A STUDY OF SOME ORGANIC CRYSTAL STRUCTURES

A Thesis presented for the degree
of Doctor of Philosophy in the
University of Glasgow

by

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A STUDY OF SOME ORGANIC CRYSTAL STRUCTURES

PART I

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PREFACE

The research work described in this thesis was carried out in the Chemistry Department of the University of Glasgow, under the supervision of Professor J.M. Robertson. To him I am indebted not only for permission to do this work while I was assistant lecturer in the Department of Natural Philosophy of the Royal Technical College of Glasgow, but also for guiding my first steps into a most fascinating science. For this, and his constant encouragement, I wish to give him my sincerest thanks. I would also like to thank Professor J.S. Rankin who was so generous to allow me to work in the University while I was his assistant.

I wish to acknowledge also the help of Dr. E. Clar and Mr. W. Kelly who prepared all the crystals, as well as those, in particular Dr. H.H.H. Shearer, who gave persuasion or dissuasion at the right times. Lastly, I wish to thank Miss H. McNeill for typing this thesis.

It is expected that this work will be published.

SUMMARY

The crystal structure determination, using single crystal X-ray diffraction methods, of three polycyclic aromatic hydrocarbons is described. The thesis is divided into three parts, each part corresponding to one compound. An appendix is added in which the history and uses of "generalized projections" is reviewed. An ~~adoption~~ adaptation of this technique was used extensively in the analysis of 1:9 - 5:10 diperinaphthylene anthracene.

Part I of this thesis deals with the structure of 2:3-8:9 dibenzperylene. The short *b* axis of the monoclinic unit cell, and the regular nature of the rings in this aromatic compound, made the structure analysis easy. The good resolution of the atoms in the projection on the (010) plane made it possible for refinement, by means of two dimensional fourier series, to proceed to a good degree of accuracy. It was, therefore, surprising that refinement by successive difference maps did not yield the same answer as a back shift correction calculated from a comparison of electron density maps for which F_{obs} and F_{calc} values had been used as coefficients in the Fourier series. However, both methods of refinement show clearly an intermolecular approach distance of less than 3.2 A. Bond lengths appear to indicate that this is apparently due to a lack of complete

planarity of the molecule, although another explanation is possible.

The overcrowded aromatic hydrocarbon 1:9-5:10 di*peri*naphthylene anthracene is described in Part II. The work concerns itself mainly in the solution of the phase problem, for which a number of unusual methods had to be employed. Two co-ordinates of the atoms in the molecule were found by projections on the (010) plane and the third by means of generalized projections of the $(hl\ell)$ planes. No great accuracy could be achieved, but it was possible to distinguish which of the two possible methods the molecule adopted to relieve the overcrowding.

In the third part of the thesis a description is given of the analysis and refinement of anthrovalene, the third member of the coronene, ovalene series. This analysis is of very great interest because of the extraordinary nature of the chemical reaction in which anthrovalene was formed. It is possible that this process may give an understanding of graphitization. When the work was started not even the empirical formula was known. The cell dimensions showed clearly that the unknown compound was loosely {"isostructural" "isomorphous"} with coronene and ovalene. The molecular weight determination left little doubt about this, and a study of the intensities gave a final confirmation. Certain impurities were, however, found in the available crystals.

X-RAY DIFFRACTION BY A SINGLE CRYSTAL

The theory of the interpretation of the diffraction spectra of X-rays by single crystals is now well established. It has been discussed in original papers, text books, and Ph.d. theses. It was therefore thought superfluous to give yet another account, except for a very short outline as a basis for the work which follows.

A crystal may be regarded as a three dimensional repetition of a certain electron density distribution, as far as X-ray diffraction phenomena are concerned. Hence a crystal may be represented by a three dimensional Fourier summation

$$\rho(x,y,z) = \frac{1}{V} \sum_{h}\sum_{k}\sum_{\ell}{}_{-\infty}^{+\infty} F(hk\ell) \cos 2\pi[hx + ky + \ell z - \alpha(hk\ell)]$$

where $\rho(x,y,z)$ is the electron density at ax, by, cz,

$F(hk\ell)$ is the "structure factor" of the $(hk\ell)$ plane

and $\alpha(hk\ell)$ is the phase angle of the structure factor.

The quantity "structure factor" is complex. It represents the amplitude and phase of the wave "reflected" by a particular plane in the crystal as compared with the same wave "reflected" from the same plane when the cell contents are replaced by just one electron. Thus we may write

$$F(hk\ell) = A(hk\ell) + i\,B(hk\ell)$$

If the n atoms in the cell are assumed to be centred at specific points

$$A(hk\ell) = \sum_{r=1}^{r=n} f_r \cos 2\pi(hx_r + ky_r + \ell z_r)$$

$$B(hk\ell) = \sum_{r=1}^{r=n} f_r \sin 2\pi(hx_r + ky_r + \ell z_r)$$

It then follows that $\tan \alpha(hk\ell) = \frac{B(hk\ell)}{A(hk\ell)}$

f_r is known as the "scattering factor" of an atom and accounts for the fact that the electron density of an atom is not confined to a point, but is spread out over a volume stretching to infinity.

The magnitude of the amplitude of a diffracted wave, as compared to what would be diffracted by a single electron in the cell, is thus the modulus of the structure factor

$$|F(hk\ell)| = \sqrt{A^2 + B^2}$$

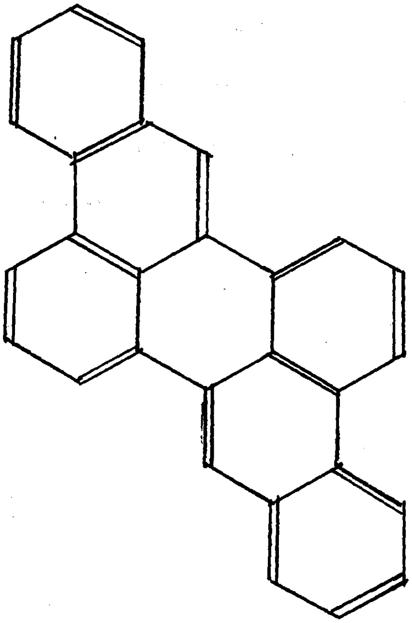
The intensity of any reflected ray will be a function of the square of the amplitude. Hence the moduli of structure factors can be measured experimentally, but not their phases.

A rough knowledge of the phase angles can, therefore, only be obtained by indirect methods. Once a trial structure has been found various iteration processes are available to approximate more and more closely to the correct phase angles. Consequently the electron density in a cell can be calculated with a precision only limited, in the end, by the errors involved in the measurements of intensity.

PART I

2:3 - 8:9 DIBENZPERYLENE

$C_{28}H_{16}$



Introduction

The experimental determination of bond lengths, bond angles and bond energies has for some time been the topic of many investigations (Evans & others, 1951). These experiments have been proceeding hand-in-hand with theoretical investigations aimed at calculating the bond properties, based on assumptions and approximations about the nature of the electronic configuration in atoms and molecules. It is hoped that these studies will lead to a more fundamental and exact understanding of the properties of compounds. X-ray crystallographic investigations are particularly suitable for this work as it is possible to discover the total electron distribution as well as the inter-atomic distances and angles. Aromatic hydrocarbons have had particular attention in this work because the C - C bond "orders" can be calculated fairly easily, and variations in the corresponding bond lengths are sufficiently large to be detected and measured by means of single crystal X-ray analyses.

This X-ray crystallographic study of 2:3 - 8:9 dibenzperylene is meant as a further contribution towards the experimental determination of bond lengths and angles in aromatic hydrocarbons. Recently, theoretical calculations on this compound (Watson, 1956), based on molecular orbital ideas, have been started in the University of Glasgow.

Preliminary Studies

The crystals were prepared by Clar (1932), and crystallized by sublimation into long, thin, yellow needles. On some specimens the (1,0,0) and on nearly all the (0,0,1) faces could be recognized. The needle axis was found to be parallel to the unique axes of the monoclinic unit cells. Good extinction of polarized light was observed under the polarizing microscope when the needle was parallel and perpendicular to the plane of polarization.

Attempts at cutting the crystals were unsuccessful, because the needles tended to split along the needle axis to form large numbers of very small crystals. Even if this did not occur visually, cracks, invisible under the microscope, must have been formed. If any crystal which had been cut was examined with X-rays, partial powder rings were observed.

Crystal Data

2:3 - 8:9 Dibenzperylene, $C_{28} H_{16}$; M = 352.1; m.p. 343°C; d, calc 1.375, found 1.348 gm./c.c.; monoclinic system, $a = 16.59 \pm .04$, $b = 5.23 \pm .01$, $c = 20.6 \pm 0.1$, A., $\beta = 107.8^{\circ} \pm 0.3^{\circ}$; Absent spectra, $(hk\ell)$ when $k + \ell$ is odd, $(h0\ell)$ when h is odd and when ℓ is odd, (oko) when k is odd; Space group C_{2h}^{6} (A2/a), although C_{s}^{4} (Aa) is permissible according to the absent spectra; four molecules per unit cell; Volume of unit cell 1702 A^3; Absorption coefficient for X-rays, $\lambda = 1.542$ A, $\mu = 6.84$ cm^{-1}; Total number of electrons per unit cell = F(000) = 736.

Analysis of the structure

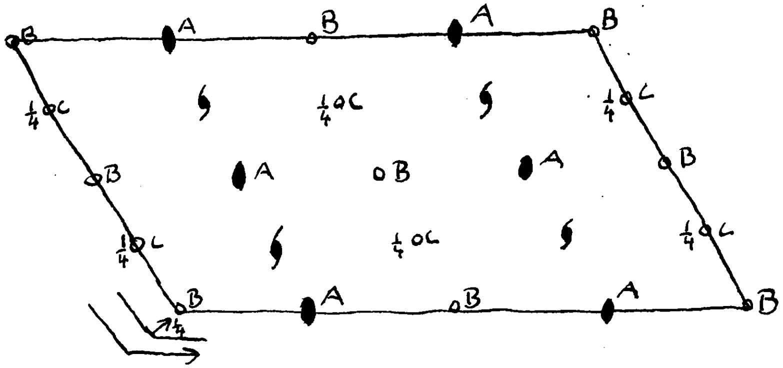
The outstanding feature of the particular habit of dibenzperylene is the short b axis of 5.23 A. Other aromatic polycyclic hydrocarbons such as Coronene (Robertson and White, 1945) and Ovalene (Donaldson and Robertson, 1953) have short unique axes of 4.70 A. In these compounds the planar molecule is inclined at roughly 45° to the short axis. Thus it seemed almost inevitable that the arrangement of the molecule in the unit cell would be similar in dibenzperylene, except for the presence of the face centred lattice. Therefore a study of the (hoℓ) reflections appeared to be the most rewarding procedure.

Two space groups were possible C_{s}^{4} (Aa) without a centre of symmetry, or C_{2h}^{6} (A2/a) with a centre of symmetry. In the non-centred space group the atoms of the molecule would have to lie in general fourfold positions, while in the centred space group there were three possibilities:-

(i) the centre of the molecule co-incident with a twofold axis at Ⓐ,

(ii) the centre of the molecule co-incident with the centre of symmetry at Ⓑ,

(iii) the centre of the molecule co-incident with the centre of symmetry at Ⓒ.



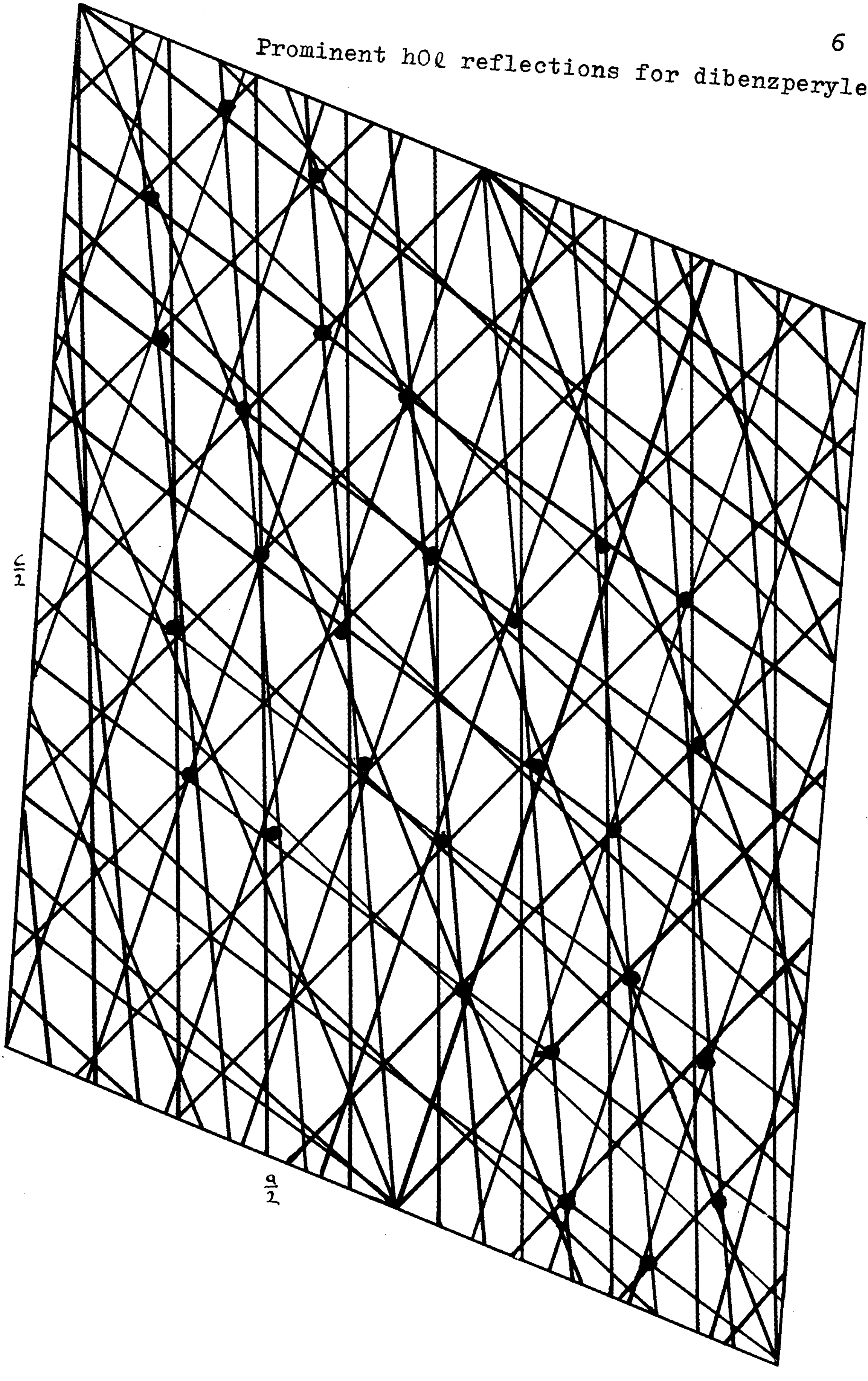
The first of these possibilities (centre at Ⓐ) can be ruled out at once from packing considerations. This would require the molecular plane to be parallel to (010), but the a axis is not long enough to allow such packing.

Perylene (Donaldson, Robertson & White, 1953) has a molecular centre of symmetry according to the chemical formula, but it is not made use of crystallographically, although two molecules are related to each other across a centre of symmetry. Perylene is known to have a dipole moment when in solution. It is believed that no measurement of the dipole moment of 2:3 - 8:9 dibenzperylene has yet been made. As no two molecules could be related to each other across a centre of symmetry with ~~a b axis of only 5.23 A.~~ only four molecules in the unit cell, and as the simpler assumption was that the molecular centre of symmetry was utilized in the space group, it was assumed that the structure employed the space group A2/a. Although the projection down the b axis refined well and quickly when this assumption was made, yet this by itself is no proof that the space group possesses a centre of symmetry. The molecule will in any case have, if not an exact centre of symmetry, something approaching very closely indeed to a centre of symmetry. Since the origin is not fixed in the ac plane for space group Aa, we are at liberty to choose the origin at the centre of the molecule. Thus the projections down the *b* axis, if not identical, will be nearly identical whatever space group is assumed. The essential difference between the two space groups is in the position of the centre of the molecule with respect to the glide plane *a*. While for space group A2/a the molecular centre may only be either on glide planes *a* (position Ⓑ or exactly halfway between glide planes *a* (position Ⓒ, in space group Aa the molecular centre may be at any distance from a glide plane *a*.

The position of the centre of the molecule can, therefore, only be discovered by studying the structure factors of reflections other than those with k = 0. However, if the stacks of oppositely inclined molecules were to be related to each other by a twofold screw axis, as is the case in coronene and ovalene, then the centre of symmetry at Ⓒ would have to be made use of in space group A2/a. This, indeed, was found to be so from a study of the (0kℓ) reflections.

A survey of the reflections from planes of the [010]

Prominent h0ℓ reflections for dibenzperylene.



zone, with moving film methods, showed that the following small spacing planes gave outstandingly strong reflections: (18,0,2), (18,0,4), (8,0,6), (6,0,16), (4,0,16), ($\bar{6}$,0,20), ($\overline{14}$,0,12). After several trials it was found possible to arrange traces, drawn to scale, representing these planes in projection on the (010) plane, in such a way that the lines joining points where all the traces tended to intersect formed a lattice of hexagons. Due regard had also been taken of the centre of symmetry at the origin. These planes must have had strong X-ray reflections because all atoms are on or near planes represented in projection by the traces. Thus atoms must occur, in projection, where all these traces intersect. The hexagons then represent the benzene rings and showed clearly the tilt of the molecule. There were, however, six possible ways of fitting the molecule to this hexagonal lattice. The molecule has a very definite length to it, for there are five benzene rings joined in a row. Now the (202) plane was the most intensely reflected plane. Thus it was assumed that the lengths of the molecule lay along this plane. There were now only two possible structures. Trials indicated clearly which of these was the correct structure.

Refinement of the [010] zone

The initial work was done on intensities estimated only roughly from a moving film exposed for only a relatively short time. The agreement factor, which was defined in the usual way as

$$R = \frac{\sum |(|F_{obs}| - |F_{calc}|)|}{\sum |F_{obs}|}$$

expressed as a percentage, was found to be 43% for the trial structure over the 59 observed planes on this film. A Fourier synthesis using 48 of the F observed factors as coefficient was constructed on which 12 out of the 14 atoms in the asymmetric unit were resolved. The atoms could, therefore, be placed far more accurately, so that the agreement factor was reduced to 25.4%. At this stage a multiple film moving film series was available. 85 planes were observed representing 40% of all the independent observable planes inside the copper sphere of reflection. The same structure gave an agreement factor of only 25.6% over all these 85 planes. The extra terms were included in a second Fourier synthesis. This not only showed every carbon atom resolved, but gave considerable evidence of most of the hydrogen atoms as well. The structure taken from this electron density map gave an agreement factor of 21.9% when the hydrogens were taken into account as well as the carbon atoms. The C - H bonds were assumed to be 1.0 A. long.

Most of the signs of the structure factors had now been determined, thus further refinement was continued by means of $(F_{obs} - F_{calc})$ difference syntheses. The first difference synthesis indicated considerable atomic shifts, causing the agreement factor to fall to 16.7% when both carbon and hydrogen atoms were taken into account. The second difference synthesis indicated much smaller atomic shifts as well as a suggestion of anisotropic motion of the whole molecule. Most atoms appeared to be vibrating more in a direction roughly parallel to the length of the molecule, and less in a direction perpendicular to its length. Correcting for atomic shifts only, not taking into account the probable anisotropic motions of the atoms, the agreement factor was now 15.6%.

An empirical scattering curve due to Robertson (1935) had been used in the initial stages of refinement. This was replaced by theoretical scattering curves for carbon and hydrogen due to McWeeny (1951) after the second electron density map had been completed. These curves were corrected for thermal vibrations in the following manner. We may write

$$|F_{obs}| = |(s\, f_T + s'\, f'_T)|$$

where s and s' are the geometrical structure factors for carbon and hydrogen respectively,

and f_T and f'_T are the temperature corrected scattering factors for carbon and hydrogen respectively.

If f_0 and f'_0 are the uncorrected scattering factors for these atoms respectively, it can be shown that

$$f_T = f_o \, e^{-B\left(\frac{\sin\theta}{\lambda}\right)^2} \quad \text{and} \quad f_T' = f_o' \, e^{-B\left(\frac{\sin\theta}{\lambda}\right)^2}$$

where θ is the Bragg angle at wavelength λ.

B and B' are constants, known as temperature or Debye factors. Let us assume that the degree of vibration of the carbon and hydrogen atoms are the same, as the molecule is probably fairly rigid. $\therefore$ B = B'

$$\therefore \quad |F_{OBS}| = |(s f_o + s' f_o')| \, . \, e^{-B\left(\frac{\sin\theta}{\lambda}\right)^2}$$

$$\therefore \sum |F_{OBS}| = e^{-B\left(\frac{\sin\theta}{\lambda}\right)^2} \, . \sum |(s f_o + s' f_o')|$$

if the sum Σ is taken over structure factors with roughly equal θ values.

Thus $$\ln\left\{\frac{\sum |F_{OBS}|}{\sum |(s f_o + s' f_o')|}\right\} = -B\left(\frac{\sin\theta}{\lambda}\right)^2$$

or

$$\ln\left\{\frac{\sum |F_{OBS}|}{\sum |(s f_o + s' f_o')|}\right\} = -B\left(\frac{\sin\theta}{\lambda}\right)^2 - \ln k$$

where k is the unknown scaling factor of the observed structure factors (which are known only on a relative scale).

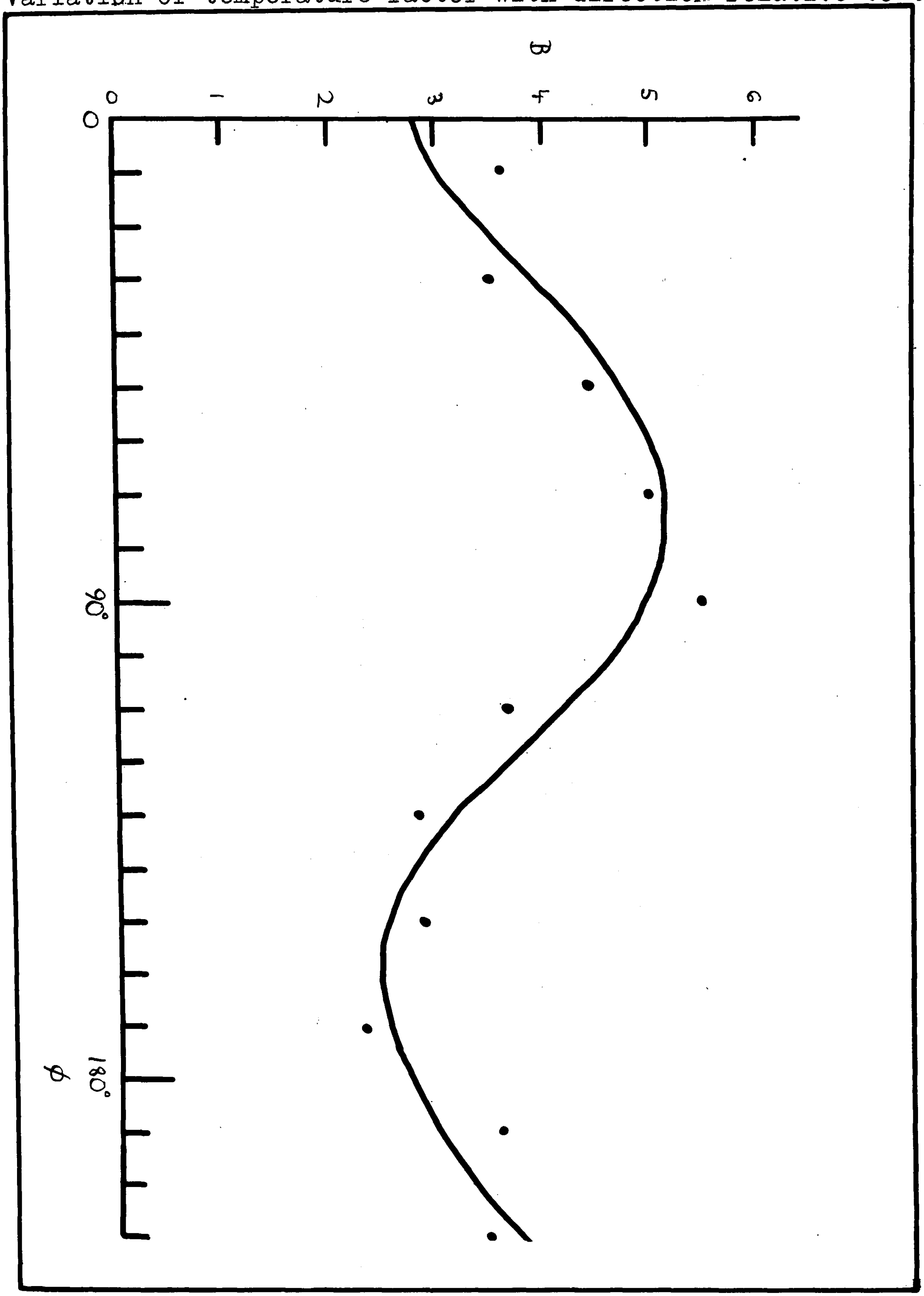
The expression $\ln\left\{\frac{\sum |F_{OBS}|}{\sum |(s f_o + s' f_o')|}\right\}$ was evaluated for angles of sin θ of 0.0 - 0.05, 0.05 - 0.10, 0.10 - 0.15, ... 0.95 - 1.00, and plotted against $\left(\frac{\sin\theta}{\lambda}\right)^2$.

The slope of the resulting straight line then gave the value of $-B$, where B is the temperature factor. A first determination of B gave $B \simeq 3.5$ A.^{2}

As has already been said, it was found from the second difference map that there was a slight suggestion of anisotropic motion of the molecule as a whole, which was visible to a greater or lesser extent in 11 out of the 14 carbon atoms of the asymmetric unit. To determine the magnitude and direction of this anisotropic motion more accurately the temperature factors for planes lying in roughly the same direction were calculated. The planes were divided into groups whose normals made angles of $\phi = 0 - 20^\circ$, $20^\circ - 40^\circ$, $40^\circ - 60^\circ$, ... $160^\circ - 180^\circ$ with the c axis. The temperature factors, B, were then plotted against the mean value of ϕ and the resulting curve fitted very beautifully to the theoretical curve $B = \alpha + \beta \sin^2 (\phi - \psi)$, where α and β are constants and ψ is the angle the direction of maximum vibration makes with the c axis (Cochran, 1951, a and b). Values found were $\alpha = 2.5$ A.^{2}, $\beta = 2.7$ A.^{2}, $\psi = 160^\circ$, which means that 2.5 A.$^2 \leqslant B \leqslant 5.2$ A.^{2} to give a mean $B = 3.9$ A.^{2}, in good agreement with the previous determination of $B = 3.5$ A.^{2}

The agreement factor was found to be 16.2% ~~for~~ neglecting the hydrogen atoms, and 15.1% when they were taken into account, using the ~~when this~~ anisotropic scattering curve ~~was used~~; an

Variation of temperature factor with direction relative to the a^* axis.



improvement of 0.5% over the isotropic curve. A third difference map was calculated using the anisotropic corrected structure factors. From this map it appeared that the anisotropic motion had been correctly accounted for, and that most of the carbon atoms had been moved to the positions in best agreement with the experimental data. There was also a very slight suggestion that there is a denser electron distribution in the neighbourhood of chemical bonds. This has also been previously observed by Cochran (1953) on salicylic acid, but not by Sim, Robertson and Goodwin (1955) on benzoic acid nor by Cruickshank (private communication) on Anthracene. 5 out of the 14 atoms were moved slightly, but the agreement factor went up to 16.3%, probably because these atoms had been overshifted. Thus the structure indicated by the second difference map was therefore assumed to be nearest to physical reality.

A final electron density map using 83 out of the 85 observed structure factors was calculated.

Orientation of the molecule in the crystal

The projection of the structure onto the (010) plane gave two co-ordinates of each atom with a good degree of accuracy. A projection along another crystal axis was not worthwhile because of insufficient resolution and lack of information. Thus only indirect evidence of the third coordinate could be obtained. A study of the projection onto the (010) plane makes it clear that it represents the dibenzperylene molecule built from approximately regular planar hexagons of carbon atoms. It was therefore assumed that the molecule was planar. With this assumption the agreement in the $(0k\ell)$ zone between observed and calculated structure factors was as good as in the $(h0\ell)$ zone. It does, however, appear conceivable, from a study of bond lengths and angles, that there is a slight divergence from an exactly planar structure. This can, therefore, only be detected with certainty by methods such as Booth's bounded projection or a three dimensional fourier series. A generalized projection may possibly detect such a variation, but probably not with any great certainty.

The usual method for determining the molecular orientation (cf. Coronene; Robertson & White, 1945) could not be used because of the irregular nature of the central carbon ring, and hence the uncertainty of determining ψ_M. The relations given in the above paper must and are, however, be satisfied.

Orthogonal axes were chosen parallel to the a and b axes and their perpendicular c'. These axes were called X, Y and Z, respectively. The oblique axes, x, y, z are then related to the orthogonal axes by the relationships

$$X = x + z \cos \beta \; ; \quad Y = y \; ; \quad Z = z \sin \beta$$

The molecule had then to lie on the plane $Y = AX + BZ + C$, where X and Z are the known coordinates for each atom. If the space group is A2/a, then $Y = 0$ or $\frac{b}{4}$; If the space group is Aa then Y may vary between $0 < Y < \frac{b}{4}$ at the molecular center. Whatever the value of C the orientation of the molecule is given by A and B. To determine the orientation of the molecule a method of least squares described below was used.

Let R be the "real" bond length - which is what we are trying to determine.

Let Y_1^R and Y_2^R be the "real" coordinates of two atoms at the ends of a chemical bond.

$$\therefore (Y_1^R - Y_2^R)^2 = R^2 - (X_1 - X_2)^2 - (Z_1 - Z_2)^2$$

$$\text{or } (Y_1^R - Y_2^R) = \pm\sqrt{R^2 - (X_1 - X_2)^2 - (Z_1 - Z_2)^2} \quad \ldots(1)$$

[the sign of this root can be determined from a rough knowledge of $(Y_1^R - Y_2^R)$]. Hence, using the method of least squares, we see that we have to minimize the function

$$F = \Sigma[(Y_1^R - Y_2^R) - (Y_1 - Y_2)]^2$$

where Σ is taken over all bonds in the molecule.

But $Y_1 = AX_1 + B2_1 + C$ and $Y_2 = AX_2 + B2_2 + C$

$$\therefore F = \Sigma[(Y_1^R - Y_2^R) - A(X_1 - X_2) - B(Z_1 - Z_2)]^2$$

To minimize F we require $\frac{\partial F}{\partial A} = 0$ and $\frac{\partial F}{\partial B} = 0$.

When the resulting two simultaneous equations in A and

B are solved for A and B we find that

$$B = \frac{\left\{\sum (Y_1^R - Y_2^R)(X_1 - X_2) . \sum (X_1 - X_2)(Z_1 - Z_2)\right\} - \left\{\sum (Y_1^R - Y_2^R)(Z_1 - Z_2) . \sum (X_1 - X_2)^2\right\}}{\left\{\sum (X_1 - X_2)(Z_1 - Z_2)\right\}^2 - \left\{\sum (X_1 - X_2)^2 . \sum (Z_1 - Z_2)^2\right\}}$$

$$A = \frac{\left\{\sum (Y_1^R - Y_2^R)(X_1 - X_2) . \sum (Z_1 - Z_2)^2\right\} - \left\{\sum (Y_1^R - Y_2^R)(Z_1 - Z_2) . \sum (X_1 - X_2)(Z_1 - Z_2)\right\}}{\left\{\sum (X_1 - X_2)^2 . \sum (Z_1 - Z_2)^2\right\} - \left\{\sum (X_1 - X_2)(Z_1 - Z_2)\right\}^2}$$

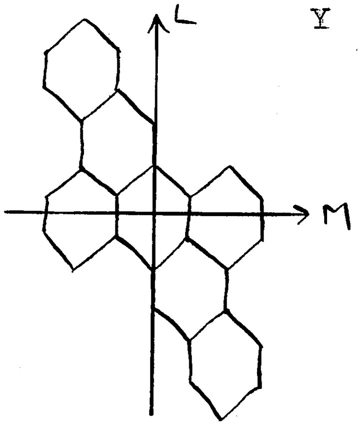
Thus to determine the values of A and B it is necessary to calculate the quantities $\Sigma(Y_1^R - Y_2^R)(X_1 - X_2)$, $\Sigma(Y_1^R - Y_2^R)(Z_1 - Z_2)$, $\Sigma(X_1 - X_2)^2$, $\Sigma(Z_1 - Z_2)^2$, $\Sigma(X_1 - X_2)(Z_1 - Z_2)$. To determine the factors $(Y_1^R - Y_2^R)$ equation (1) was used, but to use equation (1) it is necessary to have a knowledge of R, the real bond length! An estimate of R was obtained by drawing all possible 25 Kekulé structures (Gordon, Davison, 1951) and hence finding an estimate of the bond order of each bond. From a bond order - bond length curve, the values of R were read off. The points selected for drawing this graph were:-

Compound	Double bond character	Bond length in A.
Diamond	0%	1.50 (corrected for sp^3 hybridization)
Graphite	33%	1.42
Benzene	50%	1.39
Ethylene	100%	1.34

It must be admitted that there is no theoretical foundation for the application of Kekulé structures to large compounds of this sort; yet it cannot be denied that, in practice, surprisingly good agreement between bond lengths estimated by this method and experimental determinations is invariably obtained (e.g. for coronene, ovalene, perylene and pyrene). A good approximation to the truth might therefore be expected. Any difference between the assumed value of R and its correct value should cancel out between the different bonds.

Values of A and B were determined by this method, and hence values of the fractional co-ordinates could be calculated for each atom, provided a value of C was assumed. First C was assumed to be equal to zero, so that the molecule was in space group A2/a with its centre at (0,0,0)(origin as in international tables). A study of the reflections in the [100] zone was carried out. Poor agreement was obtained for reflections with k odd, and hence ℓ odd also; but reasonable agreement was found for reflections with k even, and hence ℓ even also. The two centres of symmetry, Ⓑ and Ⓒ, in space group A2/a are removed from each other by $y = \frac{b}{4}$, $z = \frac{c}{4}$, $x = 0$. Thus only the magnitude of the structure factors with even indices would not be affected by a change in position of the molecular centre from Ⓑ to Ⓒ, as the change of angle involved for such planes will be $0, 2.\frac{\pi}{2}, 4.\frac{\pi}{2}, \ldots\ldots$ that is $0, \pi, 2\pi, \ldots\ldots$ No such systematic error was found when the molecule was assumed to be at the centre of symmetry Ⓒ when hydrogen atoms were included. The agreement factor came to 15.3% over the 21 observed reflections. A number of slightly different values of A and B were tried (thus slightly changing the molecular tilt), but no improvement could be obtained on the agreement factor. No trials were made in changing the actual position of the molecular centre slightly, that is placing the molecule into space group Aa, rather than A2/a. This would have involved the accurate determination of the three constants in the equation Y = AY + BZ + C for the molecular plane, when all three were already known to a fair degree of accuracy. Such determination could only have proceeded by either trial and error or a least square method on rather scanty experimental data. This was not thought worthwhile. The best temperature factor, B, was found to be B = 5.2 A^2 equal to the maximum temperature factor in the (010) projection. The best plane was found to be:-

$$Y = -1.068X - 0.512Z + 2.148$$



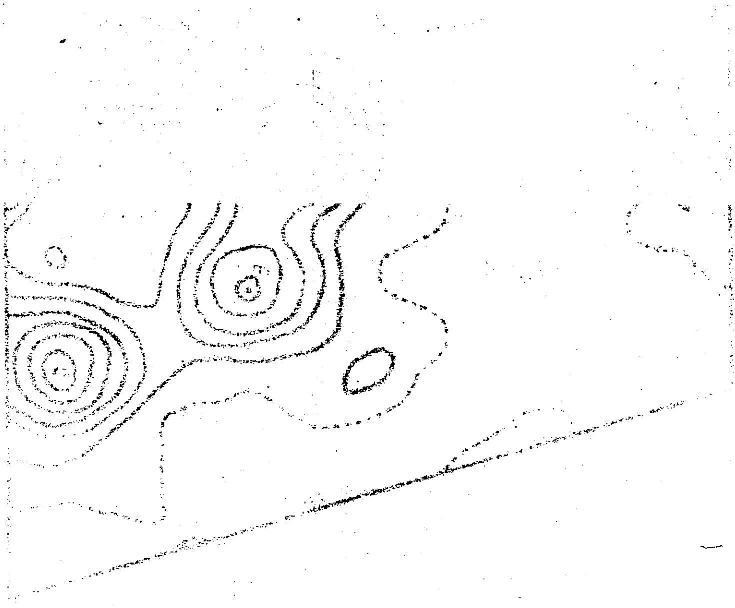
The orientation of the molecule in the crystal is given in Table I where χ_L, ψ_L, ω_L; χ_M, ψ_M, ω_M; χ_N, ψ_N, ω_N, are the angles which the molecular axes L, M and their perpendicular N make with the orthogonal axes a, b, c' chosen above. The figures in brackets are those obtained by the Booth back shift method of refinement. This will be discussed in more detail in the section on accuracy.

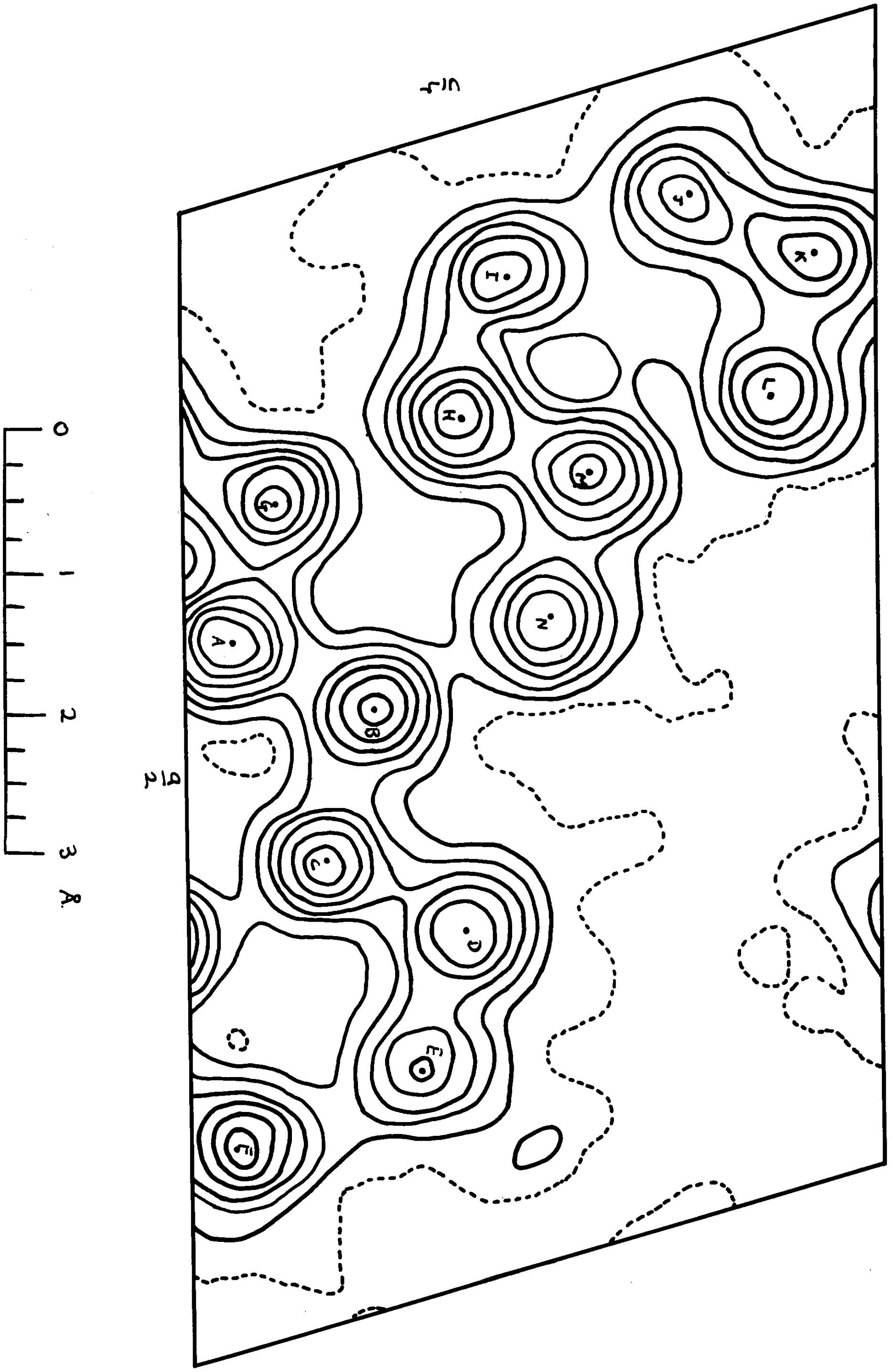
χ_L 121°25' (115° 0°)	cos χ_L −0.5208 (−0.4225)
ψ_L 96°55' (90° 8')	cos ψ_L −0.1204 (−0.0047)
ω_L 32°33' (24°56')	cos ω_L +0.8446 (+0.9068)
χ_M 53°25' (53°32')	cos χ_M +0.5937 (+0.5944)
ψ_M 139°43' (139°12')	cos ψ_M −0.7624 (−0.7571)
ω_M 75° 5' (74°17')	cos ω_M +0.2574 (+0.2709)
χ_N 46°36' (46°48')	cos χ_N +0.6870 (+0.6844)
ψ_N 49°42' (49°13')	cos ψ_N +0.6468 (+0.6532)
ω_N 70°39' (71° 5')	cos ω_N +0.3314 (+0.3241)

TABLE I.

The results show that the angle between the plane of the molecule and the (010) plane, which is expressed by ψ_N, the angle between the normal to the molecular plane and the b axis, is 49°42'. It is interesting that while in the case of coronene (43.7°) and ovalene (42.8°) the molecules are inclined at less than 45° to the (010) plane, the inclination is greater than 45° for dibenzperylene, as might be expected from its slightly longer b axis. The results also show that the L axis of the molecule is very nearly, but not exactly, in the (010) plane, as ψ_L is very nearly 90° according to the difference map refinement. This is also varified because the mean angle between the L and M directions projected on the (010) plane make an angle of 92°30' with each other, not 90°.

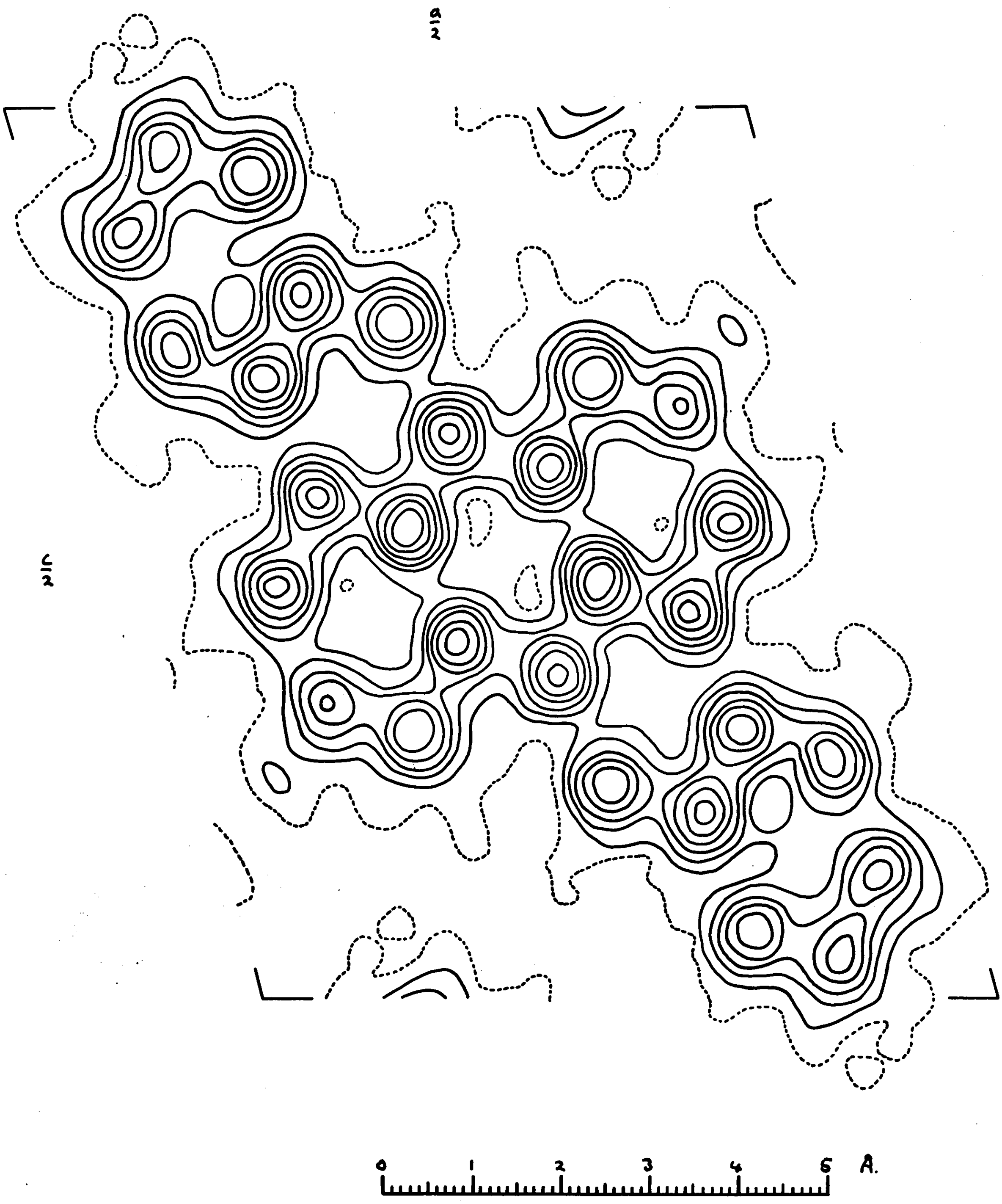
The perpendicular distance between the molecular planes is given by b cos ψ_N, or $\frac{b}{\sqrt{A^2 + B^2 + 1}}$, which is 3.38 A. (3.42 A.) almost identical with the inter planar distance in graphite (3.40 A.)



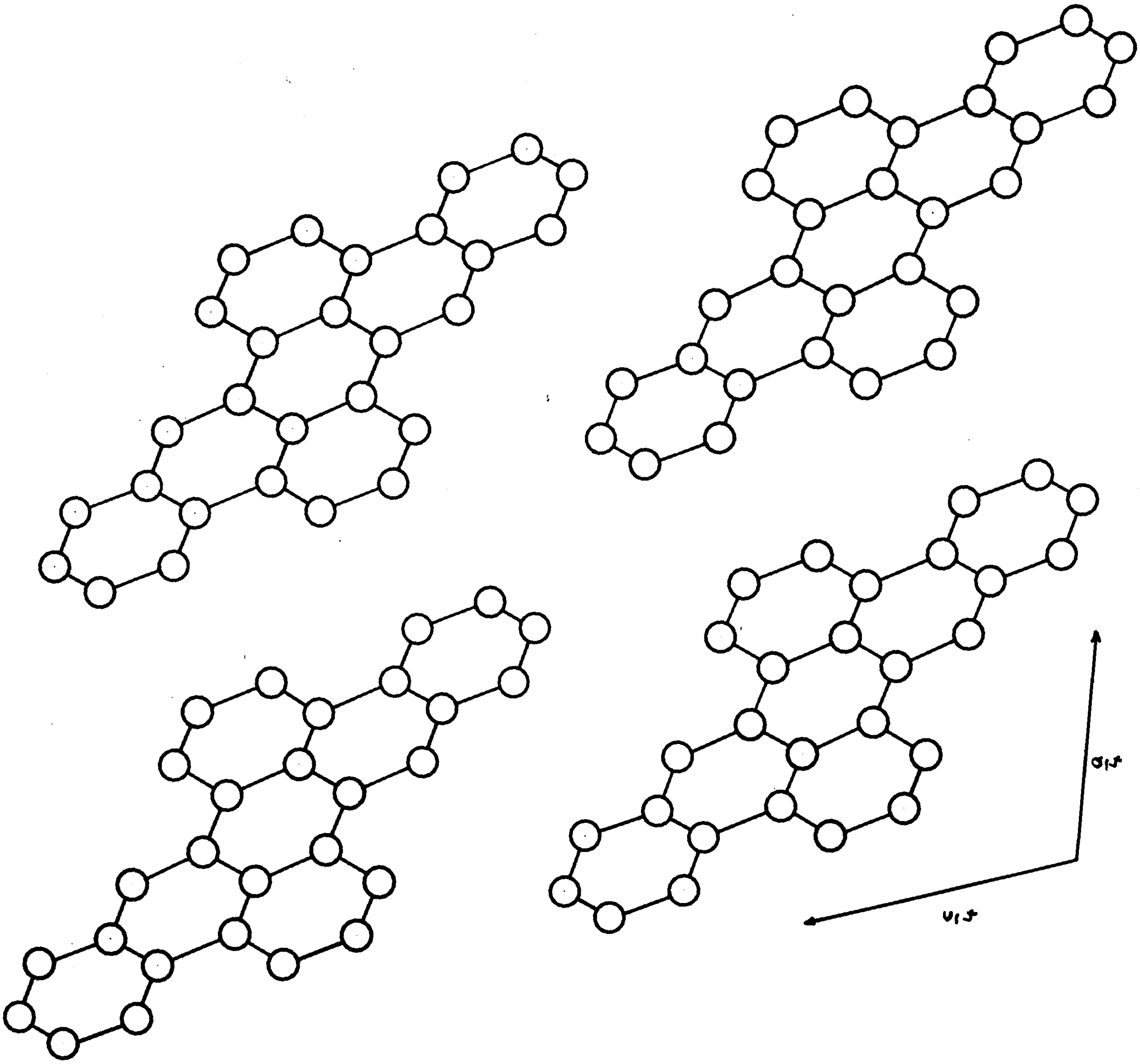


The atoms in the asymetric crystal unit.

Contours at intervals of 1 e. A.$^{-2}$ The first line is dotted.



Projection of the dibenzperylene structure on (010). Contour scale, one electrom per A., the first 1e/A.² line being dotted.



The atomic arrangement corresponding to the projection on (010).

Accuracy

When bond bond lengths and inter-molecular distances had been calculated there were found some rather unusual distances. It was also noted that the final positions of a number of atoms had refined to positions which did not coincide with the maxima on the final electron density map. It was therefore regarded as important to obtain a check on the results obtained by means of successive $(F_o - F_c)$ synthesis. This was done by correcting the apparent positions of the maxima on the final electron density map by means of the back shift method suggested by Booth (1946). These 'back shifts' are the difference in position of the maxima on an 'observed' and 'calculated' electron density map, and should account for any error due to the finite termination of the infinite Fourier series employed, and the effect which the electron cloud of one atom has on the apparent position of another neighbouring atom in projection.

The electron density on the ac plane was computed at 1,800 in the asymmetric unit from the series

$$\rho(x, z) = \frac{1}{ac \sin\beta} \sum_{h} \sum_{l} F(h0l) \cos 2\pi\left(h\frac{x}{a} + l\frac{z}{c}\right)$$

The a axis was subdivided into 120 parts, the intervals being 0.138 A. The c axis was also subdivided into 120 parts, which gave intervals of 0.173 A. along this axis. The summations were carried out sometimes by means of three figure strips and masks, or else with Beevers-Lipson strips. The position of the contour lines was obtained by graphical interpolation from the summation totals, by making sections of rows. The positions of the maxima were fixed by means of a numerical method due to Booth (1948), which uses the electron density at points in the vicinity of maxima. These calculations were carried out for both F_{obs} and F_{calc} synthesis.

The results show that the magnitude of the back shifts are small, all being smaller than 0.03 A. Thus, in general, the centres from the F_{obs} and F_{calc} synthesis are close together, but considerably removed from the centres obtained by means of successive difference maps. These results are illustrated in Tables II and III.

TABLE II: Showing magnitude of back shifts.

Atom	F_o synthesis		"Booth" corrected centres		Magnitude of backshift in A	
	$\frac{x}{a}.360$	$\frac{z}{c}.360$	$\frac{x}{a}.360$	$\frac{z}{c}.360$	Δx	Δz
A	-21.2	95.3	-21.3	95.1	.005	.011
B	-4.8	113.6	-4.6	113.5	.009	.006
C	17.0	107.8	16.5	107.9	.023	.006
D	33.7	125.6	33.4	125.8	.014	.011
E	52.6	120.3	52.4	119.9	.009	.023
F	57.6	96.6	58.1	97.1	.023	.029
G	-41.7	101.1	-41.5	101.3	.009	.011
H	-45.8	125.6	-46.1	125.4	.014	.006
I	-66.4	131.4	-66.6	131.4	.009	.000
J	-68.9	155.1	-69.1	154.8	.009	.017
K	-54.5	171.5	-54.2	171.7	.014	.011
L	-35.6	166.3	-35.5	166.3	.005	.000
M	-30.7	143.0	-31.2	142.9	.023	.006
N	-9.7	136.7	-9.6	137.0	.005	.017

TABLE III: Showing divergence between positions of atomic centres according to both methods of refinement.

Atom	"Booth" corrected centres		Difference map centres		Magnitude of divergence in A	
	$\frac{x}{a}.360$	$\frac{z}{c}.360$	$\frac{x}{a}.360$	$\frac{z}{c}.360$	Δx	Δz
A	-21.3	95.1	-21.6	95.7	.014	.034
B	-4.6	113.5	-4.8	114.0	.009	.029
C	16.5	107.9	16.2	107.7	.014	.011
D	33.4	125.8	33.6	126.0	.009	.011
E	52.4	119.9	52.8	119.7	.018	.011
F	58.1	97.1	57.6	98.0	.023	.052
G	-41.5	101.3	-40.8	101.4	.032	.006
H	-46.1	125.4	-46.2	126.0	.005	.034
I	-66.6	131.4	-65.4	132.0	.055	.034
J	-69.1	154.8	-69.6	156.0	.023	.069
K	-54.2	171.7	-54.6	171.9	.018	.011
L	-35.5	166.3	-34.8	166.2	.032	.006
M	-31.2	142.9	-31.2	142.8	.000	.006
N	-9.6	137.0	-10.8	137.4	.055	.023

The "Booth" corrected x, z, co-ordinates were used to obtain a new set of y co-ordinates for all atoms, by precisely the same least square method as was used for the co-ordinates found originally from the difference map refinement. The values of A and B thus found for the best molecular plane $Y = AX + BZ + C$ were assumed to be accurate, and hence were not varied to reduce the agreement factor any further as had been done previously. It was assumed also that the molecular center was at $\left(0, \frac{b}{4}, \frac{c}{4}\right)$.

The agreement factors were found to be:-

	Booth corrected centres	Difference Map centres
In the ($h0\ell$) projection for 85 planes	15.1%	15.1%
In the ($0k\ell$) projection for 21 planes	14.5%	15.3%

Agreement factor for uncorrected centres from F_o synthesis was 16.2%.

The plane of the molecule could be represented by the equation as:-

Booth corrected structure $Y = -1.0478X - 0.4962Z + 2.019$

Difference map structure $Y = -1.0621X - 0.5123Z + 2.148$

It is far from clear why both these methods of refinement should give answers which are so different. This is not a question of significant error, since we are starting with the same numerical data in both cases, and should therefore be interpreted unambiguously. Dr. A. Vos (1955), however, found it desirable to do two or even three back shifts corrections, while in this work it has been tacitly assumed that <u>one</u> back shift correction should completely account for the incorrect position of the maxima on the observed electron density map. It is possible, therefore, that less emphasis should be placed on the Booth method of correction. Significance tests were carried out to investigate this more fully.

Significance Tests

Booth (1946) showed that for centrosymmetrical structures

$$\sigma(\rho_0) \propto \sigma(F_{obs}) \qquad \text{and} \qquad \sigma(x_n) \propto \sigma(F_{obs})$$

where ρ_0 and x_n is the density and x co-ordinate of the n^{th} atom at its centre, respectively, and σ represents the standard deviation.

The difficulty was the exact determination of the constant of proportionality. This difficulty does not arise in the formulae given by Cruickshank (1949 and 1954). He shows that, provided the centre of an atom is at

$$\frac{\partial\rho}{\partial x} = \frac{\partial\rho}{\partial y} = \frac{\partial\rho}{\partial z} = 0$$

and $\frac{\partial^2\rho}{\partial x^2}$, $\frac{\partial^2\rho}{\partial y^2}$, $\frac{\partial^2\rho}{\partial z^2}$ are negative, we have

$$\sigma\left(\frac{\partial\rho}{\partial x}\right) = \frac{2\pi}{aV}\left\{\sum_h \sum_k \sum_l m\, h^2 \Delta F^2\right\}^{\frac{1}{2}}$$

and similar expressions for $\sigma\left(\frac{\partial\rho}{\partial y}\right)$ and $\sigma\left(\frac{\partial\rho}{\partial z}\right)$;

where $\Delta F = F_{obs} - F_{calc}$

V is the volume of the unit cells

and m is the multiplicity of the plane.

Then $$\sigma(\rho) = \frac{1}{V}\left\{\sum_h \sum_k \sum_l m\,\Delta F^2\right\}^{\frac{1}{2}}$$

and $$\sigma(x) = \frac{\sigma\left(\frac{\partial\rho}{\partial x}\right)}{\frac{\partial^2\rho}{\partial x^2}}, \quad \sigma(y) = \frac{\sigma\left(\frac{\partial\rho}{\partial y}\right)}{\frac{\partial^2\rho}{\partial y^2}}, \quad \sigma(z) = \frac{\sigma\left(\frac{\partial\rho}{\partial z}\right)}{\frac{\partial^2\rho}{\partial z^2}}.$$

When applying these results to two dimensional data it is necessary to observe that the above conditions under which these formulae hold are valid. Thus all atoms must be resolved. The above formulae will reduce to

$$\sigma\left(\frac{\partial\rho}{\partial x}\right) = \frac{2\pi}{aA}\left\{\sum_h \sum_l m\,h^2\,\Delta F^2\right\}^{\frac{1}{2}}$$ and a similar

expression for $\sigma\left(\frac{\partial\rho}{\partial z}\right)$ for the [010] zone, where A is the area of projection; and

$$\sigma(\rho) = \frac{1}{A}\left\{\sum_h \sum_l m\,\Delta F^2\right\}^{\frac{1}{2}}$$

All quantities required in the above formulae can be calculated easily except $\frac{\partial^2\rho}{\partial x^2}$, $\frac{\partial^2\rho}{\partial y^2}$, $\frac{\partial^2\rho}{\partial z^2}$. In order to estimate these, it was assumed that the atoms can be represented by Costain's formula $\rho = A\,e^{-pr^2}$. ρ is the density at a distance r from the centre of the atom. p is a constant. It was found that this represented the shape of the carbon atoms in dibenzperylene extremely well. The best fit was found to be $\rho = 7.24\ e^{-3.84\ r^2}$. Values of A and p were obtained by plotting $\ln\rho$ against r^2 to obtain a straight line of slope p, making an intercept of A on the $\ln\rho$ axis.

Now $$\frac{\partial^2\rho}{\partial r^2} = 2Ap\left(2pr^2-1\right)e^{-pr^2}$$

∴ when r = 0 (at centre of atom)

$$\left(\frac{\partial^2\rho}{\partial r^2}\right)_{r=0} = -2Ap = -55\cdot60$$

$$\therefore \left(\frac{\partial^2\rho}{\partial^{\cancel{2}} x^2}\right)_{r=0} = \left(\frac{\partial^2\rho}{\partial y^2}\right)_{r=0} = \left(\frac{\partial^2\rho}{\partial^{\cancel{2}} z^2}\right)_{r=0} = -55\cdot60$$

The results of the significance tests are given in Table IV.

TABLE IV.

Results of significance tests.

Quantity	Booth corrected centres	Difference map centres
$\sigma(F)$ for $(h0\ell)$ reflections	7.1	6.5
$\sigma(F)$ for $(0k\ell)$ reflections	6.9	7.0
$\sigma(\rho)$ for (010) projection	0.285 e.A.$^{-2}$	0.263 e.A.$^{-2}$
$\sigma(x)$ in (010) projection	0.0149 A.	0.0154 A.
$\sigma(y)$ from $(0k\ell)$ reflection	0.0302A.	0.0222 A.
$\sigma(z)$ in (010) projection	0.0156 A.	0.0154 A.
$\sigma(r)$	0.0214 A.	0.0180 A.
σ(dist)	0.0303 A.	0.0254 A.

$\sigma(r)$ is the R.M.S. value of $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$. $\sigma^2(\text{dist.}) = \sigma^2(r) + \sigma^2(r)$, i.e. $\sigma(\text{dist.}) = \surd 2\ \sigma(r)$, where σ(dist.) = standard deviation of interatomic distances (Cruickshank & Robertson, 1953). As is seen, Cruickshank's tests were applied to the [100] zone. The tests are, however, not quite applicable as there is little resolution of atoms when they are projected onto the (100) plane. It is hoped that these tests might give a little indication of the error involved in the y co-ordinate.

Co-ordinates and Dimensions

Two of the co-ordinates of the atoms were measured from the various projections onto the (010) plane. The third was calculated from the last equation of the molecular plane $Y = AX + BZ + C$, using orthogonal co-ordinates. As the molecule has an exact centre of symmetry, only half the atoms, those of the asymmetric crystallographic unit, are listed. All other atoms in the unit cell may be derived from the operations:-

$$(x,\ y,\ z),\ (\bar{x},\ \bar{y}+\frac{b}{2},\ \bar{z}+\frac{c}{2});\ (x+\frac{a}{2},\ \bar{y}+b,\ z),\ (\bar{x}+\frac{a}{2},\ y+\frac{b}{2},\ \bar{z}+\frac{c}{2});$$

$$(x,\ y+\frac{b}{2},\ z+\frac{c}{2}),\ (\bar{x},\ \bar{y}+b,\ \bar{z}+c);(x+\frac{a}{2},\bar{y}+\frac{b}{2},z+\frac{c}{2}),(\bar{x}+\frac{a}{2},y,\bar{z}+c).$$

Tables V and VI give the co-ordinate of the fourteen atoms in the asymmetric unit obtained by difference map and "Booth" correction refinement methods respectively. The oblique co-ordinates x, y, z are given along the unit cell edges a, b, c and the orthogonal co-ordinates, X, Y, Z are measured parallel to the unit cell edges a and b, and parallel to the c' axis perpendicular to a and b.

TABLE V: Atomic co-ordinates and dimensions in A. - Difference map refinement.

Atom	Fractional co-ordinates			Oblique co-ordinates		
	$\frac{x}{a}.360$	$\frac{y}{b}.360$	$\frac{z}{c}.360$	x	y	z
A	-21.6	159.0	95.7	-0.995	2.313	5.476
B	-4.8	90.7	114.0	-0.221	1.320	6.523
C	16.2	24.1	107.7	0.746	0.352	6.163
D	33.6	-46.4	126.0	1.548	-0.680	7.210
E	52.8	-107.1	119.7	2.433	-1.562	6.849
F	57.6	-107.9	98.0	2.654	-1.574	5.493
G	-40.8	220.1	101.4	-1.880	3.200	5.802
H	-46.2	222.4	126.0	-2.129	3.234	7.210
I	-65.4	283.3	132.0	-3.014	4.118	7.553
J	-69.6	281.8	156.0	-3.207	4.097	8.927
K	-54.6	221.1	171.9	-2.516	3.215	9.836
L	-34.8	158.1	166.2	-1.604	2.299	9.510
M	-31.2	161.1	142.8	-1.438	2.343	8.171
N	-10.8	95.8	137.4	-0.498	1.394	7.862

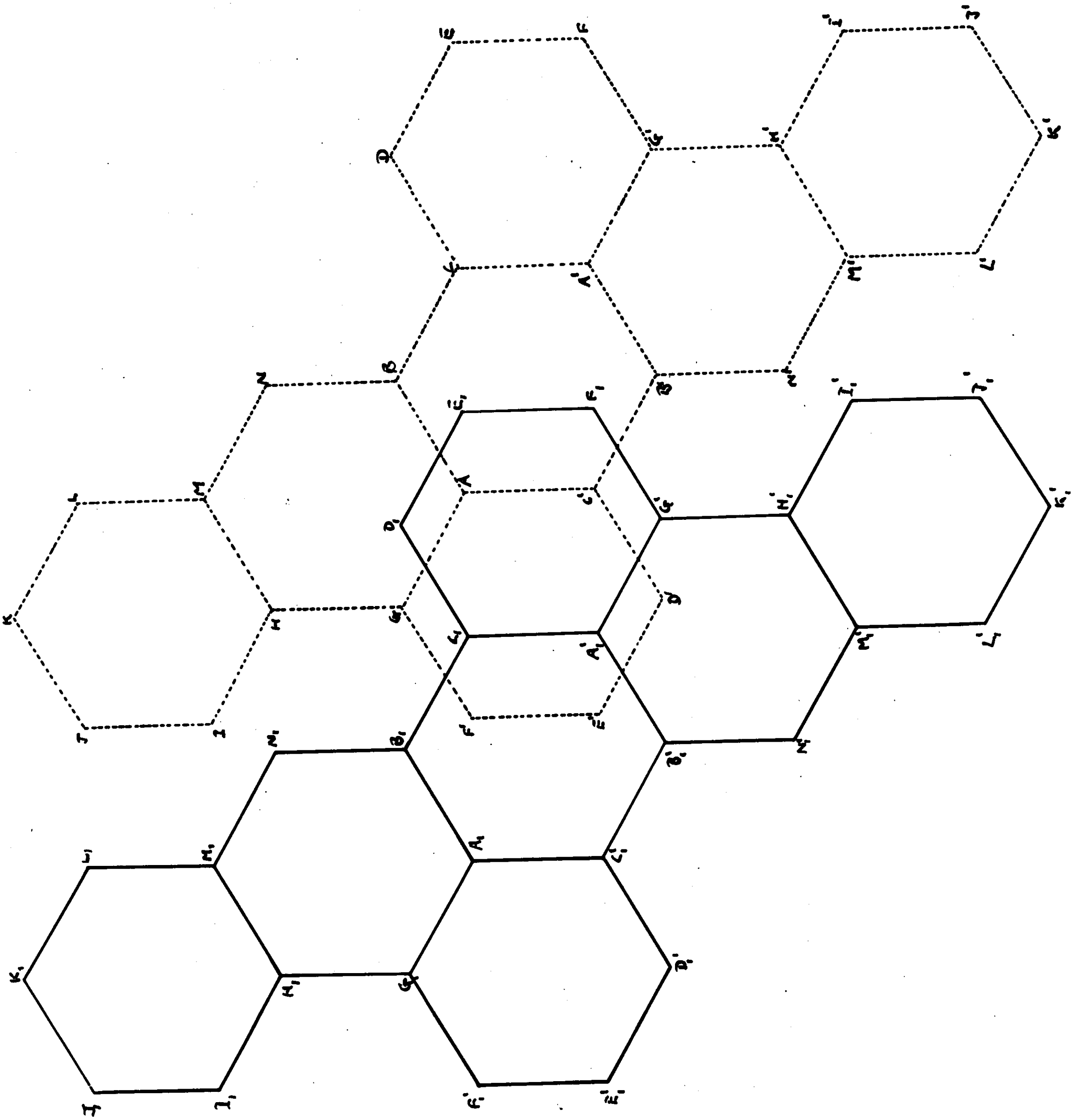
Orthogonal co-ordinates			
X	Y	Z	
-2.665	2.313	5.214	A
-2.211	1.320	6.212	B
-1.134	0.352	5.869	C
-0.652	-0.680	6.866	D
0.344	-1.562	6.522	E
0.978	-1.574	5.231	F
-3.650	3.200	5.525	G
-4.329	3.234	6.866	H
-5.318	4.118	7.192	I
-5.930	4.097	8.501	J
-5.517	3.215	9.366	K
-4.505	2.299	9.056	L
-3.931	2.343	7.781	M
-2.896	1.394	7.487	N

TABLE VI: Atomic co-ordinates and dimensions in A.
- "Booth" correction to atomic positions.

Atom	Fractional co-ordinates			Oblique co-ordinates		
	$\frac{x}{a}.360$	$\frac{y}{b}.360$	$\frac{z}{c}.360$	x	y	z
A	-21.3	158.1	95.1	-0.982	2.297	5.442
B	-4.6	92.5	113.5	-0.212	1.344	6.494
C	16.5	25.4	107.9	0.760	0.369	6.174
D	33.4	-40.4	125.8	1.539	-0.587	7.198
E	52.4	-100.4	119.9	2.415	-1.459	6.861
F	58.1	-106.9	97.1	2.677	-1.553	5.556
G	-41.5	221.7	101.3	-1.912	3.221	5.796
H	-46.1	224.0	125.4	-2.124	3.255	7.175
I	-66.6	288.9	131.4	-3.069	4.198	7.519
J	-69.1	284.4	154.8	-3.184	4.132	8.858
K	-54.2	225.7	171.7	-2.498	3.279	9.825
L	-35.5	166.5	166.3	-1.636	2.419	9.516
M	-31.2	164.9	142.9	-1.438	2.396	8.177
N	-9.6	96.3	137.0	-0.442	1.399	7.839

Orthogonal co-ordinates			Atom
X	Y	Z	
-2.708	2.297	5.161	A
-2.273	1.344	6.158	B
-1.199	0.369	5.855	C
-0.745	-0.587	6.826	D
0.238	-1.459	6.506	E
0.915	-1.553	5.269	F
-3.751	3.221	5.496	G
-4.401	3.255	6.804	H
-5.455	4.198	7.130	I
-5.995	4.132	8.400	J
-5.615	3.279	9.317	K
-4.655	2.419	9.024	L
-4.033	2.396	7.754	M
-2.929	1.399	7.434	N

An inaccurate value of $\beta = 108.5°$, instead of $\beta = 107.8°$, was used for calculating these co-ordinates.



Normal projection of two parallel molecules.

Inter Molecular Distances

The perpendicular distance between molecular planes is 3.38 A. by difference map refinement and 3.42 A. by Booth back shift refinement, but the individual atoms do not occur vertically above each other. There is a pronounced tendency to avoid such overlap. The closest approach distances are between atoms A and D_1, where the distance is 3.44 A. The atom to atom distances $F' B_1$, $C_1 G$, and $E' B'_1$ are 3.46, 3.48 and 3.50 A. The distances $L_1 J$, $M_1 I$, $N_1 H$, $B_1 G$ are 3.76, 3.78, 3.73, 3.71 A. respectively. All distances refer to the difference map structure.

The approach of one molecule to another is in places very close, the closest approach distance being 3.18 A (difference map structure) or, according to the Booth structure this distance is 3.17 A.

If the molecules whose centres are at $(0, \frac{1}{4}b, \frac{1}{4}c)$, $(0, \frac{5}{4}b, \frac{1}{4}c)$, $(\frac{1}{2}a, \frac{3}{4}b, \frac{1}{4}c)$ $(0, \frac{3}{4}b, \frac{3}{4}c)$ are denoted by Ia, Ib, IIa, IIIa, respectively then the inter-molecular approach distances less than 4.0 A. are listed in Table VII. All distances refer to the difference map structure.

TABLE VII.

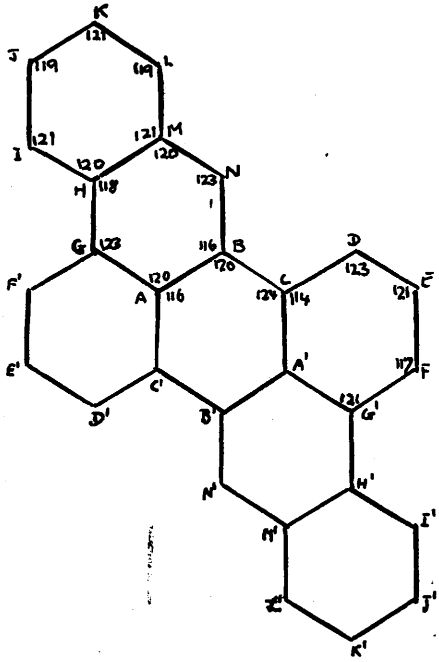
Showing Inter-molecular distances less than 4.0 A.

Ia	IIIa	distance	Ia	IIa	distance	Ib	IIa	distance
L	L'	3.18 A.	E	J	3.90 A.	E	J	3.80 A.
L	K'	3.94 A.	E	I	3.81 A.	E	I	3.73 A.
K	N'	3.54 A.	F	I	3.81 A.	F	I	3.79 A.
IIa	IIIa							
J	K'	3.72 A.						
J	J'	3.78 A.						
K	K'	3.67 A.						

TABLE VIII: Showing bond lengths in A.

Bond	Difference map length	Booth corrected length	Kekulé length	Kekulé double bond order
AB	1.48	1.45	1.46	0.2
BC	1.49	1.48	1.50	0.0
CD	1.50	1.43	1.36	0.6
DE	1.38	1.35	1.39	0.4
EF	1.44	1.42	1.36	0.6
FG'	1.45	1.44	1.39	0.4
CA'	1.44	1.40	1.39	0.4
AG	1.37	1.43	1.39	0.4
GH	1.50	1.46	1.46	0.2
HI	1.37	1.45	1.39	0.4
IJ	1.45	1.38	1.36	0.6
JK	1.29	1.31	1.39	0.4
KL	1.41	1.32	1.36	0.6
LM	1.39	1.41	1.39	0.4
MN	1.43	1.52	1.46	0.2
NB	1.45	1.44	1.35	0.8
MH	1.34	1.33	1.39	0.4

Bond angles are shown on diagram below for difference map structure.



Assuming the Kekulé bond lengths as correct, it was found that:-

Quantity	Booth corrected structure	Difference map structure
Discrepancy	3.1%	3.4%
Standard deviation	0.050 A.	0.062 A.
Maximum difference	(NB) 0.09 A.	(CD) 0.14 A.
Largest bond	(MN) 1.52 A.	(CD) 1.50 A. (GH) 1.50 A.
Shortest bond	(JK) 1.31 A.	(JK) 1.29 A.
Mean bond length	1.41 A.	1.42 A.

Discussion

Perhaps the most unexpected result is the very close intermolecular distance of 3.18 A. The hydrogen atoms attached to the two atoms concerned clear each other by 2.9 A. Nevertheless these two carbon atoms approach each other far closer than one would expect from earlier measurements, although such short non-bonded C - C distances have also been observed by Herbstein and Schmidt (1954a). It is true that there is a possibility that the correct space group might be Aa, not A2/a as has been assumed, ~~so that~~ hence the molecular centres may have been placed a little incorrectly. But even if this were the case it would not affect this distance as the two molecules concerned must always be related to each other by the translation $\frac{\vec{b}}{2} + \frac{\vec{c}}{2}$. The only difference a change to the lower symmetry space group could make is to make possible a slight ~~different~~ change of inclination of the molecule to the b axis. However, a considerable change would be required to bring the two atoms concerned 3.40 A. apart. It therefore appears to be extremely probable that this short intermolecular distance is significant. There are two possible explanations:-

(i) The distance of 3.40 A. assumed to be the non-bonded radius of carbon atoms has only been measured in a direction perpendicular to the three bonds of aromatic carbon compounds, such as the inter layer spacing for graphite or for large hydro-carbons. Because of the presence of hydrogen atoms there is in general little opportunity for carbon atoms to approach each other in the direction of the plane of their aromatic bonds. It is therefore possible that a slightly shorter Van der Waals distance is operative in a direction perpendicular to the normal of planar hydro-carbons. The two molecules which approach each other too closely are, in fact, very nearly co-planar.

(ii) The assumption that the molecule is planar was wrong, and had this assumption not been made the two atoms concerned would not have been nearer to each other than 3.40 A. There is some evidence for this, because perylene itself has a dipole moment, although X-ray studies appear to show it to be planar. Any change from planarity should, however, be amplified in the two outer benzene rings of dibenzperylene. The long bond length CD might indicate a strain due to the slight overcrowding, hence causing a deviation from planarity. If this is the case it might possibly explain the rather unusual bond lengths and angles. For instance, JK appears to be shorter than a double bond. If, however, atoms J and K are considerably displaced from the mean plane, as one would expect since they are in the outermost ring, then the real bond length would be longer than that calculated when a planar molecule is assumed.

Dibenzperylene is of particular interest because the bonds BC and B'C', as in perylene itself, have completely single bond character according to the Kekulé structures. The bond length found was 1.48 - 1.49 A., as compared with 1.50 A. in perylene.

Discussion of Molecular Orbital Calculations

The results of the theoretical calculations of bond orders from molecular orbital theory were obtained from Watson & Goodwin (1956) after this thesis had been nearly completed. The results are quoted in Tables IX and X, where they are also compared with the experimental X-ray measurements. Bond orders were converted to bond lengths by means of the bond order-length graph proposed by Coulson (1951).

There is less agreement between these theoretical calculations and the difference map results than there is between these calculations and the Booth back shift refinement results. It may, therefore, be possible that the latter is a better method of refinement when all atoms are resolved. In any case the molecular orbital calculations bear out the prediction made in the general discussion that the outermost ring has a slight distortion. These results indicate that atoms K, L and M are either on a slightly different plane than the rest of the atoms in the asymmetric unit, or that the whole of the outermost ring has a slightly greater inclination to the (010) plane than the rest of the molecule. Whatever the case may be, bonds JK, KL, LM, MN and MH must be regarded as inaccurately measured according to the two dimensional X-ray data, which can only give the projected lengths onto the mean plane.

If we accept that this distortion indicated in the outermost ring is real, then it is of interest to know why this should be so. Two possible tentative explanations are offered below, although at present there is no supporting evidence.

The molecule may be distorted either due to internal or external forces. The most likely internal overcrowding is that present in perylene also, between atoms N and D and also atoms N' & D'. In a completely regular molecule these atoms would be 2.82 A. apart, while a study of overcrowded molecules (Hornik, Hedstein & Schmidt, 1954) indicates that such atoms are never closer than 2.9 - 3.0 A. Perylene itself has a dipole moment. Although the X-ray investigation of it did not reveal any non-planarity, if this were only slight, then it would be amplified due to the "lever" of the outermost ring in 2:3 - 8:9 dibenzperylene. On the other hand, if the molecule is distorted due to external overcrowding, we must assume that the energy of packing is decreased more by straining the molecule from its planar form, than the chemical energy is increased by the process.

[illegible]	1.4[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]		
[illegible]		[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	1.46	.05	[illegible]	[illegible]
[illegible]	[illegible]	.05	1.44	[illegible]
[illegible]	1.45	.0[illegible]	1.5[illegible]	[illegible]
[illegible]	1.40	.00	1.50	[illegible]
1.41	1.45	.04	1.47	[illegible]
1.50	1.28	.00	[illegible]	[illegible]
1.40	1.3[illegible]	.00	[illegible]	
[illegible]	[illegible]	.03	[illegible]	[illegible]
[illegible]	1.4[illegible]	.02	[illegible]	[illegible]
[illegible]	[illegible]	.09	[illegible]	[illegible]
[illegible]	1.44	.06	1.45	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	.09

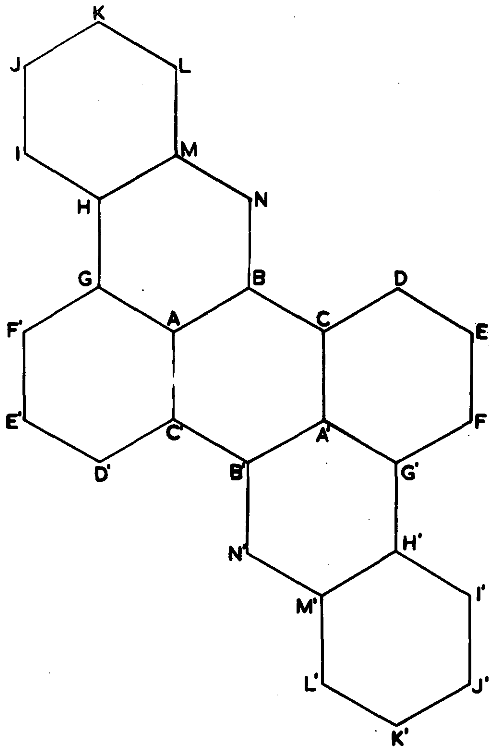
[illegible] lengths, due to [illegible]

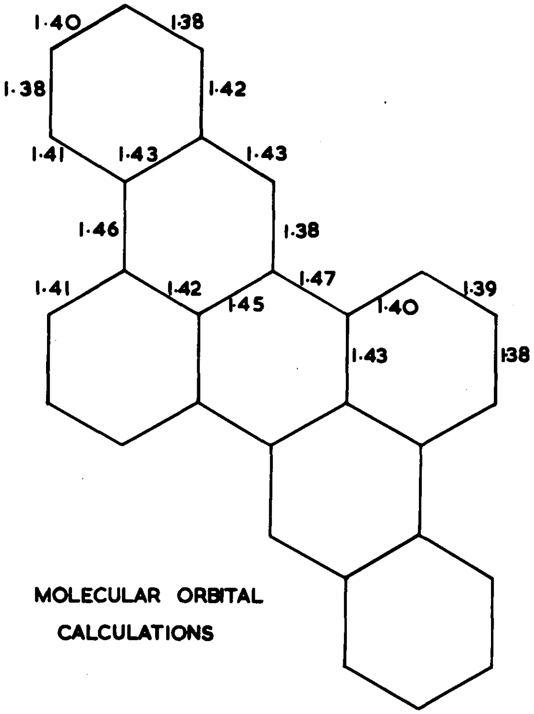
TABLE IX: Comparison of X-ray and molecular orbital results

Bond	M.O. length	Booth refinement		$(F_o - F_c)$ refinement	
		length	$\|\Delta\|$	length	$\|\Delta\|$
AB	1.45	1.45	.00	1.48	.03
BC	1.47	1.48	.01	1.49	.02
CD	1.40	1.43	.03	1.50	.10
DE	1.39	1.35	.04	1.38	.01
EF	1.38	1.42	.04	1.44	.06
FG'	1.41	1.44	.03	1.45	.04
CA'	1.43	1.40	.03	1.44	.01
AG	1.42	1.43	.01	1.37	.05
GH	1.46	1.46	.00	1.50	.04
HI	1.41	1.45	.04	1.37	.04
IJ	1.38	1.38	.00	1.45	.07
JK	1.40	1.31	.09	1.29	.11
KL	1.38	1.32	.06	1.41	.03
LM	1.42	1.41	.01	1.39	.03
MN	1.43	1.52	.09	1.43	.00
NB	1.38	1.44	.06	1.45	.07
MH	1.43	1.33	.10	1.34	.09

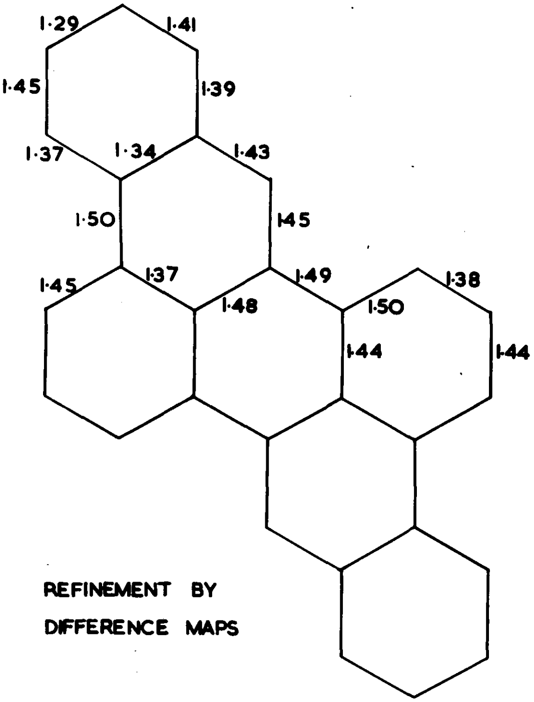
"Doubtful" experimental bond lengths, due to a possible distortion of the molecule, are in red.

All distances are in Angstrom.

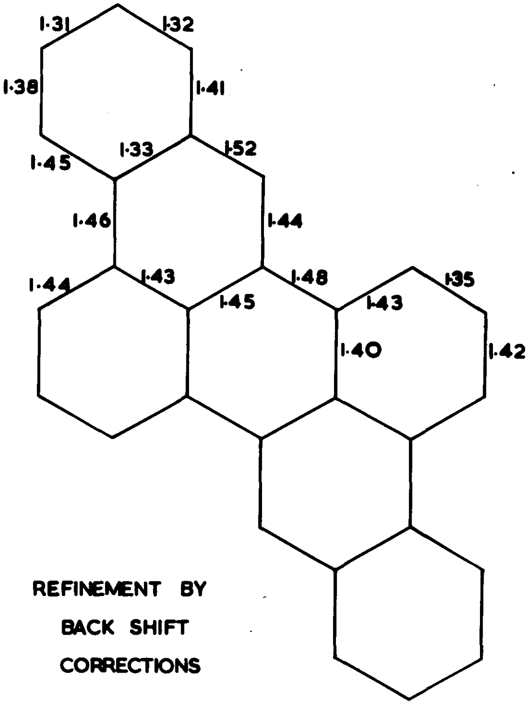




MOLECULAR ORBITAL CALCULATIONS



REFINEMENT BY DIFFERENCE MAPS



REFINEMENT BY BACK SHIFT CORRECTIONS

BOND LENGTHS IN ÅNGSTRÖM

TABLE X: Standard deviations

	All bonds	Without doubtful bonds	Cruickshank's test
Booth refinement	0.0492 A.	0.0258 A.	0.0303 A.
$(F_o - F_c)$ refinement	0.0605 A.	0.0487 A.	0.0254 A.

Experimental

Copper K_α radiation, $\lambda = 1.542$ A. was employed in all measurements. Rotation, oscillation, and moving-film photographs were used, the latter chiefly for intensity records. In the $(h0\ell)$ zone of reflections only those with h even and ℓ even appeared; in the $(h1\ell)$ layer line the only reflections recorded were those with $1 + \ell = 2n$. In the $(0k\ell)$ zone of reflections only those with $k + \ell = 2n$ were present. Thus the space group was Aa or A2/a.

Unit cell lengths were measured from rotation photographs on which copper powder lines had been superimposed for calibration of the camera. The β angle was calculated by measuring the length of the [101] and also the [$\bar{1}$01] diagonals.

Density measurements were made by floatations in solutions of potassium iodide at room temperature.

The $(h0\ell)$ and $(0k\ell)$ zone of reflections were explored in detail by moving-film exposures of the equatorial layer lines for crystals rotated about the b and a axes. The multiple-film technique was used to correlate strong and weak reflections, the total range of intensities covered was about 5,000:1. Very long exposures (up to 70 hours at 10 m.a. and 35 kV) were made of both these zones so that it was possible to record 48% of the total possible number of independent reflections in the $(h0\ell)$ zone, and 26% of the independent reflections in the $(0k\ell)$ zone. Even fewer reflections were present in a moving film of the (hk0) zone. The absolute value of the F values was not determined directly, but obtained by correlation with the calculated F values, in such a way that

$$\Sigma|F_{obs}| \text{ (scaled)} = \Sigma|F_{calc}|$$

Small crystal specimens were employed which completely bathed in a uniform X-ray beam. The specimen used for the $(h0\ell)$ zone was 2 mm. long (parallel to the b axis), 0.2 mm. broad and 0.15 mm. wide. The specimen used for the $(0k\ell)$ zone was 0.43 mm. long (b axis) and 0.07 mm. wide (c axis). Because of the difference in the X-ray path lengths through the crystal for different positions of the crystal in the latter case, absorption corrections were carried out graphically by drawing and measuring a mean path for the X-ray beam through the crystal for each reflection (Albrecht, 1939).

The calculated correction factors varied from 1.05 to 1.35.

There was considerable evidence of extinction of the (002) reflection in the (0kℓ) zone. This could easily be seen by comparing the (00ℓ) reflections in the (h0ℓ) and (0kℓ) zones. Most X-rays will have had to pass through the whole length of the crystal to be reflected off the (002) planes, which explains why extinction should occur in this reflection.

The (h0ℓ) reflections had also been estimated by using another specimen, but using a rather shorter exposure. The intensity of the reflections which were observed on this series of films were estimated and found in good agreement with those from the other specimen.

The method of summing Fourier series representing electron density projections has been discussed in the section on "Accuracy". Difference syntheses were summed in the same way using the series

$$\rho_{OBS}(x,z) - \rho_{CALC}(x,z) = \frac{1}{ac\sin\beta} \sum_{h} \sum_{\ell} \Delta F(h0\ell) \cos 2\pi\left(h\frac{x}{a} + \ell\frac{z}{c}\right)$$

This series was summed at 900 points in the asymmetric unit. Both the a and c axes were subdivided into 60 parts. Thus the summation intervals were $\frac{a}{60} = 0.277$ A., $\frac{c}{60} = 0.344$ A. The atomic centres were adjusted independently to make

$$\underline{\text{grad}} \left\{ \rho_{OBS}(x,z) - \rho_{CALC}(x,z) \right\} \rightarrow 0$$

Calculated and observed values of structure factors:

(1) From difference map refinement
(2) From Booth back shift refinement

$\lambda = 1.542$ A.

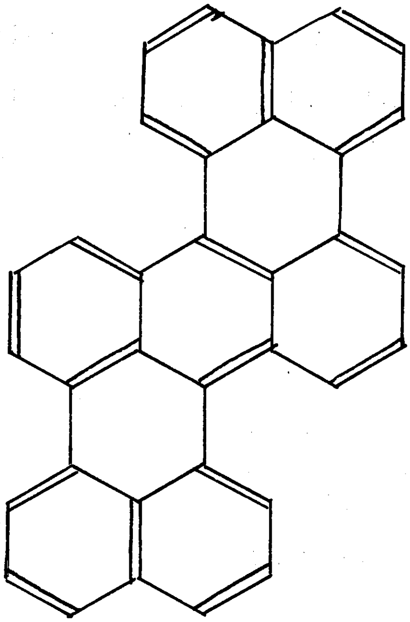
			F_c						F_c		
hkℓ	2 sin θ		(1)	(2)	$\lvert F_o \rvert$	hkℓ	2 sin θ		(1)	(2)	$\lvert F_o \rvert$
002	.157	-	110	102	102	4016	1.428	+	62	66	78
004	.315	-	32	34	36	4018	1.535	-	6	8	18*
006	.472	+	30	34	34	600	.586	+	38	42	36
008	.629	+	32	28	27	602	.655	-	43	42	38
0010	.786	-	30	28	31	604	.749	-	15	12	15
0012	.943	-	14	12	17	606	.857	+	58	61	66
0016	1.258	-	10	13	14	6010	1.118	+	12	15	14
200	.195	+	94	94	82	6012	1.255	+	15	14	15
202	.290	-	168	162	156	6016	1.345	+	27	22	31
204	.425	-	104	111	95	6018	1.690	-	18	18	18
206	.565	-	13	9	6	800	.781	-	16	10	19
2010	.870	-	10	8	10	806	1.030	+	76	73	90
2012	1.018	-	18	19	17	808	1.149	-	38	38	54
2014	1.175	-	14	19	26	8016	1.670	-	19	18	18
400	.391	-	144	142	141	1002	1.038	+	14	11	11
402	.468	+	10	14	8	1202	1.232	-	21	23	14
404	.580	-	6	10	6	14012	1.888	-	11	13	10
406	.700	-	34	38	33	1602	1.618	-	16	19	8
4012	1.130	-	12	12	21	1604	1.689	-	2	0	13*
4014	1.275	-	24	22	26	1606	1.765	-	8	6	9

		F_c						F_c			
hkℓ	2 sin θ		(1)	(2)	$\lvert F_o \rvert$	hkℓ	2 sin θ		(1)	(2)	$\lvert F_o \rvert$
1802	1.813	-	32	34	24	$\bar{8}08$	.840	+	18	18	14
1804	1.880	+	43	45	41	$\bar{8}012$	1.020	+	15	7	13
$\bar{2}02$	.210	+	24	21	23	$\bar{8}014$	1.135	-	16	19	14
$\bar{2}04$	.316	+	92	98	96	$\bar{8}018$	1.390	+	17	22	20
$\bar{2}06$	.450	+	34	32	34	$\overline{10}02$	.935	+	44	46	47
$\bar{2}010$	.750	+	79	97	98	$\overline{10}04$	.925	-	77	84	87
$\bar{2}012$	.900	-	13	11	14	$\overline{10}012$	1.128	-	21	22	22
$\bar{2}014$	1.055	-	27	26	23	$\overline{10}014$	1.225	+	14	12	9
$\bar{4}02$	.373	-	14	24	17	$\overline{12}02$	1.130	+	55	59	54
$\bar{4}04$	.423	-	37	40	36	$\overline{12}04$	1.115	-	8	10	16
$\bar{4}06$	.510	-	26	28	19	$\overline{12}012$	1.255	+	14	11	22
$\bar{4}08$	.632	-	104	94	94	$\overline{12}014$	1.340	-	46	44	54
$\bar{4}010$	.764	+	90	93	106	$\overline{12}016$	1.432	-	18	12	10
$\bar{4}014$	1.050	+	14	11	13	$\overline{14}04$	1.300	+	26	23	28
$\bar{4}020$	1.500	-	24	18	10	$\overline{14}012$	1.398	+	97	95	87
$\bar{6}02$	.555	+	20	18	20	$\overline{14}014$	1.465	-	40	46	35
$\bar{6}04$	.575	+	14	10	14	$\overline{14}016$	1.545	-	8	8	9
$\bar{6}06$	.627	-	14	26	22	$\overline{16}010$	1.515	-	17	11	9
$\bar{6}08$	.717	-	6	10	14	$\overline{16}012$	1.555	+	22	26	30
$\bar{6}010$	.827	-	32	29	26	$\overline{16}014$	1.610	+	18	11	10
$\bar{6}012$	.944	-	2	9	8	$\overline{16}016$	1.675	+	18	20	20
$\bar{6}018$	1.355	+	25	24	27	$\overline{18}012$	1.720	-	26	26	22
$\bar{6}020$	1.500	-	22	25	19	011	.307	+	90	82	78

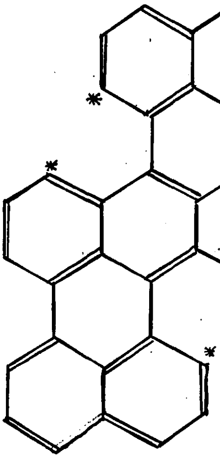
hkℓ	2 sin θ		F_c (1)	F_c (2)	$\lvert F_o \rvert$
013	.380	+	29	41	41
015	.498	+	26	25	32
019	.770	+	38	43	46
0,1,11	.917	-	29	30	34
0,1,15	1.214	-	40	54	47
020	.590	-	53	55	53
022	.614	+	18	25	19
024	.673	+	54	56	59
026	.758	-	22	28	18
0,2,16	1.392	-	22	18	18
0,2,20	1.685	+	12	27	17
035	.972	-	30	42	29
0,4,16	1.728	+	16	22	16
060	1.769	-	16	18	26

PART II

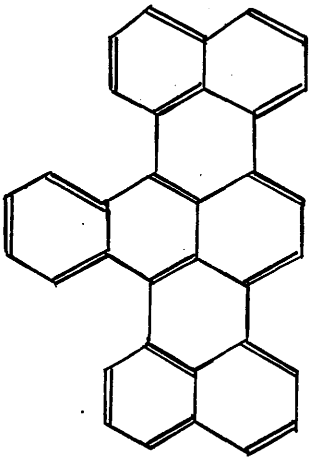
1:9 - 5:10 - DIPERINAPHTHYLENE-ANTHRACENE



Introduction



I

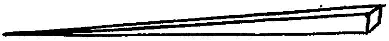


II

The absorption visible and infra red spectrum of the two chemically related compounds 1:9 -5:10 - Di*peri*naphthylene-anthracene (I) and 1:9 - 4:10 - Di*peri*naphthyleneanthracene (II) had been predicted by Dewar (1952). These compounds were, therefore, prepared by Clar and Kelly (1954) in order to verify this prediction. Dewar's calculations were found to be incorrect in the case of I, but this left a little doubt as to whether the compound believed to be I had been correctly synthesized.

The X-ray work had therefore first to establish that the correct formula had been assigned to the compound. It was hoped also to carry this work further in order to establish the bond lengths and angles, because in this compound they were of even more than usual interest in view of the overcrowding between the atoms marked *. When the work had been in progress for a little time it became apparent that it would be impossible to obtain very accurate atomic co-ordinates by means of two-dimensional data only. Thus the work of refinement was stopped once the chemical formula had been established without doubt, and the nature of the distortion due to the overcrowding had been determined.

Preliminary studies



The crystals were prepared by Clar and Kelly (1954) and crystallized by sublimation into what appeared to be long thin prismatic needles to the naked eye. Under the microscope it could be seen that the crystals were, in fact, very thin pyramids. Faces could be recognized on some specimens. These were probably the (001) and (101) surfaces. Single crystals were very dark red and opaque, but in quantity or in a finely powdered form, their colour appeared to change to a very dark blue. On nearly all crystals there were considerable overgrowths which were impossible to cut off because of the pliable nature of the crystals. These overgrowths and the ease with which the crystals could be distorted made it very difficult to find good specimens for X-ray work. The needle axis was found to be parallel to the unique axis of the monoclinic unit cell.

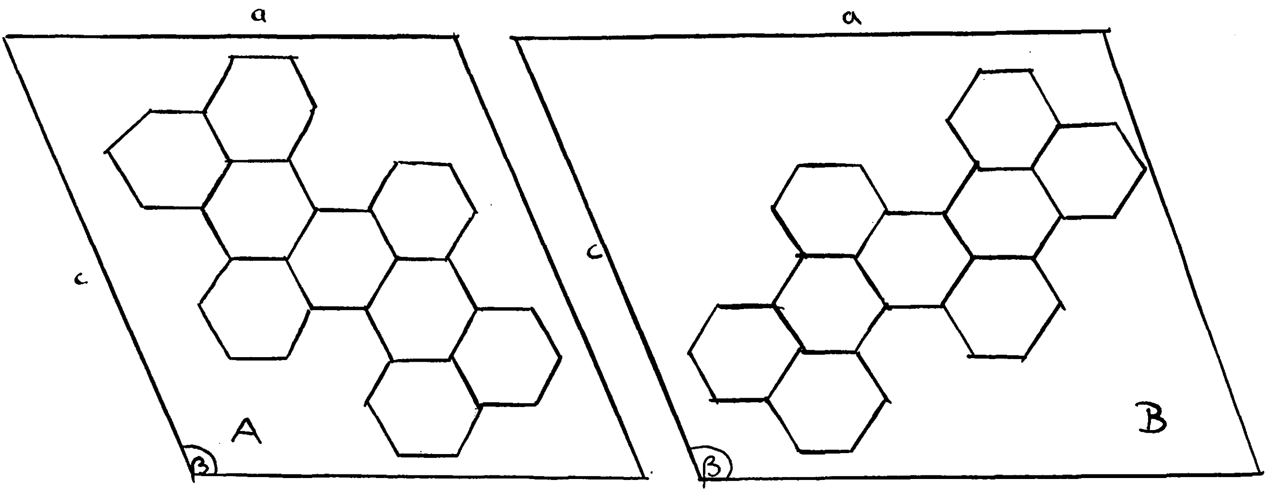
Crystal Data

1 : 9 - 5:10 Diperinaphthylene anthracene, C_{34} H_{18}; M = 426.1; m.p. 333-334°C.; d, calc., 1.356 gm./c.c., found 1.359 gm./c.c.; monoclinic system; a = 11.95 $\pm$ .03 A., b = 7.83 $\pm$ .02 A., c = 11.17 $\pm$ .03 A., β = 92°18' $\pm$ 12'. Absent spectra, (0k0) when k is odd. Space group C_2^2 ($P2_1$), although C_{2h}^2 ($P2_{1/m}$) is permissible according to the absent spectra; Two molecules per unit cell; Molecular symmetry, the possibility of either a centre of symmetry or two fold axis; Absorption coefficient for X-rays, λ = 1.542, μ = 6.50 m^{-1}; Total number of electrons per unit cell = F(000) = 444.

Partial Analysis of the structure by consideration of molecular packing and statistical distribution of intensities

By far the strongest reflection was found to be from the (020) plane. This suggested a layer structure with the mean plane of the molecule roughly perpendicular to the b axis. The two molecules in the cell would then be stacked roughly on top of each other as a result of the 2_1 screw axis. The molecule is overcrowded as shown by the asterisk on the diagram in the introduction. It is therefore to be expected that the molecule will depart slightly from the planar configuration as has been found previously in the case of similar molecules (McIntosh, Robertson and Vand, 1954, and Herbstein and Schmidt 1954 a and b). The usual thickness for non-overcrowded planar molecules such as coronene (Robertson and White, 1945), Ovalene (Donaldson, Robertson, 1953), as well as the inter layer distance in graphite, is 3.40 A. Thus two molecules stacked on top of each other, as suggested here, would require the length of the b axis to be at least 6.80 A. In fact, b = 7.83 A., suggesting that one molecule is (3.4 + 0.5) A. thick, and lying very nearly perpendicular to the b axis. The 0.5 A. extra thickness would then account for the overcrowded nature of the molecule.

This packing was also in good agreement with the lengths of the a and c axes. If the molecule was regarded as completely planar and made of regular benzene rings of 1.4 A. sides, then it could just be fitted into the area $a \wedge c$ leaving just sufficient space (3.4 A.) between it and the molecule in the next cell. There were only two such ways in which a molecule could be fitted into the cell (A) or (B) as shown in the diagram. It must be remembered that the plane of the molecule is roughly parallel to the (010) plane of projection, which fixes the angle of tilt of the molecule. The other molecule in the unit cell is $\frac{b}{2}$ above that shown in the diagrams and has the same relationship to its neighbours. This type of packing is very similar to that found in the overcrowded hydrocarbon tetrabenznaphthalene (Herbstein and Schmidt, 1954 b).



Two space groups were possible according to the absent spectra: C_2^2 ($P2_1$) without a centre of symmetry, or C_{2h}^2($P2_1/_m$) with a centre of symmetry. Statistical tests should distinguish between these two space groups. These tests should really be applied to three dimensional data, but have been found almost equally successful when applied to two dimensional data. Space group $P2_1$ possesses a centre of symmetry when projected onto the (010) plane, thus it would be useless to apply statistical tests to the $(h0\ell)$ planes. Consequently either the (hk0) or $(0k\ell)$ planes must be employed to distinguish between the two space groups with only two dimensional data. In fact the (hk0) planes were employed. There were 49 observed planes, the remainder were assumed to have half the intensity of the weakest observed plane, inside the copper sphere. Each had a multiplicity of 4, except for the axial planes which only had a multiplicity of 2.

Two types of tests were applied. The first is due to

Wilson (1949). He shows that the ratio $\frac{\{\text{Mean } |F|\}^2}{\text{Mean } F^2}$ should have a different value for centro- and non-centrosymmetrical structures. The other test is due to Howells, Philips and Rogers (1950). Their test is perhaps a little more satisfying for it does not depend on drawing a conclusion from a single value. They show that the function N(z) has a different distribution with z according to whether the structure is centro- or non-centrosymmetrical. N(z) is defined as the number of reflections whose intensities are less than or equal to z of the mean intensity. Both the Wilson test as well as the distribution curves derived by Howells, Philips and Rogers are derived on the assumption that the scattering factors for the planes remain roughly constant. Thus when applying these tests the reflections must be divided into ranges of roughly equal scattering factors.

The ranges selected in the present case were:-

Range I	$\sin\theta$	:	$0 \rightarrow 0.10$	(neglected, as it only contained one reflection)
Range II	$\sin\theta$	:	$0.10 \rightarrow 0.40$	
Range III	$\sin\theta$	:	$0.40 \rightarrow 0.60$	
Range IV	$\sin\theta$	:	$0.60 \rightarrow 0.77$	

The Wilson ratios for these ranges were:-

Range II	Range III	Range IV	Mean
0.379	0.643	0.784	0.603

Theoretical values of Wilson's ratio:

Non-centred	0.785
centred	0.637

It is, therefore, obvious that Wilson's test completely fails to distinguish between the two possible space groups.

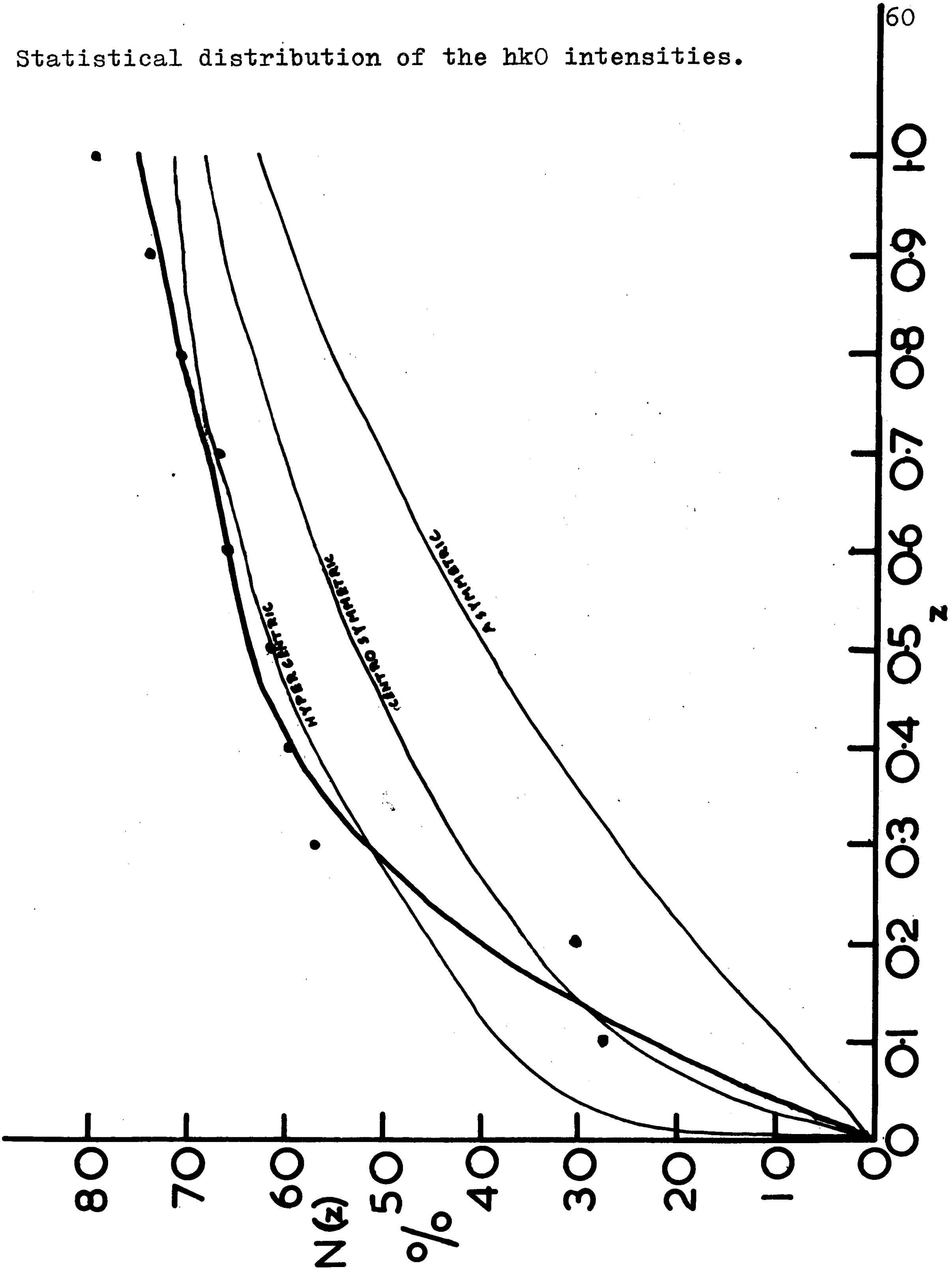
The result for the distribution curve are given in Table I (page 59). From this table it will be seen that the experimental distribution is in general above the centro-symmetrical curve. It therefore appeared possible that the space group was $P2_{1/m}$. Lipson and Woolfson (1952) who showed that if the molecular structure possessed a centre of symmetry which was not made use of in a centro-symmetrical structure, as for instance in Pyrene (Robertson and White, 1947), then a different distribution would result. Lipson and Woolfson called this a "hypercentric" distribution. The results in this case appeared to be hypercentric, but that may well be due to internal symmetry of the molecule. The molecule could certainly not be related across a centre of symmetry to another molecule in space group $P2_{1/m}$ as this would require four molecules per unit cell, while there are only two molecules in the cell. A later paper by Rogers and Wilson (1953) showed that both centro and non-centro-symmetrical structures could correspond to the experimental distribution, because there is considerable symmetry in the

Range	z = 0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
II	0.0	43.6	51.2	64.2	64.2	69.2	82.0	82.0	82.0	87.2	92.3
III	0.0	38.4	38.4	38.4	46.2	46.2	46.2	46.2	57.6	61.4	72.9
IV	0.0	0.0	0.0	67.8	67.8	67.8	67.8	71.6	71.6	71.6	71.6
Mean	0.0	27.3	29.9	56.8	59.4	61.1	65.3	66.6	70.4	73.4	78.9
*non-centro symmetrical	0	9	18	26	33	39	45	50	55	59	63
*centro symmetrical	0	25	35	42	47	52	56	60	63	66	68
*hypercentric	0	38	45	51	57	61	64	67	69	70	71

* Theoretical curves

TABLE I: Distribution of intensities of (hk0) reflections: N(z) in %.

Statistical distribution of the hk0 intensities.



molecule as a result of it being composed of six membered carbon rings. Thus no really satisfactory conclusion could be drawn from these statistical tests.

The space group $P2_{1/m}$ demands that the two molecules in the cell are related by a mirror plane with the molecular centre of both molecules on the 2_1 screw axis separated by $\frac{b}{2}$. This packing leaves large gaps between molecules. Nevertheless it was noted that the following high order planes were very strongly reflected: (600), (601), (304), (305), (905), (009), (109), $(\bar{3}04)$, $(\bar{8}04)$, $(\bar{8}05)$. These fitted in well with the only two possible molecular arrangements (A and B) allowed by packing considerations, for these structures demand that certain small spacing planes on which the atoms lie must have very strong reflections. This suggested that the space group was $P2_{1/m}$, as it would be unlikely that these planes would still be enhanced if the molecular centres were no longer restricted to lie exactly on top of each other along the b axis. Structure factors were accordingly calculated from which it appeared that structure A was more likely. An electron density map was plotted on which every atom was found to be resolved, and there even appeared to be evidence of some hydrogen atoms. However, the structure factors did not appear to improve sufficiently after the atoms had been adjusted according to the electron density map.

At this stage it was realized that the unit cell would have been approximately halved along the b axis if the structure had been correct. The halving would be exact if the molecule were exactly planar with its plane perpendicular to the b axis. In other words if the space group were $P2_1/m$ all layer lines on the b-axis rotation photograph with k odd should be weak in intensity. In fact, the first layer line was even stronger than the zero layer line. Hence the space group must be $P2_1$, not $P2_{1/m}$ as had been assumed.

The essential difference between the packing in space groups $P2_1$ and $P2_{1/m}$ ~~lies~~ is that the molecular centre is fixed to lie on the 2_1 screw axis in the latter case, so that there are four asymmetric units per unit cell; but for space group $P2_1$ the molecular centre may lie anywhere in the unit cell (say at X, Y, Z, where these are axial ratios). Once the position of the molecular centre could be decided upon it was only necessary to know whether the lengths of the molecule lay parallel to [101] (structure A) or parallel to [$\bar{1}$01] (structure B). Two independent methods were used to determine the position of the molecular centre, both of which lead to the same result. These will now be described.

First method for obtaining trial structure

According to the convention of the International Tables, the origin in space group $P2_1$ requires to be fixed on the 2_1 screw axis, but its position on this axis cannot be fixed. Let us therefore choose the position of the molecular centre to make $Y = \frac{1}{4}$. Hence the two molecules in the unit cell lie roughly in the planes $y = \frac{1}{4}$ and $y = \frac{3}{4}$.

The structure factor formulae for this space group are

$$\left.\begin{aligned} A &= 2 \sum_{N} f.\cos 2\pi (hx + \ell z).\cos 2\pi ky \\ B &= 2 \sum_{N} f.\cos 2\pi (hx + \ell z).\sin 2\pi ky \end{aligned}\right\} \qquad k = 2n$$

$$\left.\begin{aligned} A &= -2 \sum_{N} f.\sin 2\pi (hx + \ell z).\sin 2\pi ky \\ B &= 2 \sum_{N} f.\sin 2\pi (hx + \ell z).\cos 2\pi ky \end{aligned}\right\} \qquad k = 2n + 1$$

where x, y and z are the positions of atoms expressed as ratios of the unit cell edges, a, b, and c respectively.

Let x', y', z' be the co-ordinates of the atoms with respect to the molecular centre of symmetry at X, Y, Z. Then for every atom at $x_1 = X + x'$, $y_1 = Y + y'$, $z_1 = Z + z'$ there is an atom at $x_2 = X - x'$, $y_2 = Y - y'$, $z_2 = Z - z'$. Hence when $k = 2n$

$$\begin{aligned} A &= 2 \sum_{\frac{N}{2}} f.\Big[\cos 2\pi\left\{(hX + \ell Z) + (hx' + \ell z')\right\} . \cos 2\pi kY \\ &\qquad + \cos 2\pi\left\{(hX + \ell Z) - (hx' + \ell z')\right\} . \cos 2\pi kY\Big] \\ &= 4 \sum_{\frac{N}{2}} f.\cos 2\pi (hX + \ell Z) . \cos 2\pi (hx' + \ell z').\cos 2\pi kY \end{aligned}$$

It has been assumed that the molecule is planar with its plane perpendicular to the b axis. Thus y' has been put equal to zero as a first approximation.

Since the product $\cos 2\pi(hX + \ell Z).\cos 2\pi kY$ is common to each atom, we may write:-

$$A = 4 \cos 2\pi(hX + \ell Z).\cos 2\pi kY \sum_{\frac{N}{2}} f \cos 2\pi(hx' + \ell z')$$

But we have chosen the origin so that $Y = \frac{1}{4}$.

$$\therefore A = 4 \cos 2\pi(hX + \ell Z) \sum_{\frac{N}{2}} f.\cos 2\pi(hx' + \ell z') \text{ when } k = 2n$$

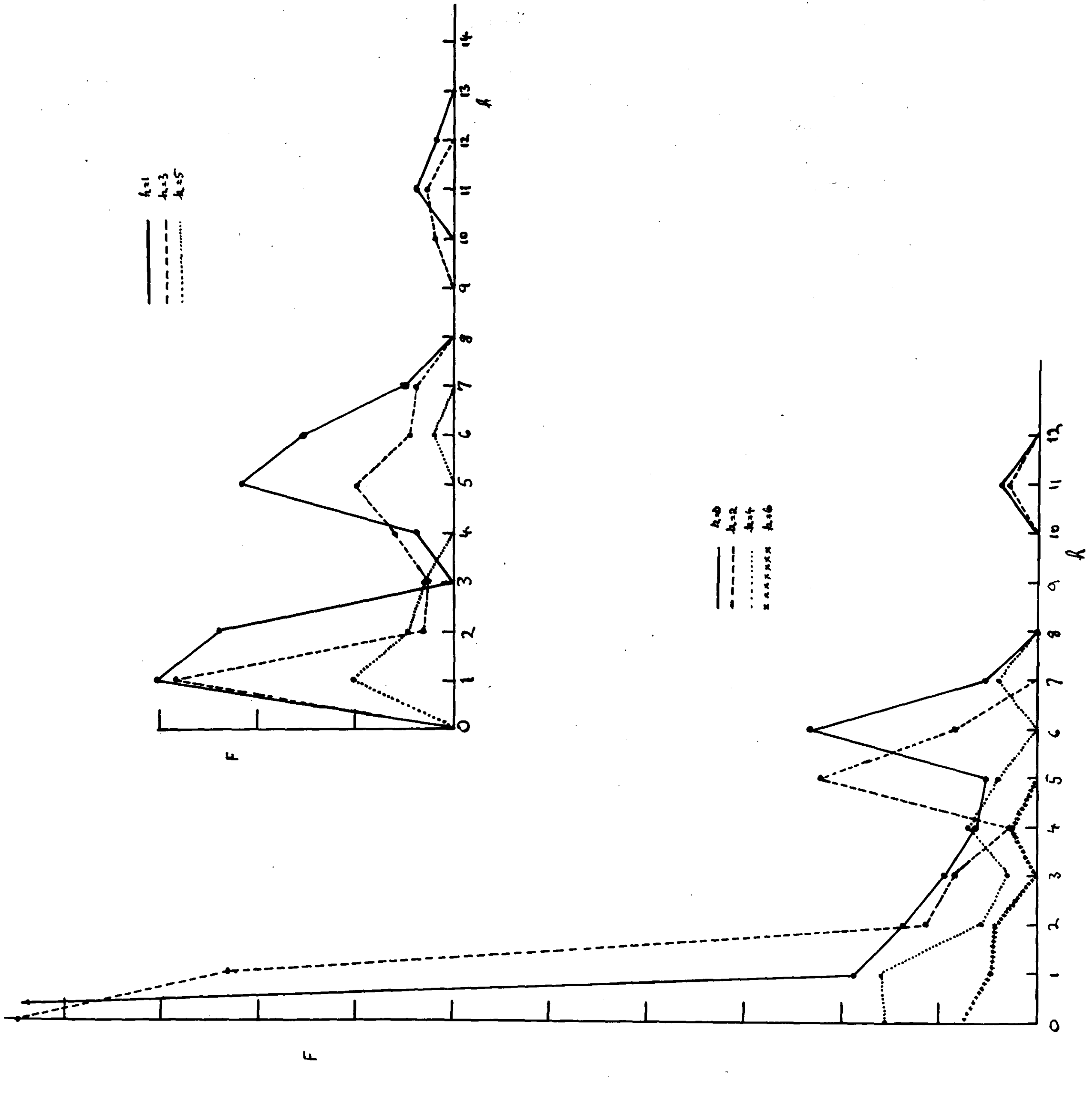
Treating all parts of the structure factors similarly we find that

$$\left.\begin{array}{ll} A = & (-1)^n.4.\cos 2\pi(hX + \ell Z) \sum_{\frac{N}{2}} f \cos 2\pi(hx' + \ell z') \\ B = & 0 \end{array}\right\} k = 2n$$

$$\left.\begin{array}{ll} A = & (-1)^{n+1}.4.\sin 2\pi(hX + \ell Z) \sum_{\frac{N}{2}} f.\cos 2\pi(hx' + \ell z') \\ B = & 0 \end{array}\right\} k = 2n + 1$$

The approximation that the molecule is planar, and perpendicular to the b-axis, does not affect the $(h0\ell)$ structure factors, but has increasing effect as k increases since all errors are multiplied by k. That this approximation was, however, quite reasonable could be seen by plotting the

Structure factor graphs of the hk0 reflections, showing how F (on a relative scale) varies with h, for constant k.



modulus of the structure factors against h for the (hk0) reflections, first for k even, then for k odd. The approximation shows that all the geometrical structure factors with the same value of h and k = 2n should be equal in magnitude and similarly, all the geometrical structure factors with the same value of h and k = 2n + 1 should also be equal in magnitude. Hence these plots should show the same variation in the magnitude of F(hk0) as h increases for different even values of k, and likewise the variation should be the same for the plots of the odd values of k. Emphasis must be placed on variation rather than actual magnitudes since F(hk0) must diminish in magnitude as k increases because of the smaller scattering factors for larger values of k. The diagrams of these plots show that the approximation was fairly reasonable.

Thus we have

$$S(h0\ell) = 4 \cos 2\pi(hX + \ell Z) \sum_{\frac{N}{2}} \cos 2\pi(hx' + \ell z') \quad \text{for carbon atoms.}$$

where S is the geometrical structure factor. The only approximation for the (h0ℓ) structure factors is that the molecular centre of symmetry is exact.

Also

$$S(h1\ell) = -4 \sin 2\pi(hX + \ell Z) \sum_{\frac{N}{2}} \cos 2\pi(hx' + \ell z')$$

In this case the planar approximation to the molecule is only small as k is only one.

Hence it follows that

$$\frac{S(h1\ell)}{S(h0\ell)} = -\tan 2\pi(hX + \ell Z)$$

or

$$\frac{F(h1\ell)\ /\ f(h1\ell)}{F(h0\ell)\ /\ f(h0\ell)} = -\tan 2\pi(hX + \ell Z)$$

that is

$$\tan 2\pi(hX + \ell Z) = -\frac{F(h1\ell)\ .\ f(h0\ell)}{F(h0\ell)\ .\ f(h1\ell)}$$

where $f(hk\ell)$ is the scattering factor for the carbon atoms for the plane $(hk\ell)$ for the particular X-radiation used. The effect of the hydrogen atoms has been neglected.

From this equation it follows that

$$|\tan 2\pi hX| = \frac{|F(h10)|\ .\ f(h00)}{|F(h00)|\ .\ f(h10)} \qquad \ldots\ldots\ldots\ldots \quad (1)$$

and

$$|\tan 2\pi\ell Z| = \frac{|F(01\ell)|\ .\ f(00\ell)}{|F(00\ell)|\ .\ f(01\ell)} \qquad \ldots\ldots\ldots\ldots \quad (2)$$

Equations (1) and (2) can be applied provided $F(h10)$ is on the same relative scale as $F(h00)$, and likewise if $F(01\ell)$ is on the same relative scale as $F(00\ell)$. They need not have absolute values since the equations are in the form of divisions; hence the scaling factor to relative values cancels out. $F(h10)$ and $F(h00)$ were placed on the same relative scale by taking a moving film of the (hk0) reflections, and $F(01\ell)$ was placed on the same relative scale as $F(00\ell)$ by using the $(0k\ell)$ reflections. The possible values of X and Z were limited to lie between

$$0 \leqslant X \leqslant +\frac{1}{4} \quad \text{and} \quad -\frac{1}{4} \leqslant Z \leqslant +\frac{1}{4}$$

Any values of X or Z outside these ranges would produce an identical structure as corresponding values of X and Z inside this range, except that the position of the origin would be changed. Hence the ambiguity of equation (1) is h fold, and the ambiguity of equation (2) is ℓ fold.

No knowledge of the scattering curve could be had at this stage, except by the rather uncertain statistical method due to Wilson (1942). But this did not greatly matter as it was not necessary to obtain accurate values of the scattering factors in order to apply equations (1) and (2). The reason for this is that $f(h0\ell) \simeq f(h1\ell)$, so that

$$\frac{f(h0\ell)}{f(h1\ell)} \simeq 1$$

whatever the temperature vibration. More accurately this ratio is slightly larger than one, but its actual value is not likely to change much whatever temperature factor is chosen. Consequently an empirical curve due to Robertson (1935) was used. The results, which leave little doubt as to the position of the centre of the molecule, are shown in Tables II and III. Unobserved intensities were assumed to be half the intensity of the weakest observed intensity in these calculations.

h00	|F(h00)|	f(h00)	h10	|F(h10)|	f(h10)	|tan 2πhX|	360X hX	X . 360								
100	23.3	4.95	110	36.5	4.26	1.815	61°	(61)								
200	16.9	4.20	210	30.0	4.02	1.855	62°	31	(59)							
300	11.8	3.60	310	0.7	3.39	0.0792	5°	2	(59)	(62)						
400	7.7	3.00	410	5.0	2.85	0.680	34°	9	37	(56)	82					
500	6.4	2.49	510	27.3	2.43	4.38	77°	15	20	51	(56)	87				
600	29.2	2.07	610	19.4	2.01	0.685	34°	6	24	38	(54)	66	73			
700	6.7	1.74	710	6.4	1.68	0.989	45°	6	19	32	45	(58)	71	83		
1100	4.6	0.78	1110	5.5	0.78	1.040	46°							(53)	(61)	70

Mean value of X = 58°

TABLE II: Application of the equation $|\tan 2\pi hX| = \frac{|F(h10)| . f(h00)}{|F(h00)| . f(h10)}$

00l	$\|F(00l)\|$	f(00l)	01l	$\|F(01l)\|$	f(01l)	$\|\tan 2\pi l Z\|$	$l Z.360$	360 . Z									
001	64.2	4.83	011	22.7	4.26	0.401	22°	㉒									
002	36.9	4.11	012	8.7	3.81	0.256	15°	⑧	82								
003	14.7	3.39	013	11.0	3.18	0.798	39°	⑬	47	73							
005	1.4	2.28	015	3.5	2.19	2.53	68°	⑭	22	50	58	86					
006	1.6	1.89	016	2.7	1.83	1.74	60°	⑩	⑳	40	50	70	80				
008	4.1	1.26	018	8.7	1.23	2.17	65°	8	⑭	30	37	53	59	75	82		
009	10.4	1.02	019	16.7	0.99	1.625	58°	6	⑭	26	34	46	54	66	74	86	
0010	2.2	0.81	0110	6.9	0.81	3.14	72°	7	⑪	25	29	41	47	61	65	77	83

Mean value of Z = 14°

TABLE III: Application of the equation $|\tan 2\pi l Z| = \dfrac{|F(01l)| . f(00l)}{|F(00l)| . f(01l)}$

Thus $X = 58^\circ$, $Y = 90^\circ$, $Z = \pm 14^\circ$.

To distinguish between these two possibilities was very easy by visual inspection of the $(h1\ell)$ reflection, and comparing them with the $(h0\ell)$ reflections, using the knowledge

$$\tan\,(h\,58^\circ \pm \ell 14^\circ) \simeq \frac{|F(h1\ell)|}{|F(h0\ell)|} .$$

It was then clear that the molecular centre was at $X = 58^\circ$, $Z = 14^\circ$. After refinement the mean centre was found to be at $X = 56^\circ$, $Z = 13^\circ$, hence this shows how sensitive the method was.

What remained to be done was to distinguish whether the length of the molecule lay along [101] (structure A) or along [$\bar{1}$01] (structure B). This was done by calculating the agreement factor over the $(h0\ell)$ planes for both structures based on a completely regular molecule whose centre of symmetry was at $X = 58^\circ$, $Z = 14^\circ$. A good deal of computational work was saved by observing the following simplifications.

It has been shown that for the $(h0\ell)$ reflections, assuming a molecular centre of symmetry at X, Z that

$$S(h0\ell) = 4\cos 2\pi(hX + \ell Z) \sum_{\frac{N}{2}} \cos 2\pi(hx' + \ell z')$$

where x' and z' are the atomic co-ordinates expressed as axial ratios with respect to the molecular centre.

$$\therefore F(h0\ell) = \cos 2\pi(hX + \ell Z)\left\{4\, f(h0\ell) \sum_{\frac{N}{2}} \cos 2\pi(hx' + \ell z')\right\}$$

$$= \cos 2\pi(hX + \ell Z) \;.\; \Phi(h0\ell)$$

where $\Phi(h0\ell)$ is the structure factor of plane $(h0\ell)$ with respect to the molecular centre. To compute $\Phi(h0\ell)$ is twice as quick as it has to be taken over only 17 atoms, while to compute $F(h0\ell)$ requires a summation over 34 atoms. $\Phi(h0\ell)$ is then modulated by the factor $\cos 2\pi(hX + \ell Z)$ to give $F(h0\ell)$ for structure A.

However structure B is related to structure A, since every atom at (x',z') in structure A corresponds to an atom at approximately $(-x',z')$ in structure B, since $\beta \approx 90^{\circ}$. Hence the geometrical structure factor of the n^{th} atom of structure A is $\cos 2\pi(hx' + \ell z')$, but is $\cos 2\pi(-hx' + \ell z')$ for structure B. This can be written as $\cos 2\pi(\bar{h}x' + \ell z')$. Thus it follows that for structure A

$$F(h0\ell) = \cos 2\pi(hX + \ell Z) \;.\; \Phi(h0\ell)$$

but for structure B

$$F(h0\ell) = \cos 2\pi(hX + \ell Z) \;.\; \Phi(\bar{h}0\ell)$$

Therefore no additional computation was involved in calculating the structure factors for structure B.

Structure A was found to give much better agreement between observed and calculated structure factors.

Second method for obtaining trial structure

It has been shown that $F(h0\ell) = \cos 2\pi(hX + \ell Z) . \Phi(h0\ell)$.

$\overline{\Phi}(h0\ell)$ was calculated for nine low order planes with large ~~unitary~~ structure factors. The expression $\cos 2\pi(hX + \ell Z)$. $\overline{\Phi}(h0\ell)$ was then calculated very readily at 6° intervals with Beevers Lipson strips. $\left|\cos 2\pi(hX + \ell Z) . \overline{\Phi}(h0\ell)\right|$ was then plotted for $-90^\circ \leqslant Z \leqslant +90^\circ$ at $X = 0^\circ, 6^\circ, 12^\circ, \ldots 90^\circ$. Each structure factor was allocated a different colour. Also, on a separate sheet of paper the values of $|F(h0\ell)|$ were arranged in order on a relative scale in the same colours. The same was done for the corresponding values of $|F(\bar{h}0\ell)|$. It was then necessary to find a position on the graphs where

$$|F(h0\ell)| = \left|\cos 2\pi(hX + \ell Z) . \overline{\Phi}(h0\ell)\right|$$ if structure A were correct

or

$$|F(\bar{h}0\ell)| = \left|\cos 2\pi(hX + \ell\bar{Z}) . \overline{\Phi}(h0\ell)\right|$$ if structure B were correct

In other words it was necessary to find a position on the graphs where the colour order was the same as the experimentally determined colour order, which was plotted on the separate sheet of paper. Only one reasonable fit was found at $54 < X < 60$ and $8 < Z < 15$ for structure A. Thus this method yielded the same result as before, although the molecular centre could not be fixed as accurately as with the first method.

Statistical methods can sometimes show whether there is a centre of symmetry in the molecule which is not made use of in the crystal structure, as for instance in the case of perylene (Donaldson, Robertson and White, 1953) or in pyrene (Robertson and White, 1947). However, frequently statistical methods give a rather uncertain answer, as in the present case, and at any rate do not give any indication where the molecular centre is situated. In comparison the two methods given above give more information, and the information is more certain. On the other hand, these two methods are far less generally applicable than statistical methods, for they were developed for the particular problem in hand.

Refinement of the [010] zone

The accuracy of any particular structure was assessed from the agreement factor, R, defined in the usual way as

$$R = \frac{\Sigma \left| \left(|F_{obs}| - |F_{calc}| \right) \right|}{\Sigma |F_{obs}|}$$

The value of R was usually multiplied by 100 to express it in terms of a percentage.

The trial structure gave an agreement factor of 39%, using an empirical scattering curve. The signs of 71 planes could be fixed with a fair degree of certainty. These were included in a Fourier summation representing the electron density projected onto the (010) plane. It was very difficult to place the atomic centres because of the lack of resolution. Consequently the molecule was treated as if it had a centre of symmetry, and structure factors $\Phi\,(h0\ell)$ were calculated for 17 atoms and then modulated according to the formula

$$F(h0\ell) = \cos 2\pi(hX + \ell Z).\,\Phi(h0\ell).$$

The agreement factor of 36.8% was found, thus no great improvement had taken place. This was rather disappointing, but it was thought that the lack of improvement may be due to the lack of resolution and the assumption that the molecule is centro-symmetric.

Further refinement had therefore to proceed by a different method. Thus a difference map (Cochran, 1951 a) was constructed using the same planes. Hydrogen atoms were, however, first subtracted because the lack of resolution of the carbon atoms. If they had not been subtracted peaks of significant size would have remained on the difference map, which would have obscured the gradients produced by carbon atoms in wrong positions. The C-H bond lengths were assumed to be 1.1 A. long. This is roughly the value found in anthracene (Mathieson, Robertson and Sinclair, 1950) and naphthalene (Abrahams, Robertson and White, 1949). However, Cochran (1953) found a rather smaller value of 0.9 A. for salicylic acid, while spectroscopic data (see, for instance, Coulson, 1952) indicates a C-H bond of 1.09 A. between the atomic nuclei. When structure factors had been re-calculated using the new positions of all the 34 atoms suggested by this difference map the agreement factor came down to 30.9%. The value of the temperature factor had been found to be 6.75 A^2., using the same method as described for 2:3 - 8:9 dibenzperylene in this thesis. McWeeny (1951) scattering curves for carbon and hydrogen were used as before.

Further difference maps were constructed. The agreement factors found for the new structures suggested by each successive map in turn are given below:-

Structure suggested by 1st difference map gave an agreement factor of 30.9%.

" " " 2nd " " gave an agreement factor of 25.3%.

" " " 3rd " " gave an agreement factor of 24.1%.

" " " 4th " " gave an agreement factor of 20.9%.

" " " 5th " " gave an agreement factor of 19.1%.

After the structure according to the 2nd difference synthesis had been completed it was seen that the calculated large structure factors tended to be on the small side. This was no temperature effect, as it involved large structure factors of both high and low order planes. Consequently a small increase in the scaling factor made but little difference in the magnitude of the small structure factors, but gave the desired increase for the large structure factors. Hence, instead of calculating the scaling factor by assuming that

$k\,\Sigma\left|F_{obs}\right| = \Sigma\left|F_{calc}\right|$ (where k is the scaling factor), it was assumed that we require to minimize the expression

$$E = \Sigma\,(k\,F_{obs} - F_{calc})^2$$

$$\therefore \frac{\partial E}{\partial k} = 2\Sigma\,(k\,F_{obs}^2 - F_{obs}\,F_{calc})$$

Hence when $\frac{\partial E}{\partial k} = 0$, $k = \frac{\Sigma\,F_{obs}\,F_{calc}}{\Sigma\,F_{obs}^2}$

When the scaling factor was calculated according to this expression - which gives more weight to larger structure factors as it involves their square - the agreement factor fell from 27.6 to 25.3% on the structure obtained from the 2nd difference map. The scaling factor was re-calculated for each structure in this manner for succeeding structures.

The third difference map showed that most atoms lay on negative areas. When the temperature factor was recalculated a value of B = 7.05 $A.^2$ was indicated. No further change in the temperature factor was found necessary after this increase. This temperature factor is extraordinarily large. In the similar compounds 3:4 benzophenanthrene (Herbstein and Schmidt, 1954 b) the scattering curve found most suitable was the curve used for anthracene (Mathieson, Robertson and Sinclair, 1950) (Private communication). It corresponds to a value of B $\simeq$ 3.5 $A.^2$. A partial explanation of the large temperature factor in the case of 1:9 - 5:10 di<u>peri</u>-naphthylene anthracene may be that the melting point (334°C.)

of this substance is more than 100°C. lower than that of similar compounds. It is, however, difficult to believe that this totally accounts for such a high value of B. Consequently it may be possible that there is some kind of disorder in the crystal, although another explanation is offered in part III of this thesis in connection with the compound anthrovalene which shows the same phenomenon. It is also of interest to note that the similar compounds listed above have normal melting points and are colourless and transparent, unlike di*peri*naphthylene anthracene which has dark opaque crystals.

Refinement had not yet come to an end after the fifth cycle, nevertheless it was decided that physical reality would probably not be approached any closer by further iteration. There were 99 observed structure factors and 34 independent atoms, that is 68 parameters had to be determined with only 99 observational equations. No great accuracy could therefore be expected in view of the unusually large number of independent parameters. The accuracy is in this case still further reduced because of the poor resolution of the atoms. In the final Fourier synthesis only 15 out of the 34 atoms were separately resolved. The resolution is, in fact, even less than usual because of the large temperature factor. For these reasons, as well as the possibility that there may be a certain degree of randomness, further refinement was regarded as fulfilling no useful purpose.

A final F_{obs} synthesis was calculated. All but 12 structure factors whose phase angles still remained in doubt (those marked with an asterisk in the structure factor tables) were included. Two peculiarities were noted. Atom M_2 was well resolved, but the final co-ordinate of atom M_2 was about 0.2 A. from the centre of the peak. Atom O_2 was not resolved. It appeared to be - according to the position found by the $F_{obs} - F_{calc}$ syntheses - in the middle of a slope, where the electron density was not as large as that associated with other atoms. Also bond P_2 O_2 was far too long to be sensible even in projection. Thus atoms O_2 and M_2 were moved to more "reasonable" positions indicated by the final F_{obs} synthesis. It is possible that because of the large number of parameters (68 in number) in comparison to the number of structure factors, even fairly large errors in only 4 parameters can be marked by suitable adjustment to the other 64 parameters. When structure factors were calculated with atoms M_2 and O_2 in their new sites, the discrepancy between observed and calculated structure factors went up from 19.1% to 20.0%. Perhaps if the 32 other atoms were now re-adjusted, so that they no longer masked the large errors in the atoms M_2 and O_2, the agreement factor would again be lowered. The structure factor tables give the

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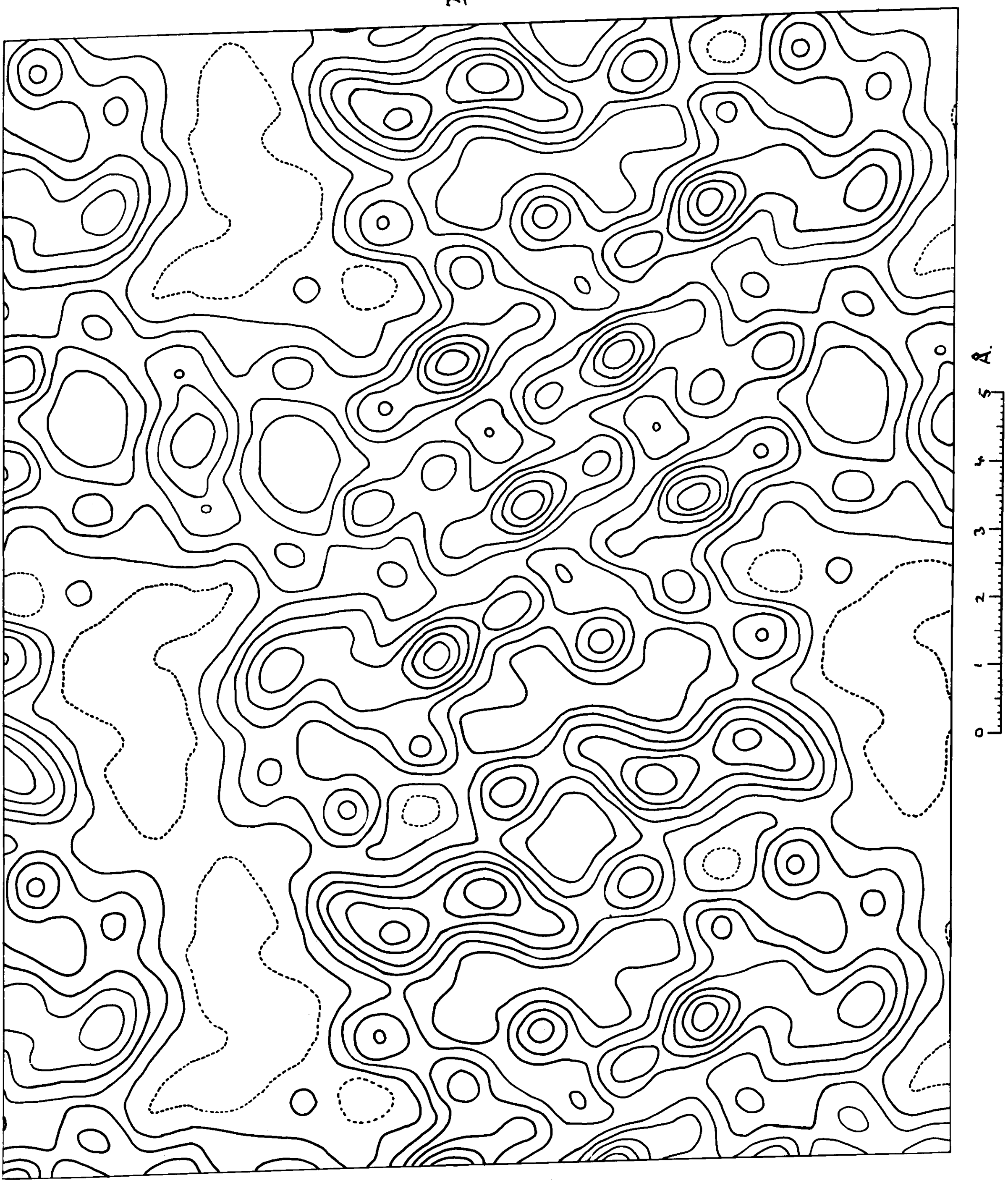
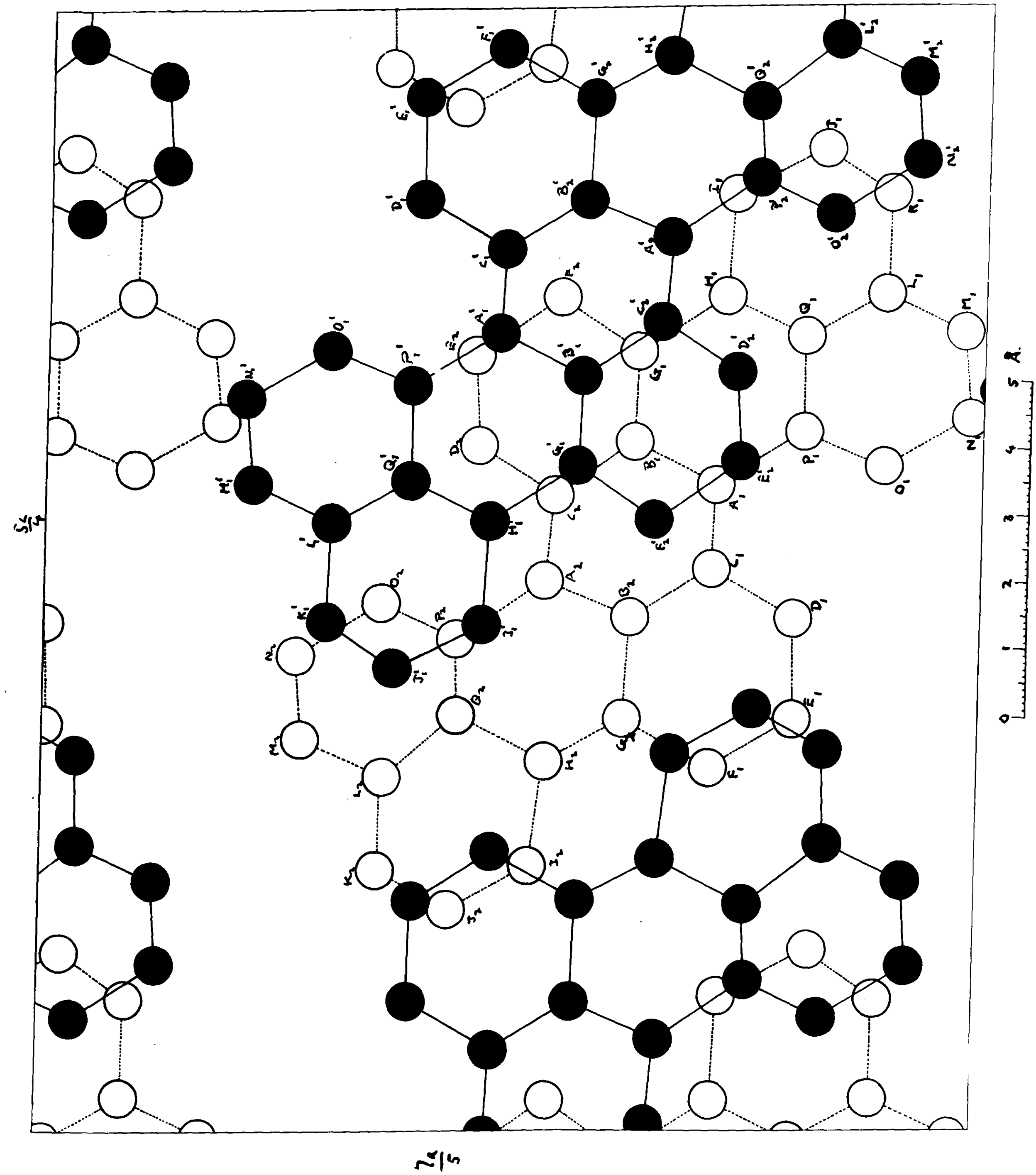


Projection of the diperinaphthylene anthracene structure on (010). Contour scale, one electron per A^2., the first line being dotted.

The atomic arrangement corresponding to the projection on (010), showing molecules at different levels.



value of only the F_{calc} (h0ℓ) according to the atomic positions determined by the difference map refinements. Since, however, the atoms M_2 and O_2 seemed in more reasonable positions in the sites indicated by the final F_{obs} synthesis, these positions were used for all other calculations.

The hydrogen atoms bonded to atoms O_1 and D_1 approach close to each other. Their combined electron densities produce a resolved peak of just over 2e/A^2. Resolved carbon atoms produce an electron density of about 5e/A^2. This low value is no doubt due to the large temperature factor and the small number of reflections in comparison to the large number of atoms. These circumstances give undoubtedly a large termination of series effect, but it is difficult to believe that this effect causes a shift of 0.2 A. in the position of atom M_2.

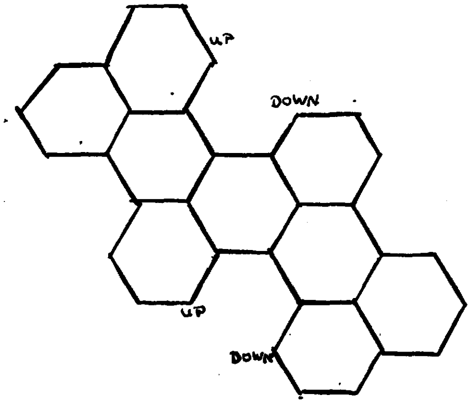
The nature of the molecular distortion due to overcrowding

At this stage fairly accurate values of the x and z axial ratios were known from the (h0ℓ) projection, but the y axial ratios were only roughly known and were all about $y \simeq \frac{1}{4}$ for atoms in one molecule. Thus any endeavour to refine the (hk0) or (0kℓ) zones would not yield any very reliable information. Short of complete three dimensional work, the only possible way of obtaining more accurate y axial ratios was by means of a generalized projection of the (h1ℓ)

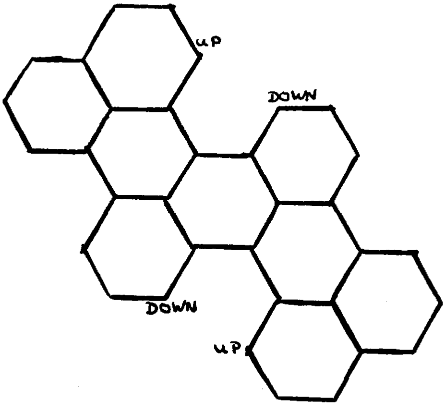
reflections or of higher (hKℓ) layer lines.

If the approximation is made that $y = \frac{1}{4}$ for all atoms in one molecule, greater symmetry is now introduced. Were this approximation true, the crystals would be in space group $P2_{1/m}$, with each molecule lying in a mirror plane at $y = \frac{1}{4}$ and $y = \frac{3}{4}$. Consequently if any atom is moved out of the mirror plane it will produce another "spurious" atom on the other side of the plane. Hence whatever method of refinement is used, provided we start with the assumption that $y = \frac{1}{4}$ for one molecule, the refinement must produce one ambiguous result per atom. Thus, after the first cycle of refinement, there will be 2^n possible structures, where n is the number of atoms in the asymmetric unit. It is therefore necessary to return to trial structures at this stage in order to discover the nature of the distortion of the molecule produced by the overcrowding. A study of the ways in which the molecule might be distorted would therefore be useful.

It has been found in the crystallographic studies of overcrowded aromatic molecules (Harnik, Herbstein and Schmidt, 1954) that the relief to overcrowding is obtained by sharing the strain throughout the molecule. If this is so there are only two ways in which the molecule under consideration could be distorted:- the "centro-symmetrical" and the "two fold axis" geometrical isomers, as shown below:



Centro-symmetrical
distortion



Two fold axis
distortion

The centro-symmetrical distortions should also produce a centro-symmetrical molecule in projection, but this is not true for the two fold axis distortion. The projection down the <u>b</u>-axis appeared to show that there is no centre of symmetry of the molecule in projection, but, in view of the lack of accuracy, there was considerable doubt whether this indication was significant.

If the molecule had a two fold axis there are two possible enantiomorphic forms. Since the space group has no centre of symmetry, mirror plane or glide plane, only one enantiomorphic form can be present in one single crystal. Thus a two fold axis distortion would require the assumption that there is spontaneous resolution on crystalization into (+) and (-) crystals. Such resolution occurs in 3:4 benzophenanthrene (Herbstein and Schmidt, 1954 a). However, in the case of tetrabenzonaphthalene (Herbstein and Schmidt, 1954 b) for which the packing is almost identical to that of di<u>peri</u>naphthylene anthracene, both enantiomorphic forms could be present, as the crystal habit adopts space group $P2_{1/c}$. Considerable effort was made to discover reflections which would show a doubling of cell size **of** the cell given in this paper and thus be able to produce a packing identical, instead of nearly identical to tetrabenzonaphthalene. These reflections would be weak in any case, because of the nature of the packing. No such reflection was found. In the case of tetrabenzonaphthalene there was no difficulty in finding these reflections (private communication). The space group must, therefore, be $P2_1$.

It was thought unlikely that spontaneous resolution would occur on crystalization, and hence the centro-symmetrical distortion seemed the more likely method for relief of overcrowding.

The Generalized Projection

The theory of generalized projection is given in the appendix. Suffice it to say that, in general, there are always two possible generalized projections of, say, the $(hK\ell)$ planes, K being constant: the cosine and the sine series. These are so called because, to a first approximation, the electron density of the atoms in the corresponding ordinary projection (say onto (010)) is multiplied by $\cos 2\pi Ky$ or $\sin 2\pi Ky$ respectively, in the case of the K^{th} layer line. Representing the two possible generalized projections as C_K and S_K, we have

$$C_K(x,z) = \frac{1}{A}\sum_h \sum_\ell \left\{ A(hK\ell)\cos 2\pi(hx+\ell z) + B(hK\ell) \sin 2\pi(hx+\ell z)\right\}$$

and

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

where A is the area of projection and $A(hK\ell)$, $B(hK\ell)$ are the real and imaginary parts of the structure factor of plane $(hk\ell)$.

Now for space group $P2_1$

$A(hK\ell) = A(\overline{h}\overline{K}\overline{\ell})$ and $B(hK\ell) = B(\overline{h}\overline{K}\overline{\ell})$ when $K = 2n$;

also

$A(hK\ell) = -A(\overline{h}\overline{K}\overline{\ell})$ and $B(hK\ell) = -B(\overline{h}\overline{K}\overline{\ell})$ when $K = 2n + 1$.

Hence when $K = 2n + 1$, for instance $K = 1$

$$C_{K=1}(x,z) = \frac{2}{A}\sum_h \sum_\ell \left|F_{obs}(hK\ell)\right| \sin\alpha \sin 2\pi(hx + \ell z)$$

and

$$S_{K=1}(x,z) = -\frac{2}{A}\sum_h \sum_\ell \left|F_{obs}(hK\ell)\right| \cos\alpha \sin 2\pi(hx + \ell z)$$

where α is the phase angle of $F(hk\ell)$.

If the approximation is made that the molecule is planar and perpendicular to the b axis then $\alpha = \pm 180^\circ$, for the molecule has now been placed into the centro-symmetrical space group $P2_{1/m}$. Thus $C_{K_1}(x,z) = 0$. Consequently the sine generalized projection was calculated for the ($h1\ell$) reflections, using the signs obtained for a completely planar structure. The heights of the peaks, from which the y axial ratios would have to be calculated appeared to vary more or less randomly and were of much the same size as those in the ordinary projection onto (010). Now both the termination of series effect and the variation of the y axial ratio should produce variation in peak height. This method of generalized projection can, however, only be applied if the termination of series effect can be neglected. This was quite obviously not the case.

In order to eliminate errors due to termination of series a difference sine generalized projection was calculated, using the same signs as before. If the difference sine generalized density is expressed as $D^{S_K}(x,z)$, then

$$D^{S_1}(x,z) = -\frac{2}{A}\sum_h\sum_\ell \left(|F_{obs}| - |F_{calc}|\right)\cos\alpha\,\sin 2\pi(hx+\ell z)$$

This synthesis gave a far more sensible result. The shift of the atoms from the plane $y = \frac{1}{4}$ were calculated from

$$D^{S_1} = \rho\sin 2\pi y_{obs} - \rho\sin 2\pi y_{calc}$$

$$\therefore \sin 2\pi y_{obs} = \frac{D^{S_1}}{\rho} + \sin 2\pi y_{calc}$$

In this case $y_{calc} = \frac{1}{4}$ for all atoms

$$\therefore \sin 2\pi y_{obs} = \frac{D^{S_1}}{\rho} + 1$$

where y_{obs} is the new atomic co-ordinate and ρ is the electron density on the ordinary projection at the centre of the atom.

From this it is impossible to decide whether the co-ordinate

$$y_{obs} = \frac{1}{4} - \Delta \quad \text{or} \quad y_{obs} = \frac{1}{4} + \Delta$$

(Δ being the atomic shift) since $\sin (90^{\circ} - \phi^{\circ}) = \sin (90^{\circ} + \phi^{\circ})$

This ambiguity arises because the assumption that $y = \frac{1}{4}$ for all atoms produces the higher symmetry space group $P2_{1/m}$. Since the centro-symmetrical structure appeared more likely the sign of Δ was decided for each atom so as to make the molecule centro-symmetrical. The structure factors were re-calculated and indeed they had improved.

Another difference generalized projection was calculated. This time the cosine function could be employed since α, the phase angle, was now continuously variable. This projection measured the quantity $\cos 2\pi y_{obs}$, which changes far more rapidly near $y = \frac{1}{4}$, and should therefore give more accurate y axial ratios. There was little improvement in the structure factors. The ambiguities found in the first generalized projection must have been wrongly resolved.

It was observed that for the completely planar structure (for which all the imaginary parts of the structure factors were by necessity equal to zero) that a number of intense reflections, in particular those from (211), $(\bar{1}19)$ and $(\overline{10}13)$, calculated far too small. The real parts of the structure factors could not change greatly since they were of the form

$$A = -2 \sum_{N} \sin 2\pi(hx + \ell z) . \sin 2\pi ky$$

The only variable is y, but sin 2π ky changes slowly near $ky = \frac{1}{4}$. However the imaginary parts must change quickly with y for

$$B = 2 \sum_{N} \sin 2\pi(hx + \ell z) . \cos 2\pi ky$$

and cos 2π ky changes rapidly at $ky = \frac{1}{4}$. Thus large imaginary parts should be expected for these structure factors. Hence all, or nearly all, the contributions to the imaginary parts of these structure factors must act in the same direction. For instance, when B is positive, cos 2πky is positive if sin $2\pi(hx + \ell z)$ is positive, but cos 2πky is negative if sin $2\pi(hx + \ell z)$ is negative. The signs for all sin $2\pi(hx + \ell z)$ values for all atoms in these planes were listed (see Table IV), except for those atoms where sin $2\pi(hx + \ell z)$ was less than 0.25, when a weight of zero was assumed. It will be seen by an inspection of Table IV that these signs for the three planes have the same sequence. Hence it was easy to decide whether $\cos 2\pi ky$ was positive or negative for each atom by observing the above rule; that is, whether the atom was below or above the plane $y = \frac{1}{4}$.

The above argument in the reverse direction is easier to understand and will make this logic a little clearer. Each of the 34 atoms is, in fact, either a little above or a little below the plane $y = \frac{1}{4}$. It has been shown that certain planes must have large imaginary parts. Now $\cos 2\pi \cdot \ell \cdot y$ must be positive for all atoms with $y < \frac{1}{4}$, and it must be negative for those atms with $y > \frac{1}{4}$. Thus if B is positive then $\sin 2\pi(hx + \ell z)$ must be positive for those atoms with $y < \frac{1}{4}$, and negative for those atoms with $y > \frac{1}{4}$. The reverse is true if B is negative. Hence, whether B is positive or negative, the same <u>sequence</u> of the signs of $\sin 2\pi(hx + \ell z)$ for the atoms taken in order must result for these planes.

(<u>Table IV is given on page 91</u>)

There could be no doubt that a non-centro-symmetrical molecule was required. A similar inspection of the (610) and (611) planes, both of which calculated rather low, showed that the structure could be further improved by tilting the molecule very slightly about an axis roughly parallel to $[\bar{1}01]$.

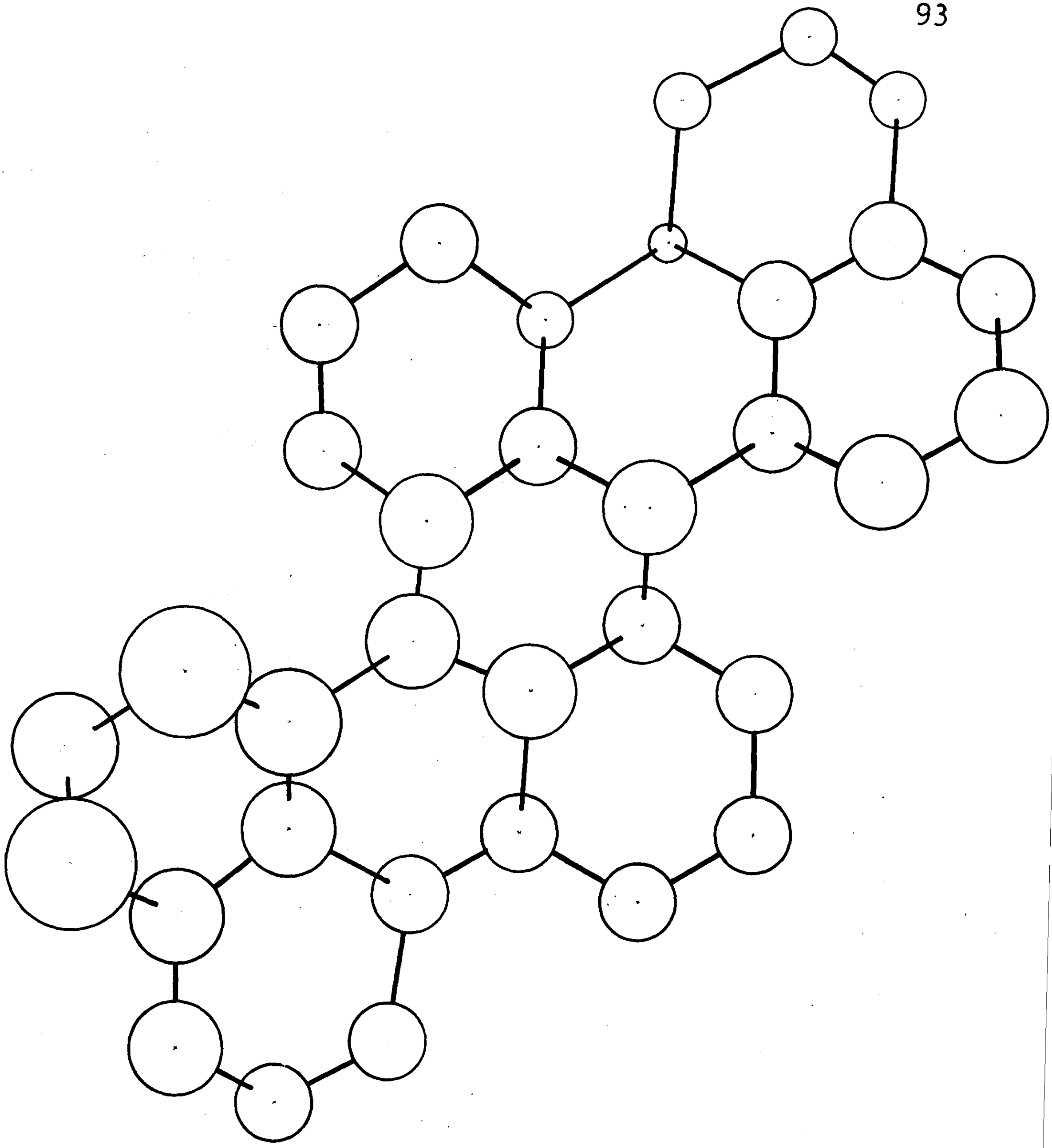
The improvement in the structure was very good. Two

$hl\ell$	A_1	B_1	C_1	D_1	E_1	F_1	G_1	H_1	I_1	J_1	K_1	L_1	M_1	N_1	O_1	P_1	Q_1
$+(211)$	+	+	-	-	0	+	-	-	-	-	-	+	+	0	0	+	+
$+(\bar{1}19)$	+	+	+	0	-	+	-	-	-	-	+	+	+	+	+	+	+
$-(\overline{10}13)$	0	+	-	-	+	+	+	+	-	-	+	0	-	-	-	0	+

$hl\ell$	A_2	B_2	C_2	D_2	E_2	F_2	G_2	H_2	I_2	J_2	K_2	L_2	M_2	N_2	O_2	P_2	Q_2
$+(211)$	+	-	+	-	-	-	-	-	+	+	-	-	+	+	+	+	-
$+(\bar{1}19)$	+	0	+	+	0	-	-	-	-	-	-	-	0	0	+	-	-
$-(\overline{10}13)$	+	0	+	0	-	-	-	-	0	-	-	0	+	+	+	+	+

TABLE IV: Signs of the quantities $\sin 2\pi\,(hx + \ell z)$

cycles of refinement by means of difference cosine generalized projections of the $(h1\ell)$ planes were carried out. The nature of the molecular distortion was well established. Owing to the inaccuracy of the x and z fractional co-ordinates no effort was made at further refinement, or at refinement of a higher layer line. The rates of refinement for the wrong "centrosymmetrical structure", and the correct "two fold axis structure" can be seen from Table V. Structure factors were also calculated for the 49 independent observed (hk0) reflections and 53 independent observed $(0k\ell)$ reflections with the structure obtained after the final difference generalized projection had been completed. When these were compared with the corresponding structure factors for the completely planar molecule (as shown in Table VI) no doubt can exist of the nature of the distortion of the molecule. The value of $B = 7.05\ A^2$ was found a suitable temperature factor for all reflections, indicating that the molecule is vibrating roughly equally in all directions.



Diagramatic representation of the molecular distortion of di<u>peri</u>naphthylene anthracene.

TABLE V: Agreement factors at different stages of refinement of $(hl\ell)$ planes

Structure	Centro-symmetrical	Two-fold axis
Planar	50.0%	50.0%
Trial	42.4%	38.6%
After 1st diff. cos gen. proj.	40.0%	32.4%
After 2nd diff. cos gen. proj.	-	30.4%

TABLE VI: Agreement factors at different stages of refinement of $(hk0)$ and $(0k\ell)$ planes

Structure	hk0 reflections	0kℓ reflections
Planar	58.7%	59.9%
Refined	27.5%	27.3%

After the refinement had been completed it was pointed out by Dr. Herbstein that a centred molecule in a non-centred cell is very unusual. This is in agreement with the present structure.

A model of the molecule was cut from cardboard. From this it was seen that the cardboard preferred to twist itself into a two fold axis distortion in preference to a centro-symmetrical distortion.

Since there was no centre of symmetry in the space group a "double shift" rule was used, as is usual for conventional difference maps (Cochran (1951 b) and also Shoemaker & others (1950)). Thus since

$$D^{C_1} = \rho \cos 2\pi y_{obs} - \rho \cos 2\pi y_{calc}$$

$$\cos 2\pi y_{obs} = \frac{D^{C_1}}{\rho} + \cos 2\pi y_{calc}$$

But all values of D were multiplied by 2. ρ was assumed equal to six.

$$\therefore \cos 2\pi y_{obs} = \frac{D^{C_1}}{3} + \cos 2\pi y_{calc} .$$

The number 3 by which D^{C_1} was divided was roughly correct, for it was found that some atoms had been over-, and others undershifted after the first cycle on the correct structure.

The method used for calculating the generalized and difference generalized densities was a little unusual. The time taken to calculate one projection was cut to less than one quarter of the time these same calculations would have taken with either Beevers Lipson strips or Robertson masks, by adopting the scheme described below.

In generalized and difference generalized projections two atomic co-ordinates are assumed. Therefore it is only necessary to find the generalized or difference generalized densities at the specific atomic sites. For instance

$$D^{C_1}(x_n, z_n) = -\frac{2}{A} \sum_h \sum_\ell \left(|F_{obs}| - |F_{calc}| \right) \sin\alpha \sin 2\pi(hx_n + \ell z_n)$$

at the nth atom. Hence if the quantity $\sin 2\pi(hx_n + \ell z_n)$ is listed for every atom in all observed reflections, as shown in Table VII, then each term in one row (corresponding to a particular reflection) must be multiplied by the common factor $\frac{2}{A}(|F_{obs}| - |F_{calc}|).\sin\alpha$. This could be done quicker on a slide rule than any calculating machine, as only two figure accuracy was needed. Finally, all columns (each column corresponding to a particular atom) were added up to give the difference generalized density at each atomic site. An easy cross-check could be obtained by also multiplying the sum of each row by the row's common multiplication factor. Then the sum of these products should be equal to the sum of the densities at all atomic sites, if no mistake had been made.

Atom $hl\ell$	A_1	B_1	C_1	D_1	E_1	F_1
110	.56	.24	.95	1.00	.64	.33
210	.93	.48	.59	$.\overline{17}$	$.\overline{98}$	$.\overline{60}$
310	.97	.68	$.\overline{59}$	$.\overline{97}$	.86	.83
410	.68	.85	$.\overline{95}$	.33	$.\overline{33}$	$.\overline{96}$
510	.16	.95	.00	.91	.36	1.00

TABLE VII:

Corner of table showing arrangement of sin $2\pi(hx_n + \ell z_n)$ quantities.

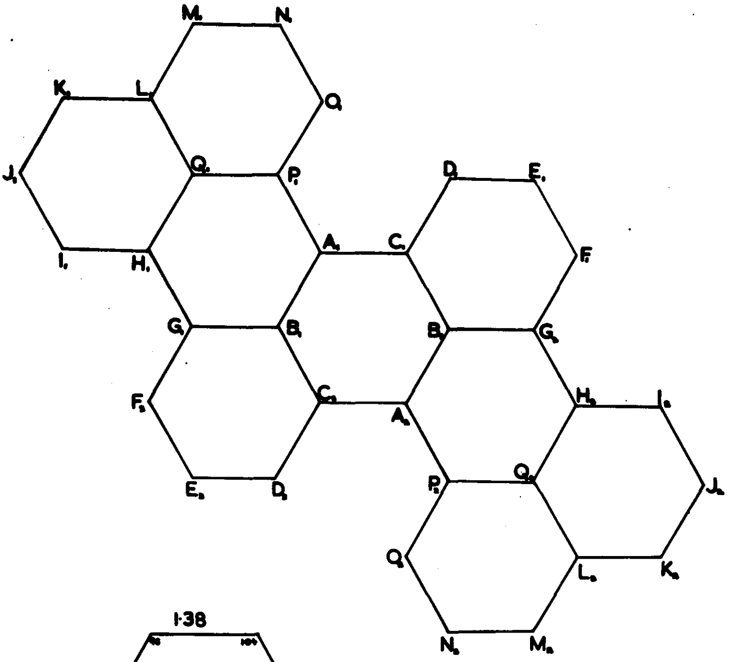
From the same table listing sin $2\pi(hx_n + \ell z_n)$ both real and imaginary parts to the structure factors could be calculated. In this case every column (corresponding to atoms) was multiplied by the common factor sin $2\pi y_n$ or cos $2\pi y_n$ according to whether the real or imaginary parts were being calculated, respectively. Finally all rows were added to give the required value of $A(hl\ell)$ or $B(hl\ell)$.

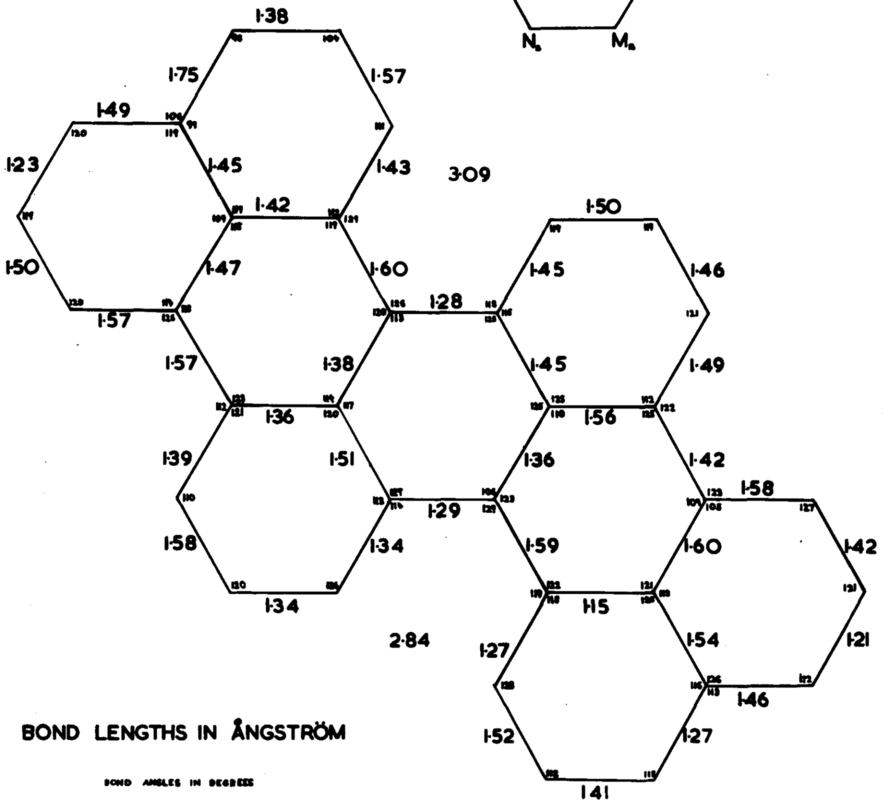
Bond lengths, bond angles and inter-molecular distances

Bond lengths are given in Table VIII and bond angles are shown on the diagram. Both bond lengths and angles vary considerably, because, no doubt, of the inaccuracy of the structure determination rather than any real variation, although some of the trends may have a little significance. The R. M. S. ~~standard~~ deviation between bonds in the two chemical equivalent halves of the molecule is 0.15 A. The mean bond length is 1.43 A. The R. M. S. ~~standard~~ deviation can be regarded as a measure of the accuracy of the inter-atomic distances. Cruickshank (1949) tests of significance could not be applied as a condition of the tests is resolution of all atoms - as is always the case for three dimensional analyses.

TABLE VIII: Bond distances in Angstrom

Bond	d_1	Bond	d_2	$d_1 - d_2$	$\frac{d_1 + d_2}{2}$
A_1 B_1	1.38	A_2 B_2	1.36	.02	1.38
B_1 C_2	1.51	B_2 C_1	1.45	.06	1.48
C_2 D_2	1.34	C_1 D_1	1.45	.11	1.40
D_2 E_2	1.34	D_1 E_1	1.50	.16	1.42
E_2 F_2	1.58	E_1 F_1	1.46	.12	1.52
F_2 G_1	1.39	F_1 G_2	1.49	.10	1.44
G_1 H_1	1.57	G_2 H_2	1.42	.15	1.50
H_1 I_1	1.57	H_2 I_2	1.58	.01	1.57
I_1 J_1	1.50	I_2 J_2	1.42	.08	1.46
J_1 K_1	1.23	J_2 K_2	1.21	.02	1.22
K_1 L_1	1.49	K_2 L_2	1.46	.03	1.48
L_1 M_1	1.75	L_2 M_2	1.27	.48	1.51
M_1 N_1	1.38	M_2 N_2	1.41	.03	1.40
N_1 O_1	1.57	N_2 O_2	1.52	.05	1.55
O_1 P_1	1.43	O_2 P_2	1.27	.16	1.35
P_1 A_1	1.60	P_2 A_2	1.59	.01	1.59
B_1 G_1	1.36	B_2 G_2	1.56	.20	1.46
P_1 Q_1	1.42	P_2 Q_2	1.15	.27	1.29
Q_1 L_1	1.45	Q_2 L_2	1.54	.09	1.50
Q_1 H_1	1.47	Q_2 H_2	1.60	.13	1.54
A_1 C_1	1.28	A_2 C_2	1.29	.01	1.29
O_1 D_1	3.09	O_2 D_2	2.84	.25	2.97





BOND LENGTHS IN ÅNGSTRÖM

BOND ANGLES IN DEGREES

The bonds G_1H_1, G_2H_2, A_1P_1, A_2P_2 should all be purely single bonds according to the Kekulé structures. The shortest of these four bonds is 1.42 A., and their mean value is 1.54 A., in good agreement with the bond length 1.54 A. observed in Diamond.

The distances between the atoms O_1D_1 and O_2D_2 which repel each other due to overcrowding are 3.09 and 2.84 A. respectively, giving a mean of 2.97 A. Previously observed distances between atoms in similar circumstances (Harnik, Herbstein and Schmidt, 1954) were found to be between 2.9 and 3.0 A. apart.

All inter-molcular distances below 4.0 A. are listed in Table IX. Molecule Ia, the standard molecule, has its centre at $x = \frac{56}{360}$, $y = \frac{90}{360}$, $z = \frac{13}{360}$. The centres of molecules IIa, IIIa, IVa and Va are then at $x, y, z + c$; $x + a, y, z$; $x, y, z - c$; $x - a, y, z$. Similarly the centres of molecules Ib, IIb and IIIb are at $\bar{x}, y + \frac{b}{2}, \bar{z}$; $\bar{x}, y + \frac{b}{2}, \bar{z} + c$; $\bar{x} + a, y + \frac{b}{2}, \bar{z}$; and the centres of molecules Ic, IIc and IIIc are at $\bar{x}, y - \frac{b}{2}, \bar{z}$; $\bar{x}, y - \frac{b}{2}, \bar{z} + c$; $\bar{x} + a, y - \frac{b}{2}, \bar{z}$.

I_a	I_h	d	I_a	I_c	d	I_a	II_b	d	I_a	III_c	d	I_a	V_a	d	I_a	IV_a	d
A_1	E_2	3.34	G_1	C_2	3.96	N_1	N_1	3.95	I_2	G_2	3.72	J_1	E_1	3.47	N_2	D_1	3.84
A_1	F_2	3.66	G_1	B_1	3.69	M_1	N_1	3.59	I_2	F_1	3.45	J_1	F_1	3.09	N_2	E_1	3.93
B_1	F_2	3.79	I_1	P_2	3.66	I_a	II_c	d	J_2	F_1	3.82	I_1	F_1	3.40	M_2	E_1	3.84
B_1	G_1	3.69	I_1	A_2	3.72	M_1	N_1	3.95	J_2	E_1	3.49	F_2	I_2	3.57			
C_1	F_2	3.94	J_1	P_2	3.87				K_2	E_1	3.35	F_2	J_2	3.22			
G_1	C_2	3.96	J_1	O_2	3.51							E_2	J_2	3.71			
H_1	D_2	3.88	K_1	N_2	3.65												
			K_1	O_2	3.84												

TABLE IX: Inter-molecular distances in angstrom

Only four of the inter-molecular distances are less than 3.40 A. The smallest of these is 3.09 A., that is 0.31 A. less than the generally assumed minimum distance between non-bonded carbon atoms. Since this is only twice the ~~standard~~ R.M.S. deviation, it need not be regarded as significant.

Co-ordinates and dimensions

All co-ordinates of the atoms in one molecule, which forms one asymmetric unit, are given in Table X. The co-ordinates of the atoms of the other molecule in the unit cell may be derived from these by the operation

$$(x, y, z) \qquad\qquad (\bar{x}, y + \frac{b}{2}, \bar{z})$$

The x and y co-ordinates given are those obtained after the completion of the fifth difference synthesis of the $(h0\ell)$ planes, except for atoms M_2 and O_2, which have been adjusted to give better agreement with the first electron density map. The y co-ordinates are those derived from the second difference generalized projection of the $(h1\ell)$ planes.

Atom	Fractional coordinates			Oblique Angstrom			Orthogonal Angstrom		
	x	y	z	X	Y	Z	X'	Y'	Z'
A_1	.095	.286	.147	1.14	2.24	1.64	1.07	2.24	1.64
B_1	.040	.286	.037	0.48	2.24	0.41	0.46	2.24	0.41
C_1	.200	.261	.142	2.39	2.05	1.58	2.33	2.05	1.58
D_1	.263	.225	.252	3.15	1.76	2.81	3.03	1.76	2.81
E_1	.388	.242	.255	4.64	1.89	2.85	4.53	1.89	2.85
F_1	.448	.197	.145	5.36	1.68	1.62	5.29	1.68	1.62
G_1	$.\overline{070}$	.242	.038	$\overline{0.84}$	1.89	0.43	$\overline{0.85}$	1.89	0.43
H_1	$.\overline{138}$	.242	.155	$\overline{1.65}$	1.89	1.73	$\overline{1.72}$	1.89	1.73
I_1	$.\overline{267}$	.203	.163	$\overline{3.19}$	1.59	1.82	$\overline{3.26}$	1.59	1.82

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Atom	Fractional co-ordinates			Oblique Angstrom			Orthogonal Angstrom		
	x	y	z	X	Y	Z	X'	Y'	Z'
J_1	$.\overline{322}$	.197	.282	$\overline{3.84}$	1.68	3.15	$\overline{3.97}$	1.68	3.14
K_1	$.\overline{265}$	.261	.370	$\overline{3.17}$	2.05	4.13	$\overline{3.33}$	2.05	4.13
L_1	$.\overline{141}$	.258	.367	$\overline{1.68}$	2.02	4.10	$\overline{1.84}$	2.02	4.09
M_1	$.\overline{093}$	.411	.472	$\overline{1.12}$	3.22	5.27	$\overline{1.33}$	3.22	5.27
N_1	.015	.350	.483	0.18	2.74	5.40	$\overline{0.37}$	2.74	5.40
O_1	.073	.422	.370	0.88	3.31	4.13	0.71	3.31	4.13
P_1	.030	.342	.263	0.36	2.68	2.94	0.24	2.68	2.94
Q_1	$.\overline{088}$	.325	.262	$\overline{1.06}$	2.55	2.92	$\overline{1.17}$	2.55	2.92

TABLE X: Atomic co-ordinates

Atom	Fractional co-ordinates			Oblique Angstrom			Orthogonal Angstrom		
	x	y	z	X	Y	Z	X'	Y'	Z'
A_2	.215	.250	$.\overline{080}$	2.57	1.96	$\overline{0.89}$	2.61	1.96	$\overline{0.89}$
B_2	.260	.233	.033	3.11	1.83	0.37	3.09	1.83	0.37
C_2	.108	.242	$.\overline{070}$	1.30	1.89	$\overline{0.78}$	1.33	1.89	$\overline{0.78}$
D_2	.045	.217	$.\overline{170}$	0.54	1.70	$\overline{1.90}$	0.61	1.70	$\overline{1.90}$
E_2	$.\overline{067}$	.208	$.\overline{178}$	$\overline{0.80}$	1.63	$\overline{1.99}$	$\overline{0.72}$	1.63	$\overline{1.99}$
F_2	$.\overline{138}$	.244	$.\overline{065}$	$\overline{1.65}$	1.91	$\overline{0.73}$	$\overline{1.62}$	1.91	$\overline{0.73}$
G_2	.387	.186	.028	4.62	1.46	0.32	4.61	1.46	0.32
H_2	.440	.128	$\overline{.075}$	5.26	1.00	$\overline{0.84}$	5.29	1.00	$\overline{0.84}$
I_2	.570	.147	$.\overline{093}$	6.81	1.15	$\overline{1.04}$	6.85	1.15	$\overline{1.04}$

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Atom	Fractional co-ordinates			Oblique Angstrom			Orthogonal Angstrom		
	x	y	z	X	Y	Z	X'	Y'	Z'
J_2	.623	.181	$.\overline{202}$	7.45	1.41	$\overline{2.25}$	7.54	1.41	$\overline{2.25}$
K_2	.575	.161	$.\overline{298}$	6.87	1.26	$\overline{3.33}$	7.01	1.26	$\overline{3.33}$
L_2	.459	.219	$.\overline{298}$	5.48	1.72	$\overline{3.33}$	5.62	1.72	$\overline{3.33}$
M_2	.412	.219	$.\overline{402}$	4.92	1.72	$\overline{4.49}$	5.10	1.72	$\overline{4.48}$
N_2	.307	.303	$.\overline{410}$	3.67	2.37	$\overline{4.58}$	3.85	2.37	$\overline{4.58}$
O_2	.242	.283	$.\overline{297}$	2.89	2.22	$\overline{3.31}$	3.02	2.22	$\overline{3.31}$
P_2	.287	.239	$.\overline{197}$	3.43	1.87	$\overline{2.20}$	3.51	1.87	$\overline{2.20}$
Q_2	.382	.214	$.\overline{192}$	4.56	1.68	$\overline{2.14}$	4.65	1.68	$\overline{2.14}$

TABLE X: Atomic co-ordinates

In Table X the oblique axial ratios, x, y, z are given measured parallel to the cell edges a, b, c, as well as the actual oblique distances X, Y, Z in angstrom. Finally, a set of co-ordinates is given with respect to orthogonal axes. These axes OX', OY' and OZ' are so chosen that OX' is parallel to OX, OY' is parallel to OY, and OZ' is perpendicular to OX' and OY'.

Experimental

Copper K_α radiation, $\lambda = 1.542$ A. was employed in all measurements. Rotation, oscillation, and moving-film photographs were used, the latter chiefly for intensity records. The only systematic absences were found to be 0k0 reflections with k odd. Thus the space group could have been $P2_1$ or $P2_{1/m}$.

Unit cell lengths were measured from rotation photographs on which copper powder rings had been superimposed in order to measure the effective radius of the camera. The β angle was calculated by measuring the [101], and [201] axes. From each, together with the lengths of the a and b axes, β could be calculated. The mean of the two values was taken as correct. Since β was so very close to 90° the length of the axes alone was insufficient for recognition of an axis; thus a moving film had also to be taken of the corresponding zero layer for each axis.

Density measurements were made by floatation in solutions of potassium iodide at room temperature (about 19°C.)

Three zones of reflections, the (h0ℓ), (hk0) and (0kℓ) reflections, as well as the (h1ℓ) reflections were explored in detail by moving-film methods. The (h1ℓ) reflections were taken by means of an equi-inclination Weisenberg of the first layer line of a crystal rotated about its needle axis (b). The three zones of reflections (0kℓ), (h0ℓ), (hk0) were each photographed from the equatorial layer of crystals rotating about their a, b and c axes respectively. Very long exposures (up to 70 hours at 10 mA and 35 KV) were made in all cases. As a result 99 (h0ℓ) independent reflections were observed representing 28% of the independent (h0ℓ) reciprocal lattice points inside the copper sphere of reflection; 99 (h1ℓ) independent reflections were observed corresponding to 347 of the possible number, 49 (hk0) independent reflections were observed corresponding to 133 of the possible number and 53 (0kℓ) independent reflections were observed corresponding to 122 of the possible number of reflections.

The fairly rapid fall off in intensity was probably due to the large temperature factor. The absolute value of the F values was not determined directly, but obtained by correlation with the calculated F values in each of the four sets of reflections. The agreement of the absolute scale so found in each case could be compared by using the common axial planes, and was found to be good. For the $(h0\ell)$ planes the scaling factor was defined as

$$k = \frac{\Sigma F_{obs} F_{calc}}{\Sigma F_{obs}^{2}}$$

For all other planes the usual definition $k = \frac{\Sigma |F_{calc}|}{\Sigma |F_{obs}|}$ was used.

For the calculation of structure factors the method of multiple additions on adding machines was used to compute the angle $2\pi(hx + \ell z)$ correct to 0.1° for the $(h0\ell)$ and the $(h1\ell)$ planes. The corresponding cosine or sine was found from two figure tables. However, the less accurate Robertson sorting board (Robertson, 1936) was made use of to calculate the structure factors of the $(hk0)$ and $(0k\ell)$ planes.

Small crystal specimens were employed which were completely bathed in a uniform X-ray beam. Two records were made of the $(h0\ell)$ zone of reflections with two different crystals. There was good agreement between the intensities measured from both crystal specimens. These were small and roughly square in cross-section with the dimensions 0.030 x 0.010 x 1.00 cm. and 0.010 x 0.006 x 1.00 cm. Thus absorption corrections (Albrecht, 1939) were only necessary for the $hk0$ and $0k\ell$ reflections for which the crystals measured 0.017 x 0.077 cm. and 0.014 x 0.100 cm. in cross-section perpendicular to the axis of rotation, respectively.

The longer distance in each case is the b axis.

Intensities were measured by the multiple film technique (Robertson, 1943) and corrected for the Lorentz and polarization factors in all cases. The $(hl\ell)$ planes, whose reflections had been recorded by means of equi-inclination photographs, had also to be corrected for the relative time any crystal plane spends reflecting, compared to the zero layer line, given by the Tunnell factor (1939). Measurements were made to establish the variation of the film factor - the increase of X-ray absorption due to longer path lengths at angles of incidence other than normal - and were found to be negligible up to about 10° inclination. This was confirmed by an investigation of this subject by H.J. Grenville-Wells (1955) published a little later.

The Fourier summations were carried out by means of Beevers-Lipson strips. For the difference synthesis intervals of $\frac{a}{30} = 0.398$ A. and $\frac{c}{60} = 0.186$ A. were used; but the F_o syntheses were calculated at 1,800 points, at intervals of $\frac{a}{60} = 0.199$ A. and $\frac{c}{60} = 0.186$ A. The positions of the contour lines were obtained by graphical interpolation from the summation totals, by making sections of the rows.

The agreement factor was reduced to 19.1% over the $(h0\ell)$ planes, but refinement had not yet stopped. After atoms M_2 and O_2 were adjusted to more reasonable sites according to the final F_o synthesis the agreement factor, R, went up to 20.0%. Refinement of the (h1ℓ) generalized projection was stopped when R = 30.4% and this structure gave R = 27.5% and 27.3% for the (hk0) and (0kℓ) planes, respectively.

[illegible]	$\lvert F_o\rvert$	$\lvert F_c\rvert$	[illegible]	[illegible]	[illegible]	$\lvert F_o\rvert$	[illegible]
[illegible]	[illegible]	[illegible]	0	202	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	0	302	.47[illegible]	[illegible]	[illegible]
.487	[illegible]	14.5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	15.0	[illegible]	180	[illegible]	[illegible]	[illegible]	[illegible]
.445	8.6	8.3	180	[illegible]	1.[illegible]	[illegible]	[illegible]
.774	44.6	[illegible]	180	[illegible]	[illegible]	[illegible]	19.[illegible]
[illegible]	[illegible]	7.2	0	[illegible]	.427	17.[illegible]	[illegible]
[illegible]	[illegible]	5.6	0	303	.553	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	0	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	0	[illegible]	.780	[illegible]	[illegible]
[illegible]	[illegible]	4.0	0	[illegible]	.930	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	180	204	.620	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	0	304	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	0	404	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	180	[illegible]	.840	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	180	[illegible]	[illegible]	[illegible]	[illegible]

Structure factor tables for diperinaphthylene anthracene [$\lambda = 1.542$ A.]

* Not included in final Fourier summation of $h0\ell$ reflections.

§ Cut off by beam stop. Estimated from oscillation photographs.

$h0\ell$	2 sin θ	$\|F_c\|$	$\|F_o\|$	α	$h0\ell$	2 sin θ	$\|F_c\|$	$\|F_o\|$	α
100	.129	27.8	30.4§	0	202	.377	26.4	30.4	0
200	.254	19.4	20.8	0	302	.473	16.0	19.6	180
300	.387	16.2	14.8	0	402	.580	10.8	7.6	0
400	.517	13.0	10.8	180	602	.806	11.2	9.0	0
500	.645	5.6	8.2	180	902	1.170	5.0	2.6	0
600	.774	44.6	42.6	180	003	.414	9.8	13.4	180
700	.902	9.2	7.2	0	203	.487	17.4	16.6	180
1100	1.419	1.4	5.6*	0	303	.563	3.6	3.4	180
001	.138	63.6	59.4§	0	403	.662	1.6	2.6	0
101	.190	32.6	30.8	0	503	.758	5.2	8.6	0
201	.290	8.2	4.0	0	703	.980	3.6	4.0	180
301	.405	44.6	44.2	180	204	.610	25.4	25.4	0
401	.530	4.4	7.2	0	304	.670	29.8	33.6	0
501	.647	2.2	3.2	0	404	.753	0.0	4.6*	-
601	.770	32.8	34.6	180	504	.840	6.4	6.8	0
801	1.020	2.0	4.6	180	704	1.045	1.8	7.0*	180
1201	1.525	5.0	3.2	180	804	1.150	9.6	8.0	180
002	.276	34.4	30.2	180	904	1.265	5.0	9.2	180

h0ℓ	$2\sin\theta$	$\|F_c\|$	$\|F_o\|$	α	h0ℓ	$2\sin\theta$	$\|F_c\|$	$\|F_o\|$	α
005	.690	2.0	2.2	180	$\bar{1}01$	.190	27.6	24.8	180
205	.735	0.4	4.2*	0	$\bar{3}01$	.405	15.6	17.0	0
305	.787	37.0	34.2	0	$\bar{4}01$	.530	21.2	20.2	180
405	.857	6.0	5.6	180	$\bar{5}01$	.647	12.8	12.6	0
505	.935	0.4	5.4*	180	$\bar{7}01$	.898	7.8	4.6	180
605	1.025	3.4	2.8	180	$\overline{11}01$	1.400	1.0	2.8	180
705	1.120	1.4	5.4*	0	$\bar{1}02$	.308	51.2	48.6	0
805	1.220	14.6	14.8	180	$\bar{3}02$	.473	4.2	6.8	180
905	1.330	25.8	24.0	180	$\bar{4}02$	.580	10.8	9.2	180
1005	1.440	1.0	5.0*	180	$\bar{5}02$	.692	0.8	2.2*	0
106	.840	8.2	7.8	0	$\bar{6}02$	.806	5.8	4.4	180
706	1.210	2.0	3.8	180	$\bar{7}02$	.928	5.6	3.0	0
806	1.305	5.4	4.0	0	$\bar{1}03$	.435	25.0	28.8	180
906	1.410	6.0	8.8	180	$\bar{2}03$	.487	3.8	4.4	0
1006	1.510	0.4	3.8*	180	$\bar{3}03$	.563	8.4	2.8	180
107	.975	5.6	2.8	180	$\bar{4}03$	.662	0.6	6.4*	0
407	1.090	4.2	3.2	0	$\bar{5}03$	.758	2.8	3.2	180
008	1.103	3.4	3.2	180	$\bar{7}03$	.980	5.0	4.2	0
108	1.115	6.0	3.0	0	$\bar{9}03$	1.210	1.2	4.2*	0
009	1.241	16.4	13.4	180	$\overline{10}03$	1.330	4.0	7.8	180
109	1.250	13.4	11.0	180	$\bar{1}04$	.565	13.2	14.8	0
1,0,10	1.382	13.2	13.6	180	$\bar{2}04$	.610	7.8	5.6	180

$h0\ell$	2 sin θ	$\lvert F_c \rvert$	$\lvert F_o \rvert$	α
$\bar{3}04$	.670	29.4	24.4	0
$\bar{4}04$	.753	7.6	5.8	0
$\bar{7}04$	1.045	8.0	6.0	180
$\bar{8}04$	1.150	22.8	25.4	0
$\bar{9}04$	1.265	0.4	7.2*	180
$\bar{1}05$	.700	7.0	7.0	0
$\bar{2}05$	.735	21.2	21.2	180
$\bar{4}05$	.857	5.4	5.0	180
$\bar{7}05$	1.120	5.4	7.2	180
$\bar{8}05$	1.220	21.0	24.4	0
$\bar{9}05$	1.330	1.8	4.4	0
$\bar{1}06$	.840	11.8	9.6	0
$\bar{4}06$	.970	7.6	6.4	0
$\bar{8}06$	1.305	1.2	3.4	180
$\bar{4}07$	1.090	2.0	3.0	0
$\bar{5}07$	1.150	1.2	2.6	180
$\bar{6}08$	1.338	2.6	3.4	0
$\bar{5}09$	1.390	7.2	3.8	0
$\bar{6}09$	1.445	4.2	3.8	0

Beam stop: reflection cut off by beam stop.

† : reflection estimated by correlation with hk0 reflections.

‡ : reflection estimated by correlation with $0k\ell$ reflections.

$h1\ell$	2 sin θ	$\lvert F_c \rvert$	$\lvert F_o \rvert$	α
110	.227	46.2	53.2†	188
210	.323	39.0	43.8	357
310	.427	4.6	5.0	18
410	.542	15.8	7.2	313
510	.665	37.4	43.6	187
610	.785	20.8	30.8	197
710	.906	5.8	11.2	237
011	.241	36.2	25.2‡	249
111	.275	70.6	Beam stop	187
211	.350	42.4	43.2	289
311	.450	8.8	12.8	342
411	.565	8.0	7.4	244
511	.677	7.0	9.2	354
611	.797	11.8	19.0	128
711	.920	7.0	11.2	55
811	1.040	4.6	7.0	101
012	.338	9.0	8.2	5

h1ℓ	2 sin θ	|F_c|	|F_o|	α	h1ℓ	2 sin θ	|F_c|	|F_o|	α
112	.366	27.4	26.2	51	1014	1.390	1.4	4.4	234
212	.426	10.2	14.8	355	015	.717	4.6	4.4	282
312	.512	6.2	4.2	66	115	.727	9.0	4.4	186
412	.615	15.4	8.6	179	215	.763	12.8	13.6	282
712	.950	5.0	6.4	143	315	.813	37.0	31.4	181
912	1.180	2.2	4.4	300	415	.882	15.2	11.2	197
013	.460	13.4	10.6	325	515	.958	0.8	5.8	289
113	.478	7.0	12.0	189	715	1.138	7.6	6.6	343
213	.523	9.2	7.8	280	815	1.238	5.8	8.2	150
313	.597	3.8	4.0	333	116	.865	10.0	8.2	3
413	.681	10.8	9.6	202	216	.890	2.0	3.8	165
513	.785	4.8	5.6	202	316	.933	1.8	3.8	240
613	.890	4.8	6.4	155	416	.990	9.4	4.0	179
713	1.000	12.4	5.0	350	516	1.060	0.8	3.8	137
813	1.115	4.6	4.2	124	616	1.138	3.6	4.0	357
014	.586	1.2	2.6	323	017	.987	3.0	3.6	353
114	.600	21.8	16.0	131	018	1.122	12.8	9.8	158
214	.642	6.2	12.0	31	019	1.260	28.2	19.6	180
314	.700	28.6	17.8 ~~9.8~~	158	119	1.257	5.6	10.6	257
414	.781	5.0	11.6	12	219	1.272	3.2	4.8	163
714	1.065	16.4	7.0	323	$\bar{1}11$	.275	20.8	Beam stop	117
814	1.170	10.6	13.6	178	$\bar{2}11$	.350	30.8	31.6	324
914	1.282	5.4	8.4	262	$\bar{3}11$	.450	2.4	10.0	213

h1ℓ	2 sin θ	$\lvert F_c \rvert$	$\lvert F_o \rvert$	α
$\bar{4}11$	.565	12.0	4.6	127
$\bar{5}11$	.677	23.4	17.4	345
$\bar{6}11$	.797	6.2	9.4	83
$\bar{1}12$	.366	29.8	33.0	359
$\bar{2}12$	.426	7.6	6.2	93
$\bar{3}12$	.512	16.6	10.4	326
$\bar{4}12$	.615	5.2	4.6	166
$\bar{5}12$	.720	9.2	3.0	201
$\bar{7}12$	.951	2.4	5.6	141
$\bar{1}13$	.478	8.4	5.4	168
$\bar{2}13$	.523	7.6	9.6	157
$\bar{3}13$	.597	11.2	15.8	101
$\bar{4}13$	.681	10.6	9.4	157
$\bar{5}13$	.785	5.6	4.8	51
$\bar{8}13$	1.115	2.6	5.4	173
$\bar{9}13$	1.227	9.6	19.0	337
$\overline{10}13$	1.343	2.2	6.0	28
$\bar{1}14$	.600	6.0	4.4	24
$\bar{2}14$	.642	15.6	14.6	233
$\bar{3}14$	.700	59.8	48.0	179
$\bar{4}14$	.781	9.0	10.8	279
$\bar{5}14$	.865	4.0	5.6	345
$\bar{8}14$	1.170	16.2	13.8	24
$\bar{9}14$	1.282	23.2	19.8	3
$\overline{10}14$	1.390	4.6	4.6	117
$\bar{1}15$	.727	3.2	3.0	198
$\bar{2}15$	.763	32.8	23.2	180
$\bar{3}15$	.813	22.6	23.8	171
$\bar{5}15$	.958	9.6	6.2	187
$\bar{8}15$	1.238	6.8	5.8	335
$\bar{9}15$	1.342	2.8	6.0	289
$\bar{2}16$	.890	4.4	3.6	69
$\bar{3}16$	.933	7.6	4.8	352
$\bar{4}16$	.990	10.0	4.4	181
$\bar{1}18$	1.132	3.2	6.2	228
$\bar{1}19$	1.267	6.8	13.0	270

hk0	2 sin θ	$\lvert F_c \rvert$	$\lvert F_o \rvert$	α
100	.129	30.6	31.8	0
200	.254	22.6	23.2	0
300	.387	18.0	16.2	0
400	.517	10.4	10.6	180
500	.645	5.0	8.6	180
600	.774	43.8	40.0	180
700	.902	8.4	9.2	0
1100	1.419	1.6	6.2	0
110	.227	46.2	50.0	188
210	.323	39.0	41.0	357
410	.542	15.8	6.8	313
510	.665	37.8	37.4	187
610	.785	20.8	26.4	197
710	.906	5.8	8.6	237
1110	1.407	8.4	7.6	175
1210	1.532	2.0	2.8	168
020	.392	212.4	180.6	174
120	.409	78.0	105.4	264
220	.465	17.6	18.4	357
320	.550	10.0	14.6	217
420	.640	10.8	4.0	282
520	.745	15.4	38.6	83
620	.850	23.0	14.4	339
1120	1.448	1.0	5.4	340

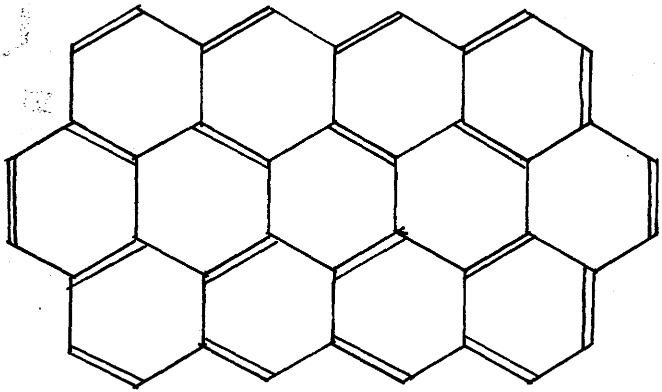
hk0	2 sin θ	$\lvert F_c \rvert$	$\lvert F_o \rvert$	α
130	.602	27.8	48.8	20
230	.640	23.0	5.0	170
330	.702	5.8	4.2	230
430	.775	16.2	10.2	124
530	.865	15.6	17.0	7
630	.957	8.6	7.8	29
730	1.065	7.8	6.4	134
1030	1.395	4.2	3.2	90
1130	1.513	5.0	4.6	356
040	.787	51.2	26.6	328
140	.795	23.2	27.2	66
240	.823	23.8	10.0	247
340	.875	6.4	5.0	202
440	.932	9.8	11.8	96
540	1.007	7.0	6.8	203
740	1.187	0.6	6.8	262
150	.988	11.4	17.4	198
250	1.010	10.0	7.8	324
350	1.052	3.8	4.6	97
650	1.240	2.6	3.4	176
060	1.181	12.8	13.0	142
160	1.179	7.6	8.0	199
260	1.199	7.4	7.4	12
460	1.278	1.4	4.4	335
170	1.378	2.8	5.4	349

$0k\ell$	$2 \sin \theta$	$\lvert F_c \rvert$	$\lvert F_o \rvert$	α
001	.138	69.2	65.6	0
002	.276	35.0	37.8	180
003	.414	14.4	15.0	180
008	1.104	3.2	4.2	180
009	1.242	16.4	10.6	180
011	.241	36.2	23.2	249
012	.338	9.0	8.8	5
013	.460	13.4	11.2	325
015	.717	4.6	3.6	282
016	.848	5.6	2.8	2
018	1.122	12.8	8.8	158
019	1.260	28.2	17.2	180
0110	1.390	4.6	7.0	126
020	.392	212.4	193.4	174
021	.417	78.8	89.4	140
022	.485	35.2	19.2	336
023	.575	5.8	8.8	322
024	.680	9.0	8.8	291
025	.795	8.2	8.8	165
026	.920	1.8	3.2	148
028	1.173	9.4	6.8	296
029	1.305	11.4	11.0	0
031	.605	25.2	29.4	84
032	.655	15.0	12.2	41
033	.725	3.8	8.4	250
034	.808	9.2	8.6	353
035	.910	4.6	5.6	144
036	1.015	1.0	4.4	148
038	1.255	7.8	6.8	330
0310	1.498	5.0	3.2	318
040	.787	51.2	37.2	328
041	.800	23.2	35.8	332
042	.835	11.4	14.4	138
043	.890	7.2	22.8	77
044	.960	7.8	2.8	173
045	1.047	10.6	3.0	335
046	1.145	6.4	7.2	293
048	1.355	4.2	9.4	119
049	1.470	5.0	3.6	162
051	.990	5.0	17.0	117
052	1.020	4.6	3.2	279
053	1.065	5.8	10.0	133
056	1.285	3.8	5.0	234
058	1.475	1.6	5.2	160

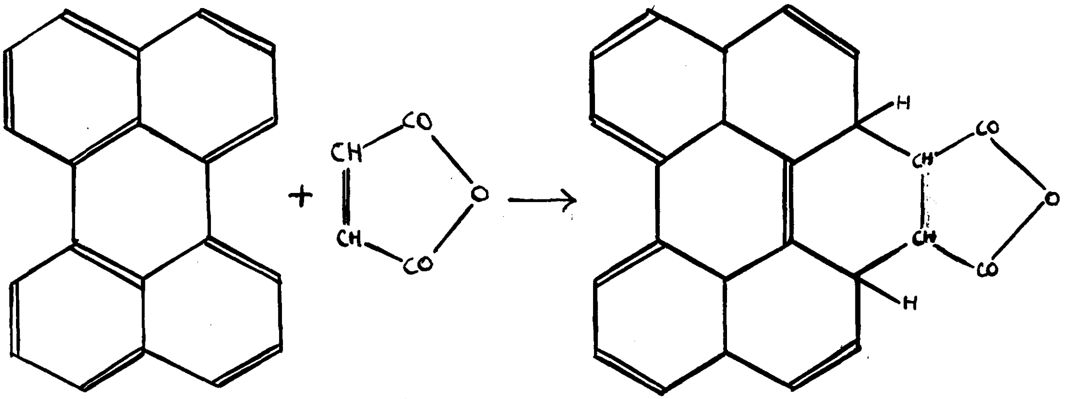
$0k\ell$	$2 \sin \theta$	$\lvert F_c \rvert$	$\lvert F_o \rvert$	α
060	1.181	12.8	11.8	142
061	1.187	3.8	14.2	154
062	1.210	5.8	6.6	238
063	1.250	5.4	12.4	257
064	1.300	6.0	5.4	40
071	1.380	0.6	7.0	359
072	1.405	3.2	3.4	183
080	1.568	2.8	3.8	306
081	1.575	2.4	3.8	336

PART III

ANTHROVALENE

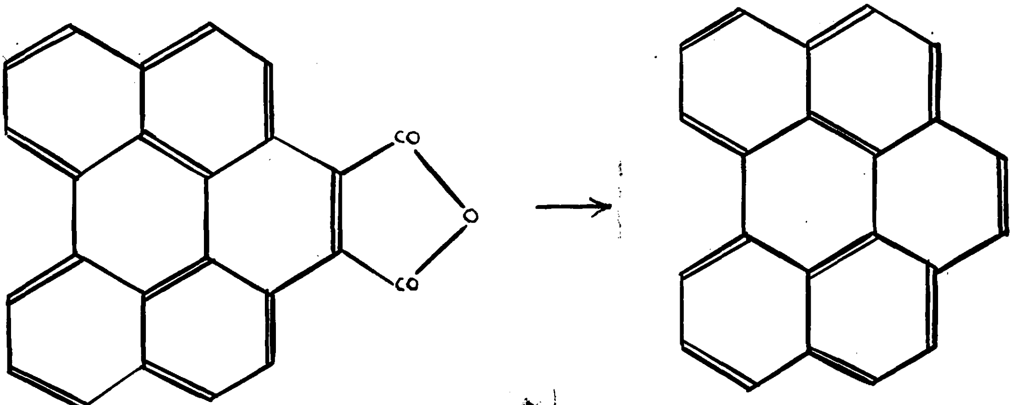


Chemical knowledge prior to the X-ray investigation



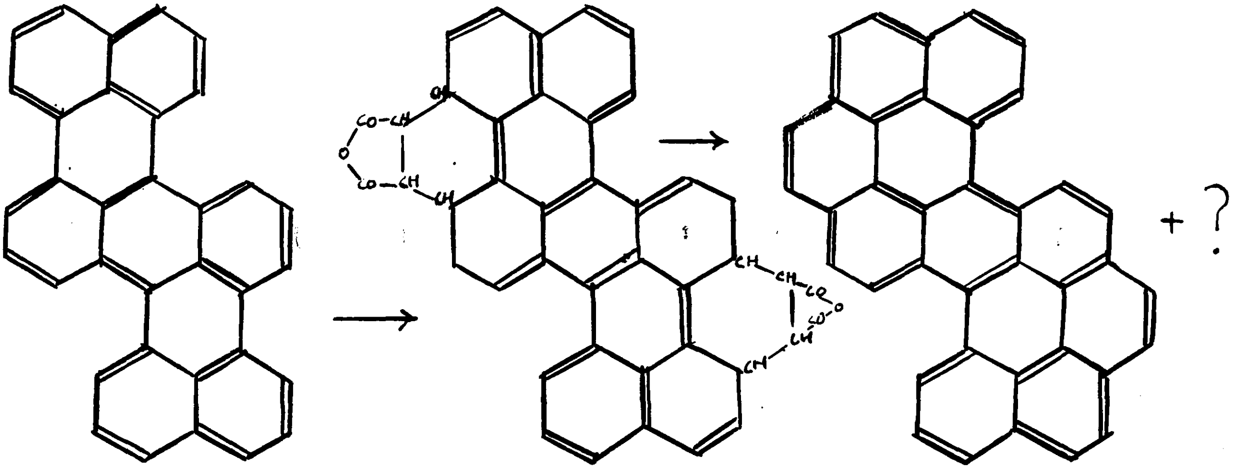
I II III

When the completely aromatic compound perylene (I) is treated with maleic anhydride II the addition product III is formed. If III is then dehydrated to IV and decarboxylated with soda lime than 6:7 benzperylene (V) is produced.



IV V

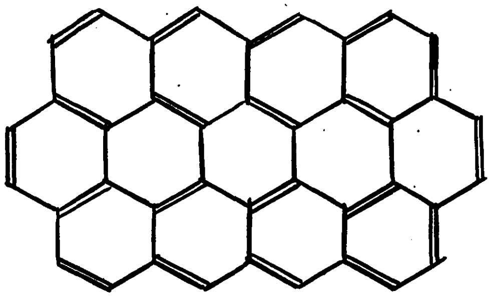
Similarly when 1:9 - 5:10 diperinaphthylene anthracene (VI), which can be regarded as a di-perylene, is treated with maleic anhydride the addition product VII is formed. However, in the chemical processes which might be expected to lead to VIII, in fact two compounds are formed, namely VIII and one unknown substance (Clar, Kelly, Robertson and Rossmann, 1956).



VI VII VIII

There could be no doubt about the nature of the starting compound VI, for its formula had been established on chemical grounds (Clar and Kelly, 1954) and confirmed by the X-ray work described in this thesis. The formula of the intermediary addition product VII was also confirmed on chemical grounds. Thus the unexpected chemical reaction must have occurred in going from VII to VIII. The result of this reaction gave small but roughly equal yields of the two different compounds. Their crystals were in one case dark translucent red needles, and in the other case black and opaque needles. The absorption spectra of the two compounds were examined in the ultra-violet range. It appeared fairly clear that the red crystals were VIII, while the black crystals had a highly condensed aromatic nature. Chemical tests further confirmed that the red crystals were Di (3':1' - 2:9)(3":1" - 6:10) pyrene anthracene (VIII). Very recently an X-ray examination of this compound has been started in the Chemistry Department of the University of Glasgow (J. Trotter, private communication). The needle axis has been found to be 3.9 A. It should be pointed out that 2 x 3.9 = 7.8 A., is the length of the needle axis in the crystals of Tetrabenzonaphthalene (Herbstein and Schmidt, 1954 b) and 1:9 - 5:10 di*peri*naphthylene anthracene (Part II of this thesis). Both these compounds are arranged in a "two layer" structure, making each molecule 3.9 A. thick. Again both compounds are overcrowded to the same degree as VIII.

The formula of the black compound was, however, quite unknown. A possible highly condensed compound of roughly the same shape as VIII is that of IX. The formula of IX was unreasonable since it requires two more carbon atoms in the molecule than is permissible by the chemical reactions in the processes from VII to VIII.



IX

The X-ray investigation was started at this juncture. Formula IX was confirmed. Buu-Hoi, Chalvet and Daudel (1950) suggest in a theoretical paper the name "Triovalene", but Dr. Clar and Mr. Kelly (who prepared the compound) prefer the name "Anthrovalene". After the X-ray work had firmly established the chemical formula, work was started in the Chemistry Department of the University of Glasgow, (J. McGlochlin and R.I. Read, 1956) aimed at tracing the "migration" of the two extra carbon atoms into the compound. A mass-spectrometer is being used to detect labelled C_6^{14} atoms. It is believed that the mechanism of the process may go a long way in explaining the natural phenomenon of graphitization.

Crystal Data

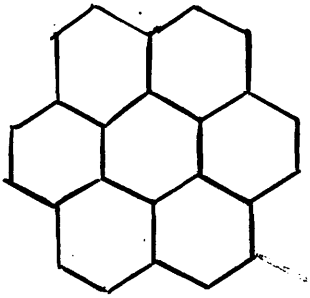
Anthrovalene, $C_{40}H_{16}$; M.W. = 496.1; m.p. –; d (calc.) 1.530 gm/ c.c. ; d (found) 1.52±.01 gm./c.c. monoclinic system; $a = 23.766 \pm .005$ A., $b = 4.59 \pm .02$ A., $c = 9.981 \pm .005$ A., $\beta = 99°54' \pm 30'$. Absent spectra, $(h0\ell)$ when h is odd, (0k0) when k is odd; space group C_{2h}^5 $(P2_{1/a})$; Two molecules per unit cell; Molecular symmetry, centre; Volume of unit cell 1075 $A.^3$. Absorption coefficient for X-rays, $\lambda = 1.542$, $\mu = 7.82$ cm.$^{-1}$. Total number of electrons per unit cell = F(000) = 512.

Anthrovalene can be crystallized by sublimation at about 400°C. into small black completely opaque crystals. These are elongated in the direction of the monoclinic b axis with (001) usually well developed. No other faces could be identified.

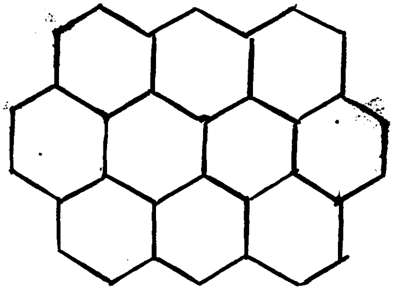
When the crystals were heated in vacuo they decomposed at about 473°C.

Analysis of the structure

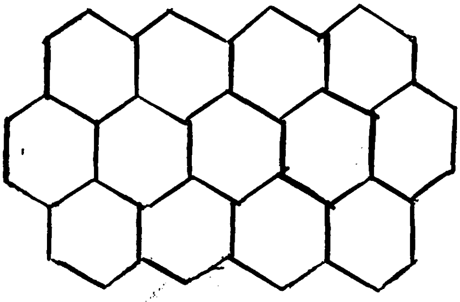
From the unit cell dimensions and the observed density the molecular weight of the molecule was calculated as 492.0 ± 5 , if there are two molecules in the unit cell. The molecular weight of the suggested chemical formula (IX) - anthrovalene - is 496.1. Hence the presence of the extra two carbon atoms in the molecule was more or less confirmed. This, in itself, made it particularly likely that the compound was (IX), since the main objection against the formula had been that the chemical process should produce a substance with 38, not 40, carbon atoms per molecule. When, however, the cell dimensions were compared to those of coronene (X) (Robertson and White, 1945) and ovalene (XI) (Donaldson and Robertson, 1953) as is shown overleaf, little doubt remained concerning the nature of the chemical formula of these crystals.



Coronene (X)



Ovalene (XI)



Anthrovalane (IX)

Compound	C_nH_m	Space Group	Mols. per cell	a in A	b in A	c in A	β	Volume A^3	Density gm./c.c.	M.W.
Coronene	$C_{24}H_{12}$	$P2_1/a$	2	16.1	4.70	10.2	111°	717	1.38	300
Ovalene	$C_{32}H_{14}$	$P2_1/a$	2	19.5	4.70	10.1	105°	894	1.49	398
Anthrovalene	$C_{40}H_{16}$	$P2_1/a$	2	23.8	4.59	10.0	100°	1075	1.53	496

The Coronene - Ovalene - Anthrovalene Series

There appears to be a type of loose $\left\{\overset{\text{iso structure}}{\text{isomorphism}}\right\}$ between these three compounds. Thus it was to be expected that the extra three rings which anthrovalene has over ovalene, add on to ovalene in the same way as the three extra rings of ovalene added to coronene. Since the b axis is so short the first projection was made onto the (010) plane, as was done for (X) and (XI). Hence the x and z co-ordinates of ovalene were plotted out relative to the ovalene cell. An extra three benzene rings were added and the origin was transferred to the centre of symmetry of anthrovalene. The cell dimensions of anthrovalene were now superimposed and the co-ordinates of the 20 independent atoms measured. Ovalene, rather than coronene was chosen for this operation as its β angle is closer to that of anthrovalene. The accuracy of this structure was estimated in the usual way by calculating the agreement factor R expressed in a percentage

$$R = \frac{\Sigma \left| \left\{ |F_{obs}| - |F_{calc}| \right\} \right|}{\Sigma \, |F_{obs}|}$$

When an empirical scattering curve (Robertson, 1935) was used R was found to be 36.6%. This was reduced to 32.1% when the McWeeny (1951) curve for carbon was employed estimating the temperature factor by the method described in Part I of this thesis. The latter was found to be $B = 10\ \text{A}^{2}$, a quite unprecedented large value. This did, however, explain why only 57 out of the 329 possible independent reflections had been observed, of which only 6 reflections were with $\sin \theta > 0.5$.

These results were fairly encouraging. Thus a first electron density map was calculated using 45 terms. The signs of these had been determined without much doubt. This map gave disappointingly little resolution of the atoms, probably because of the large temperature factor and small number of terms. Atoms were re-adjusted according to this map. The agreement factor now dropped to 25.7%. When hydrogen atoms had also been taken into account (there was considerable evidence of these on the electron density map) the agreement factor was again reduced to 23.7%. The C-H bond distances were assumed to be 1.1 A., for the same reasons as were given in Part II of the thesis.

There had only been a few minor sign changes, thus no great improvement could be expected if a new electron density map were calculated. Further refinement had therefore to be carried out by means of $(F_o - F_c)$ syntheses. The first cycle reduced the discrepancy to 22.2%. At this time a multiple film series from a rather better crystal was available on which 63 independent reflections could be observed. The new estimate of the structure factors gave 24.0% discrepancy. The second cycle reduced the discrepancy to 21.5%.

Impurities in the crystal

It was noted that atoms B and C were in the centre of negative troughs of depths 0.8 and 0.4 e/A^2 respectively, while all other atoms were very nearly at zero electron density on the second difference map. One or the other of these atoms would not have been there if only the expected compound had been formed by the maleic anhydride addition. It was therefore argued that some of this compound (VIII) was present as an impurity in the crystal arranged randomly in the two possible positions to leave either atom B or C vacant. This would have the effect of slightly reducing the electron density in these atomic sites. At the same time, since this compound would be distorted from a plane due to overcrowding in the molecule, such an impurity would set up considerable local lattice changes wherever such a molecule occurred. Uncertainty in the atomic positions of the anthrovalene molecules would be created, giving a net result of an apparently large spread in electron density around the mean centre of an atom, which shows up as the temperature factor of 10 A^2.

The following analysis was applied, making the assumption of the presence of an impurity.

Let atom B have a weight of 1- m

Let atom C have a weight of 1- n

and all other atoms a weight of unity.

Let F_c be the calculated structure factor assuming no impurity, i.e. all atoms have the same weight.

Let C_1 and C_2 be contributions to structure factor by atoms B and C respectively.

Thus the corrected value of calculated structure factor is

$$F_c - mC_1 - nC_2$$

Hence we wish to minimize the summation

$$E = \Sigma\,[F_o - (F_c - mC_1 - nC_2)]^2$$

$$= \Sigma\,[\Delta + mC_1 + nC_2]^2$$

The necessary conditions for this are that

$$m = \frac{(\Sigma\Delta C_1)(\Sigma C_2^2) - (\Sigma\Delta C_2)(\Sigma C_1C_2)}{(\Sigma C_1C_2)^2 - (\Sigma C_1^2)(\Sigma C_2^2)}$$

and $$n = \frac{(\Sigma\Delta C_2)(\Sigma C_1^2) - (\Sigma\Delta C_1)(\Sigma C_1C_2)}{(\Sigma C_1C_2)^2 - (\Sigma C_1^2)(\Sigma C_2^2)}$$

It was found that $m = 0.219$ and $n = 0.179$. When these weights for atoms B and C were used the discrepancy dropped to 19.0%.

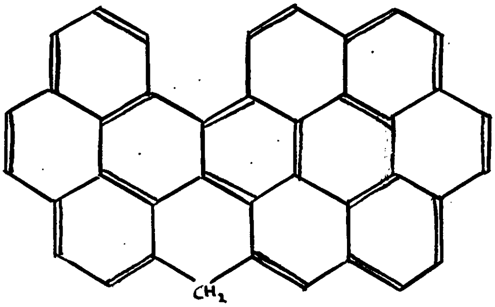
A third $(F_o - F_c)$ synthesis was calculated, from which it could be seen that atoms B and C, as well as all the other atoms were now at about zero electron density. Peaks up to 0.5 e/A^2 still remained in areas where there were no atoms at all. Since atom C lay in a trough of only 0.4 e/A^2

and since one might expect the troughs of atom B and C in the second difference map to be of equal depths (while, in fact, there was a difference of 0.4 e/A^2), the values of m and n can hardly be regarded as accurate. Only the trough of atom B appears to be of significant depth. Therefore the correct weight to apply to atom B and possibly also to atom C is probably $m - n = 0.040$; that is, we are assuming the weight n insignificant. Hence an impurity with two atoms missing of about 4-6% was expected.

At this stage, Dr. Read, of the University of Glasgow, had completed a mass-spectroscopic study of the crystals. The object of the investigation was purely to confirm, or otherwise, the presence of an impurity. The crystals were vapourized by electron bombardment with electrons of sufficient speed to make any breaking up of the molecules exceedingly unlikely. The molecular weight of the main bulk of the material could be placed to 496 ± 4 mass numbers from absolute measurements of magnetic and electric fields present in the mass spectrometer, in confirmation of the X-ray molecular weight determination. Assuming a mass number of 496 for this peak, three other subsidiary peaks were also found. These corresponded to impurities of about

1-2% molecules with roughly 4 x 12 mass numbers less than anthrovalene
8-16% " " " 1 x 12 " " "
1-2% " " " 1 x 12 " " more than anthrovalene.

The major part of the impurity was thus probably not (as had been expected) compound VIII but an intermediary (XII) between VIII and anthrovalene. The X-ray data suggests that XII is packed randomly into space group $P2_{1/a}$ to an extent of (10 ± 4)%.

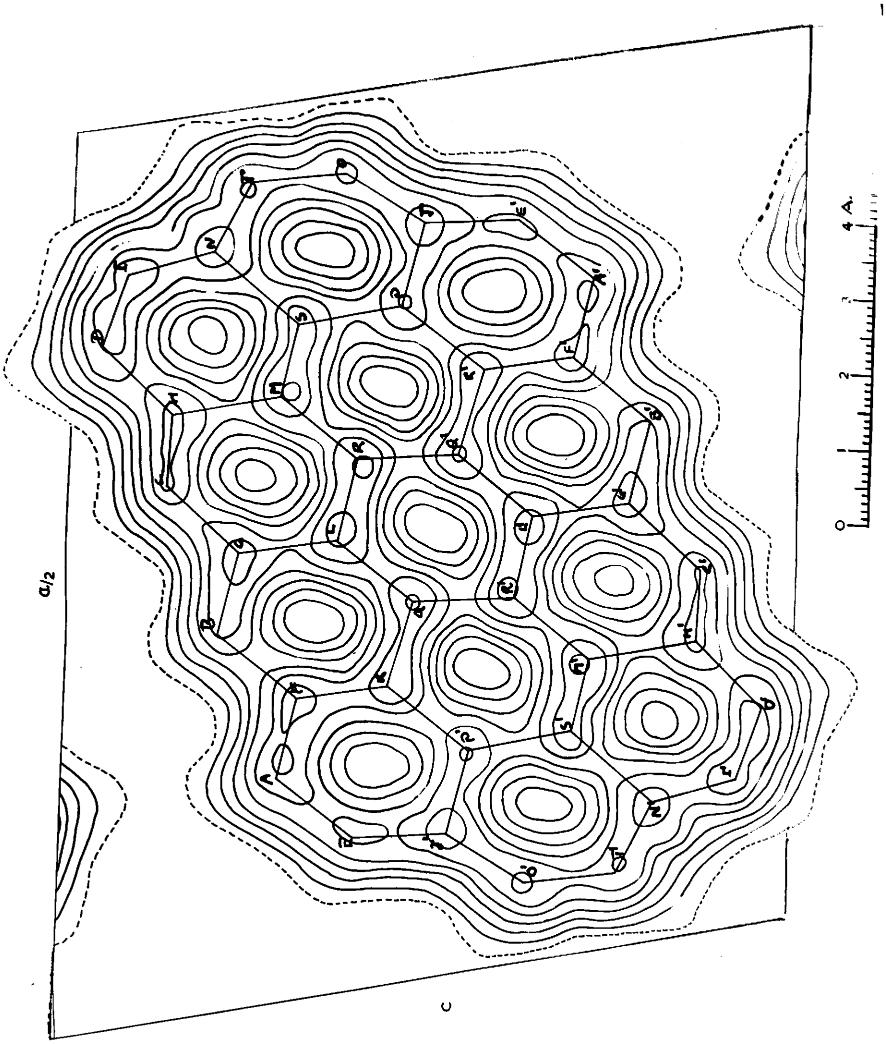


XII

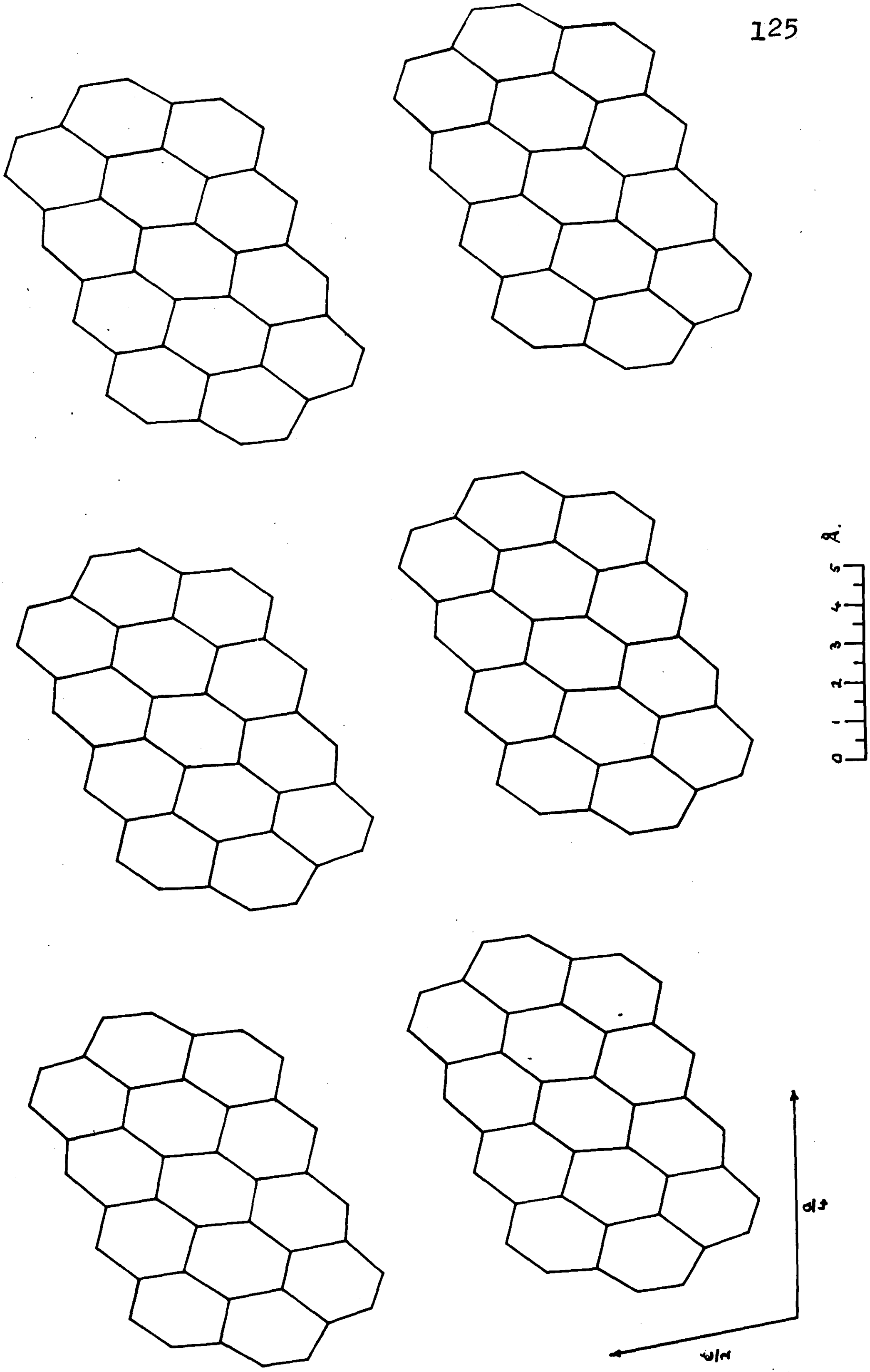
Dr. E. Clar, who had prepared Anthrovalene with Mr. W. Kelly, was able to corroborate these findings. Certain features of the U.V. spectrum had for long been a puzzle, but assuming not more than 10% of XII these difficulties were removed.

It must be said that XII is not the only possible formula for the major impurity, but it appears to be the most likely suggestion.

The X-ray work of refinement was stopped as it was now obvious that no accurate measurements, other than the determination of the chemical formula, could be made. Nevertheless, the atomic positions which had been found were used to give rough estimates of bond lengths and other quantities.



Projection of the anthrovalene structure on the (010). Contour scale, ½ electron per A.^{2}, the one electron line being dotted.



The atomic arrangement corresponding to the projection on (010).

A final electron density map was calculated and drawn up. This, together with a skeleton map showing the packing of the molecule when viewed down the b axis, is shown here.

Orientation of the molecule and bond lengths

The molecule was assumed planar. Its plane was fixed by the least squares method described in Part I for dibenzperylene. The "correct" bond lengths were taken from a paper by Buu Hoi, O. Chalvet and R. Daudel (1950) in which the method of "spin-states" is used. It is doubtful whether this method can be regarded as very reliable. The best plane was found to be

$$Y = 0.8402X - 0.2264Z$$

where X, Y and Z are orthogonal co-ordinates measured parallel to the a, b axes and the perpendicular to both these axes, c^1, respectively. The orientation of this plane relative to the three axes a, b and c^1 could now be found and expressed in the usual set of nine angles already defined in Part I of the thesis and also given for Coronene (J.M. Robertson and J.G. White, 1945) as well as for Ovalene (D.M. Donaldson and J.M. Robertson, 1953). They are given in Table I, together with the equivalent angles for Coronene and Ovalene. The molecular axes OL and OM were chosen differently for Coronene, and hence only the angles the normal ON makes with the three axes bears comparison for this compound.

It is of interest to note that the angle between the plane of the molecule and the (010) plane, ψ_N is 41.1° for anthrovalene, 42.7° for ovalene and 43.7° for coronene. The perpendicular distance between the molecular planes, given by b cos ψ_N, is thus 3.46 A., 3.45 A. and 3.40 A., respectively.

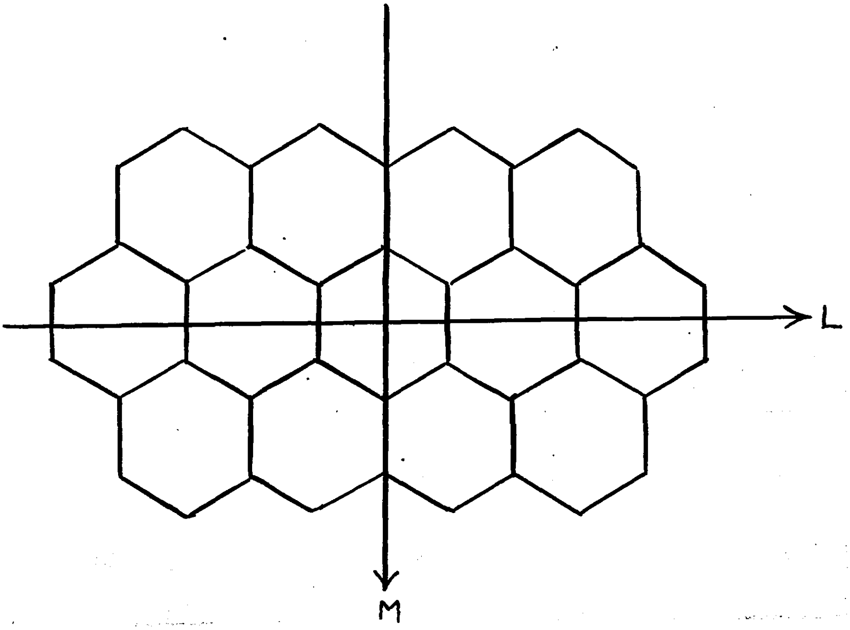


TABLE I: Orientation of Anthrovalene Molecule

Anthrovalene				Ovalene	Coronene
$\cos \chi_L$	0.760	χ_L	40.5°	44.7°	-
$\cos \psi_L$	0.564	ψ_L	55.7°	51.5°	-
$\cos \omega_L$	0.323	ω_L	71.2°	70.8°	-
$\cos \chi_M$	0.147	χ_M	81.5°	78.5°	-
$\cos \psi_M$	0.334	ψ_M	70.5°	74.4°	-
$\cos \omega_M$	-0.930	ω_M	158.4°	160.5°	-
$\cos \chi_N$	-0.633	χ_N	129.3°	132.4°	133.7°
$\cos \psi_N$	0.754	ψ_N	41.1°	42.7°	43.7°
$\cos \omega_N$	0.171	ω_N	80.2°	86.2°	89.6°

The Y co-ordinates of all atoms were calculated from the equation of the mean plane and bond lengths could then be calculated. These are given in Table II. The table also shows the mean for the chemically equivalent bonds which are compared with the expected values from the spin states calculation. The R.M.S. deviation between these experimentally determined lengths and the theoretically expectations is 0.057 A.

The closest lateral contacts between molecules in the lattice occur between atom O on the standard molecule and E on the molecule at ($\frac{1}{2}$a, $\frac{1}{2}$b) where the distance is 3.86 A. [Equivalent distances for ovalene and coronene are 3.68 A. and 3.77 A.], and between O and atom E on the molecule at ($\frac{1}{2}$a, $-\frac{1}{2}$b) where it is 3.95 A. Between atom C on the standard molecule and atom C' on the molecule one translation further along the <u>c</u> axis the distance is 3.84 A. Finally from atom D on the standard molecule and atom A' on the molecule at (0, b, c) a distance of 3.99 A. is found. All other contacts between atoms on neighbouring molecules appear to be greater than 4 A.

TABLE II: Bond lengths in Angstrom

Bond	d_1	Bond	d_2	$\|(d_1 - d_2)\|$	$\frac{d_1 + d_2}{2}$	Spin States	$\|\Delta\|$
EA	1.35	DI	1.32	.03	1.34	1.38	.04
AF	1.43	HD	1.40	.03	1.42	1.42	.00
FB	1.42	CH	1.21	.21	1.32	1.41	.09
BG	1.47	GC	1.42	.05	1.45	1.41	.04
J'E	1.33	NI	1.29	.04	1.32	1.42	.10
KF	1.30	MH	1.55	.25	1.43	1.44	.01
O'J'	1.27	NT	1.41	.14	1.34	1.42	.08
J'P'	1.53	SN	1.56	.03	1.54	1.44	.10
P'K	1.45	MS	1.32	.13	1.39	1.43	.04
KQ	1.55	RM	1.37	.18	1.46	1.43	.03
QL	1.35	LR	1.47	.12	1.41	1.43	.02
LG					1.40	1.44	.04
TO					1.32	1.38	.06
SP					1.48	1.43	.05
RQ'					1.44	1.43	.01

Co-ordinates and dimensions

The $\frac{x}{a}$ and $\frac{z}{c}$ fractional co-ordinates derived from two successive $(F_o - F_c)$ refinement cycles are listed in Table III. The $\frac{y}{b}$ fractional co-ordinates is calculated from the equation of the mean molecular plane. The co-ordinates, x, y, z are also given in Angstrom, and lastly the atomic positions are given in Angstrom relative to the orthogonal system of axes, X, Y, Z. X and Y are measured parallel to the a and b axes of the unit cell. Z is measured in a direction perpendicular to X and Y. The crystallographic centre of symmetry is taken as origin.

As the molecule has an exact centre of symmetry, only half the atoms, those of the asymmetric crystallographic unit, are listed. All the other atoms in the unit cell may be derived from these by the operations

$$(x,y,z),(-x,-y,-z),(x + \frac{a}{2}, -y + \frac{b}{2}, z),(-x + \frac{a}{2}, y + \frac{b}{2}, -z)$$

Atom	Fractional co-ordinates			Oblique co-ordinates in A.			Orthogonal co-ordinates in A.		
	$\frac{x}{a}$	$\frac{y}{b}$	$\frac{z}{c}$	x	y	z	X	Y	Z
A	-45.3	-257.5	75.6	-2.990	-3.283	2.096	-3.350	-3.283	2.065
B	-14.7	-148.3	105.6	-0.970	-1.891	2.928	-1.473	-1.891	2.884
C	16.8	-32.4	132.0	1.109	-0.413	3.660	0.480	-0.413	3.605
D	46.5	70.5	165.0	3.070	0.899	4.575	2.284	0.899	4.507
E	-59.4	-288.1	37.2	-3.921	-3.673	1.031	-4.098	-3.673	1.016
F	-30.0	-183.7	66.6	-1.980	-2.342	1.846	-2.297	-2.342	1.818
G	0.9	-72.9	96.0	0.059	-0.929	2.662	-0.399	-0.929	2.622
H	30.6	29.0	130.2	2.020	0.370	3.610	1.399	0.370	3.556

Continued overleaf/

Atom	Fractional co-ordinates			Oblique co-ordinates in A.			Orthogonal co-ordinates in A.		
	$\frac{x}{a}$	$\frac{y}{b}$	$\frac{z}{c}$	x	y	z	X	Y	Z
I	60.0	138.3	153.6	3.961	1.763	4.259	3.229	1.763	4.196
J	61.5	259.9	9.6	4.060	3.314	0.266	4.014	3.314	0.262
K	-30.3	-149.5	22.2	-2.000	-1.906	0.615	-2.106	-1.906	0.606
L	0.3	-37.1	48.0	0.020	-0.473	1.331	-0.209	-0.473	1.311
M	30.9	72.1	78.0	2.040	0.919	2.163	1.668	0.919	2.131
N	61.8	179.2	112.2	4.080	2.285	3.111	3.545	2.285	3.065
O	73.8	282.3	48.6	4.872	3.599	1.347	4.640	3.599	1.327
P	45.3	181.3	19.8	2.991	2.312	0.549	2.897	2.312	0.541

Continued overleaf/

Atom	Fractional co-ordinates			Oblique co-ordinates in A.			Orthogonal co-ordinates in A.		
	$\frac{x}{a}$	$\frac{y}{b}$	$\frac{z}{c}$	x	y	z	X	Y	Z
Q	-14.1	-69.5	10.2	-0.931	-0.886	0.283	-0.980	-0.886	0.279
R	16.2	38.3	40.2	1.069	0.488	1.115	0.877	0.488	1.098
S	45.0	140.2	69.6	2.971	1.787	1.930	2.639	1.787	1.901
T	75.0	251.0	94.2	4.951	3.200	2.612	4.502	3.200	2.573

Table III: Atomic co-ordinates

Experimental

1. Cell dimensions

The b axis was measured from different rotation photographs calibrated either with Cu or Na Cl powder lines. Difficulty was experienced in measuring the other cell dimensions by the same method because of the number of different axes with very nearly the same lengths. Hence the a and c axes and the β angle were measured from a moving Weissenberg film of the $h0\ell$ reflections. This film was calibrated with Na Cl powder lines which made it possible to calculate the $\frac{\lambda}{d_{h0\ell}}$ reciprocal distances for 15 reflections.

Now $\left(\frac{\lambda}{d_{h0\ell}}\right)^2 = h^2 a^{*2} + \ell^2 c^{*2} - 2h\ell\, a^* c^* \cos\beta$

We may write this as

$$d^{*2} = h^2 x + \ell^2 y - 2h\ell\, z$$

where $x = a^{*2}$, $y = c^{*2}$, and $z = a^* c^* \cos\beta$

The solution of this linear equation in three unknowns was found by the least squares method. Hence the three equations

$$(\Sigma\, d^{*2}h^2) = (\Sigma\, h^4)\, x + (\Sigma\, h^2\ell^2)\, y - 2(\Sigma\, h^3\ell)\, z$$
$$(\Sigma\, d^{*2}\ell^2) = (\Sigma\, h^2\ell^2)\, x + (\Sigma\, \ell^4)\, y - 2\,(\Sigma\, h\ell^3)\, z$$
$$(\Sigma\, d^{*2}h\ell) = (\Sigma\, h^3\ell)\, x + (\Sigma h\ell^3)\, y - 2(\Sigma\, h^2\ell^2)\, z$$

were solved to determine the three unknowns x, y and z. From these the cell constants a, c and β were then found. These values were then used to re-calculate the reciprocal distances d . The experimentally measured d 's and those calculated from the "best" cell dimensions only differed in the fourth place.

2. Densities

The density of the crystals were determined by flotation in potassium iodide solution. The accuracy of this method was not controlled by the accuracy with which the density of the solution, believed to be of the same density as the crystals, could be measured. Because of the very small volume of the crystals it was very difficult to distinguish whether a crystal was sinking or rising due to its weight, or due to thermal or other currents in the solution. A centrifuge was used to overcome this difficulty; however, the crystals just stuck to the walls of the containing vessel.

Determination of Crystal Data

Copper K_α radiation, $\lambda = 1.542$ A. was employed in all the measurements. Rotation oscillation and moving film photographs were used, the latter chiefly for intensity records. Of the (0k0) reflections only the (020) and (040) could be observed, and these were very weak reflections themselves. There was no exception to the (hoℓ) halving with h odd, and the space group $P2_{1/a}$ was therefore assumed.

Measurement of Intensities

The (h0ℓ) zone was explored in detail by moving film exposures of the equatorial layer lines for two different crystals rotated about the b axis. The multiple-film technique (Robertson, 1943) was used to estimate the intensities visually. The total range of intensities covered was about 4,000:1. The time of exposure was increased until the background became too thick to see the weakest reflections. Yet only 63 independent reflections could be observed. This was probably due to a combination of the apparently large temperature factor and the small size of the crystals available. The cross-section of both crystals used in these exposures were 0.03 mm. by 0.10 mm.; they were 2-3 mm. long. No absorption corrections were made.

The absolute scale of the F values was determined by correlation with the calculated F values. MacWeeny (1951) scattering curves were used.

Fourier Analysis

The electron density for all the F_o and the $(F_o - F_c)$ syntheses was computed at 900 points on the assymmetric unit with the help of Beevers Lipson strips. The <u>a</u> axis was divided into 120 parts, and the <u>c</u> axis into 30 parts, the intervals along a being 0.198 A., and along c 0.333 A. The positions of the contour lines were obtained by interpolation from the summation totals.

Structure factor tables for Anthrovalene

* Not used in final Fourier summation representing the electron density.

$\lambda = 1.542$ A.

$h0\ell$	2 sin θ	$\|F_{obs}\|$	F_{calc}	
200	.132	69	+	67
400	.264	54	-	62
600	.395	30	+	34
800	.527	7	-	13
1000	.659	10	+	4
1400	.923	6*	+	1
001	.157	79	+	84
201	.220	30	-	37
401	.335	36	+	34
601	.455	24	-	21
801	.580	6	+	8
1001	.706	8	+	5
1201	.833	9*	-	2
002	.314	20	-	25
202	.364	23	+	31
402	.448	15	-	14
1002	.780	51	-	48
003	.470	4	-	6
203	.512	10	-	9
403	.583	10	+	7
603	.672	11	+	13
803	.771	36	-	32
1003	.877	23	-	24
004	.627	10*	-	1
604	.808	6	+	5
804	.897	8	+	10
005	.784	8*	-	0
205	.818	7*	-	2
407	1.175	10	+	18
607	1.238	16	+	18
1007	1.378	9*	+	1
408	1.332	11	+	16
$\bar{2}01$	.190	82	+	81
$\bar{4}01$	.285	27	-	30
$\bar{6}01$	.403	38	+	32
$\bar{8}01$	.528	18	-	20
$\overline{10}01$	.652	7	+	9
$\overline{12}01$	.780	4	+	4
$\overline{14}01$	.914	13*	-	1
$\bar{2}02$	.322	64	-	63

$h0\ell$	2 sin θ	$\lvert F_{obs}\rvert$	F_{calc}	
$\bar{4}02$	.379	22	−	27
$\bar{6}02$	.465	22	+	28
$\bar{8}02$	.570	15	−	17
$\overline{10}02$	.681	6	+	7
$\overline{14}02$	.926	42	−	34
$\overline{16}02$	1.050	10*	−	0
$\bar{2}03$	.470	28	+	34
$\bar{4}03$	.500	26	+	29
$\bar{6}03$	.562	4	+	2
$\bar{8}03$	.649	7	−	6
$\overline{10}03$	.742	10*	−	2
$\overline{14}03$	.968	28	−	30
$\overline{16}03$	1.080	13	−	15
$\bar{2}04$	.625	10	−	12
$\bar{4}04$	.642	30	−	24
$\bar{6}04$	.690	10*	+	1
$\bar{8}04$	.750	10	+	10
$\overline{10}04$	.832	4	−	6
$\bar{4}05$	.785	51	−	50
$\bar{6}05$	.817	38	−	38
$\bar{6}06$	.957	7	−	13
$\overline{20}08$	1.655	6	+	7
$\overline{20}09$	1.756	6*	−	0

APPENDIX

GENERALIZED PROJECTIONS

Introduction

Simpler organic molecules usually require the use of two dimensional Fourier syntheses in order to solve and refine their crystal structures.[4] When the molecule is complex it is very nearly essential to use three dimensional data and the corresponding Fourier series. While for two dimensional work ordinary desk calculating machines together with aids such as Beevers Lipson strips or Robertson masks are sufficient; for three dimensional summations, involving often thousands of terms, a mechanical or electronic computor is necessary.

A technique known variously as "generalized projection method" or "weighted density method" has been developed in recent years. The three dimensional electron density is weighted by an arbitrary function in such a manner as to make most terms in a three dimensional summation disappear. This reduces the calculation to manageable size, while at the same time some of the three dimensional character is maintained. Although the choice of weighting function is infinite, only one type has so far been used. This function has the effect of employing reflections of one layer line only in the Fourier summation. Hence the data required is easy to collect by means of usual moving-film methods. Since these reflections are from planes which are not parallel but at a known angle to the direction of projection an estimate of the third co-ordinates of the electron density in the cell can be found by studying the peak height of the generalized density. An analogous case is when a distant range of hills appears flat while nearer trees and buildings give a three dimensional effect.

Clews and Cochran (1949) were the first to use a generalized projection, although they did not realize the full significance of the method at that time. Dyer (1951) was the first to make full use of the method in finding the third co-ordinate of atoms from generalized Patterson map, but he did not explain the underlying theory of the method in this paper. Raeuchle and Rundle (1952) described in outline the theory of generalized projections, but a few months later Cochran and Dyer (1952) published the first full and correct account of the method in their classic paper. The description of generalized projection theory which now follows is based on the ideas of Cochran and Dyer (1952).

The basic theory

It can easily be shown that (e.g. Robertson, 1953)

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

where ρ is the electron density at x,y,z which are the co-ordinates of a point in the unit cell expressed as fractions of the cell edges a,b,c;

and V is the volume of the unit cell.

The weighting function $e^{2\pi iKy}$ is used. Thus let us define the generalized projection onto the (010) plane as

$$\rho_K(x,z) = b \int_0^1 \rho(x,y,z) \exp[2\pi iKy]\, dy \qquad (2)$$

Substituting for $\rho(x,y,z)$ with (1) in (2) and using the fact

$$\begin{aligned} \int_0^1 \exp[2\pi i(K-k)y]\, dy &= 1 \quad \text{when } k = K \\ &= 0 \quad \text{when } k \neq K, \end{aligned}$$

we find that

$$\rho_K(x,z) = \frac{1}{A}\sum_h \sum_\ell F(hK\ell) \exp[-2\pi i(hx + \ell z)] \qquad (3)$$

If we let $F(hK\ell) = A(hK\ell) + i\,B(hK\ell)$ as usual

and put $\rho_K(x,z) = C_K(x,z) + i\,S_K(x,z)$ (4)

we have

$$C_K(x,z) + i\,S(x,z) = \frac{1}{A}\sum_h\sum_\ell \left\{A(hK\ell) + iB(hK\ell)\right\}\left\{\cos 2\pi(hx+\ell z) - i\sin 2\pi(hx+\ell z)\right\}$$

Equating real parts

$$C_K(x,z) = \frac{1}{A}\sum_h\sum_\ell \left\{A(hK\ell)\cos 2\pi(hx+\ell z) + B(hK\ell)\sin 2\pi(hx+\ell z)\right\}$$

and similarly equating imaginary parts

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

These functions reduce to

$$C_K(x,z) = \frac{1}{A}\sum_h\sum_\ell |F(hK\ell)| \cos\left\{2\pi(hx+\ell z) - \alpha(hK\ell)\right\} \qquad (5)$$

and

$$S_K(x,z) = \frac{1}{A}\sum_h\sum_\ell \left|F(hK\ell)\right| . \sin\left\{\alpha(hK\ell) - 2\pi(hx + \ell z)\right\} \qquad (6)$$

where $\alpha(hK\ell)$ is the phase angle of the structure factor of the plane $(hK\ell)$. At first sight it may appear strange that the generalized density is not completely real. This can be understood when it is realized that it is dependent not only on the physically real electron density, but also on the arbitrarily selected weighting function.

We now need to interpret the meaning of the Fourier series (5) and (6). Let us assume that the structure is composed of spherically-symmetric atoms.

$$\therefore F(hk\ell) = \sum_{n=1}^{N} f_n(hk\ell) \exp\left\{2\pi i(hx_n + ky_n + \ell z_n)\right\} \qquad (7)$$

Substituting equation (7) in the expression for the generalized density (3)

$$\rho_K(x,z) = \frac{1}{A}\sum_{n=1}^{N}\left[\sum_h\sum_\ell f_n(hK\ell)\exp\left\{2\pi i(hx_n + Ky_n + \ell z_n\right\}\exp\left\{-2\pi i\,(hx+\ell z)\right\}\right]$$

$$= \frac{1}{A}\sum_{n=1}^{N}\left[\sum_h\sum_\ell f_n(hK\ell)\exp\left\{2\pi i[h(x_n - x) + \ell(z_n - z]\right\}.\exp\left\{2\pi iKy_n\right\}\right]$$

But $\exp\{2\pi i\, Ky_n\}$ does not change with h or ℓ and may, therefore, be taken outside the summation. Hence putting

$$\sigma_{nK}(x,z) = \frac{1}{A}\sum_{h=-\infty}^{+\infty}\sum_\ell f_n(hK\ell) \exp\left\{2\pi i(hx + \ell z)\right\}$$

we find that

$$\rho_K(x,z) = \sum_{n=1}^{N} [\ \sigma_{nK}(x - x_n,\ z - z_n).\exp 2\pi i K y_n] \qquad (8)$$

Now, since $f(hK\ell) = f(\overline{hK\ell})$

$$\sigma_{nK}(x,z) = \frac{1}{A}\sum_{h}\sum_{\ell=0}^{\infty} 2\ f\ (hK\ell)\ \cos 2\pi(hx + \ell z)$$

Therefore σ_{nK} is completely real, representing what would be the projected electron density of the n^{th} atom onto the (010) plane if $f(hK\ell)$ were replaced by $f(h0\ell)$. We can now separate real and imaginary parts in (8) if we make use of (4).

Thus

$$C_K(x,z) = \sum_{n=1}^{N} \sigma_{nK}(x - x_n,\ z - z_n).\cos 2\pi K y_n \qquad (9)$$

and

$$S_K(x,z) = \sum_{n=1}^{N} \sigma_{nK}(x - x_n,\ z - z_n).\sin 2\pi K y_n \qquad (10)$$

The Fourier series (5) and (6) correspond to the summations (9) and (10). Thus the cosine generalized projection $C_K(x,z)$ can be built up by multiplying the distribution $\sigma_{nK}(x,z)$ for each atom by $\cos 2\pi K y_n$ and centring the atom at x_n, z_n. It follows that a comparison of the heights of the peaks (or troughs) in $C_K(x,z)$ or $S_K(x,z)$ with the corresponding $\sigma_{nK}(x_n,z_n)$ then gives $\cos 2\pi K y_n$ or $\sin 2\pi K y_n$, respectively. For lower layer lines (K small) the peak height of the corresponding atom in the normal projection can be assumed to equal $\sigma_{nK}(x_n, z_n)$. For higher layer lines $\sigma_{nK}(x_n, z_n)$ can easily be calculated, since

$$\sigma_{nK}(0,0) = \frac{1}{A}\sum_{h}\sum_{\ell=0}^{\infty} 2f(hK\ell)$$

A discussion of the effect of termination of series and bad resolution on peak heights, and the corresponding effect on the accuracy of a generalized projection is given in the section "The generalized projection" in Part II of this thesis.

Philips (1954) first suggested the combination of the cosine and sine parts. This has been done by Fridrichsons and Mathieson (1955) in the determination and refinement of the structure of DL isocryptopleurine methiodide. It follows from (9) and (10) that

$$\left\{C_K^2\,(x,z) + S_K^2\,(x,z)\right\}^{\frac{1}{2}} = \sum_{n=1}^{N} \sigma_{nK}(x - x_n, z - z_n) \quad (11)$$

In other words we have the ordinary electron density projection except that the peak heights are slightly altered because $f(hK\ell) \simeq f(h0\ell)$ only. Fridricksons and Mathieson term this a "modulus projection". Philips (1954) points out that the peak shape in a modulus projection is improved because the effective scattering curve generally becomes flatter in shape as the level of projection is increased, so that the corresponding atomic peak becomes sharper though smaller. Hence an increase in resolution should be obtained, but this is in part counterbalanced by the decrease in the amount of observable data for higher layer lines. Nevertheless the power of a modulus projection to increase resolution is well shown by Fridrichsons and Mathieson (1954 and 1955), who combined by summation the modulus projections of a number of different layer lines.

Some applications

Clews and Cochran (1949), who were the first to use the new method, derived accurate two dimensional co-ordinates for 4- amino -2, 6- dichloropyrimidine by making generalized projections of different layer lines down the very short c axis. From each projection two co-ordinates of each atom were measured, and these were then averaged. This is akin to the modulus projection, although Fridrichsons and Mathieson (1955) claim their method of summing modulus projections at different levels to be more accurate, as it gives the correct weight of each layer line.

Dyer (1951), Zussman (1953) and Curtis and Pasternak (1955) have used Patterson generalized projections to determine the third co-ordinate in structures where two co-ordinates were already known. Since the coefficients in a Patterson summation are all real and positive it follows from equations (5) and (6) that

$$CP_K(x,z) = \frac{1}{A} \sum_h \sum_\ell F^2(hK\ell) \cos 2\pi(hx + \ell z)$$

and

$$SP_K(x,z) = -\frac{1}{A}\sum_h \sum_\ell F^2(hK\ell)\ \sin 2\pi(hx + \ell z)$$

The n^{th} peak is then of height $\phi_{nK}.\cos 2\pi K_{yn}$ or $\phi_{nK}.\sin 2\pi Ky_n$ according to whether the cosine or sine generalized Patterson is being used. ϕ_{no} is the corresponding distribution of the n^{th} peak of the equatorial layer line projection. Dyer (1951) assumed that

$$\frac{\phi_{nK}}{\text{height of origin peak of layer K}} = \text{constant for a particular type of atom}$$

An estimate of the unknown ϕ_{nK} could, therefore, be made. It must, however, be pointed out that a full interpretation of the zero layer line Patterson is required before any meaning can be attached to a generalized Patterson.

Raeuchle and Rundle (1952), Zachariason (1954), as well as Curtis and Pasternak (1955) made use of generalized projections in order to eliminate the density due to atoms at certain heights in the unit cell, thereby increasing the resolution of the other atoms. Let us, for instance, consider a structure with atoms on the planes $y = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$. If we construct the cosine generalized $(h1\ell)$ projection all atoms at levels $y = \frac{1}{4}$ and $\frac{3}{4}$ are eliminated since

$$\cos 2\pi \frac{1}{4} = \cos 2\pi \frac{3}{4} = 0 .$$

However, the remaining atoms enter with a weight of ±1 since

$\cos 2\pi.0 = 1$ and $\cos 2\pi\frac{1}{2} = -1$. It should be explained that the apparently new weighting system used by Curtis and Pasternak is nothing else but the usual generalized projection. A generalized projection was defined as

$$\rho_K(x,z) = b\int_0^1 \rho(x,y,z)\ \exp[2\pi i K\,y]\ dy \tag{2}$$

Since $\rho(x,y,z)$ is all real we could define the two generalized projections as

$$C_K(x,z) = b\int_0^1 \rho(x,y,z).\cos 2\pi Ky.\,dy$$

and

$$S_K(x,y) = b\int_0^1 \rho(x,y,z).\sin 2\pi Ky.\,dy$$

These are the definitions used by Raeuchle and Rundle (1952). Now the weighting functions used by Curtis and Pasternak are $(1 \pm \cos 2\pi y)$ and $(1 \pm \sin 2\pi y)$. Hence

$$\text{Curtis \& Pasternak function} = b\int_0^1 \rho(x,y,z)\left(1 \pm \substack{\cos\\ \sin}\ 2\pi\,y\right)\ dy$$

$$= b\int_0^1 \rho(x,y,z)\,dy \pm b\int_0^1 \rho\,(x,y,z)\ \substack{\cos\\ \sin}\ 2\pi\,y.\,dy$$

$$= \text{zero layer projection} \pm \text{first layer cos or sin generalized projection.}$$

A very good example of how heavy atom technique can be of great assistance when used in conjunction with a generalized projection technique is given by Cochran and Dyer (1952).

Speakman (1953) gives an illustration how a generalized projection can demonstrate the non-planarity of a roughly planar molecule.

It has already been mentioned that Zachariason (1954) and Curtis and Pasternak (1955) employed generalized projections to eliminate electron density at specific heights in the unit cell. In both cases difference generalized projections were subsequently used: by Zachariason to show up the positions of hydrogen atoms in a "hydrogen synthesis"; by Curtis and Pasternak to refine the two projected atomic co-ordinates. Difference generalized projections have now also been used in some of the work described in this thesis in order to refine, not the two projected co-ordinates, but the third co-ordinate, parallel to the direction of projection.

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