variation of the valency angles from 120°, and this probably explains the retention of aromatic character in spite of the severe distortion.

Part IV is an account of the determination of the structures of diindenyl iron and diindenyl cobalt. The "sandwich" nature of these molecules is well illustrated in the projections along two crystal axes. The aromatic rings in these molecules are probably rotating freely in solution and in the vapour state, but fixed in the crystal, and it has been postulated that the configuration is probably _trans_. While the present analysis has not yielded accurate molecular dimensions (a three-dimensional analysis will be required), it does show definitely that the molecular configuration in the crystal is not _trans_, but _gauche_.

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PART I.

X-RAY CRYSTAL ANALYSIS.

1. X-RAY DIFFRACTION.

The discovery by von Laue in 1912 that the regularly-spaced building units in a crystal lattice could act as a three-dimensional diffraction grating for X-rays led to advances in two main directions. Firstly, further investigation of the nature of the radiation and the development of X-ray spectroscopy resulted in fundamental advances in the theory of the atomic structure of matter, and secondly, a powerful method was provided for investigating crystal and molecular structure on an atomic scale.

This thesis deals with the elucidation of the crystal and molecular structures of some organic molecules using X-ray diffraction methods.

Some of the earliest demonstrations of a particulate theory of matter are found in the work of Hooke and Huygens; their theories of crystal structure were based on the concept of a lattice, with continued repetition of identical units. The self-consistent sets of symmetry operations that are applicable to infinitely extended structures based on the lattice principle constitute groups of movements which are infinite but discontinuous, and these are called space groups. The geometrical aspects of the lattice theory of crystal structure had been developed and perfected some time before the discovery of X-rays in 1895, but it was not until 1912 that it became possible to verify the conclusions of space group theory experimentally, and show that the theory applied in all its detail to real crystals.

When a monochromatic X-ray beam impinges upon a crystal which is slowly rotated about some axis, one lattice plane after another comes into a position satisfying the Bragg relation, $n\lambda = 2d_{hk\ell}\sin\theta$, and the beams reflected from the planes may be recorded on a photographic film, or in a suitably-placed Geiger counter. From the positions of the diffracted beams it is possible to determine the nature of the lattice, the unit cell parameters, and in many cases the space group of the crystal. The assignment of indices $(hk\ell)$ to each reflexion is facilitated by use of the geometrical concept of the reciprocal lattice.

The precise positions of the individual atoms of the molecule in the unit cell can be found only by a detailed analysis of the intensities of the diffracted beams. If the positions of the atoms in the unit cell are known, the structure factor $F(hk\ell)$ for the plane $(hk\ell)$, which results from combining the waves scattered by the contents of the whole unit cell in the direction required for this reflexion, may be calculated. It is expressed as

$$F(hk\ell) = \sum_{1}^{n} f_j \cdot e^{2\pi i(hx_j/a + ky_j/b + \ell z_j/c)} \quad \ldots(1)$$

where x_j/a, y_j/b, z_j/c are the coordinates of the j^{th} atom expressed as fractions of the unit cell sides, and n is the number of atoms in the unit cell. f_j is the atomic scattering factor for the j^{th} atom; it is a function of the scattering angle, and depends on the distribution of electrons in the atom. These distributions have been calculated by Hartree (1928), James and Brindley (1932), McWeeny (1951, 1952), Hoerni and Ibers (1954), and others for a number of atoms, and atomic scattering factors have been derived. These theoretical scattering factors are calculated for the atoms at rest, but thermal vibrations spread the electron distribution, and decrease the scattering factor. If f_o is the factor for the atom at rest, then the temperature-corrected factor is given by

$$f = f_o \cdot e^{-B(\sin\theta/\lambda)^2} \qquad \ldots\ldots (2)$$

where B is a constant, related to the mean square displacement $\bar{u}^2$ of the atoms from their mean positions by the expression

$$B = 8\pi^2\bar{u}^2.$$

In crystal analysis an empirically-derived value of the constant B is normally used initially, and this value is corrected during the refinement process.

The structure factor is complex, characterized by an amplitude $|F|$, and a phase constant α. The actual crystal intensities depend upon the squares of the structure amplitudes (for a mosaic crystal), and it is possible to test any postulated structure by comparing calculated and measured structure amplitudes.

Since a crystal is periodic in three dimensions, it can be represented by a three-dimensional Fourier series, and the electron-density $\rho(xyz)$ at the points (x,y,z) may be expressed

$$\rho(xyz) = \sum \sum_{-\infty}^{+\infty} \sum A(pqr) . e^{2\pi i \left(px/a + qy/b + rz/c \right)} \quad \ldots (3)$$

p,q,r are integers and $A(pqr)$ the unknown coefficient of the general term. It can be shown that $A(\bar{h}\bar{k}\bar{\ell}) = F(hk\ell)/V$; that is, the Fourier coefficients are directly related to the corresponding structure factors. The Fourier series which represents the electron density distribution at every point in the crystal may now be written

$$\rho(xyz) = \frac{1}{V} \sum \sum_{-\infty}^{+\infty} \sum F(hk\ell) . e^{-2\pi i \left(hx/a + ky/b + \ell z/c \right)} \quad \ldots (4)$$

The Fourier series (4) may be written in the form

$$\rho(xyz) = \frac{1}{V} \sum \sum_{-\infty}^{+\infty} \sum |F(hk\ell)| . \cos \left[2\pi \left(hx/a + ky/b + \ell z/c \right) - \alpha(hk\ell) \right] \quad \ldots . (5)$$

where $\alpha(hk\ell)$ is the phase constant associated with the amplitude $|F(hkl)|$. In a centro-symmetrical case α is restricted to 0 or π, and (5) may be written

$$\rho(xyz) = \frac{1}{V}\sum\sum_{-\infty}^{+\infty}\sum \pm F(hkl).\cos 2\pi(hx/a + ky/b + lz/c) \quad \ldots(6)$$

The computation of a series of this type is extremely laborious, and generally in the initial stages of a structure analysis, a double Fourier series is employed; this is of the form

$$\rho(xy) = \frac{1}{A}\sum_{-\infty}^{+\infty}\sum \pm F(hk0).\cos 2\pi(hx/a + ky/b) \quad \ldots(7).$$

All the data for this series can be obtained from a single zone of reflexions, which can be conveniently recorded on one Weissenberg moving-film.

It seems then that the process of determining crystal structure is quite straightforward; the observed structure factors are used as Fourier coefficients, the series is summed, and the result is a representation of the electron density throughout the crystal. The observed intensities however provide no information about the phase constants of the structure factors, and this fundamental difficulty prevents any direct solution of the problem of finding the atomic positions.

2. THE PHASE PROBLEM.

2.1. Introduction.

In general an infinite number of electron-density distributions may be obtained by assigning phases arbitrarily to the observed structure amplitudes, and summing the Fourier series for the electron distribution. Each distribution obtained will give an exact account of the measured structure amplitudes, so that there is no unique mathematical solution to the phase problem. There may however be a unique physical solution, since the electron density must be everywhere positive (or zero), must consist of approximately spherically-symmetrical atoms, and must be chemically reasonable, and these conditions limit the number of possible combinations of phases. Some of the more important methods of overcoming the "phase problem" are outlined in the following section.

2.2. Methods of solution.

The process of crystal structure analysis cannot in general be direct, since knowledge of the phases of the diffracted beams is lost in recording the diffraction pattern. The problem that has to be solved is the determination of the distribution of scattering matter from the measured structure amplitudes, and usually it is necessary to assume initially that the scattering matter is concentrated into separate atoms. The problem is then attacked by postulating an arrangement of atoms, and comparing the structure amplitudes calculated from these atomic positions, $|F_c|$, with the measured structure amplitudes, $|F_o|$. The atomic positions are adjusted by trial until reasonable agreement between the values of F_o and F_c is obtained; this indicates that the postulated structure is probably correct, and refinement may proceed by Fourier methods.

Harker and Kasper (1948) have shown that the result of the condition that the electron density must be everywhere positive is to establish sets of inequality relations involving the structure factors, and these can be used to limit the possible values of the phases. More general inequalities have been derived by Karle and Hauptmann (1950), and the Harker-Kasper inequalities are special cases of these. Equality relations between the signs of structure factors for centrosymmetrical crystals have been discussed by Sayre (1952), Cochran (1952), and Zachariasen (1952), and these are directed particularly to the case of more complex crystals where the Harker-Kasper inequalities are inadequate.

While the positions of the atoms in the unit cell are not known in advance, knowledge of the chemical structure determines the disposition of the atoms with respect to each other, and the relative positions of the molecules may be deduced by the Fourier Transform method (Knott, 1940).

The vector representation of crystal structure, discovered by A.L. Patterson (1934; 1935), is one of the most powerful methods of crystal analysis. From the squares of the structure amplitudes, which are directly derivable from the X-ray intensities, it is possible to produce a picture of the crystal structure, showing all the interatomic vectors of the crystal. In principle the atomic positions can be derived from the vector map, but in two-dimensions the difficulties of the method are considerable due to overlap of peaks, and the use of three-dimensional syntheses, with their greater resolution, is of the greatest importance.

If the crystal contains one or more atoms of predominant scattering power at known or easily-determined positions in the unit cell, the vectors between the light atoms are relatively unimportant, and a Fourier synthesis with phases calculated from the heavy atoms alone should give a reasonable representation of the structure. There are however many difficulties associated with the method; if, for example, the unit cell contains more than one heavy atom, the contributions from the heavy atoms may have opposite phases for some of the reflexions, and cancel out. It is then necessary to proceed with an analysis based on the phase-determined structure factors alone, and use some trial method (based on knowledge of bond lengths and stereochemistry) to interpret the Fourier series. The method is, of course, limited to structures containing a heavy atom or structures into which one can be introduced (Robertson and Woodward, 1937, 1940). A good example of a structure analysed by this method is provided by diindenyl iron, which is described in Part IV.

A more powerful phase-determining method is available if a series of isomorphous compounds is available, since the phases are determined from the difference of the contributions of the replaceable atoms, and these need contain a much smaller proportion of the scattering matter than is required for the heavy atom method. Most of the triumphs of X-ray structure analysis have been achieved by the application of either the heavy atom or the isomorphous replacement method.

2.3. Conclusion.

When atomic positions have been obtained which give calculated structure amplitudes in good agreement with those observed, the crystal structure has been essentially solved, and the broad features of the molecular architecture will have been established. Many investigations however are undertaken with the object of obtaining accurate values of the bond lengths and other molecular dimensions, for comparison with those calculated by wave-mechanical methods, and for checking theories of molecular structure. For such purposes the atomic parameters must be obtained with greater precision; adjustment of the atomic parameters is called refinement of the structure. Methods of refining a trial structure are described in Part II.

PART II.

REFINEMENT PROCEDURES IN CRYSTAL ANALYSIS.

1. REFINEMENT PROCEDURES.

1.1. Introduction.

Refinement procedures are used when we have arrived, by some method, at atomic positions which are within about 0.1 - 0.2 A of the true atomic positions in the crystal. We must consider whether modifications of the Fourier series method, or methods not involving Fourier series will give more accurate atomic coordinates than the usual F_o synthesis.

The coordinates are corrected by small amounts so that the new set of coordinates gives improved agreement between observed and calculated structure factors. The structure factor agreement is usually expressed as

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

where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the summations are taken over all the reflexions. Values of R are useful in deciding whether a change in parameter has led to better agreement between observed and calculated data, but too much significance must not be attached to the actual numerical value of R. Some of the more widely-used methods of crystal structure refinement are outlined in the following sections.

1.2. F_o synthesis.

When a structure giving reasonable agreement between F_o and F_c has been obtained, a Fourier synthesis is computed using as coefficients the measured structure amplitudes with the calculated phase constants. From this Fourier synthesis more accurate atomic parameters may be obtained, and re-calculation of the structure factors generally leads to improved agreement with the measured values, and enables the phases of further structure amplitudes to be determined. Generally a number of successive syntheses must be computed, since the initial coordinates are seldom sufficiently accurate to give the correct phase angle for every reflexion.

A variant of the F_o synthesis, the differential synthesis, was suggested by Booth (1946a, b); this is subject to the same sources of error as the F_o synthesis, and greater accuracy is obtained only in that the points of maximum density are precisely located without interpolation.

It has been shown that random errors in the F_o values have a remarkably small effect on the atomic positions (Booth, 1946c; Robertson and White, 1947). More serious errors are introduced if the series is terminated when the coefficients are still large; each peak is then surrounded by diffraction "ripples", and this displaces the peaks from their true positions. Booth (1946c, 1947) has suggested a simple method of correcting the atomic coordinates for the effect of series termination - "backshift" method.

1.3. Method of least squares.

An alternative refinement method, the least squares method, which is free from the inherent errors of the F_o synthesis, was suggested by Hughes (1941). The "best" atomic parameters are those which minimize the function

$$R = \sum w\left(|F_o| - |F_c|\right)^2$$

where the sum is taken over all the terms within the limiting sphere; w is a weighting factor depending on the reliability of the F_o value. Each structure factor supplies one observational equation, and these are reduced to a set of normal equations, which are solved for the coordinate shifts, Δx_n, Δy_n, Δz_n.

1.4. $(F_o - F_c)$ synthesis.

Let us now consider the function

$$D = \rho_o - \rho_c = \frac{1}{V}\sum_3 (F_o - F_c) . \cos 2\pi\left(hx/a + ky/b + lz/c\right)$$

Cochran (1951b) has shown that if we choose atomic coordinates which make the slope of D vanish at all atomic centres, then these coordinates are exactly the same as those given by the least squares method, if each observation is given the arbitrary weight $w = 1/f$. When the slope of D is not zero at a point taken to be an atomic centre, the centre of the atom must be moved a distance Δr_n given by

$$\Delta r_n = \frac{\left(\partial D/\partial r\right)_n}{\left(\partial^2 \rho_o/\partial r^2\right)_n}$$

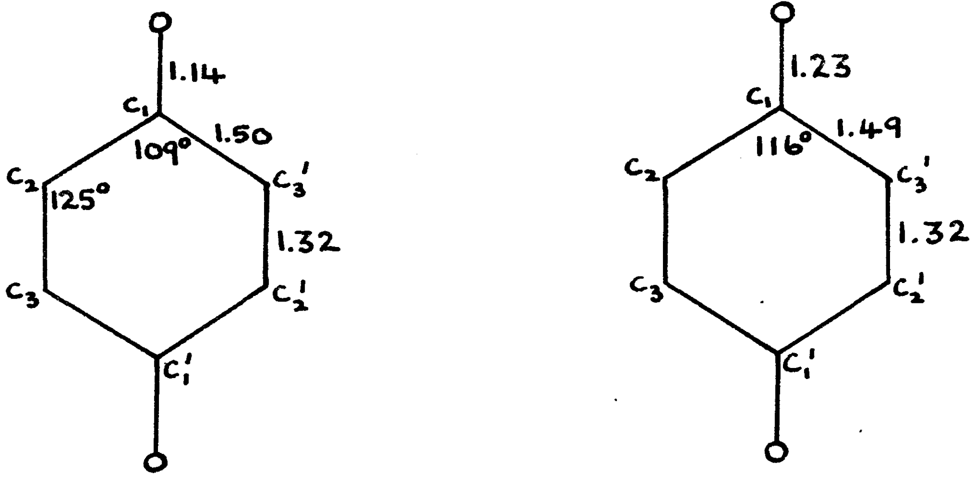
where r̲ denotes a distance measured in the direction in which D increases most rapidly. The $(F_o - F_c)$ synthesis however also shows when incorrect values of the scattering factor are being used, and expressions for correcting the temperature parameters have been given by Cochran (1951a,b). The use of $(F_o - F_c)$ synthesis in crystal structure refinement will be illustrated by the refinements of the crystal structures of two organic molecules - p-benzoquinone and coronene - which are described in the following sections.

2. REFINEMENT OF THE CRYSTAL STRUCTURE OF p-BENZOQUINONE.

2.1. Introduction.

The crystal structure of p-benzoquinone was determined by X-ray diffraction methods in 1935 (Robertson, 1934, 1935) by trial and error, followed by two-dimensional Fourier analysis. Due to overlap in all the projections however the atomic parameters can be considered as only approximately correct, and the object of the present investigation was to obtain more accurate parameters by two-dimensional $(F_o - F_c)$ syntheses.

The structure of vapourised p-benzoquinone has been studied more recently by electron-diffraction techniques (Swingle, 1954), and the molecular dimensions obtained are compared in Fig.1 with those obtained in the X-ray diffraction study of the crystalline material.



(a) Robertson (1935) (b) Swingle (1954)

Fig.1. Bond lengths and valency angles in p-benzoquinone.

In both investigations the general features of molecular structure observed are similar - the bond lengths and valency angles indicate that the ring is significantly different from the regular, hexagonal arrangement in benzene. The two investigations differ in the length assigned to the C — O bond and in the $C_2\hat{C}_1C_{3'}$ valency angle. In the original X-ray investigation however accurate atomic positions could not be found because of overlap, and the atomic positions were chosen assuming $C_2\hat{C}_1C_{3'}$ had the tetrahedral value.

Crystal data. p-Benzoquinone, m. 115.7°; a = 7.03, b = 6.79, c = 5.77 A, β = 101.0°. Volume of the unit cell 270.5 A^3. d(calc.) = 1.327, d(meas.) = 1.318 at 20°. Absorption coefft. for X-rays (λ = 1.542 A) = 9.82 cm^{-1}. Absent spectra: ($h0\ell$) when h is odd, (0k0) when k is odd. Space group, C_{2h}^5 - $P2_1/a$. Two molecules per unit cell, and hence each molecule possesses a centre of symmetry. F(000) = 112.

The intensity data used in the present two-dimensional refinement were those collected in 1935.

2.2. Refinement of the (001) projection.

Structure factors for the (hk0) zone reflections were recalculated from Robertson's final coordinates, using McWeeny's scattering curves (McWeeny, 1951), corrected for thermal vibration by the factor $\exp\left\{-B(\sin\theta/\lambda)^2\right\}$, with $B = 4.8$. Hydrogen atoms were included, approximate coordinates being obtained by assuming C-H distances of 1.0 A, and using McWeeny's curve for hydrogen, with $B = 5.7$. The structure factor agreement over the observed planes was $R = 14.3\%$ at this stage.

Further refinement of atomic coordinates and temperature parameters was now carried out by evaluating successive Fourier difference syntheses with $(F_o - F_c)$ as coefficients. From the successive difference maps, which represent the function $(\rho_o - \rho_c)$, the difference between observed and calculated electron density at each point on the (001) projection, coordinate adjustments were made until the electron density slope at the atomic centres became zero. The temperature factors B for each atom were then adjusted until $(\rho_o - \rho_c)$ was approximately zero at the atomic centres.

The first difference synthesis is shown in Fig.2a; after the corrections had been applied the final $(\rho_o - \rho_c)$ synthesis was computed (Fig.2b). It represents the difference between the electron distribution existing in the crystal, and that calculated for carbon, oxygen and hydrogen atoms at their appropriate positions in the unit cell. This map indicates anisotropic thermal vibrations of the oxygen atom, but the extent and accuracy of the data scarcely

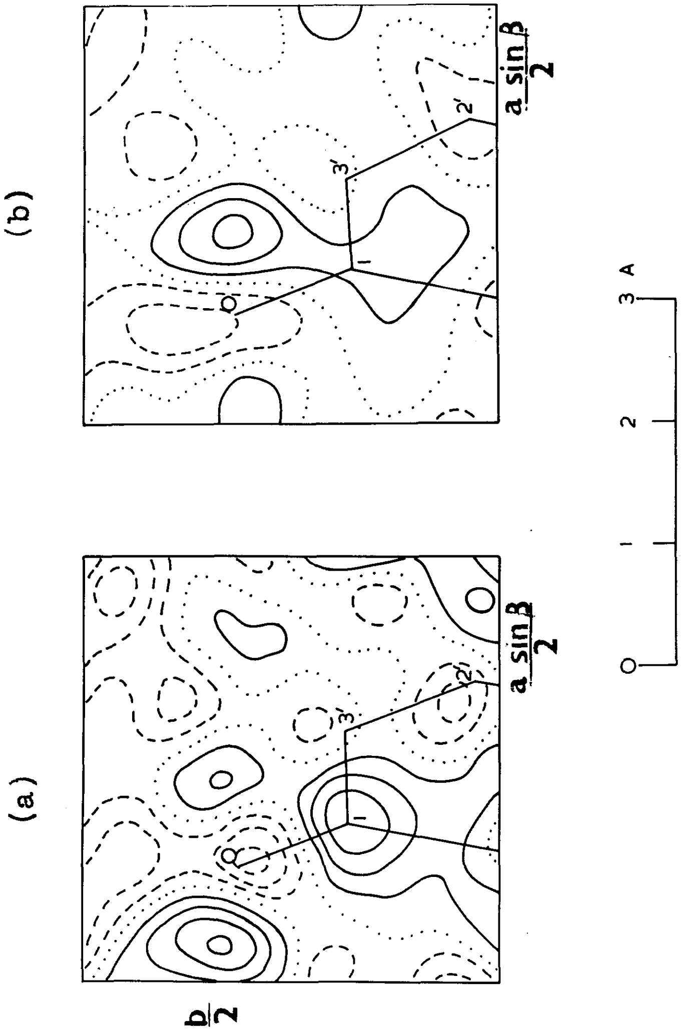


Fig.2. (a) Initial and (b) Final ($F_o - F_c$) syntheses, (hk0) zone. All atoms, including hydrogen, subtracted. Contour interval 0.2 eA^{-2}, negative contours broken, zero contour dotted.

justify allowance for this, and no anisotropic factor has been introduced. The arrangement of the anisotropic vibration peaks does however show that the direction of maximum vibration of the oxygen atom is at right angles to the C - O bond direction.

A hydrogen synthesis is shown in Fig.4a; this represents the difference between the electron distribution existing in the crystal and that calculated for carbon and oxygen atoms only. It is not possible to make any reliable assignment of coordinates to the hydrogen atoms from this map because of the poor resolution; this is due to overlap of hydrogen atoms of neighbouring molecules, and to the small number of terms included in the synthesis.

The final value of R for the (hk0) structure factors was 10.7%.

2.3. Refinement of the (100) projection.

Structure factors for the (0kℓ) zone were recalculated from Robertson's coordinates using McWeeny scattering curves and including hydrogen atoms, as for the (hk0) zone. The value of R at this stage was 12.9%. Refinement again proceeded by $(F_o - F_c)$ synthesis, with adjustment of the positional and temperature parameters; the initial and final $(\rho_o - \rho_c)$ maps and the hydrogen synthesis are shown in Fig.3a, b, 4b. As in the (001) projection, the hydrogen

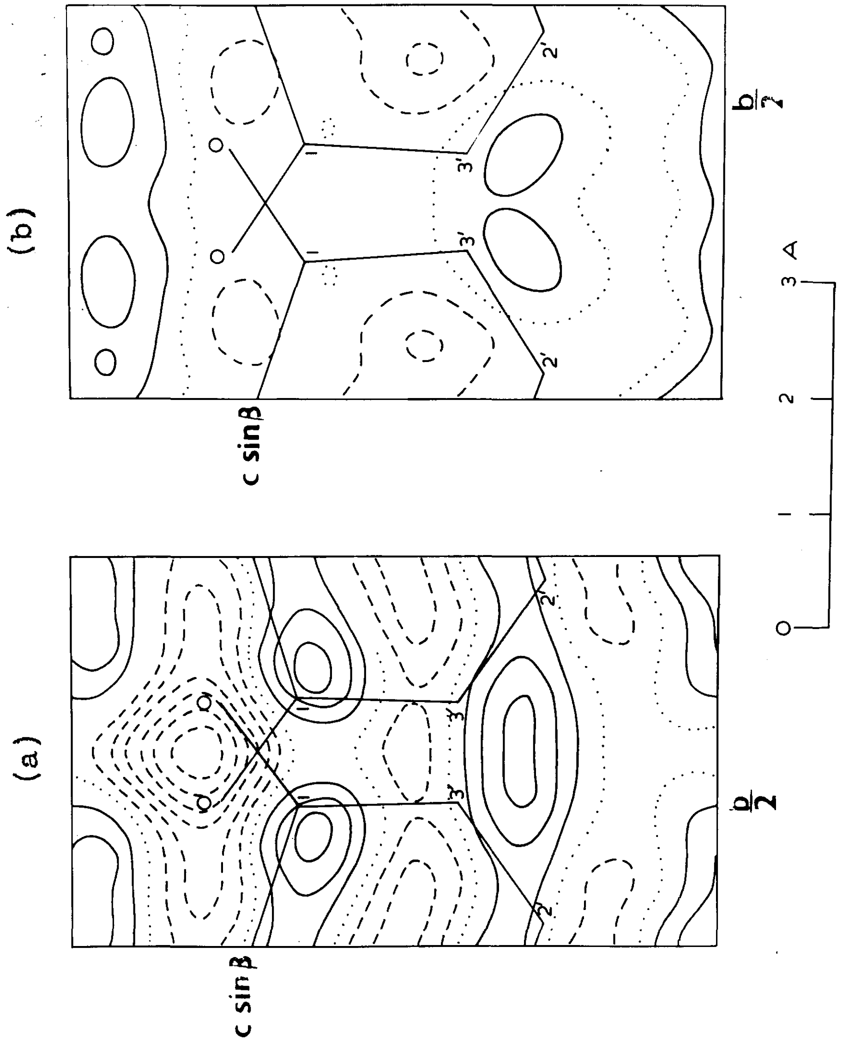
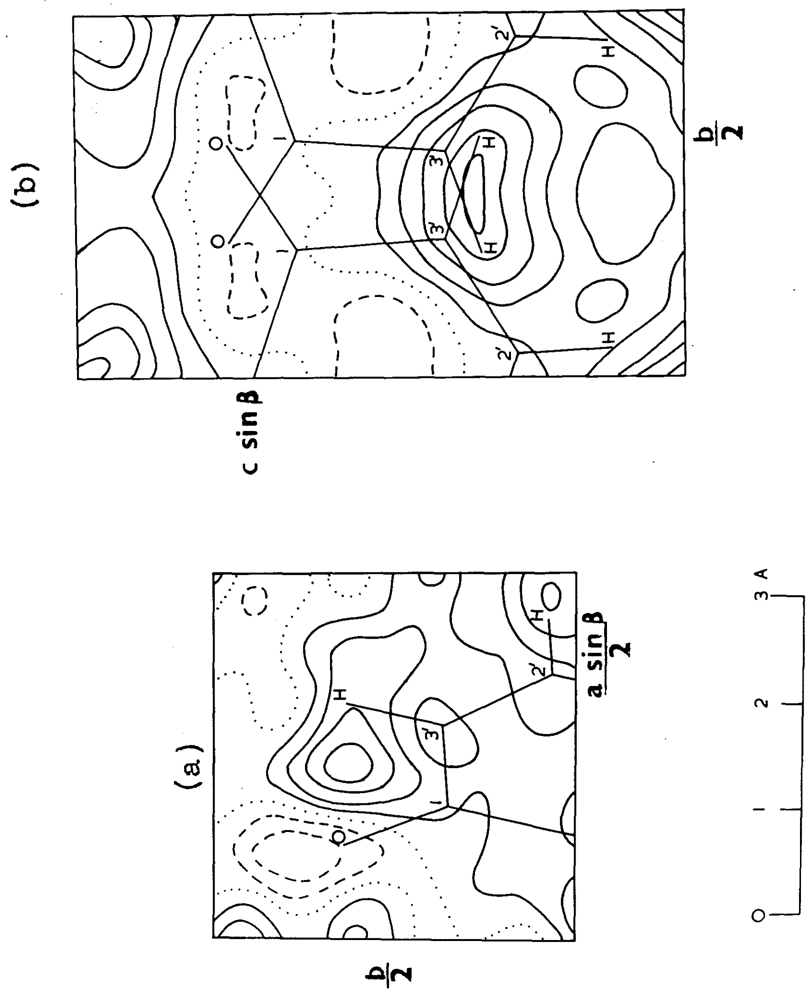


Fig.3. (a) Initial and (b) Final ($F_o - F_c$) syntheses, ($0k\ell$) zone. Contours as in Fig.2.



<u>Fig.4</u>. Hydrogen syntheses. (a), $(hk0)$ zone; (b), $(0k\ell)$ zone. Only carbon and oxygen atoms subtracted. Contours as in Fig.2.

atoms were poorly resolved, and no accurate assignment of coordinates was possible. The final value of R for this zone was 7.7%.

2.4. (010) projection.

Due to the great amount of overlap in this projection no detailed refinement was attempted. Structure factors were calculated from the x and z coordinates obtained from the (001) and (100) projections; the discrepancy was reduced from 21% (Robertson's coordinates and McWeeny scattering curves) to 15.3%. Including the $(20\bar{1})$ plane at its calculated value to allow for a secondary extinction error, R was 10.9%.

Compared with the original X-ray structure determination, only one term - (240) - has changed sign. The values of the measured and calculated structure factors are given in Table 4 (page 32).

2.5. Coordinates, molecular dimensions and orientation.

The final coordinates and temperature parameters of the carbon and oxygen atoms are given in Table 1. The coordinates x, y, z are referred to the monoclinic axes and are expressed as fractions of the unit cell edge, with the centre of symmetry as origin, and the coordinates X', Y, Z' to orthogonal axes a', b and c, a' being taken perpendicular to the b and c crystal axes, so that

$$X' = X.\sin\beta, \qquad Z' = Z + X.\cos\beta.$$

These coordinates are expressed in Angstrom units.

Table 1.

Coordinates and temperature parameters.

Atom	x	y	z	X'	Y	Z'	B_{hk0}	B_{0kl}
C(1)	0.0669	0.1753	0.1410	0.461	1.190	0.724	3.5	4.8
C(2)	0.1101	-0.0321	0.2240	0.760	-0.218	1.144	4.9	4.8
C(3')	-0.0420	0.1882	-0.1049	-0.290	1.278	-0.549	4.8	4.8
O	0.1226	0.3175	0.2537	0.846	2.156	1.300	6.0	4.8

It is found that the coordinates of the atoms can be fitted to an equation of the form

$$X' + BY + CZ' = 0.$$

B and C were determined by the method of least squares to be -0.0153 and -0.6328 respectively. The perpendicular distances of the atoms from this mean molecular plane are given in Table 2.

Table 2.

Deviations from the mean plane.

Atom	Displacement from plane (A).
C(1)	-0.013
C(2)	0.033
C(3')	0.032
O	-0.008

The maximum deviation is 0.033 A, and the mean deviation is

0.022 A. These deviations from strict planarity are probably not significant (the accuracy of the structure determination will be discussed later).

The bond lengths and valency angles in the p-benzoquinone molecule, calculated from the coordinates of Table 1, are shown in Fig.5a; Fig.5b shows the molecular dimensions after averaging over chemically-equivalent bonds and angles.

The orientation of the molecule in the crystal may be indicated by giving the angles χ, ψ and ω, which the lines L, M (Fig.5a) and the plane normal N make with the axes a', b and c. L and M are taken to be in the mean plane of the molecule, L passing through the atoms C1 and C1', and M perpendicular to L. These values are given in Table 3. The previous values of the orientation angles are included for comparison.

Table 3.

Orientation of the molecule in the crystal.

$\chi_L = 71^\circ\ 14'\ (72.6^\circ)$ $\cos\chi_L = 0.3217$
$\psi_L = 35^\circ\ 48'\ (36.9^\circ)$ $\cos\psi_L = 0.8112$
$\omega_L = 60^\circ\ 44'\ (59.3^\circ)$ $\cos\omega_L = 0.4888$

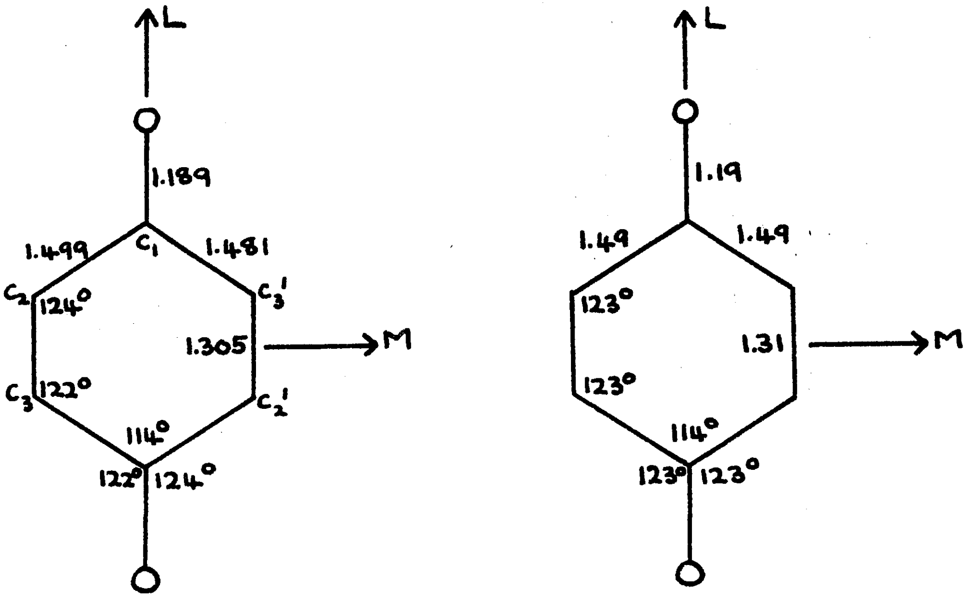
$\chi_M = 64^\circ\ 42'\ (65.7^\circ)$ $\cos\chi_M = 0.4274$
$\psi_M = 125^\circ\ 48'\ (126.9^\circ)$ $\cos\psi_M = -0.5849$
$\omega_M = 46^\circ\ 24'\ (46.6^\circ)$ $\cos\omega_M = 0.6895$

$\chi_N = 32^\circ\ 20'\ (30.5^\circ)$ $\cos\chi_N = 0.8450$
$\psi_N = 90^\circ\ 44'\ (89.5^\circ)$ $\cos\psi_N = -0.0129$
$\omega_N = 122^\circ\ 19'\ (120.5^\circ)$ $\cos\omega_N = -0.5347$

2.6. Discussion of structure and molecular dimensions.

Due to the great amount of overlap in all the projections the formulae developed by Cruickshank (1949, 1954) for estimating the accuracy of a crystal structure determination are not applicable here. However from the consistency of the values of the bond lengths and valency angles of chemically identical but crystallographically different bonds and angles, it can be estimated that the bond lengths are probably accurate to within ± 0.03 A, and the valency angles to within $\pm 2^\circ$.

The maximum displacement of the atoms from the mean



(a) (b)

Fig.5. (a) Bond lengths and valency angles calculated from atomic coordinates.

(b) Bond lengths and valency angles after averaging over chemically-equivalent bonds and angles.

plane of the molecule is 0.03 A; this displacement is probably not significant, and it is likely that the molecule is strictly planar. The bond lengths and valency angles in the p-benzoquinone molecules are very similar to those in related compounds, some of which are shown in Fig.5c (see Allen and Sutton, 1950). The bond orders in p-benzoquinone have been calculated by molecular orbital methods (Goodwin, 1956), but these bond orders cannot easily be related to bond lengths due to unreliability of the bond order - bond length correlation curves in the regions of bond order involved. This is especially true for the C - O bond; Cox and Jeffrey (1951) list C = O lengths varying between 1.14 A (acetone) and 1.22 A (formaldehyde) with a mean value of 1.185 A (in good agreement incidentally with the value found in this investigation), so that a family of correlation curves is required passing through double bond points ranging from 1.14 to 1.22 A, and converging towards the single bond end. Walsh (1947) has arranged C = O bonds in order of polarity.

The correlation curve for C - C bonds is more firmly established; calculated bond orders and bond lengths are shown below for comparison with the observed bond lengths:

Bond	Bond order	Bond length (calc.)	Bond length (obs.)
C_1-O	-	1.14 - 1.22	1.19
C_1-C_2	0.310	1.485	1.49
C_2-C_3	0.904	1.35	1.31

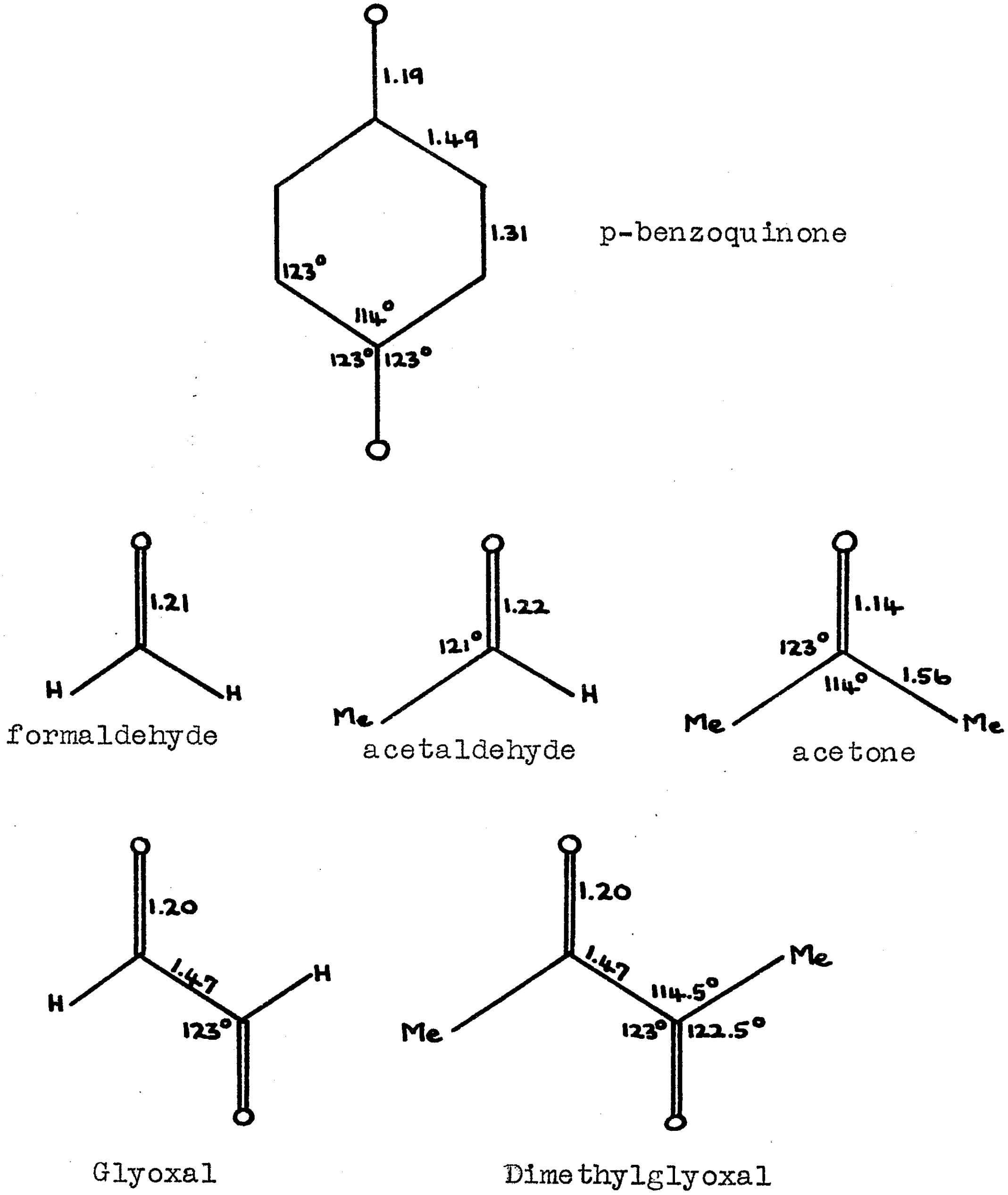


Fig.5c. Bond lengths and valency angles in p-benzoquinone and related molecules.

The observed length of the C = C bond (1.31 A) is rather less than the accepted value for a double bond, and this may be due to small errors in the positions of atoms C_2 and C_3, which also deviate by the greatest amount from the mean molecular plane. In the present refinement, no allowance has been made for anisotropic thermal motion of the atoms, and no rotational oscillation corrections have been applied (Cruickshank, 1956a, b). These factors would have to be taken into account in a full three-dimensional refinement, and they would increase all the bond lengths by small amounts. The molecular dimensions obtained in the present investigation are in good agreement with those of the electron-diffraction investigation of the vapour (Fig.1, page 15); the largest discrepancy is in the C - O distance, but even here the difference appears to be within the limits of experimental error.

All intermolecular approach distances correspond to normal van der Waals interactions. The closest distance of approach between the oxygen atoms of neighbouring molecules occurs between the molecule at (0, 0, 0) and that at ($\frac{1}{2}$, $\frac{1}{2}$, 0), where the distance is 3.57 A. Between carbon and oxygen atoms the distances are slightly smaller, the closest approach being 3.32 A, and between carbon and carbon the minimum distance is 3.45 A. These intermolecular contacts are illustrated in Fig.6.

This completes the present two-dimensional refinement of the structure of p-benzoquinone. Since the number of reflexions in the axial zones is rather small, more accurate molecular dimensions could be obtained only by a three-dimensional analysis.

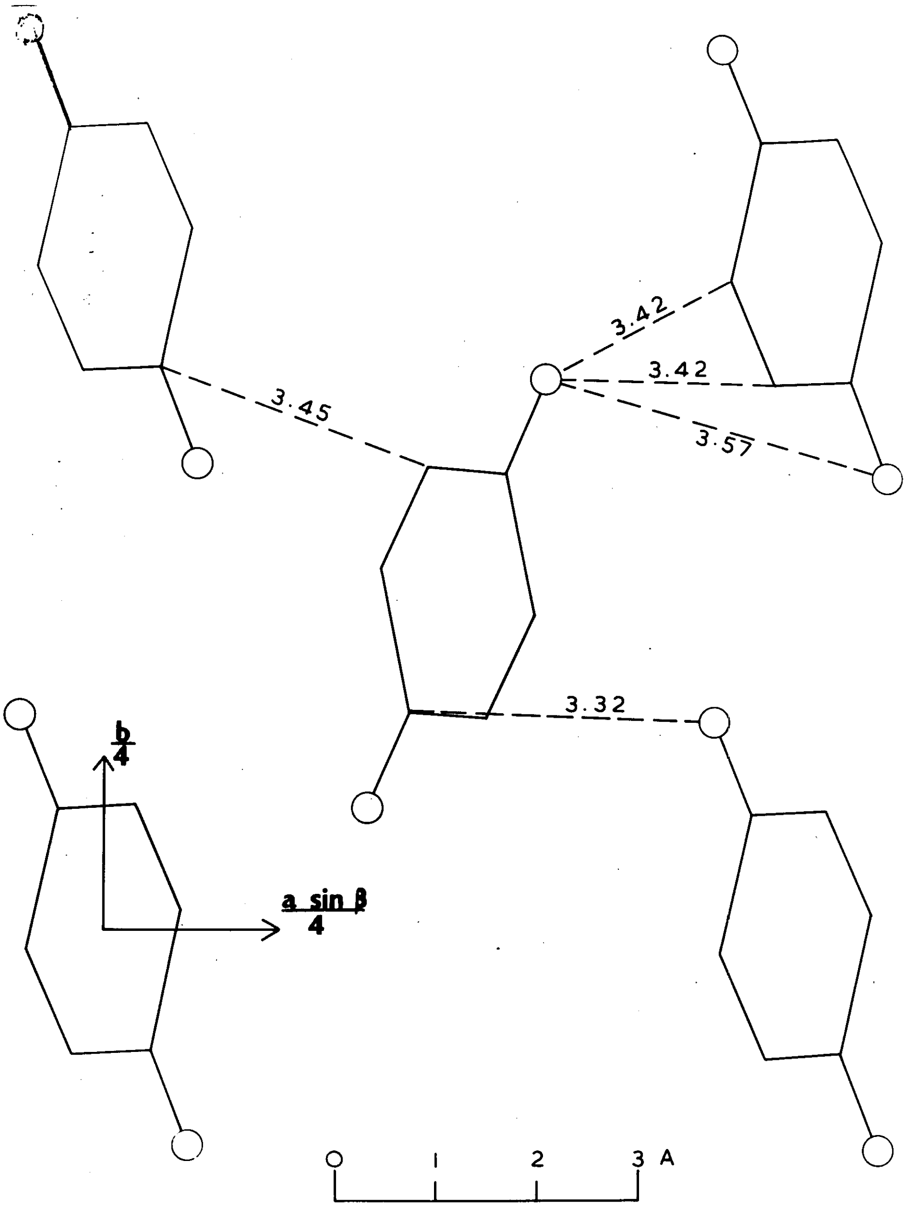


Fig.6. Arrangement of molecules in the (001) projection.

Table 4.

Observed and calculated structure factors.

hkℓ	F_o	F_c	hkℓ	F_o	F_c
000	-	112	031	8.9	9.3
200	31.2	29.3	2	<5.6	-1.2
4	12.1	-14.9	3	7.3	-6.5
6	4.6	-4.8	4	<7.3	-1.9
020	23.0	-21.7	5	<7.3	1.5
4	1.6	1.7	041	<6.2	-0.6
6	10.0	9.1	2	<6.7	-1.9
001	28.6	31.4	3	<7.3	-0.2
2	33.8	-34.3	4	<7.3	1.5
3	15.6	-13.6	051	7.8	8.1
4	<2.2	2.4	2	<7.3	1.8
5	2.2	-2.0	3	<7.3	-3.9
			061	<7.3	3.1
011	20.2	-20.6	2	<7.3	-3.4
2	4.3	2.9			
3	12.7	14.1	$20\bar{5}$	<2.3	1.1
4	<6.7	2.2	$\bar{4}$	7.6	-7.9
5	<7.3	-1.4	$\bar{3}$	18.8	-20.7
021	13.9	-13.0	$\bar{2}$	13.7	14.9
2	<5.0	1.8	$\bar{1}$	59.6	74.9
3	<6.2	2.7	1	31.4	-31.4
4	<7.3	3.4	2	19.5	-14.1
5	<7.3	4.1	3	<2.3	3.0

hk	F_o	F_c	hk	F_o	F_c
204	3.9	-2.2	210	18.5	-18.4
5	6.6	-4.5	2	11.1	-11.1
$40\bar{5}$	3.3	-3.9	3	7.2	7.8
$\bar{4}$	6.2	-9.2	4	1.8	-1.3
$\bar{3}$	4.4	5.0	5	6.6	6.8
$\bar{2}$	28.0	29.3	6	4.1	4.0
$\bar{1}$	17.0	14.4	310	2.1	2.9
1	11.5	-9.0	2	5.6	6.4
2	<2.3	2.5	3	13.9	-14.9
3	<2.3	-1.8	4	<1.7	0.2
4	5.1	-4.5	5	3.6	3.9
$60\bar{4}$	<3.5	1.5	6	1.4	2.3
$\bar{3}$	6.2	10.9	410	2.0	-1.0
$\bar{2}$	5.9	6.3	2	2.3	-0.4
$\bar{1}$	2.8	-5.9	3	<1.7	0.3
1	<2.3	1.4	4	<1.7	-1.7
2	<3.5	-1.1	5	1.7	1.7
			510	2.9	-2.6
110	23.7	22.7	2	1.9	-3.4
2	12.7	13.1	3	2.6	-3.7
3	<1.1	-0.9	4	<1.7	1.5
140	2.5	-2.1	610	<1.7	3.2
5	4.0	5.0	2	<1.7	0.7
6	3.4	2.7	3	<2.3	-2.0

3. REFINEMENT OF THE CRYSTAL STRUCTURE OF CORONENE.

3.1. Introduction.

The highly-symmetrical aromatic hydrocarbon coronene, $C_{24}H_{12}$, has a beautifully simple crystal structure, which is very suitable for detailed analysis. The crystal structure was determined by Robertson and White (1944, 1945) by trial methods, and refined by two-dimensional F_o syntheses. In the projection down the short b-axis all the carbon atoms in the molecule were clearly resolved, and it was possible to obtain accurate measurements of the bond lengths and other structural details. The agreement between the observed molecular dimensions and those obtained from theoretical investigations using the molecular orbital method (Coulson, 1944; Moffitt and Coulson, 1948) was extremely good. The present investigation describes some further refinement of the carbon atom parameters, and location of the hydrogen atoms, using $(F_o - F_c)$ syntheses.

Crystal data. Coronene, $C_{24}H_{12}$; M, 300.3; m.p. 434-436°; d, calc. 1.381, found 1.377; monoclinic, $a = 16.10 \pm 0.05$, $b = 4.695 \pm 0.005$, $c = 10.15 \pm 0.05$ A, $\beta = 110.8^\circ \pm 0.2^\circ$. Absent spectra, $(h0\ell)$ when h is odd; $(0k0)$ when k is odd. Space group, C_{2h}^5 $(P2_1/a)$. Two molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell, 717.1 A^3. Absorption coefficient for

X-rays, $\lambda = 1.542$ A, $\mu = 7.30$ cm^{-1}. Total number of electrons per unit cell = F(000) = 312.

3.2. Refinement of (010) projection.

Structure factors for the $(h0\ell)$ zone reflections were recalculated from the final coordinates of Robertson and White, using McWeeny's scattering curve for carbon corrected for thermal vibration by the factor $\exp\left\{-B(\sin\theta/\lambda)^2\right\}$ with B = 3.5. In the final F_o synthesis, there is distinct evidence in the one-electron contour of resolution of hydrogen atoms, and a contribution from the hydrogen atoms was included in the calculated structure factors. Approximate coordinates were obtained by assuming C - H distances of 1.0 A, and McWeeny's curve for hydrogen with B = 4.2 was used. The agreement between the observed and calculated values of the structure factors was 12.2%, compared with 14.0% using an empirical curve.

Further refinement of atomic coordinates and temperature parameters of the carbon atoms was now carried out by evaluating successive Fourier difference syntheses, with $(F_o - F_c)$ as coefficients. Coordinate adjustments were first made until the electron-density slope at the atomic centres became zero, and the temperature factors B were then adjusted to decrease $(\rho_o - \rho_c)$ at the atomic centres.

The first $(F_o - F_c)$ synthesis is shown in Figure 7a.

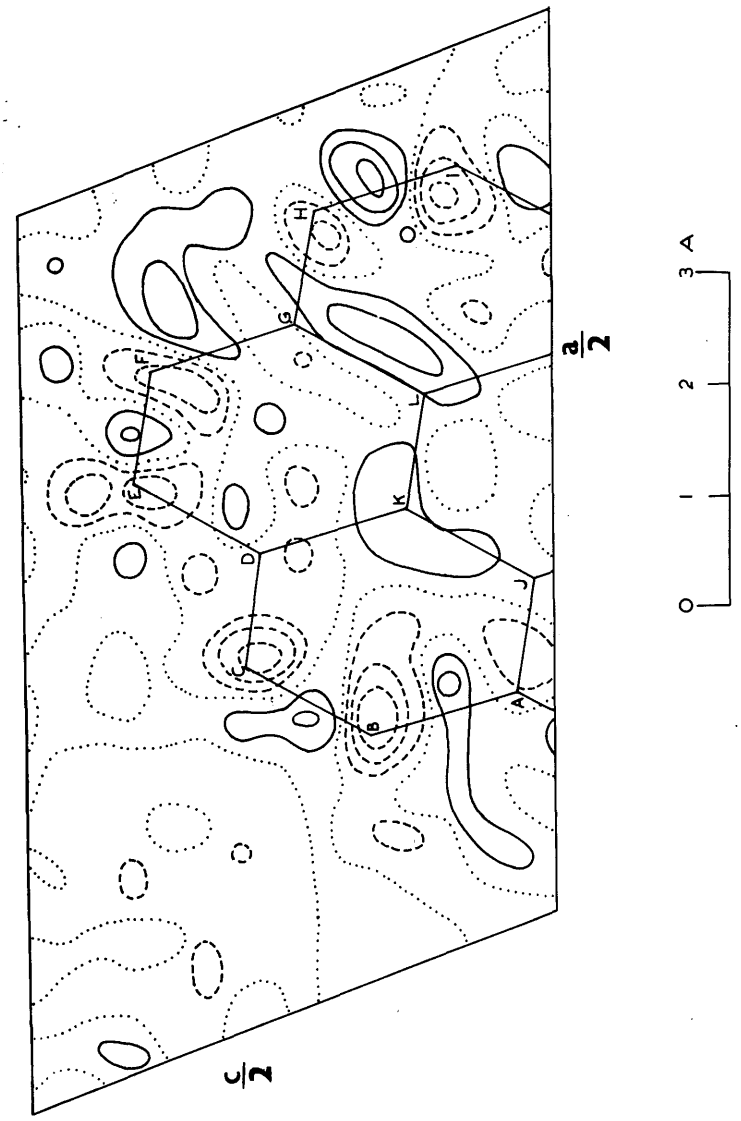


Fig.7a. First (F_o - F_c) synthesis, ($h0\ell$) zone. All atoms, including hydrogen, subtracted. Contour interval 0.2 eA^{-2}, negative contours broken, zero contour dotted.

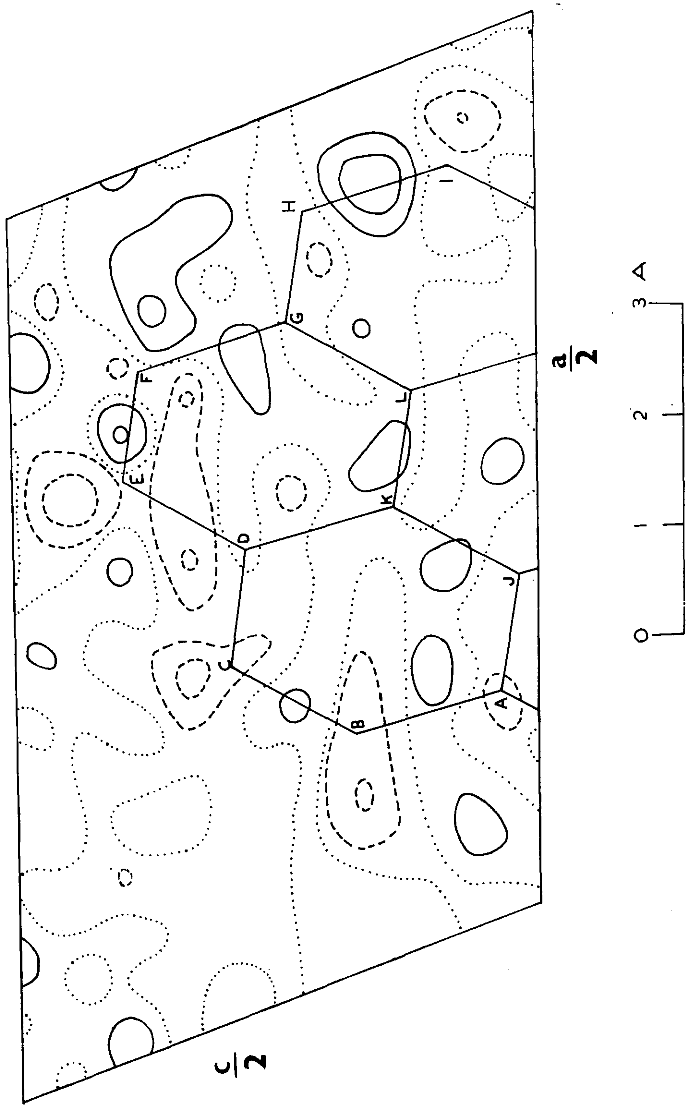


Fig.7b. Final ($F_o - F_c$) synthesis, (h0ℓ) zone. All atoms, including hydrogen, subtracted. Contours as in Fig.7a.

An outstanding feature of this map is the clear indication of thermal vibration increasing with distance from the centre of the molecule, showing that the molecule is vibrating about its centre. The temperature factor used at this stage (B = 3.5) is appropriate to the thermal vibrations of atoms A, D, and G; atoms B, C, E, F, H, I require a larger, and atoms J, K, L a smaller value of B.

After the positional and temperature parameters of the carbon atoms had been adjusted, the final $(\rho_o - \rho_c)$ map was computed (Fig.7b). It represents the difference between the electron distribution existing in the crystal and that calculated for carbon and hydrogen atoms, at their appropriate positions in the unit cell. During the refinement procedure similar vibrational parameters were used for chemically identical atoms, and no allowance was made for anisotropic thermal motion, so that the electron density is not quite zero at the position of every carbon atom, and there are density fluctuations due to thermal anisotropy. This final difference map has regions of positive electron-density at the centre of each carbon-carbon bond, and the sharpness of these peaks indicates that they cannot be assigned to bonding electrons, but rather are due to anisotropic thermal vibration of the molecule as a whole, about the normal to the molecular plane.

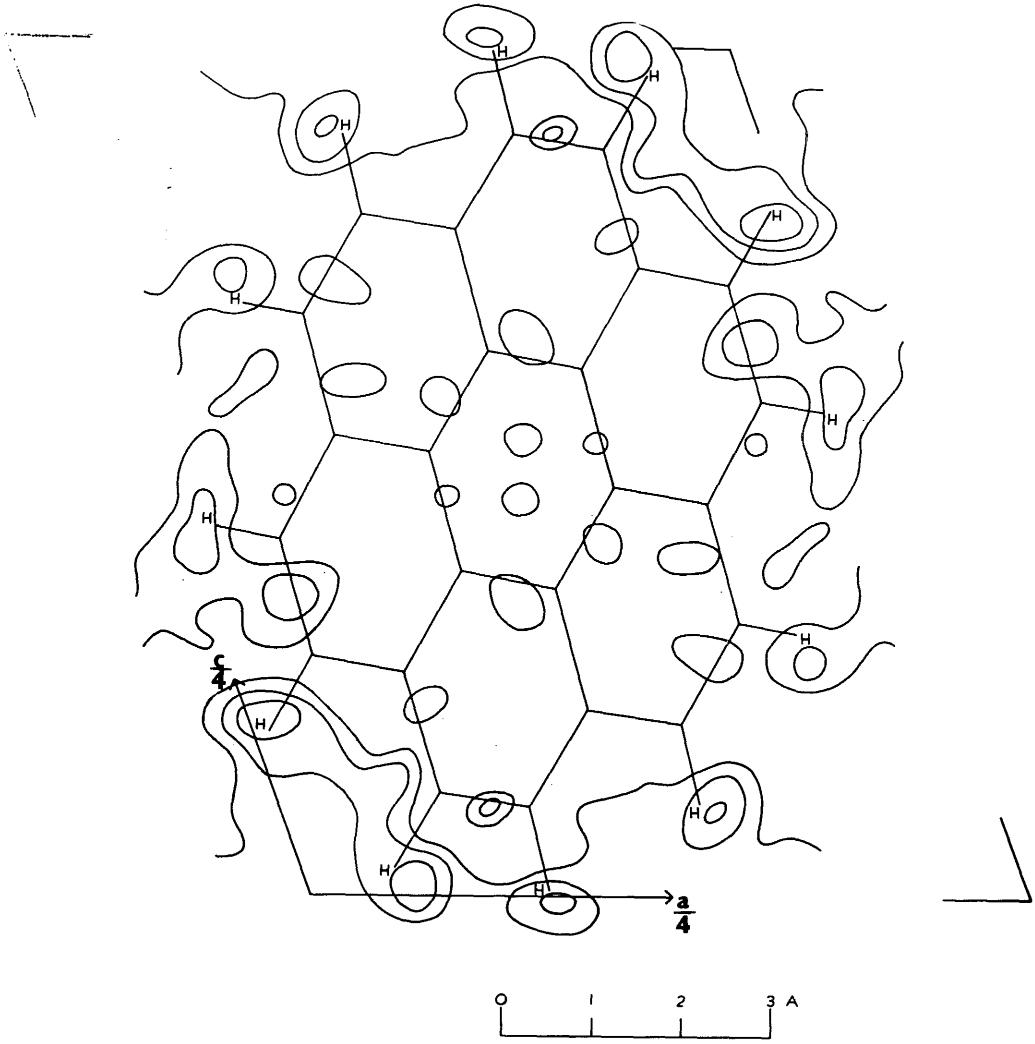


Fig.8. Hydrogen synthesis. Difference-synthesis projection on (010), showing the electron distribution due to hydrogen atoms. Contours at intervals of 0.2 eA^{-2}, starting at 0.4 eA^{-2}.

A difference synthesis projection on (010) showing the electron distribution due to hydrogen was computed (Fig.8). This map represents the difference between the electron distribution existing in the crystal, and that calculated for carbon atoms only, at the appropriate positions in the unit cell. All the hydrogen atoms in the molecule are clearly resolved.

The final value of R for the $(h0\ell)$ structure factors was 10.2%.

3.3. Coordinates, molecular dimensions, and orientation.

The projection of the structure on (010) allows two coordinates for each atom to be determined, but of course gives no information about the third coordinate (y). It was assumed that the whole molecule is planar, and the orientation of the molecule, the third coordinate, and the molecular dimensions were determined as in the original investigation.

The orientation of the molecule in the crystal may be indicated by giving the angles χ, ψ and ω, which the directions L, M (Fig.9, page 43) and the plane normal N make with the a and b crystal axes, and their perpendicular c'. These values are given in Table 5. The previous values of the orientation angles are included for comparison.

The mean plane of the molecule has equation of the form

$$Y = AX' + BZ',$$

Table 5.

Orientation of the molecule in the crystal.

$\chi_L = 84.4^\circ \quad (84.8^\circ) \qquad \cos\chi_L = 0.0971$

$\psi_L = 85.9^\circ \quad (85.6^\circ) \qquad \cos\psi_L = 0.0714$

$\omega_L = 7.9^\circ \quad (6.9^\circ) \qquad \cos\omega_L = 0.9904$

$\chi_M = 43.5^\circ \quad (44.2^\circ) \qquad \cos\chi_M = 0.7250$

$\psi_M = 47.3^\circ \quad (46.7^\circ) \qquad \cos\psi_M = 0.6782$

$\omega_M = 96.9^\circ \quad (96.8^\circ) \qquad \cos\omega_M = -0.1200$

$\chi_N = 133.0^\circ \quad (133.7^\circ) \qquad \cos\chi_N = -0.6819$

$\psi_N = 43.0^\circ \quad (43.7^\circ) \qquad \cos\psi_N = 0.7315$

$\omega_N = 89.9^\circ \quad (89.6^\circ) \qquad \cos\omega_N = 0.0014$

where the coordinates X', Y and Z' are referred to the orthogonal axes a, b and c'. A and B were determined from the direction cosines of the plane normal to be 0.9322 and -0.0019 respectively. Y-coordinates for the atoms were now calculated from the equation of the mean plane of the molecule. The final coordinates of the carbon atoms are given in Table 6. The coordinates x, y, z are referred to the monoclinic crystal axes, and are expressed as fractions of the unit cell edges. The temperature factor B for each atom is also given.

The coordinates of Table 6 were used for calculation of the structure factors of the (hk0) reflections, using B=3.9 for all the carbon atoms and 4.2 for the hydrogen atoms.

Table 6.

Coordinates and temperature factors.

Atom	x	y	z	X'	Y	Z'	B
A	-0.121	-0.412	0.036	-2.074	-1.934	0.345	3.5
B	-0.113	-0.488	0.175	-2.456	-2.292	1.657	4.4
C	-0.049	-0.367	0.294	-1.845	-1.725	2.785	4.4
D	0.013	-0.157	0.278	-0.787	-0.739	2.640	3.5
E	0.078	-0.034	0.394	-0.163	-0.159	3.739	4.4
F	0.136	0.163	0.378	0.830	0.767	3.583	4.4
G	0.132	0.251	0.238	1.269	1.179	2.262	3.5
H	0.191	0.452	0.221	2.280	2.121	2.093	4.4
I	0.184	0.531	0.082	2.674	2.492	0.778	4.4
J	-0.060	-0.204	0.018	-1.028	-0.958	0.170	3.35
K	0.006	-0.080	0.138	-0.400	-0.375	1.311	3.35
L	0.067	0.129	0.119	0.650	0.604	1.133	3.35

The discrepancy R was 10.4%. The observed and calculated values of the structure factors of the (h0ℓ) and (hk0) reflexions are listed in Table 11 (page 51).

3.4. Discussion of structure and molecular dimensions.

The bond lengths in the coronene molecule were calculated from the projected bond lengths on (010) and the molecular orientation angles. These values after averaging over chemically equivalent bonds are shown in Fig.9. The maximum difference between an individually-determined bond length and the mean value for that bond is 0.03 A, and the average difference between the observed and mean value of a bond length for all the bonds is 0.015 A.

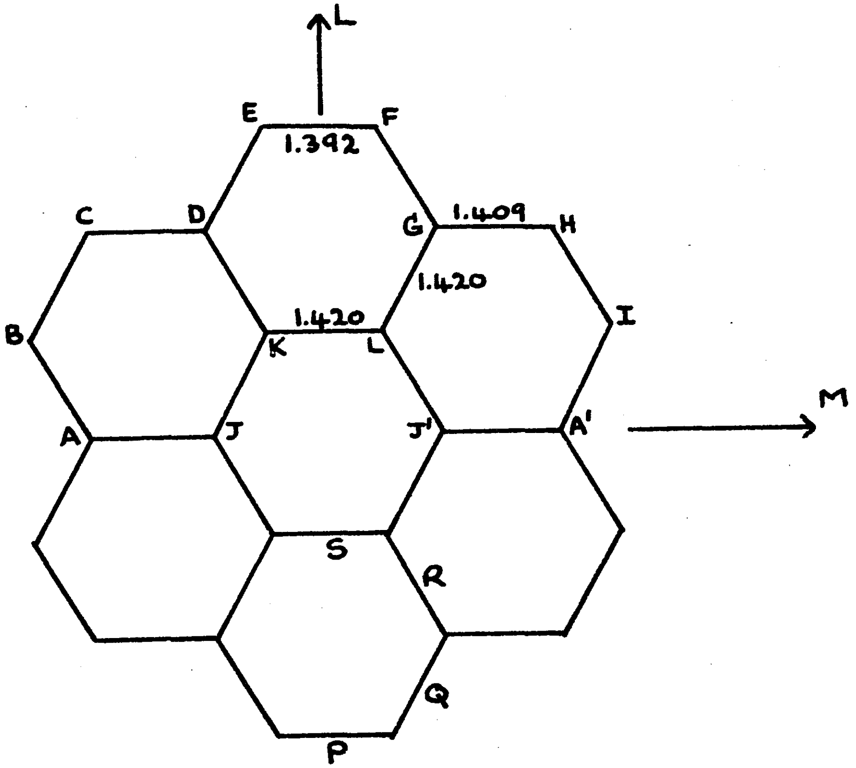


Fig.9. Dimensions of the coronene molecule.

Table 7.

Observed and calculated bond lengths in the coronene molecule (A).

	M.O.	R.W.	Δ_1	Present	Δ_2
P	1.372	1.385	0.013	1.392	0.020
Q	1.411	1.415	0.004	1.409	-0.002
R	1.411	1.430	0.019	1.420	0.009
S	1.415	1.430	0.015	1.420	0.005
Root mean square Δ over the whole molecule			0.013A		0.009A

Δ_1 = (Robertson and White) - (Molecular Orbital).

Δ_2 = (Present investigation) - (Molecular Orbital).

In Table 7 the observed bond lengths are compared with the values of the previous investigation and with those calculated by the molecular orbital method. The agreement between the observed and theoretically-determined bond lengths is extremely good, and the present refinement process has decreased somewhat the discrepancies between the observed and calculated values.

The coordinates of the hydrogen atoms are given in Table 8. These coordinates were obtained by assuming C-H bond lengths of 1.0 A, and were used in the structure factor calculations.

Table 8.

Coordinates of the hydrogen atoms.

Atom	x	y	z
H B	-0.152	-0.621	0.187
C	-0.042	-0.414	0.388
E	0.083	-0.087	0.491
F	0.185	0.256	0.467
H	0.239	0.540	0.310
I	0.225	0.666	0.073

Fig.8 shows fairly good resolution of the hydrogen atoms, but residual density on the final difference map (Fig.7b) disturbs the positions of the hydrogen peaks, and accurate parameters cannot be assigned from the hydrogen map. The final (F_o - F_c) synthesis could be further improved by introducing anisotropic vibration factors, but the hydrogen peaks would probably still be distorted by spurious residual density, due to random errors in the F_o values.

3.5. Estimation of accuracy.

The standard deviation of an atomic coordinate, $\sigma(x)$, was calculated by the formula given by Cruickshank (1949, 1954):

$$\sigma(x_n) = \frac{2\pi\left\{\sum_2 h^2 (F_o - F_c)^2\right\}^{1/2}}{a.\ A.\ C_n}$$

for a two-dimensional synthesis

where C_n is the curvature $\partial^2\rho/\partial x^2$, at the centre of the n^{th} atom. The electron distribution of the peaks in a Fourier synthesis may be represented by the expression (Costain, 1941):

$$\rho = \rho_0 \cdot \exp\left[-pr^2\right]$$

where p and ρ_0 are constants; these constants were determined from a plot of $\ln\rho$ against r^2, and the central curvature of the atoms then computed from the expression:

$$\left(\frac{\partial^2\rho}{\partial r^2}\right)_{r=0} = -2p\rho_0$$

From the final Fourier synthesis for the (h0ℓ) zone, the mean values of p and ρ_0 were $p = 3.8$, $\rho_0 = 7.2$. From the final values of $\Delta F = F_o - F_c$ for the (h0ℓ) zone structure factors, $\sigma(x)$ and $\sigma(z)$ were calculated:

$$\left.\begin{aligned}\sigma(x) &= 0.0081 \text{ A}\\ \sigma(z) &= 0.0107 \text{ A}\end{aligned}\right\} \quad \text{Mean } \sigma = 0.0094 \text{ A.}$$

From the (hk0) data, $\sigma(y) = 0.049$ A, which is much greater than $\sigma(x)$ and $\sigma(z)$. (Cruickshank's formulae however are not really applicable in this zone, because of the great amount of overlap.)

Now, in comparing the bond lengths in the coronene molecule with some standard set of bond lengths, the appropriate σ is the root mean square of $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$. However the errors in the y-coordinates are not random and unrelated, since they have been calculated from the equation of the molecular plane (making the reasonable assumption that the whole molecule is completely planar); any slight error in this equation is reflected in all the y-coordinates, so that $\sigma(y)$ might be given a reduced weight.

In the present investigation the chief interest lies in whether the bond length variations within the molecule are significant, and for this purpose $\sigma(y)$ has been neglected, since a small change in the equation of the molecular plane will alter all the bond lengths by small amounts, and the small changes in different bond lengths will be proportional.

The standard deviation of an individual bond length is given by $\sigma(d_{12}) = \sqrt{2}$ (Mean σ) = 0.013 A. Since the final length of each bond has been determined by averaging over chemically equivalent bonds, the standard deviation of the final bond lengths is given by:

$$\sigma(d_{12})_{\mathrm{mean}} = \frac{\sigma(d_{12})}{\sqrt{n}}$$

where for any bond n = number of chemically equivalent but crystallographically different bonds of this type. These values are given in Table 9.

Table 9.

Standard deviation of bond lengths.

Bond	n	$\sigma(d_{12})$	$\sigma(d_{12})_{mean}$
P	3	0.013 A	0.0075 A
Q	6	0.013	0.0053
R	3	0.013	0.0075
S	3	0.013	0.0075

In comparing the measured lengths of chemically non-equivalent bonds, the total estimated standard deviation $\sigma(t)$ was taken as:

$$\sigma(t) = \left\{\sigma^2(d_{12}) + \sigma^2(d_{34})\right\}^{\frac{1}{2}}$$

The results of this statistical analysis of the bond length variations within the coronene molecule are given in Table 10.

The final two columns of Table 10 indicate that bonds of type P are significantly shorter than the other bonds in the molecule. The difference between bonds Q and bonds R or S is however of doubtful significance; the probability that these bonds should be so much different by chance is 0.1151. Bonds R and S are of course not significantly different. It seems then that the observed bond length variations within the coronene molecule are of some significance.

Table 10.

Significance tests.

Bonds	Individual est.		$\sigma(t)$	Diff. in bond length. Δ	$\Delta/\sigma(t)$	P	Conclusion
	s. d. (A)		(A)	(A)			
P Q	0.0075	0.0053	0.0092	0.017	1.85	0.0322	Poss. signif.
P R, S	0.0075	0.0075	0.0106	0.028	2.64	0.0041	Signif.
Q R, S	0.0053	0.0075	0.0092	0.011	1.20	0.1151	Not signif.
R S	0.0075	0.0075	0.0106	0	0.00	-	Not signif.

The final ($F_o - F_c$) map (Fig.7b, page 37) shows peaks corresponding to rotational oscillations of the molecule about the normal to the molecular plane. Slight corrections are necessary to allow for these angular oscillations, which cause the atoms to appear too close to the centre of the molecule (Cruickshank, 1956a, b). Since no anisotropic factors have been introduced in the present analysis, no allowance has been made for these oscillations. The effect of the small corrections is to increase all the bond lengths slightly.

The present refinement has led to improved agreement between measured and calculated molecular dimensions, and the hydrogen synthesis (Fig.8, page 39) shows reasonable resolution of all the hydrogen atoms in the molecule.

Table 11.

Measured and calculated structure factors.

hkℓ	F_o	F_c	hkℓ	F_o	F_c
000	-	312	0011	2	-2
200	67	69	12	6	-4
4	31	-33	1401	<2	-3
6	7	6	12	5	-4
8	<2	-1	10	7	8
10	5	4	8	10	-9
12	6	-5	6	6	-5
14	6	7	4	23	21
16	17	16	2	33	-33
18	<2	1	$\bar{2}$	59	55
020	17	22	$\bar{4}$	31	-30
4	<8	-1	$\bar{6}$	13	14
001	61	60	$\bar{8}$	<2	0
2	30	-30	$\overline{10}$	<2	3
3	8	10	$\overline{12}$	<2	-1
4	2	-1	$\overline{14}$	<2	-2
5	8	9	$\overline{16}$	23	23
6	8	-7	$\overline{18}$	13	13
7	7	7	1802	<1	1
8	13	11	16	<2	2
9	7	-4	14	<2	2
10	4	2	12	<2	0

hkℓ	F_o	F_c
1002	5	6
8	17	-18
6	49	-52
4	4	-4
2	12	12
$\bar{2}$	29	-30
$\bar{4}$	24	-26
$\bar{6}$	21	21
$\bar{8}$	8	-9
$\overline{10}$	21	-20
$\overline{12}$	5	5
$\overline{14}$	3	-1
$\overline{16}$	<2	-1
$\overline{18}$	7	4
$\overline{20}$	<1	1
1603	<2	0
14	<1	1
12	<2	0
10	<2	1
8	<2	-2
6	18	-18
4	16	-15
2	2	1
$\bar{2}$	27	29

hkℓ	F_o	F_c
$\bar{4}03$	14	17
$\bar{6}$	5	5
$\bar{8}$	10	-11
$\overline{10}$	40	-40
$\overline{12}$	14	-15
$\overline{14}$	4	3
$\overline{16}$	<2	2
$\overline{18}$	<2	2
1604	<1	0
14	6	-7
12	10	-12
10	3	-3
8	<2	2
6	6	7
4	10	11
2	5	4
$\bar{2}$	18	-19
$\bar{4}$	16	-17
$\bar{6}$	3	0
$\bar{8}$	<2	-1
$\overline{10}$	3	-2
$\overline{12}$	5	-5
$\overline{14}$	3	1
$\overline{16}$	<2	1

$hk\ell$	F_o	F_c
$\overline{18}04$	2	1
$\overline{20}$	<1	2
1405	<2	1
12	8	-8
10	<2	-2
8	2	3
6	6	-7
4	7	-7
2	5	-8
$\overline{2}$	14	-11
$\overline{4}$	56	-59
$\overline{6}$	15	-13
$\overline{8}$	7	7
$\overline{10}$	4	1
$\overline{12}$	3	5
$\overline{14}$	<2	3
$\overline{16}$	<2	1
$\overline{18}$	<2	-4
$\overline{20}$	4	-5
1206	<2	0
10	<2	2
8	<2	3
6	<2	-5
4	11	11
206	5	6
$\overline{2}$	9	11
$\overline{4}$	11	-13
$\overline{6}$	8	-9
$\overline{8}$	8	8
$\overline{10}$	6	-6
$\overline{12}$	6	-6
$\overline{14}$	4	-6
$\overline{16}$	<2	-1
$\overline{18}$	<2	1
$\overline{20}$	6	-6
1207	<1	-1
10	<2	0
8	<2	1
6	6	-6
4	20	19
2	47	48
$\overline{2}$	6	-6
$\overline{4}$	6	5
$\overline{6}$	<2	2
$\overline{8}$	6	4
$\overline{10}$	6	-6
$\overline{12}$	7	10
$\overline{14}$	15	16

hkℓ	F_o	F_c
$\overline{16}07$	<2	-2
$\overline{18}$	2	0
1008	2	-2
8	<2	1
6	<2	1
4	5	-2
2	16	20
$\bar{2}$	2	-6
$\bar{4}$	<2	3
$\bar{6}$	<2	-1
$\bar{8}$	<2	2
$\overline{10}$	3	-3
$\overline{12}$	6	4
$\overline{14}$	28	28
$\overline{16}$	12	12
$\overline{18}$	<2	-2
809	7	-6
6	<2	1
4	<2	-1
2	7	-4
$\bar{2}$	4	-4
$\bar{4}$	3	4
$\bar{6}$	3	-4
$\bar{8}$	6	-6
$\overline{10}$	2	3

hkℓ	F_o	F_c
$\overline{12}09$	<2	-3
$\overline{14}$	5	3
$\overline{16}$	5	6
$\overline{18}$	3	-2
6010	5	-3
4	<2	1
2	2	2
$\bar{2}$	<2	1
$\bar{4}$	<2	2
$\bar{6}$	6	-5
$\bar{8}$	15	-14
$\overline{10}$	4	-4
$\overline{12}$	<2	2
$\overline{14}$	3	-2
$\overline{16}$	2	-2
4011	<2	1
2	2	0
$\bar{2}$	<2	0
$\bar{4}$	<2	0
$\bar{6}$	<2	0
$\bar{8}$	3	-4
$\overline{10}$	3	-3
$\overline{12}$	<2	1
$\overline{14}$	<2	1
$\bar{2}012$	10	-9

hkℓ	F_o	F_c	hkℓ	F_o	F_c
$\bar{4}012$	4	-2	420	<6	-2
$\bar{6}$	<2	1	5	6	6
$\bar{8}$	2	1	6	5	0
$\overline{10}$	2	2	7	<7	4
110	11	13	8	8	-7
2	61	-68	9	<8	4
3	59	65	10	17	16
4	20	-20	11	15	12
5	<5	-6	12	<9	5
6	8	9	13	9	6
7	<6	2	14	9	-6
8	<7	-5	15	<7	-1
9	<7	-1	130	16	-17
10	<8	-2	2	<7	-1
11	<8	3	3	10	10
12	14	14	4	<7	0
13	21	21	14	<7	4
14	14	14	15	7	-4
15	<8	5	140	8	8
120	<5	-2	2	10	-9
2	10	-9	3	10	9
3	6	6	4	8	-7

PART III.

DINAPHTHOPEROPYRENE.

$C_{38}H_{18}$.

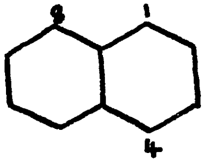
1. Overcrowded Aromatic Hydrocarbons.

In aromatic molecules each carbon atom forms three σ-bonds with neighbouring carbon and hydrogen atoms, using three sp^2 hybrid orbitals, which lie in one plane at 120° to each other. The axis of the p_z orbital of each carbon atom is normal to this plane, and overlap of these p_z orbitals leads to formation of π molecular orbitals; delocalisation of the π-electrons gives to aromatic compounds their characteristic properties. Maximum overlap of the p-atomic orbitals and maximum aromatic character will be obtained if the whole molecule is completely planar and hence the p_z atomic orbitals exactly parallel.

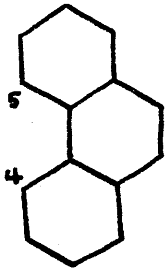
Investigation of aromatic molecules by X-ray diffraction and other techniques has demonstrated the strictly planar arrangement of atoms in the aromatic ring. Such molecules as benzene, naphthalene, anthracene, pyrene, coronene and ovalene are completely aromatic and exactly planar. These views may have to be modified slightly in view of the results of the most recent investigation of the anthracene structure. Mathieson, Robertson and Sinclair (1950) carried out an accurate three-dimensional analysis of anthracene, and found very small deviations of the atoms from strict planarity, the maximum deviation being about 0.010 A; a recent analysis by Cruickshank (1956b) has shown that this deviation is significant, and this slight molecular distortion is due to the close approach of a hydrogen atom of a neighbouring molecule in the crystal, and so is intermolecular in nature. The type of molecular distortion in the molecule which will be described in this section is very much more severe than this, and is intramolecular in nature.

There exist classes of aromatic structures in which the distance of closest approach between non-bonded atoms of the same molecule, calculated on the basis of conventional bond lengths and bond angles, and planar molecules, is smaller than the sum of the van der Walls radii of these atoms. The strain due to such abnormal approach distances is relieved by distortion of the molecule; 3:4-benzphenanthrenes (Newman and Wheatley, 1948) and 3:4:5:6-dibenzphenanthrenes (Bell and Waring, 1949) have been fully or partially resolved into optical isomers, and cannot therefore be planar molecules. Bell and Waring (1949) have suggested the term "intramolecular overcrowding" for this type of steric effect.

In directions close to the already existing bond directions however, the minimum approach distances are less than the van der Walls distance, and in particular, atoms which are bonded to the same atom can approach each other much more closely than the sum of the van der Waals radii without undue strain (Pauling, 1939).



I



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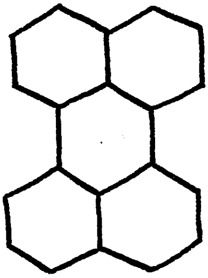
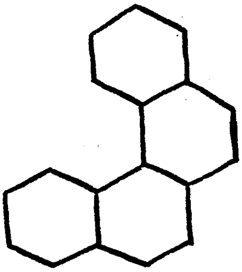


III



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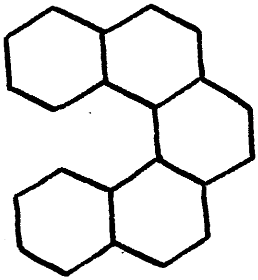
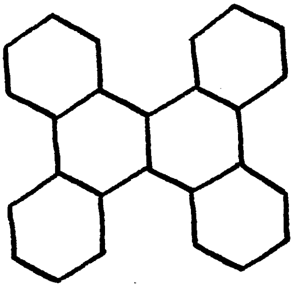


V



VI

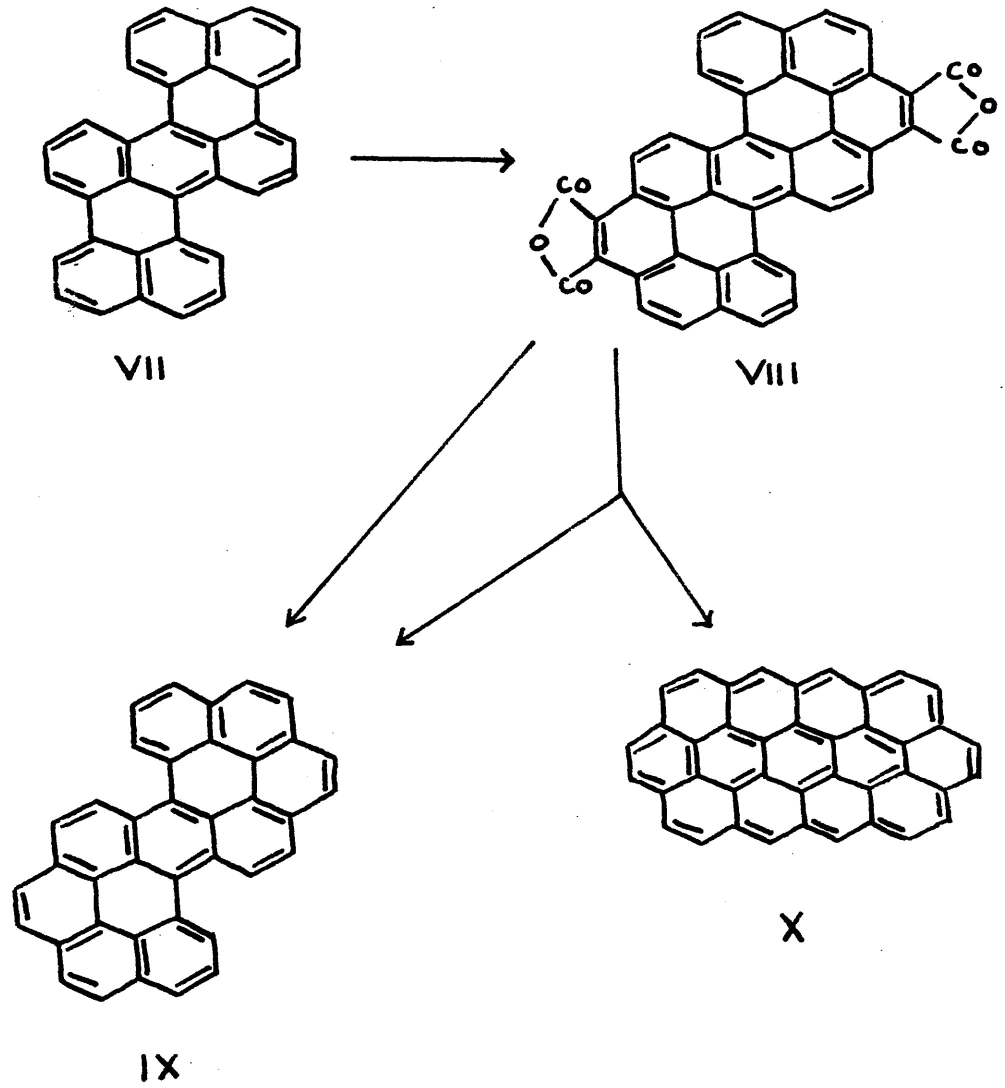
In naphthalene (I), for example, the distance between atoms 1 and 8 is only about 2.4 A, but this does not disturb the stability or planarity of the molecule; also atoms 1 and 4 are only about 2.8 A apart, but these atoms are part of the rigid aromatic framework, and do not cause any undue stress. In phenanthrene (II) atoms 4 and 5 are also separated by about 2.8 A, but in this case the hydrogen atoms attached to these carbons would be only 1.8 A apart on the basis of a planar molecule. The van der Waals radius of hydrogen is about 1.2 A, so that we might expect that these hydrogen atoms at least would deviate from the plane of the molecule; the carbon framework however does appear to be planar. Similar considerations apply to perylene (III) and, since this molecule has a dipole moment, the carbon skeleton may be slightly distorted from strict planarity; X-ray investigation (Donaldson, Robertson and White, 1953) indicates that any such deviation must be very small.

In 3:4-benzphenanthrene (IV), 3:4:5:6-dibenzphenanthrene (V) and tetrabenznaphthalene (VI), molecular overcrowding is still more severe, and detailed X-ray analysis (Herbstein, Schmidt et al., 1954; McIntosh, Robertson and Vand, 1952) has shown that these molecules are very markedly non-planar. The results of these investigations indicate that the distances between the overcrowded, non-bonded carbon atoms are about 3.0 A, representing a considerable compression below the usual van der Waals distance. The increase in intramolecular distance compared with the planar model is achieved with little change in the valency angles, and this possibility explains the retention of aromatic character in spite of the severe distortion.

This part of the thesis deals with the elucidation of the crystal and molecular structure of dinaphthoperopyrene, an overcrowded aromatic hydrocarbon, in which the distances between the overcrowded atoms, on the basis of a planar model, are similar to those in 3:4-benzphenanthrene and tetrabenznaphthalene, although the molecule is considerably larger.

2. Dinaphthoperopyrene.

When diperinaphthaleneanthracene (VII) is boiled with maleic anhydride in the presence of chloranil as dehydrating agent, two molecules are fused to it, in the same way as perylene reacts with one molecule of maleic anhydride (Clar, Kelly, Robertson and Rossmann, 1956). Decarboxylation of the adduct (VIII) with copper powder in boiling quinoline gives the orange-red dinaphthoperopyrene (IX). The additional two benzene rings compared with the starting material cause a strong violet-shift of the long-wavelength bands of the absorption spectrum, this shift being about twice that found


VII
CO
O
CO
CO
O
CO
VIII
IX
X

in the passage from perylene to 1:12-benzperylene.

If the adduct is treated with soda-lime at 400° however, there results, as well as the dinaphthoperopyrene, a higher-melting, less volatile hydrocarbon, which sublimes in dark needles. The properties of this new hydrocarbon indicate that it might be formed by "controlled graphitisation", and the structure (X) was proved by X-ray investigation. This new hydrocarbon, which is the third member of a series beginning with coronene and ovalene, has been named "circumanthracene".

The crystal structures of both diperinaphthalene-anthracene (VII) and circumanthracene (X) have been determined by X-ray analysis (Rossmann, 1956a). In both these structure analyses however the accuracy with which the molecular dimensions have been determined is not as good as might be expected, due to a rapid decrease in the intensities of the high-order spectra, which appears to be due to unusually high temperature factors. Rossmann (1956b) has related the increase in temperature factor to increase in amount of impurity in the crystals - determined by mass spectrometry. The present investigation was undertaken in an effort to define the molecular geometry of large buckled molecules of this type, and to obtain an accurate account of the molecular dimensions, particularly the intramolecular overcrowded distances.

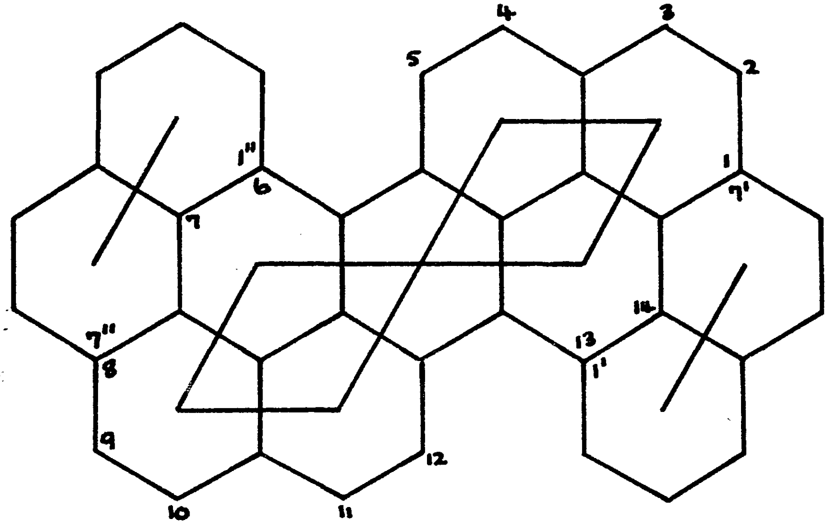
Both diperinaphthaleneanthracene and dinaphthoperopyrene could theoretically be buckled in either of two ways - so that the molecules have either centres of symmetry or two-fold axes of symmetry. Construction of wire models showed that the strain was much more evenly distributed in the two-fold axis type of distortion, and this molecular configuration has already been confirmed in the case of diperinaphthaleneanthracene.

Note on nomenclature. Molecule IX is a derivative of peropyrene, which is the largest hydrocarbon with a trivial name which can be chosen from the structural formula; so IX is named dinaphthoperopyrene (Fig.10a). It might also be considered as a derivative of anthracene, and named dipyrenoanthracene (Fig.10b).

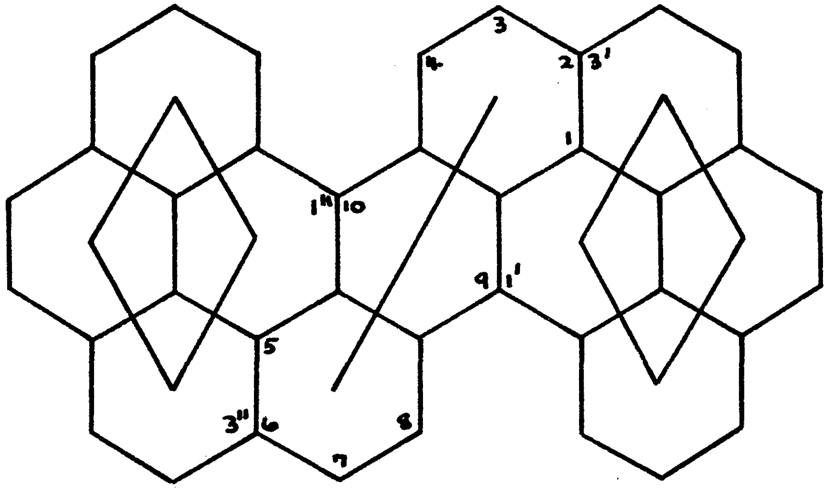
3. X-ray analysis: Experimental.

3.1. Preparation of crystals.

The crystals used in the present investigation were obtained by sublimation in a high vacuum. Examination of the sublimate revealed that it consisted mainly of stout hexagonal prisms which were dark-red in colour. There was however a small quantity of pale-red material; these crystals were generally aggregates of very small crystals, and initially it was thought the difference in colour was due to the different sizes of the crystals. After careful



(a) Dinaphtho(7':1'-1:13)(1":7"-6:8)-peropyrene.



(b) Dipyreno(3':1'-2:9)(3":1"-6:10)-anthracene.

Fig.10. Nomenclature.

examination of the batch of crystals however a very small single crystal of the pale-red form was separated by hand-picking; this crystal was rather smaller than those used for the X-ray photographs of the dark-red crystals, but it nevertheless had about the same dimensions as some of the smaller dark-red crystals, so that the colour difference did not seem to be due to different particle size.

Both the dark-red crystals (which will be called the α-form) and the single-crystal specimen of the pale-red form (β-form) have been examined and the unit cell and space group of each determined.

3.2. α-Dinaphthoperopyrene.

Crystals of the α-form were dark-red in colour, and consisted of elongated prisms with $\{100\}$, $\{001\}$ and $\{10\bar{1}\}$ faces developed. The density was determined by flotation in aqueous potassium iodide solution. The unit cell dimensions and space group were determined from rotation and oscillation photographs about the a, b, c, $[101]$, $[110]$ and $[111]$ axes, and moving-film photographs of the $(h0\ell)$, $(h1\ell)$, $(hk0)$ and $(0k\ell)$ zones.

<u>Crystal data</u>: α-Dinaphthoperopyrene, $C_{38}H_{18}$; $M = 474.5$; m. 338-339°C. Monoclinic, $a = 30.73 \pm 0.05$, $b = 3.855 \pm 0.01$, $c = 19.87 \pm 0.03$ A, $\beta = 113.0^\circ \pm 0.5^\circ$. Volume of the unit cell = 2166.7 A^3. Density, calculated (with four

molecules per unit cell) = 1.446, found 1.447. Absorption coefficient for X-rays, $\lambda = 1.542$ A, $\mu = 7.65$ cm^{-1}. Total number of electrons per unit cell = F(000) = 984.

Absent spectra: (hkℓ) when (h + k) is odd; no other systematic absences. Space group is C_2^3 - C2, C_s^3 - Cm, or C_{2h}^3 - C2/m.

3.3. β-Dinaphthoperopyrene.

Only one small single crystal of the pale-red modification was available, and all the X-ray data for this form were obtained from this one crystal, which was a plate of dimensions 0.32 x 0.07 x 0.26 mm., and weighing about 0.01 mg. The density was determined by flotation in aqueous potassium iodide solution; a larger polycrystalline aggregate was used for the density determination, so that the observed density may be in error due to included air pockets. The unit cell dimensions and space group were determined from rotation and oscillation photographs about the a, b and c crystal axes, and moving-film photographs of the (h0ℓ), (h1ℓ), (hk0) zones.

Crystal data: β-Dinaphthoperopyrene, $C_{38}H_{18}$; M = 474.5; m. 338-339°C. Monoclinic, a = 16.01 ± 0.08, b = 7.48 ± 0.02, c = 21.51 ± 0.05 A, $\beta = 118.6° \pm 0.5°$. Volume of the unit cell = 2263 A^3. Density, calculated (with four molecules per unit cell) = 1.39, found ~1.41. Absorption coefficient

for X-rays, $\lambda = 1.542$ A, $\mu = 7.35$ cm^{-1}.
Total number of electrons in the unit cell = 984.
Absent spectra: ($h0\ell$) when ℓ is odd, ($0k0$) when k is odd.
Space group is C_{2h}^{5} - $P2_1/c$.

3.4. Intending data.

α-Dinaphthoperopyrene. The intensities of all the reflexions observable with CuKα radiation were recorded on moving-film exposures for crystals rotating about the b and c axes, the multiple-film technique (Robertson, 1943) being used to correlate strong and weak reflexions. For the crystal rotating about the b-axis, layers with $k = 0$-3 were recorded, and for the crystal rotating about the c-axis, layers with $\ell = 0$-14, the equi-inclination method being used for all non-equatorial layers. The range of intensities measured was about 70,000 to 1, the estimates being made visually. The cross-sections of the crystals, normal to the rotation axes, were 0.25 x 0.18 mm., and 0.53 x 0.44 mm. for the b-axis and c-axis crystals respectively; errors due to absorption are negligible, and no absorption corrections were applied.

The values of the structure amplitudes were derived by the usual formulae for a mosaic crystal; Lorentz and polarisation corrections were applied, together with the rotation factor appropriate to equi-inclination Weissenberg photographs (Tunell, 1939). An approximately absolute scale was derived by Wilson's method (Wilson, 1942), and this scale was later adjusted by correlation with the F values of the $(h0\ell)$ zone reflexions, calculated from the final coordinates.

In estimating the intensities, the intensity of the Bragg reflexions only was considered, and no estimation was made of the intensity variation in the regions of diffuse scattering (see section 4.1, page 72).

β-Dinaphthoperopyrene. The intensities of the $(h0\ell)$ and $(h1\ell)$ zone reflexions were recorded on moving-film exposures for the crystal rotating about the b-axis, the equi-inclination method being used for the $(h1\ell)$ zone. The multiple-film technique was used to correlate strong and weak reflexions. The cross-section of the crystal normal to the rotation axis was 0.32 x 0.07 mm., and absorption errors are negligible.

3.5. General survey of intensities.

Examination of the intensity records of β-dinaphthoperopyrene reveals that there is a rapid decrease in the intensities of the high-order reflexions, apparently exactly analogous to the effect found for diperinaphthaleneanthracene and circumanthracene. A simple explanation of the rapid decrease in intensity might be that the crystal is rather small, and perhaps a larger crystal, or a microfocus tube would reveal weak high-order reflexions. However these reflexions must be weak, and the suggestion that this decrease in intensity is related to the amount of impurity in the crystal seems a very plausible explanation of the effect in this case. The presence of the small quantity of the pale-red crystals (β-form) among the larger proportion of dark-red (α-form) suggests that the former may be subliming either at the beginning or at the end of the sublimation, at a slightly lower or slightly higher temperature than the main bulk. The presence of these crystals is then most readily accounted for by the presence of a small amount of impurity, which sublimes before and after the dinaphthoperopyrene.

The pale-red crystals however do not appear to be entirely or even largely a different molecular species, since the measured density agrees reasonably well with that calculated assuming that the crystals consist entirely of $C_{38}H_{18}$ molecules. The crystals are probably polymorphic modifications of dinaphthoperopyrene. It appears reasonable to postulate that the dark-red crystals (which show no marked decrease in intensity in the higher-order spectra) are crystals of pure dinaphthoperopyrene, while the pale-red crystals are chiefly dinaphthoperopyrene, but with a small amount of impurity.

A small quantity of each type of crystal was separated by hand-sorting, and the absorption spectrum of each type in the visible region was examined (xylene was used as solvent). The two absorption spectra were identical; there was no evidence of broadening of the bands of the pale-red crystals. This evidence seems to indicate that any "impurity" in the pale-red crystals is not a different molecular species, but perhaps disoriented molecules, so that there is possibly some disorder in the crystal. The melting points of pure specimens of the α and β forms were measured. The α-form melted at 340°C, and the melting point of the β-form appeared to be slightly higher than this (about 343°C), so that it probably does not contain any impurity.

It has already been pointed out (page 63) that the molecular overcrowding can be relieved by distorting the molecule in either of two ways, and it is possible that the distortion is different in the two types of crystal. This however is unlikely, as the strain is much more evenly distributed in the 2-fold axis buckling, and the molecule would probably not exist in the centrosymmetrical form.

In view of the fact that the visible absorption spectra of the two forms are identical, the difference in colour perhaps seems rather strange. However many polynuclear hydrocarbons have different colours in solution and in the solid state, due to the presence of molecules in different electronic energy levels. In this case the colour difference is probably due to the "freezing-in" of some triplet state in one of the crystals.

The cell dimensions and space group of the α and β forms are compared in Table 12.

Table 12.

Unit cell dimensions and space group.

	α-form	β-form
	Monoclinic	Monoclinic
a	30.73 A	16.01 A
b	3.855	7.48
c	19.87	21.51
	113.0°	118.6°
Space group	C2, Cm, or C2/m	$P2_1/c$
Z	4	4

The short b-axis in the α-form, together with the more extensive range of data available, suggests that this form is much more suitable for structure analysis, in spite of the fact that the space group may be non-centred. No structure analysis of the β-form has yet been attempted, and all the following description of the analysis of the structure of dinaphthoperopyrene refers to the α-form.

4. Structure Analysis.

4.1. Space group: diffuse scattering.

The only systematically absent reflexions are (hkℓ) when (h + k) is odd, so that the space group is C2, Cm or C2/m. In the latter two space groups, the existence of a mirror plane perpendicular to the b-axis requires either the presence of two molecules within one unit translation along b, or a mirror plane within the molecule. The first of these alternatives is excluded by the short b-axis (3.855 A), while the second requires that the molecule is planar, and this is unlikely. The space group must therefore be C2.

Further examination of the photographs however reveals an interesting series of regions of diffuse scattering. These consist of diffuse rods in reciprocal space parallel to a*, and passing through the Bragg reflexions, and these rods are present for all values of k and ℓ, except when k = 0. In the (h0ℓ) zone those reflexions with ℓ even are all quite sharp, and not joined by diffuse streaks; those with ℓ odd are all extremely weak maxima on the diffuse rods parallel to a*. These diffraction features are shown in Fig.11.

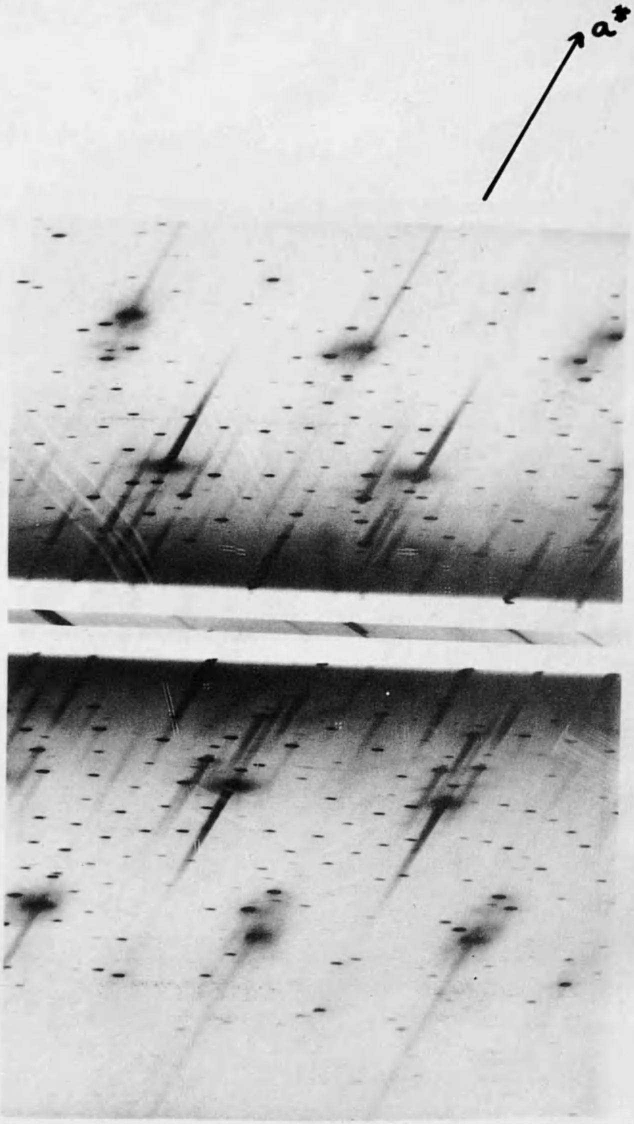


Fig.11a. Normal-beam Weissenberg photograph, $(h0\ell)$ zone, showing diffuse rods parallel to a^* when $\ell = 2n + 1$.
Note also the thermal diffuse regions surrounding the intense higher-order reflexions.

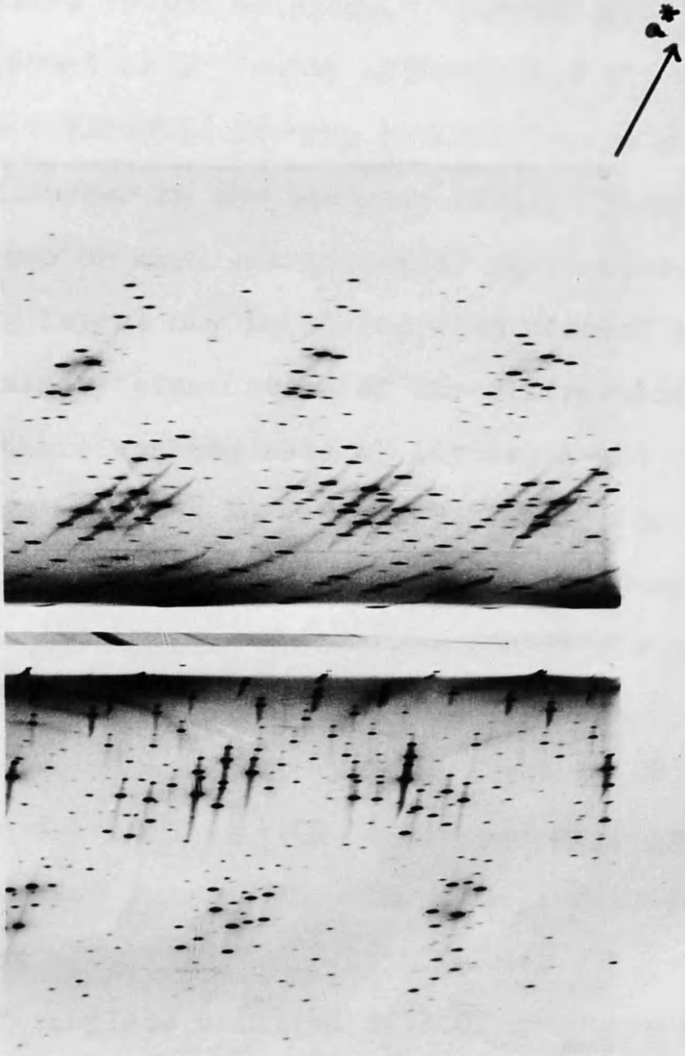


Fig.11b. Equi-inclination Weissenberg photograph, (hlℓ) zone, showing diffuse rods parallel to a* for all values of ℓ.

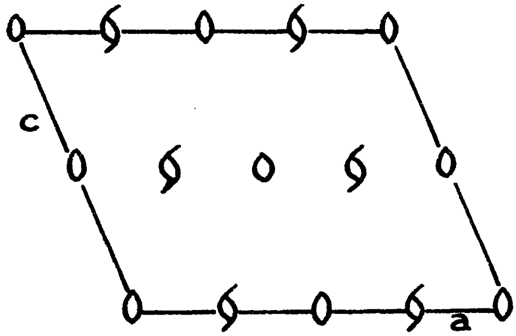
The diffraction pattern is typical of an order-disorder structure - OD structure (Dornberger-Schiff, 1956), built of layers parallel to the bc-plane. Within each layer the molecular arrangement is perfectly ordered, but the sequence of layers is such that there is no true periodicity in the *a* direction. The disorder in the stacking results from the fact that there are two or more energetically equivalent ways in which neighbouring layers may be placed with respect to one another. Preliminary examination of the diffraction data indicates that there are two sets of layers, A and B; since $(h0\ell)$ reflexions with $\ell = 2n$ are sharp, layer B can be made coincident with layer A in projection down the b-axis, simply by translation $\frac{1}{2}c$. Using Dornberger-Schiff's space group notation, the true space group of the disordered crystal is C(1)21. The Λ symmetry of each layer is C2.

In addition to the diffuse rods, there are regions of thermal diffuse scattering surrounding the intense higher-order $(h0\ell)$ reflexions (Fig.11a).

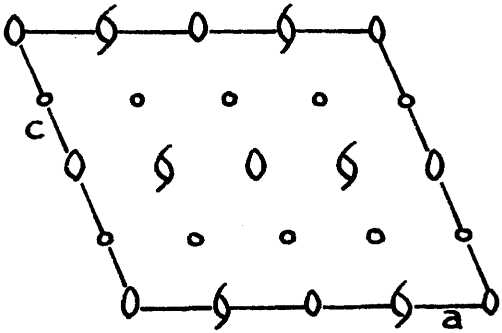
The problem of complete solution of the structure will now be approached by considering initially the projection down the short b-axis, in which all the atoms in the molecule will probably be well resolved.

4.2. (010) projection.

Examination of the $(h0\ell)$ zone intensities reveals that of about 360 independent reflexions with $\ell = 2n$ which are theoretically observable with $CuK\alpha$ radiation, 260 have been observed (72%); of a similar number of theoretically observable reflexions with ℓ odd, only 20 weak, diffuse reflexions have been observed. Since all the $(h0\ell)$ reflexions with ℓ odd are extremely weak, there must be two molecules which are almost identical in projection and separated by $\frac{1}{2}c$, and the problem of obtaining a trial structure can best be approached by neglecting the ℓ odd reflexions, so that the projection corresponds to the $(h0\ell)$ projection of space group C2/c.



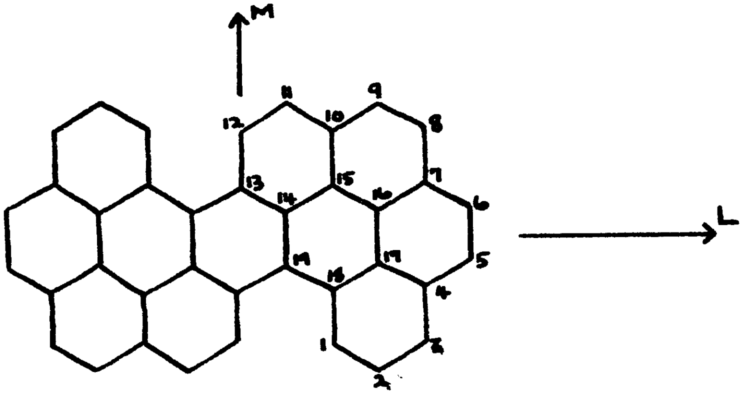
C2.



C2/c.

Since reflexions with ℓ even are all sharp, there will be obtained a projection of the disordered structure, that is a super-position of layers A and B.

As an initial approximation, we may assume that the molecule is completely planar, and consists of regular hexagons of side 1.40 A. (If the molecule was really planar, the space group could of course be Cm or C2/m. The assumption of planarity however is being used only to establish a plausible trial structure, and it will then be discarded, so that Cm and C2/m are untenable.) The distance between the molecular planes in crystals of large planar aromatic hydrocarbons (coronene, for example) is about 3.4 A - equal to the interplanar spacing in graphite. Since dinaphthoperopyrene is almost certainly buckled, we might expect a rather larger separation between mean planes drawn through the molecules, and it is likely that a mean plane through the molecule is almost parallel to (010) - this also means that the assumption of planarity of the molecule will give quite a reasonable trial structure in this projection. The problem of finding the approximate positions of the carbon atoms then reduces to finding the directions of the molecular axes L and M in the projection.



In a molecule consisting of regular hexagons of side 1.4 A, all the carbon atoms lie on planes of spacing 1.2 A, and close to planes of spacing 2.1 A, and if these planes coincide with planes in the crystal, then the crystal planes will have large values of the structure amplitudes. In an ideal case (perfectly regular hexagons of side 1.40 A), planes of spacing 1.2 A would have unitary structure factors 1.0, and those of spacing 2.1 A unitary structure factors 0.5. The spacings and unitary structure factors (based on the approximate absolute scale) of a few reflexions of spacings approximately 1.2 A and 2.1 A are given in Table 13; that these planes are of outstanding intensity is immediately obvious from examination of the (h0ℓ) zone photograph (Fig.11a, page 73).

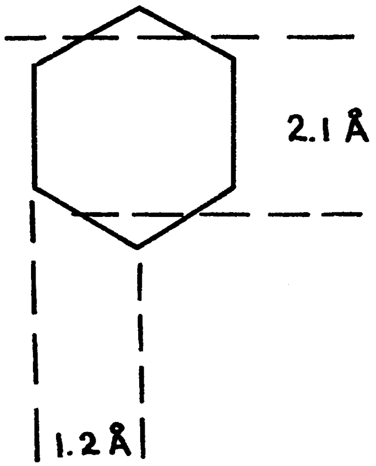


Table 13.

Outstandingly strong high-order reflexions.

Plane	d(A)	|U|
24 0 $\bar{2}$	1.24	0.85
6 0 12	1.31	0.32
8 0 12	1.24	0.41
6 0 14	1.16	0.69
18 0 $\overline{16}$	1.16	0.95
10 0 4	2.09	0.42
14 0 $\bar{6}$	2.11	0.45
4 0 $\overline{10}$	1.97	0.45

If the origin of the projection is taken at the centre of one of the molecules (this will be either at a centre of symmetry or on a two-fold axis in C2/c, and these are indistinguishable in this projection), then it is a simple matter to adjust the orientations of the molecular axes L and M so that all the atoms lie close to the traces of these planes. There are six possible molecular orientations, but the molecule is considerably elongated, and packing considerations reduce the possibilities to two (orientations I and II in Fig.16, page 88), which are related by a rotation of 180° about either L or M. In this projection the two orientations differ only in the position of one atom - atom 11.

Structure factors were calculated for about 90 of the stronger reflexions, using McWeeny's scattering curve for carbon with B = 3.5 (determined by Wilson's method; Wilson, 1942). The discrepancy between measured and calculated structure factors was 38.2% for orientation I, and 44.7% for orientation II. A Fourier synthesis was computed, using about 60 terms, whose signs did not depend on the position of atom 11 and were most probably correct. All the carbon atoms were well resolved, except 11 and 11' - which were rather poorly defined. More accurate atomic parameters were obtained from the Fourier map, and recalculation of the structure factors led to improved agreement between F_o and F_c, but it was not possible to decide between orientations I and II. It was however noted that a structure consisting of I + II (in the proportions 1:1) gave considerably better agreement than either orientation separately, and this structure probably represents superposition of layers A and B.

Refinement was continued by computing a second F_o synthesis, again using only terms whose signs did not depend on the position of atom 11 (215 terms), and choosing new centres. Structure factors were recalculated with the inclusion of a contribution from the hydrogen atoms; hydrogen coordinates were assigned assuming C-H bond lengths of 1.0 A. The process of refinement is outlined in Table 14, in terms of the discrepancy R.

Table 14.

Refinement process (R%).

	I	II	I + II
Trial structure	38.2	44.7	-
1st F_o synthesis	26.5	29.9	20.3
2nd F_o synthesis	20.1	-	11.1

The low value of the discrepancy of Orientation (I+II) leaves no doubt that this is the true molecular arrangement in the disordered structure. Using the signs of the structure factors calculated from the coordinates of the second F_o synthesis, a third Fourier synthesis (260 terms) was computed (Fig.12). In this map all the carbon atoms are very well resolved; atoms 11 and 11' have peak heights corresponding to only one-half of a carbon atom (plus a contribution from a peak where two "half-hydrogen atoms" overlap). The peak heights of atoms 11 and 11' are not quite equal, but this is due to the chance occurrence that the structure factors calculated from molecular orientation I have more signs correct than those calculated from orientation II. The positions of the carbon atoms are shown in Fig.13.

All the hydrogen atoms, except those attached to carbons 11 and 11' are reasonably well resolved; those in the overcrowded positions are of course obscured by carbons 11 and 11'.

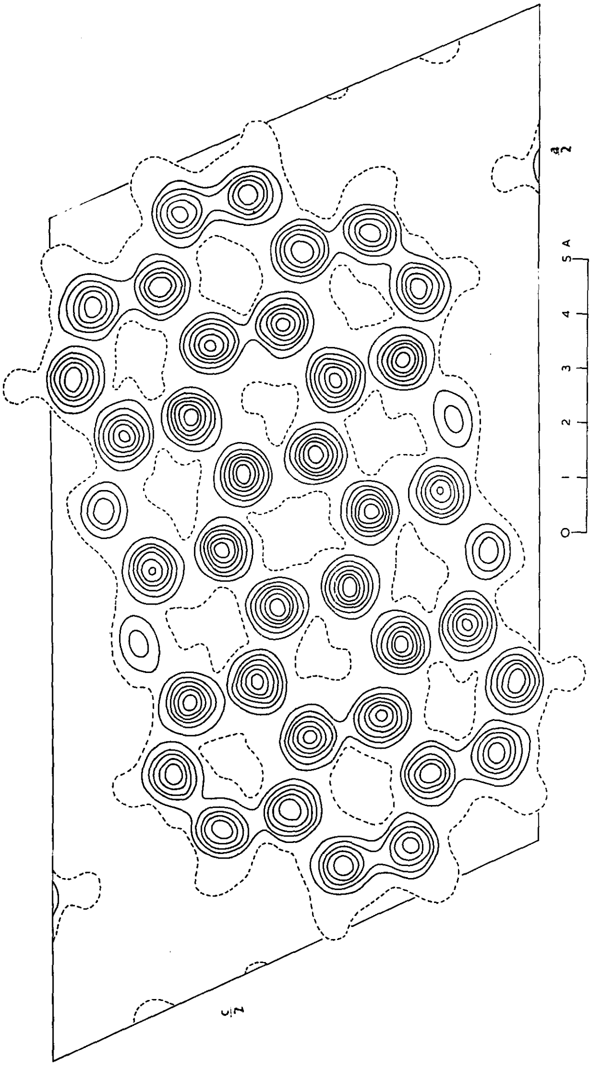


Fig.12. Final electron density projection on (010). Contours at intervals of 1 eA^{-2}, with the one-electron line dotted.

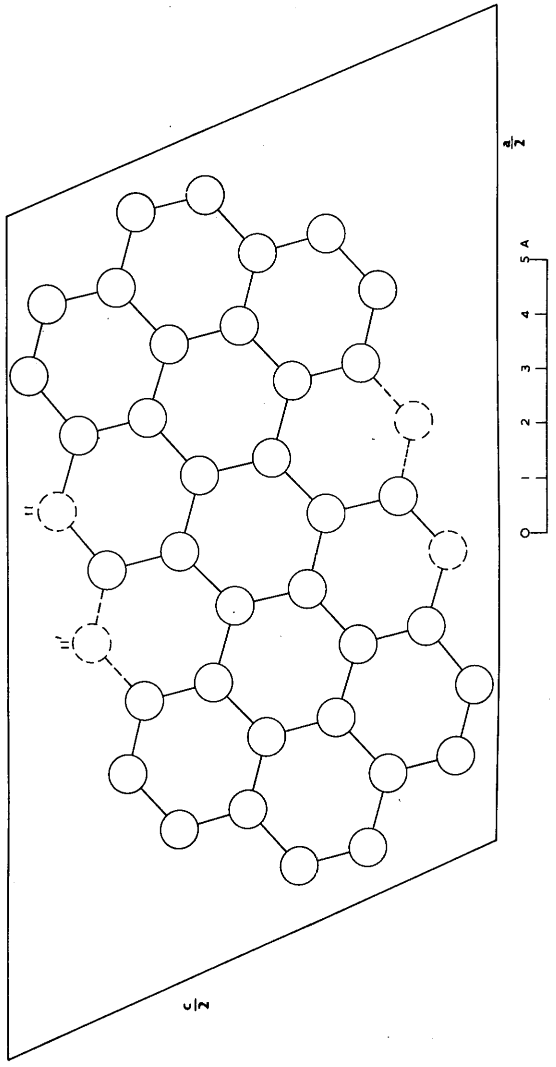


Fig. 13. Projection of the structure onto (010).

Finally an $(F_o - F_c)$ synthesis was computed (Fig.14), and 10 of the carbon atoms were shifted by small amounts to minimize the slopes at the atomic centres. The map reveals also that the atoms at the periphery of the molecule are executing larger thermal vibrations than those nearer the centre, as is usual with these large aromatic hydrocarbons, but no correction for this variation of temperature parameter has been applied. The x and z parameters of the carbon atoms have been determined with considerable precision; since however the structure is a disordered one, each atomic position is the mean of two positions which are extremely close, but nevertheless probably distinct. The complete description of the arrangement of molecules in layers A and B requires consideration of further evidence, and this will be described in the following section.

4.3. Molecular arrangement in the (010) projection.

From the results so far obtained about the disordered structure by a consideration of the sharp $(h0\ell)$ reflexions, each layer, A and B, may be constructed in two possible ways:

(a) Layer A consisting entirely of molecules of orientation I and layer B entirely of molecules in orientation II.

(b) Each layer, A or B, containing molecules in both orientations.

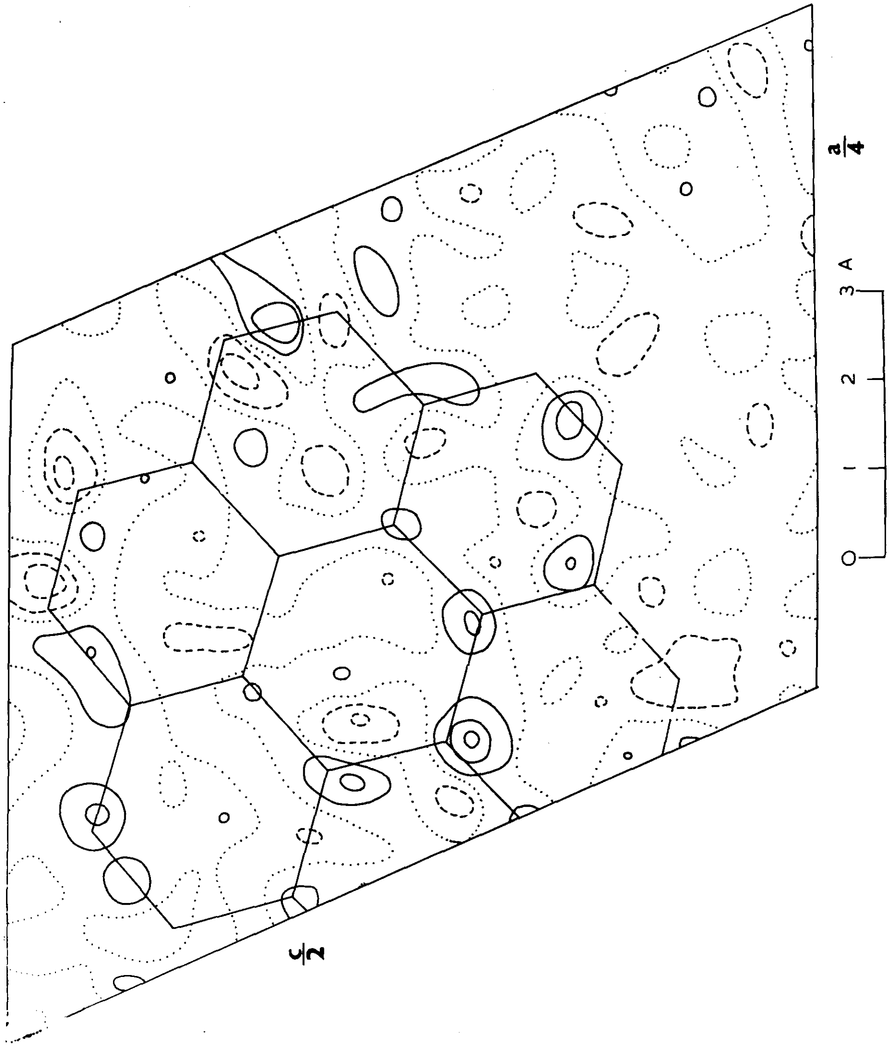


Fig.14. Difference synthesis projection on (010). Contours at intervals of 0.2 eA^{-2}, negative contours broken, zero contour dotted. Carbon and hydrogen atoms subtracted.

Examining arrangement (a) first, consideration of the following evidence shows that this molecular arrangement is untenable.

(i) Since the space group is C2 and the unit cell contains four molecules, the asymmetric unit is one molecule, and the molecular centres are in general positions and separated by $\frac{1}{2}$c. If the origin is taken at a point on a two-fold axis, the molecular centres are at either (0, 0, $\frac{1}{4}$) or ($\frac{1}{4}$, 0, $\frac{1}{4}$) - these arrangements are shown in Fig.15a and b.

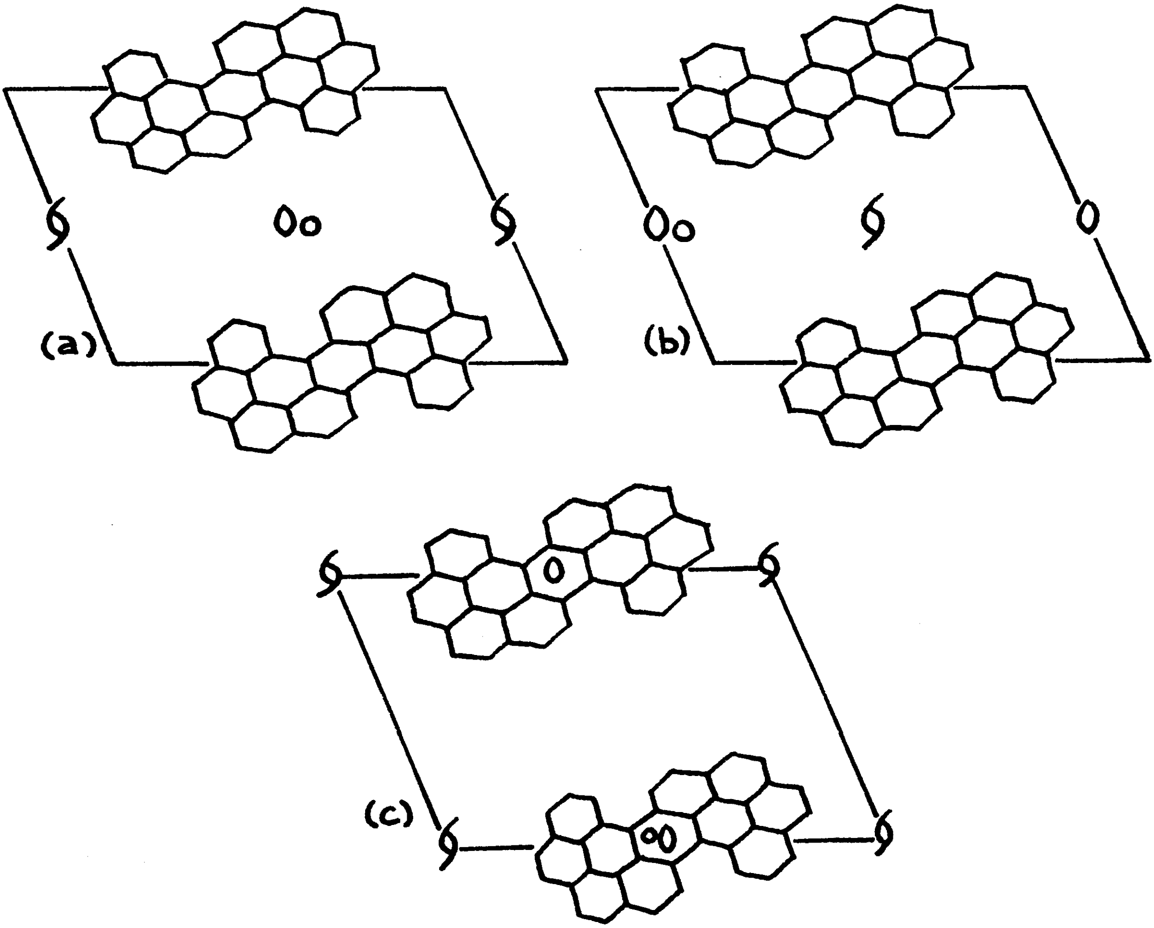


Fig.15. Possible molecular arrangements (origin at O).

The first of these arrangements would result in all reflexions with ℓ odd being weak, and the second in all reflexions with $(k + \ell)$ odd being weak. Examination of the intensities of the general reflexions immediately reveals that neither of these intensity variations is observed, so that these molecular arrangements are untenable.

A further possibility is that the molecules are situated on the two-fold axes; this would require each molecule to possess a two-fold axis, coincident with the space group two-fold axis (Fig.15c). The molecules are then situated at $(0, 0, 0)$ and $(0, d, \frac{1}{2})$, and since d can have any value, no marked systematic intensity variations would be observed (other than ℓ odd reflexions weak when $k = 0$). The two molecules are independent, and the true asymmetric unit consists of half of each molecule. It might be noted that in spite of the fact that space group C2 is one of the Sohncke "regular point systems", the two molecules, since they are not related by any symmetry element, could be optical enantiomorphs.

(ii) Since the $(h0\ell)$ reflexions with ℓ even are sharp, layer B can, in projection down b, be made identical with layer A by translation $\frac{1}{2}c$. In any of the arrangements described above, with each layer composed of a single molecular orientation, this is not possible; in any of these the (h0ℓ) reflexions with $\ell = 2n$ would also be diffuse.

The true arrangement of molecules then must be (b); if each layer contains molecules in both orientations, then the arrangement in any one layer must be of the same type as the third arrangement described above for (a), with the molecules situated on two-fold symmetry axes, the asymmetric unit being half of each molecule. The arrangement of molecules in the two layers A and B is shown in Fig.16.

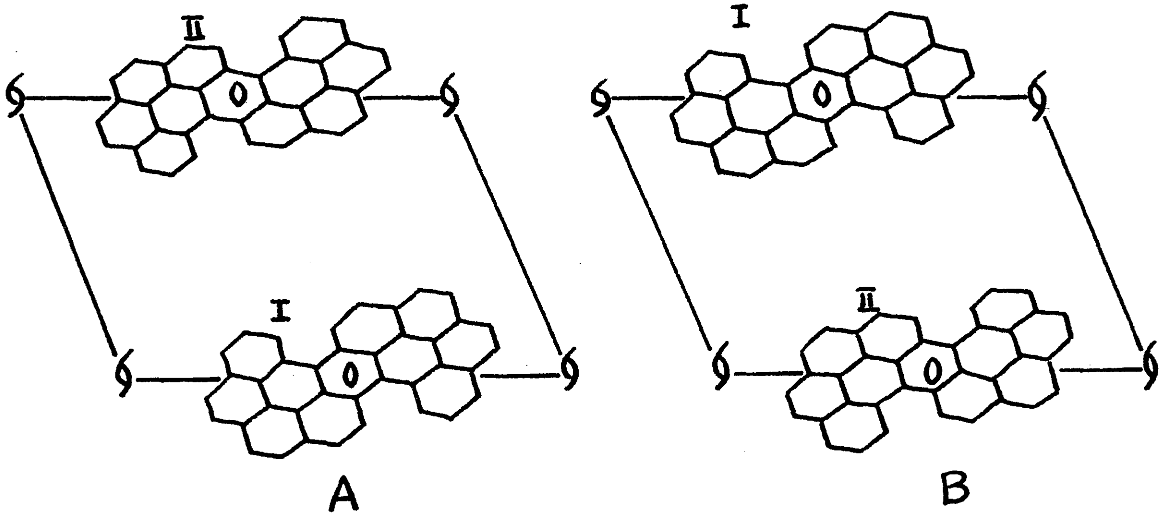


Fig.16. True arrangement of molecules in layers A and B.

Superposition of the layers gives an accurate account of the intensities of the (h0ℓ) reflexions with ℓ even (sharp reflexions) - values of measured and calculated structure factors are listed in Appendix I (page 137). An ordered structure consisting of either layer A or layer B would give sharp (h0ℓ) reflexions with ℓ odd, and the structure factors for this type of crystal may be calculated from the atomic coordinates - $F_c(A)$. In a "perfectly disordered" structure, these structure factors would be zero - $F_c(AB)$. Values of $F_c(A)$ and $F_c(AB)$ are compared with the measured values in Appendix I (page 141); this comparison reveals that the true structure may be described as a "partially-ordered superlattice", with order extending over only a few unit cells.

This completes the description of the projection of the structure onto (010). A complete description of the molecular geometry and dimensions requires the examination of further data, to determine the third coordinates of the atoms.

4.4. y-coordinates.

No resolution of the individual atoms in the molecule can be expected in projections down the long a or c axes, more especially since the structure is disordered. The problem of finding the y-coordinates will therefore be approached by considering the (h1ℓ) zone structure factors.

Approximate y-coordinates, which must be found by trial, may be refined by the use of generalized projections. All reflexions are diffuse, so that we cannot hope to obtain perfect agreement between calculated and measured structure amplitudes of the Bragg reflexions (Harker, Lucht and Kasper, 1950). A reasonable measure of agreement might be obtained however if we can find an accurate description of the structure of layer A alone.

A planar wire model of the molecule was constructed and buckled so that the distance between the overcrowded carbon atoms was 3.05 A. Approximate y-coordinates with respect to the centre of the molecule were determined from this model by projecting along the molecular axis M. It now remains to find the positions of the two molecular centres, which are not related by any symmetry element. These two centres lie, one on the two-fold axis at x = 0, z = 0, the other on the two-fold axis at x = 0, z = $\frac{1}{2}$. One molecular centre was taken at (0, 0, 0), and this molecule was arbitrarily buckled in one sense - let us call its configuration D. Then the centre of the second molecule is at (0, d, $\frac{1}{2}$). The structure factor expressions for the space group C2:

$$A = 4 \sum \cos 2\pi(hx + \ell z).\ \cos 2\pi ky$$

$$B = 4 \sum \cos 2\pi(hx + \ell z).\ \sin 2\pi ky.$$

may be written

$$A = 4 \sum_{1} \cos 2\pi(hx + \ell z).\cos 2\pi ky + 4\sum_{2} \cos 2\pi(hx + \ell z).\ \cos 2\pi k(d \pm y)$$

$$B = 4 \sum_{1} \cos 2\pi(hx + \ell z).\ \sin 2\pi ky + 4\sum_{2} \cos 2\pi(hx + \ell z).\ \sin 2\pi k(d \pm y)$$

where the + and - signs correspond to L and D configurations of molecule 2 - that is the molecule at $(0, d, \frac{1}{2})$. On expansion these expressions reduce to

$$A = A_1 + A_2 . \cos 2\pi kd \mp B_2 . \sin 2\pi kd$$

$$B = B_1 + A_2 . \sin 2\pi kd \pm B_2 . \cos 2\pi kd$$

where A_1 is the real part of the structure factor for molecule 1, etc.

$F_{hk\ell}$ ($= \sqrt{A^2 + B^2}$) was computed for a number of reflexions (h10, and h12) for values of d from $\frac{0}{60} \longrightarrow \frac{60}{60}$ y, using Beevers-Lipson strips. Only for the + sign was any general measure of agreement between F_o and F_c obtained; best agreement was obtained when d was taken as $\frac{26}{60}$ y. Structure factors were calculated for about 270 (h1ℓ) reflexions (425 were observed of a possible of about 650 independent reflexions); the discrepancy between measured and calculated values was 29.8% - an encouragingly low value considering that the structure is disordered and the reflexions are diffuse. Scaling the F_o values by making $\sum F_o$ equal to $\sum F_c$ gave a scale about 14% higher than that from the (h0ℓ) structure factors, but this higher scaling is probably not real, but due to the fact that some of the scattered radiation is diffuse, and no estimate has been made of the intensity of the diffuse scattering. This means that it would be expected that in general F_c would be greater than F_o.

In this structure the two molecules have opposite configurations, in spite of the fact that the space group is one of the Sohncke groups; while this type of arrangement is unusual it is mathematically quite sound, and there are other examples of structures which contain two non-related molecules, and in which the asymmetric unit is half of each molecule. A single crystal weighing about 0.5 mg. was dissolved in α-methylnaphthalene and examined in a polarimeter, but no rotation was observed, in agreement with the deduced crystal structure.

Refinement of the y-parameters proceeded by computing a "difference generalized projection", and this process is described in the following section.

4.5. Generalized projections.

Corresponding to the electron density

$$\rho(x,y,z) = \frac{1}{V}\sum_h\sum_k\sum_\ell F(hk\ell)\,.\,\exp\left\{-2\pi i\,(hx+ky+\ell z)\right\}$$

the generalized projection of this distribution on a plane perpendicular to the b-axis is

$$\rho_K(x,z) = \frac{1}{A}\sum_h\sum_\ell F(hK\ell)\,.\,\exp\left\{-2\pi i\,(hx+\ell z)\right\}$$

It can be shown that

$$\rho_K(x,z) = C_K(x,z) + i.\,S_K(x,z)$$

where

$$\left.\begin{aligned} C_K(x,z) &= \frac{1}{A}\sum_h\sum_\ell\left\{A(hK\ell).\cos 2\pi(hx+\ell z) + B(hK\ell).\sin 2\pi(hx+\ell z)\right\} \\ S_K(x,z) &= \frac{1}{A}\sum_h\sum_\ell\left\{B(hK\ell).\cos 2\pi(hx+\ell z) - A(hK\ell).\sin 2\pi(hx+\ell z)\right\} \end{aligned}\right\}$$

<u>For space group C2</u>:

For all structure factors

$$\left.\begin{aligned} A &= 4\sum \cos 2\pi(hx+\ell z).\cos 2\pi ky \\ B &= 4\sum \cos 2\pi(hx+\ell z).\sin 2\pi ky \end{aligned}\right\} \quad \text{and} \quad \begin{aligned} A(hk\ell) &= A(\bar{h}k\bar{\ell}) \\ B(hk\ell) &= B(\bar{h}k\bar{\ell}) \end{aligned}$$

Hence

$$\left.\begin{aligned} C_K(x,z) &= \frac{2}{A}\sum_0^\infty\sum A(hK\ell).\cos 2\pi(hx+\ell z) = \frac{2}{A}\sum_0^\infty\sum |F|.\cos\alpha.\cos 2\pi(hx+\ell z) \\ S_K(x,z) &= \frac{2}{A}\sum_0^\infty\sum B(hK\ell).\cos 2\pi(hx+\ell z) = \frac{2}{A}\sum_0^\infty\sum |F|.\sin\alpha.\cos 2\pi(hx+\ell z) \end{aligned}\right\}$$

$C_K(xz)$ represents a projection of the structure on (010), with the electron density in the nth atom multiplied by $\cos 2\pi Ky$. If the phases of the structure factors of the Kth layer line can be found from a trial structure, a cosine or sine generalized projection may be computed, and the value of $\cos 2\pi Ky$ or $\sin 2\pi Ky$ can be found for each atom. Series termination can however produce considerable errors in the values of y, and these errors can be eliminated by computing a "difference generalized projection" (Rossmann, 1956a), using as coefficients the terms $\{|F_o| - |F_c|\}.\cos\alpha$ or $\{|F_o| - |F_c|\}.\sin\alpha$. This function need not be computed over the whole area of the projection, but only at the atomic centres, and this greatly reduces the amount of computational work involved.

The sine difference generalized projection, D_s, was computed at the atomic centres for the (h1ℓ) zone using the values $\{|F_o| - |F_c|\}$ of the trial structure. If y_o is the true coordinate of an atom, y_c the coordinate included in the structure factor calculation, and ρ_o the peak height in the (h0ℓ) zone F_o synthesis, then

$$D_s = \rho_o . \sin 2\pi k y_o - \rho_o . \sin 2\pi k y_c$$

Hence

$$\sin 2\pi y_o = D_s/\rho_o + \sin 2\pi y_c$$

The shifts in the y-coordinates were calculated for all the atoms; these shifts were however applied with caution, since the structure is a disordered one, and the magnitude of a shift may be the mean of two atomic shifts. Generally however the shifts were very reasonable, and recalculation of the structure factors led to improved agreement between F_o and F_c. The discrepancy was reduced to 26% over the 425 observed reflexions; values of the measured and calculated structure amplitudes, and the calculated phase constants are listed in Appendix II. The agreement between observed and calculated structure amplitudes is not as good as in the $(h0\ell)$ zone, but it is better than might be expected with a disordered structure of this type, and does indicate that the y-coordinates have been determined fairly accurately.

Summarizing then, layer A consists of one molecule situated on the two-fold axis at $x = 0$, $z = 0$, and the centre of this molecule may be chosen as the origin of the space group; a second molecule has its centre at $(0, \frac{26}{60}, \frac{1}{2})$, and is the optical enantiomorph of the first. The arrangement of molecules in layer B is either identical with that in layer A, or related to it by some symmetry operation, such as inversion in a centre of symmetry ($D \rightarrow L$, $L \rightarrow D$). However it does not seem to be possible to describe exactly how A and B are related in the crystal, since, even if the true arrangement were found, perfect agreement between F_o and F_c for the general reflexions could not be obtained, since they are all diffuse. The agreement for the $(h1\ell)$ reflexions is remarkably good, and could scarcely be improved.

Sharp reflexions are required to give an accurate account of the relation between the layers; from the only sharp reflexions observed - $(h0\ell)$ with ℓ even - it has been possible to describe the relation between layers A and B in projection down the b-axis.

5. Coordinates and molecular dimensions.

The final coordinates of the carbon atoms are listed in Table 15, expressed as fractions of the unit cell edges. x and z have been determined from the $(h0\ell)$ zone refinement, and y from the difference generalized projection, using the $(h1\ell)$ zone data.

Table 15.

Coordinates of the carbon atoms.

	I			II		
Atom	x	y	z	x	y	z
C 1	0.0735	-0.322	-0.1101	0.1014	0.141	0.6754
2	.1123	-0.439	-0.1287	.1484	.015	.7253
3	.1584	-0.372	-0.0770	.1865	.071	.7066
4	.1648	-0.205	-0.0060	.1795	.207	.6374
5	.2115	-0.139	0.0472	.2191	.301	.6178
6	.2191	-0.003	0.1178	.2115	.431	.5472
7	.1795	0.070	0.1374	.1648	.509	.4940
8	.1865	0.203	0.2066	.1584	.640	.4230
9	.1484	0.250	0.2253	.1123	.690	.3713
10	.1014	0.192	0.1754	.0735	.623	.3899
11	.0625	0.226	0.1972	.0256	.637	.3359
12	.0149	0.105	0.1486	-0.0149	.523	.3514
13	.0077	0.005	0.0745	-0.0077	.426	.4255
14	.0470	0.010	0.0534	0.0393	.443	.4788
15	.0940	0.070	0.1060	.0797	.510	.4599

	I			II		
Atom	x	y	z	x	y	z
16	0.1326	0.013	0.0845	0.1261	0.450	0.5125
17	.1261	-0.115	0.0125	.1326	.331	.5845
18	.0797	-0.155	-0.0401	.0940	.297	.6060
19	.0393	-0.047	-0.0212	.0470	.356	.5534

The bond lengths and valency angles in the dinaphthoperopyrene molecule were calculated from these coordinates. Two independent values of each bond length and valency angle were obtained - one from each molecule - and the mean values (to the nearest 0.01 A in bond length and the nearest degree in bond angle) are shown in Fig.17. The maximum deviation of any individually-determined bond length from the mean value for that bond is 0.027 A, and the root mean square deviation for all the bonds is 0.011 A. The corresponding differences for the valency angles are 1.8° and 0.9°. The average value of the carbon-carbon bond lengths is 1.431 A.

The overcrowded non-bonded distances (1 - 12) are 2.975 A and 2.930 A, mean value 2.953 A.

The molecule has an exact two-fold symmetry axis (2), and is propeller-shaped. If the whole carbon skeleton was completely planar, the sum of the valency angles around each carbon atom would be 360°. The small deviations from 360°

(Fig.17) show that the three bonds around each carbon atom are nearly coplanar. The carbon atom hybrid orbitals are nearly pure sp^2, and the strain due to molecular distortion is evenly distributed over the whole molecule, which retains its aromatic character. These angle sums are however rather insensitive to small deviations from a planar arrangement of bonds.

The six-membered rings which are furthest from the centre of the molecule ought to show the smallest deviations from planarity; the two rings consisting of atoms 4, 5, 6, 7, 8, 9, 10, 15, 16, 17 are far from the molecular centre, and the mean planes of these atoms in the two molecules were found by the least squares method:

$$\text{I} : \quad 0.0647\,X' - 0.9345\,Y + 0.3499\,Z' - 0.2826 = 0$$

$$\text{II} : \quad 0.0652\,X' - 0.9412\,Y + 0.3379\,Z' - 4.7697 = 0$$

X', Y, Z' are coordinates expressed in A, and referred to orthogonal axes a', b, c, where a' is perpendicular to b and c.

The deviations of all the atoms in one half of each molecule from these mean planes are given in Table 16. The atoms used to determine the equations all lie close to the planes, but the deviations increase towards the centre of the molecule. The values for chemically-identical atoms

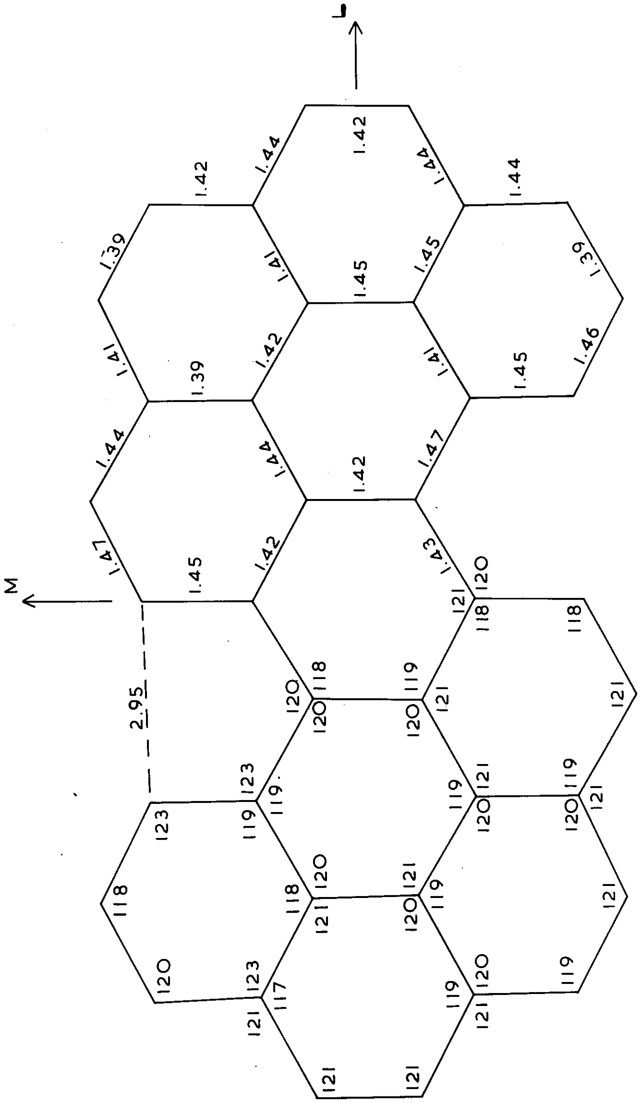


Fig.17. Bond lengths and valency angles in Dinaphthoperopyrene.

ought to have the same magnitude but opposite signs. Generally the two displacements agree closely, except for atoms 1, 11, 12, 13, 19. These atoms are furthest from the atoms used to determine the mean planes, and quite small changes in the orientation of the planes could improve the agreement considerably.

Table 16.

Deviations from mean planes.

Atom	I	II	Atom	I	II
C 1	-0.123A	-0.003A	C 11	0.125A	-0.260A
2	0.136	-0.173	12	0.337	-0.481
3	0.146	-0.181	13	0.199	-0.351
4	0.023	-0.069	14	-0.059	-0.035
5	0.044	-0.015	15	-0.021	-0.009
6	0.027	0.000	16	-0.058	0.024
7	-0.006	0.029	17	-0.081	0.061
8	-0.020	0.041	18	-0.192	0.168
9	0.031	-0.022	19	-0.354	0.243
10	0.004	-0.055			

An idealized view of the molecule along the molecular axis L is shown in Fig.18a, and the shape of the central ring in Fig.18b.

All intermolecular distances correspond to normal van der Waals interactions. The distance between any atom and

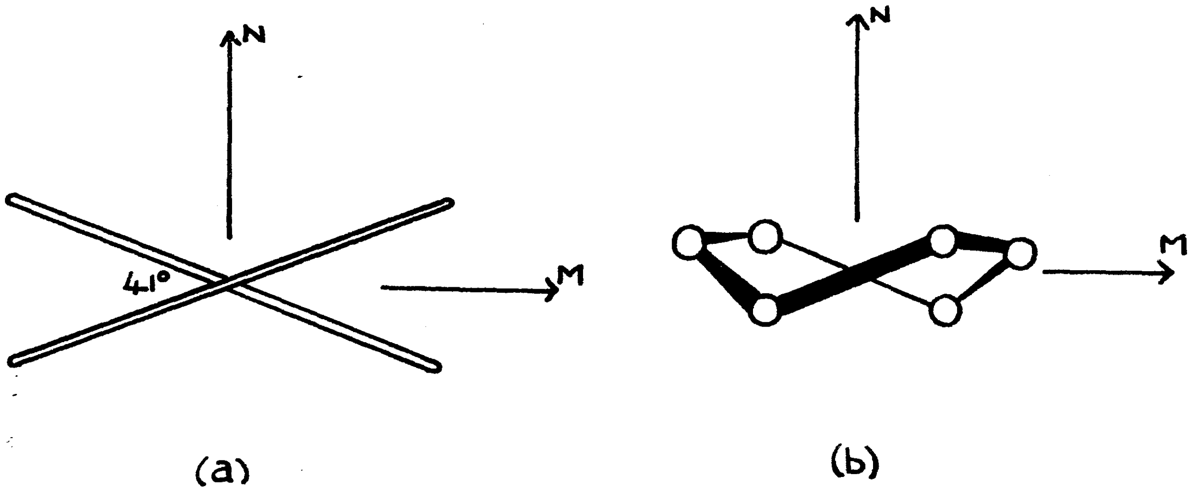


Fig.18 (a) Idealized view along molecular axis L.
(b) Atoms of the central ring (the puckering is exaggerated for clarity).

the corresponding atom in the molecule one translation along b is 3.855 A (the b-axis repeat distance). The mean perpendicular distance between the mean planes through the outer rings, of two molecules related by translation b, is 3.62 A, so that no intermolecular distance in the b direction is less than this. The shortest lateral contact, within either layer A or layer B, is 3.66 A. All the shorter intermolecular contacts are shown in Fig.19. Examination of the intermolecular distances projected onto (010) shows that there can be no unusually short distances between the molecules of layer A, and those of an adjacent layer B, so that the two layers are built into the crystal without any undue strain.

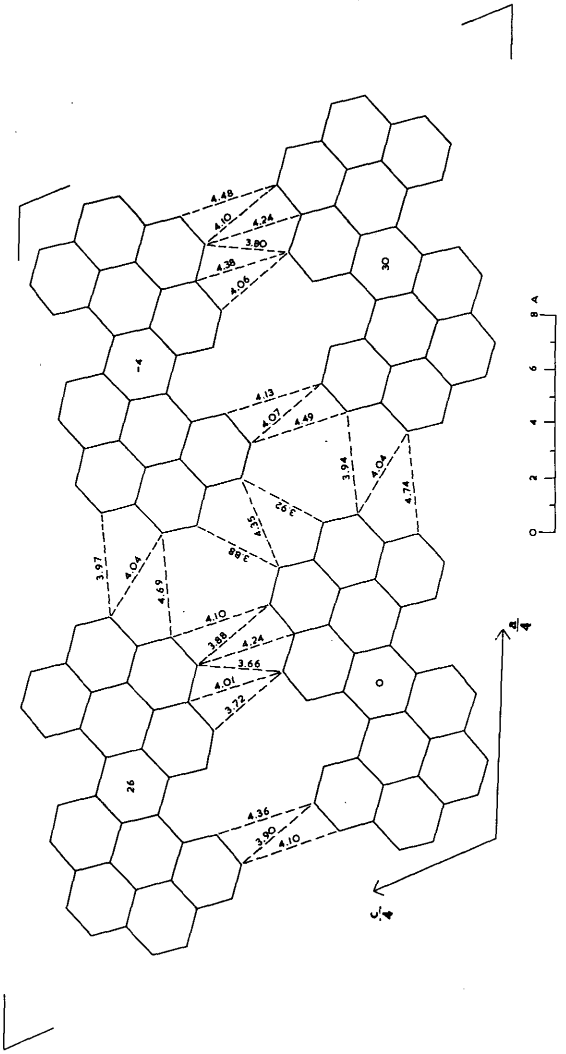


Fig.19. Intermolecular distances in Å (figures at the centre of each molecule are the y-coordinates of the molecular centres in b/60 ths.).

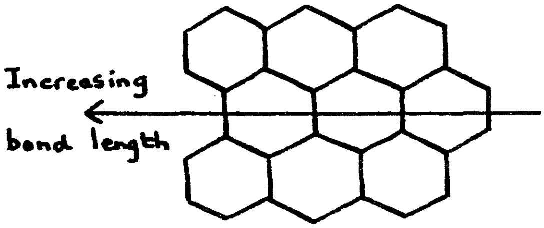
6. Discussion of the molecular dimensions and the crystal structure.

6.1. Molecular dimensions.

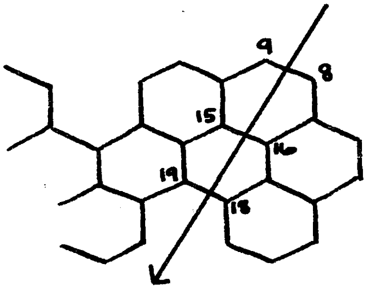
It is rather difficult to estimate the accuracy with which the bond lengths and valency angles have been determined in this analysis. Cruickshank's formulae (Cruickshank, 1949, 1954) could be applied to the $(h0\ell)$ zone data, but this would give a false impression of the accuracy, since, although the structure factor agreement is extremely good, each atomic position is really the mean of two extremely close atoms. The close agreement of the independent values of chemically-identical bonds (R.M.S. deviation from the mean 0.01 A) suggests that the molecular dimensions have been determined with considerable precision in spite of the disorder.

Since however the accuracy is rather doubtful, no detailed discussion of the bond length variations in the molecule will be attempted, but some general trends may be discussed. Since the three bonds from each carbon atom are almost coplanar and the strain is distributed over the whole molecule, it might be hoped that molecular orbital calculations, assuming that the whole molecule is planar, would give reasonable estimates of the bond orders and bond lengths. These calculations are at present being carried out (Goodwin and Roche, 1957), but at the time of writing, the results of this investigation are not available.

Consideration of the Kekulé structures of molecule XI suggests that the bond lengths should increase along the centre of the molecule, and this is in agreement with the fact that this molecule adds maleic anhydride. The crystal structure of this molecule is at present being investigated (Trotter, 1957).



XI



A similar but less extended system is present in dinaphthoperopyrene, and the bonds 8-9, 15-16, 18-19 increase in length as expected (1.387 → 1.423 → 1.472 A).

The bonds involving the overcrowded atoms are rather long —indicating maximum break-down of aromatic character around these positions. The mean bond length is 1.43 A, rather greater than the average value for planar aromatic hydrocarbons (coronene = 1.410 A, ovalene = 1.412 A), again suggesting that the aromatic character is reduced by the buckling. The mean bond length in diperinaphthalene-anthracene is also 1.43 A.

The distance between the overcrowded carbon atoms in dinaphthoperopyrene (2.95 A) is almost identical with the mean distance in diperinaphthaleneanthracene (2.97 A). The increase in intramolecular distance compared with a planar model is achieved by buckling the molecular framework, with the strain distributed over the whole molecule and with very little variation of the valency angles from the trigonal values. This results in retention of aromatic character in spite of the severe molecular distortion.

6.2. Crystal structure.

The description of the crystal structure given in section 4.5 (page 95) leads to calculated structure factors for the sharp reflexions, which are in excellent agreement with those observed. For the diffuse reflexions the agreement is encouragingly good, although not, as might be expected, as good as for the sharp spectra. The account of the structure which the present analysis has yielded is not however quite complete. The positions of all the atoms in each molecule, and the arrangement of molecules in each layer have been obtained from a consideration of sharp and diffuse reflexions. It has not been possible however to describe how the two layers A and B are packed together in the crystal, except that they are related by translation $\frac{1}{2}c$.

Since the structure factor agreement is so good, even for the diffuse reflexions, the layers A and B probably scatter nearly in phase. If the complete arrangement of layers was found, the agreement between measured and calculated structure amplitudes for the diffuse reflexions would not be much better than at present (if indeed it improved at all); it would be extremely difficult to decide whether a postulated arrangement giving reasonable agreement was the true one, and very little useful additional information would be obtained. With the large number of parameters involved, the great amount of work (and it would be largely trial and error) required to obtain any further information scarcely justifies the small improvement in the description of the structure which would result.

The present analysis has established with considerable precision the molecular dimensions and stereochemistry of this large overcrowded molecule, and has demonstrated how the strain caused by molecular distortion is evenly distributed over the molecule, which retains its aromatic character.

PART IV.

THE CRYSTAL AND MOLECULAR STRUCTURES OF DIINDENYL IRON AND DIINDENYL COBALT.

1. Introduction.

Iron biscyclopentadienyl (ferrocene), $Fe(C_5H_5)_2$, the first of a new type of organometallic compound with an unusual molecular structure, was obtained in 1951 by Kealy and Pauson (1951), and independently by Miller, Tebboth and Tremaine (1952). The chemical and physical properties led Wilkinson, Rosenblum, Whiting and Woodward (1952) to propose a highly symmetric "sandwich" model for its structure, having D_{5h} or D_{5d} symmetry. A number of analogous biscyclopentadienyl compounds, in which the iron atom is replaced by atoms of the other transition elements, have been prepared by Wilkinson, Fischer and others. A review of the work done in this field, with a comprehensive list of references, has been given by Pauson (1955).

X-ray studies on ferrocene by a number of investigators (see Pauson, 1955) have verified the structure with D_{5d} ($\bar{5}m$) symmetry; the iron, cobalt and nickel compounds have been examined, and have closely similar structures (Fischer and Pfab, 1952). A complete account of the molecular dimensions of ferrocene has been obtained by an accurate three-dimensional analysis (Dunitz, Orgel and Rich, 1956).

The first member of a new type of complex of indene with the transition metals, analogous to but rather less stable than the cyclopentadienyl compounds, was obtained in 1953 by Fischer, Seus and Jira (1953), who prepared diindenyl cobalt (dibenzocobaltocene) by reaction of the potassium salt of indene with $Co(NH_3)_4(SCN)_2$ in liquid ammonia, and decomposition of the precipitated $Co(NH_3)_6(C_9H_7)_2$. $Co(C_9H_7)_2$ is a black, paramagnetic substance which may be crystallised from petroleum ether. Measurement of the magnetic moment of $Co(C_9H_7)_2$ indicates a structure similar to the cyclopentadiene complex, $Co(C_5H_5)_2$, with the central Co^{II} situated between the five-membered rings, which are parallel and arranged antiprismatically, while the six-membered rings are probably in the trans-configuration.

Diindenyl iron, $Fe(C_9H_7)_2$, which is deep-violet in colour, sublimable in high vacuum, and diamagnetic, was obtained by Fischer and Seus (1953) by treatment of indene magnesium bromide with ferric chloride, and by Pauson and Wilkinson (1954) by reaction of indenyllithium with ferric chloride. Diindenyl iron is reasonably stable in air, soluble in organic solvents giving a red-violet solution, and insoluble in water. Powder photographs show that the iron and cobalt compounds have similar structures.

The three-dimensional X-ray investigation of ferrocene proves conclusively that in the solid state the five-membered rings are fixed in the staggered configuration; electron-diffraction investigation of the vapour shows that in the vapour state, the rings are rotating freely, and this is also the case in solution, since only one isomer can be obtained on disubstitution. It is probably safe to assume that the aromatic rings in diindenyl iron are also rotating freely in solution, but that the molecule has a fixed configuration in the solid state. The present investigation was designed to illustrate the "sandwich" nature of the molecule, and to examine whether the configuration is trans as postulated.

2. Experimental.

The crystals of diindenyl iron used in the present investigation were prepared by P.L. Pauson, and recrystallised by dissolving in boiling ether, and cooling in a Dry Ice-acetone bath. Since the material is rather unstable in solution, fairly rapid crystallisation was necessary to avoid excessive decomposition, and hence the crystals were generally small (average dimensions 0.50 x 0.20 x 0.06 mm.). Crystals were also grown by high-vacuum sublimation (120°C at 10^{-4}mm. Hg) but these crystals were rather poor and generally polycrystalline specimens.

The crystals are deep-purple in colour, reasonably stable in air, and consist of thin plates elongated along the b-axis, with $\{001\}$ developed. The density was determined by flotation in aqueous potassium iodide solution.

The data required for the X-ray investigation were collected using CuKα (λ = 1.542 A) and CoKα (λ = 1.790 A) radiations, the latter when intensity measurements were required. The following dimensions were obtained by use of single-crystal rotation, oscillation and moving-film photographs about the a, b, c and $[10\bar{1}]$ axes:

Crystal data. Diindenyl iron, $C_{18}H_{14}Fe$; M = 286.1; m. 184°-185°C (in an evacuated tube). Monoclinic a = 11.32 ± 0.03, b = 7.85 ± 0.02, c = 8.09 ± 0.02 A, β = 115.3° ± 0.5°. Volume of the unit cell = 650.0 A^3. Density, calculated (assuming two molecules per unit cell) = 1.462, found 1.457. Absorption coefficients for X-rays: λ = 1.790 A, μ = 26.4 cm^{-1}; λ = 1.542 A, μ = 98.5 cm^{-1}. Total number of electrons per unit cell = 296. When this value is corrected for the anomalous dispersion of the CoKα radiation by the K-electrons of the iron atom, F(000) = 288.5. Absent spectra: (h0ℓ) when h is odd; possibly (0k0) when k is odd. Space group is either C_s^2 - Pa, C_{2h}^4 - P2/a, or C_{2h}^5 - $P2_1/a$. The choice of space group will be discussed later.

The intensities were measured on moving-film exposures of the equatorial layers for crystals rotating about the b and c axes, the multiple-film technique (Robertson, 1943) being used to correlate strong and weak reflexions. The range of intensities measured was about 1600 to 1, the estimates being made visually. The cross-sections of the crystals, normal to the rotation axes, were 0.20 x 0.06 mm. and 0.40 x 0.20 mm. for the $(h0\ell)$ and $(hk0)$ zones respectively, and approximate absorption corrections were applied by considering the path length in the crystals of rays reflected from their centres (Albrecht, 1939). The values of the structure factors were derived by the usual formulae for a mosaic crystal and are listed in Table 20 (page 134). The absolute scale was derived by correlation with the F values calculated from the final coordinates.

The intensities of the $(h0\ell)$ zone reflexions were remeasured using zirconium-filtered MoKα radiation (for diindenyl iron, $\mu = 11.7$ cm^{-1} for $\lambda = 0.7107$ A); with the use of MoKα radiation, the effective radius of the limiting sphere of reflexion is increased, and, more important, errors due to absorption are greatly reduced. Unfortunately many of the weaker reflexions recorded with CoKα radiation were too weak to observe on these films taken with molybdenum radiation, but it was possible to remeasure the intensities of the stronger reflexions.

A sample of diindenyl cobalt was made available by E.O. Fischer, and the unit cell dimensions were obtained from a powder photograph; the lines were indexed by trial, and comparison with the single-crystal rotation and oscillation photographs of the iron analogue. The powder photograph was of rather poor quality, and the cell dimensions of the cobalt analogue are probably only approximately determined; there is no doubt however that the iron and cobalt compounds are isomorphous. The cell dimensions are compared in Table 17; the cell dimensions of the corresponding cyclopentadienyl derivatives are also included for comparison.

Table 17.

Unit cell dimensions.

	$Fe(C_9H_7)_2$	$Co(C_9H_7)_2$	$Fe(C_5H_5)_2$	$Co(C_5H_5)_2$
a	11.32 A	11.49 A	10.56 A	10.60 A
b	7.85	7.94	7.60	7.71
c	8.09	8.15	5.95	5.90
	115.3°	115.3°	121.0°	121.1°

Diindenyl cobalt is rather unstable in the presence of oxygen, due to oxidation of Co^{II} to Co^{III}, and all the single-crystal investigation was confined to the iron analogue.

3. Structure Analysis.

3.1. Space group.

Of the $(h0\ell)$ reflexions with $h = 2n$, 55 independent reflexions have been observed out of a possible 81 observable with CoKα radiation; careful examination of the ($h0\ell$) zone photographs reveals no planes with $h = 2n + 1$, so that the presence of a glide plane, a, is definitely established, and the space group is P-/a. On the photographs obtained with the use of CoKα radiation, only (040) of the (0k0) reflexions is observed; with CuKα radiation a weak (020) reflexion has also been observed. No (0k0) reflexions with k odd have been observed, and these absences establish the space group as $P2_1/a$. However, since only two (0k0) reflexions are observable, some further evidence for centrosymmetry is desirable.

Howells, Phillips and Rogers (1950) have shown that the fractions N(z) of reflexions whose intensities are equal to or less than a fraction z of the local average are given, for a centrosymmetrical crystal or projection, by the function

$$N(z) = \operatorname{erf}\,(\tfrac{1}{2}z)^{\frac{1}{2}}$$

and for a non-centrosymmetrical crystal, by the function

$$N(z) = 1 - \exp\,(-z)$$

The theoretical results apply only to the distribution of intensities produced by a random arrangement of atoms, so that they might not be expected to apply rigorously to a structure containing an atom of predominant scattering power, such as the iron atom in the present case. The two distribution functions are shown in Fig.20, and compared with the values of N(z) for the (h0ℓ) and (hk0) reflexions of diindenyl iron. In both zones the values of N(z) lie close to the centrosymmetrical curve at values of z from 0 to 0.5; at higher z, neither curve fits closely.

All this evidence appears to leave little doubt that the space group is $P2_1/a$, and structure analysis proceeded on this basis. It is as well to bear in mind however that the presence of the iron atom reduces the reliability of this type of evidence, and there is a slight possibility that the space group may still be Pa or P2/a.

3.2. (010) projection.

The space group $P2_1/a$ requires four asymmetric units per unit cell, and since the unit cell contains only two molecules, each molecule has a centre of symmetry at the iron atom, and the two iron atoms in the cell are situated at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0). The molecular centre of symmetry defines the configuration of the molecule; the six-membered rings must be trans.

The iron atoms contribute $2f_{Fe}$ or 0 towards the structure factors according as (h + k) is even or odd, and using the heavy atom technique (see page 8), preliminary analysis may be carried out in a direct manner. In the (h0ℓ) zone those reflexions to which the iron atoms do not

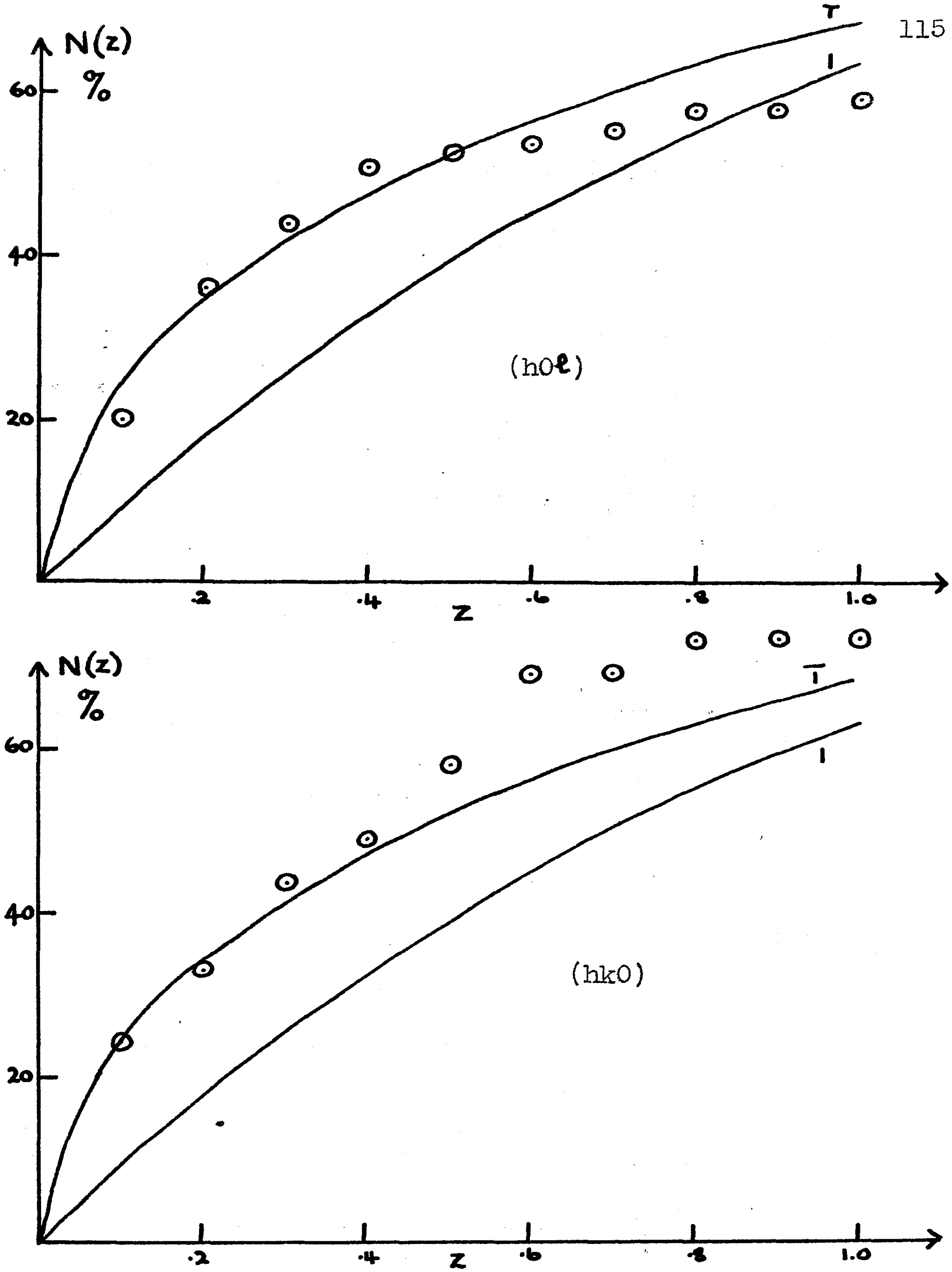


Fig.20. Intensity distributions for diindenyl iron, compared with theoretical curves for 1 and $\bar{1}$.

contribute are forbidden by the space group, so that a Fourier synthesis may be computed with the phases of all the $(h0\ell)$ terms based on the iron atoms alone - zero phase angle or positive sign.

The function $\rho(xz)$ was computed using positive signs for all $F(h0\ell)$; this function is shown in Fig.21. The iron atoms are well resolved, with peak height 33 eA^{-2}; this peak however represents one iron atom and two carbon atoms, one from each five-membered ring, which are obscured by the heavy iron peak. The other four atoms of each five-membered ring are clearly resolved, peak heights 6 - 8 eA^{-2}. The positions of the six-membered rings are less certain. Positions have to be chosen for eight carbon atoms; there are however fourteen available peaks, two of these being much heavier than the others, and probably corresponding to two overlapping carbon atoms. If the molecule has a trans-configuration, the electron-density function can be interpreted only by overlap of two molecules with different orientations, and regular repetition of these differently-oriented molecules along the b-axis would lead to a b-axis of double the present length. Careful examination of the rotation and oscillation photographs for crystals rotating about the b-axis reveals no intermediate layer lines, and so the two types of molecular orientation must be arranged randomly along the b-axis. This type of stacking would be

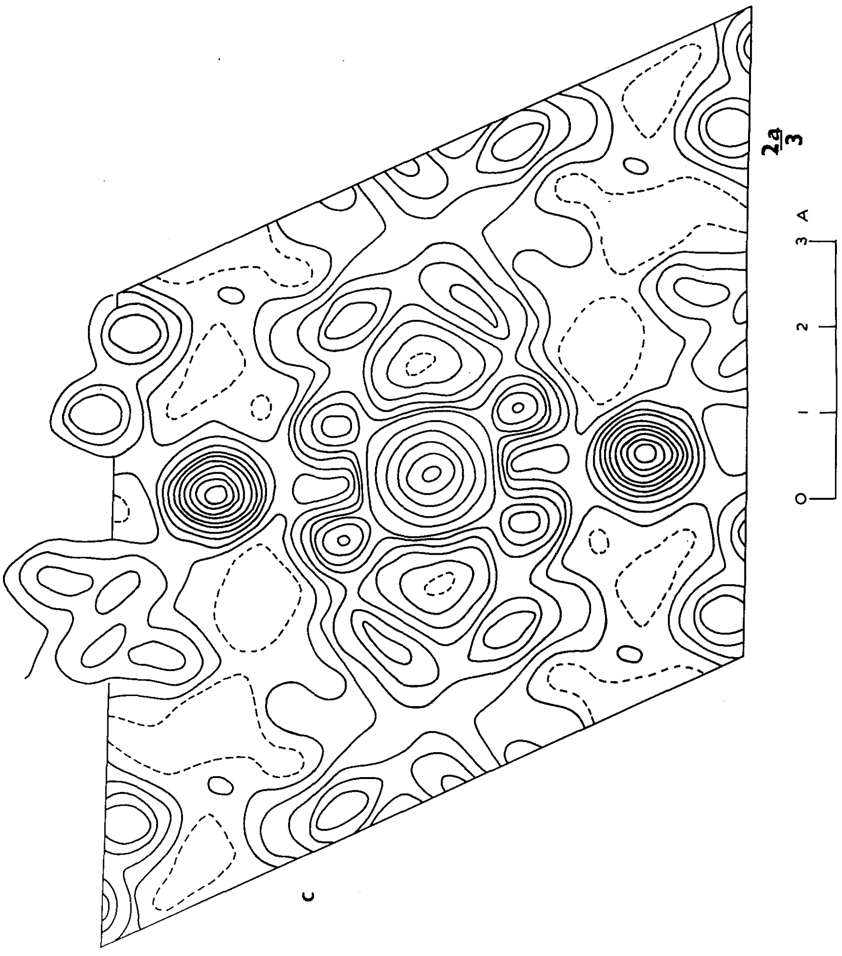


Fig. 21. Electron-density projection on (010); phase-angles based on iron atoms only. Contours at intervals of 1 eA^{-2}, one-electron line dotted, except on the iron atom, where contours are 6, 10, 15, 20 ... eA^{-2}.

expected to give rise to regions of diffuse scattering, but all the photographs showed only sharp reflexions, with no trace of diffuseness. Also any stacking disorder in the ac plane would lead to impossibly short intermolecular distances, so that only in the b-direction is any stacking disorder possible.

An interpretation of this electron-density map which is crystallographically much more reasonable can be given if the postulated trans-configuration for the molecule is discarded. Let us assume that the true space group of the crystal is Pa, and hence no molecular symmetry is required. When the space group is not determined unambiguously, it is always a wise policy to choose the one of lower symmetry, and any additional symmetry will emerge during the course of the analysis. In the present case the absent spectra determine the space group unambiguously as $P2_1/a$, but there is some doubt about the (0k0) halvings.

Now in the b-axis projection the iron atoms have positions such that, if the origin of the projection is chosen at one of the iron atoms, the phase angles of their contributions to the structure factors are 0. If these phase angles are used to compute the electron density, they must inevitably give a centrosymmetrical structure, and if the true structure is not centrosymmetrical, this electron-density map represents a superposition of two structures - the correct one, and another related to it by centres of symmetry at the iron atoms, and midway between the iron atoms. In other words, of each pair of centrosymmetrically-related peaks only one is correct; the true structure, chosen with the help of chemical evidence, is shown in Fig.22. Structure factors were calculated from these iron and carbon positions, using the structure factor expressions appropriate to space group Pa:

$$A = 2\sum_{1}^{18} f_c . \cos 2\pi(hx_j + \ell z_j) + 2f_{Fe}$$

$$B = 2\sum_{1}^{18} f_c . \sin 2\pi(hx_j + \ell z_j)$$

In general the B parts are small in comparison with A, since the contribution of the two Fe atoms to B is zero. The agreement between measured and calculated structure factors was encouragingly good, except for a few reflexions (particularly 201 and $20\bar{2}$).

A second Fourier synthesis was computed using these revised phase angles, and the resulting electron-density distribution is shown in Fig.23. Only one atom of each pair of centrosymmetrically-related peaks is now present, except that there is a six-electron peak in a position related, by a centre of symmetry at the iron atom, to the peak where two carbon atoms overlap. In spite of the height of this peak, it is probably spurious and due to errors in phase

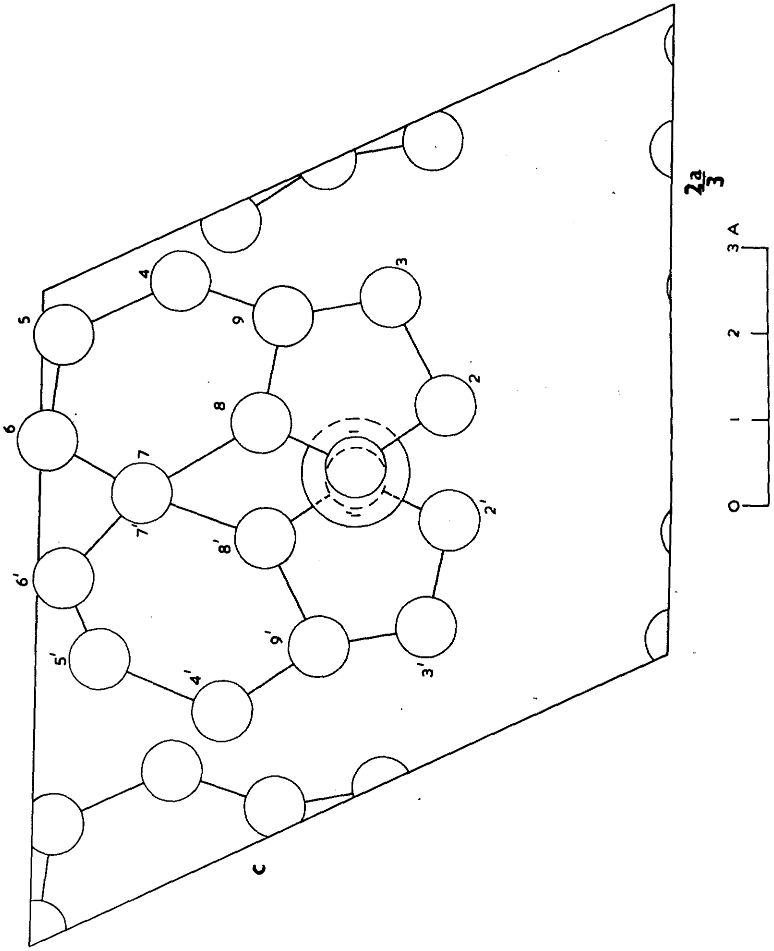


Fig.22. Projection of the structure of diindenyl iron onto (010).

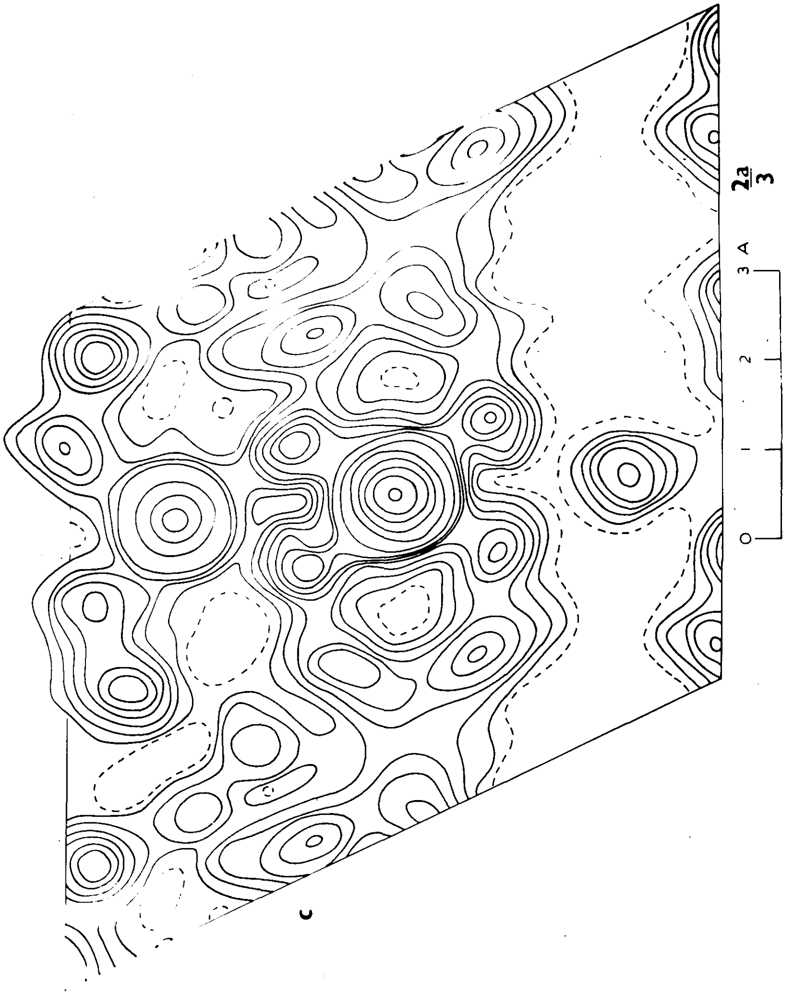


Fig.23. Electron-density projection on (010), using phase-angles calculated from the positions of iron and carbon atoms. Contours at intervals of 1 eA^{-2}, with the one-electron line dotted except on the iron atom, where the contours are 8, 10, 15, 20 ... eA^{-2}; and on the double peak, where the contours are 5, 10, 15, 18 eA^{-2}.

angle. New carbon positional parameters were chosen from this map, a double shift correction being applied. Recalculation of the structure factors led to a slight improvement in the agreement between the observed and calculated values, but the (201) and (20$\overline{2}$) planes were still grossly in error.

A difference synthesis projection on (010) was now computed (Fig.24); a feature of this map is the accumulation of density between the carbon atoms, possibly due to anisotropic vibrations of the aromatic rings about an axis, which passes through the metal atom, and is perpendicular to the planes of the aromatic rings. The scattering factor of a carbon atom may be represented by:

$$f = f_0 . \exp\left[-\left\{\alpha + \beta . \sin^2(\phi - \psi)\right\} \sin^2\theta/\lambda^2\right]$$

where α and β are constants, ψ is the angle between the direction of maximum vibration and the c axis, and (2s, ϕ) are the polar coordinates of a point in the $k = 0$ plane of the reciprocal lattice. α and β were calculated from the slopes of the function $(\rho_o - \rho_c)$ at the atomic centres (Cochran, 1951): $\alpha = 2.6$, $\beta = 2.6$. It was not to be expected however that these anisotropic factors would produce much change in the lower-order reflexions, and recalculation of the structure factors of the (201) and (20$\overline{2}$) planes showed that the changes in the calculated values of these

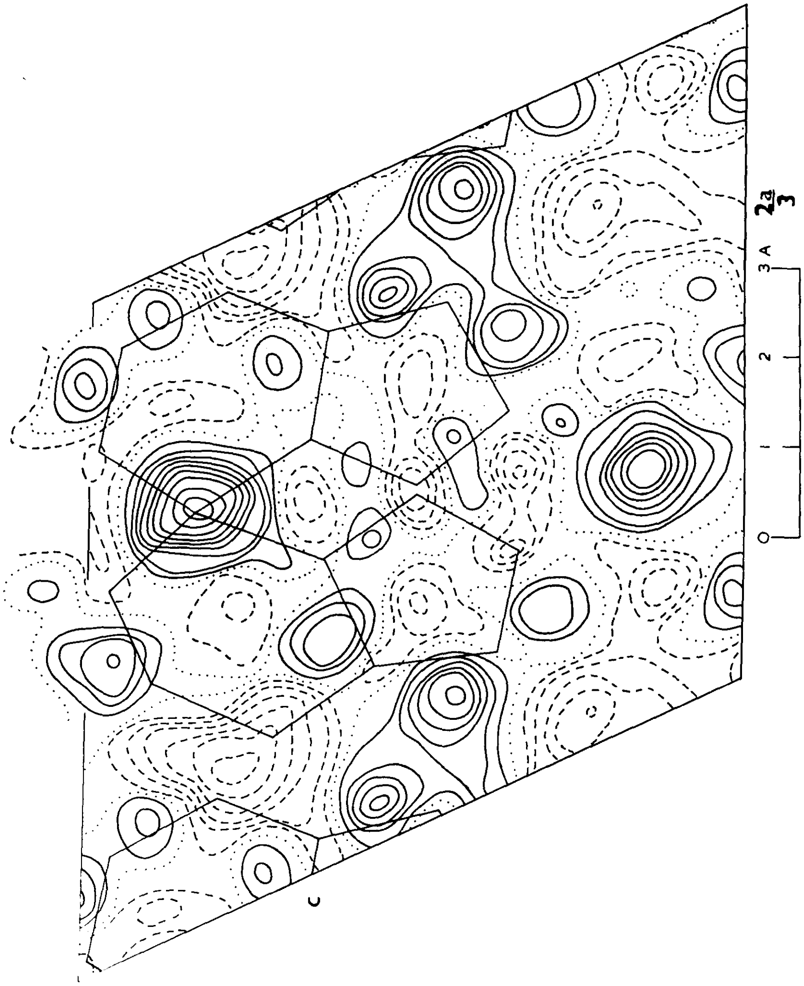


Fig.24. Difference synthesis projection on (010), iron and carbon atoms subtracted. Contours at intervals of 0.5 eA^{-2}, negative contours broken, zero contour dotted.

structure factors were negligible.

The 4-electron peaks at the position of the two overlapping atoms, and at the position related to this by inversion in the iron atom, are probably due to phase-angle errors. In a Patterson synthesis, many of the C-C vectors overlap here, so that we might expect an accumulation of errors in these positions.

At the moment little further information can be gained by further refinement of this projection; the best method of proceeding is to obtain approximate y-coordinates and proceed with a three-dimensional analysis. The discrepancy between observed and calculated structure factors over the observed reflexions (and including the unobserved 201 reflexion) is 24%, and over all the reflexions 29%. Values of measured and calculated structure factors are listed in Table 20 (page 134).

3.3. (001) projection.

Since the absent spectra correspond to space group $P2_1/a$, the iron atoms are probably situated exactly half-way between the glide-planes, and if the origin is taken at one of the iron atoms, the coordinates of the heavy atoms are (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0). In the projection down the c-axis, the aromatic rings will be viewed almost end-on, and the projection will be nearly centrosymmetric.

In computing $\rho(xy)$ all terms with $(h + k)$ even were included with + sign; of those with $(h + k)$ odd only F(120) and F(210) are of considerable magnitude, and since F(110) is large and necessarily positive, it follows from the sign relation (Cochran, 1952):

$$s(h) = s(h') . s(h + h')$$

that these two terms have the same sign, which may be taken as either positive or negative.

Examination of the Fourier map indicates that the indenyl radicals are almost normal to the projection plane, and none of the individual atoms is resolved. The "sandwich" nature of the molecule is however well illustrated. Owing to the extreme overlap in this projection, y-coordinates cannot be accurately determined; they were adjusted by trial on the Fourier map, assuming planar indenyl radicals, until satisfactory agreement between measured and calculated structure factors was obtained.

The observed and calculated structure factors are listed in Table 20 (page 134); the discrepancy over the observed planes is 23%. The final Fourier series was computed using the phase angles calculated from the final coordinates (Fig.25).

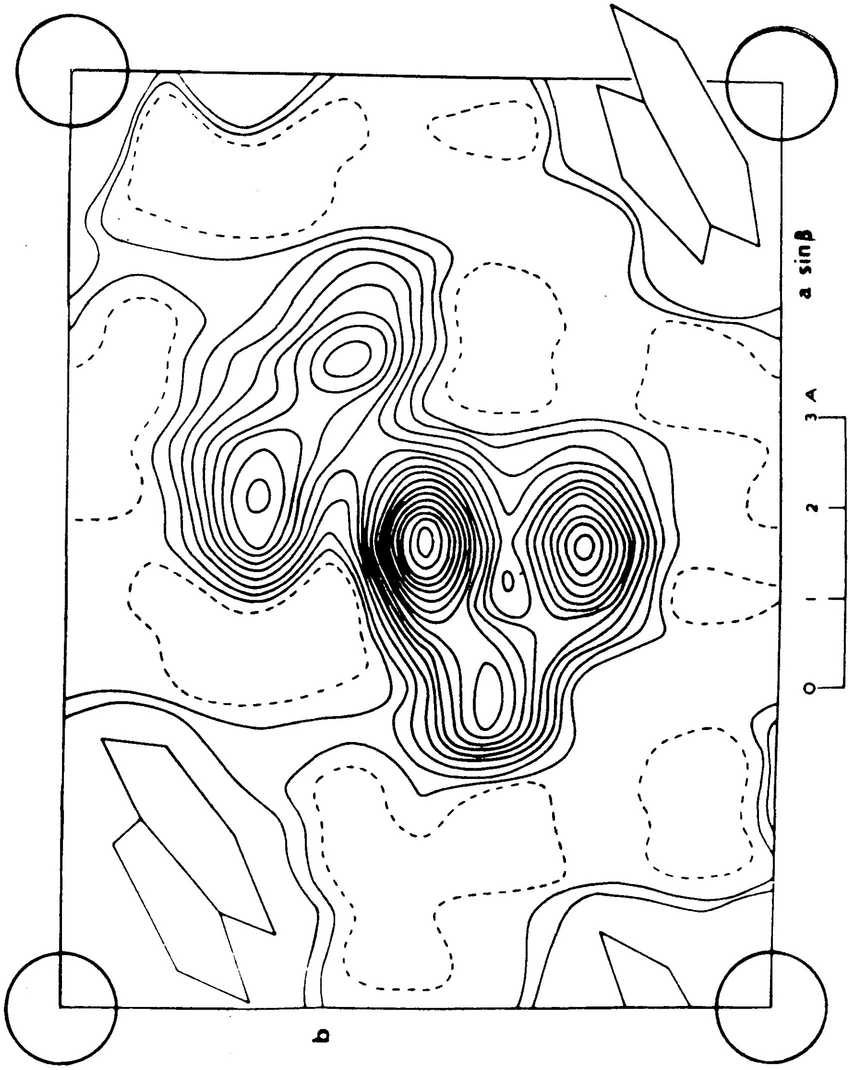


Fig.25. Electron density projection on (001), with phase angles from iron and carbon positions. Contour interval 1 eA^{-2} with the one-electron line dotted.

3.4. Scattering factors.

In the calculation of the structure factors the scattering curve used for iron was that given for Fe in the "International Tables" (1935), the curve for Fe being used in preference to that for Fe^{++} on evidence for the charge distribution in this type of molecule (Moffitt, 1954). This curve however had to be corrected for the anomalous dispersion of the CoKα radiation by the K electrons of the iron atom. A variation of the scattering factor with wavelength occurs when the wavelength of the incident radiation is near the absorption edge of the scattering atom. When the quantum of energy of the incident rays is near to that required to eject the K electrons, then the K electrons scatter with a difference of phase with respect to the rest of the electrons in the atom. Details of the corrections have been given by James (1950) who tabulates $\Delta f_K'$ and $\Delta f_K''$, the real and imaginary parts of the correction to be applied to the scattering factor on account of dispersion by the K electrons, as functions of λ/λ_K and δ_K, where

λ = wavelength of radiation scattered = 1.790 A,

λ_K = wavelength of K absorption-edge of scattering element = 1.74 A,

δ_K is a parameter characteristic of the scattering element.

From the tables: $\Delta f_K' = -3.77$

$\Delta f_K'' = 0.$

McWeeny's scattering curve was used for the carbon atoms (McWeeny, 1951).

Both curves were corrected for thermal vibrations according to the usual Debye-Waller expression:

$$f = f_o \exp\left[-B\,(\sin\theta/\lambda)^2\right].$$

B was taken as 3.86×10^{-16}, an average value estimated for the crystal by Wilson's method (Wilson, 1942).

In the Fourier summations, the axial subdivisions were a/60 = 0.189, b/30 = 0.262, c/30 = 0.270 A.

4. Discussion.

At the moment projections of the structure down two crystal axes (b and c) have been examined, and the crystal and molecular structure has been established fairly clearly. The agreement between measured and calculated structure amplitudes is on the whole quite encouraging; there are however a few poor agreements among the $(h0\ell)$ reflexions, and these do cast some doubt on the validity of the proposed structure. The first Fourier synthesis on the $(h0\ell)$ zone has been computed directly from the X-ray data, without making any assumptions about the geometry of the molecule, and it is difficult to envisage any interpretation of this Fourier map, other than the one which has been followed. The rather large variation in peak height does suggest that absorption and extinction errors are quite severe, as in the case of ferrocene (Dunitz et al., 1956).

The present doubts about the structure may be overcome by proceeding with a full three-dimensional analysis, which will be required eventually in any case, if accurate molecular dimensions are to be obtained. Absorption errors will be reduced if MoKα is used; at present the photographs obtained with this radiation are rather unsatisfactory, but the use of stouter crystals would probably produce better photographic records. A three-dimensional Patterson function may then be computed, and interpreted on the basis of the present structure; since the Fe-C peaks are much heavier than the C-C, the interpretation of the Patterson function should be fairly straightforward. At the moment however the following facts have been established:

(i) Consideration of the two projections leaves no doubt that the molecule has a "sandwich" structure. This is particularly well illustrated in the c-axis projection, where the aromatic rings are viewed end-on, with the metal atom "sandwiched" between. The b-axis projection clearly shows that the iron atom is bonded to the five-membered rings.

(ii) Attempts to interpret the observed X-ray data in terms of a trans-configuration of the molecule were unsuccessful. The planes of the two aromatic radicals are parallel, and Fig.26 shows the molecule viewed along the normal to the

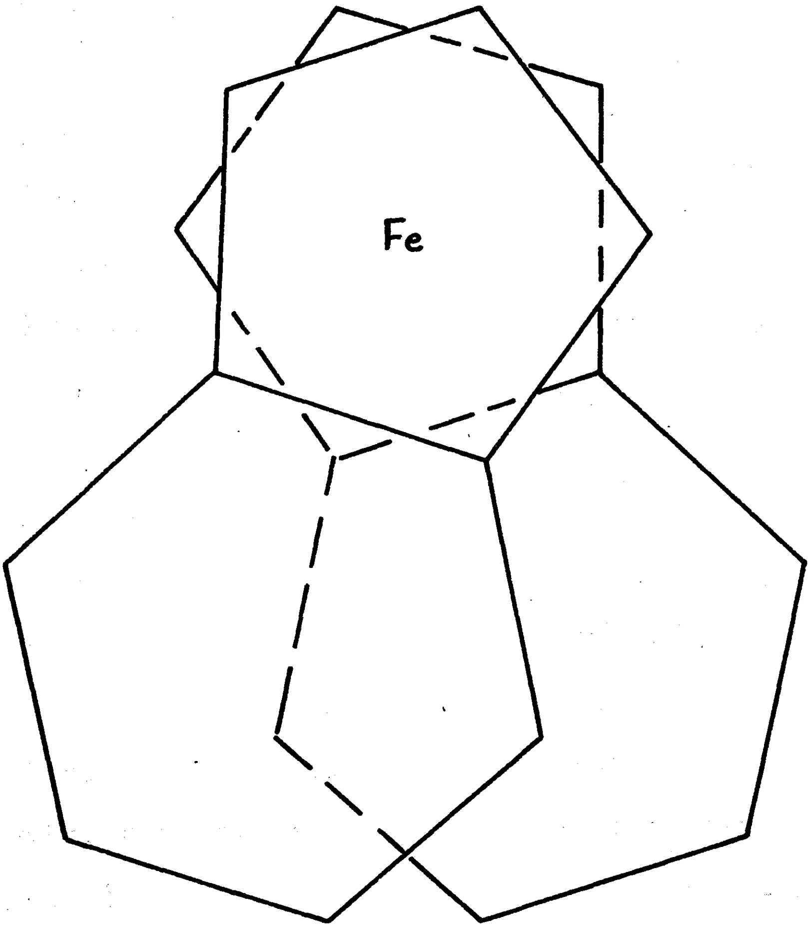


Fig.26. Projection of the diindenyl iron molecule along the normal to the planes of the aromatic rings.

planes of the aromatic rings, from which it is evident that the molecular configuration is "gauche".

(iii) In the (h0ℓ) zone, 36 carbon parameters have to be determined from only 55 independent observed reflexions, and in the (hk0) zone there are only 21 independent observed reflexions, so that the dimensions of the molecule can be determined accurately only by extending the analysis to three-dimensional data. The coordinates obtained from the two projections may nevertheless be used as a starting point for a three-dimensional refinement, and these are listed in Table 19. The coordinates x, y, z are expressed as fractions of the unit cell edges, the iron atom being taken as origin.

(iv) While no accurate determination of the dimensions of the molecule is possible by consideration of two-dimensional data only, the Fe-C and C-C bond lengths have been calculated from the coordinates of Table 19, and the mean bond lengths are compared in Table 18 with the corresponding mean bond lengths in ferrocene.

Table 18.

Mean bond lengths in $Fe(C_5H_5)_2$ and $Fe(C_9H_7)_2$.

	$Fe(C_5H_5)_2$	$Fe(C_9H_7)_2$
Mean Fe-C	2.045 A	2.13 A
Mean C-C	1.403	1.46
Perpendicular distance between planes of rings	3.32	3.4

The perpendicular distance between the planes of the aromatic rings is about 3.4 A, identical with the interplanar spacing in graphite, and the molecule is probably fixed in the gauche configuration by weak van der Waals forces between the six-membered rings, which stabilize the gauche configuration with respect to the trans.

All the intermolecular distances correspond to normal van der Waals attractions.

Table 19.

Coordinates of the atoms.

Atom	x	y	z
Fe	0	0	0
C1	0.005	0.265	0.000
2	0.037	0.164	-0.141
3	0.174	0.070	-0.045
4	0.286	0.053	0.293
5	0.278	0.143	0.457
6	0.185	0.240	0.489
7	0.079	0.300	0.338
8	0.099	0.221	0.163
9	0.200	0.110	0.139
C1'	-0.005	-0.265	0.000
2'	-0.106	-0.227	-0.157
3'	-0.198	-0.110	-0.129
4'	-0.179	-0.029	0.214
5'	-0.072	-0.050	0.400
6'	0.041	-0.149	0.468
7'	0.079	-0.246	0.338
8'	-0.026	-0.195	0.141
9'	-0.157	-0.100	0.060

Table 20.

Measured and calculated structure factors.

Plane	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α°	Plane	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α°
000	-	289	-	205	28	31	346
001	87	88	38	6	13	20	24
2	75	63	330	7	<4	6	343
3	16	13	31	$40\bar{8}$	<6	8	324
4	<6	14	343	$\bar{7}$	21	29	353
5	7	12	11	$\bar{6}$	19	24	25
6	20	24	354	$\bar{5}$	20	28	340
7	6	14	21	$\bar{4}$	60	44	8
8	5	8	331	$\bar{3}$	20	19	11
$20\bar{8}$	<5	7	7	$\bar{2}$	31	33	327
$\bar{7}$	13	16	354	$\bar{1}$	47	46	355
$\bar{6}$	18	14	27	0	41	43	29
$\bar{5}$	<7	9	356	1	21	16	347
$\bar{4}$	14	10	342	2	62	39	345
$\bar{3}$	38	40	351	3	17	19	7
$\bar{2}$	17	48	20	4	12	10	343
$\bar{1}$	68	64	350	5	7	2	338
0	61	50	6	6	<5	4	332
1	<4	35	340	$60\bar{8}$	<6	5	19
2	37	32	358	$\bar{7}$	<8	7	356
3	41	32	18	$\bar{6}$	8	12	24
4	<7	15	11	$\bar{5}$	25	20	340

Plane	$\lvert F_o \rvert$	$\lvert F_c \rvert$	α°
$60\bar{4}$	48	38	9
$\bar{3}$	<6	22	3
$\bar{2}$	44	35	350
$\bar{1}$	46	33	13
0	7	24	3
1	39	38	355
2	21	27	30
3	8	9	325
4	10	12	349
5	<4	5	10
$80\bar{8}$	<5	3	322
$\bar{7}$	9	12	28
$\bar{6}$	<8	7	348
$\bar{5}$	24	30	353
$\bar{4}$	11	15	8
$\bar{3}$	7	14	338
$\bar{2}$	<7	2	263
$\bar{1}$	<7	9	2
0	<8	2	56
1	24	25	338
2	20	20	22
3	<6	10	353
$100\bar{8}$	4	9	1
$\bar{7}$	<5	9	354
$\bar{6}$	20	22	348
$\bar{5}$	22	18	30
$\bar{4}$	<7	6	1
$\bar{3}$	<7	8	1
$\bar{2}$	<7	9	357
$\bar{1}$	<7	9	356
0	18	14	343
1	14	11	14
$120\bar{6}$	4	5	309
$\bar{5}$	12	10	19
$\bar{4}$	<5	6	18
$\bar{3}$	13	15	358
$\bar{2}$	<5	8	27
$\bar{1}$	<3	9	333

Plane	$\|F_o\|$	$\|F_c\|$	α°
010	<5	5	90
2	<7	4	180
3	<8	2	270
4	36	29	0
110	61	79	4
2	46	52	202
3	13	17	336
4	12	13	175
5	15	14	351
210	53	49	209
2	30	30	249
3	10	5	211
4	34	33	7

Plane	$\|F_o\|$	$\|F_c\|$	α°
310	7	22	317
2	<7	12	17
3	17	16	356
4	9	6	69
5	17	16	357
410	<7	5	64
2	<8	16	347
3	19	12	32
4	19	10	336
510	17	27	14

APPENDICES.

APPENDIX I.

Dinaphthoperopyrene.

Measured and calculated $(h0\ell)$ structure factors.

(i) Sharp reflexions ($\ell = 2n$).

h	ℓ	F_o	F_c
0	0	-	+984
2	0	86	+ 85
4		111	-112
6		50	+ 57
8		16	- 17
10		27	+ 31
12		10	+ 11
14		11	+ 10
16		21	- 26
18		21	+ 22
20		14	- 12
22		16	+ 8
24		19	+ 10
26		<4	0
28		15	+ 9
30		12	- 12
32		6	+ 7
34		21	- 21
36		14	- 14
0	2	164	+158
	4	70	- 74
	6	6	+ 3
	8	16	+ 20
	10	22	+ 16
	12	14	- 16
	14	7	+ 16
	16	<4	+ 6
	18	4	+ 10
	20	<4	- 3
	22	<3	- 3

h	ℓ	F_o	F_c
$\overline{36}$	2	2	- 1
$\overline{34}$		3	+ 6
$\overline{32}$		2	- 3
$\overline{30}$		8	+ 8
$\overline{28}$		19	- 18
$\overline{26}$		<4	+ 5
$\overline{24}$		162	+155
$\overline{22}$		36	+ 36
$\overline{20}$		30	- 29
$\overline{18}$		20	+ 19
$\overline{16}$		12	- 6
$\overline{14}$		19	+ 20
$\overline{12}$		10	+ 10
$\overline{10}$		29	+ 27
$\overline{8}$		28	- 30
$\overline{6}$		68	+ 62
$\overline{4}$		84	- 87
$\overline{2}$		146	+141
2		48	- 46
4		70	+ 72
6		75	- 74
8		32	+ 34
10		95	- 92
12		62	- 64
14		18	+ 22
16		21	- 21
18		12	+ 14
20		12	- 8
22		15	- 17
24		4	- 7
26		5	+ 2
28		<4	- 3
30		6	+ 7
32		<3	- 6
34		29	- 26

h	ℓ	F_o	F_c
$\bar{34}$	4	3	+ 3
$\bar{30}$		14	+ 11
$\bar{28}$		25	- 28
$\bar{26}$		49	+ 45
$\bar{24}$		71	+ 69
$\bar{22}$		19	- 18
$\bar{20}$		20	+ 24
$\bar{18}$		24	- 23
$\bar{16}$		<3	+ 1
$\bar{14}$		41	- 39
$\bar{12}$		55	- 52
$\bar{10}$		27	+ 28
$\bar{8}$		72	- 68
$\bar{6}$		65	+ 66
$\bar{4}$		20	- 12
$\bar{2}$		122	-117
2		41	+ 34
4		20	- 27
6		39	+ 39
8		19	- 20
10		197	-196
12		22	- 19
14		36	+ 37
16		9	- 8
18		<4	- 8
20		5	+ 8
22		9	+ 14
24		5	- 3
26		4	- 4
$\bar{38}$	6	6	- 5
$\bar{36}$		5	- 3
$\bar{34}$		<3	+ 2
$\bar{32}$		11	- 11
$\bar{30}$		17	+ 12
$\bar{28}$		<4	+ 2
$\bar{26}$		16	- 19
$\bar{24}$		25	- 29
$\bar{22}$		9	+ 14
$\bar{20}$		5	- 5
$\bar{18}$		19	+ 10
$\bar{16}$		<3	- 1
$\bar{14}$		198	-196
$\bar{12}$		47	- 49
$\bar{10}$		49	+ 44

h	ℓ	F_o	F_c
$\bar{8}$	6	14	- 7
$\bar{6}$		21	- 19
$\bar{4}$		25	+ 21
$\bar{2}$		87	+ 87
2		23	- 19
4		7	+ 7
6		9	+ 7
8		2	+ 2
10		5	- 1
12		4	- 1
14		12	- 6
20		27	- 30
22		28	- 27
24		5	+ 9
28		3	- 4
$\bar{38}$	8	28	- 26
$\bar{36}$		9	- 9
$\bar{34}$		3	+ 4
$\bar{32}$		4	- 3
$\bar{26}$		11	+ 14
$\bar{22}$		3	- 8
$\bar{20}$		8	- 3
$\bar{18}$		25	+ 29
$\bar{16}$		24	- 27
$\bar{14}$		31	- 27
$\bar{12}$		9	+ 5
$\bar{10}$		<3	- 7
$\bar{8}$		9	+ 5
$\bar{6}$		2	+ 3
$\bar{4}$		67	- 66
$\bar{2}$		81	- 78
2		<3	+ 1
4		21	- 25
6		<3	- 8
8		19	+ 19
12		5	- 3
14		5	- 8
18		4	- 1
20		47	- 48
22		3	- 5
24		3	+ 2
26		2	- 2

h	ℓ	F_o	F_c
$\overline{38}$	10	16	-12
$\overline{28}$		12	-7
$\overline{26}$		12	-9
$\overline{24}$		<4	-1
$\overline{22}$		7	+4
$\overline{20}$		16	-8
$\overline{18}$		6	-10
$\overline{16}$		25	+23
$\overline{14}$		20	+18
$\overline{12}$		13	-13
$\overline{10}$		21	-22
$\overline{8}$		18	+16
$\overline{6}$		7	+7
$\overline{4}$		192	-181
$\overline{2}$		35	-29
2		13	-14
4		20	+24
6		15	-15
8		16	-16
10		8	-4
12		22	+20
14		4	-8
16		2	+2
24		3	-4
26		4	+8
$\overline{38}$	12	4	+6
$\overline{34}$		5	-7
$\overline{32}$		9	+9
$\overline{30}$		<4	+4
$\overline{28}$		57	-58
$\overline{26}$		20	-21
$\overline{24}$		7	+11
$\overline{22}$		<4	-8
$\overline{20}$		12	+9
$\overline{18}$		6	-8
$\overline{16}$		26	-25
$\overline{14}$		7	-15
$\overline{12}$		25	+26
$\overline{10}$		13	-18
$\overline{8}$		10	+8
$\overline{6}$		<3	-1
$\overline{4}$		21	-18
$\overline{2}$		14	+21
2	12	19	+25
4		5	-10
6		75	+77
8		83	+83
10		8	-19
12		3	+7
14		2	+1
18		4	+2
$\overline{38}$	14	2	-5
$\overline{36}$		3	+4
$\overline{34}$		4	-6
$\overline{32}$		3	+7
$\overline{30}$		<4	-6
$\overline{28}$		21	-20
$\overline{26}$		5	+13
$\overline{24}$		9	-11
$\overline{22}$		9	+11
$\overline{20}$		5	-1
$\overline{18}$		49	+48
$\overline{16}$		71	+67
$\overline{14}$		4	-10
$\overline{12}$		15	+17
$\overline{10}$		<4	-9
$\overline{8}$		3	+4
$\overline{6}$		21	+15
$\overline{4}$		14	+15
$\overline{2}$		4	-4
2		15	-17
4		<4	-10
6		121	+124
8		25	+23
10		27	-26
12		4	+4
14		5	-7
18		5	-6

h	l	F_o	F_c
$\overline{36}$	16	7	+ 9
$\overline{30}$		5	+ 5
$\overline{28}$		5	+ 10
$\overline{26}$		<4	- 1
$\overline{24}$		7	+ 13
$\overline{22}$		13	- 12
$\overline{20}$		<4	- 15
$\overline{18}$		138	+135
$\overline{16}$		51	+ 44
$\overline{14}$		30	- 28
$\overline{12}$		4	+ 6
$\overline{10}$		5	- 10
$\overline{8}$		<4	+ 2
$\overline{6}$		11	- 12
$\overline{4}$		<4	+ 3
$\overline{2}$		8	- 11
2		5	- 3
4		5	- 9
6		3	- 3
8		5	- 9
10		12	+ 11
12		5	- 9
16		16	- 17
18		18	- 20
$\overline{28}$	18	<3	+ 2
$\overline{26}$		<4	- 4
$\overline{24}$		6	+ 9
$\overline{22}$		11	- 15
$\overline{20}$		<4	+ 4
$\overline{18}$		13	+ 14
$\overline{16}$		9	- 17
$\overline{14}$		7	+ 13
$\overline{12}$		8	- 12
$\overline{10}$		<4	+ 3
$\overline{8}$		22	- 24
$\overline{6}$		31	- 34
$\overline{4}$		<4	+ 7
$\overline{2}$		4	- 8
2		<4	+ 4
4		10	- 9

h	l	F_o	F_c
$\overline{32}$	20	13	- 10
$\overline{30}$		17	- 15
$\overline{28}$		<3	+ 3
$\overline{26}$		9	- 10
$\overline{24}$		7	+ 9
$\overline{22}$		<4	+ 6
$\overline{20}$		16	- 12
$\overline{18}$		15	- 14
$\overline{16}$		3	+ 7
$\overline{14}$		3	0
$\overline{12}$		4	+ 6
$\overline{8}$		41	- 42
$\overline{6}$		15	- 15
$\overline{4}$		11	+ 12
$\overline{2}$		<4	+ 2
2		<3	- 1
4		4	+ 8
6		2	0
$\overline{30}$	22	13	- 11
$\overline{28}$		6	+ 5
$\overline{20}$		9	+ 10
$\overline{2}$		<3	- 2
2		14	- 14
4		17	- 20
$\overline{22}$	24	14	- 10
$\overline{20}$		16	- 16

(ii) Diffuse reflexions ($\ell = 2n + 1$).

h	ℓ	F_o	$F_c(A)$	$F_c(AB)$
$\bar{6}$	1	4	+17	0
$\bar{4}$		5	+21	0
$\bar{2}$		Not obs.	+14	0
2		<1	-23	0
4		6	-34	0
6		6	-30	0
8		5	-18	0
10		5	- 5	0
$\bar{10}$	3	2	+12	0
$\bar{8}$		4	+14	0
$\bar{2}$		<1	- 2	0
2		2	+16	0
4		6	+24	0
6		5	+23	0
8		5	+13	0
10		<2	+ 1	0
12		3	- 8	0
$\bar{10}$	5	2	-20	0
$\bar{8}$		5	-25	0
$\bar{6}$		5	-21	0
$\bar{4}$		<2	-10	0
$\bar{8}$	7	2	+17	0
$\bar{6}$		5	+15	0
2		2	-14	0
4		2	-11	0
6		2	- 6	0

APPENDIX II.

Dinaphthoperopyrene.

Measured and calculated (hlℓ) structure factors.

h	ℓ	F_o	$\lvert F_c \rvert$	α°
1	0	41	39	105
3		29	44	212
5		41	36	46
7		16	18	232
9		17	23	70
11		18	16	60
13		29	36	232
15		5	4	22
17		<3	8	71
19		4	7	166
21		59	50	55
23		8	18	43
25		50	43	238
27		<4	3	332
29		<4	0	-
31		4	3	76
33		12	10	48
35		7	6	239
$\overline{35}$	1	20	15	145
$\overline{33}$		<2	1	118
$\overline{31}$		<3	2	354
$\overline{29}$		4	2	307
$\overline{27}$		9	8	135
$\overline{25}$		38	35	336
$\overline{23}$		76	55	338
$\overline{21}$		8	18	100
$\overline{19}$		16	20	348
$\overline{17}$		6	18	108
$\overline{15}$		2	16	349
$\overline{13}$		15	9	302
$\overline{11}$		16	14	300
$\overline{9}$		25	32	341
$\overline{7}$		21	39	105
$\overline{5}$		60	71	350
$\overline{3}$		44	67	79
$\overline{1}$		267	244	345
1		169	183	345
3		26	29	78
5	1	31	23	345
7		8	8	48
9		17	11	350
11		78	76	142
13		4	5	339
15		4	5	268
17		4	10	222
19		11	20	179
21		9	11	227
23		34	39	312
25		6	10	181
27		<4	9	182
29		3	4	217
31		<4	4	204
33		14	9	177
35		15	12	167
$\overline{31}$	2	4	4	219
$\overline{29}$		11	11	39
$\overline{27}$		15	14	228
$\overline{25}$		8	14	209
$\overline{23}$		22	23	73
$\overline{21}$		6	7	110
$\overline{19}$		8	8	67
$\overline{17}$		<3	5	213
$\overline{15}$		5	13	70
$\overline{13}$		7	13	56
$\overline{11}$		26	29	234
$\overline{9}$		18	9	39
$\overline{7}$		8	8	127
$\overline{5}$		23	27	176
$\overline{3}$		232	236	56
$\overline{1}$		93	111	53
1		261	239	235
3		17	28	280
5		<2	12	13
7		<2	8	142
9		77	70	53
11		29	30	240

h	ℓ	F_o	$\|F_c\|$	α°
13	2	71	56	236
15		<3	7	318
17		5	7	13
19		14	18	233
21		4	3	82
23		7	5	29
25		10	9	40
27		<4	1	180
29		3	4	227
31		3	2	330
33		9	8	242
$\overline{29}$	3	13	12	352
$\overline{27}$		9	13	67
$\overline{25}$		77	53	348
$\overline{23}$		61	45	354
$\overline{21}$		5	15	36
$\overline{19}$		15	17	352
$\overline{17}$		7	9	94
$\overline{15}$		14	16	334
$\overline{13}$		60	57	142
$\overline{11}$		10	13	342
$\overline{9}$		7	1	65
$\overline{7}$		3	15	266
$\overline{5}$		43	53	171
$\overline{3}$		50	42	188
$\overline{1}$		162	213	315
1		43	36	210
3		27	55	179
5		21	23	229
7		3	16	225
9		68	56	167
11		97	71	161
13		8	15	253
15		15	12	182
17		4	5	300
19		<3	2	37
21		7	12	118
23		8	12	115
33		11	7	158
$\overline{29}$	4	5	6	187
$\overline{27}$		51	43	58
$\overline{25}$		38	33	57
$\overline{23}$	4	59	60	232
$\overline{21}$		9	15	255
$\overline{19}$		6	7	358
$\overline{17}$		3	9	207
$\overline{15}$		68	55	56
$\overline{13}$		17	21	235
$\overline{11}$		79	75	236
$\overline{9}$		6	11	330
$\overline{7}$		4	8	334
$\overline{5}$		48	36	232
$\overline{3}$		15	45	53
$\overline{1}$		6	15	312
1		50	31	20
3		2	13	67
5		19	24	219
7		10	18	34
9		39	32	248
11		9	18	34
13		14	11	45
15		5	4	213
17		4	3	84
19		<4	3	163
21		6	4	133
23		5	11	228
29		2	1	286
31		12	10	232
$\overline{37}$	5	8	6	143
$\overline{35}$		4	4	332
$\overline{29}$		4	7	163
$\overline{27}$		4	9	161
$\overline{25}$		52	56	319
$\overline{23}$		4	9	262
$\overline{21}$		9	18	181
$\overline{19}$		7	10	227
$\overline{17}$		7	9	257
$\overline{15}$		48	43	160
$\overline{13}$		102	83	154
$\overline{11}$		8	19	260
$\overline{9}$		28	24	190
$\overline{7}$		8	18	275
$\overline{5}$		7	13	173
$\overline{3}$		17	13	117
$\overline{1}$		21	29	112
1		4	12	96

h	ℓ	F_o	$\lvert F_c\rvert$	α°
3	5	22	23	331
5		16	22	137
7		15	19	288
9		66	40	171
11		45	33	161
13		9	8	334
15		4	9	93
17		7	8	1
19		<4	2	104
21		18	24	151
23		6	2	204
25		3	4	341
$\bar{35}$	6	13	11	304
$\bar{33}$		5	2	0
$\bar{31}$		<4	3	62
$\bar{29}$		5	4	32
$\bar{27}$		19	22	308
$\bar{25}$		8	6	276
$\bar{23}$		6	7	297
$\bar{21}$		6	10	46
$\bar{19}$		18	15	217
$\bar{17}$		15	19	49
$\bar{15}$		9	13	269
$\bar{13}$		8	8	325
$\bar{11}$		<2	5	284
$\bar{9}$		9	2	289
$\bar{7}$		23	11	29
$\bar{5}$		30	29	217
$\bar{3}$		2	19	186
$\bar{1}$		8	19	223
1		9	8	52
3		<2	5	247
5		7	6	348
7		65	57	233
9		17	25	225
11		58	45	58
13		7	9	76
15		4	6	185
17		<4	2	82
19		15	24	48
21		12	8	247
23		21	16	239

h	ℓ	F_o	$\lvert F_c\rvert$	α°
$\bar{37}$	7	22	15	150
$\bar{29}$		5	8	170
$\bar{23}$		6	11	142
$\bar{21}$		7	8	315
$\bar{19}$		15	12	150
$\bar{17}$		10	11	261
$\bar{15}$		69	42	175
$\bar{13}$		61	40	174
$\bar{11}$		12	8	261
$\bar{9}$		9	23	119
$\bar{7}$		24	34	349
$\bar{5}$		4	14	51
$\bar{3}$		68	83	137
$\bar{1}$		11	13	118
1		18	32	342
3		7	18	90
5		18	29	349
7		8	12	57
9		31	43	126
11		<3	9	80
13		10	18	334
15		4	9	156
17		<4	8	212
19		16	15	188
21		27	22	172
23		<4	7	211
25		3	6	173
$\bar{35}$	8	7	4	243
$\bar{33}$		3	1	336
$\bar{29}$		11	10	225
$\bar{27}$		8	10	211
$\bar{19}$		3	5	17
$\bar{17}$		63	43	238
$\bar{15}$		41	36	232
$\bar{13}$		72	60	54
$\bar{11}$		19	21	68
$\bar{9}$		7	15	184
$\bar{7}$		4	7	107
$\bar{5}$		89	78	51
$\bar{3}$		21	16	245
$\bar{1}$		92	78	232
1		8	5	330

h	ℓ	F_o	$\lvert F_c \rvert$	α°
3	8	4	3	225
5		13	18	52
7		9	7	29
9		12	7	204
11		22	21	226
13		3	4	290
15		<4	5	5
17		12	11	243
19		7	8	246
21		<4	3	19
23		11	10	55
25		2	5	225
$\overline{37}$	9	13	8	181
$\overline{31}$		5	9	341
$\overline{27}$		15	24	128
$\overline{25}$		4	10	111
$\overline{23}$		9	17	345
$\overline{21}$		<4	9	76
$\overline{19}$		10	15	356
$\overline{17}$		9	10	9
$\overline{15}$		40	46	131
$\overline{13}$		<3	15	97
$\overline{11}$		17	24	343
$\overline{9}$		10	13	134
$\overline{7}$		<3	11	230
$\overline{5}$		62	43	182
$\overline{3}$		97	65	176
$\overline{1}$		11	23	229
1		13	23	168
3		5	11	256
5		9	14	178
7		<3	9	288
9		12	20	305
11		3	14	178
13		3	7	255
15		<4	5	187
17		6	6	315
19		17	18	144
21		10	13	143
27		6	1	168
$\overline{37}$	10	11	11	51
$\overline{29}$		19	21	55
$\overline{25}$		20	28	235
$\overline{19}$		11	6	44

h	ℓ	F_o	$\lvert F_c \rvert$	α°
$\overline{17}$	10	3	4	245
$\overline{13}$		17	21	219
$\overline{7}$		18	18	250
$\overline{5}$		12	9	281
$\overline{3}$		7	10	275
$\overline{1}$		27	28	47
1		12	12	218
7		19	14	260
9		23	38	50
11		11	7	75
15		6	6	41
17		8	13	233
21		12	13	58
$\overline{29}$	11	14	13	171
$\overline{27}$		26	23	174
$\overline{25}$		4	10	248
$\overline{23}$		4	11	168
$\overline{13}$		9	11	190
$\overline{11}$		4	12	254
$\overline{9}$		12	15	187
$\overline{7}$		12	14	291
$\overline{5}$		66	45	151
$\overline{3}$		47	44	148
$\overline{1}$		9	4	297
1		<3	7	288
7		62	76	326
9		22	12	346
11		7	11	127
13		7	7	348
17		7	11	336
$\overline{27}$	12	3	6	289
$\overline{25}$		5	8	34
$\overline{21}$		6	2	200
$\overline{19}$		5	6	0
$\overline{15}$		17	27	49
$\overline{13}$		4	4	210
$\overline{11}$		<3	1	347
$\overline{9}$		9	12	36
$\overline{7}$		45	36	234
$\overline{5}$		47	26	232
$\overline{3}$		54	38	56
$\overline{1}$		5	5	139
5		53	61	230
7		20	14	75
9		59	49	58

h	l	F_o	$\lvert F_c \rvert$	α°
$\overline{29}$	13	18	17	161
$\overline{27}$		19	19	158
$\overline{17}$		56	68	321
$\overline{15}$		15	17	318
$\overline{13}$		9	17	148
$\overline{11}$		8	5	335
$\overline{9}$		4	5	57
$\overline{7}$		19	20	340
$\overline{5}$		18	23	135
$\overline{3}$		10	10	343
$\overline{1}$		3	7	45
1		10	13	8
3		4	14	40
5		40	36	3
7		79	60	347
9		9	16	45
11		7	3	323
$\overline{31}$	14	15	14	234
$\overline{29}$		11	14	236
$\overline{27}$		11	17	55
$\overline{19}$		59	59	234
$\overline{15}$		61	66	57
$\overline{13}$		6	10	100
$\overline{9}$		10	7	63
1		4	7	64
3		13	10	80
5		27	27	65
9		35	26	232
15		5	5	75
$\overline{37}$	15	12	5	166
$\overline{31}$		4	7	337
$\overline{29}$		10	14	133
$\overline{23}$		8	8	3
$\overline{21}$		<4	9	68
$\overline{19}$		38	33	356
$\overline{17}$		82	66	345
$\overline{15}$		14	20	53
$\overline{13}$		10	20	356
$\overline{7}$		4	6	300
$\overline{1}$		6	13	135
1		4	10	322
3		13	16	141
5		36	26	330
7	15	35	32	326
9		8	8	165
17		13	17	148
19		<2	4	163
$\overline{31}$	16	5	6	234
$\overline{27}$		4	5	73
$\overline{23}$		9	8	49
$\overline{21}$		9	3	112
$\overline{19}$		11	11	86
$\overline{15}$		15	20	226
$\overline{9}$		3	6	72
$\overline{7}$		8	11	54
$\overline{5}$		12	18	236
$\overline{3}$		4	6	256
$\overline{1}$		<4	4	43
1		5	10	217
3		34	31	54
5		14	25	47
7		36	31	239
17		<4	3	254
$\overline{23}$	17	7	9	337
$\overline{21}$		9	10	61
$\overline{19}$		36	28	341
$\overline{17}$		42	35	334
$\overline{15}$		5	3	138
$\overline{11}$		5	5	166
$\overline{7}$		20	30	147
$\overline{5}$		9	9	155
1		5	9	192
3		12	15	168
5		10	20	310
15		6	5	189
$\overline{29}$	18	4	7	232
$\overline{27}$		4	2	270
$\overline{23}$		5	9	215
$\overline{21}$		39	30	55
$\overline{19}$		26	24	48
$\overline{17}$		38	37	237
$\overline{15}$		15	13	252
$\overline{9}$		13	20	53
$\overline{5}$		14	19	235

h	ℓ	F_o	$\lvert F_c\rvert$	α°
1	18	6	9	236
3		4	5	207
5		<3	0	243
7		10	8	42
$\bar{31}$	19	12	12	149
$\bar{23}$		3	6	199
$\bar{21}$		12	16	166
$\bar{19}$		13	25	309
$\bar{15}$		7	12	170
$\bar{9}$		10	10	178
$\bar{7}$		27	25	159
5		4	11	116
$\bar{33}$	20	7	9	53
$\bar{29}$		12	12	236
$\bar{23}$		8	7	234
$\bar{21}$		3	2	94
$\bar{17}$		5	6	27
$\bar{13}$		4	7	216
$\bar{9}$		7	11	246
$\bar{5}$		7	10	55
7		3	3	248

h	ℓ	F_o	$\lvert F_c\rvert$	α°
$\bar{31}$	21	17	15	155
$\bar{15}$		4	8	347
$\bar{11}$		3	5	331
$\bar{9}$		5	6	168
$\bar{7}$		8	10	152
3		10	14	157
5		6	6	184
$\bar{11}$	22	9	10	238
$\bar{9}$		6	12	230
$\bar{7}$		9	11	62
$\bar{5}$		2	2	85
1		3	9	44
$\bar{21}$	23	10	13	144
$\bar{19}$		7	7	159
$\bar{23}$	24	7	10	49
$\bar{19}$		9	11	238
$\bar{7}$		3	6	223

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