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THE CRYSTAL AND MOLECULAR STRUCTURE OF SOME
ORGANIC COMPOUNDS

Being a thesis presented for the Degree of
Doctor of Philosophy in the University of
St. Andrews by ROBERT FIELD ENTWISTLE, B.Sc.



DECLARATION

I hereby declare that the work recorded in this thesis was carried out by me in the Physics Department of Queen's College, Dundee under the supervision of Dr. J. Iball, and has not previously been presented for a higher degree.

UNIVERSITY TRAINING

I entered Queen's College (then University College), Dundee in October 1948 and gained First Class Honours in Natural Philosophy in June 1952. From September 1952 until December 1955 I was engaged in research, in the Physics Department of Queen's College, Dundee under the supervision of Dr. J. Iball.

CERTIFICATE

I certify that Robert Field Entwistle has spent nine terms on research work under my supervision, and that he has fulfilled the condition of Ordinance No. 16 of the University of St. Andrews, so that he is qualified to submit the following thesis in application for the degree of Doctor of Philosophy.

ACKNOWLEDGEMENTS

I wish to thank Mr. J. Ball for his constant advice and encouragement.

I would like to thank my fellow research students and the staff of the Physics Department for their interest and helpful discussions and particularly Mr. J. Stark for his assistance with the diagrams.

I would also like to thank members of the Department of Chemical Crystallography of University College, London for invaluable guidance in the preparation of data for computing.

Finally I must express my gratitude to the Department of Scientific and Industrial Research for the award of a maintenance allowance during the tenure of which the greater part of this work was carried out, and to the University of St. Andrews for an additional grant covering the three months up to December 1955.

ABSTRACT

The crystal and molecule structure of 1.2.cyclopentenophenanthrene has been elucidated by standard x-ray diffraction and Fourier synthesis techniques. The significance of observed departures of the molecule from a planar configuration is assessed statistically. The use of weighted reciprocal lattices and Fourier transforms in structure analysis is outlined. The similarity between corresponding axial reciprocal lattices of 1.2.cyclopentenophenanthrene and chrysene is shown to arise from the similarity of the structures themselves.

The crystal and molecular structure of 1.2.5.6.dibenzanthraquinone has been solved, and refinement of two axial projections continued by the method of least squares using electronic digital computers. Although the state of refinement of these projections is good, there are some abnormal features which make further study necessary before any statements about the shape of the molecule can be made with confidence.

A comparison of the coordinates derived by the application of two distinct refinement techniques to the (h0l) projection of 1.2.cyclopentenophenanthrene, and also to the (0kl) projection of 20.methylcholanthrene is shown to cast doubt on the usual statistical criteria of accuracy.

Some theoretical limitations on the use of the difference Fourier technique are discussed and an estimate of the resolving power is attempted. Methods of Fourier peak determination are examined and a simplified method for the determination of molecular centres is outlined.

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I INTRODUCTION

The main part of this work is devoted to a study of the crystal and molecular structures of two polycyclic organic compounds. A preliminary account of the structure of the first, 1.2.cyclopentenophenanthrene, was given at the Third International Congress of Crystallography in Paris in 1954. This compound is of importance as the basic structure contained in many substances which exhibit strong biological action. These include the sterols, the bile acids, the sex hormones, the toad poisons and the plant glucosides, all of which are derived from 1.2.cyclopentenophenanthrene by substitution, at certain preferred positions, of hydroxyl or quinone groups or of carbon chains of varying length. Some positions at which substitutions frequently occur are numbered 5, 6, 10, 13 in fig. 2.

The second compound, 1.2.5.6.dibenzanthraquinone, is of interest as a member of the 1.2.benzanthracene family of compounds many of which, notably 1.2.5.6.dibenzanthracene and 20.methylcholanthrene are powerful carcinogens. It is not itself carcinogenic, the potency of 1.2.5.6.dibenzanthracene apparently having been destroyed by the substitution of oxygen atoms in the 9 and 10 positions. There is clearly scope for detailed comparison of these structures when the limits of crystallographic refinement have been reached.

The biological activity of this type of compound has been related in a general way to properties of the electron density

distributions in certain parts of the molecule. A view which finds much favour is that the activity of phenanthrene and 1,2-benzanthracene derivatives is primarily associated with the K region (1), the region surrounding atoms 16 and 17 in fig. 2 and the two chemically equivalent regions around atoms 5 and 6 and 16 and 17 in fig. 17.

It is generally agreed that the region should be treated as a whole rather than the atoms individually. While the exact property of the K region which governs the activity of the molecule is not clear and may not be unique, some possibilities may be mentioned. The first is that the K bond should have a high bond order, loosely defined as a high degree of double-bondedness. The bond should therefore be noticeably shorter than 1.41 \AA the mean benzene ring bond length. The second is that the total charge on the K region, taken as the sum of the mobile bond order, the free valencies of the two atoms and any charge migrations due to substitutions in the rest of the molecule, should be high. While being valuable pointers these conditions are not inevitable requirements as Coulson (1) points out in a review devoted particularly to carcinogenic activity in relation to electronic configuration. Instances are given of methyl and cyanide substitutions which lower both total charge on the K region and the order of the K bond and yet produce strong carcinogens.

Pullman and Pullman (2) have derived a correlation between carcinogenic activity and calculated electron distributions for 37

hydrocarbons related to anthracene. Two conditions for greatest potency emerge. Firstly the region surrounding carbon positions 3 and 4 in the anthracene nucleus should have a high electron density. It may be noted that with suitable additions to the molecule as for example in 1.2.benzanthracene this region becomes a K region. Secondly the electron density in the region of the meso positions 9 and 10, the L region, should be low. The first condition approximates to that suggested for phenanthrene. No condition comparable to the second has been suggested for phenanthrene.

Returning briefly to 1.2.5.6.dibenzanthracene and the 9.10 quinone: it is now clear that the substitution has occurred at the sensitive L region and since two oxygen atoms have taken the place of two hydrogen atoms it is to be expected that the total charge on the region will have increased. The loss of carcinogenic activity is therefore in accordance with prediction.

It seems then that, despite various exceptions and qualifications, an index, if not a primary cause, of biological activity is to be sought in some peculiarity of the K region of the molecule and in the L region if such exists. Since this peculiarity will inevitably be electronic in nature it should emerge or at least be extractable from an experimental plot of the molecular electron density if only sufficiently accurate data are available and computing techniques of sufficient sophistication can be brought to bear. The latter

requirement is now being met with the increasing use of digital computers for three-dimensional Fourier syntheses.

To have a reasonable hope of success this investigation should cover as many as possible of the derivatives of phenanthrene and anthracene, both active and inactive. This would enable some idea to be obtained of what, if anything, constitutes a normal electron density distribution and variations from it to be correlated with the observed biological properties of the molecules. The programme of study suggested is naturally beyond the scope of this work. The solution and refinement of the structures of 1.2.cyclopentenyphenanthrene and 1.2.5.6.dibenzanthraquinone are small but essential parts of the larger pattern.

Many of the terms and concepts employed in the work which follows are standard and are introduced with a minimum of explanation. It seems advisable to remedy some of these omissions here and at the same time to attempt a brief description of the process of organic structure analysis so that the various sections of the work may be more easily related to the whole.

The data on which the work is based are the spacings and intensities of the x-ray diffraction maxima obtained using the crystal as a three-dimensional diffraction grating. The spacing of the reflexions gives the dimensions of the unit cell. Each diffraction maximum is assigned the Miller indices (hkl) of the reflecting plane.

Systematic absences from the observed reflexions are used to deduce the internal arrangements of the asymmetric units and so the space group into which the structure falls. Statistical treatment of the intensity data is sometimes necessary to decide whether or not the structure has a centre of symmetry.

The true intensity, that is, the measured intensity corrected for polarization and for geometrical factors connected with the means of recording and placed on an absolute scale, depends on the fine structure of the cell contents, that is on the electron density distribution. The square root of the true intensity is the structure factor $F(hkl)$ the coefficient of the Fourier series for $\rho(xyz)$ the electron density. Thus

$$\rho(xyz) = \frac{1}{V_0} \sum_h \sum_k \sum_l F(hkl) \exp 2\pi i \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)$$

so that the latter is in principle determinable. Unfortunately there is no means of deciding whether to use the positive or the negative square root of any particular intensity so that the summation cannot be performed at once. It is necessary therefore to deduce the sign or, more generally, the phase of $F(hkl)$ by indirect means.

Structure factors for a trial structure may be calculated from the expression

$$F(hkl) = \sum_{r=1}^N f_r \exp - 2\pi i \left(\frac{hx_r}{a} + \frac{ky_r}{b} + \frac{lz_r}{c} \right)$$

where (x_r, y_r, z_r) are the coordinates of the r^{th} atom and f_r is the scattering factor depending on atom type and angle of reflexion.

These are compared with the observed structure factors. When a measure of agreement between observed and calculated factors has been obtained for the larger values the summation for $\rho(xyz)$ may be performed using observed $F(hkl)$'s combined with calculated phases where the latter are reasonably certain. If the trial structure is a reasonable approximation to the true one the Fourier synthesis will enable a better set of coordinates to be obtained and the result will be improved agreement between observed and calculated structure factors and more usable phases for the next synthesis. When the trial structure has been shown capable of refinement in this way the crystal structure may be considered solved. This process is normally carried out in two dimensions only, the electron density map produced being the projection of the contents of the unit cell onto one of its faces. It is possible to do this using only $F(hkl)$'s with one index zero e.g. the projection on the (0K) face is produced from the (h0l) structure factors, thereby effecting a great saving in calculation time. From two projections all three coordinates of the atoms are obtainable although the accuracy is sometimes limited by masking between neighbouring molecules.

The problem remaining is that of obtaining the best possible atomic coordinates. The criterion of accuracy adopted is the reliability index $R = \frac{\sum |F_o - F_c|}{\sum |F_o|}$ where F_o and F_c are the observed and calculated structure factors. Methods of reducing R , termed

refinement techniques are described in relation to the solution and refinement of 1.2.cyclopentenophenanthrene and 1.2.5.6.dibenzanthraquinone in Sections III and IV. Section V is also concerned with refinement techniques and in the Appendices some aspects of these techniques not directly related to the remainder of the work are discussed.

Section V deals with a practical comparison of the effectiveness of the normal difference Fourier method and the Masking and Series Termination method devised by Burns and Iball (3). The b axis projection of 1.2.cyclopentenophenanthrene and the a axis projection of 20.methylcholanthrene (4) were subjected to refinement by both methods. The results tended to favour the difference Fourier and it is shown that this method is generally to be preferred when high accuracy is sought. The simple masking correction has, however, been found useful in the early stages of refinement.

One result which emerged from this study was that the two refinement techniques did not produce coordinates which were identical within the currently accepted criteria of accuracy. The view taken is that these criteria give a somewhat optimistic estimate of the accuracy of individual atomic coordinates. An attempt is made to calculate the necessary correction to the standard deviation of the atomic coordinates but the position remains uncertain. The effect of this is seen in the discussions of the refined structures where many

reservations are necessary when estimating the significance of observed deviations from uniformity. Thus, referring to 1.2.cyclopentenophenanthrene we find that an apparent twist of the molecule about its long axis (fig. 13) would be regarded as highly significant on the old criteria but barely so on the new. On the other hand the non-planarity of the pentene ring is sufficiently pronounced to be beyond doubt.

II EQUIPMENT

The following is a brief catalogue of the equipment used during the course of the present research.

X-Ray Generator

This was designed and built as a preliminary to the main research programme. The generating equipment was housed in a 'Dexion' framework for ease of construction. Controls, instruments, warning lights and fuses were mounted in a vertical aluminium panel. The mounting, supplied by the makers, for the x-ray tube itself was screwed to the mild steel top of the housing which also carried the crystal goniometers. High tension supplies were led from the middle of the back of the housing to the top of the x-ray tube mounting by a heavily insulated cable. The x-ray tube used was of the type Miller MC 50/Cu4F, a sealed tube with copper anode. Four windows were available. The two normally used gave pencil-shaped beams of x-rays. The remaining two gave strap-shaped beams one of which was occasionally used with needle-shaped crystals. The output, 20mA at 38KV was sufficient for most purposes. The circuit diagram, shown in fig. 1, is self explanatory.

Other x-ray generators used when beams of higher intensity were required were the Phillips sealed tube type and the Metropolitan Vickers 'Raymax', with demountable continuously evacuated tube, modified to incorporate a rotating anode.

The Weissenberg Moving Film Goniometer

Two models, one built at Leeds University and the other at Cambridge by Unicam Instruments Ltd., were used to obtain x-ray diffraction data for 1,2-cyclopentenophenanthrene and 1,2,5,6-dibenzanthraquinone. The film is mounted in a cylindrical holder which sits with its axis coincident with the axis of rotation of the crystal on the goniometer arcs. The film holder moves parallel to this axis while the crystal rotates, the two motions being geared so that 1 mm. travel corresponds to 2° rotation. Opaque screens shield the film from all reflexions but those of the equatorial layer line. These are spread over the entire film in a manner which makes for easy identification of all reflexions. Other layer lines may be obtained by inclining the axis of rotation to the x-ray beam and adjusting the screens accordingly.

The Unicam oscillation goniometer was also used. In this machine the crystal can be oscillated through 5° , 10° or 15° by means of a heart-shaped cam or rotated continuously. Reflexions are collected on a stationary film in a cylindrical holder coaxial with the rotation of the crystal.

The Bragg Structure Factor Balance

The instrument used is an enlarged version of the original model described by Bragg (5). It is designed to sum up to 24 terms of the type $\cos 2\pi \frac{hx}{a} \cos 2\pi \frac{ky}{b}$ commonly met with in structure factor formulae.

The instrument consists of 24 identical dials set on an aluminium board which, supported at the centres of its ends, forms the balance. Each dial has two scales. The rim is divided into 100 units corresponding to values of $\frac{X}{a}$ from 0 to 1. The diametral scale is marked from 0 to 1.00 in hundredths, the marks being a distance from the centre of the dial proportional to the value of $\cos 2\pi \frac{Y}{b}$. Thus with a small brass weight fixed at any mark $\frac{ky}{b}$ by a screw, its moment about the centre is proportional to $\cos 2\pi \frac{ky}{b}$, and with the outer scale set at $\frac{hx}{a} = 0$ the moment about the fulcrum of the balance is proportional to $\cos 2\pi \frac{ky}{b}$. With the outer scale turned to read a value $\frac{hx}{a}$ the moment of the weight about the fulcrum is also proportional to $\cos 2\pi \frac{hx}{a}$, that is, it is proportional to $\cos 2\pi \frac{hx}{a} \cos 2\pi \frac{ky}{b}$. The balance is controlled by a torsion wire running under its length. Torsion is applied to level the balance by a vertical dial graduated 0 to 100 divisions. The balance point is determined by means of a spirit level mounted on the board. The constant of proportionality is obtained by reading values of $\cos 0.000 0$ for different numbers of dials.

Great use was made of the structure factor balance in the early stages of structure solution and refinement. It was felt to be insufficiently accurate for use in the later stages of refinement. The maximum calculating rate achieved for a structure of 17 atoms was 40 structure factors in one hour. It was found necessary to check the zero adjustment of the instrument from time to time by means of a

levelling screw in the base since movement of the central scales was occasionally found to alter the balance point slightly.

The 'Madas' Calculating Machine

This was used for the most accurate calculations of structure factors and for much general work. Summations of the form $a.b$ and a^2 are performed quickly and easily while $a.b.c$ and $\frac{a}{b} \cdot \frac{c}{d} \cdot \frac{e}{f} \dots$ are possible.

Also used were a National Cash Register adding machine, an 'Addmaster' adding machine, an Olivetti 'Divisumma' and a 'Facit' hand calculator.

The Hilger Non-Recording Microphotometer

This instrument is designed for the accurate comparison of photographic densities on exposed film. The film is held between dust- and scratch-free glass plates on a horizontal frame which can be moved at will in its own plane. Vernier scales give accurate distance measurements if required. A parallel beam of light passes through the film and is refracted into the variable slit mouth of a photoelectric cell. A viewing attachment enables the portion of the film to be measured to be seen on a large scale. The image is deflected onto the slit of the photocell when the shutter is opened for measurement. The photoelectric current is detected by a conventional galvanometer. The moving mirror is engraved with a linear scale which is projected, greatly magnified, onto the back surface of the

screen of a convenient viewing attachment.

When comparing diffraction spots of similar shape and intensity it was found sufficiently accurate to take readings across the profiles at (say) 0.05 mm intervals and to plot the profiles on graph paper using the relation,

$$\text{density} = -K \log (\text{scale reading}).$$

Sufficient readings for the background density close to the spots were taken to average out variations due to the large grain size of the fast x-ray film used. With the background density subtracted the constant K vanishes and the areas under the curves, or even simply their maximum values, are directly comparable.

The Beavers-Lipson Strips (6)

The Beavers-Lipson Strips are tables of sines and cosines, of the form $F \cos 2\pi \frac{hx}{a}$, designed to simplify the calculation of Fourier syntheses.

III (1) 1.2.cyclopentenophenanthrene C₁₇H₁₄
unit cell, space group and x-ray
diffraction data

The crystal structure of 1.2.cyclopentenophenanthrene was first studied by Bernal and Crowfoot (7) and by Iball (8) in 1935. A choice of several monoclinic unit cells is possible. The non primitive unit cell originally chosen was suggested by a comparison of the unique b axis x-ray diffraction pattern with the equivalent diffraction pattern of chrysene, the structure of which was determined by Iball (9) in 1934. The comparison is detailed in Section III (11).

With the unit cell so chosen the space group is designated $B2_1/c$ and the cell dimensions are

$$\begin{aligned} a &= 18.35 \pm .05 \text{ \AA} \\ b &= 5.869 \pm .002 \text{ \AA} \quad \beta = 114.3 \pm 0.1^\circ \\ c &= 23.700 \pm .005 \text{ \AA} \end{aligned}$$

These values were obtained by graphical extrapolation to $\theta = 90^\circ$ from high angle reflexions on equatorial layer line photographs (10). Moving film x-ray photographs were taken by rotation of the crystal about the three axes of the cell and about the $[101]$ and $[10\bar{1}]$ axes.

Halvings observed are

hkl	h + 1 odd
Ok1	l odd
h0l	h or l odd
hk0	h odd
Ok0	k odd

This unit cell was used during the solution and much of the refinement of the structure, but in the later stages of the work it was decided to change to a primitive unit cell, when the space group is $P2_1/a$, in order to facilitate future refinement on a digital computer. The cell dimensions then are

$$\begin{aligned} a &= 18.35 \pm .05 \text{ \AA} \\ b &= 5.869 \pm .002 \text{ \AA} & \beta &= 142.5 \pm 0.1^\circ \\ c &= 17.73 \pm .03 \text{ \AA} \end{aligned}$$

Halvings observed are

hkl	none
h0l	h odd
0k0	k odd

The new Miller indices are obtained from the old ones by the transformation

$$\begin{aligned} h' &= h \\ k' &= k \\ l' &= \frac{l-h}{2} \end{aligned}$$

where the primes indicate the new indices.

The crystal density measured by a flotation method is 1.23 gm per cm^3 at 20°C (8) giving 8 and 4 molecules per unit cell for the respective unit cells. The volume of the new cell is 1163.4 \AA^3 and $F(000)$ the number of electrons in the unit cell is 464. The crystal shows the forms $\{010\}$ $\{001\}$ $\{10\bar{1}\}$ $\{20\bar{1}\}$.

Intensity measurements of reflexions recorded on Weissenberg moving film photographs were made by visual comparison with a graded series of spots which was produced by the multiple exposure of a film to strip oscillation photographs with the output from the x-ray tube carefully regulated. A range of intensity from 1 to 12 was normally used. The full range of reflected intensities was correlated using Robertson's multiple film technique (11). A modification of this method described by Iball (12) employs a fast Ilford type Industrial "G" film in front of a slow Ilford type Industrial "B" film. When this combination is exposed to x-rays the corresponding densities recorded on the two films are approximately in the ratio 10:1. The normal ratio for like films is about 3:1. Measurement of this ratio for a given batch of films was made by photometric comparison of the intensities of lines on multiply exposed powder photographs using a Hilger non-recording microphotometer. A second method used was the comparison of copper $K\beta$ spots on the "G" film with the corresponding $K\alpha$ spots on the "B" film. The direct comparison of $K\alpha$ spots on "G" and "B" films is not reliable as it is rarely found that one reflexion is accurately measurable on both.

With this high ratio between films it was found possible to record all reflexions for one layer line in measurable form with only one long and one short exposure. Considerable economy both in exposure time and in time required to measure the intensities was thus effected.

An effort has been made to collect full three-dimensional intensity data with the object in view of eventual refinement of the structure on a digital computer by the differential Fourier synthesis method. The number of possible reflexions inside the limiting sphere for copper K α radiation is about 2700. These appear on h axis layer lines with k ranging from 0 to 7. Only the zero and the first three of these layer lines are obtainable using copper K α radiation due to the limitations imposed by the geometry of the Weissenberg camera. The fourth layer line has been recorded using molybdenum K α radiation. Exposures required for higher layer lines with molybdenum radiation have proved prohibitively long but the reflexions on them will be obtainable from photographs about other axes.

Two methods were used to put the layer line structure factors on an absolute scale. In the first a calculation was made of all the structure factors for the first three h axis layer lines and the scale of the observed structure factors was adjusted independently for each layer line so that sums of observed and calculated factors were equal. In the second method use was made of short exposures taken for each layer line with the output from the x-ray tube carefully regulated. Corrections to the exposure times were applied for the change in the obliquity of the x-ray beam to the film from layer line to layer line by the method of Cox and Shaw (13) and the corresponding sets of intensities were then scaled to the zero layer line by direct

comparison of exposure times. The structure factors of the zero layer lines were originally scaled by means of Wilson's statistical method (14). The scale was later adjusted by comparison with the calculated values. The scales found for the layer lines by the two methods agreed to within about 5%, suggesting that either could have been used alone with equal confidence.

Two-dimensional structure factors are given in Table 7.

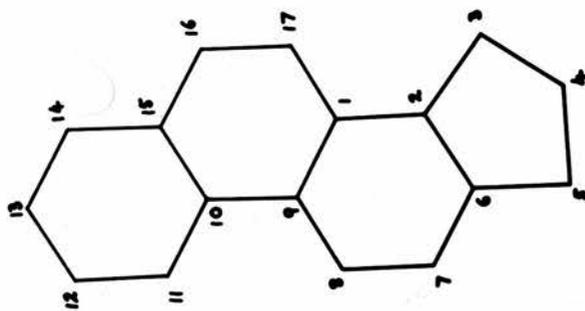
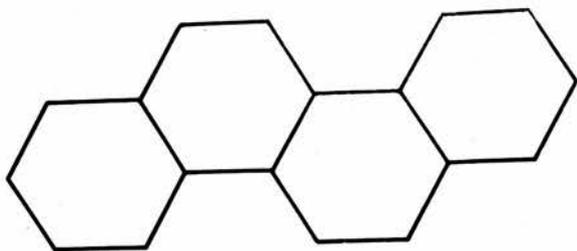


Fig. 2

Carbon skeletons of 1,2-cyclopenteneanthrene
(left) and chrysene.

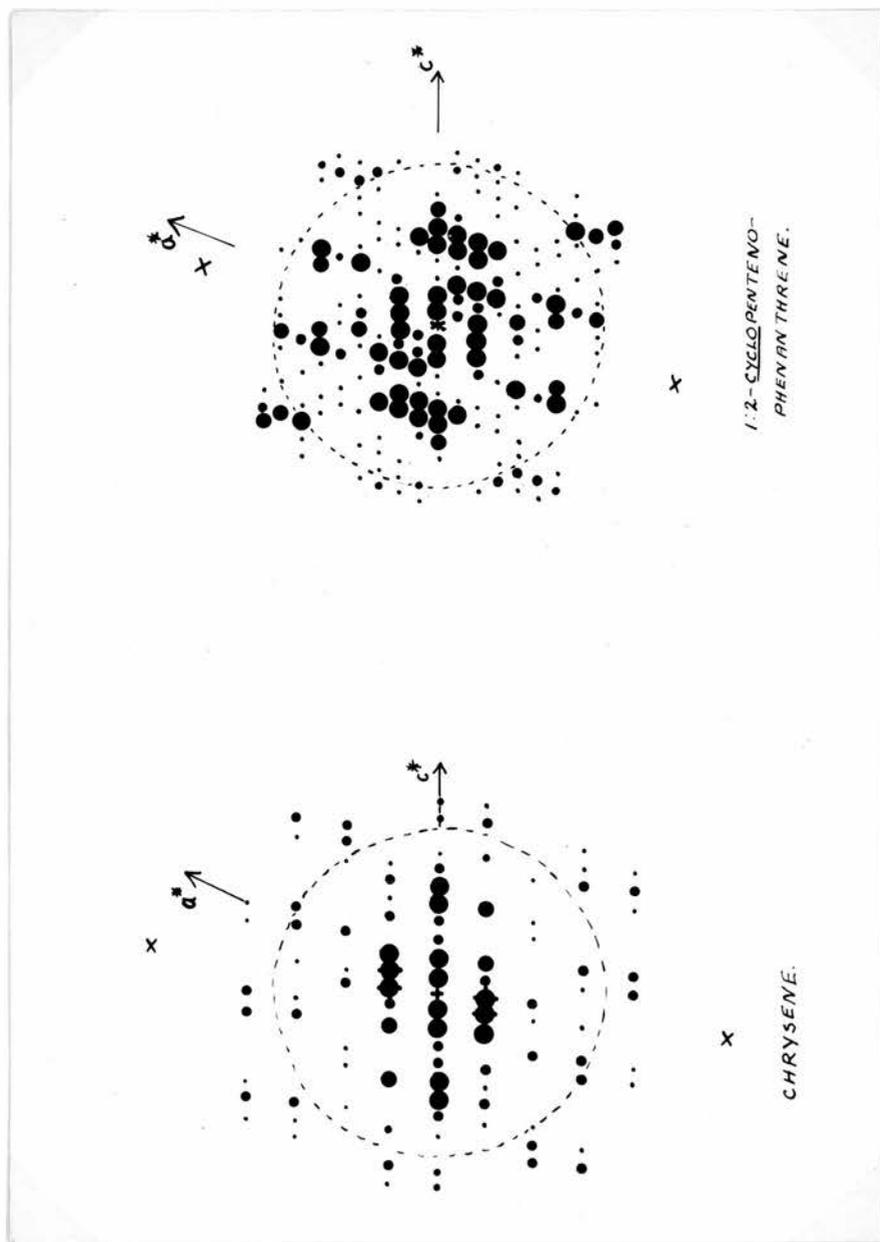


Fig. 3

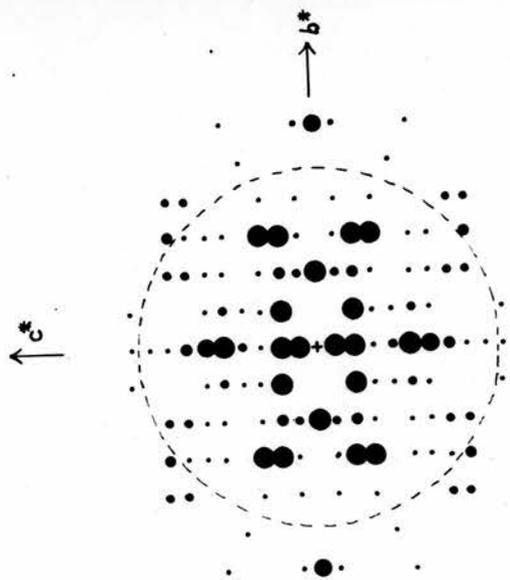
Showing the resemblance between the b^* axis weighted reciprocal lattices.

III (11) A comparison of the diffraction patterns of chrysene and 1.2.cyclopentenophenanthrene

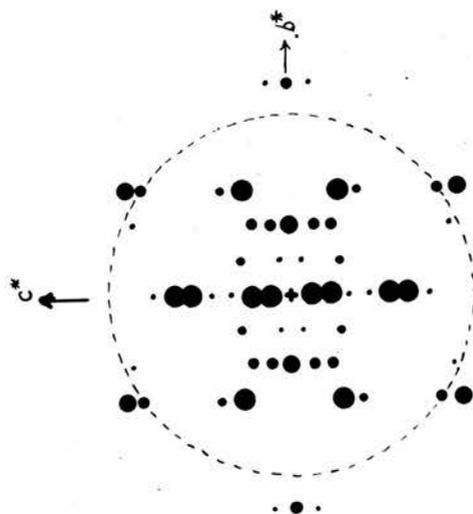
The molecules of 1.2.cyclopentenophenanthrene and chrysene (fig. 2) are similar in appearance and size, the difference being that the former has an atom fewer in one, fully substituted, end ring and so is non centrosymmetric. Weighted reciprocal lattices for the b axis projections (fig. 3) were first drawn. It was found most suitable to give the reflexions weights proportional to their structure factors, that is to the square root of the intensities of the reflexions after application of Lorentz and polarization factors. The use of weights proportional to the intensities is not advisable since too little notice may be taken of high angle reflexions with large unitary factors but small scattering factors. The importance of these will appear presently. The strengths of the c axis reflexions were seen to be remarkably similar in the two cases and the correspondence between the positions and shapes of the outer groups of strong reflexions was striking. These formed part of a fringe system nearly perpendicular to the c^x axis which suggested that the molecules lay approximately parallel to the c axis while the spacing of the fringes corresponded to a separation of the molecules of about 4.6 \AA at right angles to this direction in 1.2.cyclopentenophenanthrene and slightly less in chrysene. The fixing of the direction of the long axis of the molecule close to the c axis agreed with the observation that the direction of

maximum refractive index made an angle of 6° with the c axis (Bernal and Crowfoot). The outermost groups of strong reflexions are from planes coinciding roughly with the direction and spacing of benzene ring bonds. From these groups the approximate shapes, in projection, of the benzene rings were constructed and found to be almost identical in the two structures. The orientation of the rings so obtained was: one principal diagonal making an angle of 6° to the c axis and lying in the first quadrant of the (010) plane, and the plane of the ring tilted about this diagonal 60° out of the (010) plane. The diagonal coincided with the long axis of the molecule.

From the foregoing considerations it was evident that the b axis projections would be very similar. In fact with 1.2.cyclopentenophenanthrene in the space group $B2_1/c$ and chrysene in the space group $I2/c$ the cells also were found to be closely similar in size and shape and packing of the molecules except that for chrysene the a axis was halved and a double cell had to be used for comparison. Although in 1.2.cyclopentenophenanthrene the molecules are in general positions, the similarity to chrysene indicated that they were almost equally spaced along the a axis, the separation being $\frac{1}{4}a$ or 4.6 \AA , agreeing well with the spacing obtained from the fringe system. The spacing was confirmed by the great strength of the (400) reflexion, showing that a large proportion of the scattering matter lay in that plane, and by the apparently complete absence of the (200) reflexion.



1:2-CYCLOPENTENO-
PHENANTHRENE.



CHRYSENE.

Fig. 4

Showing the resemblance between the a axis
weighted reciprocal lattices.

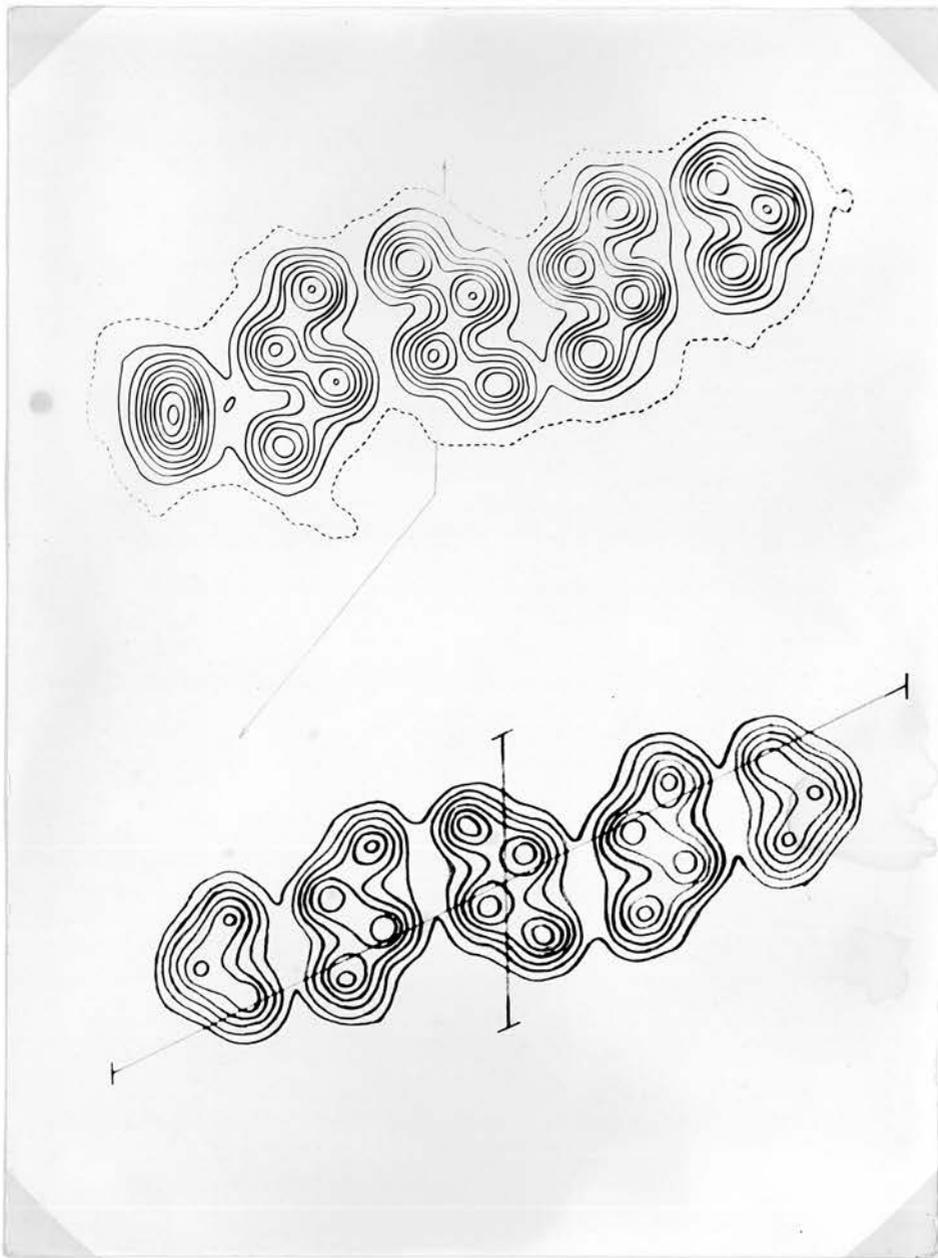


Fig. 5

The (0 1 0) Fourier projections of 1.2-cyclopentene-phenanthrene and chrysene. The latter is due to Dr. D.M.Burns.

The presence of a weak (600) reflexion shows that the halving of the (200) plane is not exact.

A study of the a axis reciprocal lattices (fig. 4) revealed the same qualitative similarity as for the b axis. In both structures the great strength of the (060) reflexion gave the orientation of the benzene ring and so the direction of the long axis of the molecule to within a degree or so. The remaining groups defining the benzene ring are clearer in chrysene than in 1.2.cyclopentenophenanthrene. This is a measure of the greater symmetry of the former structure since the molecules are situated at centres of symmetry and only two overlap in projection. In 1.2.cyclopentenophenanthrene the molecules are slightly displaced from the centres of symmetry of the projection and four molecules overlap. No useful information was obtained from Fourier syntheses on this projection whereas the chrysene structure was partly determined in this way (Iball, 1934).

The structure of 1.2.cyclopentenophenanthrene postulated by Iball on the basis of this comparison has been confirmed in its major details. As predicted the b axis projections of the two structures are very much alike (fig. 5). The Fourier projection of chrysene is due to Dr. D.M. Burns. While the a axis projections are not directly comparable for the reasons mentioned, refinement of the y coordinates from other projections has left no doubt that the molecules are similarly oriented here also.

It is clear from this comparison that such similarities in

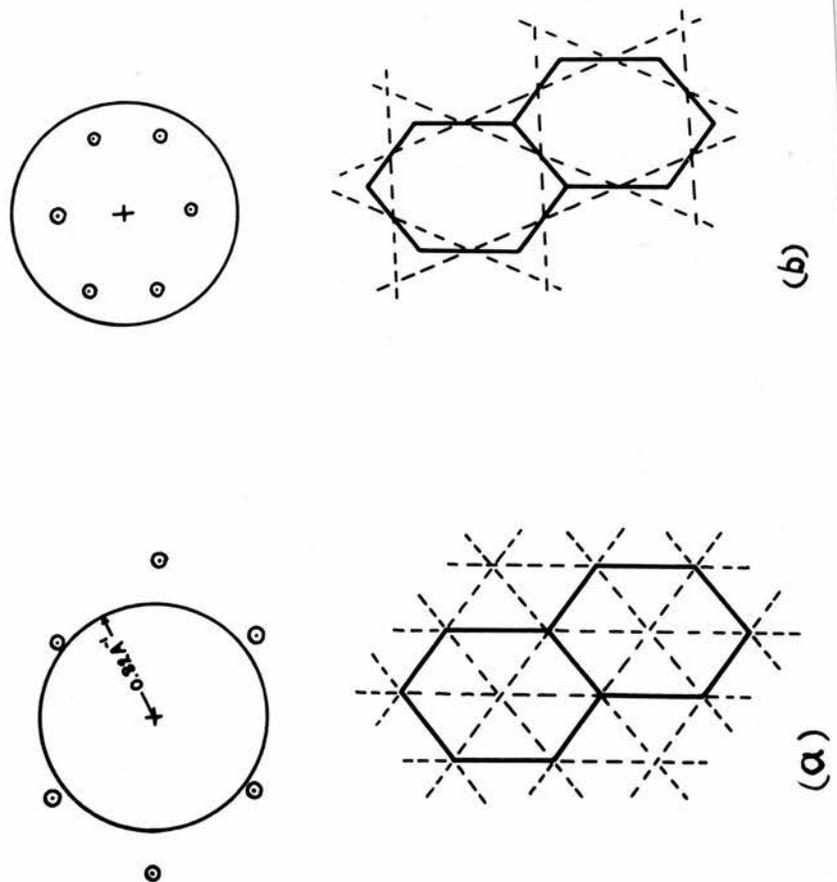


Fig. 6

The main features of the weighted reciprocal lattices of aromatic hydrocarbons, and the molecular planes giving rise to them.

diffraction patterns as have been mentioned necessarily imply at least a measure of similarity in the underlying structures and that the information obtainable from them can be of great help in the solution of one structure if the other has been determined.

Some properties of the weighted reciprocal lattices of polycyclic aromatic compounds are of interest. They depend on the symmetry in projection of the benzene ring. The use of the outer groups of strong reflexions in the fixing of the orientation of the benzene rings has already been mentioned. These groups consist of reflexions from planes corresponding to the spacings between rows of atoms in the molecules. In compounds composed of benzene rings the rows are parallel to the ring bonds with a spacing of half the width of the ring (fig. 6(a)). If the ring is tilted out of the plane of projection the rows are closer together in projection and the corresponding reflexions appear at higher angles. The inner limit for these groups is given by the reciprocal of the internal radius of the benzene ring i.e. 0.82 \AA^{-1} (15). The inner groups of intense reflexions also have hexagonal symmetry and correspond to the spacing between the zigzag rows of atoms formed when two or more rings are placed side by side (fig. 6(b)). The groups are naturally more diffuse than those of the benzene circle. These planes are of wider spacing than the benzene ring bonds so that the reflexions from them appear closer to the origin than the benzene groups. It can be shown analytically that the 'centres of gravity' of these

inner groups lie at the centroids of the triangles formed by two adjacent groups of the benzene circle and the origin of the lattice. Further, calculation shows that a line passing through two adjacent inner groups passes also through two benzene ring groups and the groups are equally spaced along the line. This fact can be used to construct the ring when it is tilted so sharply that one, and possibly two, pairs of groups fall outside the limiting circle of reflexion. In fact only two non equivalent groups and the origin are required to reconstruct the whole set. The difficulty in this case is mainly in recognizing the groups. The normal method of construction of the benzene ring is to join the groups to the origin and draw perpendiculars to the lines at a distance from the origin inversely proportional to their length. The hexagon formed by the perpendiculars is the desired ring. However, it can be shown that the hexagon formed by the ring groups is similar in shape to the benzene ring producing it and needs only to be turned through 90° in the plane of the diagram to give the required shape and orientation. The scale may be obtained by consideration of the reciprocal of one group spacing.

The use made of the properties of the weighted reciprocal lattice is not confined to comparison with other structures. It will always be worth while examining the distribution of structure factors in this way for such clues to orientation and principal spacings as have been outlined since an approximate knowledge of the molecular orientation can be of great value in limiting the number of trial structures to be investigated.

III (iii) The use of the Fourier Transform to obtain approximate molecular structures

Although the structure of 1.2.cyclopentenophenanthrene postulated from the comparison with chrysene was subsequently shown to be a close approximation to the truth, some preliminary calculations on that basis produced only limited agreement between observed and calculated structure factors and the b axis Fourier projection calculated with the signs so obtained was unrecognizable. Rather than spend longer on such calculations it was decided to apply the Fourier Transform method (16-21) to the problem. This is a systematic method of comparing observed and calculated structure factors which requires very little computation so that a series of trial structures can be tested very rapidly. An account of the theory underlying the method will now be given.

A polycyclic aromatic hydrocarbon, of which 1.2.cyclopentenophenanthrene is a particular example may be represented as a plane structure consisting of regular hexagons of side 1.41 \AA . Other types of ring such as the pentene ring and added groups such as quinone and methyl groups may be idealized for the purposes of calculation as parts of such regular hexagons. When this is done the coordinates of all the atoms in the molecule may be referred to the centre of the molecule as origin and a set of suitably chosen rectangular axes in terms of multiples of short distances, say r , s and t , parallel to

these axes. If the molecule possesses no centre of symmetry an origin of coordinates is chosen so that as many pairs of atoms as possible are centrosymmetrically related. This, like the idealization of the molecular structure is designed to simplify calculation. The Fourier transform of the molecule, or molecular transform is then given by

$$T_M(XYZ) = \sum_{r=1}^N \exp 2\pi i(u_r X + v_r Y + w_r Z)$$

the sum being taken over the N atoms of the molecule with integral coordinates (u_r, v_r, w_r) , which are expressed in units of r, s and t respectively. The points (XYZ) occur on a lattice of spacings $\frac{1}{r}, \frac{1}{s}, \frac{1}{t}$ which is comparable to the normal reciprocal lattice though the axes chosen are arbitrary. In fact, since a planar molecule is being considered it is possible to make the Z axis perpendicular to the plane of the molecule when all w_r become zero and the function T_M is independent of Z .

Since T_M consists of a real and an imaginary part for a non centrosymmetric molecule it will usually be necessary to evaluate the two parts separately and combine their values at any point (XY) as required. The functions are periodic and may be evaluated in the form of contour maps by means of the Beavers-Lipson strips (6). Although the form of the contour maps will depend on the molecular origin and axes chosen, the modulus T_M is unique for any set of points chosen to represent the structure. It remains to correlate this

function with the observed distribution of structure factors over the actual reciprocal lattice of the crystal structure under investigation.

If the position of the previously selected centre of the molecule relative to the origin and axes of the unit cell is represented by (α, β, γ) and the coordinates of the atoms relative to the centre of the molecule and the cell axes by $(u_r^!, v_r^!, w_r^!)$ the general structure factor formula may be written

$$F(hkl) = \sum_{r=1}^N f_o(hkl) \exp 2\pi i [h(u_r^! + \alpha) + k(v_r^! + \beta) + l(w_r^! + \gamma)]$$

or $\frac{F(hkl)}{f_o(hkl)} = \exp 2\pi i (h\alpha + k\beta + l\gamma) \sum_{r=1}^N \exp 2\pi i (hu_r^! + kv_r^! + lw_r^!)$

where $f_o(hkl)$ is assumed the same for all atoms in the molecule.

With the coordinates of the equivalent positions inserted the relation is of the form

$$\frac{F(hkl)}{f_o(hkl)} = \phi(h\alpha, k\beta, l\gamma) \sum_{r=1}^N \exp 2\pi i (hu_r^! + kv_r^! + lw_r^!)$$

Now the expression $\sum_{r=1}^N \exp 2\pi i (hu_r^! + kv_r^! + lw_r^!)$ is equivalent to the original definition of T_M , the coordinates of the atoms being merely referred to different, and not necessarily orthogonal, axes, so that if $\frac{F(hkl)}{f_o(hkl)}$ is called the cell transform $T_o(hkl)$ the relation becomes

$$T_o(hkl) = \phi(h\alpha, k\beta, l\gamma) T_M(XY)$$

The modulating function $\phi(h\alpha, k\beta, l\gamma)$ relating the two transforms takes account of the symmetry elements of the unit cell. Its form does not depend on the molecular structure assumed. The problem is

now to determine the projection of the true reciprocal lattice on the arbitrary lattice used for computing the contour maps, after which the values of $T_o(hkl)$ can be obtained by reading off T_M at the appropriate lattice points and multiplying by $\phi(h\alpha, k\beta, l\gamma)$. As a rule it is possible to deal only with $T_o(hkl)$ when at least one index is zero. The axial structure factors, with two indices zero are most useful in fixing the projections of the reciprocal axes since in these cases the modulating function reduces to an exponential function of one variable only. The presence of one or more large axial structure factors of small spacing is generally sufficient to fix the axis to within a few degrees. Consideration of all the axial structure factors determines the position more definitely though it may still be impossible to choose between two widely differing positions. A choice must then be made from a calculation of selected general structure factors. Additional evidence from the weighted reciprocal lattice may be extremely useful, since in favourable circumstances it can give both the approximate direction of the length of the molecule and the angle of tilt of the benzene ring to the plane of projection (Section III (ii)). The only quantities still unknown are the coordinates (α, β, γ) of the centre of the molecule. These can be obtained roughly from a consideration of the distribution of intensities as is usual in trial and error methods but may also be expected to be obtained fairly rapidly during the process of fitting the reciprocal

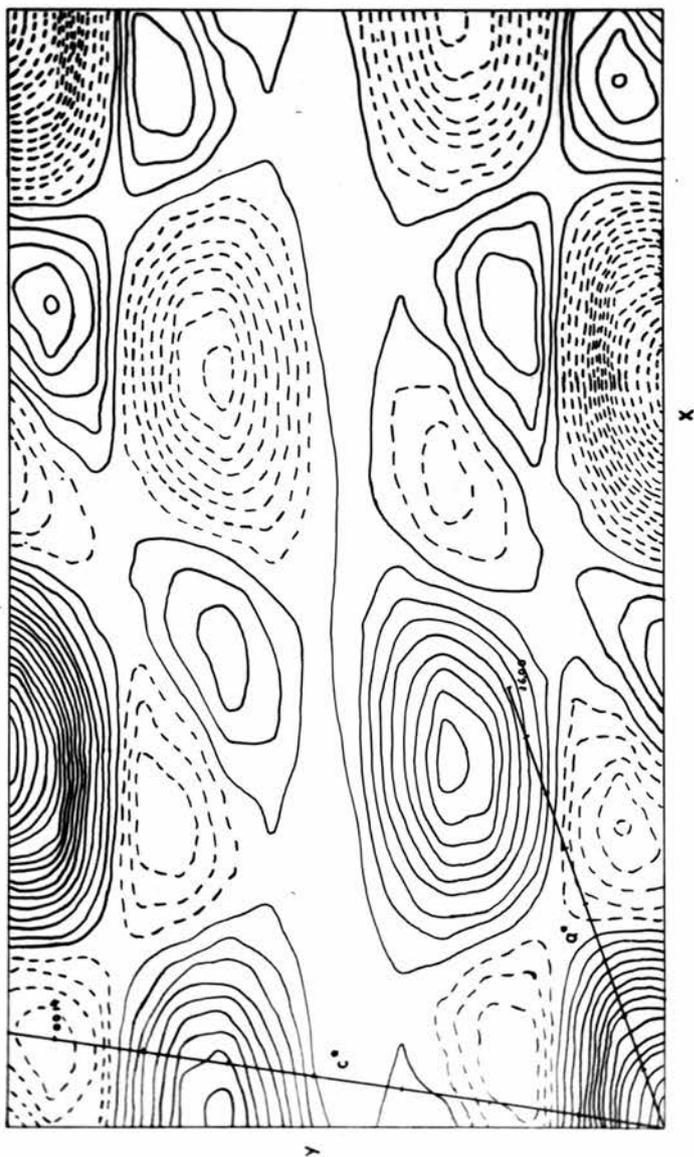


Fig. 1

The real part of the molecular transform of 1.2-cyclopentene-phenanthrene. The positions of the reciprocal axes are shown.

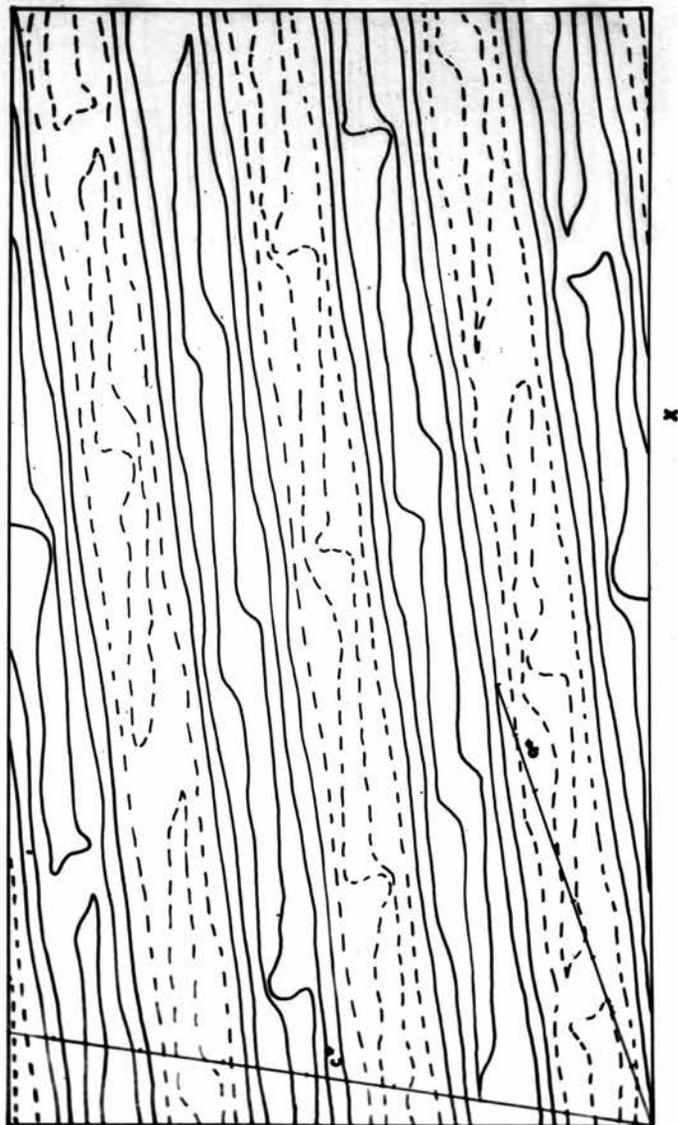


Fig. 6

The imaginary part of the molecular transform.

axes to the transform. Once this has been done and the values of $T_c(hkl)$ obtained from the real and imaginary parts of the molecular transform it is possible to use the phases associated with these values in combination with the observed structure factors to produce a Fourier synthesis which gives an approximate structure capable of refinement. A difficulty inherent in the method, when used for a non-centrosymmetric molecule, will appear when the derivation of the structure of 1.2.cyclopentenophenanthrene is discussed.

The structure of 1.2.cyclopentenophenanthrene, which consists of 17 carbon atoms and 14 hydrogen atoms, may be looked upon as being approximately planar with three complete benzene rings and one benzene ring with one atom missing. The hydrogen atoms are neglected. It is centrosymmetric but for one atom in the completed end ring which is unpaired so that the imaginary part of the transform has a maximum height of one atom and is generally overshadowed by the real part with a maximum height of 17 atoms. The two contour maps are shown in figs. 7 and 8. In the space group $B2_1/c$ the expressions for the cell transform are as follows.

In the $(h0l)$ zone $T_c(h0l) = R \cos(h\alpha + l\gamma) - I \sin(h\alpha + l\gamma)$ where R and I are the values of the real and imaginary parts of the transform. In the $(0kl)$ zone, when k is even

$$T_c(0kl) = R_+ \cos(k\beta + l\gamma) - I_+ \sin(k\beta + l\gamma) + R_- \cos(k\beta - l\gamma) - I_- \sin(k\beta - l\gamma)$$

when k is odd

$$T_c(Ok1) = R_+ \cos(k\beta + 1\gamma) - I_+ \sin(k\beta + 1\gamma) - R_- \cos(k\beta - 1\gamma) \\ + I_- \sin(k\beta - 1\gamma)$$

$$\text{where } R_+ = \sum_{v=1}^N \cos(kv_+ + lw_+) \\ R_- = \sum_{v=1}^N \cos(kv_- - lw_-) \\ I_+ = \sum_{v=1}^N \sin(kv_+ + lw_+) \\ I_- = \sum_{v=1}^N \sin(kv_- - lw_-)$$

with the symbols as used previously.

From the evidence of the weighted reciprocal lattice it was clear that the long axis of the molecule lay in the angle between the c axis and the perpendicular to the a axis so that the c^* axis should be close to the Y axis of the transform. It was a simple matter to fix its position with the aid of the (002), (004) and (00,10) structure factors and to see that $\gamma = \frac{1}{120} c$. The positions of the axes finally chosen are shown in figs. 7 and 8.

The a^* axis was known to be tilted at an angle of about 60° to the plane of the transform so that the (200) position fell inside the central peak of the transform and since the (400) reflexion was very large it had to do likewise. But the (200) reflexion was unobservably small so that the value of a was fixed at almost exactly $\frac{1}{8} a$ in agreement with the evidence mentioned in Section III(ii). Further refinement using other (h00) reflexions fixed the a^* axis in the position shown. From the (h0l) reciprocal net so constructed the signs of 50 of the larger structure factors were read off. 49 of

these were later shown to be correct. A Fourier synthesis computed with these structure factors as coefficients produced a recognizable picture of the molecule. During the process of reading off the signs of the structure factors, the question arose of what signs to give the imaginary components, since these depend on the sense in which the axes are chosen while the signs of the real components do not. This is equivalent to deciding at which end of the trial molecule to place the pentene ring. The course chosen was to omit all terms whose sign depended on the sign of the imaginary component. The result was that the Fourier map also failed to distinguish between the end rings. Some accidental asymmetry of the map caused the wrong alternative to be selected and some time was spent in fruitless attempts at refinement. During this time the reliability index never dropped below 0.4. However, once the mistake had been realized the structure proved capable of rapid refinement.

This ambiguity of sign is most likely to be overlooked when the imaginary component is small. In this case very little notice was taken of it during the actual fitting of the axes and no attempt was made to compare the agreement between observed factors and factors calculated for the two possible alternatives. In view of the approximations made in the calculation of the transform it is not certain that it would be possible to decide between the two structures in this way but the information which might be gained would probably

make the attempt worthwhile. With a larger imaginary component it would obviously be easier to distinguish between the alternatives but the fitting of the axes would become correspondingly more difficult.

A further difficulty arose in the case of 1.2-cyclopenteno-phenanthrene due to the fact that in the (h0l) zone all planes are halved when h is odd. This means that there are two unique positions along the a axis which the molecule can occupy without affecting the structure factor agreement and which cannot in consequence be distinguished by the transform. It is not until general structure factors, in which odd values of h can occur, are evaluated that the position of the centre of the molecule can be fixed definitely.

An attempt was made to obtain a trial structure for the (0kl) zone from the transform. Some difficulty was found in deciding between two possible positions for the b^* axis situated about 15° apart since only three (0k0) reflexions were available. The signs of 25 structure factors were found to be the same on either assumption and a Fourier synthesis was calculated using these. The contour map showed evidence of four rings superposed in pairs, corresponding to a pair of centrosymmetrically related molecules, which in addition were overlapped by other pairs of molecules on either side. It was found impossible to fix even approximate atomic coordinates from this map and it appeared more promising to use the y coordinates found by Iball (9) for chrysene, combined with an arbitrarily shaped pentene

ring, in future calculations. By this means the reliability index for the zone was reduced to 0.23, but as the structure factor agreement was insensitive to shifts of the molecule along the b axis and as no information was obtainable concerning the shape of the pentene ring, further attempts at refinement were abandoned.

It can be seen from this account that, while the Fourier transform method of solution of crystal structures is a powerful one in suitable cases, its application is subject to all the pitfalls normally met with in trial and error investigations. It is in fact a systematization of the trial and error method, its chief merit being the speed with which it can lead to an approximate structure.

III (iv) Refinement of the structure of 1.2.cyclopentanophenanthrene

x and z coordinates

Attention was at first concentrated on the (h0l) zone Fourier projection derived from the transform. Since there was little overlapping between atomic peaks of the same molecule and none at all between different molecules in this zone, it was hoped to obtain a very accurate set of x and z coordinates before attempting to refine a more confused projection.

The correct choice of position for the pentene ring produced a reliability index, $R = \frac{\sum |F_o - F_c|}{\sum |F_o|}$, of 0.33 compared with $R = 0.40$ for the incorrect alternative (Section III (iii)). A further adjustment, of the shape of the ring, was suggested by a large discrepancy in peak heights in the ring. The reliability index then fell to 0.27. At this stage, shifts of coordinates derived from a difference Fourier (Section V and Appendix I) with $F_o(h0l) - F_c(h0l)$ as coefficients in the synthesis, failed to improve the structure, suggesting that the coordinates were still far from their true values.

Although all atoms except numbers 4 and 5, in the pentene ring, were by this time resolved, many of the peak separations were less than 1 \AA in projection and it could be seen that a systematic correction for overlapping would probably be worthwhile. Peak positions were therefore determined from the figure field of the Fourier synthesis by the Burns and Iball 9-point method (22) based on Booth's parabolic

sectioning method (19). Corrections to the coordinates were made by the method of Burns and Iball (Section V). The simple masking correction was extended to deal with the unresolved double peak (Appendix II). In this way the reliability index of the (h0l) zone was reduced in two stages to 0.22 and then by means of a difference Fourier to 0.19. A further application of the masking correction improved this figure to 0.164.

The subsequent refinement of this zone formed part of an investigation into refinement techniques which is detailed in Section V. The final Fourier synthesis (fig. 11) was computed using 193 structure factors whose signs were definitely known, out of 215 observed factors. Peak positions were estimated, structure factors were calculated using these coordinates uncorrected for masking effects and the contributions of the 14 hydrogen atoms, in arbitrarily assigned positions, (Table 1) calculated. The reliability index was 0.150. The final cycle of refinement by difference synthesis reduced this figure to 0.122.

Final coordinates are shown in Table 3. A general view of the [010] projection, showing the packing of the molecules in the cell is given in fig. 12.

TABLE 11.2.cyclopentenophenanthrene, hydrogen atom coordinates

A CH distance of 1.08 Å is assumed.

<u>Atom</u>	<u>x Å</u>	<u>y Å</u>	<u>z Å</u>
1	5.865 5.675	2.467 2.327	-3.44 -3.193
2	7.475 7.231	1.468 1.323	-2.37 -2.835
3	4.585 4.178	0.992 0.982	-6.03 -6.557
4	3.027 2.547	1.873 1.592	-6.38 -6.702
5	2.695 3.677	-1.469 -1.267	-6.73 -6.156
6	2.165 1.482	0.176 -0.687	-6.38 -7.157
7	2.880 2.951	-2.405 -2.217	-3.97 -3.959
8	5.155 5.220	-2.449 -2.306	-0.21 -0.166
9	7.100 7.165	-2.364 -2.333	2.84 2.899
10	9.400 9.532	-2.259 -2.268	6.66 6.777
11	11.830 11.839	-0.554 -0.375	8.86 8.891
12	12.280 12.195	1.357 1.318	7.62 7.521
13	11.125 10.991	2.350 2.238	4.50 4.211
14	9.020 8.853	2.290 2.195	0.89 0.791

Atomic scattering factors

Of great assistance in speeding the reduction of the reliability index is the use of the correct atomic scattering curve for the calculation of structure factors, and the correct adjustment of

temperature factors.

The atomic scattering factor is the function $f_0(hkl)$ appearing in the expression for $F(hkl)$ namely

$$F(hkl) = \sum_{r=1}^N f_0(hkl) \exp 2\pi i \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)$$

The value of $f_0(hkl)$ is dependent on the spacing of the plane (hkl) , the form of the curve f_0 against $\sin \theta$ being somewhat similar to a Gaussian distribution curve, and on the character of the reflecting atoms and their modes of vibration. The last two quantities determine the shape of the atomic profile, of which the atomic scattering factor is the Fourier integral (Section V). Since the vibration of an atom bound into a molecule is not necessarily isotropic it follows that the atomic profile may have different shapes taken in different directions, so that the value of $f_0(hkl)$ may depend also on the orientation of the plane (hkl) with respect to a given direction in the crystal. The scattering factors used in this work are average values and no account has yet been taken of any possible anisotropy of vibration (see III (v), Hydrogen atoms).

At the beginning of refinement the scattering curve used to calculate structure factors was that derived empirically by Robertson (23) for anthracene. Although reasonable agreement between observed and calculated factors was obtained using this curve, it was evident that its fall off with increasing θ , the angle of reflexion, was too slow. That is, the values of F_0 were on the average higher than

corresponding values of F_o at high values of θ . In order to reduce this discrepancy a new curve f_t was calculated from the old curve f_o from the relation

$$f_t = f_o \exp\left(-B \frac{\sin^2 \theta}{\lambda^2}\right)$$

B, the 'temperature factor', was calculated from the assumed form of the relation between F_o and F_c thus

$$F_o = F_c A \exp\left(-B \frac{\sin^2 \theta}{\lambda^2}\right)$$

$$\therefore \sin^2 \theta = \frac{\lambda^2}{B} \left(\log_{e} \frac{F_o}{F_c} + \log_e A \right)$$

Mean values of $\log_{e} \frac{F_o}{F_c}$ were calculated for five ranges of $\sin^2 \theta$ and the results graphed. If the relation assumed is correct then the graph is roughly a straight line, the gradient giving B and the intercept on the $\log_{e} \left(\frac{F_o}{F_c} \right)$ axis giving A, the scale factor. In this case the relation was too indefinite to give clear cut values of A and B. If the curve then in use had been the most appropriate one these quantities should have taken the values one and zero respectively. It appeared then that the observed and calculated curves could not be more closely correlated by this method.

This apparent impasse was resolved when it was observed that the scattering curve as given by Robertson included contributions of the hydrogen atoms in the anthracene molecule, assumed to be divided evenly among the carbon atom positions. The hydrogen atoms only make an appreciable contribution to the structure factors for which θ is less

than 30° so that this part of the scattering curve was too high by comparison with the remainder. It was then necessary to draw out the curve with its maximum height proportional to the total number of electrons in the anthracene molecule, reduce the maximum to correspond with the total number of electrons in the carbon atoms of the molecule, and smooth off the curve to this new maximum.

A comparison of the smoothed anthracene curve with the curve calculated for carbon valence states by McWeeny (24) from theoretical considerations revealed that the two were identical if a temperature factor $\frac{B}{\lambda^2} = 1.22$ was applied to McWeeny's curve. Such agreement between empirical and theoretical approaches is very satisfactory. Table 2 shows the scattering curve used.

Table 2

Smoothed atomic scattering curve for anthracene

$\sin \theta$	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	24.0	23.9	23.8	23.7	23.6	23.4	23.3	23.1	22.9	22.7
0.1	22.4	22.1	21.7	21.3	20.9	20.4	19.9	19.4	18.8	18.3
0.2	17.7	17.2	16.7	16.1	15.7	15.3	14.9	14.5	14.1	13.7
0.3	13.3	12.9	12.5	12.1	11.7	11.3	11.0	10.8	10.5	10.1
0.4	9.7	9.4	9.1	8.9	8.5	8.1	7.8	7.5	7.3	7.1
0.5	7.0	6.7	6.5	6.3	6.1	5.9	5.7	5.5	5.3	5.1
0.6	5.0	4.8	4.7	4.6	4.4	4.2	4.1	4.0	3.8	3.8
0.7	3.7	3.5	3.4	3.3	3.2	3.1	3.0	2.9	2.8	2.7
0.8	2.6	2.5	2.4	2.4	2.4	2.4	2.3	2.2	2.1	2.0
0.9	2.0	1.9	1.9	1.9	1.9	1.9	1.8	1.7	1.7	1.6

The maximum value of the curve is given by the product of atomic number (carbon = 6) and number of asymmetric units in the unit cell. Structure factors were calculated using this curve and hydrogen contributions were evaluated separately. The immediate improvement in the reliability index for the (h0l) projection was estimated to be about 2%. Since the x and z coordinates were already well refined, this represented a substantial gain and it was thought unnecessary to

make further adjustments to scale or temperature factors.

y coordinates

A number of possible ways of obtaining accurate y coordinates demanded consideration. The [100] zone proved unfruitful owing to the large degree of overlapping between molecules (Section III (iii)) and in the [001] zone the molecules are viewed end on. Of the two no diagonal projections the positive [101] projection seemed the most hopeful since it appeared that the pentene ring would be free from overlapping from other molecules. A series of Weissenberg photographs was therefore taken by rotation of the crystal about the [101] axis and attempts were made to correlate the structure factors observed with those calculated using the x and z coordinates from the (h0l) zone and y coordinates derived from a comparison of the molecular orientation with that of chrysene (9). It quickly became obvious that while a good measure of agreement could be obtained for factors with h even, no reasonable agreement was to be expected for factors with h odd. This anomaly persisted until it was realized that the structure factors with h odd could be changed in value by a shift of the centre of the molecule in the xz plane from $\frac{a}{8}$ to $\frac{3a}{8}$, while those with h even suffered at most a change of sign. The appearance of the molecule in the (h0l) Fourier projection would be unchanged.

Recalculation of the [101] zone after this change had been made showed an improvement of the reliability index from 0.47 to 0.33 and

refinement by an F_o synthesis and a series of difference syntheses further reduced it to 0.22. However, the shift of the molecule along the g axis had defeated the purpose of the investigation since it resulted in the complete masking of the pentene ring by its centrosymmetrically related partner in this projection. It was apparent that the use of difference syntheses would not overcome this difficulty which was aggravated by the presence in the five-fold peak (fig. 9) of six hydrogen atoms in undetermined positions.

Since it was essential to obtain an accurate picture of the pentene ring for a complete description of the structure, a reconsideration of the $[10\bar{1}]$ projection followed. It appeared that some resolution might be expected in the pentene ring in this zone but very little in the rest of the molecule. It was therefore decided to proceed with the refinement of the $[101]$ and $[10\bar{1}]$ projections simultaneously.

At this stage the change of unit cell was made, the space group now being referred to as $P2_1/a$ instead of $B2_1/c$. The $[101]$ projection retained the same designation but the $[10\bar{1}]$ became the $[00\bar{1}]$, i.e. the new g axis, projection and will be referred to in this way.

Complete zero layer line diffraction data were collected for these two projections. The F_o syntheses were computed and refinement proceeded by difference syntheses on the two projections alternately, attention being confined in each case to the atoms which were moderately well resolved. No attempt was made to improve the x and z coordinates.

Approximate positions for the 14 hydrogen atoms were estimated (Table 1) and their contributions to the structure factors calculated. Their effect on the reliability indices was small.

With the reliability index for the 101 projection at 0.184 and for the 001 projection at 0.204 further efforts at refinement were abandoned. The final reliability indices for the three zones are therefore

$$R(010) = 0.122$$

$$R(101) = 0.184$$

$$R(001) = 0.204$$

The final Fourier syntheses are shown in figs. 9, 10 and 11. x , y and z coordinates are shown in Table 3.

TABLE 31.2.cyclopentenophenanthrene, atomic coordinates

<u>Atom</u>	<u>x Å</u>	<u>y Å</u>	<u>z Å</u>
1	7.157	0.487	-0.089
2	5.817	0.399	-2.304
3	5.835	1.397	-3.421
4	3.780	0.957 *	-5.903
5	3.101	-0.569	-5.991
6	4.294	-0.634	-3.687
7	4.055	-1.655	-2.943
8	5.377	-1.596	-0.727
9	6.936	-0.634	0.709
10	8.331	-0.511	2.978
11	8.239	-1.567	3.864
12	9.597	-1.526	6.133
13	10.918	-0.411	7.339
14	11.157	0.587	6.576
15	9.781	0.558	4.325
16	9.927	1.632	3.439
17	8.716	1.485	1.365

* Indicates low accuracy

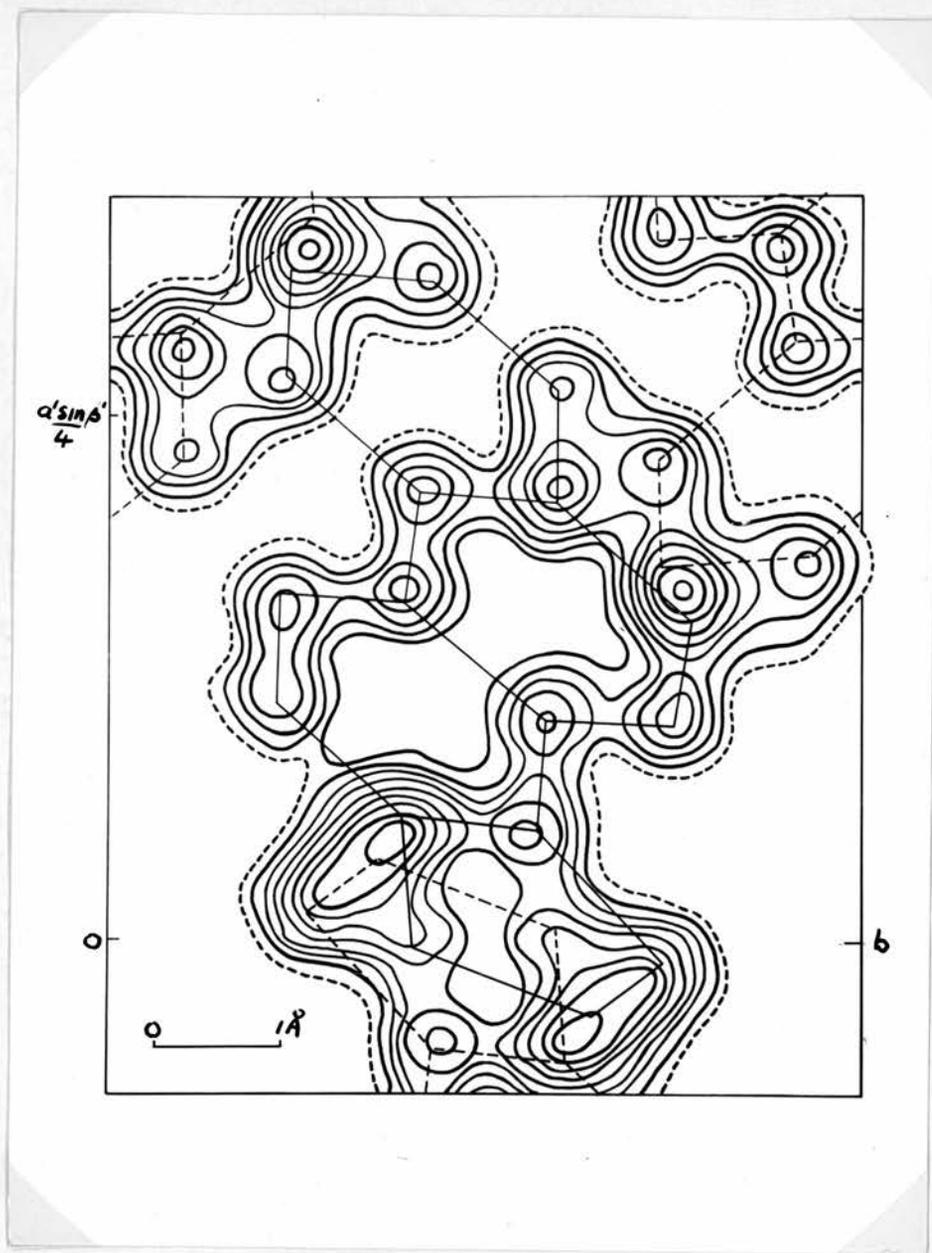


Fig. 9

1.2.cyclopentenophenanthrene (1 0 1) Fourier projection.
 The $4 e\text{\AA}^{-2}$ contour is shown dotted.

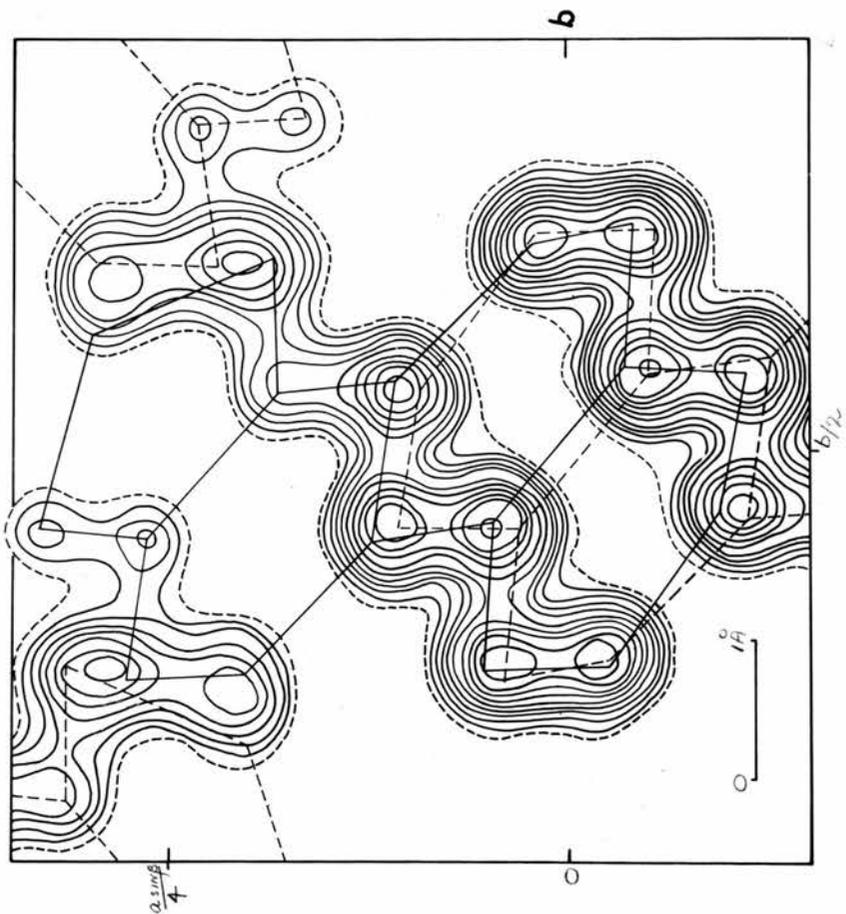


Fig. 10

1,2-cyclopentadienanthrene (0 0 1) Fourier projections.
The 7 e⁻² contour is shown dotted.

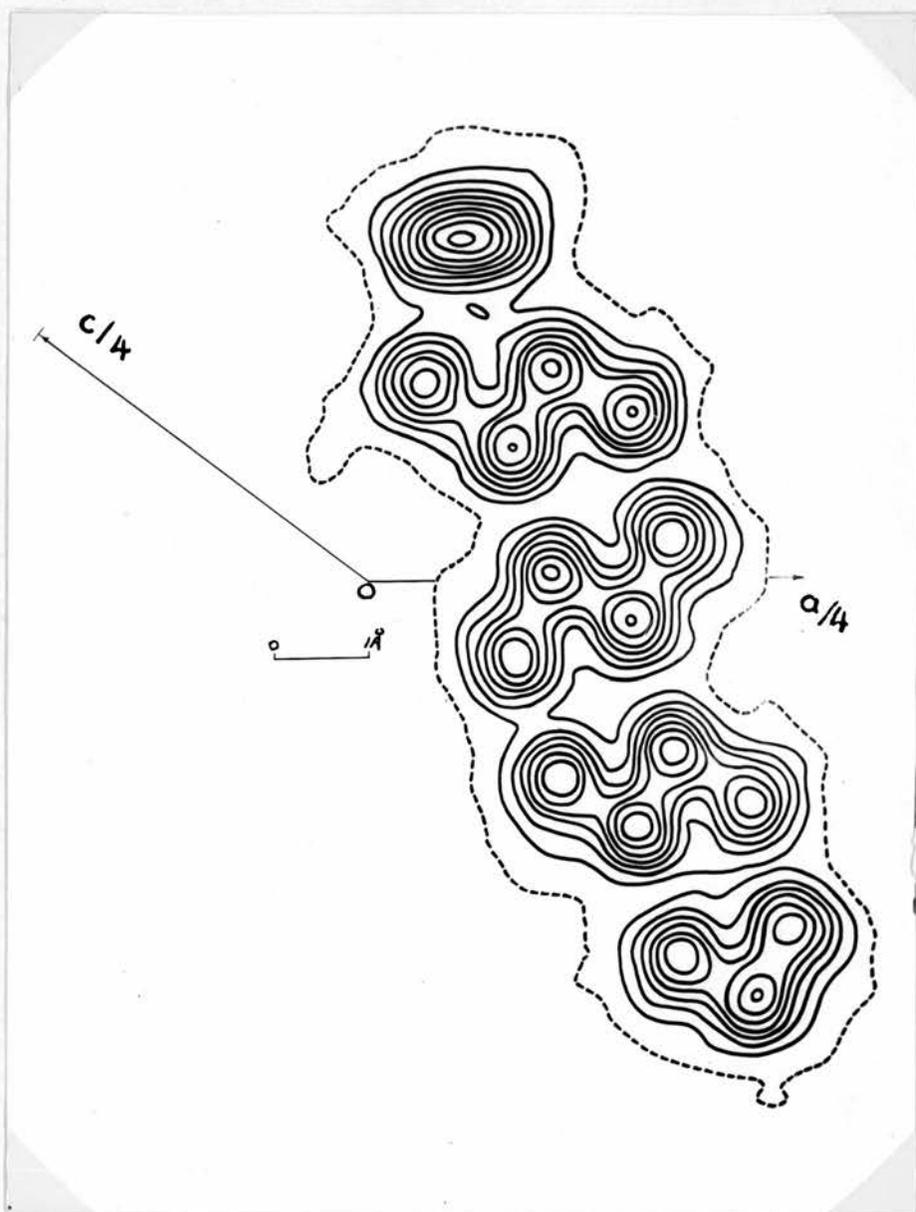


Fig. 11

1,2-cyclopentenophenanthrene (0 1 0) Fourier projection.
The 1 e\AA^{-2} contour is shown dotted.

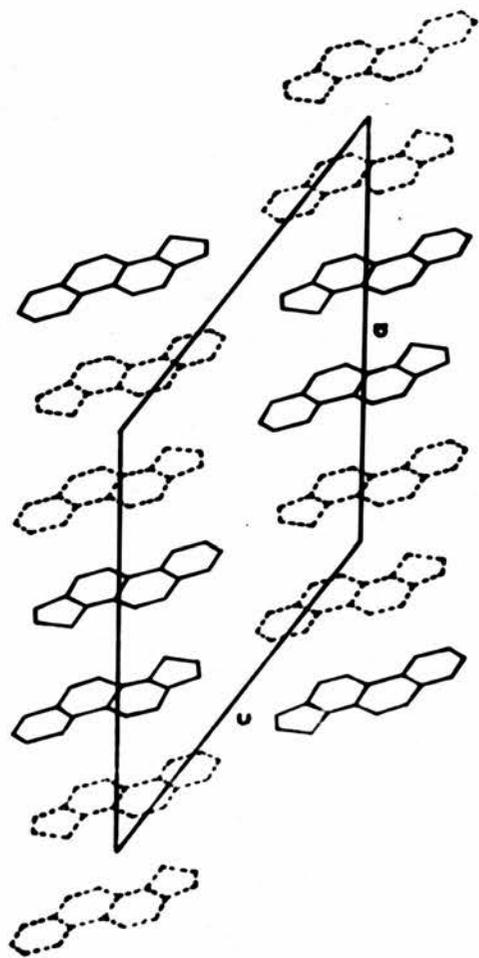


Fig. 12

1,2-cyclopentaphenanthrene. Extended view of the
 (0 1 0) projection. The molecules at \bar{y} are shown
 dotted.

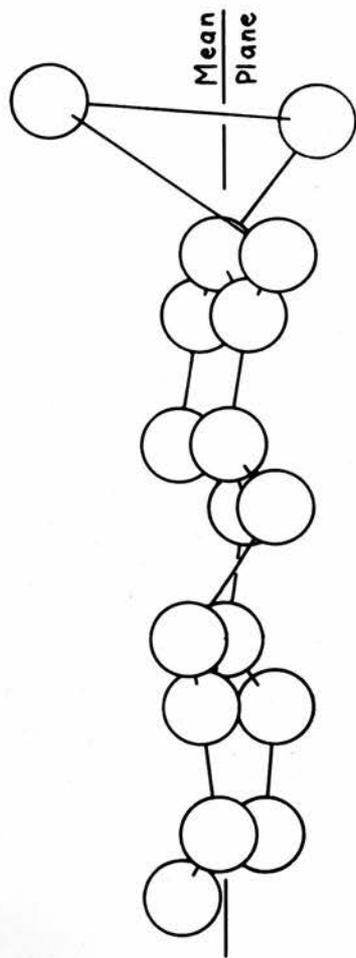


Fig. 13

1,2-cyclopentadienylphenanthrene, the molecule viewed parallel to the mean plane. The distances perpendicular to the plane are magnified $\times 10$.

III (v) Discussion of the structure of 1.2.cyclopentenophenanthreneThe Carbon Skeleton

The chief interest in the structure lies in the configuration of the phenanthrene K region (Section I) and the planarity or otherwise of the molecule, particularly of the five-membered ring.

The phenanthrene group has been found to be approximately planar although the R.M.S. deviation from the mean plane is large (0.034 Å) and the possibility of distortion is not ruled out. The plane, referred to the a and b axes of the cell and the perpendicular to them, is

$$0.8113x - 0.5199y + 0.2674z - 5.5919 = 0$$

The distances of the atoms from the mean plane are given in Table 4, and are plotted on a greatly increased scale in fig. 13. In the five-membered ring the atoms C₃ C₄ C₅ are distant from the plane 0.060, -0.187 and 0.098 Å respectively. The atoms C₂ C₃ C₅ C₆ appear to be coplanar while C₄ is 0.30 Å distant from that plane. The non-planarity of the five-membered ring is therefore definitely established.

TABLE 4

Deviation of atoms from the mean molecular plane

<u>Atom</u>	<u>Deviation \AA</u>	<u>Atom</u>	<u>Deviation \AA</u>
C ₁	.005	C ₁₀	.001
C ₂ [*]	.027	C ₁₁	.051
C ₃ [*]	.060	C ₁₂	.041
C ₄ [*]	-.187	C ₁₃	-.047
C ₅ [*]	.098	C ₁₄	-.005
C ₆ [*]	-.007	C ₁₅	-.025
C ₇	-.028	C ₁₆	-.039
C ₈	-.050	C ₁₇	.052
C ₉	.024		

* indicates a member of the pentene ring.

The R.M.S. deviation for the remaining atoms is 0.034 \AA

The phenanthrene group appears to deviate from a planar configuration in a systematic manner. A twist is indicated about the long axis of the molecule, the angle between the planes of the first and third benzene rings being about 3.6° . The possible significance of this result will now be examined.

An estimate of the accuracy of the atomic coordinates may be

obtained from Cruickshank's expression for the standard deviation (25).

Considering only two-dimensional reflexions, the standard deviation is

$$\sigma(x) = \frac{1}{N \sum_{h,l} A_{hl}} \left(\frac{V}{p}\right)^{\frac{5}{2}} \left\{ \sum_{-H}^H \sum_{-L}^L h^2 \Delta F^2 \right\}^{\frac{1}{2}}$$

and a similar expression for $\sigma(z)$, where N is the atomic number, a the axial length, A_{hl} the area of the $(h0l)$ projection, $\Delta F = F_o(h0l) - F_o(h0l)$ and p is estimated by fitting the function $\rho_r = \rho_o \exp -pr^2$ to the atomic profile.

From the $(h0l)$ projection were obtained the values

$$\sigma(x) = 0.0095 \text{ \AA}$$

$$\sigma(z) = 0.0083 \text{ \AA}$$

and from the $(h'k0)$ and $(hk0)$ projections

$$\sigma(y) = 0.020 \text{ \AA}$$

The standard deviation in any direction may be taken as

$$\sigma(r) = \left[\sum \sigma(x)^2 \right]^{\frac{1}{2}} = 0.024 \text{ \AA}$$

The standard deviation in any interatomic distance will then be

$$\sigma(d) = \sqrt{2} \sigma(r) = 0.033 \text{ \AA}$$

However, when dealing with deviations from a plane it is permissible to resolve the standard deviations of the coordinates along the perpendicular to the plane before combining them as shown above.

$\sigma(r)$ then becomes 0.014 \AA and $\sigma(d)$ becomes 0.019 \AA .

The standard deviation of the angle between the rings is given by

$$\sigma(\tan\theta) = \frac{2\sigma(d)}{2.44} = 0.016 \text{ radians}$$

2.44 \AA being the width of a benzene ring.

The significance of differences between observed values of

similar quantities may be tested by estimation of the probability, P, of the differences occurring by chance. The levels of significance commonly used are indicated, with the difference given in terms of the standard deviation σ .

Δ/σ	P	
≤ 1.65	$\geq 5\%$	not significant
$2.33 - 1.65$	$1\% - 5\%$	possibly significant
> 2.33	$< 1\%$	significant
> 3.09	$< 0.1\%$	highly significant

For the deviation of the benzene rings from a planar configuration we therefore have

$$\frac{\tan\theta}{\sigma(\tan\theta)} = \frac{0.061}{0.016} \doteq 4.0$$

so that the twist of 3.6° in the molecular plane appears to be established beyond doubt. However, the work on refinement techniques detailed in Section V has thrown considerable doubt on the validity of the standard deviation calculated from Cruickshank's formula.

It is suggested that Cruickshank's value may legitimately be increased by a factor $\sqrt{2}$ while it is possible that the true value may be about 2.5 times that given by the formula. On the first assumption the value $\frac{\tan\theta}{\sigma(\tan\theta)} = 2.8$ indicates that the observed twist of the molecule is definitely significant. On the second assumption the value falls to 1.6, just below the level of possible significance. This state of affairs is far from satisfactory but further work will be

required both on the structure of 1.2-cyclopentenophenanthrene and on the statistical assessment of the accuracy of atomic coordinates in general before the reality or otherwise of the effect under consideration can be settled.

For comparison of the benzene ring bond lengths, some of which show considerable variation from the observed mean value of 1.414 \AA , the standard deviation of interatomic distances parallel to the mean plane may be calculated. The value is 0.027 \AA . In addition, the lengths of bonds which lie parallel to the xz plane are independent of small changes in y coordinates so that the standard deviation falls to 0.013 \AA . The latter group of bonds are six in number, the lengths of five of them lying between 1.42 \AA and 1.45 \AA ; the sixth $C_{16} - C_{17}$ is 1.34 \AA . The variation of this bond length from the mean is 0.09 \AA which is of considerable significance even if the value of the standard deviation 0.013 \AA is increased by a factor 2.5. The atoms C_{16} and C_{17} and the bond connecting them, together comprise the K region (Section I). It is interesting to find a significantly low value for this bond length. It is also in good qualitative agreement with its high degree of unsaturation, stemming from the fact that it appears as a double bond in four out of its possible five Kekule structures. For the remaining ten benzene ring bonds (Table 5) the average length is 1.41 \AA , the largest deviation from it being $C_1 - C_9$ at 1.49 \AA . The significance of this difference depends too closely

on the value of the standard deviation to be accurately assessed.

TABLE 5

1.2.cyclopentenophenanthrene, bond lengths

<u>Bond</u>	<u>Length Å</u>	<u>Bond</u>	<u>Length Å</u>
1 - 2	1.42	9 - 10	1.45
1 - 9	1.49	10 - 11	1.43
2 - 6 *	1.40	10 - 15	1.40
2 - 3 *	1.51	11 - 12	1.45
3 - 4 *	1.58	12 - 13	1.38
4 - 5 *	1.64	13 - 14	1.39
5 - 6 *	1.54	14 - 15	1.43
6 - 7	1.39	15 - 16	1.47
7 - 8	1.42	16 - 17	1.34
8 - 9	1.37	17 - 1	1.40

* indicates part of pentene ring.

The four single bonds of the pentene ring vary in length from $C_2 - C_3$ at 1.51 Å to $C_4 - C_5$ at 1.64 Å. While the latter bond is sufficiently long to be viewed with suspicion, deliberate attempts to shorten it during refinement failed to produce an improvement in the structure factor agreement. Failing that, the evidence of the g-axis Fourier projection had to be accepted. Although C_4 is not resolved

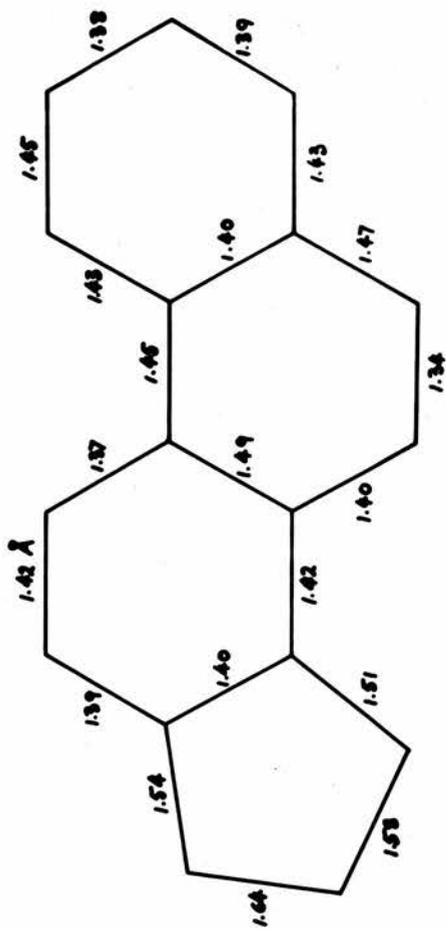


Fig. 14

1,2-cyclopentaphenanthrene, bond lengths.

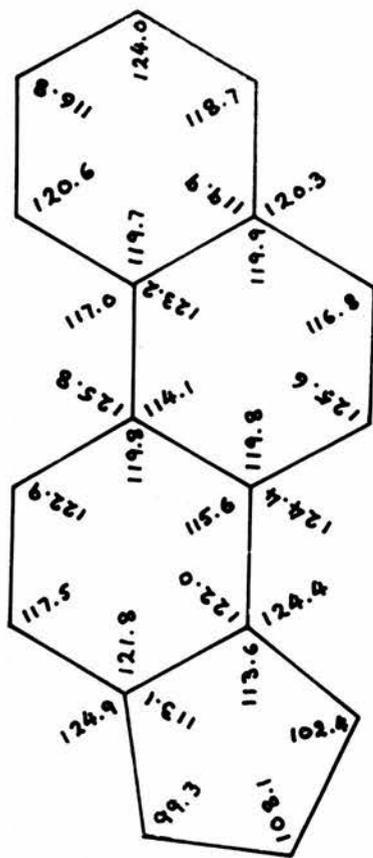


Fig. 15

1,2-cyclopenteneanthrone, bond angles.

in this or any other projection it seems unlikely that it can be placed any nearer to C_5 and may even be further away than the distance given. The bond $C_3 - C_4$ is also rather long and it may be that this bond and $C_4 - C_5$ are identical and significantly longer than $C_2 - C_3$ and $C_5 - C_6$ which are both nearly equal to the normal carbon-carbon single bond length. This might be expected supposing that resonance effects of the adjacent benzene ring tended to make the angles $C_5 - C_6 - C_2$ and $C_3 - C_2 - C_6$ approach the benzene ring angle of 120° . In fact these angles are almost equal (Table 6) and are midway between 120° and 108° , the angle which a regular five-membered ring would contain. In contrast the angle $C_3 - C_4 - C_5$ is 108° and the two remaining angles are 99.3° and 102.4° . The sum of these angles is 536.5° compared with 540° for a planar ring.

Bond lengths and bond angles are also shown in figs. 14 and 15.

TABLE 61.2.cyclopentenophenanthrene, bond angles

<u>Bond angle</u>	<u>θ°</u>	<u>Bond angle</u>	<u>θ°</u>
123 *	124.4	9,10,15	123.2
126	122.0	15,10,11	119.7
623 *	113.6	10,11,12	120.6
234 *	102.4	11,12,13	116.8
345 *	108.1	12,13,14	124.0
456 *	99.3	13,14,15	118.7
562 *	113.1	14,15,10	119.9
267	121.8	10,15,16	119.9
567 *	124.9	15,16,17	116.8
678	117.5	14,15,16	120.3
789	122.9	16,17, 1	125.6
891	119.8	17, 1, 9	119.8
1,9,10	114.1	17, 1, 2	124.4
8,9,10	125.8	2 1 9	115.6
9,10,11	117.0		

* indicates part of the pentene ring.

The mean benzene ring bond angle is 120.3° . The sum of the angles for each ring is consistent with a planar structure though this test for planarity is somewhat insensitive.

Intermolecular distances are similar to those found in other

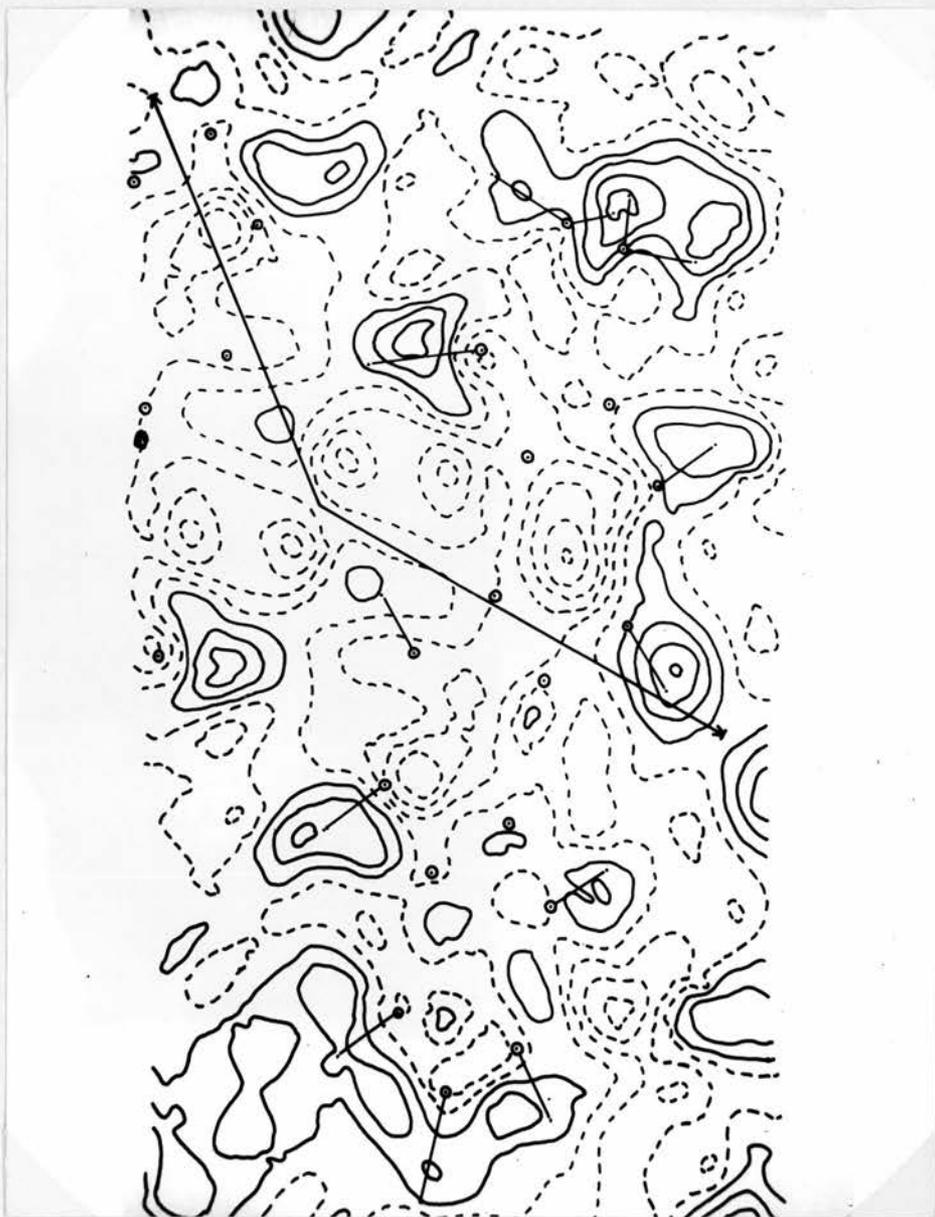


Fig. 16

1,2-cyclopentenophenanthrene (0 1 0) projection difference Fourier. Carbon positions and carbon-hydrogen bonds are indicated. Contours are at intervals of 0.2 eA^{-2} . The zero and all negative contours are shown dotted.

structures of this nature. The minimum distance between carbon atoms is 3.55 \AA which occurs between atom 10 in the molecule (xyz) and atom 8 in the molecule ($\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$). This pair of molecules is not related by a centre of symmetry. The distance between the planes of such related pairs is 3.70 \AA rather greater than the closest distance of approach quoted above.

Hydrogen Atoms

The calculation of a final difference Fourier synthesis for the (h0l) zone (fig. 16) using the coordinates of Table 3 enables some speculations to be made on the true positions of the hydrogen atoms, as distinct from those given in Table 1. Other points of interest arising from the difference map are discussed at the end of this section.

Referring to fig. 16; contours are drawn at intervals of 0.2 electrons \AA^{-2} , the zero contour and all negative contours are shown dotted. The residual electron density is generally negative in the regions inside the carbon skeleton of the molecule. Positive regions occur more or less in the positions which hydrogen atoms are expected to occupy though some interesting discrepancies are noticeable and the peak heights are somewhat diverse.

In the five-membered ring, hydrogen atoms numbered 1 - 6 are attached in pairs to carbon atoms 3, 4 and 5. H_1 and H_2 form one peak of height $0.7e\text{\AA}^{-2}$ at a distance 0.68 \AA from C_3 . This position of the centre of gravity of H_1 and H_2 is inconsistent both with the usual

tetrahedral angle of 109.2° between CH bonds in these positions and with the assumption of symmetrical placing of the H atoms with respect to the plane $C_2 C_3 C_4$. The latter discrepancy can be reduced by assuming a smaller angle between the CH bonds. In the expected positions C_3H_2 would lie flat in the (h0l) plane and C_3H_1 would be almost perpendicular to it so that the peak corresponding to H_2 should appear at the position of C_3 , if not actually inside the five-membered ring. It is hard to escape the conclusion that the absence of a peak at C_3 (there is actually a slight minimum) indicates some departure from the expected orientation of the C_3H_1 bond. A cause of the deformation may reasonably be sought in intra or inter molecular repulsion from other hydrogen atoms. Hydrogen atoms 13 and 14 in the adjacent molecule are too far (3.8 \AA) away to cause steric hindrance. (The critical distance is 2.48 \AA , twice the Van der Waals radius of the hydrogen atom.) However, H_{14} in the same molecule lies at a distance of 2.3 \AA from the assumed position of H_2 which may be close enough for repulsion to take place. The peak H_1H_2 is displaced slightly in a direction away from H_{14} suggesting that this has occurred. The peak H_{14} is also slightly displaced but since it is also much reduced in height its position cannot be regarded as established.

Concerning the remainder of the hydrogen atoms in the five-membered ring: H_4 and H_5 appear to fall in their predicted positions while H_3 and H_6 seem to be displaced away from the molecule parallel

to its long axis. The regions between the ends of the four molecules appear to have sufficient room for such expansion if necessary, for the end hydrogen atoms are all separated by upwards of 3 Å.

In a regular five-membered ring there would be no interference between hydrogen atoms if all were placed tetrahedrally. Since we know that H_1 and H_2 are not so placed but are nearer to H_3 than they should be we may suggest with confidence that the displacement of H_3 is a secondary result of the interaction of H_2 and H_{14} .

The peak corresponding to H_7 is consistent with the expected orientation of the CH bond but is not such that accurate coordinates can be obtained from it. There is no reason to expect displacement since the hydrogen position is not closely approached by any other atom.

The assumed positions of H_8 and H_9 are 2.0 Å apart. The apparent positions in projection are 2.33 Å apart, the displacement of each being about the same. A possible method of increasing their separation would be by a movement out of the plane of the molecule with the two atoms presumably moving to opposite sides of the plane. This supposition does not seem to be borne out for the displacements are such that they could only be produced by movement of both the CH bonds towards the (010) plane. The increase in separation would then be negligible. The alternative, which is supported by the evidence, is for the CH bonds to remain more or less coplanar with the molecule while being turned out of the line of the benzene ring diagonals.

The atoms H_{10} H_{11} H_{12} appear on the difference map as a continuous L shaped ridge of electron density with the upright of the L extending nearly 1 \AA beyond the assumed position of H_{12} . The peaks are ill-defined but such evidence as they have to offer is at variance with prediction. The peak corresponding to H_{10} is displaced so as to suggest that it has been affected by the displacement of H_9 previously discussed. In fact the displacement is too great to be credible. The H_{11} peak is too close (0.80 \AA) in projection to C_{13} suggesting that the bond between them which should be practically in the (010) plane has been displaced from this plane and possibly also from the plane of the molecule. It is of interest to note that in the F_0 Fourier synthesis for this zone (fig. 11) this atom appears about to resolve at a distance of 1.05 \AA from C_{13} but slightly to one side of its expected position. The significance of such small irregularities in the one electron contour is of course open to doubt. The only other hydrogen peak indicated in fig. 11 is that of H_2 which appears in the position originally assigned to it.

Returning to the difference Fourier, the peak corresponding to H_{12} appears in the expected position but is flanked by two large spurious peaks forming part of the L. These seem to be unrelated to any hydrogen atom and are referred to again at the end of this section. H_{13} is slightly displaced so as to suggest a movement of the CH bond towards the (010) plane. The H_{14} peak is too low for any significance

to be attached to a slight departure from its expected position.

The dimensions of a benzene ring are such that the six hydrogen atoms ranged around the periphery are almost exactly at the critical distance for mutual interference. For an isolated ring one would therefore expect little or no distortion. The same applies for two rings with a common bond. However, in a staggered arrangement of rings such as 1.2.cyclopentenophenanthrene certain of the atoms would be required to approach one another to within about 2.0 \AA . It is to be expected that deformations resulting from this will upset the delicate balance of nearby atoms so that deformations will be introduced which decrease with distance from the centre of disturbance.

In 1.2.cyclopentenophenanthrene the disturbance is centred on the atoms H_8 and H_9 which are attached to carbon atoms 8 and 11 respectively. The distortion here is clearly visible in the difference Fourier, the separation in projection having been increased to 2.33 \AA . Unfortunately, although some displacements of hydrogen atoms 10, 11 and 12 are indicated, the general confusion in this region previously referred to renders estimates of their magnitude unreliable in the extreme. The most that can be said is that if they exist they are probably in the expected direction, that is, away from H_9 . In the other direction H_7 , attached to C_7 does not appear to be disturbed at all.

It seems pointless and might be misleading to extract a new set

of hydrogen coordinates from this difference Fourier. Instead the coordinates as originally assumed without regard for mutual interference have been plotted on the contour map so that the suggested shifts may be seen in their context.

Certain small regions of positive density occur unrelated to any hydrogen atoms. Several of these occur along the line of carbon-carbon bonds and may very plausibly be regarded as being due to bonding electrons unaccounted for in the structure factor calculations.

Examples of this may be seen in the bonds $C_5 - C_6$, $C_7 - C_8$, $C_9 - C_{10}$, $C_{11} - C_{12}$, $C_{14} - C_{15}$. A small such area lying close to C_{10} in the angle $C_{15} - C_{10} - C_{11}$ is probably compounded of contributions from both these bonds. None of these peaks is higher than 0.2 e\AA^{-2} . It will be noticed that with the exception of the last pair of bonds, all those mentioned lie flat in this plane. The significance of this is probably not very great, although one might perhaps expect sharper peaks where the bonds are sharply inclined to the plane of projection.

A further possible cause of some positive regions still not disposed of may be the neglect of asymmetric temperature factors. All carbon atoms have been assumed for ease of calculation to have spherically symmetrical electron density distributions. This is implicit in the use of a single scattering curve for all atoms and all structure factors. Departure of this model from the truth may be due to vibration of some of the atoms in preferred directions, in particular

perpendicular to the plane of the molecule rather than parallel to it. It is clear that the energy required to deform the bonds would be very much less in the former than in the latter mode of vibration. The effect is to broaden the atomic profile in the direction of vibration and when a spherically symmetrical profile is subtracted from it regions of positive density should appear on the vibration axis. A calculation may be performed to show the magnitude of the effect to be looked for. Let the true and assumed profiles be $\rho_1 = A \exp(-p_1 r^2)$ and $\rho_2 = A \exp(-p_2 r^2)$. The difference Fourier $\Delta \rho$ in the region of $r = 0$ is represented by the difference of these functions and peaks should appear where

$$\frac{d(\Delta \rho)}{dr} = 0$$

$$\text{i.e. } p_1 \exp(-p_1 r^2) = p_2 \exp(-p_2 r^2)$$

$$\therefore r = \pm \left[\frac{1}{p_2 - p_1} \log_e \frac{p_2}{p_1} \right]^{\frac{1}{2}}$$

$$\text{if for example } p_1 = 4 \quad p_2 = 5 \quad A = 6$$

$$r = \pm 0.47 \text{ \AA}$$

$$\Delta \rho = 0.48 \text{ e\AA}^{-2}$$

Returning to 1.2.cyclopentenophenanthrene, the only peak still to be noted lies inside the end ring between C_{12} and C_{14} . This turns out to be 0.47 \AA from C_{14} , to be 0.16 e\AA^{-2} high and to be balanced by the higher peak on the far side of C_{14} which was mentioned in connection with the hydrogen atoms 10, 11 and 12. When it is noted that the line

through these peaks and C_{14} lies at an angle of about 60° to the molecular plane, it seems quite likely that an asymmetric vibration of the atom is implied. It is also possible to imagine C_{13} as lying between two of the peaks in the L shaped ridge so that this atom would have a similar vibration axis to the previous one.

Although the above calculations are interesting they do not lead to a simple correction to the temperature factor. This is provided by Cochran (26) in the formula

$$B_j = \frac{4A \left(\frac{\partial^2 D}{\partial r^2} \right)_j}{2\pi \sum f_j s^4}$$

where B_j is the temperature factor in the relation

$$f_j = f_0 \exp\left(-\frac{B_j}{\lambda^2} \sin^2 \theta\right)$$

the suffix j referring to the j th atom. This method also has the advantage that it is not dependent on the recognition of features of the difference map at a distance from the atomic centre. Refinement of individual temperature factors was not attempted for this molecule, but the subject is further discussed in Section IV in connection with the refinement of 1.2.5.6.dibenzanthraquinone.

TABLE 7

1.2.cyclopentenophenanthrene - observed and calculated structure factors for axial and ac diagonal projections.

h	k	l	sin θ	F _o	F _c	h	k	l	sin θ	F _o	F _c
0	0	0	-	464	-	0	2	6	.505	4.2	- 6.1
0	0	1	.072	71.5	+77.9	0	2	7	.568	18.8	+23.3
0	0	2	.143	64.5	-64.0	0	2	8	.631	14.8	+18.0
0	0	3	.215	10.0	+10.7	0	2	9	.697	2.3	+ 2.2
0	0	4	.286	15.8	-20.0	0	2	10	.764	< 2.3	- 0.4
0	0	5	.358	72.0	+67.5	0	2	11	.831	< 2.1	- 2.4
0	0	6	.429	36.5	+38.1	0	2	12	.897	< 1.8	+ 0.4
0	0	7	.501	26.5	-29.9	0	2	13	.966	< 1.2	+ 1.9
0	0	8	.572	11.5	-11.4						
0	0	9	.644	7.0	+ 6.8	0	4	0	.530	4.2	- 5.2
0	0	10	.715	5.0	- 4.3	0	4	1	.535	5.3	+ 11.2
0	0	11	.787	3.0	- 3.1	0	4	2	.548	3.5	- 3.1
0	0	12	.858	3.5	+ 4.0	0	4	3	.572	5.9	-14.3
0	0	13	.930	4.5	- 5.3	0	4	4	.603	< 2.0	0.0
						0	4	5	.640	< 2.0	- 1.7
0	2	0	.265	50.5	-47.5	0	4	6	.682	< 2.0	- 0.5
0	2	1	.275	16.7	-17.0	0	4	7	.730	4.7	- 5.9
0	2	2	.301	26.6	+24.6	0	4	8	.780	6.4	- 6.1
0	2	3	.341	10.1	+11.5	0	4	9	.833	< 2.0	- 1.5
0	2	4	.391	2.2	- 0.6	0	4	10	.888	2.9	+ 3.5
0	2	5	.446	6.2	- 9.0	0	4	11	.945	< 1.2	+ 3.5

h	k	l	sin θ	F _o	F _c	h	k	l	sin θ	F _o	F _c
0	6	0	.795	23.7	-24.6	0	3	1	.404	7.3	-11.7
0	6	1	.796	8.8	-6.0	0	3	2	.422	36.0	+42.0
0	6	2	.809	2.3	+2.8	0	3	3	.451	39.0	+38.5
0	6	3	.823	1.8	+2.1	0	3	4	.490	< 1.4	+1.4
0	6	4	.846	1.8	+1.0	0	3	5	.541	3.8	+8.4
0	6	5	.872	5.9	-9.0	0	3	6	.585	6.1	-11.3
0	6	6	.902	1.8	-2.1	0	3	7	.640	10.6	+9.1
0	6	7	.940	2.3	+3.2	0	3	8	.696	18.8	+25.0
0	6	8	.979	< 1.2	+0.3	0	3	9	.758	1.8	-3.2
						0	3	10	.819	2.4	-1.6
0	1	1	.151	2.6	+1.3	0	3	11	.882	< 1.6	-0.7
0	1	2	.196	28.3	-30.5	0	3	12	.945	< 1.3	-1.5
0	1	3	.253	9.0	-7.0						
0	1	4	.316	7.6	-7.5	0	5	1	.615	< 2.2	+4.2
0	1	5	.382	16.5	-11.7	0	5	2	.676	3.5	0.0
0	1	6	.450	5.8	-4.7	0	5	3	.696	1.8	-2.6
0	1	7	.520	< 1.9	+3.0	0	5	4	.720	4.7	-6.6
0	1	8	.589	2.9	-2.7	0	5	5	.753	2.3	-2.7
0	1	9	.658	< 2.2	+0.6	0	5	6	.788	1.8	+1.1
0	1	10	.728	8.0	+10.8	0	5	7	.830	2.9	-3.2
0	1	11	.799	< 2.2	+2.1	0	5	8	.874	< 1.8	-1.4
0	1	12	.868	< 1.9	+0.6	0	5	9	.923	1.8	+3.2
0	1	13	.939	< 1.4	+0.3	0	5	10	.973	2.9	+3.3

h	k	l	sin θ	F_o	F_g	h	k	l	sin θ	F_o	F_g
0	7	1	.929	1.8	+ 3.5	2	0	$\bar{5}$.263	13.0	+15.4
0	7	2	.936	< 1.2	- 1.6	2	0	$\bar{6}$.328	42.0	-40.8
0	7	3	.950	< 1.2	- 2.1	2	0	$\bar{7}$.400	41.0	-43.2
0	7	4	.970	< 1.2	+ 2.9	2	0	$\bar{8}$.470	19.5	+20.9
0	7	5	.992	< 1.2	- 1.6	2	0	$\bar{9}$.538	3.0	- 2.1
2	0	0	.140	7.3	+ 8.7	2	0	$\bar{10}$.607	2.5	+ 0.8
2	0	1	.205	19.0	+14.5	2	0	$\bar{11}$.690	19.0	+18.7
2	0	2	.271	3.0	+ 2.1	2	0	$\bar{12}$.750	13.0	+13.3
2	0	3	.336	12.5	-13.2	2	0	$\bar{13}$.821	< 2.5	+ 1.8
2	0	4	.405	31.0	+34.8	2	0	$\bar{14}$.890	< 2.1	+ 1.5
2	0	5	.479	3.7	+ 3.2	2	0	$\bar{15}$.962	3.0	- 4.5
2	0	6	.550	18.5	-20.1	4	0	0	.275	23.0	+19.8
2	0	7	.618	8.0	+ 6.2	4	0	1	.340	< 1.8	- 1.1
2	0	8	.692	1.8	- 0.1	4	0	2	.403	13.5	+15.4
2	0	9	.762	2.7	- 1.1	4	0	3	.467	12.0	-17.0
2	0	10	.836	< 2.5	0.0	4	0	4	.533	4.0	- 4.3
2	0	11	.906	< 2.1	- 0.7	4	0	5	.605	5.0	+ 6.7
2	0	12	.978	2.0	+ 2.4	4	0	6	.675	< 2.8	- 0.9
2	0	$\bar{1}$.092	< 0.9	+ 0.5	4	0	7	.743	10.0	-10.8
2	0	$\bar{2}$.089	22.5	-19.0	4	0	8	.814	< 2.7	- 1.9
2	0	$\bar{3}$.136	21.5	+21.9	4	0	9	.881	< 2.2	+ 0.2
2	0	$\bar{4}$.196	28.8	-31.1	4	0	10	.950	3.0	- 4.3

h	k	l	sin θ	F _o	F _c	h	k	l	sin θ	F _o	F _c
4	0	$\bar{1}$.225	46.5	+44.8	6	0	6	.805	< 2.7	+ 1.1
4	0	$\bar{2}$.187	170.0	-172.0	6	0	7	.870	2.3	- 4.9
4	0	$\bar{3}$.169	79.0	-72.7	6	0	8	.942	2.5	- 3.3
4	0	$\bar{4}$.181	23.5	+22.5	6	0	$\bar{1}$.360	15.0	- 9.6
4	0	$\bar{5}$.216	53.2	-54.1	6	0	$\bar{2}$.315	8.0	+ 0.4
4	0	$\bar{6}$.269	5.5	+ 7.2	6	0	$\bar{3}$.276	7.5	+ 6.6
4	0	$\bar{7}$.329	42.5	-42.2	6	0	$\bar{4}$.254	6.4	+ 1.7
4	0	$\bar{8}$.390	51.0	-51.8	6	0	$\bar{5}$.252	11.8	-10.8
4	0	$\bar{9}$.454	6.3	+ 7.0	6	0	$\bar{6}$.271	30.0	+30.4
4	0	$\bar{10}$.519	2.6	- 2.5	6	0	$\bar{7}$.305	21.5	-20.9
4	0	$\bar{11}$.588	13.5	-12.3	6	0	$\bar{8}$.350	8.0	+ 4.8
4	0	$\bar{12}$.658	10.0	+10.8	6	0	$\bar{9}$.401	42.5	+41.6
4	0	$\bar{13}$.726	11.5	+12.8	6	0	$\bar{10}$.460	1.2	- 1.9
4	0	$\bar{14}$.794	4.5	- 3.4	6	0	$\bar{11}$.520	12.5	+13.7
4	0	$\bar{15}$.865	3.3	+ 2.1	6	0	$\bar{12}$.586	12.0	+14.4
4	0	$\bar{16}$.931	< 1.7	- 1.4	6	0	$\bar{13}$.648	14.5	-16.1
6	0	0	.415	3.0	+ 7.4	6	0	$\bar{14}$.713	18.0	-19.0
6	0	1	.480	12.0	+ 9.5	6	0	$\bar{15}$.783	3.2	- 4.3
6	0	2	.540	13.3	-12.0	6	0	$\bar{16}$.845	< 2.5	- 1.4
6	0	3	.602	6.8	+ 4.8	6	0	$\bar{17}$.910	1.9	+ 2.7
6	0	4	.667	13.0	-12.1	8	0	0	.550	8.0	- 8.8
6	0	5	.735	22.8	-21.2	8	0	1	.613	8.5	- 8.2

h	k	l	sin θ	F_o	F_c	h	k	l	sin θ	F_o	F_c
8	0	2	.674	11.0	+ 9.5	8	0	$\overline{17}$.837	< 2.4	+ 1.1
8	0	3	.734	22.8	+25.1	8	0	$\overline{18}$.900	< 2.0	- 1.6
8	0	4	.796	9.0	+ 7.9	8	0	$\overline{19}$.970	< 1.1	+ 0.3
8	0	5	.865	4.3	+ 5.2	10	0	0	.689	5.8	+ 6.7
8	0	6	.932	1.4	- 2.1	10	0	1	.749	2.3	+ 1.9
8	0	7	.995	< 1.1	- 1.7	10	0	2	.810	22.0	+23.9
8	0	$\overline{1}$.496	12.5	+ 9.0	10	0	3	.870	13.5	+14.2
8	0	$\overline{2}$.448	37.0	+37.4	10	0	4	.931	5.5	- 8.1
8	0	$\overline{3}$.399	3.5	- 5.6	10	0	$\overline{1}$.634	6.3	- 5.5
8	0	$\overline{4}$.366	13.0	-12.0	10	0	$\overline{2}$.585	3.8	- 4.6
8	0	$\overline{5}$.344	23.8	-19.3	10	0	$\overline{3}$.531	21.0	+17.8
8	0	$\overline{6}$.335	26.0	-24.6	10	0	$\overline{4}$.492	3.3	+ 1.9
8	0	$\overline{7}$.340	14.0	+17.0	10	0	$\overline{5}$.460	5.3	- 5.8
8	0	$\overline{8}$.361	3.3	- 1.3	10	0	$\overline{6}$.434	11.3	+ 9.1
8	0	$\overline{9}$.393	12.8	-12.9	10	0	$\overline{7}$.420	9.0	+10.1
8	0	$\overline{10}$.432	4.5	+ 3.4	10	0	$\overline{8}$.419	7.0	- 9.5
8	0	$\overline{11}$.481	12.3	+ 9.5	10	0	$\overline{9}$.429	21.5	+22.6
8	0	$\overline{12}$.536	6.0	+ 8.1	10	0	$\overline{10}$.450	2.0	+ 2.1
8	0	$\overline{13}$.593	10.0	+10.8	10	0	$\overline{11}$.480	15.0	-15.0
8	0	$\overline{14}$.652	2.1	- 1.3	10	0	$\overline{12}$.520	9.5	+ 9.0
8	0	$\overline{15}$.715	13.0	-13.2	10	0	$\overline{13}$.565	2.4	- 0.2
8	0	$\overline{16}$.775	5.0	+ 2.3	10	0	$\overline{14}$.615	2.0	+ 0.7

h	k	l	sin θ	F _o	F _o	h	k	l	sin θ	F _o	F _o
10	0	$\overline{15}$.670	4.8	+ 2.4	12	0	$\overline{14}$.606	10.5	+ 9.3
10	0	$\overline{16}$.723	< 2.8	- 1.3	12	0	$\overline{15}$.649	20.0	+18.5
10	0	$\overline{17}$.779	< 2.7	+ 1.6	12	0	$\overline{16}$.695	2.6	- 2.5
10	0	$\overline{18}$.840	1.9	+ 1.5	12	0	$\overline{17}$.742	2.6	+ 2.8
10	0	$\overline{19}$.904	3.4	+ 2.2	12	0	$\overline{18}$.796	4.5	- 3.5
10	0	$\overline{20}$.971	3.0	- 2.8	12	0	$\overline{19}$.854	2.0	- 2.8
12	0	0	.829	12.5	-13.2	12	0	$\overline{20}$.914	4.3	+ 4.7
12	0	1	.890	17.5	-19.2	12	0	$\overline{21}$.971	< 1.0	+ 0.9
12	0	2	.950	2.0	+ 0.3	14	0	0	.964	8.8	-12.2
12	0	$\overline{1}$.775	4.0	+ 6.0	14	0	$\overline{1}$.910	2.3	- 1.3
12	0	$\overline{2}$.722	2.7	+ 2.6	14	0	$\overline{2}$.858	< 2.4	- 2.2
12	0	$\overline{3}$.666	5.5	- 4.8	14	0	$\overline{3}$.801	2.4	+ 2.1
12	0	$\overline{4}$.624	34.8	-32.9	14	0	$\overline{4}$.755	2.6	+ 1.4
12	0	$\overline{5}$.585	26.3	-25.3	14	0	$\overline{5}$.714	10.5	-10.6
12	0	$\overline{6}$.551	5.5	+ 7.3	14	0	$\overline{6}$.675	< 1.0	+ 1.1
12	0	$\overline{7}$.527	6.8	+ 8.7	14	0	$\overline{7}$.635	4.8	+ 5.0
12	0	$\overline{8}$.510	7.5	+ 5.8	14	0	$\overline{8}$.616	3.3	- 3.9
12	0	$\overline{9}$.503	26.3	+22.9	14	0	$\overline{9}$.598	2.0	- 1.7
12	0	$\overline{10}$.506	30.5	+25.6	14	0	$\overline{10}$.588	1.4	- 0.8
12	0	$\overline{11}$.519	9.0	+10.1	14	0	$\overline{11}$.586	22.0	-21.9
12	0	$\overline{12}$.541	4.0	+ 6.1	14	0	$\overline{12}$.592	6.0	- 4.7
12	0	$\overline{13}$.570	10.5	-11.5	14	0	$\overline{13}$.608	11.0	+10.6

h	k	l	sin θ	F _o	F _c	h	k	l	sin θ	F _o	F _c
4	0	$\overline{14}$.630	6.8	- 8.7	16	0	$\overline{16}$.720	7.5	- 5.7
4	0	$\overline{15}$.660	11.3	- 9.6	16	0	$\overline{17}$.748	28.0	-30.3
4	0	$\overline{16}$.694	28.8	-30.4	16	0	$\overline{18}$.782	4.8	- 4.7
4	0	$\overline{17}$.732	14.8	-16.6	16	0	$\overline{19}$.821	1.9	+ 0.9
4	0	$\overline{18}$.776	10.5	+12.4	16	0	$\overline{20}$.865	< 2.4	+ 0.5
4	0	$\overline{19}$.828	4.3	+ 5.4	16	0	$\overline{21}$.908	1.9	+ 3.5
4	0	$\overline{20}$.880	1.7	0.0	16	0	$\overline{22}$.960	3.8	- 5.8
4	0	$\overline{21}$.930	7.0	- 7.9	18	0	$\overline{5}$.980	2.0	- 3.5
5	0	$\overline{2}$.997	< 1.3	+ 2.2	18	0	$\overline{6}$.935	< 1.9	- 0.3
5	0	$\overline{3}$.937	2.1	- 4.3	18	0	$\overline{7}$.895	2.3	+ 2.9
5	0	$\overline{4}$.892	< 2.2	+ 2.3	18	0	$\overline{8}$.860	< 2.0	- 3.5
5	0	$\overline{5}$.848	< 2.5	+ 2.0	18	0	$\overline{9}$.827	< 2.0	+ 1.8
5	0	$\overline{6}$.803	7.3	+ 5.8	18	0	$\overline{10}$.800	< 2.2	+ 0.4
5	0	$\overline{7}$.768	10.0	+10.2	18	0	$\overline{11}$.780	< 2.2	- 4.7
5	0	$\overline{8}$.735	2.6	+ 3.4	18	0	$\overline{12}$.765	< 2.2	- 2.2
5	0	$\overline{9}$.710	7.5	+ 5.9	18	0	$\overline{13}$.756	7.0	+ 7.4
5	0	$\overline{10}$.690	10.5	+12.3	18	0	$\overline{14}$.754	5.0	+ 3.3
5	0	$\overline{11}$.677	11.0	- 5.1	18	0	$\overline{15}$.759	5.0	- 4.4
5	0	$\overline{12}$.672	27.3	-27.0	18	0	$\overline{16}$.769	< 2.0	+ 0.2
5	0	$\overline{13}$.673	8.0	- 6.0	18	0	$\overline{17}$.786	2.5	- 2.4
5	0	$\overline{14}$.684	1.8	- 0.2	18	0	$\overline{18}$.808	20.3	+21.1
5	0	$\overline{15}$.699	9.5	+10.4	18	0	$\overline{19}$.838	26.0	+24.2

h	k	l	sin θ	P_o	P_o	h	k	l	sin θ	P_o	P_o
18	0	$\overline{20}$.872	2.3	- 3.4	22	0	$\overline{17}$.916	1.8	- 0.8
18	0	$\overline{21}$.908	< 2.0	+ 0.3	22	0	$\overline{18}$.920	2.1	- 3.7
18	0	$\overline{22}$.950	1.6	- 0.1	22	0	$\overline{19}$.929	2.5	+ 5.7
20	0	$\overline{8}$.985	0.9	+ 2.0	22	0	$\overline{20}$.943	3.0	- 1.0
20	0	$\overline{9}$.948	< 1.7	+ 2.6	22	0	$\overline{21}$.963	7.8	-10.4
20	0	$\overline{10}$.918	3.0	+ 0.7	22	0	$\overline{22}$.987	< 1.0	+ 1.5
20	0	$\overline{11}$.891	3.0	+ 2.5	1	1	0	.148	74.9	-75.9
20	0	$\overline{12}$.868	2.2	+ 0.5	3	1	0	.245	5.0	+ 1.7
20	0	$\overline{13}$.852	1.6	- 3.0	5	1	0	.368	40.3	+33.2
20	0	$\overline{14}$.841	5.8	+ 8.4	7	1	0	.500	6.6	- 2.0
20	0	$\overline{15}$.836	< 2.0	+ 1.2	9	1	0	.635	5.5	- 7.0
20	0	$\overline{16}$.837	1.9	- 2.9	11	1	0	.770	< 1.1	- 3.0
20	0	$\overline{17}$.843	< 2.0	- 0.9	13	1	0	.905	11.0	+ 8.7
20	0	$\overline{18}$.856	< 2.0	- 0.7	2	2	0	.297	8.2	- 4.4
20	0	$\overline{19}$.875	10.5	+11.5	4	2	0	.380	59.0	-49.6
20	0	$\overline{20}$.900	3.4	+ 3.6	6	2	0	.490	10.2	-12.3
20	0	$\overline{21}$.926	< 1.9	+ 0.3	8	2	0	.610	10.0	+10.0
20	0	$\overline{22}$.960	3.2	+ 2.3	10	2	0	.738	3.7	+ 0.9
22	0	$\overline{12}$.978	< 1.3	- 1.6	12	2	0	.868	4.9	+ 8.1
22	0	$\overline{13}$.954	< 1.6	+ 2.1	1	3	0	.400	5.9	- 8.4
22	0	$\overline{14}$.937	< 1.8	0.0	3	3	0	.445	2.9	- 2.0
22	0	$\overline{15}$.925	2.0	+ 1.6	5	3	0	.524	9.1	-12.2
22	0	$\overline{16}$.919	< 2.0	+ 1.4	7	3	0	.612	3.8	+ 7.3

h	k	l	sin θ	F_o	F_c	h	k	l	sin θ	F_o	F_c
9	3	0	.735	2.6	- 2.0	2	1	0	.190	7.2	- 4.9
11	3	0	.855	< 1.0	+ 0.9	4	1	0	.305	40.6	-32.6
13	3	0	.930	< 0.9	+ 0.9	6	1	0	.434	6.1	- 6.4
2	4	0	.544	6.7	+ 7.7	8	1	0	.567	1.8	- 1.2
4	4	0	.594	18.8	+20.5	10	1	0	.701	2.7	- 3.5
6	4	0	.670	8.9	+ 8.8	12	1	0	.837	4.8	+ 5.3
8	4	0	.761	6.4	- 9.0	14	1	0	.974	7.5	+11.3
10	4	0	.866	< 1.0	- 0.9	1	2	0	.272	3.4	+ 3.0
12	4	0	.980	1.6	- 2.3	3	2	0	.334	21.0	+15.0
1	5	0	.660	19.0	+23.9	5	2	0	.433	15.2	+ 5.5
3	5	0	.688	4.2	+ 5.6	7	2	0	.550	2.9	+ 0.9
5	5	0	.741	7.0	- 6.8	9	2	0	.674	19.2	+16.8
7	5	0	.815	1.4	+ 1.2	11	2	0	.802	2.1	- 2.5
9	5	0	.904	< 0.8	+ 2.7	13	2	0	.935	< 0.7	+ 2.0
2	6	0	.800	6.6	- 7.5	2	3	0	.417	5.6	+ 7.5
4	6	0	.835	2.0	+ 0.7	4	3	0	.476	17.3	-16.4
6	6	0	.890	< 1.0	- 0.4	6	3	0	.571	2.7	- 1.5
8	6	0	.961	< 0.8	+ 0.2	8	3	0	.678	8.9	-12.1
1	7	0	.922	4.1	+ 2.3	10	3	0	.795	10.7	-10.7
3	7	0	.942	4.2	- 4.3	12	3	0	.916	2.6	- 3.9
5	7	0	.981	1.5	- 2.4	1	4	0	.530	12.2	+16.9
						3	4	0	.565	3.4	- 6.0

h	k	l	$\sin\theta$	F_c	F_o	h	k	l	$\sin\theta$	F_c	F_o
4	0		.629	12.7	+13.0	13	1	$\overline{13}$.609	< 0.8	- 0.5
4	0		.713	7.9	+ 9.8	15	1	$\overline{15}$.699	1.7	- 4.6
4	0		.812	5.1	+ 4.5	17	1	$\overline{17}$.790	< 0.8	+ 1.6
4	0		.922	< 1.0	+ 1.2	19	1	$\overline{19}$.879	13.8	-13.4
						21	1	$\overline{21}$.970	1.4	+ 2.3
5	0		.670	6.8	+ 9.9						
5	0		.711	8.0	- 6.9	2	2	$\overline{2}$.279	1.9	0.0
5	0		.776	2.9	+ 0.7	4	2	$\overline{4}$.320	22.8	+19.3
5	0		.857	1.4	- 1.4	6	2	$\overline{6}$.381	17.8	-16.6
5	0		.951	< 0.8	+ 0.3	8	2	$\overline{8}$.453	17.5	-15.0
						10	2	$\overline{10}$.528	1.7	+ 1.1
6	0		.791	11.4	-15.8	12	2	$\overline{12}$.609	12.5	- 9.7
6	0		.815	0.8	- 0.4	14	2	$\overline{14}$.693	7.5	+ 8.4
6	0		.860	2.8	- 3.7	16	2	$\overline{16}$.778	4.8	+ 5.7
6	0		.924	< 0.9	- 0.9	18	2	$\overline{18}$.865	1.1	- 3.2
						20	2	$\overline{20}$.954	3.5	+ 2.9
7	0		.930	4.2	+ 0.8						
7	0		.960	4.7	+ 6.9						
						1	3	$\overline{1}$.395	6.6	+ 8.8
1	$\overline{1}$.139	71.0	-72.8	3	3	$\overline{3}$.418	10.0	+14.3
1	$\overline{3}$.191	35.2	-29.3	5	3	$\overline{5}$.455	11.8	+17.3
1	$\overline{5}$.264	16.1	-15.1	7	3	$\overline{7}$.508	5.1	- 5.3
1	$\overline{7}$.347	24.6	+15.0	9	3	$\overline{9}$.572	1.9	- 2.6
1	$\overline{9}$.433	4.6	- 4.6	11	3	$\overline{11}$.640	< 0.9	- 1.1
1	$\overline{11}$.520	13.1	+ 8.4	13	3	$\overline{13}$.714	< 0.9	- 1.4

k	l	sin δ	F _o	F _c	h	k	l	sin δ	F _o	F _c
3	$\overline{15}$.791	< 0.9	+ 1.4	2	6	$\overline{2}$.792	5.3	+ 8.2
3	$\overline{17}$.873	1.3	- 0.2	4	6	$\overline{4}$.808	1.5	- 1.0
3	$\overline{19}$.955	1.2	- 1.7	6	6	$\overline{6}$.836	1.0	- 1.9
4	$\overline{2}$.532	1.1	- 3.5	8	6	$\overline{8}$.869	< 0.7	0.0
4	$\overline{4}$.557	14.7	-14.7	10	6	$\overline{10}$.911	2.7	- 4.3
4	$\overline{6}$.593	7.1	+ 7.3	12	6	$\overline{12}$.960	1.2	- 4.2
4	$\overline{8}$.641	7.4	+ 6.8	1	7	$\overline{1}$.919	2.5	+ 1.0
4	$\overline{10}$.697	3.8	+ 3.6	3	7	$\overline{3}$.929	2.5	+ 5.8
4	$\overline{12}$.762	6.6	+ 7.0	5	7	$\overline{5}$.947	2.0	+ 4.3
4	$\overline{14}$.828	5.4	- 5.9	7	7	$\overline{7}$.975	3.7	- 3.1
4	$\overline{16}$.900	1.1	- 1.1	2	1	$\overline{2}$.160	12.8	+12.8
4	$\overline{18}$.977	< 0.4	+ 0.4	4	1	$\overline{4}$.225	38.4	-30.7
5	$\overline{1}$.657	12.7	+16.5	6	1	$\overline{6}$.304	11.4	-11.2
5	$\overline{3}$.670	10.0	-10.2	8	1	$\overline{8}$.390	28.6	-19.6
5	$\overline{5}$.696	< 0.9	- 4.3	10	1	$\overline{10}$.476	9.3	-10.1
5	$\overline{7}$.731	1.4	0.0	12	1	$\overline{12}$.564	< 0.8	+ 1.2
5	$\overline{9}$.777	1.1	+ 0.4	14	1	$\overline{14}$.653	< 0.8	+ 0.9
5	$\overline{11}$.829	0.9	0.0	16	1	$\overline{16}$.743	1.4	- 0.9
5	$\overline{13}$.886	< 0.7	+ 1.0	18	1	$\overline{18}$.834	2.9	- 2.5
5	$\overline{15}$.953	< 0.6	+ 1.6	20	1	$\overline{20}$.925	5.3	- 4.4

k	l	sin θ	F _o	F _e	h	k	l	sin θ	F _o	F _e
2	$\bar{1}$.266	2.4	- 2.1	1	4	$\bar{1}$.527	2.1	+ 2.3
2	$\bar{3}$.296	14.7	+17.0	3	4	$\bar{3}$.542	9.1	-12.6
2	$\bar{5}$.349	9.9	-12.6	5	4	$\bar{5}$.574	14.3	-17.1
2	$\bar{7}$.415	45.2	+33.9	7	4	$\bar{7}$.615	3.7	+ 5.2
2	$\bar{9}$.490	1.9	- 1.7	9	4	$\bar{9}$.668	4.0	- 9.0
2	$\bar{11}$.569	13.1	-10.6	11	4	$\bar{11}$.727	5.9	- 5.9
2	$\bar{13}$.650	0.9	- 1.9	13	4	$\bar{13}$.793	< 0.9	+ 0.6
2	$\bar{15}$.735	2.5	+ 2.3	15	4	$\bar{15}$.864	< 0.8	- 2.7
2	$\bar{17}$.822	1.4	- 1.1	17	4	$\bar{17}$.940	< 0.6	+ 1.6
2	$\bar{19}$.909	1.3	- 0.7						
2	$\bar{21}$.996	0.8	- 1.8	2	5	$\bar{2}$.662	10.9	+12.9
					4	5	$\bar{4}$.681	1.2	+ 1.0
3	$\bar{2}$.404	1.2	+ 0.7	6	5	$\bar{6}$.712	3.7	+ 8.3
3	$\bar{4}$.435	17.0	+16.0	8	5	$\bar{8}$.753	2.7	+ 0.1
3	$\bar{6}$.480	5.3	- 4.7	10	5	$\bar{10}$.801	< 0.9	- 1.7
3	$\bar{8}$.539	4.6	+ 6.6	12	5	$\bar{12}$.856	< 0.8	+ 0.2
3	$\bar{10}$.604	1.7	+ 1.4	14	5	$\bar{14}$.917	< 0.7	- 1.0
3	$\bar{12}$.676	15.0	+19.5	16	5	$\bar{16}$.984	3.8	- 5.9
3	$\bar{14}$.752	7.9	- 9.8						
3	$\bar{16}$.840	3.8	+ 4.4	1	6	$\bar{1}$.788	2.9	- 3.1
3	$\bar{18}$.914	2.0	+ 1.1	3	6	$\bar{3}$.799	3.2	- 2.5
3	$\bar{20}$.996	1.8	+ 3.9	5	6	$\bar{5}$.819	< 0.8	- 0.6

h	k	l	sin θ	F_0	F_0
7	6	$\bar{7}$.850	< 0.7	- 2.2
9	6	$\bar{9}$.889	< 0.7	+ 1.1
11	6	$\bar{11}$.935	2.2	+ 2.9
13	6	$\bar{13}$.987	1.3	+ 2.5
2	7	$\bar{2}$.922	< 0.8	0.0
4	7	$\bar{4}$.936	< 0.7	- 0.3
6	7	$\bar{6}$.959	1.6	0.0
8	7	$\bar{8}$.990	2.2	+ 1.6

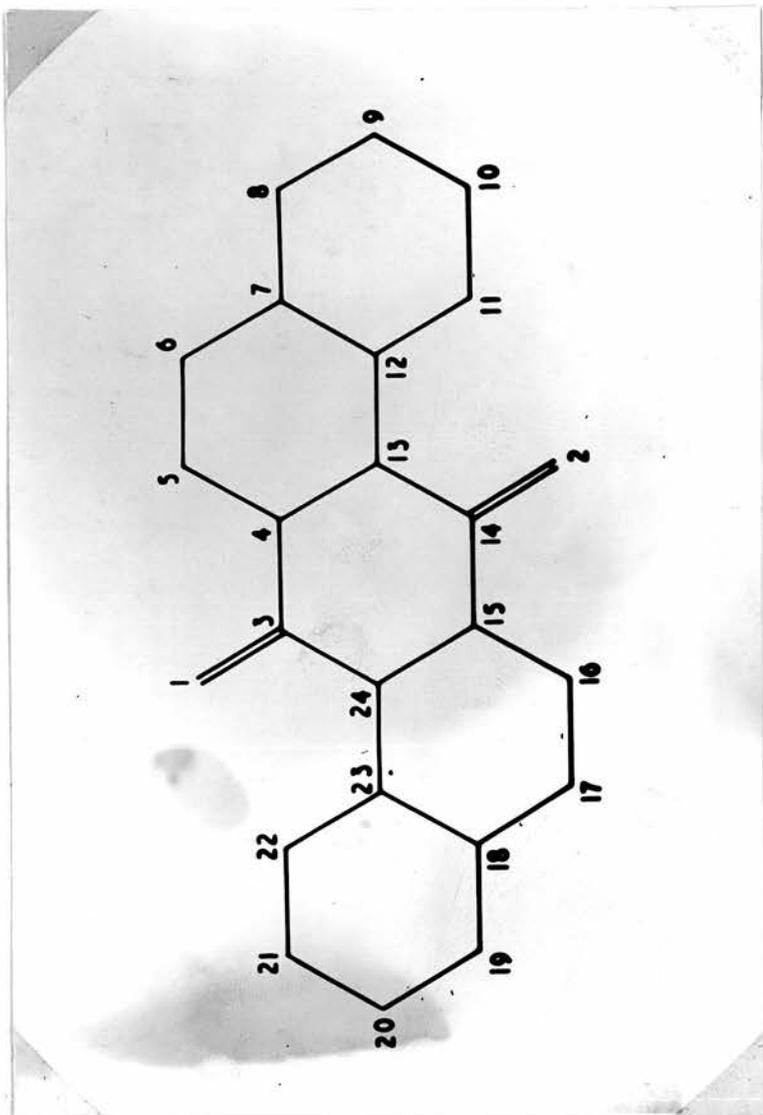


Fig. 17

1-2-5-6-dibenzanthraquinone, molecular skeleton.

IV 1.2.5.6.dibenzanthraquinone. $C_{22}H_{12}O_2$

(1) Unit cell and space group

1.2.5.6.dibenzanthraquinone (fig. 17) crystallizes in orange needles. The crystals are orthorhombic and the b axis is parallel to the length of the needles. As the faces are not well developed and there is a strong tendency for mechanical twinning to take place parallel to the needle axis, it was difficult to find a crystal of any thickness. Although this permitted measurements to be made of intense reflexions many of the weaker reflexions were not observed at all. The (h0l) projection in particular suffers from this defect. b axis Weissenberg photographs were taken using a crystal 0.7 mm long by 0.02 mm thick approximately. a and c axis photographs were taken with a larger crystal of dimensions 0.31 by 0.15 by 0.10 mm. The cell dimensions are

$$a = 28.6 \text{ \AA}$$

$$b = 3.85 \text{ \AA}$$

$$c = 12.90 \text{ \AA}$$

$$\text{Volume of unit cell} = 1419 \text{ \AA}^3$$

$$\text{Calculated density} = 1.44 \text{ gm cm}^{-3}$$

$$\text{Measured density} = 1.47 \text{ gm cm}^{-3} \text{ by flotation in carbon}$$

tetrachloride and methylated spirit

$$\text{Molecular weight} = 308.32$$

There are four molecules per unit cell and $F(000) = 640$.

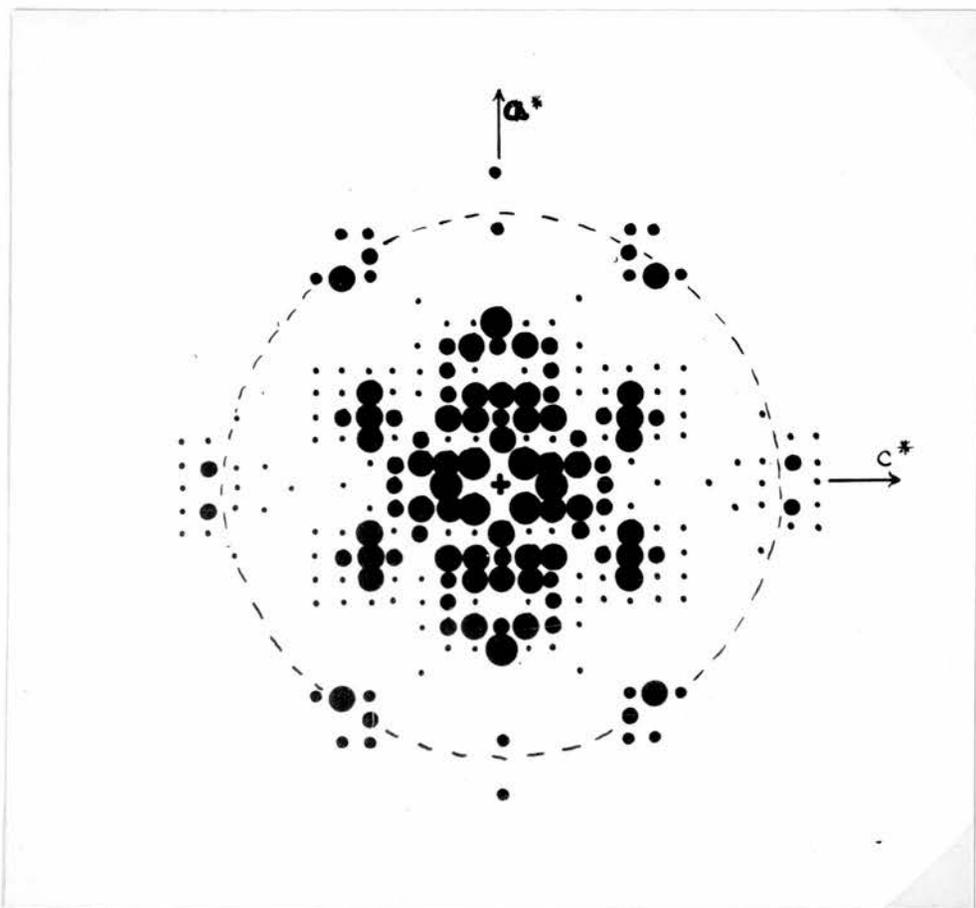


Fig. 18

1.2.5.6. dibenzanthraquinone, (0 1 0) weighted reciprocal lattice.

Halvings observed are (h0l) when h is odd

(0kl) when l is odd.

The space group is therefore either D_{2h}^4 - Pbcm No. 57 or C_{2v}^5 - Pca2₁ No. 29, the former being centrosymmetric. Intensity data (Table 10) was collected from Weissenberg photographs taken about the three principal axes and correlated using the high film to film ratio as described in Section III(1).

The b axis reciprocal lattice (Fig. 18) shows six well defined benzene ring groups the positions of which indicate that the molecule lies almost flat in the (0k) plane and that its length is approximately parallel to the a axis in this projection.

The statistical test for centrosymmetry suggested by Howells, Phillips and Rogers (27) gave a distribution curve for the structure factors of the (h0l) zone which strongly suggested that the projection possessed a centre of symmetry. On this assumption the space group is Pbcm and the representative molecule may be placed either at (0,0,0) or $(\frac{1}{4}, 0, 0)$. Either way a fit may be found for the (h,0,0) reflexions except that the (2,0,0) reflexion has a calculated value of about 150 compared with the maximum observed value of 30. To obtain agreement for this plane it is necessary for the centre of the molecule to lie very close to, but not exactly at, $\frac{1}{8} \underline{a}$, which in turn necessitates the adoption of the non-centrosymmetric space group Pca2₁. In fact packing considerations rule out the space group Pbcm since the existence of the

mirror plane requires parts of adjacent molecules to approach within 1.5 Å of one another. The usual minimum separation observed is in the region of 3.5 Å .

IV (ii) 1.2.5.6.dibenzanthraquinone, crystal and molecular structure. x and z coordinates

From the (h0l) weighted reciprocal lattice it was evident that the plane of the molecule was not far from the (010). The benzene ring derived from this pattern was ambiguous to the extent that a rotation of about 20° about the a axis was possible and also an inclination of the axis of the ring of about 5° to the a axis in projection. Packing considerations in the long flat cell required that the long axis of the molecule should be roughly parallel to the a axis. The limitation of $\pm 5^\circ$ was accepted for the fitting of preliminary trial structures to the (h,0,0) reflexions.

The position of the molecule in the z direction is arbitrary so that it was only necessary to find the x coordinate of the molecular centre. For this purpose 16 (h,0,0) reflexions were available so that the fitting could be done with some precision. The smallness of the (2,0,0) reflexion showed that the centre was close to $a/8$. However, other reflexions with $h = 4n + 2$ were large indicating some displacement from this position. The centre was finally fixed at 0.107 \AA . Fitting of the (0,0,1) reflexions required some tilting and turning of the molecule which tended to worsen the agreement of the (h,0,0) reflexions. This was taken to indicate some departure of the molecule from the symmetry implied by its structural formula. Rather than explore a series of bent structures at this stage it was decided to seek

a reasonable compromise position using the plane structure and to refine it by means of F_0 Fourier syntheses. A calculation of 81 large planes of the zone gave a reliability index of 0.394. 54 of these were included in an F_0 Fourier synthesis which gave a well resolved picture of the three central rings. The atoms in the end rings were resolved but the peaks were less regular and generally lower than in the central rings. The end rings themselves were also somewhat distorted. However, coordinates taken from this Fourier gave a reliability index of 0.337 so that prospects of refinement seemed good. A second F_0 Fourier was calculated whereupon it was seen that some errors observed in the previous synthesis had tended to persist. In particular spurious peaks appeared between the quinones and the end rings in such positions as to give the impression of badly formed benzene rings. Changes in coordinates from the previous set were generally slight suggesting that improvement of reliability might be small. These considerations cast some doubt on the correctness of the structure. It was decided to investigate a different orientation which was obtainable from the original by completing the badly formed rings and identifying two other peaks with the quinones. This was equivalent to reversing the positive direction of the z axis. Structure factors were calculated in parallel for the two structures, giving reliabilities for the old and new orientations of 0.298 and 0.280 respectively. This was taken as sufficient justification for

changing to the new orientation.

From this point onwards refinement of this zone was carried out on the Ferranti 'Pegasus' Electronic Computer at Northampton Polytechnic with the kind assistance of members of the Chemical Crystallography Department of University College, London.

The method used for the most part was that of Least Squares (28,29). After the calculation of the structure factors a series of partial differential equations are set up in terms of $F_o - F_c$ and the coordinate shifts required to reduce this difference to zero. The form of the equations is:-

$$\begin{aligned} \Delta F(h0l) = & \frac{\partial F(h0l)}{\partial x_1} \Delta x_1 + \dots + \frac{\partial F(h0l)}{\partial x_n} \Delta x_n \\ & + \frac{\partial F(h0l)}{\partial z_1} \Delta z_1 + \dots + \frac{\partial F(h0l)}{\partial z_n} \Delta z_n \end{aligned}$$

There is one equation for each structure factor to be used in the refinement. These should number at least twice the number of individual coordinates to be refined. The observational equations are reduced to the normal equations by a process of least squares and the latter are solved for Δx and Δz .

Although by suitable approximations the work may be kept within reasonable bounds, one cycle of refinement using a desk calculating machine might take a week or more. Using an electronic digital computer with a standard crystallographic programme it is possible, after spending perhaps two hours punching tapes of structure factors, cell

and space group data, to perform cycles of least squares refinement at the rate of one cycle in 40 minutes. The degree of accuracy obtainable is also considerably greater than with manual computation.

Starting with the x and z coordinates which gave a reliability index of 0.280 for the (h0l) zone, three cycles of refinement were computed. The improvement produced by the first cycle was small, about 1.6%, but after the second cycle the reliability improved to 0.230. The reason for this sudden improvement seemed to be that the coordinate shifts at first produced were much too large and that these were largely corrected for by smaller reversed shifts in the second cycle.

After the second cycle it was thought advisable to compute a difference Fourier and this was done using the structure factors which were calculated from the second cycle coordinates and which were the starting point of the third cycle. At this point the third cycle coordinates had been obtained but structure factors not calculated for them. The purpose of the difference Fourier was partly to check that the refinement was not being forced in the wrong direction. This might be recognizable as the appearance of large peaks where none should be. Since no such peaks were visible it was possible to use the difference map, both to improve the coordinates and to calculate changes in the individual atomic temperature factors. The latter had been assigned arbitrarily according to atom type, i.e. oxygen, carbon bonded to three other carbon atoms or carbon bonded to two carbon and one

hydrogen atom, and some changes were to be expected.

Changes of temperature factor were estimated following the formula of Cochran (26) namely

$$\Delta B_j = \frac{4 A \left(\frac{\partial^2 D}{\partial r^2} \right)}{2\pi \sum (f_j s^4)}$$

where B is the constant in the relation

$$f_j = f \exp\left(\frac{-B}{\lambda^2} \sin^2 \theta\right)$$

the suffix j referring to the jth atom.

The curvature $\frac{\partial^2 D}{\partial r^2}$ was estimated by drawing profiles of the difference map through the atomic positions. In view of the uncertainties of this procedure it was decided to compare ΔB 's for chemically identical pairs of atoms and to make these equal if at all plausible. Changes of B indicated for atoms where a large gradient suggested great positional inaccuracy were accepted with caution if at all. The values of B adopted were not changed during subsequent refinement and are given with the final coordinates in Table 8. These are average temperature factors and take no account of anisotropic vibrations.

The coordinates obtained from the difference Fourier were now combined with those from the third cycle of least squares in such a way as to preserve as far as possible the symmetry of the molecule. Hydrogen atom coordinates were assigned using a C - H distance 1.08 Å before proceeding with the refinement.

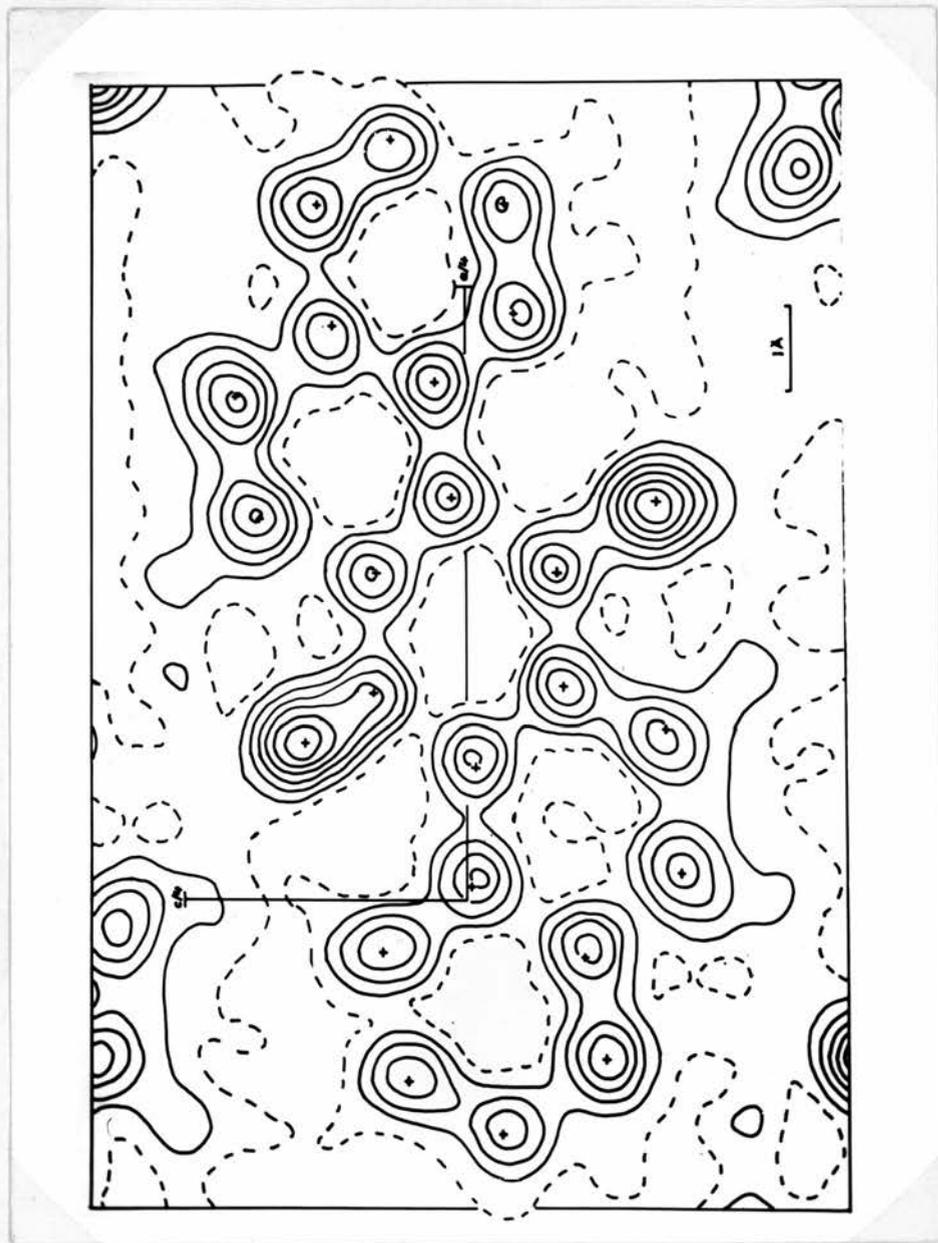


Fig. 12

1.2.5.6-dibenzanthraquinone (0 1 0) Fourier projection.

The 1 eÅ⁻² contour is shown dotted.

The combined effect of these modifications was to improve the reliability to 0.190. After the fourth cycle the computer indicated changes both of scale and overall temperature factor. These were regarded with suspicion in view of the inclusion of a number of unobserved reflexions in the calculations. A scale factor 1.04 was finally settled on and a reliability of 0.205 was obtained for the fourth cycle coordinates. This setback suggested that the refinement had begun to oscillate again. To correct for this the mean coordinates from the fourth and fifth cycles were taken and in subsequent cycles only half the indicated shifts were applied. The compromise coordinates produced a reliability of 0.160. The sixth cycle reduced it to 0.152 and the seventh to 0.135. The final coordinates for this projection are the product of the eighth cycle of refinement, the final structure factor tables the product of the seventh cycle coordinates. These structure factors were used to compute a final F_o Fourier synthesis including 110 of the 111 visible reflexions (fig. 19).

x and y coordinates

Although the refined x and z coordinates gave a molecule of peculiar shape with many bonds abnormally long or short in projection they were thought sufficiently good for the x coordinates to be used unaltered during the search for an approximate structure in the (hk0) projection. From the (h0l) projection the molecule was obviously bent but the form of bending was unclear. Such evidence as there was

was contradictory or even misleading, and the x coordinates were such that it was not possible to construct regular benzene rings for the $(hk0)$ projection.

The first possibilities to be explored were those in which bending of the molecule was consistent with a molecular centre of symmetry. Fitting of the four $(0,k,0)$ reflexions presented no problem but it proved impossible to obtain agreement for more than a very few of the large general reflexions. Unsymmetrical positions of the oxygen atoms were also tried without success. The best reliability index obtained was 0.43.

The aspect of the quinone bonds in the $(h0l)$ projection seemed slightly to favour a bending of the molecule about the line of these bonds. The quinone bonds would tend to be bent in the opposite direction and being no longer parallel to one another they would be of different lengths in projection. The observed projected lengths were 0.95 \AA and 1.30 \AA for bonds 1 - 3 and 2 - 14 respectively. The possibility of this type of deformation had been foreseen as a convenient way of reducing the steric hindrance between the quinone groups and the end rings of the molecule. It was also viewed with favour since the non-centrosymmetry of the space group argued the lack of such a centre in the molecule itself.

The bend suggested was such that the molecule presented an obtuse angle of about 175° to the positive direction of y . A considerable time was spent proving the incorrectness of this trial structure.

Finally, in direct contradiction to the evidence from the quinone bonds mentioned, it was found possible to obtain a fit with the bend of the molecule reversed. To obtain the best structure factor agreement it was also necessary to reverse the tilt of the quinone bonds with the result that the bond 2 - 14 became almost twice as long as 1 - 3. This structure gave a reliability index of 0.38.

When further adjustment of orientation of the molecule and minor changes to the oxygen atoms produced no further improvement, a process of manual refinement was embarked upon with the object of proving that the structure was essentially correct before attempting least squares refinement by mechanical means.

The course adopted was to set up the differential equations for ΔF in terms of $\frac{\partial F}{\partial y}$, Δy , as for least squares, in the form of a table of gradients. The direction of shift of each coordinate which would produce a net improvement was found by averaging the requirements for all the planes. It was found useful to prepare a second table showing the direction of shift required to reduce ΔF , together with the magnitude of the effect which unit shift in that direction would produce. A summation over all the planes for each atom then gave the direction of the shift and an indication of its magnitude. This table allowed the changes in ΔF to be computed quickly and enabled a second set of shifts to be estimated without recalculation of the gradients.

Attempts to use a limited number of reflexions, about half the total number, for which agreement was poor, were unsuccessful, since

the reflexions not included because worse more rapidly than those included improved. Some success was obtained when all available reflexions were included and the reliability index was reduced to 0.29 in three such double cycles. Although the molecule had by now assumed a somewhat irregular shape, it was decided to persevere with it.

Least squares refinement of this zone was performed at the University of London Computer Unit using the newly installed Ferranti 'Mercury' computer.

It was decided to refine x , y and B for carbon and oxygen atoms but, since only 87 observed reflexions were available, it was impossible, or inadvisable, to refine all three at once. In addition, the limited capacity of the machine prevented the inclusion of the 12 hydrogen atoms. Their contributions were calculated separately and included at the end of refinement.

Since the x coordinates were to be relied upon to a great extent, the refinement of y and B was first undertaken. The values of B used were taken directly from the (h0l) zone for want of a better approximation. The first cycle of refinement produced changes in y of up to 0.2 \AA and the actual shifts applied were one third to one half of those indicated unless the full shift tended to improve the general appearance of the molecule. The changes in B were very large so that some B 's became negative. It was decided to use only one tenth of the indicated changes. The reliability index then improved from 0.291 at

at the start to 0.265.

Since adjustment of the coordinates and temperature factors between cycles was time consuming and prevented their being fed directly into the machine for a second cycle, refinement of the temperature factors was postponed until the y coordinates had been improved when it was hoped that ΔB 's would be more reasonable. x and y coordinates were therefore refined for 4 cycles. Some shifts of 0.2 \AA were obtained for both x and y coordinates and the reliability index fell first to 0.205 and then hovered about 0.180. Refinement of B was resumed in the sixth cycle. The maximum value of ΔB in this cycle was -2.82 and of Δy was 0.069 \AA . These were accepted since all the B 's were still positive and a calculation of the structure factors with the new parameters gave a reliability index of 0.142. Cycle seven produced maximum changes $B = 1.30$ and $y = 0.033 \text{ \AA}$ and a reliability index of 0.130. The changes in parameters produced by the eighth cycle were too small to warrant recalculation of structure factors.

The inclusion of the hydrogen atom contributions at the conclusion of refinement had the unfortunate effect of worsening the reliability index to 0.147. The same corrections were applied to the previous set of structure factors when the same degree of deterioration was obtained. The indication is that the hydrogen contributions should have been introduced at an earlier stage to prevent spurious shifts in the oxygen and carbon coordinates. This is the more necessary in

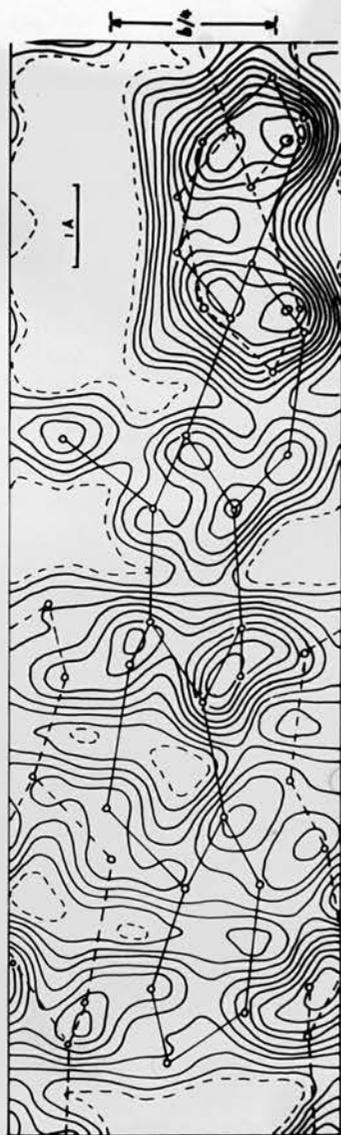


Fig. 20

1.2.5.6-dibenzanthracene (0 0 1) Fourier projection.
 The $3 \text{ e}\text{\AA}^{-2}$ contour is shown dotted.

the present instance since the total number of parameters refined is not much less than the number of reflexions used. However, this same paucity of data makes the continuation of refinement seem unrewarding so that further efforts have been left until more complete data can be obtained. The need for full-scale three dimensional refinement will become apparent during the discussion of the structure in its present state of refinement.

The reliability indices at this stage are

$$R(0,0,1) = 0.147$$

$$R(0,1,0) = 0.135$$

$$R(1,0,0) = 0.189$$

R for the (1,0,0) projection was calculated neglecting the contribution of the (0,1,2) reflexion which clearly suffers severely from extinction. Practically all the atoms lie in or close to this plane.

The final carbon and oxygen parameters are shown in Table 8 and the hydrogen parameters in Table 9. Fourier syntheses for the two projections studied are shown in figures 19 and 20.

TABLE 8

1.2.5.6.dibenzanthraquinone, oxygen and carbon parameters

<u>Atom</u>	<u>x Å</u>		<u>y Å</u>		<u>z Å</u>	<u>B(hk0)</u>	<u>B(h0l)</u>
1	1.824	± .01	0.398		1.837	5.27	5.0
2	4.605	± .025	2.430		-2.153	9.19	5.0
3	2.387	± .015	0.373		1.062	3.96	4.1
4	3.788	± .06	0.469		1.009	2.80	4.1
5	4.414	± .02	-0.135		2.351	2.25	4.1
6	5.854	± .035	-0.350		2.625	4.19	3.6
7	6.662	± .07	0.273		1.514	4.17	4.1
8	8.084	± .02	-0.274		1.679	4.33	4.1
9	8.829	± .05	0.038		0.845	5.68	4.9
10	8.090	± .025	0.823		-0.456	5.58	4.9
11	6.804	± .07	1.125		-0.545	3.92	4.1
12	6.008	± .01	0.507		0.345	2.71	4.1
13	4.655	± .075	1.008		0.159	1.24	4.1
14	3.793	± .055	1.386		-1.023	4.16	4.1
15	2.467	± .005	1.424		-1.103	4.66	4.1
16	1.979	± .08	1.661		-2.255	6.59	4.1
17	0.308	± .025	1.932		-2.416	1.66	3.6
18	-0.647	± .005	1.034		-1.325	4.71	4.1
19	-1.829	± .06	1.408		-1.526	5.87	4.1

TABLE 8 (contd.)

<u>Atom</u>	<u>x Å</u>	<u>±</u>	<u>y Å</u>	<u>z Å</u>	<u>E(hk0)</u>	<u>E(h0l)</u>
20	-2.696	± .025	1.219	-0.391 ✓	6.39	4.9
21	-2.094	± .005	0.333	0.665 ✓	2.53	4.9
22	-0.607	± .03	0.159	0.941 ✓	4.14	4.1
23	0.166	± .045	0.580	-0.056 ✓	2.87	4.1
24	1.529	± .01	0.829	-0.104 ✓	3.12	4.1

The x coordinates are the mean of those derived from the (hk0) and (h0l) projections. The degree of divergence between them is indicated by the possible errors assigned.

TABLE 91.2.5.6.dibenzanthraquinone, assumed hydrogen parameters

<u>Atom</u>	<u>x Å</u>	<u>y Å</u>	<u>z Å</u>
1	3.80	-0.43	3.19
2	6.67	-0.83	3.60
3	8.68	-0.89	2.64
4	9.92	-0.12	1.01
5	8.65	1.31	-1.33
6	6.34	1.68	-1.65
7	2.66	2.31	-3.12
8	-0.20	2.50	-3.30
9	-2.29	2.03	-2.40
10	-3.69	1.62	-0.46
11	-2.69	0.10	1.32
12	-0.14	-0.41	1.84

A temperature factor B = 5.0 was used throughout.

TABLE 10

1.2.5.6.dibenzanthraquinone, observed and calculated structure factors

h	k	l	sin θ	$ F_o $	$ F_c $	cos α	sin α	$ \Delta F $
0	0	0	-	640	-	-	-	-
0	0	2	.120	155.3	147.5	.989	.148	7.8
0	0	4	.239	39.6	41.0	-.855	.516	1.4
0	0	6	.359	19.7	20.2	.861	-.507	0.5
0	0	8	.479	18.8	20.7	-.774	-.633	1.9
0	0	10	.599	14.4	10.9	.960	.288	3.5
0	0	12	.718	21.2	16.9	.397	-.915	4.3
0	0	14	.838	4.8	6.8	-.047	-.993	2.0
0	0	16	.958	6.8	9.4	.428	.908	2.6
0	1	0	.200	93.5	90.5	1.000	.000	3.0
0	1	2	.234	83.0	197.0	.253	.968	114.0
0	1	4	.312	10.9	15.5	-.208	.975	4.6
0	1	6	.411	26.7	26.3	-.745	.668	0.4
0	1	8	.519	< 4.2	3.6	.850	-.520	-
0	1	10	.631	21.6	19.4	-.223	-.975	2.2
0	2	0	.401	12.1	12.6	1.000	.000	0.5
0	2	2	.419	40.3	69.2	-.655	.756	28.9
0	2	4	.468	40.1	53.2	-.652	.758	13.1
0	2	6	.539	13.5	13.5	-.784	.616	0.0
0	2	8	.625	33.3	24.5	-1.000	.000	8.8

h	k	l	sin θ	$ F_o $	$ F_c $	cos α	sin α	$ \Delta F $
0	2	10	.720	23.8	5.8	-.582	.812	18.0
0	3	0	.601	< 4.0	14.1	1.000	.000	-
0	3	2	.615	13.7	9.8	.246	-.972	3.9
0	3	4	.649	15.9	19.4	-.790	-.615	3.5
0	3	6	.702	< 4.8	14.4	-.946	.326	-
0	3	8	.770	16.5	7.2	-1.000	.000	9.3
0	4	0	.802	6.5	3.8	-1.000	.000	2.7
2	0	0	.054	17.0	22.1	1.000	.000	5.1
2	0	1	.081	55.7	76.0	-.149	.990	20.3
2	0	2	.131	45.4	57.5	.092	-.997	12.1
2	0	3	.188	54.0	58.2	-.016	-1.000	4.2
2	0	4	.246	42.4	41.4	-.464	.886	1.0
2	0	5	.304	31.1	25.0	-.101	.995	6.1
2	0	6	.362	9.1	7.5	-.271	.962	1.6
2	0	7	.423	5.0	4.6	.930	.360	0.4
2	0	8	.482	9.5	14.4	.314	.950	4.9
2	0	9	.541	16.8	13.8	-.915	-.400	3.0
2	0	10	.600	16.8	15.9	.742	-.670	0.9
2	0	11	.661	29.2	29.6	-.591	.806	0.4
2	0	12	.719	22.0	26.4	.662	-.750	4.4
2	0	13	.779	13.8	12.3	-.075	1.000	1.5
4	0	0	.108	32.7	38.2	1.000	.000	5.5

h	k	l	$\sin\theta$	$ F_o $	$ F_c $	$\cos\alpha$	$\sin\alpha$	$ \Delta F $
4	0	1	.124	13.2	14.2	-.422	-.903	1.0
4	0	2	.162	16.6	21.4	.764	.646	4.8
4	0	3	.210	32.1	39.5	-.970	-.234	7.4
4	0	4	.264	18.8	13.5	.955	-.299	5.3
4	0	5	.318	55.2	51.6	.907	-.420	3.6
4	0	6	.375	29.2	27.8	.538	-.843	1.4
4	0	7	.433	29.8	33.2	.980	.193	3.4
4	0	8	.491	16.8	19.7	.994	-.126	2.9
4	0	9	.549	11.2	10.7	-.915	-.405	0.5
4	0	10	.608	8.2	3.8	.727	.705	4.4
4	0	11	.669	19.6	9.7	.987	.190	9.9
4	0	12	.725	20.1	16.4	-.903	-.428	3.7
4	0	13	.785	15.7	13.5	.528	.852	2.2
6	0	0	.162	23.6	29.1	-1.000	.000	5.5
6	0	1	.173	31.6	34.2	-.397	-.917	2.6
6	0	2	.202	37.9	43.0	-.970	-.242	5.1
6	0	3	.242	7.4	6.0	-.452	.892	1.4
6	0	4	.290	42.8	42.4	.676	.737	0.4
6	0	5	.340	73.2	70.0	.216	.977	3.2
6	0	6	.394	44.8	45.8	.589	.808	1.0
6	0	7	.450	26.7	36.1	.395	.918	9.4
6	0	8	.505	15.3	12.8	-.985	.160	2.5
6	0	9	.562	11.5	12.5	-.650	.760	1.0

k	l	$\sin\delta$	$ F_o $	$ F_e $	$\cos\alpha$	$\sin\alpha$	$ \Delta F $
0	10	.620	17.1	14.4	.990	.169	2.7
0	11	.680	12.6	13.2	-.997	-.079	0.6
0	0	.216	37.0	43.3	-1.000	.000	6.3
0	1	.224	33.0	37.3	.566	.823	4.3
0	2	.247	24.6	25.9	.340	-.940	1.3
0	3	.281	13.1	6.9	1.000	.058	6.2
0	4	.323	21.6	19.7	.550	-.833	1.9
0	5	.369	57.7	56.5	.206	.980	1.2
0	6	.418	36.1	37.5	-.663	-.747	1.4
0	7	.471	29.6	36.1	.613	.790	6.5
0	8	.525	10.2	11.8	-.559	-.823	1.6
0	9	.580	11.7	11.2	.240	-.970	0.5
0	10	.636	< 9.0	6.1	.873	-.486	-
0	11	.694	< 9.0	3.1	1.000	-.052	-
0	0	.270	5.0	6.3	1.000	.000	1.3
0	1	.276	12.3	9.8	-.500	-.866	2.5
0	2	.295	24.6	24.9	.734	.680	0.3
0	3	.324	28.3	30.8	.020	1.000	2.5
0	4	.361	23.8	26.4	.968	.293	2.6
0	5	.402	15.8	16.1	-1.000	-.042	0.3
0	6	.448	27.6	24.1	-.932	.361	3.5
0	7	.499	16.0	15.6	-.399	-.915	0.4
0	8	.549	< 8.1	6.4	-.918	-.380	-

h	k	l	sin θ	$ F_o $	$ F_c $	cos α	sin α	$ \Delta F $
10	0	9	.603	< 8.5	4.4	.837	.548	-
10	0	10	.656	< 9.0	6.6	.950	-.313	-
12	0	0	.323	36.0	39.1	1.000	.000	3.1
12	0	1	.330	58.5	62.9	.315	-.950	1.4
12	0	2	.345	30.5	31.5	.070	-.997	1.0
12	0	3	.370	18.4	21.7	.597	.803	3.3
12	0	4	.404	10.9	19.1	-0.94	.996	8.2
12	0	5	.441	15.6	13.8	-.547	.835	1.8
12	0	6	.483	15.0	18.7	.930	-.370	3.7
12	0	7	.530	8.4	8.1	-1.000	.010	0.3
12	0	8	.579	< 8.3	8.0	-.765	-.640	-
14	0	0	.377	84.4	90.8	1.000	.000	6.4
14	0	1	.382	27.7	20.6	.980	.180	7.1
14	0	2	.396	19.1	14.7	.183	.988	4.4
14	0	3	.418	10.1	16.7	-.275	-.960	6.6
14	0	4	.448	13.7	16.9	-.941	.340	3.2
14	0	5	.482	13.0	12.8	-.875	.481	0.2
14	0	6	.520	8.3	10.1	1.000	.055	1.8
14	0	7	.564	< 8.2	6.7	.880	.485	-
14	0	8	.610	< 8.5	5.2	-.338	.946	-
16	0	0	.431	8.0	7.5	-1.000	.000	0.5
16	0	2	.446	< 8.3	2.3	-.310	.950	-
16	0	3	.467	16.9	15.9	.530	.850	1.0

h	k	l	$\sin\theta$	$ F_o $	$ F_c $	$\cos\alpha$	$\sin\alpha$	$ \Delta F $
16	0	4	.493	7.9	9.1	-.215	.978	1.2
16	0	5	.524	< 7.7	10.4	.061	1.000	-
16	0	6	.560	< 8.1	2.9	-.930	.328	-
16	0	7	.600	< 8.5	13.0	-.068	-.996	-
16	0	8	.644	< 8.8	2.4	.000	1.000	-
8	0	0	.485	4.6	4.3	1.000	.000	0.3
8	0	2	.498	10.1	7.9	-.963	.252	2.2
8	0	3	.517	< 7.4	7.4	-.994	.027	-
8	0	4	.541	7.6	8.2	.985	.175	0.6
8	0	5	.570	28.7	25.7	.996	-.064	3.0
8	0	6	.603	43.7	45.6	.930	-.366	1.9
8	0	7	.640	31.4	34.1	.970	.245	2.7
8	0	8	.682	19.5	23.0	1.000	-.030	3.5
0	0	0	.539	6.4	10.4	-1.000	.000	4.0
0	0	2	.553	12.0	8.1	-.995	-.093	3.9
0	0	3	.569	10.1	12.1	-.798	-.608	2.0
0	0	4	.591	17.3	26.2	.831	-.557	8.9
0	0	5	.618	38.1	44.2	-.289	.958	6.1
0	0	6	.648	15.4	19.3	1.000	.035	3.9
0	0	7	.684	19.0	18.1	.086	1.000	0.9
2	0	0	.593	14.9	17.6	-1.000	.000	2.7
2	0	3	.619	< 8.6	9.7	.616	-.790	-
2	0	4	.639	15.7	10.2	.590	-.817	5.5

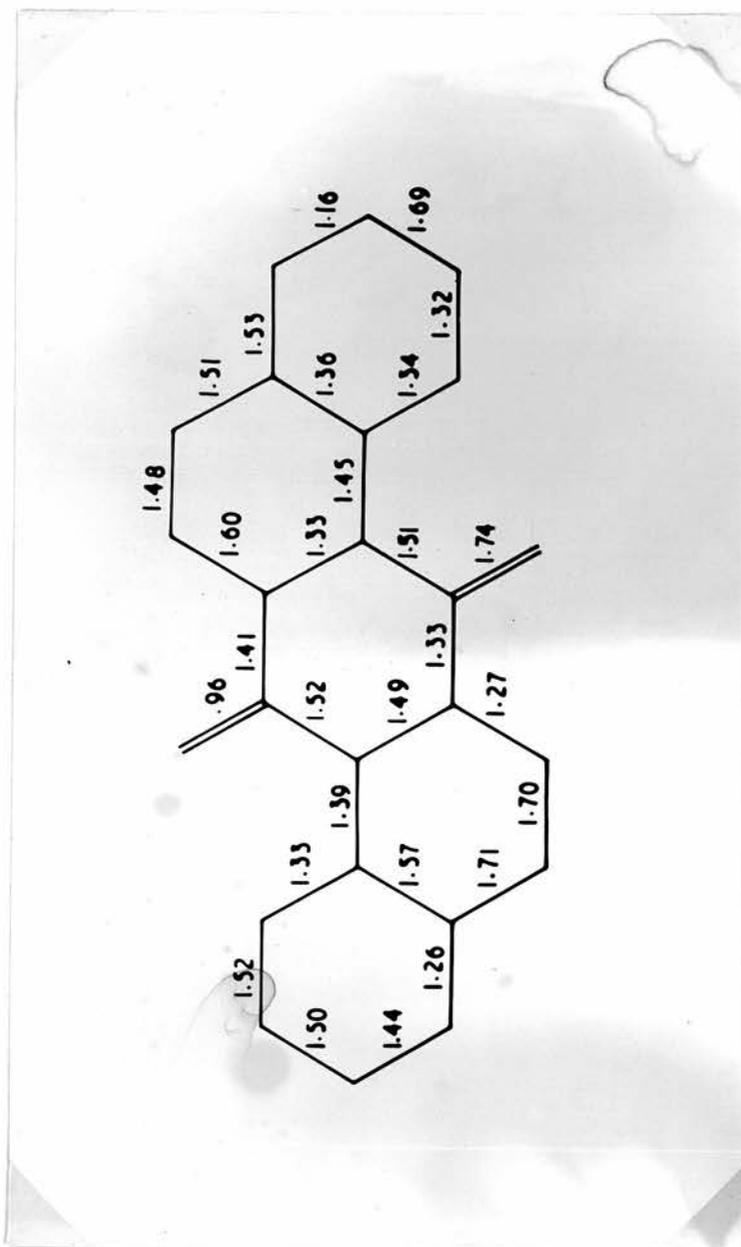
h	k	l	sin θ	$ F_o $	$ F_c $	cos α	sin α	$ \Delta F $
22	0	5	.664	25.3	23.6	.779	.631	1.7
22	0	6	.692	24.9	22.7	-.592	-.805	2.2
22	0	7	.725	19.9	17.4	.705	.710	2.5
24	0	0	.648	6.4	1.6	1.000	.000	4.8
24	0	3	.671	13.5	12.0	-.411	.910	1.5
24	0	4	.691	12.2	15.4	1.000	-.070	3.2
24	0	5	.713	15.3	14.8	-.850	-.522	0.5
26	0	0	.702	6.8	12.4	-1.000	.000	5.6
28	0	0	.754	12.6	13.5	-1.000	.000	0.9
30	0	0	.808	3.8	3.2	1.000	.000	0.6
32	0	0	.862	3.7	3.0	1.000	.000	0.7

h	k	l	sin θ	F_o	F_c	ΔF
1	1	0	.202	-61.65	-55.46	-6.19
1	2	0	.402	-11.68	-9.80	-1.88
1	3	0	.601	7.14	7.39	-0.25
-1	4	0	.802	5.19	3.52	1.67
2	1	0	.205	-49.86	-47.45	-2.41
2	2	0	.403	4.76	5.88	-1.12
-2	3	0	.602	-14.17	-11.47	-2.70

h	k	l	$\sin\theta$	F_o	F_o	ΔF
3	1	0	.216	4.43	5.12	-0.69
3	2	0	.408	-13.20	-12.85	-0.35
3	3	0	.606	-10.38	-10.23	-0.15
3	4	0	.805	5.19	5.48	-0.29
4	1	0	.227	39.59	37.55	2.04
4	2	0	.414	4.22	2.06	2.16
5	1	0	.241	-16.87	-21.32	4.45
5	2	0	.423	-7.57	-8.42	0.85
5	3	0	.615	-3.79	-5.27	1.48
5	4	0	.812	3.68	3.60	0.08
6	1	0	.257	-5.08	-2.67	-2.41
6	2	0	.431	7.68	3.53	4.15
7	1	0	.275	27.58	23.91	3.67
7	2	0	.443	-5.95	-8.12	2.17
8	2	0	.455	-7.03	-3.93	-3.10
9	1	0	.315	-3.35	-5.78	2.43
9	2	0	.468	-3.79	-1.39	-2.40
10	1	0	.336	4.65	4.61	0.04
10	2	0	.482	11.90	12.49	-0.59
10	4	0	.845	-3.46	-5.69	2.23
11	2	0	.498	4.00	8.54	-4.54
11	3	0	.670	-7.25	-7.14	-0.11
12	1	0	.380	-21.96	-23.87	1.91

h	k	l	sin θ	F _o	F _e	ΔF
12	2	0	.515	6.81	7.26	-0.45
12	3	0	.682	4.54	5.31	-0.77
12	4	0	.863	7.36	6.95	0.41
13	1	0	.404	31.80	29.49	2.31
13	3	0	.696	- 3.89	- 2.86	-1.03
13	4	0	.874	- 6.17	- 4.57	-1.60
14	1	0	.427	26.39	26.53	-0.14
14	2	0	.550	10.38	12.78	-2.40
14	4	0	.885	- 6.92	- 9.40	2.48
15	1	0	.451	5.30	1.89	3.41
15	2	0	.569	8.33	7.35	0.98
15	3	0	.724	3.89	3.70	0.19
15	4	0	.897	4.65	6.73	-2.08
16	1	0	.475	- 7.25	- 5.63	-1.62
16	3	0	.740	- 9.52	-11.39	1.87
17	1	0	.500	- 4.00	- 3.43	- 0.57
17	3	0	.756	-16.12	-16.11	-0.01
17	4	0	.923	- 3.79	- 0.90	-2.89
18	1	0	.525	- 7.79	- 7.31	-0.48
18	2	0	.629	-14.49	-12.17	-2.32
18	3	0	.772	- 7.14	- 8.74	1.60
19	1	0	.550	- 7.36	- 3.52	-3.84
19	2	0	.650	- 8.11	- 3.40	-4.71

h	k	l	sin θ	F_o	F_o	ΔF
19	3	0	.789	3.79	4.85	-1.06
19	4	0	.951	4.54	1.84	2.70
20	2	0	.671	- 6.71	- 4.22	-2.49
21	1	0	.601	5.19	4.95	0.24
21	2	0	.693	- 5.41	- 7.18	1.77
21	3	0	.825	6.06	11.41	-5.35
21	4	0	.980	2.49	4.65	-2.16
22	3	0	.843	- 4.76	- 4.37	-0.39
23	2	0	.738	- 6.71	-10.20	3.49
24	2	0	.762	- 5.41	- 4.82	-0.59
25	3	0	.903	- 4.11	- 4.01	-0.10
26	1	0	.729	3.89	2.89	1.00
27	1	0	.755	-14.28	- 9.59	- 4.69
28	1	0	.781	7.46	6.03	1.43
29	1	0	.807	4.11	3.40	0.71



IV (iii) 1.2.5.6.dibenzanthraquinone: discussion of the structure

The state of refinement of the structure, judged solely by the reliability indices quoted in the previous section, seems to be quite good. It is to be expected that the standard error of coordinates will be about 0.02 \AA . It is distressing therefore to find discrepancies between x coordinates in the (h0l) and (hk0) projections of up to 0.18 \AA . If this were not enough the calculated bond lengths using the mean coordinates, as shown in fig. 21 and Table 11, show such extreme variations from the accepted mean benzene ring bond length that the worth of the structure is a matter of some doubt. Thus the longest benzene ring bond is 1.71 \AA and the shortest is 1.16 \AA . The mean length, 1.45 \AA , is about 2.5% longer than the usual mean length of $1.41 - 1.42 \text{ \AA}$. The quinone double bonds are similarly improbable. Whereas an acceptable length would be about 1.3 \AA , the bond 1 - 3 is 0.96 \AA and the bond 2 - 14 is 1.74 \AA .

The quinone bonds are inclined to the plane of the central ring towards the positive direction of y relative to the molecule, making angles of 25° and 15° with it respectively, and are approximately coplanar with one another. There is a general tendency for the remainder of the molecule to be bent in the opposite direction. This trend is most marked in the ring containing atoms 8, 9, 10, 11, and is to some extent reversed in the ring containing atoms 19, 20, 21, 22. The apparent shape of the molecule is thus that of a much elongated S.

TABLE 11Bond lengths in 1.2.5.6.dibenzanthraquinone

Chemically equivalent bonds are shown side by side.

<u>Bond distance</u> Å		<u>Bond distance</u> Å	
≡ 1 - 3	0.96	≡ 2 - 14	1.74
3 - 4	1.41	14 - 15	1.33
4 - 5	1.60	15 - 16	1.27
4 - 13	1.33	15 - 24	1.49
5 - 6	1.48	16 - 17	1.70
6 - 7	1.51	17 - 18	1.71
7 - 8	1.53	18 - 19	1.26
7 - 12	1.36	18 - 23	1.57
8 - 9	1.16	19 - 20	1.44
9 - 10	1.69	20 - 21	1.50
10 - 11	1.32	21 - 22	1.52
11 - 12	1.34	22 - 23	1.33
12 - 13	1.45	23 - 24	1.39
13 - 14	1.51	24 - 3	1.52

≡ indicates C = O bonds.

The effects of steric hindrance between the oxygen atoms and the end rings of the molecule are seen in the intramolecular distances

1 - 22 and 2 - 11 (fig. 17). These are 2.57 Å and 3.00 Å respectively and may be compared with the usual width, 2.44 Å, of an undistorted benzene ring structure. It seems likely that the almost normal value of the 1 - 22 distance indicates a degree of hydrogen bonding between these two atoms which is absent between atoms 2 and 11. It is worth noting that the oxygen atom 2 is associated with two very short intermolecular distances, 2-13' = 3.36 Å and 2 - 14' = 3.14 Å, where the primes refer to the molecule at the next lattice point in the b direction. Unfortunately atoms 13 and 14 have no hydrogen atoms attached so that intermolecular hydrogen bonding is not a possibility unless atoms 11' and 16' are considered. These are both about 3.5 Å distant from 2 and their hydrogen atoms would probably exert too feeble a bonding effect to account for the short distances mentioned. It may be more realistic to regard them as due to the same displacement of atom 2 which makes the 2 - 14 bond abnormally long. It is only fair to add that to do this would be contrary to all the evidence, in the form of data employed, so far adduced.

Supposing that the structure is essentially correct, i.e. that the phase problem has been solved, but that the coordinates are subject to large random errors it remains to find the source or sources of the latter.

The unevenness comes about equally from both projections used for refinement. For the (h0l) projection there is an adequate supply

of data. 111 reflexions were observed and a further 17 unobserved ones were used in the least squares refinement. The number of parameters refined was 50, including overall scale and temperature factors so that the least squares refinement should be valid. On the other hand the observed reflexions total less than half the number possible for this zone. In particular there are very few observed outside the benzene circle. Without these high angle reflexions it is probably not possible to get a very good degree of accuracy. There is also a suspicion that some systematic errors have crept into the estimation of the reflexion intensities. On account of the length and curvature of the needle shaped crystal used, some of the large spacing reflexions are elongated while a focussing effect has tended to reduce the length of certain other reflexions and hence to increase their peak intensity. The effect of this on the structure factor tables is not expected to be large but clearly should be removed before the highest accuracy can be claimed.

The position in the (hk0) projection is roughly the reverse of that described above. The data is regarded as accurate since the crystal used was a more suitable shape and corrections for variable spot shape were applied to the measured intensities. It is also more complete and the reflexions not observed are evidently very small. However, there are only 87 observed reflexions which is strictly inadequate for least squares refinement of 3×24 parameters even if

taken only 48 at a time. The remaining unobserved reflexions were unfortunately excluded from the calculations since the least squares programme used with 'Mercury' did not permit them to be used until the calculated values had fallen below the maximum possible values of F_o and thereafter ignored. This facility was available in the 'Pegasus' computer programme. The suspicion is therefore that a spurious refinement may have taken place in this zone, the true structure not being greatly different from the one obtained but both being equally plausible on the available data. This view is fortified by the wide variations in the individual atomic temperature factors (Table 8) and also by the confused nature of the (hk0) Fourier synthesis (fig. 20).

The possibility that the structure may actually be incorrect is not thought to be very great. This is a feeling chiefly based on the respectability of the (h0l) Fourier synthesis, on the ease with which the refinement of the (hk0) projection proceeded, in the early stages mainly by adjustment of the y coordinates, and on the satisfactory reliability index obtained. Also in favour of this view is the fact that, although an exhaustive search was made, no trial structure for the (hk0) projection could be found with more desirable attributes than the one used.

In sum, it seems necessary both to enlarge the quantity of data used and to improve on the accuracy of the present data. It should then be a simple if time consuming matter to estimate the significance of the results so far obtained.

Fourier syntheses

These were performed by the 'Mercury' computer using the standard programme devised by G.S. Mills.

(h0l) projection. As expected a good picture of the molecule is obtained in this projection (fig. 19). It was unexpected that atom 3 in the central ring would fail to be resolved from oxygen atom 1. The rest of the atoms are satisfactorily resolved and the peak positions are in moderate accord with the coordinates on which the synthesis is based. It was not thought profitable to extract peak coordinates from the figure field for the reasons advanced in V. The carbon peaks are generally low, five of them being less than $5e\text{\AA}^{-2}$ and only two reaching $6e\text{\AA}^{-2}$. These two are the K region atoms 5 and 6 where a high total charge would be of interest in relation to biological potency. However, this bond is of greater than average length where a short bond would be more in keeping with a high total charge. The only other points of interest in the two K regions are the hydrogen 'peaks' of $1.8 - 2.8 e\text{\AA}^{-2}$ attached to them. No other hydrogen peaks of this height occur and while some are $1.0 - 1.5 e\text{\AA}^{-2}$ high there are a number of spurious peaks of this height so that it would appear to be a case of special pleading to attach significance to some while ignoring others. The evidence as to the existence of intramolecular hydrogen bonding is thus unreliable, equally so for both oxygen atoms which were thought to differ in this respect on the basis of the intramolecular distances mentioned above. There is also a $2.1 e\text{\AA}^{-2}$ peak

close to atom 1 for which no explanation can be found. The attractive possibility that it might form a hydrogen bridge between atom 1 of the molecule at (x, y, z) and atom 19 of the molecule at $(\bar{x}, \bar{y}, \frac{1}{2} + z)$ has to be rejected since these atoms are 3.6 \AA apart and so should require no stabilizing influence. It is probably merely a curiosity which combined with the spurious detail at the $1\text{e}\text{\AA}^{-2}$ level indicates that series termination and possibly other errors are not negligible.

(hk0) projection. The curious distortion produced by the least squares refinement is well seen in the molecule drawn on this projection (fig. 20). The atomic positions all lie in regions of electron density greater than $5.8 \text{ e}\text{\AA}^{-2}$ and are more or less plausibly related to single or multiple peaks in the Fourier synthesis. The latter is, however, too confused to give a good picture of the molecule. A better picture could have been expected with the reliability index at 0.147 before the synthesis so that there are some grounds for being suspicious of the genuineness of these coordinates.

The peak heights are roughly in accord with the individual temperature factors derived from the least squares refinement. Thus oxygen atom 2 with $B = 9.2$ is lower than carbon atoms 4, 5 and 13 with $B = 2.8, 2.3$ and 1.2 respectively, and atom 20 at $5.8 \text{ e}\text{\AA}^{-2}$ has $B = 6.4$.

The peak corresponding to oxygen atom 2 is of interest since, although it is not very well formed, the degree of resolution is good and tends to confirm the long 2 - 14 distance. The height and

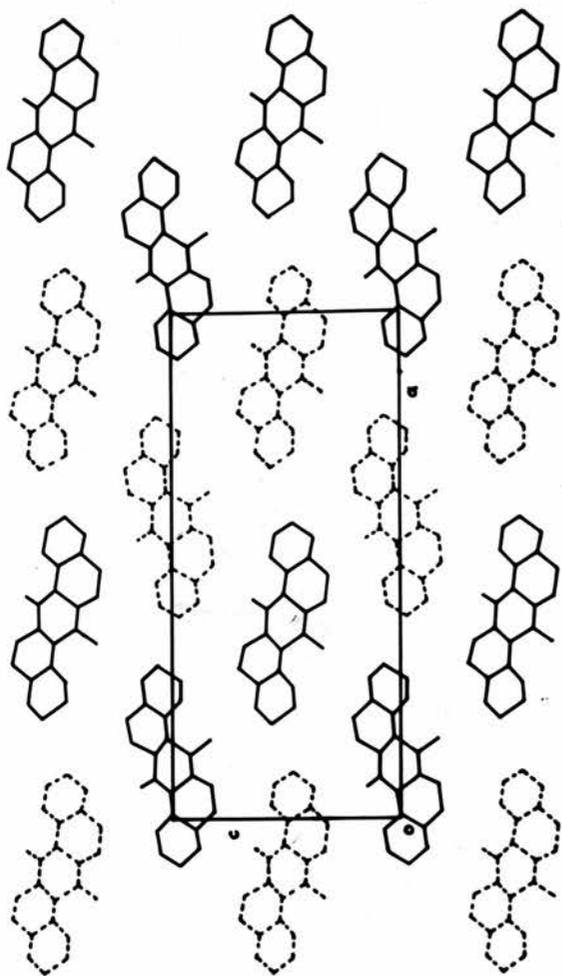


Fig. 22

1,2,5,6-dibenzanthraquinone, extended view of the
 (0 1 0) projection. The molecules at \bar{y} are
 shown dotted.

definition of the seven-fold peak and its mirror image in $x = a/4$ suggests that the position of this end ring, if not its somewhat original shape, is reasonably certain. This view is supported by the large area of low density immediately adjacent to the peak. Beyond this the electron density plot can offer very little evidence either for or against the present structure.

Packing in the unit cell

An extended view of the (h0l) projection is shown in figure 22. Molecules at \bar{y} are shown dotted.

The high calculated crystal density of 1.44 gm cm^{-3} indicates that packing is fairly close. A comparison of this structure with 1.2.5.6.dibenzanthracene in its orthorhombic form (30) reveals that the two molecules occupy almost exactly the same volume in the crystal, the unit cell volumes being 1419 \AA^3 and 1415 \AA^3 respectively with 4 molecules in each. The density of the latter compound is 1.28 gm cm^{-3} so that the high density of the former is almost exactly accounted for by the increase in molecular weight.

The extra space required by the quinone groups is gained in the (0,1,0) plane by the destruction of the centrosymmetry of the unsubstituted compound and a relative translation of the molecules in the x direction of about 6 \AA . These groups then no longer clash with one another and there is no atom of another molecule approaching closer to them than 3.6 \AA . In the y direction the short b axis and the long

2 - 14 bond are responsible for the very short distances, 2 - 13' and 2 - 14' between molecules at adjacent lattice points, previously mentioned. In contrast the 1 - 3 bond is so short and is, moreover, parallel to (0,1,0) that the oxygen atom comes no closer than 3.6 Å to any other atom in any direction.

One other close distance of approach is noteworthy. The distance 9 - 20' between molecules at (x,y,z) and at ($\frac{1}{2} + x, \bar{y}, z$) is 3.28 Å. This distance is greatly dependent on the accuracy of the x coordinates. In particular the x coordinate of atom 9 has a possible error of ± 0.05 Å. It is also necessary to note that the intramolecular distance 9 - 20 is 11.7 Å where a distance of 11.4 Å would be normal. This abnormally close approach of molecules is therefore not well established.

V. A comparison of two techniques of refinement

A direct practical comparison of the two refinement techniques used was undertaken to test their relative efficiency. Neither had been proved entirely satisfactory, the difference Fourier method making only slow progress at the start of refinement while it seemed that the ultimate accuracy of the masking and series termination correction method would be limited by the accuracy with which peak positions could be located. The latter trouble does not arise in difference Fourier refinement.

The chief errors arising in coordinates taken from reasonably well resolved Fourier projections are:-

1. Those due to masking or overlapping between atoms situated less than about 1.0 \AA apart in projection. The effect is to draw the apparent peak positions together.
2. Those due to termination of the Fourier series at the limit imposed by the X-ray wavelength used. Each peak is liable to be affected by all peaks lying within about 3 \AA of it. The separation may be increased or decreased, the displacement being only in the line of centres. Individual displacements may be added vectorially. At its maximum the effect is much smaller than the average masking effect.
3. Those due to diffuseness of the observed Fourier peak. Occasionally a peak appears to be more like a plateau and no amount of analysis of the figure field can do more than suggest an area within which the

atomic centre will lie.

The method of refinement normally used is that of the difference Fourier. The function $F \exp 2\pi i(hx + lz)$ is computed as for an ordinary Fourier projection with $F = F_0 - F_0'$, and corrections to the assumed atomic positions are estimated from the gradients of the function at these positions. The Fourier map obtained from this function is a plot of the electron density remaining after the atoms in their assumed positions have been removed from the 'true' electron density map. If the positions have been assumed correctly then both gradient and density should be zero there. With the atoms incorrectly sited the density should still be small but the gradient may be large and the atoms must be moved up the gradient a distance depending on the steepness.

The shift r is given by

$$r = \frac{d\rho(\text{diff})}{dr} / \frac{d^2\rho_0}{dr^2}$$

where $\rho(\text{diff})$ is the electron density of the difference synthesis and ρ_0 is the peak height of the F_0 synthesis. The process is equivalent to minimizing the function $R = \frac{F_0 - F_0'}{F_0}$, the value of which is generally taken as being a measure of the accuracy of the structure.

The difference Fourier refinement if continued over a sufficient number of cycles should clearly correct for series termination errors in the coordinates from the original Fourier synthesis and also for any errors in the graphical location of the peaks. The refinement may be greatly hindered by incorrect choice of scale or temperature factor (Section III (iv) and IV (ii)). It is advisable to adjust these at

the earliest stage possible and to complete refinement by adjusting the temperature factor of each atom individually.

The effect of random errors in the magnitudes of the observed structure factors has been shown in a particular hypothetical case (31) to have little effect on the coordinates derived from an F_o Fourier synthesis. The effect of these random errors on refinement by difference Fourier has apparently not been investigated. It is clear that an error of a few percent in the value of F_o may cause a large percentage error in $F_o - F_c$ and may even change its sign. The effect of a number of such errors may be either to prevent the convergence of the refinement process or to lead to a wrong set of coordinates. It is not obvious whether these effects will be large or whether they will be small enough to be neglected. The most likely method of assessing the possible errors from this source appears to be the application of the difference Fourier process to a series of hypothetical structures with random errors introduced into the calculated structure factors.

A fresh approach to the problem of structure refinement by Burns and Iball (22) attempts to apply systematic corrections for masking between adjacent atoms. The profile of the projected atom is assumed to be of the form $\rho(r) = A \exp(-pr^2)$ where ρr is the electron density at distance r from the peak, A is the peak density and p is a constant which can be determined graphically from the figure field. If two

such atoms are placed at $r = a$ and $r = -a$ respectively, the combined electron density is given by

$$\rho(r) = A \exp(-p(r - a)^2) + A \exp(-p(r + a)^2)$$

a function which has maxima at $r = \pm s$ where

$$(s - a) \exp(-p(s - a)^2) + (s + a) \exp(-p(s + a)^2) = 0$$

hence

$$a = s \coth(2psa) .$$

The authors give a table of corrections $(s - a)$ in terms of the observed separations, $2s$, of the atoms for various values of p ranging from 3.0 to 5.0. The effect of masking is seen to be negligible at a peak separation greater than 1.3 \AA . Where more than two atoms are involved it has been found possible to deal with them in pairs and to combine the resultant shifts of coordinates vectorially.

A further extension of the above technique was made (3) to correct for masking and series termination effects simultaneously.

The number of structure factors available for any Fourier synthesis is limited by the wavelength of the X radiation used so that the scattering curve may be thought of as cut off abruptly at $\sin\theta = 1.0$ or $s_{\text{max}} = \frac{2\sin\theta}{\lambda} = 1.3$ for copper K α radiation. After the correct temperature factor has been applied to the scattering curve the Fourier integral of the latter may be calculated to give the corresponding atomic profile. The relation is (25)

$$\rho(r) = 2\pi \int_0^s f(s) J_0(2\pi sr) ds$$

where $s = \frac{2\sin\theta}{\lambda}$, $f(s)$ is the value of the scattering factor at s , r is

the distance from the atomic centre and J_0 is the Bessel function.

If s_{max} is infinite $\rho(r)$ is a smooth curve but if s_{max} is small the smooth peak is surrounded by a series of diffraction ripples beginning at about 1.0 \AA from the centre. Two such curves may be combined in the same way as for the simple masking correction. The shifts ($a - s$) may be obtained by calculating the slope at all points of the profile but a simpler and scarcely less accurate way is to combine the two curves numerically and calculate the peak position and hence the required shift, assuming the peak to be of parabolic form over a small range. The corrections used for the b axis projection of 1,2-cyclopentenopiperanthrene, and the profile from which they were calculated are given in Table 12 (a) and (b).

Since the series termination effects extend to about 3.0 \AA from the atomic centre, in projection, the correction due to the presence of as many as ten other atoms may require to be calculated. It has been found useful to plot the peak positions taken from the F_0 Fourier on a large scale on millimetre graph paper, when the separations can be measured directly and the corrections read from the table drawn in on the diagram and summed geometrically.

It is clear that the accuracy of the coordinates produced by this method depends very largely on the accuracy with which the peak positions can be estimated, which in turn depends on the sharpness of the peaks. Since the rate of convergence of the difference Fourier refinement depends in the same way on the sharpness of the peaks there

may be little to choose between the two methods on this score.

TABLE 12 (a)

Rippled atomic profile calculated from terminated scattering
curve for Anthracene

<u>Distance from</u> <u>peak</u>	<u>Electron</u> <u>density</u>	<u>Distance from</u> <u>peak</u>	<u>Electron</u> <u>density</u>
0.0 Å	7.3155 eÅ ⁻²	1.6 Å	0.0276 eÅ ⁻²
0.1	6.9726	1.7	0.0687
0.2	6.0222	1.8	0.0918
0.3	4.4316	1.9	0.0756
0.4	3.3072	2.0	0.0324
0.5	2.1012	2.1	-0.0132
0.6	1.2426	2.2	-0.0366
0.7	0.7536	2.3	-0.0312
0.8	0.5460	2.4	-0.0012
0.9	0.4836	2.5	0.0276
1.0	0.4434	2.6	0.0372
1.1	0.3594	2.7	0.0252
1.2	0.2334	2.8	0.0036
1.3	0.1044	2.9	-0.0228
1.4	0.0198	3.0	-0.0312
1.5	-0.0027		

TABLE 12 (b)

Series termination and masking corrections calculated
for the rippled atomic profile

<u>Separation (2s)</u> <u>of atoms</u>	<u>Correction</u> <u>Δs</u>	<u>Separation (2s)</u> <u>of atoms</u>	<u>Correction</u> <u>Δs</u>
0.2 Å	0.1940 Å	1.7 Å	-0.0050 Å
0.3	0.1650	1.8	0.0005
0.4	0.1345	1.9	0.0045
0.5	0.1040	2.0	0.0054
0.6	0.0717	2.1	0.0040
0.7	0.0403	2.2	0.0013
0.8	0.0140	2.3	-0.0025
0.9	0.0070	2.4	-0.0043
1.0	0.0095	2.5	-0.0028
1.1	0.0165	2.6	0.0002
1.2	0.0185	2.7	0.0026
1.3	0.0147	2.8	0.0035
1.4	0.0072	2.9	0.0024
1.5	-0.0005	3.0	0.0005
1.6	-0.0052		

Two subjects, the (h0l) projection of 1.2.cyclopentenophenanthrene and the (0kl) projection of 20.methylcholanthrene (4), were selected for a comparison of the efficiencies of the difference Fourier and series termination correction methods of refinement.

1.2.cyclopentenophenanthrene

In the (h0l) zone 15 out of 17 carbon atoms are well resolved and masking corrections, while large enough to make a fair test of the method, are not too numerous to make estimation tedious. Intermolecular distances are large enough for masking from this source to be negligible.

In the earlier stages this projection was refined using the simple masking correction in conjunction with difference syntheses. When 197 of the signs of the 215 observable planes had been determined the final F_o Fourier synthesis was computed and the peak positions found by the 9-point method of Burns and Iball (22). In this method the highest points on rows in the figure field are found and joined to form ridge lines. The intersection of two such ridge lines is the peak. Megaw (32) suggests that a third ridge line should be drawn when possible using diagonal rows. If the three lines are of equal reliability the area enclosed at their intersections gives a measure of the accuracy of the peak coordinates.

Calculation of the structure factors using these uncorrected coordinates gave a reliability index $R = 0.150$ for the zone. The rippled atomic profile was then calculated from the Anthracene scattering

curve given by Robertson (23) with the hydrogen atom contributions removed. This corresponds to McWeeny's curve for carbon (24) with a temperature factor $B = 2.9$. The series termination and masking corrections were determined graphically as described above. These coordinates produced a reliability index of 0.131. A single difference Fourier was also carried out using the structure factors calculated for the uncorrected peak coordinates. The reliability index then fell to 0.122. The R.M.S. shifts in atomic positions from the uncorrected coordinates were 0.0245 \AA and 0.0187 \AA for series termination and difference Fourier respectively. The R.M.S. difference between the two sets of atomic positions was 0.016 \AA .

If the improvement in the reliability index is taken as a measure of the improvement in the structure, it is clear that the difference Fourier is superior in this instance. Whether the difference between the two sets of atomic coordinates is greater or less than the expected experimental error remains to be investigated.

An estimation of the accuracy of the atomic coordinates may be made by the method of Cruickshank (25). The expression for the standard deviation of the x coordinates is :-

$$\sigma(x) = \frac{\sigma(A_h)}{A_{hh}}$$

where $\sigma(A_h) = \frac{2\pi}{aV} \left\{ \sum_{-h}^h h^2 \Delta F^2 \right\}^{\frac{1}{2}}$

$$A_{hh} = \left(\frac{\partial^2 \rho}{\partial x^2} \right)_0 = -2\rho_0$$

$$\Delta F = F_0 - F_0$$

and the remaining symbols have the usual meaning. The quantity A_{hh} is taken as the curvature of the calculated atomic profile at the peak. On fitting the profile to the formula $\rho_x = \rho_0 e^{-px^2}$ a value of 73.0 was obtained for the product $2pp_0$. Standard deviations for the x coordinates were then found to be 0.0101 \AA and 0.0095 \AA respectively and for the z coordinates 0.0083 \AA . Since these apply to the actual coordinates they are not immediately comparable with the R.M.S. differences of position quoted above.

The effective standard deviation to be applied to the discussion of the significance of an apparent difference in atomic positions will vary somewhat with the direction of the vector joining them. For a random distribution of difference vectors the only course available is to derive the overall standard deviation as the square root of the sum of the squares of its components. When the difference vectors have only a small spread about a common direction then the relevant standard deviation is that relating to changes of position along the common direction. An approximation to this quantity may be obtained by constructing a parallelogram of sides equal to the standard deviations of the coordinates and drawing a line in the required direction through the origin to cut the parallelogram again. The length of this line is the value of the required standard deviation. This is equivalent to saying that the area in which an atomic centre probably lies is a parallelogram whose sides are proportional to the

TABLE 13 (a)

x coordinates (\AA) 1.2.cyclopentenophenanthrene

<u>Atom No.</u>	<u>1. Uncorrected</u>	<u>2. Corrected by difference Fourier</u>	<u>3. Corrected for masking and series termination</u>	<u>$\Delta x (= 2 - 3)$</u>
1	7.1561	7.1579	7.1630	-.0051
2	5.8033	5.8169	5.8294	-.0125
3	5.8262	5.8262	5.8485	-.0223
4	3.7996	3.7856	3.7939	-.0083
5	3.0600	3.0990	3.0670	.0320
6	4.3200	4.3028	4.2924	.0104
7	4.0689	4.0493	4.0247	.0246
8	5.3963	5.3708	5.3644	.0064
9	6.9517	6.9417	6.9476	-.0059
10	8.3514	8.3368	8.3113	.0255
11	8.2534	8.2449	8.2112	.0337
12	9.6488	9.6043	9.6019	.0024
13	10.9123	10.9263	10.9526	-.0263
14	11.1280	11.1590	11.1577	.0013
15	9.7697	9.7767	9.8056	-.0289
16	9.8911	9.9271	9.9370	-.0099
17	8.7091	8.7091	8.7469	-.0378

The R.M.S. value of $\Delta x = .021 \text{ \AA}$

TABLE 13 (b)

s coordinates (\AA) 1.2.cyclopentenaphenanthrene

<u>Atom No.</u>	<u>1. Uncorrected</u>	<u>2. Corrected by difference Fourier</u>	<u>3. Corrected for masking and series termination</u>	<u>$\Delta s(-2 - 3)$</u>
1	-0.0857	-0.0912	-0.0972	.0060
2	-2.3174	-2.3174	-2.3059	-.0115
3	-3.4355	-3.4355	-3.4273	-.0082
4	-5.8903	-5.8813	-5.9018	.0205
5	-5.9966	-5.9606	-5.9859	.0253
6	-3.6556	-3.6649	-3.6835	.0186
7	-2.9126	-2.9203	-2.9380	.0177
8	-0.7214	-0.7284	-0.7263	.0021
9	0.6942	0.7047	0.7155	-.0108
10	3.0119	2.9995	2.9807	.0188
11	3.8860	3.8966	3.8712	.0254
12	6.1541	6.1401	6.1328	.0073
13	7.2893	7.3239	7.3402	-.0163
14	6.5774	6.5874	6.5840	.0034
15	4.3099	4.3099	4.3312	-.0213
16	3.4213	3.4353	3.4451	-.0098
17	1.3568	1.3568	1.3667	-.0099

The R.M.S. value of Δs is .015 \AA

calculated standard deviations of the coordinates. The usefulness of this formulation is particularly apparent in the present case where the extremely large β angle of 142.5° has to be considered.

On comparing the two sets of coordinates obtained as explained above (Table 13(a) and (b)) it is seen that the vector differences of position of all but two of the atoms lie in the obtuse angle between the $[0,0,1]$ and the $[1,0,0]$ axes: that is Δx and Δz are of the same sign. The appropriate standard deviation can therefore be estimated as 0.008 \AA . This may be compared directly with R.M.S. difference, 0.016 \AA between the atomic positions. Since the latter quantity is twice as great as the former some interpretation is necessary.

The first possibility is that the difference between the sets of coordinates is probably significant, the chance of the difference occurring accidentally being about 3 in 100. In view of the fact that both sets of coordinates were obtained from the same data and in view of the satisfactory values of the reliability indices this seems most unlikely. The second alternative is to reject the standard deviation given by Cruickshank's analysis as being too optimistic. This will be discussed later.

20-methylcholanthrene $C_{21}H_{16}$

In the (0kl) projection of this structure all 21 carbon atoms are well resolved so that determination of peak positions is a simple matter and effects of pure masking are small. When the final F_0

Fourier synthesis was computed for the zone the structure had already undergone two cycles of three-dimensional difference Fourier refinement. The reliability index over all observed reflexions was then 0.178. Subsequently two further cycles were performed, the reliability then being 0.156.

The F_0 Fourier synthesis was treated as described for 1.2.cyclopentenophenanthrene. The series termination corrections were smaller in the present case since the atoms are all well separated but a greater number of atoms contributed to each correction due to the fact that other molecules approached to within 3 \AA in projection.

These coordinates produced the rather high reliability index of 0.212 or allowing 2% for the inclusion of the hydrogen atoms, 0.190.

The uncorrected coordinates and the two sets of "final" coordinates are compared in Table 14(a) and (b). Table 14 (c) contains the actual differences between the atomic positions. In 15 cases out of 21 the series termination corrections can be seen to have brought the uncorrected Fourier peak positions closer to the differential synthesis coordinates. The sizes of the differences are of some interest. The R.M.S. series termination correction is 0.014 \AA while the R.M.S. difference between uncorrected and differential synthesis positions is 0.035 \AA , showing plainly that the series termination corrections are inadequate in their present form. This may be contrasted with the previous case in which the R.M.S. series termination

TABLE 14 (a)

y coordinates (Å) 20-methylanthrene

<u>tem No.</u>	<u>1. Uncorrected from F Fourier</u>	<u>2. 4th cycle differential synthesis</u>	<u>3. Corrected for series termination and masking</u>	<u>$\Delta y = 2 - 3$</u>
A	4.6941	4.6801	4.6896	-.0095
B	5.4423	5.4909	5.4558	.0351
C	5.2660	5.2646	5.2730	-.0084
D	6.1188	6.1549	6.1346	.0203
E	5.9345	5.9466	5.9495	-.0029
F	4.8063	4.8279	4.8136	.0143
G	4.5870	4.6097	4.5910	.0187
H	3.5111	3.5196	3.5159	.0037
I	3.4740	3.4391	3.4820	-.0429
J	2.4218	2.4465	2.4278	.0187
K	1.5422	1.5074	1.5281	-.0207
L	1.5520	1.5988	1.5407	.0581
M	2.6718	2.6392	2.6573	-.0181
N	2.8771	2.8471	2.8606	-.0135
O	3.9590	3.9301	3.9520	-.0219
P	4.1816	4.1568	4.1723	-.0155
Q	3.3360	3.3337	3.3232	.0105
R	3.5980	3.5849	3.5805	.0044
S	5.3704	5.3529	5.3566	-.0037
T	4.5276	4.5847	4.5389	.0458
V	2.2764	2.3091	2.2764	.0327

TABLE 14 (b)

xsirB coordinates (Å) 20-methylcholanthrene

<u>Atom No.</u>	<u>1. Uncorrected from F_o Fourier</u>	<u>2. 4th cycle differential synthesis</u>	<u>3. Corrected for series termination and masking</u>	<u>$\Delta z = z - z_0$</u>
A	8.3163	8.3481	8.3338	.0143
B	7.8162	7.8112	7.8215	-.0103
C	6.4826	6.5157	6.4768	.0389
D	5.9742	5.9913	5.9742	.0171
E	4.7678	4.7506	4.7608	-.0102
F	3.9417	3.9368	3.9394	-.0026
G	2.6741	2.6720	2.6781	-.0061
H	1.8902	1.9106	1.8849	.0257
I	0.6927	0.6515	0.6904	.0389
J	-0.2216	-0.2041	-0.2211	.0170
K	0.2087	0.2234	0.2057	.0157
L	1.4459	1.4498	1.4582	-.0084
M	2.3877	2.3723	2.3839	-.0116
N	3.6493	3.6493	3.6583	-.0090
O	4.4207	4.4326	4.4187	.0139
P	5.7445	5.7472	5.7445	.0027
Q	6.3011	6.3061	6.3146	-.0085
R	7.5967	7.5899	7.5987	-.0088
S	1.9027	1.8808	1.8822	-.0014
T	0.4944	0.5314	0.4974	.0340
V	-1.5751	-1.5660	-1.5889	.0229

TABLE 14 (c)

20.methylcholanthrene. Distances between atomic positions
for three sets of coordinates (Å)

<u>Atom No.</u>	<u>1. Series termination</u> <u>- Uncorrected</u>	<u>2. Differential</u> <u>synthesis -</u> <u>Uncorrected</u>	<u>3. Differential</u> <u>synthesis - Series</u> <u>termination</u>
A	.0181	.0358	.0172
B	.0145	.0488	.0366
C	.0091	.0332	.0398
D	.0158	.0400	.0266
E	.0165	.0210	.0106
F	.0076	.0222	.0145
G	.0057	.0228	.0197
H	.0071	.0221	.0260
I	.0083	.0540	.0579
J	.0060	.0303	.0253
K	.0139	.0378	.0260
L	.0167	.0470	.0186
M	.0150	.0361	.0215
N	.0188	.0300	.0162
O	.0073	.0221	.0259
P	.0093	.0250	.0157
Q	.0186	.0055	.0135
R	.0176	.0148	.0098
S	.0247	.0280	.0040
T	.0117	.0680	.0571
V	.0138	.0339	.0395
R.M.S. difference	.014	.035	.031
Mean difference	.013	.032	.025

shift, 0.0245 \AA , was greater than that due to a single difference Fourier

The R.M.S. difference between the two sets of "final" coordinates is 0.031 \AA which may be compared with the radial standard deviation 0.014 \AA calculated from Cruickshank's formula. The ratio of these is 2.21:1 indicating that, according to accepted statistical criteria, the two sets of coordinates are significantly different to about the same degree as was found for 1.2. cyclopentenophenanthrene.

Before the possibility of the differences being significant is allowed, it is necessary to examine the basis of Cruickshank's formula. No fault has been found with the mathematical treatment. Two symbols only in the formula require interpretation. The quantity A_{hh} was evaluated from the calculated atomic profile rather than graphically since the latter would involve averaging over all the Fourier peaks, a process which had in effect been carried out previously when an overall temperature factor correction was applied to the zone. The calculated profile was derived directly from the corrected scattering curve and so was the best average available.

ΔF was equated simply to the difference $F_o - F_c$ and Cruickshank rejected the idea that errors in the estimation of intensities should be used to get an approximate value for each $|\Delta F|$. It is clear that a value of σ , the standard deviation, obtained from ΔF 's estimated as errors in the observed data alone would be independent of the state of refinement of the structure and might be taken as the lowest value

attainable, the reliability index then being zero. Errors of this kind will have a considerable effect on the accuracy of coordinates at all stages of refinement since for individual F_o measurements they may be as large as 10%, while errors of 20%, due to extinction, in some low angle reflexions are not unknown. The latter are more tractable than the former since their signs are known and their existence may be suspected from the occurrence of excessively large values of ΔF .

If the true, but unknown, value of the structure factor is F_T two relations may be written,

$$F_o - F_c = \Delta F_1$$

$$F_T - F_o = \Delta F_2$$

whence the true F , which should appear in the formula for σ , becomes

$$\Delta F = F_T - F_c = \Delta F_2 + \Delta F_1$$

$$\begin{aligned} \therefore \sigma &= \frac{2\pi}{aV} \left\{ \sum_{-H}^H h^2 \Delta F^2 \right\}^{\frac{1}{2}} \\ &= \frac{2\pi}{aV} \left\{ \sum_{-H}^H h^2 [\Delta F_2^2 + 2\Delta F_2 \Delta F_1 + \Delta F_1^2] \right\}^{\frac{1}{2}} \end{aligned}$$

Making the intuitive assumption that $\sum_{-H}^H h^2 \Delta F_2 \Delta F_1$ is small compared to the remainder of the expression, we have the result

$$\sigma = (\sigma_2^2 + \sigma_1^2)^{\frac{1}{2}}$$

where σ_1 is the standard deviation calculated with $\Delta F = F_o - F_c$ and σ_2 is that which could be obtained from a consideration of the random errors of measurement of the structure factors. If these errors are not random the assumption that $\sum_{-H}^H h^2 \Delta F_2 \Delta F_1$ is small is invalid so

that the true value of σ may be very different from the postulated value.

In the later stages of refinement σ_1 and σ_2 will not be very different so that

$$\sigma \doteq \sigma_1 \sqrt{2}$$

Beyond this point σ will approach the limiting value σ_2 .

For the present purposes Cruickshank's value is therefore increased by a factor 1.4 and the ratios of R.M.S. difference between sets of coordinates to calculated standard deviation are reduced from 2.0 and 2.2 to 1.4 and 1.6. The latter figures indicate that the differences between coordinates are not significant (Section III (v)).

The foregoing discussion suggests that the line of approach adopted will not yield an accurate value for the standard deviation. The approximation given may serve as a rough guide, but it will probably be insufficiently precise to determine the significance or otherwise of results to any degree of accuracy. It is possible that the R.M.S. difference between the sets of atomic positions obtained as described, is as true a measure of the accuracy of the structure as can be obtained.

This conclusion is a disappointing one. It was hoped that the two refinement techniques would produce sets of atomic positions which were equivalent within the limits imposed by the errors in the observed data and by the degree of refinement of the structure. It

now appears impossible to fix these limits other than by reference to the difference between the atomic positions whose accuracy it is desired to test.

To sum up the merits of the techniques discussed. The difference and differential syntheses seem to be superior in that they improve the reliability index more rapidly. Their chief merit is that each succeeding cycle of refinement takes up exactly where the previous one finished, i.e. the uncorrected coordinate is already known and only the correction to be applied has to be estimated. Further, any minor mistakes are automatically compensated for in the subsequent refinement.

In contrast, the determination of Fourier peak positions is liable to errors of the order of 0.01 \AA , even under the best possible conditions, as is discussed in Appendix II. These errors are random and are liable to occur each time the technique is employed. While it does not seem likely that they would reinforce to any significant extent over several refinements, it is quite obvious that errors of this order will remain, however many cycles of refinement are carried out.

For this reason the use of the F_0 Fourier should be limited to the initial stages of refinement, particularly when the amount of data put into successive syntheses is small but increasing rapidly. The improvement in the peak shapes may then lead to significant improvement in the reliability index. If in addition, there is much

overlapping of adjacent atoms, it will be worthwhile to apply systematic masking corrections while ignoring the interaction of peaks further away than about 1.3 \AA . The speed of refinement may then compare favourably with or surpass that of the difference Fourier (e.g. see Section III (iv)).

When all the available data has been put into the F_0 Fourier and the best coordinates extracted, the refinement must proceed by means of difference syntheses since, as has appeared, the series termination corrections do not provide a short cut to the same coordinates. Improvement of the reliability index is still possible in this way after the F_0 Fourier has ceased to be of use, and as the reliability index is the only currently available criterion of the worth of a structure, the coordinates which give the best value must be accepted.

It may be noted that this argument is not strictly applicable to a non centrosymmetric projection, since phase changes will take place and will presumably improve the Fourier synthesis as long as refinement is continued. It seems unlikely, however, that this approach will be as profitable as refinement by difference synthesis.

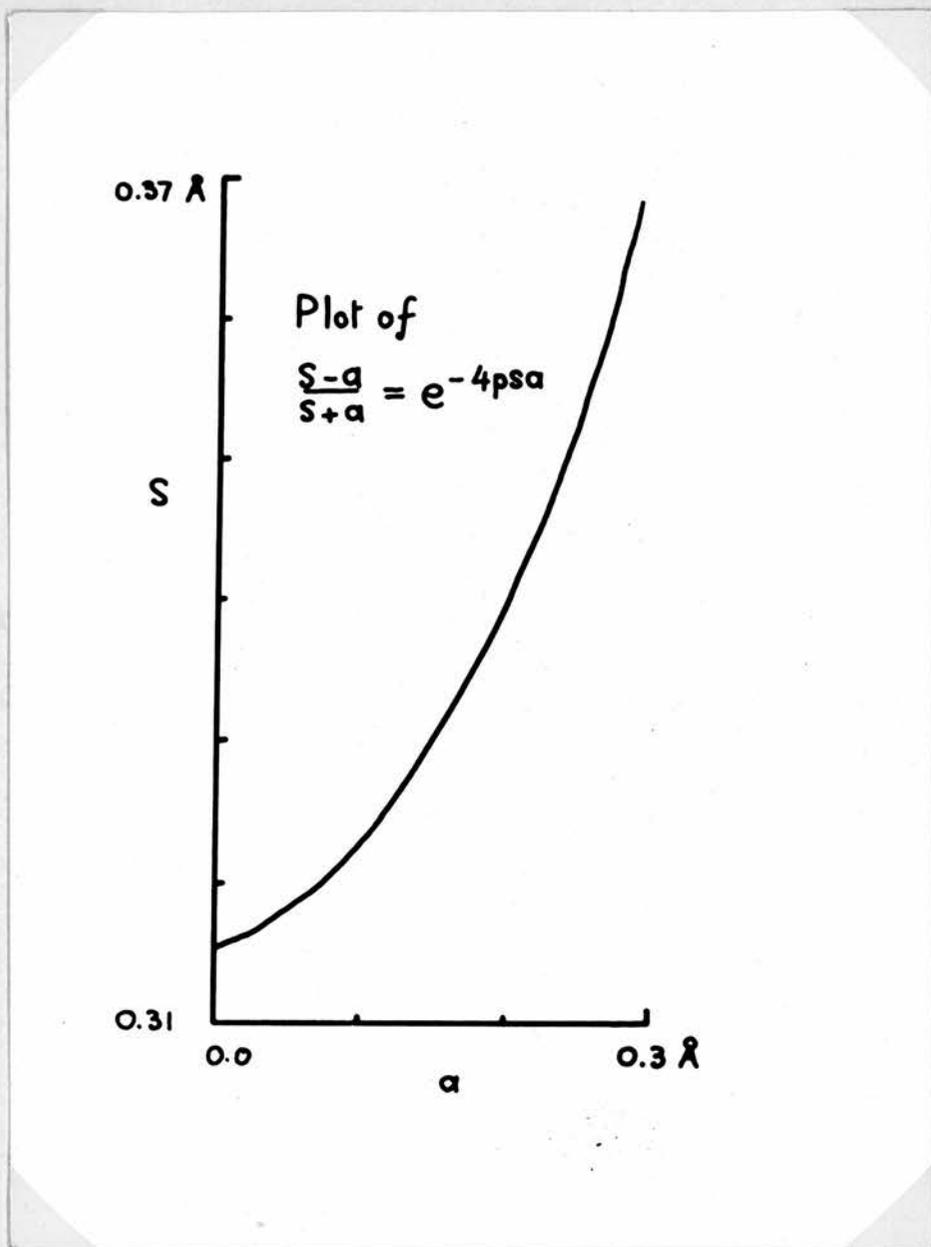


Fig. 21

Showing the relation between peak to trough distance ($2s$) and positional error of coordinate ($2a$) in a difference Fourier ($p = 5.0$).

APPENDIX IOn the limits of usefulness of the difference Fourier in two dimensions

Two considerations limit the use of the difference Fourier in structure refinement. The first is the slow or zero rate of refinement when the atomic coordinates are placed too far from their true positions. The second is the disturbing effect on any coordinate shift, taken from a difference map, of the errors in placing other nearby atoms. Some of these effects are discussed and an estimate of the resolving power of the method is attempted.

Supposing an atomic profile to be given by $\rho r = A \exp -p(r - a)^2$ (35), the atom being centred at $r = a$, we may represent the result of computing a difference Fourier for one atom by subtracting from this an atom $\rho r' = A \exp -p(r + a)^2$, the position $r = -a$ being the assumed position and $r = +a$ the true position of the atom. The required shift is then $\Delta r = 2a$. The resultant electron density is

$$\Delta \rho = \rho r - \rho r' = A \exp -p(r - a)^2 - \exp -p(r + a)^2$$

Differentiating

$$\frac{d(\Delta \rho)}{dr} = 2pa (r + a) \exp -p(r + a)^2 - (r - a) \exp -p(r - a)^2$$

ρ has maximum or minimum at $r = \pm s$ where

$$\frac{s - a}{s + a} = \exp(-4psa)$$

The function s against a is plotted in fig. 23, for $p = 5.0$ as found for 1.2.cyclopentenophenanthrene. The value of $\frac{d(\Delta \rho)}{dr}$ at $r = -a$ is given by

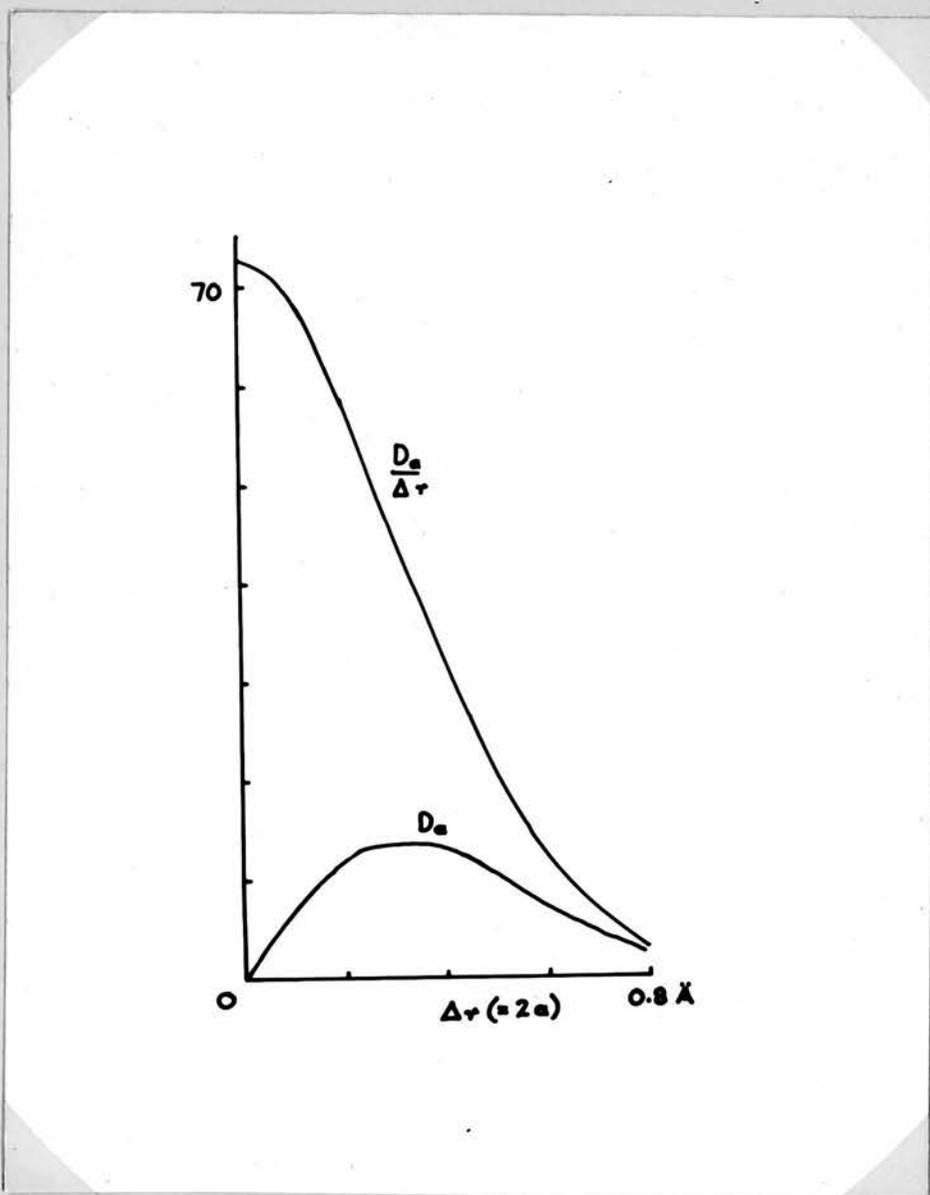


Fig. 24

Plot of $D_e \left[= \left(\frac{d(\Delta p)}{dr} \right)_{r=a} \right]$, and of $D_e/\Delta r$, against Δr .

$$D_a = 4pAa \exp(-4pa^2)$$

• taking $2pA = 73$ (Section V)

$$D_a = 73 \Delta r \exp(-pa\Delta r)^2$$

This function and the ratio $\frac{D}{\Delta r}$ are plotted in fig. 24.

$$\text{The expression } \Delta r = \frac{D \exp(4pa^2)}{2pA}$$

may be compared with the usual formula (Section V).

$$\Delta r = \frac{D}{2pA}$$

The range over which these two formulae are approximately equivalent is given by the initial straight portion of the graph of D_a against Δr . This extends to $\Delta r \doteq 0.15 \text{ \AA}$. Beyond this point the gradient D_a indicates too small a shift unless the exponential term is taken into account. Although the gradient is still measurable at $\Delta r = 0.6 \text{ \AA}$, the possibility of refinement at this distance seems remote, except in very exceptional circumstances. It is more likely that structure factor agreement would be so poor in the first instance that insufficient data could be included in the difference Fourier to produce a fair approximation to the quantity $pr - pr'$. Uncertainty in the scale and temperature factors and also errors in the observed structure factors must reduce the refining power still further. The figure 0.6 \AA may be four or five times greater than the upper limit for refinement to take place.

Considering now the resolving power of the method, we see from fig. 23 that the misplacement of an atom by a distance of not more than 0.15 \AA produces a positive and a negative peak at a separation of about

0.64 Å along the line of the required shift. The effect of these peaks will be noticeable a further 0.32 Å beyond their maxima so that spurious shifts may be indicated to other atoms within a distance of about 0.7 Å in either direction. The maximum possible value of this shift is equal to the shift applied to the original atom and is opposite in direction to it.

With two atoms close enough to be unresolved in Fourier projection it is likely that the principal corrections required will be along the line of centres, the centre of gravity remaining stationary unless the peak position has been incorrectly located. Lateral shifts may be required if the line of centres has not been accurately placed or if series termination effects from nearby atoms are appreciable. Since the resolving power of the F_0 Fourier synthesis is about 0.7 Å for CuK α radiation, it might appear at first sight that the use of the difference Fourier brings no improvement in resolution. However, it is possible to analyse a double Fourier peak to give moderately accurate coordinates (Appendix II(a)), from which refinement can proceed in not too large steps once it is realized that more than one interpretation of the relevant portions of the difference map may be possible. Thus if the gradients at the two assumed positions are equal and opposite it may mean that the two are to be moved towards or away from the centre by equal amounts; alternatively that the wrong placing of one atom is producing its maximum spurious effect while the other is correctly

placed. A continuous variation between these extremes is possible. It may then be possible to select the correct shifts by locating the troughs or peaks corresponding to the peak or trough between the atoms. If the shifts indicated are in the same direction it may be impossible to distinguish between the case where two equal shifts are required and that which calls for a large and a small or zero shift. An average shift may then be taken as applying to the centre of gravity of the pair. If this is placed correctly the next cycle of refinement will indicate equal and opposite shifts.

If one atom requires a lateral shift relative to the line of centres, a lateral shift in the other atom is indicated, the gradient being given by

$$D = 4apA \exp -p(d^2 + 4a^2)$$

where d is the separation of the atoms and $2a$ is the original shift. The ratio of spurious to original gradient is then

$$\frac{D}{D_a} = \exp(-pd^2)$$

and the indicated shift is $2a \exp(-pd^2)$. The ratio $\frac{D}{D_a}$ is less than 0.1 for d greater than 0.7 \AA , but at $d = 0.3 \text{ \AA}$ it is 0.64 which is by no means negligible.

This calculation may have its use if the principal ridge line has been misorientated as may happen when the atoms are almost on top of one another. The calculated separation is also likely to be in error (Appendix II(a)), but this can be dealt with separately. The

true lateral shifts should then be equal and opposite and the effect of each will be to reduce the other by an equal fraction. Suppose that $d = 0.3 \text{ \AA}$ and that shifts required are 0.03 \AA . The indicated shifts will be $+0.03 - 0.02 = 0.01 \text{ \AA}$.

A lateral shift produces no gradient along the line of centres at the other position, neither does a shift along the line of centres produce a lateral gradient.

A calculation may be made of the height and extent of the peak or trough between closely adjacent atoms assuming small equal and opposite shifts in the line of centres.

Let the assumed atomic positions be $\pm(t - a)$ and the true positions be $\pm(t + a)$. If the atomic profile is given by $\rho r = A \exp(-pr^2)$ then the result of the difference synthesis is given by

$$\Delta \rho = A \exp -p(r - [t+a])^2 - \exp -p(r - [t-a])^2 + \exp -p(r + [t+a])^2 - \exp -p(r + [t-a])^2$$

$$\Delta \rho = 2A \left[\exp -p(r^2 + [t+a]^2) \cosh 2pr(t+a) - \exp -p(r^2 + [t-a]^2) \cosh 2pr(t-a) \right]$$

$$\Delta \rho = -4A \exp -p(r^2 + a^2) \left[\cosh 2prt \cosh 2apr \sinh 2apt - \sinh 2prt \sinh 2apr \cosh 2apt \right]$$

The value of $\Delta \rho$ when $r = 0$ is given by

$$\Delta \rho_0 = -4A \exp(-pa^2) \sinh 2apt$$

or for a and apt small and $2Ap = 73$, $\Delta \rho_0 = -292$ at $e\text{\AA}^{-2}$

The value of r for which $\Delta \rho = 0$ is of interest and is given by

$$\tanh 2prt \tanh 2apr = \tanh 2apt$$

or since the arguments are still small

$$r^2 = \frac{1}{2p}$$

$$\therefore r = \pm 0.32 \text{ \AA} \text{ for } p = 5.0$$

The constancy of $r(\Delta\rho = 0)$ suggests that it might be possible to detect an incorrect scale factor by the departure of $\Delta\rho$ from zero at this distance: also that this figure might be used to obtain a more accurate value of $\Delta\rho$ at $r = 0$. We may calculate $\Delta\rho_0$ for various assumed and true separations of atoms noting that these quantities are given by $2(t - a)$ and $2(t + a)$ respectively. Thus

TABLE 15

<u>Assumed separation</u>	<u>True separation</u>	<u>$\Delta\rho_0$</u>
0.06 \AA	0.14 \AA	- 0.3 e\AA ⁻²
0.16	0.24	- 0.6
0.36	0.44	- 1.2

In each case a shift of 0.04 \AA to both atoms is postulated. If the true and assumed separations are interchanged $\Delta\rho_0$ is of course positive.

The value of $\Delta\rho_0$ which is detectable and measurable with certainty will naturally vary with the circumstances. Assuming a minimum detectable value for $\Delta\rho_0$ of 0.6 e\AA⁻² we may calculate the

true separation if zero separation has been assumed. Then $a = t$ and

$$292 a^2 = 0.6$$

$$a = 0.045 \text{ \AA}$$

and the true separation is 0.180 \AA .

The reduction of $|\Delta\rho_o|_{\min}$ to 0.3 e\AA^{-2} gives a separation of 0.128 \AA . This figure then corresponds to the minimum separations distinguishable from zero in the two cases, i.e. the resolving power of the difference Fourier. If we regard $|\Delta\rho_o|_{\min}$ as the smallest change in $\Delta\rho$ to be regarded as significant, we may write

$$\text{Resolving power} = \left[\frac{2|\Delta\rho_o|_{\min}}{\rho\Delta} \right]^{\frac{1}{2}}$$

where $|\Delta\rho_o|_{\min}$ is given by the formula

$$|\Delta\rho_o|_{\min} = 2.33 \sigma(\rho) = \frac{2.33}{A_o} [\sum \Delta F^2]^{\frac{1}{2}} \quad (25)$$

where $\sigma(\rho)$ is the standard deviation of the electron density in the F_o Fourier and A_o is the area of the unit cell projection. The interpretation of ΔF is subject to the considerations outlined in Section V.

The value of $\sigma(\rho)$ for 1,2-cyclopentenophenanthrene (h01) zone was calculated from $\Delta F = F_o - F_c$ to be 0.225 e\AA^{-2} . Multiplying $\sigma(\rho)$ by $\sqrt{2}$ as in Section V, we obtain 0.318 e\AA^{-2} and

$$|\Delta\rho_o|_{\min} = 0.74 \text{ e\AA}^{-2}$$

so that Resolving power = 0.20 \AA .

Although the figure for $|\Delta\rho_o|_{\min}$ seems rather high and may in

fact refer to the significance of differences of electron density in different parts of the cell rather than to differences over a range of two or three net points, the value of the resolving power calculated from it is probably a reasonable approximation to the truth.

A practical evaluation of the resolving power might be attempted using a hypothetical structure. This would seem eminently desirable were it not for the increasing tendency to complete structure refinements using full three-dimensional diffraction data and electronic computation. The problem of overlapping is then non-existent as far as light atoms are concerned.

APPENDIX IIDetermination of Fourier Peaks(a) Analytical resolution of double peaks

The electron density on the long axis of the double peak may be represented as the sum of two atomic profiles with centres at $r = \pm a$ thus

$$\rho_r = A \exp -p(r - a)^2 + A \exp -p(r + a)^2$$

so that at $r = 0$ the peak height is give by

$$\rho_0 = 2A \exp(-pa^2)$$

which gives the value of the half distance between the atoms

$$a = \left[\frac{1}{p} \ln \frac{2A}{\rho_0} \right]^{\frac{1}{2}}$$

An average value of A , the height of a single peak may be taken from well resolved atoms in the same Fourier projection or from the rippled atomic profile as in Section V. The former is the least time consuming. The value of A/ρ_0 is not quite independent of scale factor since $F(000)$ must be subtracted from each before a change of scale is made. The value of A taken from the Fourier map becomes critical when a is very small. In particular, the mean peak height may be overestimated due to masking between atoms, though this may be allowed for if recognized. The effect is to increase the calculated value of a . An error of 5% in A in these circumstances will produce an error of 0.2 Å in the calculated separation. At the other extreme when the atoms are approaching resolution the error is only one tenth

of this for the same error in A.

(b) Location of maxima

It is common practice to fit the figure field surrounding a Fourier peak to a series of parabolas, so finding the electron density maxima along a number of net lines. The peak is taken as the intersection of the 'ridge lines' drawn smoothly through the maxima of parallel net lines (Booth (19), Burns and Iball (22)). The calculation of the peak as the maximum of a parabolic surface has been given by Ladel and Katz (33) and Burns (34).

The assumption of an exponential form for the Fourier peak seems to offer some saving in drawing time over the former method and in ease of calculation over the latter. Perhaps not a very strong argument in its favour is the desire for consistency with the previously assumed form of the peak.

Two methods of arriving at the peak position are available. The results will be seen to be identical.

Method 1

Let the electron densities at the net points 1, 2, 3 be given by

$$\rho_0 = A \exp -pr_0^2$$

$$\rho_1 = A \exp -p(r_0 - r)^2$$

$$\rho_2 = A \exp -p(r_0 - 2)^2$$

where $A = \rho_{\max} = \rho(r_0)$ and $p = \text{constant}$

Then $\frac{\rho_1}{\rho_0} = \exp -p(1 - 2r_0)$

$$\frac{\rho_2}{\rho_0} = \exp -4p(1 - r_0)$$

let $a_1 = \ln \frac{\rho_1}{\rho_0} = p(2r_0 - 1)$

$$a_2 = \ln \frac{\rho_2}{\rho_0} = 4p(r_0 - 1)$$

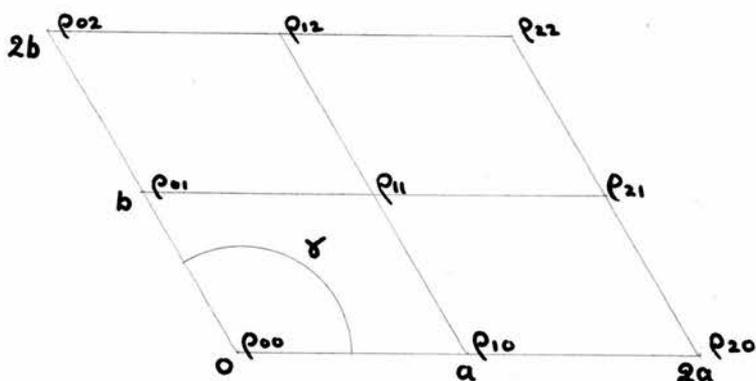
$$\therefore r_0 = \frac{4a_1 - a_2}{4a_1 - 2a_2} = \frac{4 - t}{4 - 2t}$$

where $t = \frac{a_2}{a_1}$

This becomes identical with the formula for x_m given by Booth (19) if $(\ln p - \ln p_0)$ is replaced by $(\rho - \rho_0)$. The use of $\ln p$ in place of ρ is mentioned by Burns (3) but the reason for doing so is not given.

Method 2

Consider a lattice with constants a , b and γ and electron densities ρ_{00} , ρ_{01} etc. as shown.



Let the peaks have coordinates (ax, by) where $0 < x, y < 2$.

$$\text{Define } ax' = ax - by \cos \gamma^{\#}$$

$$by' = by - ax \cos \gamma^{\#}$$

That is ax' and by' are the distances from the origin of the feet of the perpendiculars from (ax, by) on to the respective axes.

$$\text{Then } P_{00} = A \exp -p(a^2x^2 + b^2y^2 - 2abxy \cos \gamma^{\#})$$

$$P_{01} = A \exp -p(a^2x^2 + b^2[y-1]^2 - 2abx[y-1] \cos \gamma^{\#})$$

$$P_{02} = A \exp -p(a^2x^2 + b^2[y-2]^2 - 2abx[y-2] \cos \gamma^{\#})$$

Eliminating A

$$\begin{aligned} a_{01} = \ln \frac{P_{01}}{P_{00}} &= -p [b^2(1-2y) + 2abx \cos \gamma^{\#}] \\ &= -pa^2(1-2x') \end{aligned}$$

$$\begin{aligned} a_{02} = \ln \frac{P_{02}}{P_{00}} &= -p [4b^2(1-y) + 4abx \cos \gamma^{\#}] \\ &= 4pb^2(1-y') \end{aligned}$$

Eliminating p

$$y' = \frac{4a_{01} - a_{02}}{4a_{01} - 2a_{02}}$$

Repeating the analysis for P_{10} P_{11} P_{12} and P_{20} P_{21} P_{22} , two further expressions for y' are obtained

$$y' = \frac{4a_{11} - a_{12}}{4a_{11} - 2a_{12}} - \frac{a}{b} \cos \gamma^{\#}$$

$$\text{and } y' = \frac{4a_{21} - a_{22}}{4a_{21} - 2a_{22}} - 2 \frac{a}{b} \cos \gamma^{\#}$$

Similar expressions may be obtained for x' and the coordinates (x, y) from the relations

$$ax = \frac{ax' + by' \cos \gamma^{\#}}{\sin^2 \gamma^{\#}}$$

$$by = \frac{bx' + ax' \cos \gamma^{\#}}{\sin^2 \gamma^{\#}}$$

These equations are sufficient to determine the peak positions without recourse to drawing.

Examining the three expressions for y' it may be seen that e.g.

$\frac{4a_{o1} - a_{o2}}{4a_{o1} - 2a_{o2}}$ is the value y_0 previously obtained for the peak

coordinate along the net line $x = 0$ and similarly for y_1 and y_2 on the net lines $x = 1$ and $x = 2$ so that the expressions become

$$y' = y_0$$

$$y' = y_1 - \frac{a}{b} \cos \gamma^{\#}$$

$$y' = y_2 - \frac{2a}{b} \cos \gamma^{\#}$$

In other words, the ridge line is a line of constant y' , that is a line perpendicular to the y axis. A little consideration renders this conclusion obvious, although it does not seem to have been explicitly stated elsewhere.

For the particular case of an orthogonal lattice the relations reduce to

$$y = y' = y_0 = y_1 = y_2$$

It is now evident that the graphical and analytical methods are entirely equivalent. The only difference likely to be encountered in practice might arise from the method of taking the average of x' and y' if as sometimes happens there are small variations from one net line to another.

A study of a number of peaks in the orthogonal (0kl) projection of 20-methylcholanthrene (Section V) confirmed this conclusion to a very good degree of accuracy. Values of y_0, y_1, y_2 agreeing to 0.005 Å or better, were common. These peaks were well resolved and shapely. Any effects of masking or of asymmetric vibration would presumably show up either in the curvature of the ridge lines or their inclination to the net lines or in the different values of p which are calculable for the profile $A \exp(-px^2)$ for the two axial directions.

Some peak positions calculated for 20-methylcholanthrene using the exponential and the parabolic forms are shown below.

TABLE 16

<u>Atom</u>	<u>Coordinates</u>	<u>Exponential</u>	<u>Parabolic</u>	<u>Difference (Å)</u>
		<u>120ths</u>		
M	y	28.368	28.273	.0090
	z	11.439	11.441	.00042
Q	y	35.210	35.302	.0087
	z	30.223	30.192	.0065
S	y	56.882	56.830	.0049
	z	9.131	9.117	.0029

The figures would seem to indicate that the assumption of exponential or parabolic form for the peak is a matter for personal choice. This is so, provided that the coordinates are not accepted as final or subjected only to masking and series termination

corrections. Clearly such corrections would do nothing to remove inaccuracies in the peak determination.

It is evident that if the uncertainties of the peak positions are too great to be acceptable, the way to correct for them is by means of a difference Fourier. It is shown in Section V that even when the peak positions are apparently determinable with great accuracy and masking and series termination corrections applied, a difference Fourier will produce shifts of coordinates greater than the assumed uncertainties and a corresponding improvement in reliability. For this reason it seems pointless to search for greater accuracy in peak determination, but since the accuracy at present obtainable is very useful as a starting point it is worth a little effort to obtain the best possible coordinates systematically rather than by visual estimation only.

APPENDIX IIIA rapid method of fixing molecular centres

In the structure analysis of condensed ring compounds the orientation of the molecule is often easier to determine than its precise position in the cell. Some methods of fixing orientation have been indicated in Section III (ii) and (iii). Trouble may be experienced if an axial projection is very confused or if molecular positions are not obviously limited by packing considerations.

When the position is not immediately clear, it is helpful to calculate structure factors systematically, varying one set of coordinates only. If sufficient reflexions with two indices zero are available or if one set of coordinates is already known, this can easily be done. It is common to plot these values of the structure factors against the position of the molecular centre and to find the position at which observed and calculated factors show the greatest measure of agreement. This position is not always easy to spot. The innovation suggested here is to plot the values of $[|F_o| - |F_c|]$, a function which is zero at or close to the required position. With a number of such curves plotted the true position of the centre should be obvious at once. In any case, not more than two positions should need investigation. Small errors in coordinates relative to the centre, due to the idealization of the molecule, appear to have comparatively little effect on the shape of the curves.

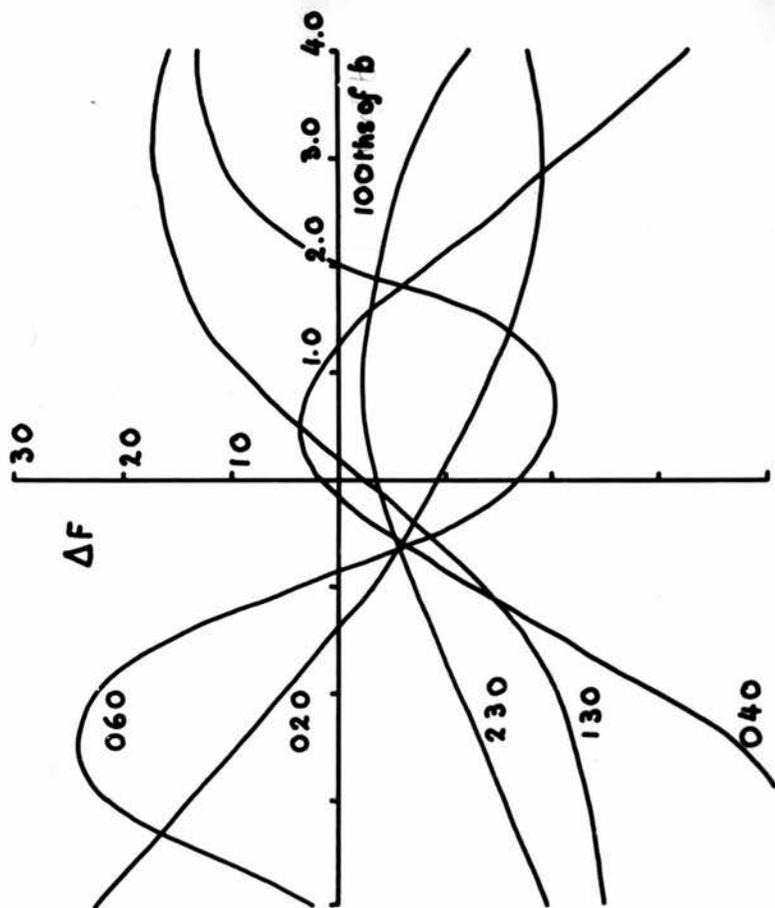


Fig. 25

Showing the variation of some structure factors with movement of the molecular model parallel to the b axis (1.2-cyclopentaphenanthrene).

This method was used to fix the y coordinate of the centre of 1.2-cyclopentenophenanthrene. Fig. 25 shows the variation of five structure factors along the b axis for the $[001]$ projection. The centre is at $-0.0065 b$ which compares very favourably with the value $-0.008b$ taken from the refined y coordinates. The difference in \AA is 0.009. The fact that the curves all cross slightly below the axis suggests the possibility of an incorrect scale factor. Its magnitude could not be estimated from this graph but a plot of the function $\frac{|F_c| - |F_c|}{|F_c|}$ suggested a value of 20%. An increase of this order in the magnitude of the observed structure factors was noticed independently during later refinement. The plot of the latter function is of less value in fixing the position of the molecule since curves corresponding to small or zero values of F_c are intractable. The curves of $[|F_c| - |F_c|]$ for F_c small or zero, on the other hand, are easily dealt with and may be of value.

The curves in Fig. 25 were drawn when the x coordinates of the atoms were already well refined. However, it can be seen that the evidence from the (1,3,0) and (2,3,0) planes merely confirms the position suggested by the (0k0) planes. The latter are almost sufficient in themselves and with more than three axial reflexions available the position of the molecule must be determinable unequivocally and with fair accuracy.

The calculation of the necessary structure factors was considerably simplified by the use of the Bragg structure factor balance (Section II). The constant factors $\cos 2\pi \frac{hx}{a}$ were set up on the centre scales and the values of $\frac{ky}{b}$ for an arbitrary position of the molecule were set up on the rim scales. It was then possible to calculate the structure factor with the molecule moved a distance Δy parallel to b by altering the settings of the rim scales by an amount $\frac{k\Delta y}{b}$. The complete calculation for each structure factor curve then took only a few minutes.

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