The Crystal and Molecular Structure of Ovalene, Perylene and Octamethylnaphthalene

THESIS

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Part III. The Crystal and Molecular Structure of Octamethylnaphthalene.

Preface

This thesis describes research into crystal and molecular structures of organic compounds which has been carried out since October 1948 in the Chemistry Department of the University of Glasgow. It is expected that the work will be published.

I wish to offer my sincere thanks to Professer J. Monteath Robertson for suggesting the research problems, and for his constant interest and encouragement throughout the work. I would also like to thank Dr. E. Clar for the crystal specimens of ovalene and Professor J. W. Cook for the crystal specimens of perylene and octamethylnaphthalene.

In conclusion I am indebted to the Department of Scientific and Industrial Research for a maintenance allowance during the first two years of this research.

D. M. D.

Summary

Described in this thesis are the results of research on three main problems. These three problems are separated into Parts I, II and III, which contain reports on investigations into the crystal and molecular structures of ovalene, perylene and octamethylnaphthalene respectively, by means of X-ray diffraction methods. The appendix contains a short account of the crystal structure of benzfurazane oxide.

Part I. The crystal and molecular structure of ovalene has been determined by quantitative X-ray analysis. The monoclinic crystals, space group $P2_1/a$, have two centro-symmetrical molecules of $C_{32}H_{14}$ per unit cell, and the structure resembles that of coronene. The cell dimensions of $\underline{a}$ = 19.47A, $\underline{b}$ = 4.70A, $\underline{c}$ = 10.12A and β = 105.0° bear a remarkable similarity to coronene in the $\underline{b}$ and $\underline{c}$ axial directions. The tilt of the molecular plane to the (010) crystal plane, 43°, and the distance of 3.45A between the molecular planes are almost identical to the corresponding values in the coronene structure. In the (h0l) projection, all of the 16 carbon atoms in the asymmetric unit are clearly resolved, and the measured values of the bond distances between these atoms vary from 1.345A to 1.45A. Reference

is made to the calculations on this problem by the methods of molecular orbitals, and of spin states. The variations in bond distances in different parts of the molecule have also been discussed in terms of the 50 stable valence-bond structures for ovalene.

Part II. The crystal and molecular structure of perylene has been determined by quantitative X-ray analysis. The monoclinic crystals, space group $P_{2_1/a}$, have four molecules of $C_{20}H_{12}$ per unit cell, and the structure resembles that of 1:12 benzperylene. The molecule has been shown to be planar if only the carbon atoms are considered, and so has a centre of symmetry. It is possible that some of the hydrogen atoms are not in the same plane, and so this may destroy the centre of symmetry. The cell dimensions are $\underline{a}$ = 11.35A, $\underline{b}$ = 10.87A, $\underline{c}$ = 10.31A and $\underline{\beta}$ = 100.8°. The tilt of the molecular plane to the (010) crystal plane is 55°, and the distance between the molecular planes is 3.47A. In the (h01) projection only 11 of the 20 crystallographically distinct carbon atoms were resolved, and in some cases the resolution was poor. These 11 resolved atoms were sufficient to give a measure of every chemically distinct bond in the molecule except one. The measured values of the bond distances vary from 1.375A to 1.50A. This latter value is the longest bond which has so far been measured in a polycylic aromatic hydrocarbon. Reference is made to molecular orbital calculations on this problem, and the bond length variations are discussed in terms of the 9 non-excited or Kekulé structures.

<u>Part III</u>. The crystal and molecular structure of octamethylnaphthalene has been investigated by X-ray diffraction methods. The orthorhombic crystals, space group Ccca, have four molecules of $C_{18}H_{24}$ per unit cell. Since the space group requires 16 asymmetric units, the asymmetric unit consists of one-quarter of the molecule. The cell dimensions are $\underline{a}$ = 16.66A, $\underline{b}$ = 11.31A and $\underline{c}$ = 7.64A. The molecular plane lies in the (001) crystal plane. Only 2 of the 5 crystallographically distinct atoms are resolved in the (hk0) projection. A new type of difference synthesis has been used to resolve another atom in this zone. In the (h0l) projection only one atom was resolved. This was the methyl group in the α-position, and it does not lie in the molecular plane, but is displaced by 0.73A. The remaining z co-ordinates were obtained by trial and error using the (h0l) and (0kl) reflections. It has been shown that the methyl group in the β -position is very probably displaced from the

molecular plane by about 0.25A or 0.3A. There is also a distinct possibility that the naphthalene nucleus is not planar, i.e. it may be distorted. It has also been shown that the contribution of the hydrogen atoms to the structure factors cannot be neglected. A full three-dimensional analysis of this structure will be required before the structure is completely known.

Appendix. The crystal structure of benzfurazane oxide has been determined by X-ray methods. The triclinic crystals, space group P1 or $P\bar{1}$, have four molecules of $C_6H_4N_2O_2$ per unit cell. The molecular symmetry is unknown. So also is the structure. The cell dimensions are $\underline{a}$ = 10.76A, $\underline{b}$ = 7.83A, $\underline{c}$ = 7.51A, $\underline{\alpha}$ = 99.2°, $\underline{\beta}$ = 95.5° and $\underline{\gamma}$ = 94.0°.

Introduction

There are many methods available for the precise measurements of bond lengths in molecules. Calculations based on spectroscopic data undoubtedly yield the most accurate results for simple types. This method however can only be applied to gaseous molecules of the simplest type, ~~i.e.~~ e.g. diatomic or triatomic molecules (1). The results obtained here are very accurate though, and give very reliable values for the pure carbon-carbon single and double bond links.

Diffraction methods however have a much greater range of application. Both gas diffraction and crystal diffraction are now being widely employed. For the more complex types of structures now being investigated crystal diffraction methods are the most suitable. The diffraction of high velocity electrons by gases and vapours has been extensively used in the analysis of structures. A good account of the development of this method and a list of structures investigated has been published by Brockway (2). This method of investigating structures however, only applies to compounds which exist in the gaseous state or to solids with a high vapour pressure, i.e. they can be easily converted to the vapour. An example of this latter type is the investigation of the dimethylketene dimer (3), where the melting-point of the compound was 113°- 114°, but, due to its high vapour pressure near the melting-point, it passed directly into the vapour stage. Electron diffraction methods differ from spectroscopic methods in that a trial structure of the compound under investigation is required and also a theoretical curve to compare with the intensity data. In a recent structure investigation, that of trifluoromethyl acetylene (4), both the spectroscopic and electron diffraction methods of analysis have been used. From a combination of both results, the best agreement for a set of parameters was obtained. The advantages accruing from this are a lessening of the limits of error.

One other method of structure determination, which is in the process of development and is worthy of mention, is neutron diffraction. Most of the work attempted so far has utilised the powder method. However, there is a very good probability that the single-crystal method will soon be developed. One difficulty is the comparative weakness of the available sources of neutrons. The greatest disadvantage at the present is that, as the dimensions of the crystal increase so also do the effects of secondary extinction. Bacon and Lowde (5) have concluded that with crystals large enough to permit the observation of many reflections, secondary extinction would be of overriding importance, intensities being more strongly dependent on the mosaic spread of the specimen than on the structure factors. They also concluded that, in general, crystal specimens would have to be thinner than about 0.1 mm. to avoid these difficulties. Peterson and Levy (6) however, have shown that this is not so. Certainly as the dimensions of the specimen increase, the effect of extinction becomes greater, but it is not greatly so. Advantages of this method include greatly increased resolution and greatly reduced sample size.

For the complex types of structure now being investigated, by far the best method at present is the diffraction of X-rays by a crystal. A short account of the development of X-ray analysis and the technique employed is given in a paper by Robertson (7). This method can be used to investigate the structure of the simplest of molecules in the crystalline state and to obtain an accurate measurement of the bond lengths within the molecule such as in the structure of hexamethylbenzene (8). Or it can be used in the investigation of an unknown structure of a very complex type as was the case in the structure of penicillin (9). In the investigation of the compounds reported in this thesis the method of X-ray diffraction was employed.

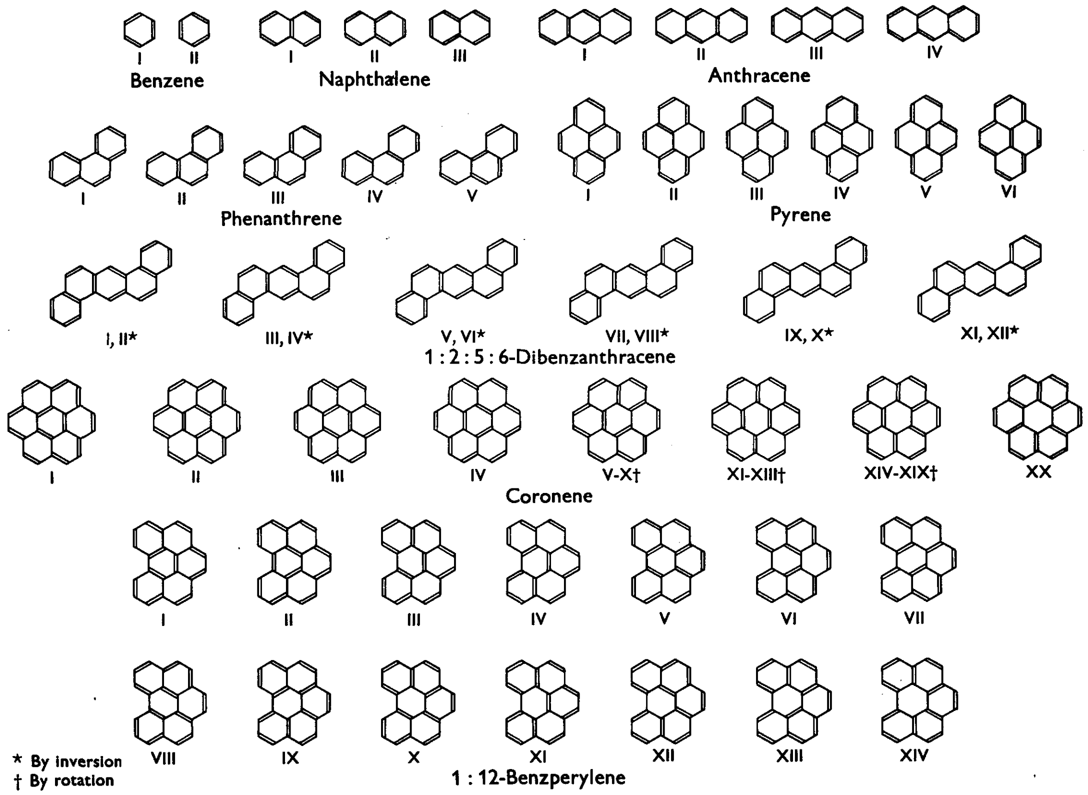
Carbon-carbon bond length measurements have been made by the method of X-ray crystal analysis on various condensed ring hydrocarbons. These are pyrene, $C_{16}H_{10}$ (10), 1:2:5:6-dibenzanthracene, $C_{22}H_{14}$ (11), coronene, $C_{24}H_{12}$ (12), 1:12-benzperylene, $C_{22}H_{12}$ (13), which have been done by the usual two-dimensional methods of analysis, and naphthalene, $C_{10}H_8$ (14, 15), and anthracene, $C_{14}H_{10}$ (16, 17) which have been investigated more fully by the triple Fourer series method. In all these cases evidence has been obtained that the bond lengths vary to some extent in different parts of the molecule.

Parts I and II of this thesis contain accounts of another two aromatic hydrocarbons, viz. ovalene and perylene, which have been investigated fully by the two-dimensional methods of analysis. The results obtained are in full agreement with this variation in bond length within polycyclic aromatic molecules. In the two cases reported the carbon-carbon bond length variation is even larger than has been observed in any of the compounds previously investigated. Part III of the thesis contains an account of an investigation into the structure of octamethylnaphthalene. In this case no definite measurement of bond lengths can be made, but once again it seems highly probable that there is a variation of bond length within the naphthalene nucleus. The structure of octamethylnaphthalene is of more importance for other reasons, which will be discussed later.

The interest centring around these polycyclic aromatic hydrocarbons lies in this variation of bond distances within the molecule. There are several methods of calculating the carbon-carbon bond distance in a planar molecule, and with the advent of X-ray crystal analysis, a method arose by which experimentally obtained values could be compared with those calculated.

Probably the best known method of calculation is that derived from the use of the Kekulé structures of the molecule in conjunction with a curve relating distance and double bond character (18). The manner in which this method of calculation is applied is as follows. In these hydrocarbons, for a fixed position of the carbon atoms the bonds can be arranged in a distinct number of ways. These different arrangements are the Kekulé or stable-valence bond structures. Figure 1 shows the stable-valence bond structures for the hydrocarbons previously mentioned(10-17) and also benzene. Thus benzene has 2 Kekulé structures, naphthalene 3, coronene 20, and etc. The percentage double bond character is now obtained by taking linear summations of corresponding and chemically equivalent bonds. For instance, consider the "spokes" in the coronene molecule (see Fig. 1). There are 20 stable-valence bond structures of which each contains 6 "spokes". Hence there is a total of 120 bonds. Of these 48 are double bonds. Hence the "spokes" have 40% double bond character. With pyrene there are 6 stable-valence bond structures of which each contains one central bond. Hence there is a total of 6 central bonds of which 2 are double bonds in the 6 structures. This gives the central bond of pyrene a 33% double bond character.

Figure 1.

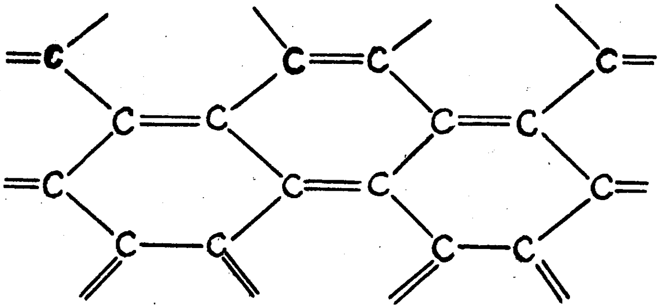


The bond distance corresponding to this double bond character can now be found from the empirical Pauling - Brockway curve. This curve is derived from four values of the carbon-carbon bond.

%age double bond character	Bond length (A)
0 (pure single bond)	1.54
33 (from graphite)	1.42
50 (from benzene)	1.39
100 (pure double bond)	1.33 (or 1.34)

The value for a carbon-carbon single bond has been derived from various hydrocarbons (18), and the results are found to lie between 1.52 and 1.55A. These are all equal to the diamond value of 1.542A within their probable experimental errors. The value for the carbon-carbon double bond has been obtained from spectroscopic values of 1.325 ± 0.005A (19) and 1.331 ± 0.005A (20) for ethylene and 1.330 ± 0.005A (19) for allene. The less accurate electron diffraction values are 1.34 ± 0.02A for the two substances (18) The resonance of the benzene molecule between the two Kekulé structures (see Fig. 1) can be considered to give each of the six carbon-carbon bonds fifty percent single-bond character and fifty percent double-bond character. The value now accepted for this bond, representing 50% double bond character, is 1.39A. The same value for this bond has been obtained from various benzene derivatives such as hexamethylbenzene (8). The fourth point on the curve is given by the value of 1.42A for graphite. The structure of the graphite crystal consists of hexagonal layers of molecules which are separated by a distance so large (3.40A), that there can be no covalent bonds between them. Each of the layers is a giant molecule, and the superimposed layer molecules are held together only by weak van der Waal's forces. The four valences of each carbon atom are used to form bonds with its three neighbours. The layer molecule resonates among many valence bond structures as depicted in Fig. 2.

Figure 2.



In this way each carbon-carbon bond achieves one-third double-bond character i.e. 33% double bond character. This then leads to the value of 1.42A for a bond with 33% double-bond character.

As previously stated the value of any bond length can now be obtained from a knowledge of its percentage double bond character. The carbon-carbon bond distances for all the polycyclic aromatic hydrocarbons shown in Fig. 1 have been calculated by this method and compared with the values obtained from the observed data. Remarkably good agreement has been obtained in most cases, even more so than would be expected considering this method takes no account of the numerous first and second excited structures of which more will be said later. In fact it would not be expected that the non-excited Kekulé structures alone would make a dominant contribution to the larger molecules and yet it is found that, in the large and highly symmetrical molecules of pyrene and coronene, there is a distinct qualitative resemblance between the measured values and those predicted by the Kekulé structures. This agreement breakes down somewhat in the case of 1:2:5:6 dibenzanthracene. In the case of ovalene (Part I of this thesis), the agreement is even more remarkably good, and here the molecule is even larger than any of those previously mentioned. With perylene (Part II) however, the agreement is not so good. The agreement obtained for six of the polycyclic aromatic hydrocarbons in Fig. 1 is shown below

	Average Δ	Maximum Δ
coronene	0.013A	0.02A
pyrene	0.021A	0.04A
1:2:5:6 dibenzanthracene	0.025A	0.06A
1:12 benzperylene	0.013A	0.03A
naphthalene	0.009A	0.025A
anthracene	0.012A	0.045A

Δ = the difference between the measured and calculated values of the bond lengths.

Average Δ = the sum of the discrepancies of all the bonds in the molecule divided by the number of bonds.

Another method of calculating bond distances in molecules is that of molecular orbitals. This method gives more weight to the excited structures. Coulson has published a very good qualitative account of the molecular orbital theory (21). Each electron in any individual atom is assigned to a definite particular orbit. This orbit is no longer precise as in the older quantum theory of Bohr, but is described by a wave function ψ which is termed an atomic orbital. The value of ψ for any electron varies from point to point, and the value of ψ^2 at any place measures the probability that the electron will be found at that place. In considering any atom the various atomic orbitals to be filled are s, p, d, etc. The s type of atomic orbital is spherically symmetrical. The p type on the other hand exhibit directional properties and hence are separated into p_x, p_y and p_z.

Now it is well known that the ground state of the carbon atom is $(1s)^2$ $(2s)^2$ $(2p)^2$ in which there are two unpaired electrons - $(2p)^2$. These electrons will be in the $2p_x$ and $2p_y$ atomic orbitals. This corresponds to bivalency. The characteristic quadrivalency can only be obtained by starting from a state of four unpaired electrons. This state may be attained by exciting one of the 2s electrons to the empty $2p_z$ orbit. This leads to the four valence electrons being one in each of the atomic orbitals 2s, $2p_x$, $2p_y$, and $2p_z$, but they are still not equivalent. To get equivalent bonds these four "pure" orbitals must be mixed to give "hybridised" orbitals. There are three linear combinations of importance - tetrahedral, trigonal and diagonal. In dealing with aromatic compounds the trigonal combination is the one of importance. In trigonal hybridisation 2s, $2p_x$ and $2p_y$ are compounded to give three equivalent coplanar orbitals pointing at angles of 120° in the xy plane. The compounded orbital is given from the equation:- $\psi = \sqrt{\tfrac{1}{3}}\,\psi(2s) + \sqrt{\tfrac{2}{3}}\,\psi(2p_x)$. The remaining orbital is the undisturbed $2p_z$, usually referred to as the π orbital. The energy required to convert the carbon atom from the ground state is amply compensated by the correspondingly greater gain in energy through the formation of more stronger bonds.

The peculiar stability of benzene and other aromatic hydrocarbons lies in this trigonal (or sp^2) hybridisation. Here there are six atoms in the ring and the atomic orbitals are at angles of 120° - an ideal position for combination. The molecular orbitals are obtained by a linear combination of the atomic orbitals. This is only an approximation, but is accurate enough. The work involved in calculating the true molecular orbital is prohibitive. This pairing of two overlapping atomic orbitals provides a molecular orbital that will accommodate two electrons. This then leaves one unused electron, the $2p_z$ electron, on each carbon atom. Thus benzene would have six unused electrons. The orbitals, π orbitals, of these unused electrons tend to overlap forming non-localised molecular orbitals. The electrons in these π orbitals, the π electrons, make a contribution to the energy of binding. Hence there is nothing in the molecular orbital theory which remotely resembles the individual Kekulé structures.

Now in using this theory to obtain bond distances, an approximate description of a particular link is given by assigning to it an order. This order is the sum of two parts, one from the σ bonds (obtained by the overlapping of the atomic orbitals which are at 120° and in the same plane), and the other from the π bonds. The first contribution is assumed to have the value of unity in all cases, and the latter contribution is called the "mobile order", p. For a pure single bond such as ethane, the total order is 1. for a pure double bond as in ethylene, the total order is 2 and for a pure triple bond as in acetylene, the total order is 3. This leads to corresponding values of 0, 1 and 2 respectively for p. Hence for bonds intermediate between pure single and pure double bonds, the value of p will be a fraction. This idea has been improved by Coulson (22). Here the problem of determining the order of a given bond resolves itself into the calculation of the partial orders of the individual electrons. These partial orders are then added together to give the total mobile order. The technique involved is the setting up of the electronic wave function of the π electrons, which is expressed as a product of linear combinations of atomic orbitals, and thus obtaining the contribution of the π electrons to the bond order. This method thus takes into account the excited canonical structures.

The next point is to obtain the length of the bond from a knowledge of the bond order. This is done by using a curve relating bond order and bond distance. The curve is obtained by a knowledge of certain points which lie on it (some have been already mentioned - pure single, double and triple bonds). A list of points on the curve is given below.

	Total Order	Mobile Order	Bond Length (A)
ethane (pure single bond)	1.000	0	1.54
graphite	1.535	0.535	1.42
benzene	1.667	0.667	1.39
ethylene (pure double bond)	2.000	1.000	1.33
acetylene (pure triple bond)	3.000	2.000	1.20

These points are found to lie on a smooth curve.

Two of the polycyclic aromatic hydrocarbons previously mentioned have been investigated by this method, viz. pyrene (23) and coronene (Coulson). The agreements between the measured and calculated values of the bond lengths are given below (Δ and average Δ as before).

	Average Δ	Maximum Δ
pyrene	0.020A	0.038A
coronene	0.011A	0.019A

Calculations of the bond lengths of ovalene and perylene have also been made by this method. These will be discussed later in the appropriate sections.

The one other method of calculating bond distances is that termed the method of "spin states" (24). This method corresponds to the earlier method of Penney (25), and proceeds by measuring the bond order in terms of energy. In their paper Vroelant and Daudel have shown an approximation which can be used and is still sufficiently accurate. This approximation, which classifies a bond according to the bonds which surround it, has been applied to a number of cases including naphthalene, anthracene, pyrene and coronene (26). The agreements are remarkably good, especially in the case of coronene, although not completely satisfactory in the cases of naphthalene and anthracene where the measured values were obtained by the three-dimensional methods of analysis, and so would be expected to be very accurate. The agreements are shown below (Δ and average Δ as before).

	Average Δ	Maximum Δ
naphthalene	0.014A	0.026A
anthracene	0.013A	0.020A
pyrene	0.020A	0.045A
coronene	0.003A	0.005A

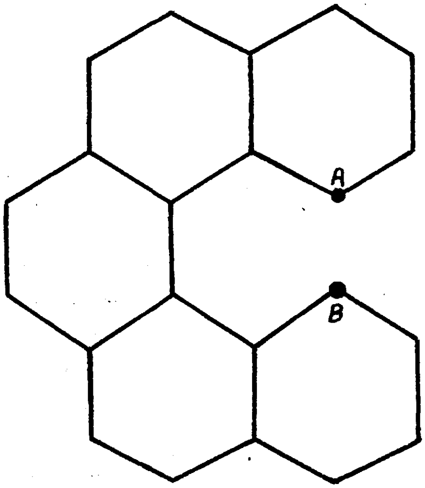
The bond lengths of ovalene have been calculated by this method and will be discussed later in the appropriate section.

Part III of the thesis contains an account of the investigation into the structure of octamethylnaphthalene. It will be of interest here to compare the values of the bond lengths in the naphthalene nucleus with those obtained in the three-dimensional analysis of naphthalene and also with those predicted for naphthalene. No great change would ordinarily be expected, since the only difference between the two molecules appears to be that the eight hydrogen atoms in naphthalene have been replaced by methyl groups.

This compound is much more interesting however from the point of view of steric hindrance. The methyl groups substituted in the α-positions of naphthalene would have a much closer distance of approach than that between two adjacent methyl groups in hexamethylbenzene (approximately 2.4A in the former case and 2.8A in the latter). It has been shown that the molecule of hexamethylbenzene is completely planar (27, 8), but it is questionable if this will be so in the case of octamethylnaphthalene. Undoubtedly there will be restriction of rotation of the methyl groups, but there is also a possibility that the methyl groups in the α-positions will not be coplanar with the naphthalene ring.

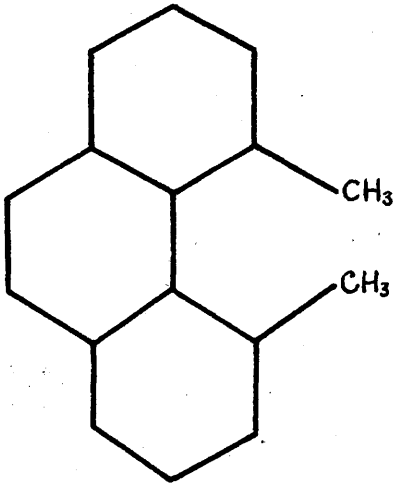
Cook has given a brief review of the sterochemistry of and steric factors involved in polycyclic aromatic compounds (28), and discussed them in terms of their chemical reactivity. The compounds reviewed however have no direct bearing on the problem here. One interesting compound mentioned however is that of 3:4:5:6-dibenzphenanthrene (see Fig. 3). The atoms at A and B are not joined by a bond and yet, if the molecule was planar, the distance between them would be of the order of 1.4A. It has now been shown that this molecule is not planar, but actually resembles a spiral so that A. and B. are almost 3.4A apart (McIntosh and Robertson - unpublished communication). Another interesting compound which has recently been prepared is 4:5 dimethylphenanthrene (29) Fig. 4). The structure of this has not been studied by X-ray diffraction, but its spectra consists of absorption curves which are definitely "phenanthroid" in character, although some of the fine structure exhibited by phenanthrene itself has been smoothed

Figure 3.



out. The details of the spectra are rather interesting. The methyl groups are undoubtedly displaced from the molecular plane, and this could explain the smoothing out of the fine structure. However this need not necessarily rule out the possibility that the phenanthrene group is not completely planar. Even with the methyl groups displaced and the phenan:threne structure being slightly distorted, the absorption curves would still be "phenanthroid" in character. Thus no conclusions can be arrived at regarding the nature of the phenanthrene ring structure.in 4:5 dimethylphenanthrene other than the fact that, if it is not completely planar, then the distortion is slight.

Figure 4.



At the present moment a similar state of affairs exists in the octamethylnaphthalene structure. It has been shown conclusively that the methyl groups in the α-positions are displaced from the molecular plane, and proved that there is a high probability that the methyl groups in the β-positions are also displaced, although in this case the displacement is not so great. No information is available however regarding the nature of the naphthalene nucleus, other than the fact that it is either planar, or slightly distorted from the molecular plane.

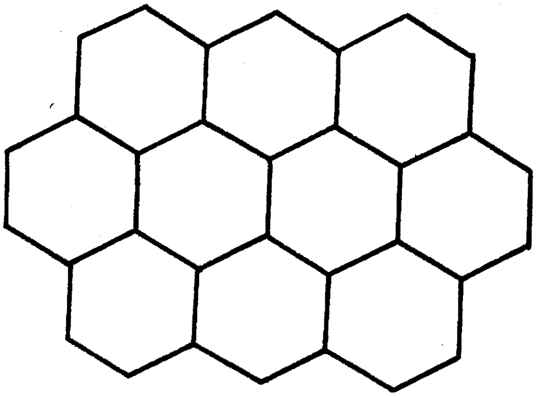
Part 1

The Crystal Structure of Ovalene (A Quantitative X-ray Investigation)

Introduction

Ovalene, or octabenzonaphthalene (Fig. 5), has recently been synthesised by E. Clar (30). It is a condensed-ring hydrocarbon analogous to coronene (12,31).

Figure 5.



The symmetry of the molecule is lower than that of coronene, and a greater range of bond length variations within the molecule is possible. If this is the case, it will afford a good experimental comparison of the measured bond lengths with those predicted by theory.

Since ovalene has only two centrosymmetric molecules per unit cell and a short b-axis of 4.70A, good resolution of all the atoms, as in the case of coronene, may be expected. Hence a better estimation of all the atomic centres should be obtained than in the cases of other aromatic hydrocarbons such as pyrene (10), 1:12 benzperylene (13), anthracene (16, 17), etc., due in the latter cases to lack of resolution in the two-dimensional Fourier methods of analysis employed. The accuracy will not be as great, however, as in the coronene structure, where, because of the higher molecular symmetry, it was possible to average certain crystallographically distinct, but chemically equivalent bonds within the molecule.

The investigation was carried out with the purpose, as previously stated, of obtaining experimental values of the bond lengths for comparison with those predicted, and with the view of obtaining a sufficiently good refinement of the structure to enable a possible analysis by the three-dimensional Fourier methods.

Crystal Data.

Ovalene, $C_{32}H_{14}$, M, 398.4 m.p. 473°(uncorrected)
d, calc. 1.477 d, found 1.496
monoclinic prismatic, $a = 19.47 \pm 0.05$A, $b = 4.70 \pm 0.01$A.
$c = 10.12 \pm 0.04$A, $\beta = 105.0^\circ \pm 0.3^\circ$

Absent Spectra - (h0l) when h is odd; (0k0) when k is odd.

Space Group - C_{2h}^5 ($P_{2_1/a}$)

Two molecules per unit cell. Molecular symmetry, centre.

Volume of the unit cell, 894.3A^3

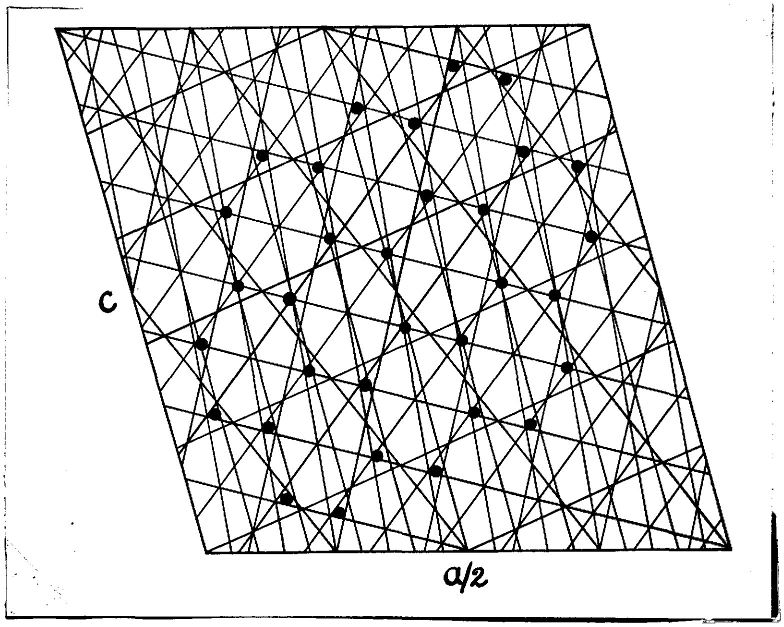
Absorption coefficient for X-rays, $\lambda = 1.54A$, $\mu = 7.78$ per cm.
Total number of electrons per unit cell = F(000) = 412.
The crystals are elongated in the b-axial direction, with cleavage parallel to the needle axis. The (001) face is well-developed on most specimens, but no end faces could be identified. On some specimens the (101) face could be observed.

Crystal Structure.

The most prominent feature of the crystal structure is the relatively short b-axis of 4.70A. This short axis is exactly the same length, within experimental error, as the corresponding axis in the coronene structure (12). The crystal habits are very similar also. This periodicity and crystal habit are also closely similar to those of phthalocyanine and many of its metal derivatives (32, 33). The similarity between ovalene and coronene also exists in the c-axial direction, where once again the axial lengths are the same, within experimental error. These data suggest that the arrangement in the crystal, especially the inclination of the molecular plane to the (010) crystal plane, will be similar in the two cases.

For ovalene it is necessary to proceed by trial and error methods in the first instance. However it can be assumed that the molecular plane is tilted at about 44° to the (010) crystal plane. Two remaining degrees of freedom now remain to be fixed before the orientation of the molecule is specified. An investigation of the (h0l) zone, by moving film methods, showed that the following small-spacing planes gave strong reflections: $(20,00)$, $(20,0\bar{1})$, $(16,0\bar{8})$, $(12,0\bar{3})$, (802), $(40\bar{5})$, (407). Only one trial was necessary to obtain the one position of the molecule which would satisfactorily explain the enhancement of these reflections (see Fig. 6).

Figure 6.

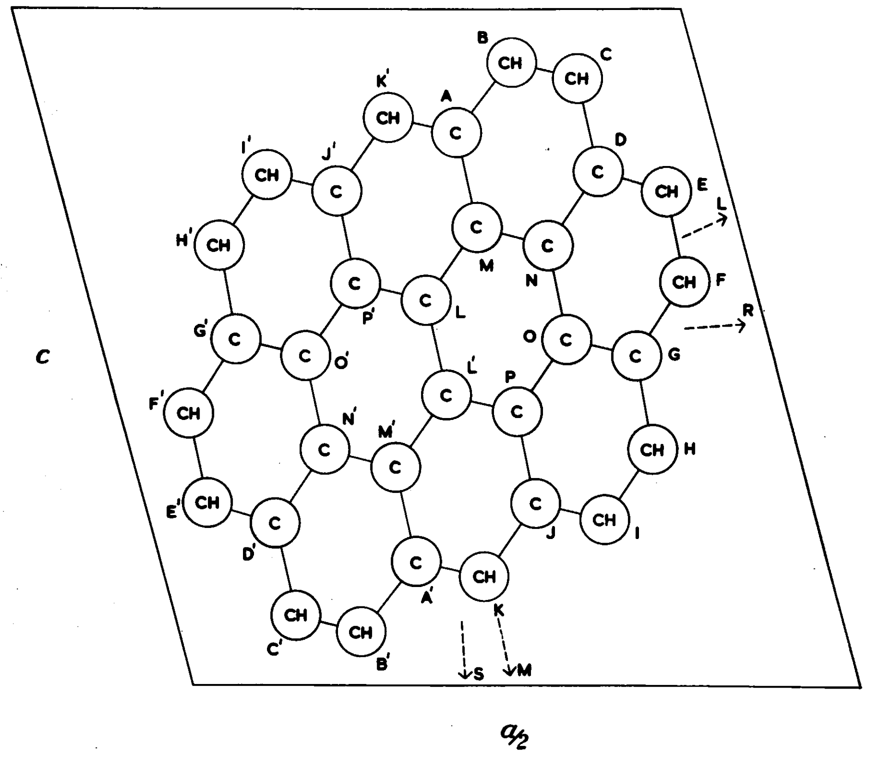


Prominent (h0l) reflections for ovalene.

The atomic positions of the molecule will lie either on or midway between the traces of the above planes, thus making the structure factors of these planes either strong positive or strong negative. Once again, because of the strong resemblance to coronene, the phase constants of these small-spacing planes were known, and hence the necessity for only one attempt. The complete orientation of the molecule can now be calculated, as explained in the experimental section.

$\chi_L, \psi_L, \omega_L; \chi_M, \psi_M, \omega_M;$ and $\chi_N, \psi_N, \omega_N;$ are the angles which the molecular axes L and M (Fig. 7) and their perpendicular N make with the a and b crystallographic axes and their perpendicular c'.

Figure 7.



Projection along b-axis of ovalene.

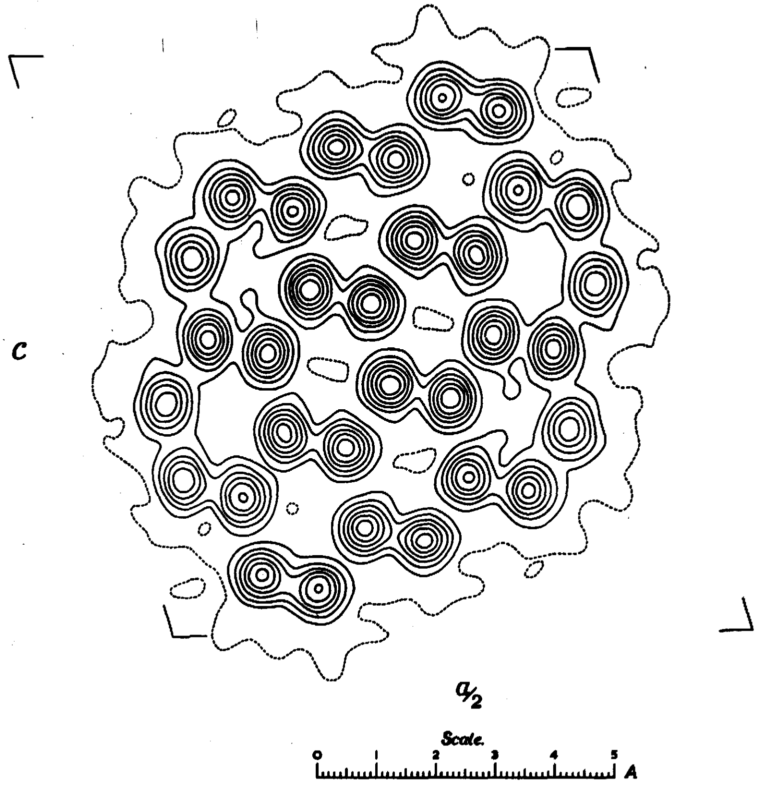
Assuming a regular hexagonal structure for the molecule, a trial structure can now be obtained.

From this point the refinement of the atomic positions proceeded by a straightforward application of double Fourier Series methods. In all, three Fourier Series in the (h0l) zone were carried out. In the first only 80 reflections were used, and only partial resolution of the atomic positions obtained. For the most part, the atoms appeared on the electron density diagram in pairs. The discrepancy, obtained in the usual manner (i.e. the sum of all the discrepancies divided by the total of the measured structure factors) for the 80 planes included was 26.1%.

The result of the second Fourier analysis and the projection of the structure obtained from this refinement have already been reproduced (34). 146 reflections were included this time, the discrepancy for this number of planes being 28.7% (the discrepancy for the 80 structure factors previously used was now only 21.1%). Complete resolution of all atoms was obtained.

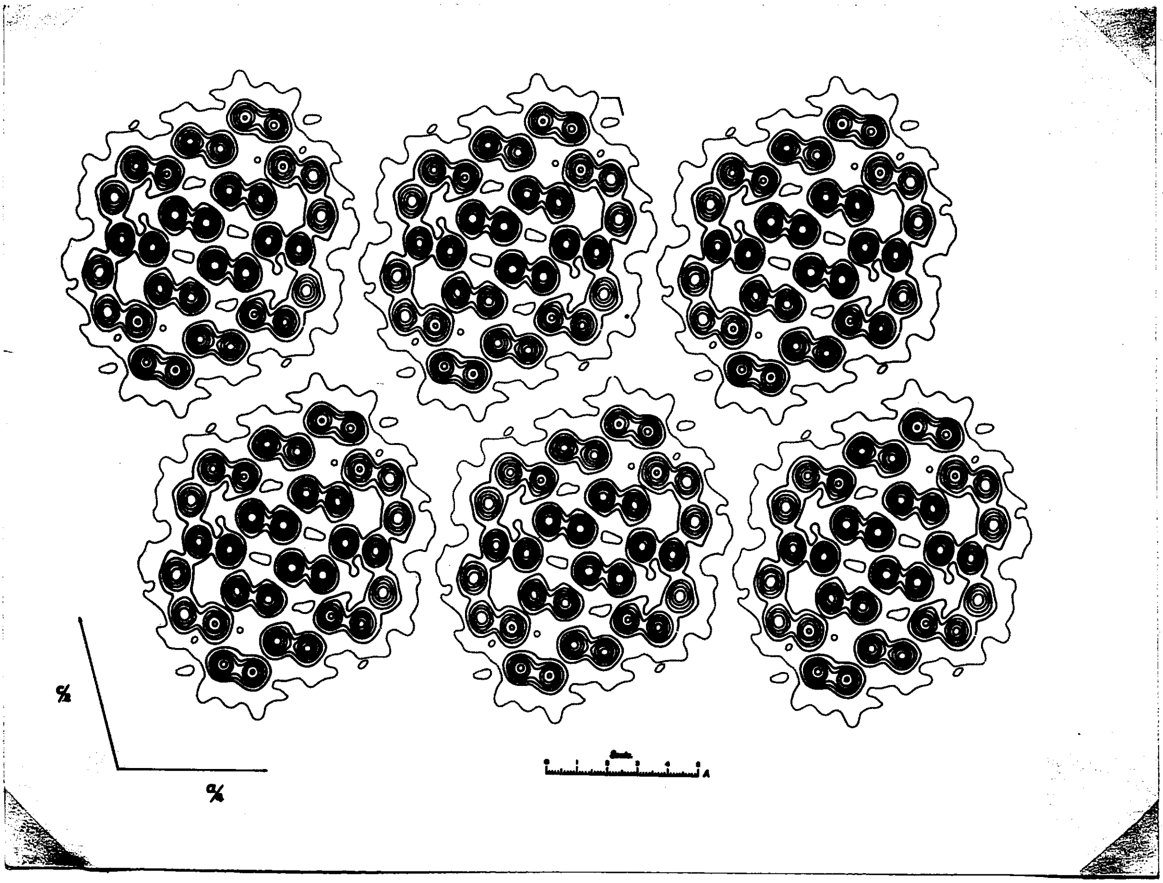
156 reflections were included in the third and final refinement. This represents 62.7% of the total possible reflections in the (h0l) zone. The discrepancy for these planes was 17.3%. This series contained almost all the

Figure 8.



Projection along the b-axis, showing one ovalene molecule. Each contour line represents a density increment of approximately one electron per Å^2, the one-electron line being dotted. The plane of the molecule is inclined at about 43° to the projection plane, (010).

Figure 9.



A group of six ovalene molecules in the b axis projection showing the comparatively large gap of low density around each molecule.

reflections obtained from the (h0l) zone with copper radiation. A few reflections of very small geometric structure factor were omitted since the phase constants would be doubtful. The projection of the structure obtained from this final synthesis is reproduced in Fig. 8. This is the projection of one complete molecule (half the unit cell) on the (010) plane. Fig. 9 shows how a group of six ovalene molecules are arranged in the crystal, with a comparatively large gap of low density around each molecule. As in the case of coronene, this explains the well-developed (001) plane in the crystal, since Fig. 9 shows that the molecular alinement in this direction involves very little interlocking.

Co-ordinates and Dimensions

Fig. 8 (the projection on the (010) plane) allows of direct measurement of the x and z crystal co-ordinates with considerable accuracy. Assuming the molecule to be planar and knowing the orientation, the y co-ordinates can be calculated. The values obtained for the y co-ordinates for various orientations were tested by calculating structure factors in other zones, viz. (hk0) and (0kl), until satisfactory results were obtained. The orientation finally accepted is shown in Table 1.

Table 1.

$\chi_L = 44.9^\circ$	$\cos\chi_L = 0.7078$
$\psi_L = 51.3^\circ$	$\cos\psi_L = 0.6257$
$\omega_L = 70.9^\circ$	$\cos\omega_L = 0.3278$
$\chi_M = 78.4^\circ$	$\cos\chi_M = 0.2018$
$\psi_M = 74.6^\circ$	$\cos\psi_M = 0.2656$
$\omega_M = 160.5^\circ$	$\cos\omega_M = -0.9428$
$\chi_N = 132.6^\circ$	$\cos\chi_N = -0.6769$
$\psi_N = 42.8^\circ$	$\cos\psi_N = 0.7334$
$\omega_N = 86.5^\circ$	$\cos\omega_N = 0.0617$

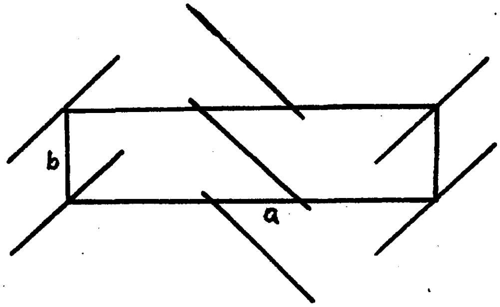
The molecular axes chosen for coronene were not suitable in the ovalene molecule. For comparison, however, the orientation of the ovalene molecule with respect to molecular axes L' and M', corresponding to those of coronene, was calculated. The orientation with respect to these axes is shown in Table 2. (corresponding values for coronene in brackets).

Table 2.

$\chi_{L'} = 79.7^\circ$	(84.8)	$\cos\chi_{L'} = 0.1791$	(0.0912)
$\psi_{L'} = 85.2^\circ$	(85.6)	$\cos\psi_{L'} = 0.0829$	(0.0765)
$\omega_{L'} = 11.4^\circ$	(6.9)	$\cos\omega_{L'} = 0.9803$	(0.9928)
$\chi_{M'} = 44.4^\circ$	(44.2)	$\cos\chi_{M'} = 0.7139$	(0.7174)
$\psi_{M'} = 47.6^\circ$	(46.7)	$\cos\psi_{M'} = 0.6747$	(0.6865)
$\omega_{M'} = 100.8^\circ$	(96.8)	$\cos\omega_{M'} = -0.1875$	(-0.1188)
$\chi_N = 132.6^\circ$	(133.7)	$\cos\chi_N = -0.6769$	(-0.6905)
$\psi_N = 42.8^\circ$	(43.7)	$\cos\psi_N = 0.7334$	(0.7233)
$\omega_N = 86.5^\circ$	(89.6)	$\cos\omega_N = 0.0617$	(0.0078)

No direct measurement of the y co-ordinates is possible, as in the case of the x and z co-ordinates, since no resolution of the atomic positions can be obtained, either from projections of the (hk0) or of the (0kl) zones. For example the structure, viewed along c' (i.e. perpendicular to the a and b crystal axes), would give an end view of the molecules as depicted roughly in Fig. 10

Figure 10.

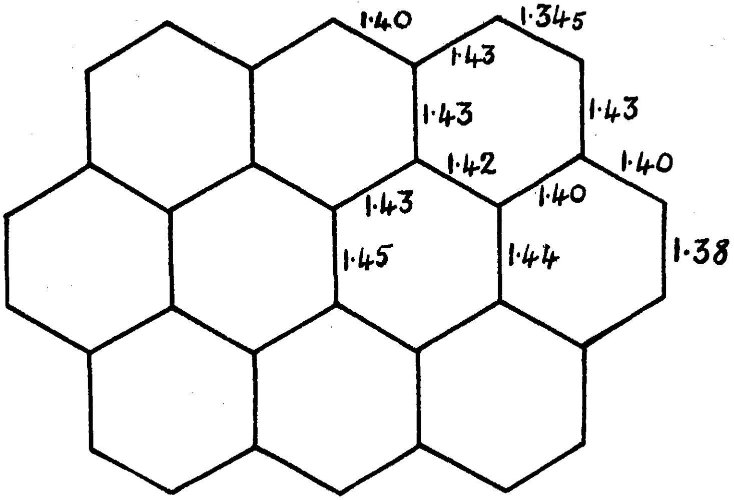


In Fig. 7, R represents the line of maximum inclination of the molecular plane to the projection plane, (010), and S lies in the (010) plane, i.e. S represents the line of zero inclination. Since S is almost perpendicular to the a-axis this explains the above projection viewed along c'.

In the (0kl) zone, successive molecules viewed in the direction of the a-axis, although identical in the projection of Fig. 9, are inclined in opposite directions and may be derived by the operation of a glide plane of symmetry a. Hence no reasonable resolution of the atoms can be expected in this zone.

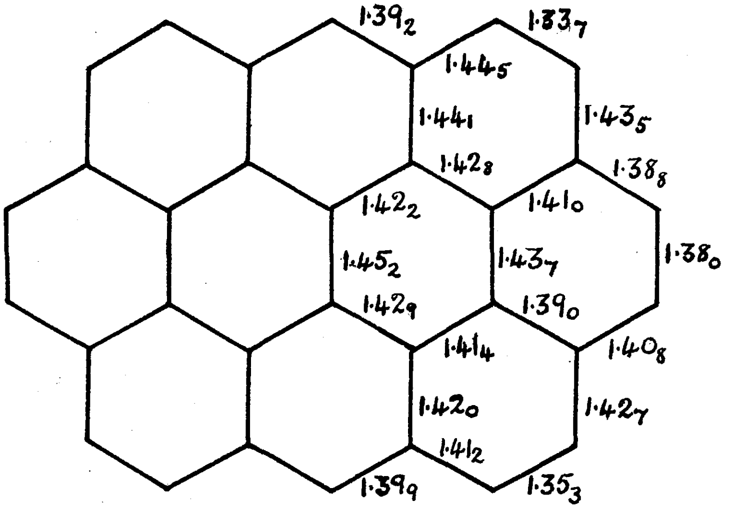
The co-ordinates of the atoms are collected in Table 3.

Figure 11(a).



Dimensions of the ovalene molecule.

Figure 11(b).



Bond distances obtained from co-ordinates before averaging.

Under the column headed (b) are the co-ordinates directly measured for x and z. As the molecule has an exact centre of symmetry it is possible to average the bond lengths, and hence under column (a) are the co-ordinates of the atoms after this averaging. These are the co-ordinates finally accepted, as they are probably more correct. Also since the molecule has an exact centre of symmetry which lies on the origin of the unit cell, only half the atoms, those of the asymmetric crystallographic unit, are listed. The positions of all the other atoms in the unit cell may be derived from the operations (x,y,z,); (-x,-y,-z,); (x+a/2,-y+b/2,z); (-x+a/2,y+b/2,-z).

Table 3.

Atom (Fig.7)	x, A (a)	x, A (b)	y, A (a)	z, A (a)	z, A (b)
A	1.118	1.118	0.011	3.192	3.197
B	2.159	2.178	0.628	4.264	4.270
C	3.056	3.072	1.536	4.010	4.025
D	3.023	3.032	1.948	2.632	2.638
E	3.941	3.936	2.889	2.340	2.330
F	3.872	3.877	3.256	0.993	0.988
G	2.881	2.871	2.695	-0.114	-0.114
H	2.767	2.751	3.043	-1.526	-1.526
I	1.804	1.785	2.489	-2.574	-2.585
J	0.829	0.830	1.521	-2.360	-2.354
K	-0.179	-0.179	0.934	-3.431	-3.429
L	0.036	0.040	-0.193	0.708	0.710
M	1.067	1.068	0.407	1.803	1.800
N	2.017	2.023	1.367	1.547	1.540
O	1.945	1.938	1.749	0.143	0.132
P	0.922	0.920	1.157	-0.957	-0.960

Table 3 (contd.)

Atom (Fig.7)	$2\pi x/a$ (a)	$2\pi x/a$ (b)	$2\pi y/b$ (a)	$2\pi z/c$ (a)	$2\pi z/c$ (b)
A	20.7°	20.7°	0.8°	113.6°	113.7°
B	39.9°	40.3°	48.1°	151.7°	151.9°
C	56.5°	56.8°	117.7°	142.7°	143.2°
D	55.9°	56.1°	149.2°	93.6°	93.8°
E	72.9°	72.8°	221.3°	83.2°	82.9°
F	71.6°	71.7°	249.4°	35.3°	35.1°
G	53.3°	53.1°	206.4°	-4.1°	-4.1°
H	51.2°	50.9°	233.1°	-54.3°	-54.3°
I	33.4°	33.0°	190.7°	-91.6°	-92.0°
J	15.3°	15.3°	116.5°	-84.0°	-83.7°
K	-3.3°	-3.3°	71.5°	-122.1°	-122.0°
L	0.7°	0.7°	-14.8°	25.2°	25.3°
M	19.7°	19.7°	31.2°	64.1°	64.0°
N	37.3°	37.4°	104.7°	55.0°	54.8°
O	36.0°	35.8°	134.0°	5.1°	4.7°
P	17.1°	17.0°	88.6°	-34.0°	-34.2°

Fig. 11(a) expresses the results of the averaged co-ordinates in terms of actual bond distances, taking into account the orientation of the molecular axes L and M. Fig. 11(b) shows the bond distances obtained from the co-ordinates before averaging but using the same orientation. The atomic co-ordinates with respect to these molecular axes are given in Table 4. For comparison purposes, the atomic co-ordinates of a regular model with respect to these molecular axes are listed alongside.

Table 4.

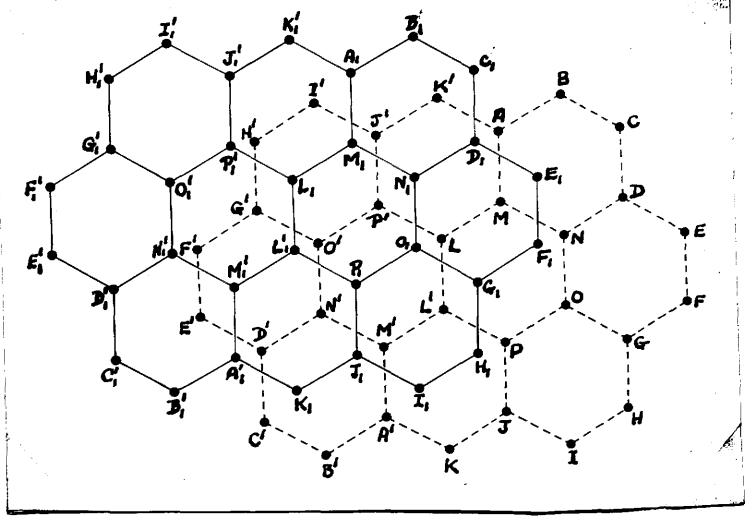
Atoms	Fig.11a		Regular Model (1.39A)	
	L,A	M,A	L,A	M,A
A and J.......	1.224	2.844	1.204	2.780
B and I.......	2.491	3.503	2.407	3.475
C and H.......	3.659	2.836	3.611	2.780
D and G.......	3.710	1.406	3.611	1.390
E and F.......	4.910	0.690	4.814	0.695
K and K.......	0	3.515	0	3.475
L and L.......	0	0.726	0	0.695
M and P.......	1.250	1.413	1.204	1.390
N and O.......	2.490	0.719	2.407	0.695

Intermolecular Distances

The shortest distance between two molecules is the perpendicular distance between their planes i.e.3.45A.(=b $\cos\psi_N$) Since the individual atoms do not occur vertically over each other (see Fig. 12, which shows the normal projection of two parallel molecules separated by translation b), the shortest distance between carbon atoms of two adjacent molecules is slightly greater than this. The closest approaches are between atoms A and D_1, L and O_1, and J' and M_1, where the distance is 3.48A.; between N and F_1 and between P and H_1, it is 3.49A. The other pairs of atoms are separated by more than 3.5A. Between other molecules the separation is greater. From atom B on the standard molecule to K on the molecule one translation along the c-axis (Figs. 7 and 9) the distance is

3.79A. On the same pair of molecules the distance from B to I is 3.87A., and from K to K$'$ it is 3.85A. From atom F on the standard molecule to H$'$ on the reflected molecule at $(\frac{1}{2}a, \frac{1}{2}b)$ the distance is 3.69A. On this same pair the distance from F to G$'$ is 3.77A., and from F to F$'$ it is 3.93A. All other distances between atoms on neighbouring molecules appear to be greater than 4A.

Figure 12.



Normal projection of two parallel molecules.

Discussion of Results.

The most striking result of this analysis is the large variation in bond length within the molecule (Fig. 11a). The six exposed bonds BC, EF, HI, etc., are all considerably shorter than any of the others, especially short are the bonds BC, HI, etc., which are only 1.34_5A. All the remaining bonds are 1.40A or more. The variation of bond lengths in the naphthalene nucleus is not so pronounced - the hexagon could almost be regular. However, the central bond LL' is probably longer than any of the others.

In the case of ovalene, it was possible to average the bond lengths of the asymmetric unit in pairs, e.g. due to the symmetry of the molecule, bonds BC and HI should be identical. Hence any variations inbonds, which should be identical, have been assumed to be due to experimental errors. In all cases this difference in bond length is 0.02A or less, except on comparing bonds AB and IJ where the difference is 0.03_5A (see Fig.11b). Therefore, in all cases, but the one exception mentioned, the average values have a variation of 0.01A or less.

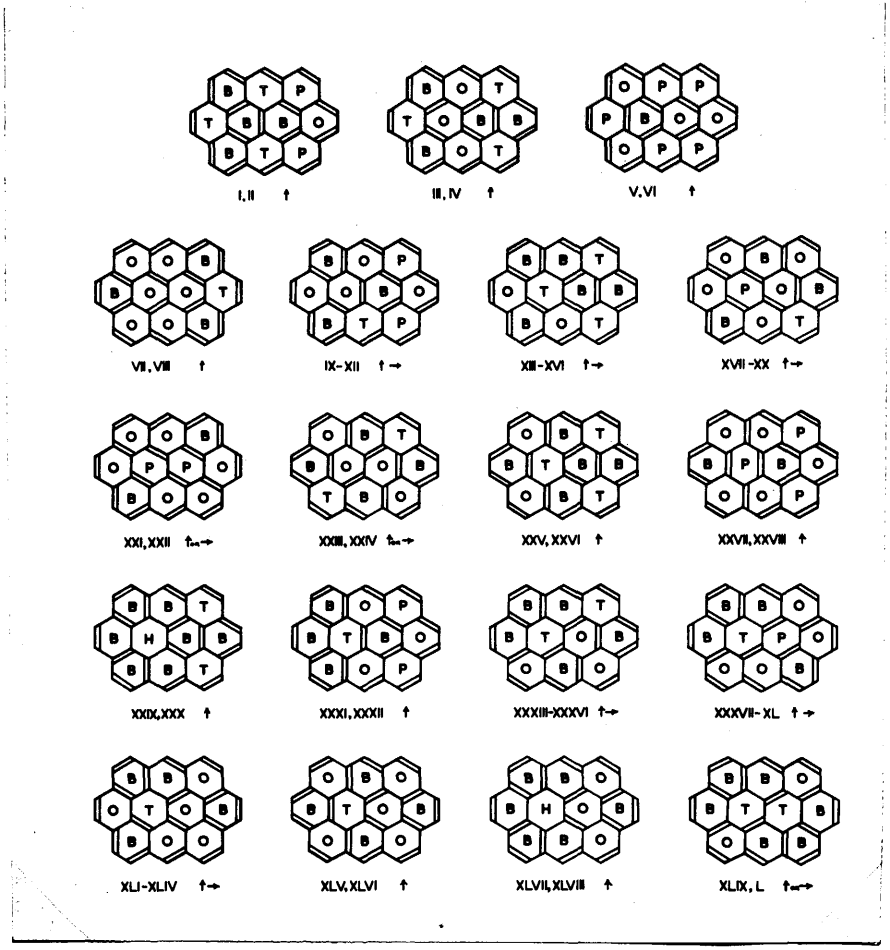
Many other factors must be taken into account, before the accuracy of the results obtained can be discussed. The accuracy must obviously depend on the range and accuracy of the intensities, the size of the crystal specimens, etc. Recently a direct approach to the accuracy obtainable by Fourier series methods has been attempted (35).

Booth has estimated that there are probable errors of ±0.003A in the co-ordinates obtained from a three-dimensional synthesis, due to the usual experimental errors (36). Applied to the two-dimensional case these errors are estimated at three times this value, i.e. ± 0.01A (37). This has been borne out by checking the two-dimensional analysis of oxalic acid (38).

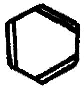
A greater source of error however, is due termination of series, i.e. an incomplete series. In this case errors in co-ordinates of the order of ± 0.02A may be encountered (36, 37). The correction suggested by Booth to allow for this error was not applied in this structure analysis, and so certain errors due to this cause probably still remain. However since the series was fairly complete up to a 2sinθ = 2.0, these errors are probably small. In the principal projection zone, i.e. the (h0l) zone, 62.7% of the possible terms were included. Of the planes which had a 2sinθ between 1.9 and 2.0, 46% were observed, and of those which had a 2sinθ between 1.8 and 1.9, 33% were observed. Also the final agreement between the observed and calculated values of the structure factors was very good, viz. 15.2%.

It seems probable however, that, though the accuracy will not be as great as in the coronene structure, the accuracy of the bond lengths obtained will be between ± 0.02A and ± 0.03A.

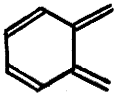
Figure 13.



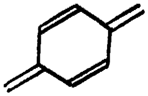
B denotes



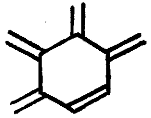
O denotes



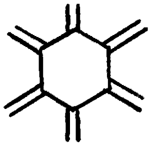
P denotes



T denotes

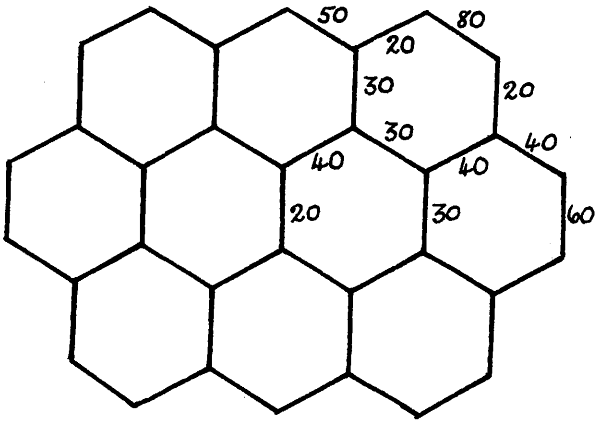


H denotes



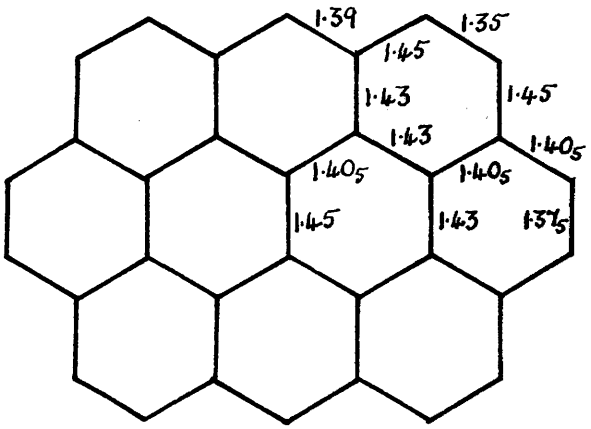
The 50 Kekulé structures of ovalene.

Figure 14 (a)



Percentage double bond character.

Figure 14 (b)



Corresponding bond lengths.

These results have been compared with those obtained from various theoretical methods of calculation, and in each case the agreement is favourable.

Remarkably good agreement with the experimental results is obtained from a treatment of the problem in terms of the stable valency bond structures for ovalene. For a fixed position of the carbon atoms the bonds can be arranged in 50 distinct ways (Fig. 13). The double-bond character for any particular set of links may now be computed by summing the number of double bonds occurring in them and dividing by the total number of these links in all the structures. The double-bond characters obtained for the bonds are shown in Fig. 14a. On the basis of Pauling and Brockway's empirical curve relating double-bond character and distance (18), the bond lengths corresponding to these values are shown in Fig. 14b. The mean deviation of these predicted values from the experimental values is 0.010A. The maximum deviation of any one bond is 0.025A (c.f. Figs. 11a and 14b)

The bond lengths of ovalene have also been obtained theoretically by the method of spin states (39) and by the method of molecular orbitals (40). Once again the agreements between predicted values and experimental values are remarkably good. The values of the individual bonds by these method are shown in Table 5.

Table 5.

Bond	Spin States	Molecular Orbitals	X-ray Results
AB	1.420A	1.427A	1.43A
BC	1.380	1.380	1.34_5
CD	1.420	1.425	1.43
DE	1.420	1.418	1.40
EF	1.380	1.387	1.38
AK'	1.410	1.410	1.40
AM	1.436	1.428	1.43
DN	1.436	1.422	1.40
LM	1.425	1.421	1.43
MN	1.425	1.424	1.42
NO	1.425	1.425	1.44
LL'	1.425	1.430	1.45

As can be seen from this table, in the case of the bond lengths, calculated by the method of spin states, the mean deviation from the experimental values is 0.015A, and the maximum deviation for any one bond is 0.036A. In the case of the bond lengths of ovalene calculated by the method of molecular orbitals, the mean deviation from those obtained experimentally is 0.012A., and the maximum deviation for any one bond is 0.035A.

Experimental

Determination of Crystal Data.

Copper K_α radiation, $\lambda = 1.54$A, was employed in all the measurements. Rotation, oscillation and moving-film photographs were used, the latter to determine the space group and for intensity purposes. The space group was established as $P_{2_1/a}$, since there was no exception to the (h01) absences when h was odd. Of the (0k0) reflections, both (020) and (040) were observed.

Measurement of Density and Number of Molecules per Unit Cell.

The density (d) was found by flotation of small crystals in a solution of silver nitrate at 20°C. The value obtained was 1.496. The number of molecules (n) per unit cell can now be calculated using the formula $n = VdN/M$, where V is the volume of the unit cell; N is Avogadro's number = 6.023×10^{23} ; M is the molecular weight of the compound. In this way n is calculated as 2.024, and rounded off to the nearest whole number i.e. 2. The calculated value of the density, using n = 2, is found to be 1.477 which is in good agreement with the measured value of 1.496.

Measurement of Intensities.

All three zones, i.e. (h01), (hk0) and (0kl), were explored in detail by moving-film methods. Long exposures of the equatorial layer lines for crystals rotated about the a, b and c axes were obtained. The multiple film technique (41) was used in the correlation of the intensities, all of which were estimated visually. The total range of intensities covered was about 6,000 to 1. The absolute scale of F values was not obtained directly, but by correlation with the calculated F values. Since this involves a scattering curve, the scale may not be quite accurate. This, however, will not affect the positions of the atomic centres, but only the vertical scale of the contour maps. The atomic scattering factor used was based mainly on absolute measurements obtained from anthracene(42).

Small crystal specimens were employed. The two specimens used in the (h0l) zone had cross-sections of 0.19mm by 0.22mm, and 0.31 mm by 0.45mm. These crystals were both sufficiently long to cut completely through the X-ray beam. In the (hk0) and (0kl) zones the crystal specimen had the more extreme cross-section of 0.25 mm by 0.91 mm. In these cases, the crystal was completely bathed in the X-ray beam. No absorption corrections were applied. An absorption correction was applied to the (hk0) zone originally, but the discrepancy in this zone improved considerably on removal of this correction factor.

The observed values of the structure factors for the planes (200), (001) and $(20\bar{1})$ are considerably lower than the calculated values. This is probably due to extinction.

The (001) plane observed in the (0kl) zone gave a better agreement, and this was adopted as most likely to be correct. In the (h0l) zone not only had the (001) plane a lower observed value of the structure factor than in the (0kl) zone, but all the (00l) planes were decidedly lower. Since the agreement in the (0kl) zone between F obs. and F calc. was better, it was decided to adopt these observed values as correct. However the final Fourier analysis had included the values obtained from the (h0l) zone. Instead of repeating the analysis, the maximum possible shift of any atomic co-ordinate was calculated, assuming that this would arise when all the increases contributed in the same direction at one point.

$$\text{Thus} \quad \frac{\text{F obs. for (0kl) - F obs. for (h0l)}}{\text{Area of projection}} = 0.021 \text{ electron per A}^2$$

Taking the greatest distance between two subsequent contour lines at a peak on the electron density diagram (this value being 0.116A), the greatest possible shift of any individual atomic centre of the 16 atoms in the asymmetric unit would be 0.116 x 0.021A = 0.0024A. This is well within the probable experimental error in the position of atomic centres, which will be of the order 0.02 or 0.03A.

Trial Analysis

From the tracing of the small-spacing planes of strong intensity, an approximate estimate of the atomic positions was obtained. From this the orientation of the molecule was calculated. The first trial structure was obtained by assuming the ovalene molecule to be planar, and to consist entirely of regular hexagons of side 1.39A. Knowing the orientation of the molecule and the molecular dimensions, the co-ordinates of the atoms can be calculated. A refinement of these atomic positions was carried out, using the double Fourier Series methods.

Fourier Analysis

The electron density on the ac plane (010), was computed at 1,800 points on the asymmetric unit from the series

$$\rho(x,z) = \frac{1}{ac\sin\beta}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} F(h0l)\cos 2\pi\left(\frac{hx}{a}+\frac{lz}{c}\right)$$

The a-axis was divided into 120 parts, and the c-axis into 60 parts, the intervals along a being 0.162A., and along c 0.169A., and the summation was carried out by means of three-figure strips (43). The positions of the contour lines were obtained by graphical interpolation of the summation totals, by making sections of the rows and columns. The final contour map obtained is shown in Fig. 8

Calculation of the Orientation

In order to calculate the orientation it is necessary to assume some distance in space of the molecule. In this case it was assumed that the distance LN was that of a similar distance in a regular hexagon of side 1.43A; i.e. LN = $1.43\sqrt{3}$ A. It is also necessary to know the angles which the L and M molecular axes make with the a crystallographic axis, i.e. η_L and η_M. The complete orientation of the molecule may then be obtained from the relations

(1) $\cos^2\chi_L + \cos^2\psi_L + \cos^2\omega_L = 1$ (7) $\cos\omega_L = \cos\chi_L \tan\eta_L$

(2) $\cos^2\chi_M + \cos^2\psi_M + \cos^2\omega_M = 1$ (8) $\cos\omega_M = \cos\chi_M \tan\eta_M$

(3) $\cos^2\chi_N + \cos^2\psi_N + \cos^2\omega_N = 1$ (9) $\psi_L = 51.3^\circ$

(4) $\cos\chi_L\cos\chi_M + \cos\psi_L\cos\psi_M + \cos\omega_L\cos\omega_M = 0$

(5) $\cos\chi_L\cos\chi_N + \cos\psi_L\cos\psi_N + \cos\omega_L\cos\omega_N = 0$

(6) $\cos\chi_M\cos\chi_N + \cos\psi_M\cos\psi_N + \cos\omega_M\cos\omega_N = 0$

The value of ψ_L is obtained from the relation $\sin\psi_L = r/R$, where r = length of LN in projection and R = the real length of LN. In actual fact the distance used was that joining the mid-points of LL$'$ and NO, since this line will lie along the L molecular axis.

When equations (7) and (8) are taken in conjunction with the equations relating orientation, monoclinic co-ordinates and rectangular co-ordinates (see later), and also the fact that L_A (L molecular co-ordinate of A) = L_J and $M_A = -M_J$ due to the molecular symmetry, the following relations may be derived.

$$\tan\eta_L = \frac{(z_J + z_A)\sin\beta}{(x_J + x_A) + (z_J + z_A)\cos\beta} \qquad \tan\eta_M = \frac{(z_J - z_A)\sin\beta}{(x_J - x_A) + (z_J - z_A)\cos\beta}$$

From these relations it is possible to calculate several values of η_L and η_M for different pairs of atoms (e.g. A and J; B and I; etc.) The mean value was the one finally used. Thus η_L is found to be 24.85° ± 0.25°, and η_M to be - 77.9° ± 0.45°. The results of the calculation, i.e. the orientation obtained, are given in Table 1.

Co-ordinates of Atoms and Molecular Dimensions

If all the hexagons in ovalene were regular, no distortion effects would be seen. This is not so, however. Atoms, which would be expected to lie on a straight line, if the hexagons were regular, are considerably displaced. This effect was also noticed in coronene. The finally accepted model of ovalene was that whose molecular co-ordinates are given in Table 4. When these co-ordinates are combined with the orientation angles according to the relations

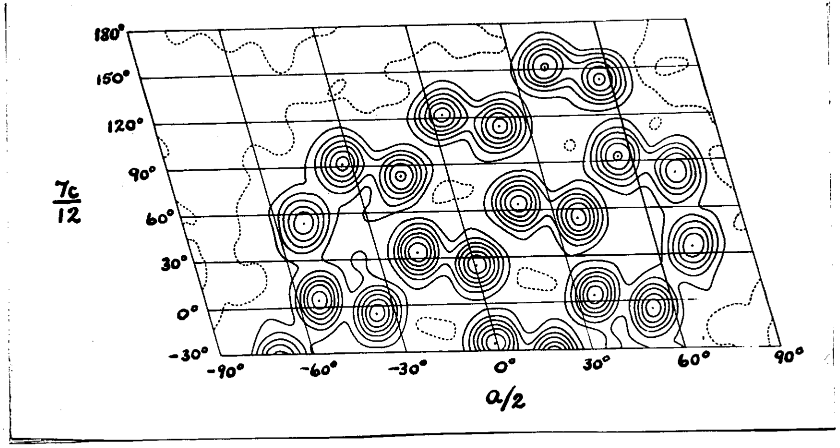
$$x' = L\cos\chi_L + M\cos\chi_M \qquad x = x' - z'\cot\beta$$

$$y = L\cos\psi_L + M\cos\psi_M \qquad z = z'\operatorname{cosec}\beta$$

$$z' = L\cos\omega_L + M\cos\omega_M$$

we obtain the rectangular co-ordinates (x', y, z') referred to the a and b crystal axes and their perpendicular c', or the monoclinic crystal co-ordinates. The latter are collected in Table 3 under column (a), and also plotted in Fig. 15 which is the contour map of the asymmetric unit.

Figure 15.



Structure Factors.

The co-ordinates of Fig. 15 and Table 3(a) were used in the final calculation of the structure factors, which are shown in the following Table under F calc. The agreement between the observed and calculated values of F, expressed in the usual way as a sum of all the discrepancies divided by the sum of the measured structure factors, is 15.2% for the (h0l) reflections, 14.3% for the (hk0) reflections and 12.9% for the (0kl) reflections. The overall agreement between the observed and calculated values of F for the three zones is 14.8%. This is of about the order usually encountered in such investigations.

Measured and calculated values of the structure factor. (Ovalene)

hkl	2sinθ	F meas.	F calc.	hkl	2sinθ	F meas.	F calc.
200	0.164	55.5	+69.6	$20\bar{7}$	1.078	6.4	- 6.8
400	0.328	44.9	-44.9	$20\bar{8}$	1.233	2.7	- 4.7
600	0.492	20.6	+19.3	$20\bar{9}$	1.390	4.8	- 6.6
800	0.656	2.5	- 2.7	$20\overline{10}$	1.548	< 2.7	- 1.3
10,00	0.820	2.0	+ 0.1	$20\overline{11}$	1.701	< 2.4	+ 0.8
12,00	0.984	4.0	- 5.0	$20\overline{12}$	1.860	5.0	+ 5.0
14,00	1.148	4.3	+ 6.0	40,11	1.854	< 1.9	+ 0.1
16,00	1.312	7.0	- 6.8	40,10	1.698	< 2.4	- 0.8
18,00	1.476	12.3	+10.2	409	1.542	10.2	+ 8.2
20,00	1.640	29.3	+29.1	408	1.388	24.2	-26.2
22,00	1.804	3.0	+ 1.5	407	1.234	61.2	-66.5
24,00	1.968	< 1.2	- 2.8	406	1.082	3.5	- 3.0
001	0.158	67.1	+74.2	405	0.932	5.9	+ 5.6
002	0.316	32.0	-37.9	404	0.786	5.2	- 4.5
003	0.474	8.5	+ 8.6	403	0.645	2.4	- 6.3
004	0.632	3.4	+ 2.4	402	0.513	7.5	- 2.8
005	0.790	11.1	+11.4	401	0.401	25.7	+23.4
006	0.948	12.3	-11.2	$40\bar{1}$	0.326	27.3	-31.0
007	1.106	8.7	+ 8.3	$40\bar{2}$	0.392	19.9	-26.6
008	1.264	6.6	+ 9.2	$40\bar{3}$	0.502	19.3	+18.5
009	1.422	5.6	+ 5.6	$40\bar{4}$	0.634	24.1	-19.3
00,10	1.580	< 2.7	- 1.1	$40\bar{5}$	0.773	66.4	-72.8
00,11	1.738	< 2.3	- 0.2	$40\bar{6}$	0.920	11.4	-11.1
00,12	1.896	19.5	+15.4	$40\bar{7}$	1.071	6.2	+ 5.4
20,12	1.949	7.6	+ 5.1	$40\bar{8}$	1.220	< 2.7	+ 2.4
20,11	1.789	2.1	- 0.3	$40\bar{9}$	1.376	3.5	+ 4.7
20,10	1.631	6.6	- 4.3	$40\overline{10}$	1.528	< 2.7	+ 2.2
209	1.477	10.5	+ 7.9	$40\overline{11}$	1.682	< 2.5	+ 0.7
208	1.318	21.1	-18.8	$40\overline{12}$	1.840	< 1.9	- 2.7
207	1.161	9.7	- 9.1	$40\overline{13}$	1.992	< 0.9	- 3.2
206	1.003	7.0	+ 6.7	60,11	1.929	< 1.5	- 0.1
205	0.849	7.8	- 7.2	60,10	1.778	< 2.2	+ 0.3
204	0.694	3.9	+ 4.1	609	1.623	< 2.6	- 0.9
203	0.540	5.8	- 6.5	608	1.474	6.0	+ 5.5
202	0.394	14.4	+14.6	607	1.325	22.6	-18.0
201	0.257	27.6	-31.6	606	1.179	10.4	- 5.0
$20\bar{1}$	0.196	43.3	+59.1	605	1.037	10.5	+ 9.4
$20\bar{2}$	0.317	42.7	-43.1	604	0.900	16.4	-16.0
$20\bar{3}$	0.460	34.3	+34.9	603	0.771	25.4	+26.0
$20\bar{4}$	0.610	21.7	-19.9	602	0.654	1.7	- 2.7
$20\bar{5}$	0.764	12.5	-13.3	601	0.557	20.6	-13.1
$20\bar{6}$	0.920	10.3	+11.3	$60\bar{1}$	0.478	21.3	+17.5

hkl	2sinθ	F meas.	F calc.	hkl	2sinθ	F meas.	F calc.
$60\bar{2}$	0.513	22.3	+22.5	$10,0\bar{5}$	0.980	3.4	- 2.4
$60\bar{3}$	0.588	< 1.6	+ 1.5	$10,0\bar{6}$	1.084	7.4	- 8.9
$60\bar{4}$	0.694	< 1.8	- 1.4	$10,0\bar{7}$	1.197	5.7	- 6.5
$60\bar{5}$	0.808	17.3	-21.3	$10,0\bar{8}$	1.319	< 2.8	- 3.0
$60\bar{6}$	0.951	11.1	-10.1	$10,0\bar{9}$	1.448	4.2	+ 5.8
$60\bar{7}$	1.090	4.3	+ 2.3	$10,0\overline{10}$	1.585	7.6	- 4.8
$60\bar{8}$	1.233	< 2.7	- 1.6	$10,0\overline{11}$	1.719	4.1	- 4.6
$60\bar{9}$	1.380	2.8	- 1.9	$10,0\overline{12}$	1.863	5.3	+ 5.5
$60\overline{10}$	1.530	5.9	- 1.5	12,09	1.935	11.4	- 9.1
$60\overline{11}$	1.679	< 2.5	+ 0.7	12,08	1.801	< 2.1	+ 1.0
$60\overline{12}$	1.830	< 2.0	+ 0.1	12,07	1.670	< 2.5	- 0.4
$60\overline{13}$	1.984	< 1.0	+ 2.3	12,06	1.542	< 2.7	+ 2.6
80,10	1.864	< 1.9	+ 1.3	12,05	1.422	2.8	+ 3.7
809	1.709	< 2.4	- 2.2	12,04	1.308	3.9	+ 3.7
808	1.572	2.7	- 1.3	12,03	1.203	< 2.7	- 2.4
807	1.429	8.4	+10.9	12,02	1.114	9.5	- 8.8
806	1.290	3.5	+ 6.5	12,01	1.042	7.2	- 9.0
805	1.156	5.6	+ 5.9	$12,0\bar{1}$	0.959	3.9	- 3.8
804	1.028	10.5	-11.9	$12,0\bar{2}$	0.956	29.9	+26.9
803	0.908	30.8	+27.4	$12,0\bar{3}$	0.978	52.5	+46.7
802	0.802	64.8	+59.1	$12,0\bar{4}$	1.026	< 2.4	+ 1.5
801	0.718	< 1.8	+ 1.4	$12,0\bar{5}$	1.094	3.5	- 5.0
$80\bar{1}$	0.637	8.9	- 7.4	$12,0\bar{6}$	1.176	4.5	+ 3.5
$80\bar{2}$	0.652	15.6	-12.8	$12,0\bar{7}$	1.279	6.7	+ 6.8
$80\bar{3}$	0.706	8.0	- 8.8	$12,0\bar{8}$	1.388	3.5	+ 3.1
$80\bar{4}$	0.784	< 1.9	+ 1.2	$12,0\bar{9}$	1.506	2.8	- 4.2
$80\bar{5}$	0.887	10.0	+11.6	$12,0\overline{10}$	1.616	< 2.6	+ 3.1
$80\bar{6}$	1.004	7.0	+10.6	$12,0\overline{11}$	1.763	2.2	+ 0.7
$80\bar{7}$	1.131	3.6	+ 5.0	$12,0\overline{12}$	1.902	1.7	+ 2.3
$80\bar{8}$	1.268	< 2.7	+ 1.7	14,08	1.925	3.5	- 2.2
$80\bar{9}$	1.407	6.9	- 7.9	14,07	1.799	< 2.1	- 0.1
$80\overline{10}$	1.546	22.2	-18.5	14,06	1.678	< 2.5	+ 1.5
$80\overline{11}$	1.689	3.8	- 3.8	14,05	1.562	2.7	- 2.6
$80\overline{12}$	1.840	< 1.9	+ 2.6	14,04	1.453	2.8	- 3.5
$80\overline{13}$	1.988	< 1.0	- 1.0	14,03	1.358	< 2.8	- 0.3
10,0,10	1.965	6.2	- 5.7	14,02	1.274	3.9	+ 3.6
10,09	1.822	2.0	+ 3.4	14,01	1.205	8.0	+ 7.5
10,08	1.681	< 2.5	+ 0.5	$14,0\bar{1}$	1.121	< 2.5	+ 0.3
10,07	1.547	4.2	- 4.0	$14,0\bar{2}$	1.112	4.4	- 7.4
10,06	1.413	2.8	- 5.4	$14,0\bar{3}$	1.115	19.2	+17.7
10,05	1.285	4.8	- 5.2	$14,0\bar{4}$	1.158	2.6	+ 1.0
10,04	1.161	2.6	- 1.3	$14,0\bar{5}$	1.214	4.6	- 7.3
10,03	1.052	< 2.4	- 0.3	$14,0\bar{6}$	1.286	8.2	+ 9.2
10,02	0.957	18.4	+16.0	$14,0\bar{7}$	1.372	10.5	-10.2
10,01	0.878	6.4	+ 8.9	$14,0\bar{8}$	1.470	4.8	+ 0.4
$10,0\bar{1}$	0.798	2.0	- 0.7	$14,0\bar{9}$	1.579	< 2.7	+ 2.0
$10,0\bar{2}$	0.803	8.4	+ 5.1	$14,0\overline{10}$	1.695	< 2.5	- 2.8
$10,0\bar{3}$	0.838	6.5	+ 7.2	$14,0\overline{11}$	1.818	< 2.1	+ 0.9
$10,0\bar{4}$	0.899	< 2.1	+ 0.1	$14,0\overline{12}$	1.944	< 1.4	- 0.7

hkl	2sinθ	F meas.	F calc.
16,07	1.930	< 1.5	+ 1.8
16,06	1.816	< 2.1	+ 0.9
16,05	1.703	12.6	-14.2
16,04	1.604	17.1	-17.0
16,03	1.513	< 2.8	+ 2.1
16,02	1.436	< 2.8	- 0.1
16,01	1.369	5.0	- 2.9
16,0$\bar{1}$	1.288	< 2.7	+ 1.2
16,0$\bar{2}$	1.274	4.7	+ 4.8
16,0$\bar{3}$	1.280	8.2	- 7.2
16,0$\bar{4}$	1.304	3.9	- 3.0
16,0$\bar{5}$	1.349	< 2.8	- 3.1
16,0$\bar{6}$	1.414	6.9	+ 8.2
16,0$\bar{7}$	1.484	25.1	-24.2
16,0$\bar{8}$	1.568	40.3	-36.4
16,0$\bar{9}$	1.669	< 2.5	+ 0.6
16,0$\overline{10}$	1.774	3.1	+ 2.4
16,0$\overline{11}$	1.888	< 1.7	+ 0.1
18,06	1.962	< 1.3	+ 1.1
18,05	1.855	< 1.9	+ 0.5
18,04	1.757	10.6	- 8.5
18,03	1.671	< 2.5	+ 4.0
18,02	1.597	< 2.7	+ 0.8
18,01	1.532	4.8	- 4.4
18,0$\bar{1}$	1.448	4.0	- 2.9
18,0$\bar{2}$	1.432	< 2.8	+ 1.0
18,0$\bar{3}$	1.434	2.8	+ 1.7
18,0$\bar{4}$	1.450	< 2.8	- 0.3
18,0$\bar{5}$	1.487	< 2.8	+ 0.5
18,0$\bar{6}$	1.539	< 2.7	+ 0.4
18,0$\bar{7}$	1.602	< 2.7	+ 1.8
18,0$\bar{8}$	1.678	18.9	-17.3
18,0$\bar{9}$	1.764	3.9	- 3.6
18,0$\overline{10}$	1.865	2.6	+ 3.5
18,0$\overline{11}$	1.969	4.9	- 4.2
20,04	1.914	2.8	+ 3.0
20,03	1.830	< 2.0	+ 1.1
20,02	1.756	< 2.3	- 0.4
20,01	1.694	< 2.5	- 4.8
20,0$\bar{1}$	1.614	34.5	+28.2
20,0$\bar{2}$	1.596	< 2.7	- 4.5
20,0$\bar{3}$	1.592	< 2.7	+ 0.4
20,0$\bar{4}$	1.606	< 2.6	- 0.4
20,0$\bar{5}$	1.630	< 2.6	+ 1.8
20,0$\bar{6}$	1.676	< 2.5	- 2.6
20,0$\bar{7}$	1.730	< 2.3	- 0.3
20,0$\bar{8}$	1.798	6.4	+ 7.4
20,0$\bar{9}$	1.875	4.4	+ 3.7
20,0$\overline{10}$	1.960	5.8	+ 3.7
22,03	1.988	< 1.1	- 0.8
22,02	1.919	< 1.6	+ 0.4
22,01	1.860	< 1.9	- 2.3
22,0$\bar{1}$	1.780	17.8	+16.0
22,0$\bar{2}$	1.760	< 2.3	- 1.4
22,0$\bar{3}$	1.750	< 2.3	- 0.7
22,0$\bar{4}$	1.758	< 2.3	+ 2.4
22,0$\bar{5}$	1.778	6.0	- 6.1
22,0$\bar{6}$	1.810	< 2.1	+ 3.4
22,0$\bar{7}$	1.859	< 1.9	- 0.9
22,0$\bar{8}$	1.918	< 1.6	- 1.9
22,0$\bar{9}$	1.956	< 1.0	- 2.3
24,0$\bar{1}$	1.942	5.7	- 6.2
24,0$\bar{2}$	1.918	4.8	- 3.9
24,0$\bar{3}$	1.911	< 1.6	- 1.8
24,0$\bar{4}$	1.912	< 1.6	+ 4.1
24,0$\bar{5}$	1.928	10.8	-11.5
24,0$\bar{6}$	1.956	8.4	- 9½.3
020	0.656	7.9	- 5.7
040	1.312	5.4	- 6.5
060	1.968	< 2.4	+ 2.1
110	0.339	5.2	- 7.3
210	0.367	29.6	-40.4
310	0.412	81.6	+82.6
410	0.464	53.3	-56.0
510	0.525	12.0	+11.2
610	0.592	11.6	+ 9.0
710	0.661	7.2	- 8.1
810	0.733	8.6	- 6.6
910	0.806	3.9	+ 2.3
10,1,0	0.883	5.1	+ 2.9
11,1,0	0.959	< 4.4	- 0.6
12,1,0	1.038	< 4.7	+ 0.3
13,1,0	1.118	4.9	- 4.1
14,1,0	1.193	< 5.1	- 1.6
15,1,0	1.280	12.5	+11.7
16,1,0	1.354	29.8	+28.0
17,1,0	1.435	28.3	+24.1
18,1,0	1.508	11.4	+ 9.9
19,1,0	1.597	5.2	+ 0.9
20,1,0	1.670	< 4.9	- 3.3
21,1,0	1.758	< 4.4	- 3.5
22,1,0	1.831	< 3.9	+ 0.1
23,1,0	1.919	2.9	+ 3.4
24,1,0	1.988	< 2.0	+ 0.3
120	0.664	13.9	-15.9
220	0.677	6.0	+ 3.9

hkl	2sinθ	F meas.	F calc.
320	0.703	4.3	+ 6.5
420	0.734	6.8	- 4.6
520	0.776	3.8	+ 2.2
620	0.823	7.4	- 5.2
720	0.874	< 4.1	+ 0.8
820	0.928	< 4.3	- 0.9
920	0.989	4.5	+ 7.8
10,2,0	1.050	< 4.7	- 3.7
11,2,0	1.114	6.7	- 6.5
12,2,0	1.184	10.9	+11.4
13,2,0	1.249	21.4	+18.3
14,2,0	1.322	11.5	+ 9.9
15,2,0	1.393	< 5.4	+ 3.6
16,2,0	1.466	< 5.4	+ 2.3
17,2,0	1.538	10.6	- 8.0
18,2,0	1.612	< 5.1	+ 1.2
19,2,0	1.689	< 4.8	+ 3.5
20,2,0	1.766	< 4.3	- 0.6
21,2,0	1.842	< 3.8	- 1.2
22,2,0	1.918	< 2.9	+ 0.6
23,2,0	1.990	< 0.9	- 0.4
130	0.992	18.4	+18.5
230	0.998	4.6	+ 3.4
330	1.016	9.7	-10.7
430	1.040	< 4.7	- 1.7
530	1.066	6.5	+ 8.8
630	1.101	< 4.9	- 0.8
730	1.138	< 5.0	- 3.2
830	1.185	< 5.1	- 0.5
930	1.235	8.3	- 9.1
10,3,0	1.282	< 5.3	+ 2.6
11,3,0	1.334	5.4	- 7.1
12,3,0	1.392	< 5.4	- 1.6
13,3,0	1.450	< 5.4	- 2.0
14,3,0	1.516	< 5.4	- 0.9
15,3,0	1.575	< 5.2	+ 3.0
16,3,0	1.646	< 5.0	+ 2.5
17,3,0	1.704	< 4.7	- 3.1
18,3,0	1.776	6.7	- 4.4
19,3,0	1.842	8.0	+ 6.0
20,3,0	1.913	4.3	- 5.2
21,3,0	1.983	< 1.2	+ 5.0
140	1.317	6.6	- 4.3
240	1.328	12.1	+11.2
340	1.338	12.7	-12.5
440	1.354	11.5	+11.5
540	1.375	5.4	- 5.5
640	1.406	< 5.4	- 3.8
740	1.432	< 5.4	- 1.0
840	1.468	< 5.4	- 3.6
940	1.505	< 5.4	- 2.9
10,4,0	1.552	< 5.3	+ 0.3
11,4,0	1.591	< 5.2	+ 1.4
12,4,0	1.646	< 5.0	+ 2.8
13,4,0	1.690	< 4.8	- 2.8
14,4,0	1.748	< 4.4	- 0.5
15,4,0	1.798	< 4.1	- 0'5
16,4,0	1.856	5.2	+ 4.2
17,4,0	1.916	5.6	+ 5.0
18,4,0	1.978	< 1.4	+ 2.6
150	1.645	< 5.0	+ 0.5
250	1.654	< 5.0	+ 2.8
350	1.661	< 4.9	+ 1.2
450	1.677	< 4.9	+ 2.0
550	1.693	4.8	+ 5.1
650	1.720	4.6	- 5.1
750	1.738	4.5	+ 5.2
850	1.772	< 4.3	- 3.0
950	1.798	< 4.1	+ 0.1
10,5,0	1.835	< 3.9	- 0.1
11,5,0	1.873	< 3.5	+ 0.1
12,5,0	1.906	< 3.2	+ 4.2
13,5,0	1.956	< 2.2	+ 6.5
011	0.365	< 2.5	- 1.3
012	0.457	9.3	+10.8
013	0.578	8.2	- 8.7
014	0.715	36.7	+36.3
015	0.856	13.8	+11.3
016	1.002	< 4.7	+ 1.6
017	1.156	9.9	-11.2
018	1.307	29.6	-32.9
019	1.460	< 5.6	- 5.4
0,1,10	1.614	< 5.2	+ 2.4
0,1,11	1.770	< 4.4	+ 0.3
0,1,12	1.929	< 2.8	+ 1.3
021	0.677	7.1	- 1.0
022	0.730	7.9	- 8.0
023	0.814	17.9	+17.4
024	0.914	27.4	+30.6
025	1.030	< 4.7	+ 1.6
026	1.156	< 5.1	+ 1.5
027	1.290	< 5.5	+ 3.0
028	1.430	< 5.6	- 3.7
029	1.568	< 5.6	- 3.2
0,2,10	1.712	< 4.8	- 1.6
0,2,11	1.860	< 3.7	+ 0.8
031	1.000	17.0	-17.9
032	1.037	< 4.8	- 1.8

hkl	2sinθ	F meas.	F calc.
033	1.095	< 5.0	- 2.5
034	1.175	< 5.2	- 3.5
035	1.266	< 5.4	- 3.0
036	1.371	< 5.6	+ 2.3
037	1.486	< 5.5	+ 0.8
038	1.607	< 5.3	- 1.9
039	1.734	< 4.7	- 0.6
0,3,10	1.866	< 3.7	- 0.4
0,3,11	1.997	< 1.8	- 0.6
041	1.329	< 5.6	+ 0.5
042	1.354	< 5.6	- 1.7
043	1.404	< 5.6	+ 3.6
044	1.460	10.4	- 6.7
045	1.540	17.3	-15.4
046	1.628	< 5.2	- 0.9
047	1.725	< 4.7	- 5.7
048	1.828	4.0	- 4.1
049	1.942	< 2.5	- 0.1
051	1.657	< 5.1	- 1.3
052	1.678	< 5.0	+ 0.7
053	1.716	13.4	+12.9
054	1.769	< 4.4	+ 1.1
055	1.825	< 4.0	- 2.1
056	1.900	< 3.4	- 0.6
057	1.986	< 2.1	+ 0.4
061	1.982	< 2.1	- 5.0

Part 2.

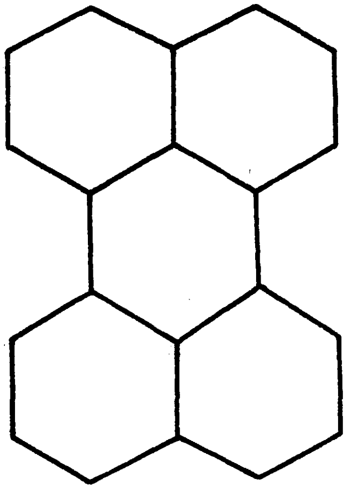
The Crystal Structure of Perylene (A Quantitative X-ray Investigation)

Introduction

Perylene (Fig. 16), is a condensed-ring hydrocarbon. The cell dimensions and space group have already been recorded (44). This work has since been repeated by White and separately by the author. A simpler unit cell has now been chosen.

The molecule, presuming it to be planar, has a centre of symmetry and three planes of symmetry at right angles. Since there are four molecules of perylene per unit cell and the space group is $P2_1/a$ (axial lengths 11.35A; 10.87A; 10.31A;) the molecular centre does not lie at the origin of the unit cell. Because of this, good resolution of all the atoms as in the cases of coronene (12, 31) and ovalene, cannot be expected. The resolution of the atoms on the most favourable projection will be only partially complete due to overlapping of molecules, as in the pyrene (10) and 1:12 benzperylene structures (13). Hence the estimation of the atomic centres will probably not be as accurate as those in the previous structure analysis (i.e.

Figure 16.



ovalene), and it is doubtful if it will be possible to obtain values for all the bond distances.

The investigation was carried out with the purpose of obtaining experimental values of as many of the bond lengths as possible for comparison with those predicted. Also, if a sufficiently good refinement of the structure is obtained by the two-dimensional Fourier methods of analysis, it will enable a possible analysis by the three-dimensional Fourier methods.

Crystal Data

Perylene, $C_{20}H_{12}$, M, 252.3 m.p., 266° - 268°

d. calc. 1.341 d, found 1.322

monoclinic prismatic, $\underline{a} = 11.35 \pm 0.02$A, $\underline{b} = 10.87 \pm 0.03$A,

$\underline{c} = 10.31 \pm 0.03$A, $\underline{\beta} = 100.8^\circ \pm 0.2^\circ$.

Absent Spectra - (h0l) when h is odd; (0k0) when k is odd.

Space Group - C^5_{2h} ($P_{2_1/a}$).

Four molecules per unit cell. Molecular symmetry centre.

Volume of the unit cell, 1,249A^3

Absorption coefficient for X-rays, $\lambda = 1.54$A, $\mu = 6.96$ per cm.

Total number of electrons per unit cell = F(000) = 528.

The crystals are square plates which cleave parallel to the sides. The a and b crystal axes are the diagonals of the square, and the c crystal axis is almost perpendicular to the plane of the plates. These specimens were most unsuitable for intensity measurements in the investigation of the (h0l) zone. By extremely slow crystallisation from amyl acetate, it was possible to grow a crystal considerably thicker in the c-axial direction, and which could be cut to give an almost regular piece of crystal suitable for intensity measurements.

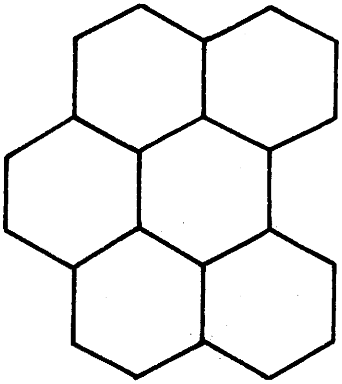
Crystal Structure.

The asymmetric crystal unit consists of one complete molecule, and it is reasonable to assume, as a first approximation, a regular planar structure in accordance with the chemical evidence. Now the b-axis in perylene is appreciably larger than the corresponding axis in pyrene (9.24A) and smaller than the b-axis of 1:12 benzperylene (11.88A). This suggests that there are two perylene molecules accommodated in one b-axis translation as in the case of these two compounds, but tilted at an angle to the (010) plane which is rather more than the corresponding tilt in the pyrene structure and slightly less than in the 1:12 benzperylene structure.

It is necessary now to proceed by trial and error methods in the first instance. A tilt of the molecular plane to (010) of about 56° being assumed, there remain five more degrees of freedom to be fixed, viz., two more orientation angles and the free translations x_0, y_0 and z_0 of the molecular centre along the three crystal axes from the origin (the molecule being assumed planar, the molecular centre is then the centre of symmetry, i.e. the centre of the central hexagonal ring).

An inspection of the (h0l) zone, by moving-film methods, showed that the following small-spacing planes gave strong reflections:- (204); (800); (10,000); (805); $(80\bar{9})$.
It was also noticed that the reflection from the large-spacing (201) planes was almost too weak to be visible. Since the perylene molecule probably contains an inherent centre of symmetry, it seems that the molecular centre almost lies on a line one-quarter of the way between the (201) planes. Use was made of this fact in investigating the structure of 1:12 benzperylene (13) (Fig. 17). Rotation photographs taken about the corresponding axes of this compound and perylene show a remarkable similarity in intensity distribution, which can only be due to a very close, three-dimensional similarity in structure. In 1:12 benzperylene the (201)

Figure 17.



reflection was recorded, since the two additional carbon atoms make appreciable contributions to this reflection, but it was assumed that the molecular centre of 1:12 benzperylene would also lie in the same relative position as that of perylene, i.e. on a line one-quarter of the way between the (201) planes.

An approximate orientation of the perylene molecule can be obtained from the small-spacing planes, which gave strong reflections. The contributions from most of the atoms must be in phase for these planes and, from a diagram similar to that used for coronene and ovalene, an orientation of the molecule was obtained which accounted for the enhancement of these reflections. This fact taken in conjunction with the molecular centre lying one-quarter of the way between the (201) planes fixes the remaining five degrees of freedom. Assuming regular hexagons of 1.41A for the molecular model to begin with, values of 37.5° for x_0 and 8.0° for z_0 are obtained.

Calculations of the (h0l) structure factors on the above basis led to fairly good agreements with the observed values, and it was possible to refine the atomic parameters from this stage by the application of double Fourier series methods. Three successive Fourier analyses of the (h0l) zone were carried out.

The first analysis was carried out by White. 57

reflections were included. The discrepancy between the calculated and observed values of the structure factors for these 57 planes, after the analysis had been completed, was approximately 19%. The crystal used by White had the extreme dimensions of 0.85 mm. by 0.24 mm. It was now that the attempt to grow better crystals, in order to obtain a better moving-film series for intensity estimation, was made. A more uniform crystal (dimensions of 0.35 mm. by 0.38 mm.) was obtained. Another moving-film series was taken, and the intensities re-estimated. This time 80 reflections were observed, and the discrepancy between the calculated and observed values of the structure factors for these 80 reflections was 22.5%.

In the second Fourier analysis 74 reflections were included, 6 being omitted because the values of the phase angle were doubtful. The discrepancy between the observed and calculated values of the structure factors, after this refinement had been completed, was 22.5%. Since there was no reduction in the discrepancy, and the resolution of the atoms was not very good, leaving ample scope for alternative positions of the atomic centres, other estimates of the positions of the centres had to be made. Booth's Method of locating maxima (45) was used.

The following is a short account of this method. Since Fourier syntheses give density values at equidistant points, usually 1/60th of the unit-cell side, the information can be assumed to be in the form

$$\begin{array}{c|c|c|c|} x & 0 & 1 & 2 \\ \hline d & 0 & d_1 & d_2 \end{array}$$

where d represents electron density, and $d_1 \geq d_2 \geq 0$

Assume that $d = ax^2 + bx$

then $a = (d_2 - 2d_1)/2$ and $b = -(d_2 - 4d_1)/2$.

The value of x which makes d a maximum is given by

$$x = -b/2a = (d_2 - 4d_1)/(2d_2 - 4d_1)$$

$$= (r - 4)/(2r - 4) \qquad \text{where } r = d_2/d_1$$

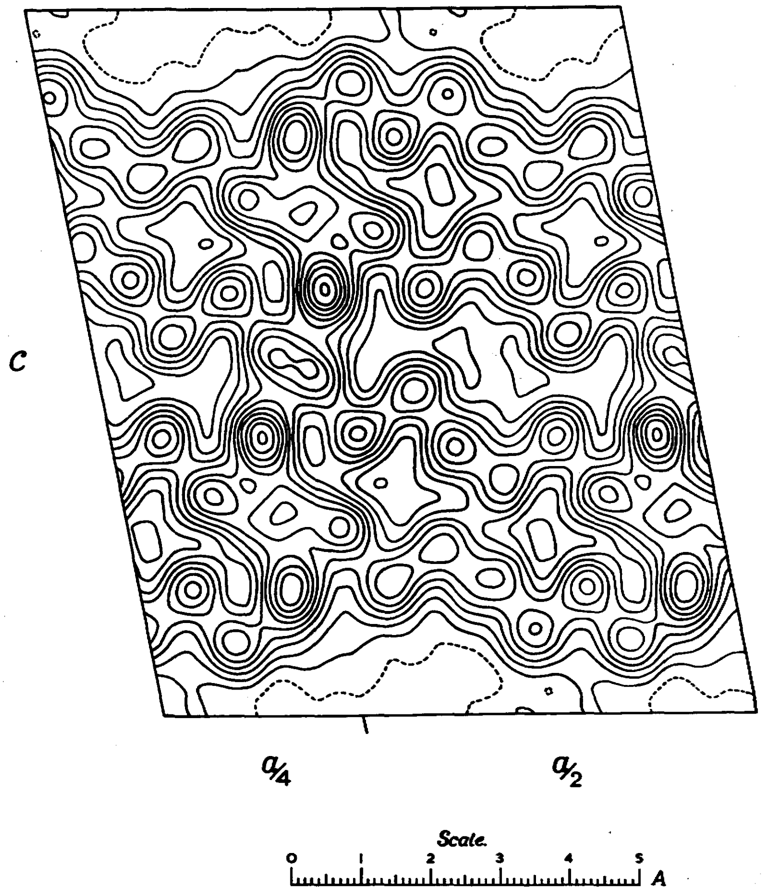
Since $0 \leq d_2 \leq d_1$, then $0 \leq r \leq 1$.

Booth has tabulated values of x for the whole range of r, and hence, if d_1 and d_2 are known then x is obtained from a Table. It can be seen from the above explanation, that the method simply makes use of the gradients at either side of the peak. The procedure then, to obtain the position of the centre, is to take three electron densities along a row d_1; d_2; d_3 (in that order) such that d_2 is the greatest. Then subtract the smallest value (d_1 or d_3) from the three values leaving one value zero. The maximum point can then be obtained as above. This is then repeated for another row and two columns, and so four points are obtained. The intersection of the two lines joining the two points on the rows and the two points on the columns is then taken as the position of the centre.

New values for the centres of the atoms were obtained. The new z co-ordinates improved the discrepancy between the observed and calculated values of the structure factor of the (001) planes but the new x co-ordinates considerably worsened the discrepancy between the observed and calculated values of the structure factors of the (h00) planes. These new z co-ordinates were adopted as being correct, but the new x co-ordinates were abandoned for the old values. This accepted set of co-ordinates was now used for calculating structure factors in the (h0l) zone, and the discrepancy between these calculated values and the observed values for the 80 planes observed became 19.1%. There were several sign changes in the 80 structure factors calculated, but of the 74 included in the Fourier analysis only one, (405), changed in sign.

In the final refinement of the structure 79 reflections were included in the Fourier series, representing all the reflections which could be observed with copper-K_α radiation, except one. In the moving-film series used for estimating intensities towards the latter part of the work, the (201) planes appeared very weakly. The calculated value of the structure factor for these planes was extremely small, and hence its sign was very doubtful. This was the one observed reflection which was omitted. The discrepancy between the observed and calculated values of the structure factors, after this refinement had been completed and the positions of the atomic centres re-estimated, was 16.9%. The projection of the structure obtained from this final synthesis is reproduced in Fig. 18.

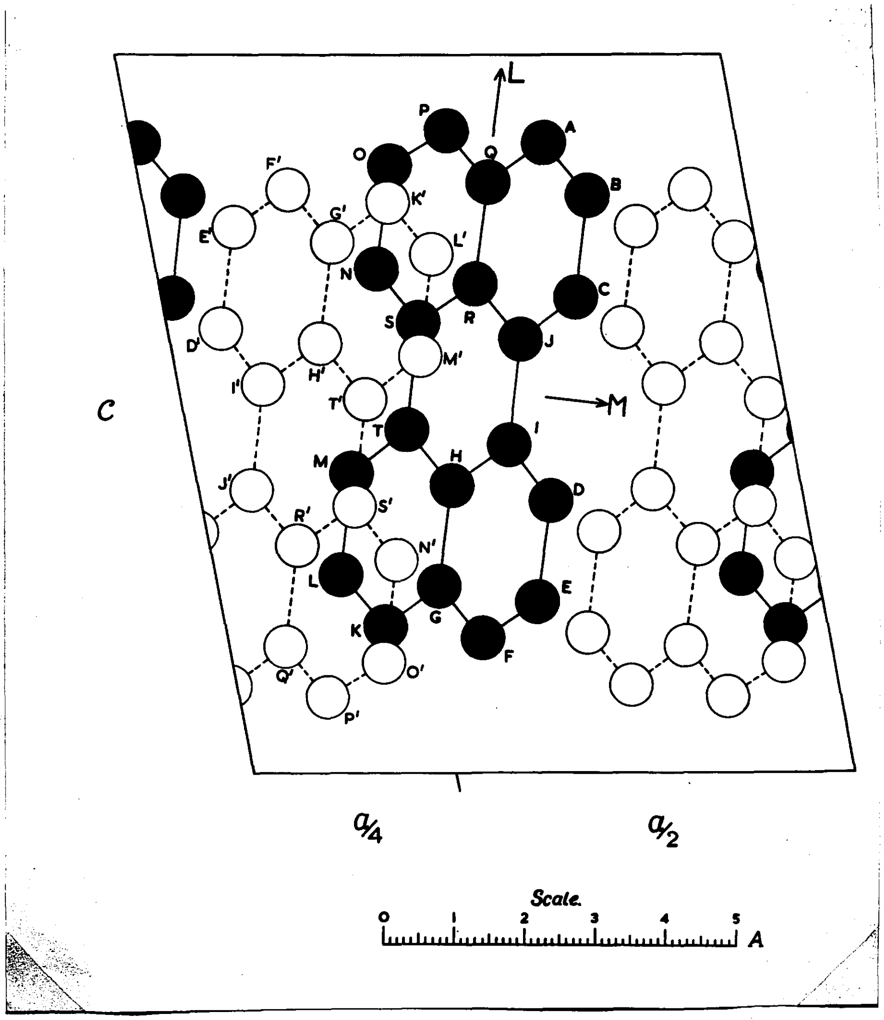
Figure 18.



Projection on (010) plane.

Only 11 of the 20 crystallographically independent atoms are separately resolved, the others being obscured by overlapping effects of adjoining molecules, as shown in Fig. 19.

Figure 19.



Projection on (010) plane showing overlapping of perylene molecules.

Because of the centre of symmetry in the molecule the x and z co-ordinates of the unresolved atoms can be obtained from a knowledge of the co-ordinates of the resolved atoms (see experimental section). These positions are in accordance with the observed double peaks in Fig. 18.

Orientation, Co-ordinates and Dimensions.

By assuming a planar molecule, with molecular axes L and M at right angles and meeting at the molecular centre, (see Fig. 19) it is possible to calculate the orientation of the molecule as explained in the experimental section. The finally accepted orientation is shown in Table 6, where χ_L, ψ_L, ω_L; χ_M, ψ_M, ω_M; χ_N, ψ_N, ω_N; are the angles which the molecular axes L and M and their perpendicular N, make with the a and b crystal axes and their perpendicular c'.

Table 6.

$\chi_L = 83.3^\circ$ $\cos\chi_L = 0.1173$ $\chi_M = 55.4^\circ$ $\cos\chi_M = 0.5681$

$\psi_L = 89.2^\circ$ $\cos\psi_L = 0.0138$ $\psi_M = 35.0^\circ$ $\cos\psi_M = 0.8192$

$\omega_L = 6.8^\circ$ $\cos\omega_L = 0.9930$ $\omega_M = 94.5^\circ$ $\cos\omega_M = -0.0785$

$\chi_N = 144.5^\circ$ $\cos\chi_N = -0.8146$

$\psi_N = 55.0^\circ$ $\cos\psi_N = 0.5733$

$\omega_N = 84.9^\circ$ $\cos\omega_N = 0.0883$

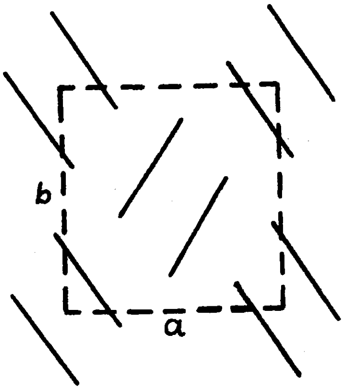
Fig. 18 (the projection on the (010) plane) allows of a direct measurement of the x and z crystal co-ordinates of some of the atoms, viz., A, B, C, D, E, F, H, I, J, P, Q. (See Fig. 19). These are the atoms which are separately resolved, and bond distances between these atoms alone can be measured directly. Due to the high molecular symmetry however, these are sufficient to give a measure of every type of chemically equivalent bond in the molecule, except GH and QR. The remaining unresolved atoms can be assigned co-ordinates using the molecular symmetry. This then allows of a measure of these two bond lengths, but the accuracy of this measurement will be much less than for the others.

The y co-ordinates can be calculated by assuming the molecule to be planar and knowing the orientation and also the free translation, y_0, of the molecular centre along the b crystal axis. This latter was found by trial and error. The values obtained for the y-co-ordinates were tested by calculating structure factors in the (hk0) zone. This zone is extremely sensitive to the tilt of the planar molecule and y-co-ordinates were calculated for various values of this tilt. At a tilt of 54.7° (ψ_N), the discrepancy between the observed and calculated structure factors in the (hk0) zone was 16.3%. Trials of making this tilt 1° more and 1° less made this discrepancy worse. One trial, however, which made this tilt greater by 0.3°, reduced the discrepancy in the (hk0) zone to 14.1%. This was the result finally accepted.

No direct measurement of the y-co-ordinates is possible, since no resolution of the atomic positions can be obtained, either from projections of the (hk0) or of the (0kl) zones. For example the structure, viewed along c' (i.e. perpendicular to the a and b crystal axes), would give an end view of the molecules as depicted roughly in Fig. 20.

The co-ordinates of the atoms are collected in Table 7.

Figure 20.



Under the column headed (b) are the x and z co-ordinates directly measured for the 11 resolved atoms. As the molecule has a centre of symmetry, it is possible to average the lengths of chemically equivalent but crystallographically distinct bonds, and hence, under column (a), are the co-ordinates of the atoms after this averaging. These are the co-ordinates finally accepted as they are probably more correct. Since the molecular centre does not lie on the origin of the unit cell, the asymmetric unit consists of one complete molecule i.e. 20 atoms. The position of all the other atoms in the unit cell may be derived from the operations:-

(x,y,z); (-x,-y,-z); (x + a/2,-y + b/2, z);(-x+a/2,y +b/2,-z).

Table 7.

Atom	x, A. (a)	$2\pi x/a$ (a)	y, A. (a)	$2\pi y/b$ (a)	z, A. (a)	$2\pi z/c$ (a)
A	2.922	92.7°	-0.500	- 16.6°	3.889	135.8°
B	3.410	108.2°	0.499	16.5°	3.156	110.2°
C	2.980	94.5°	0.502	16.6°	1.686	59.9°
D	2.097	66.5°	0.463	15.3°	-1.223	- 42.7°
E	1.636	51.9°	0.420	13.9°	-2.689	- 93.9°
F	0.764	24.2°	-0.597	- 19.8°	-3.224	-112.6°
G	0.287	9.1°	-1.586	- 52.5°	-2.480	- 86.6°
H	0.730	23.2°	-1.566	- 51.9°	-1.020	- 35.6°
I	1.646	52.2°	-0.510	- 16.9°	-0.430	- 15.0°
J	2.105	66.8°	-0.490	- 16.2°	1.085	37.9°
K	-0.582	-18.5°	-2.593	- 85.9°	-3.030	-105.8°
L	-1.070	-33.9°	-3.591	-118.9°	-2.298	- 80.2°
M	-0.640	-20.3°	-3.594	-119.0°	-0.828	- 28.9°
N	0.243	7.7°	-3.554	-117.7°	2.082	72.7°
O	0.704	22.3°	-3.511	-116.3°	3.547	123.9°
P	1.576	50.0°	-2.494	- 82.6°	4.083	142.6°
Q	2.053	65.1°	-1.506	- 49.9°	3.339	116.6°
R	1.610	51.1°	-1.526	- 50.5°	1.879	65.6°
S	0.694	22.0°	-2.581	- 85.5°	1.288	45.0°
T	0.235	7.4°	-2.602	- 86.2°	-0.226	- 7.9°
U (molecular centre)	1.171	37.1°	-1.546	- 51.2°	0.429	15.0°

Table 7 (contd.)

Atom	x, A. (b)	z. A. (b)
A	2.928	3.890
B	3.411	3.153
C	2.979	1.690
D	2.100	-1.220
E	1.633	-2.692
F	0.758	-3.222
H	0.730	-1.020
I	1.645	-0.430
J	2.106	1.085
P	1.582	4.081
Q	2.052	3.339

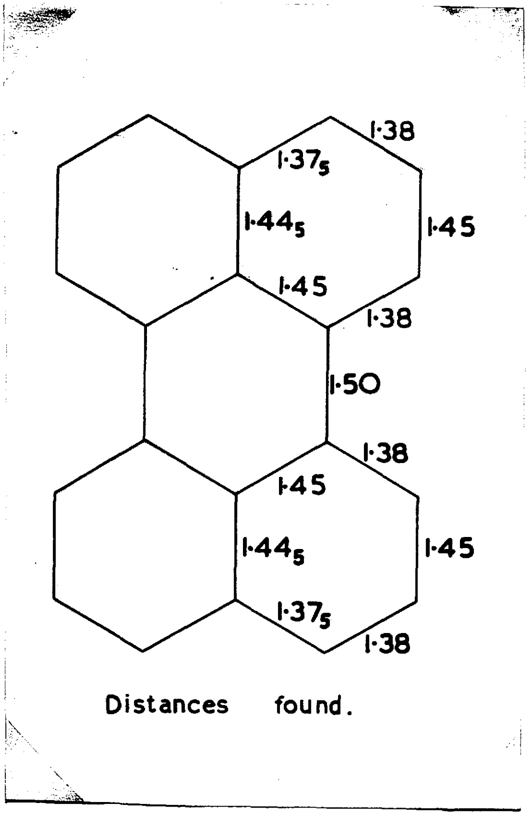
The molecular dimensions and bond distances can be calculated from the observed crystal co-ordinates by combination with the orientation angles of Table 6. Below are the bond distances obtained between the resolved atoms before corresponding pairs of bonds were averaged.

AB = 1.378A EF = 1.384A
BC = 1.446A DE = 1.459A
CJ = 1.380A DI = 1.386A
AQ = 1.386A PQ = 1.367A
IJ = 1.499A
HI = 1.448A

The mean values of these bonds are collected in Fig. 21(a). These bond distances are the values obtained from the averaged co-ordinates.

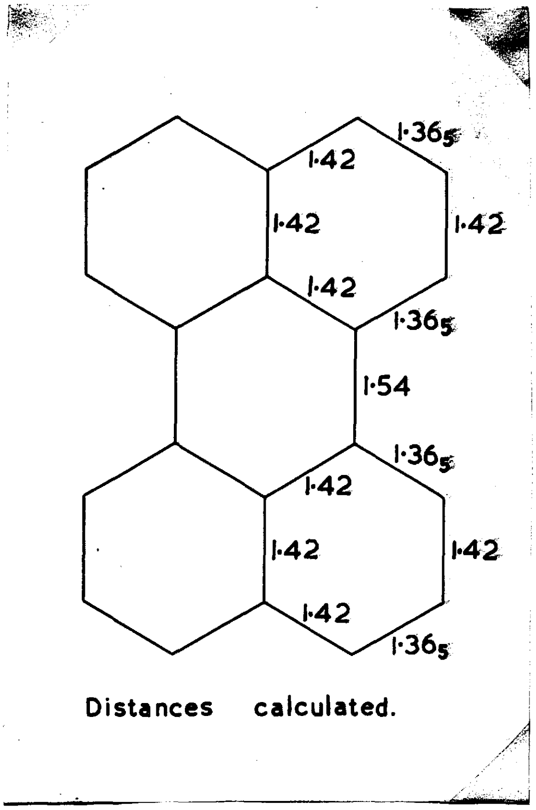
The apparently good agreement is really spurious. Use was made of this molecular symmetry in plotting the co-ordinates in the final contour diagram (Fig. 18), since even the resolution of the separately resolved atoms was not very good, and it was difficult to decide the exact centres of the peaks. Fig. 21 (b) shows the bond lengths calculated from the Kekulé structures, but these will be discussed later.

Figure 21(a).



Distances found.

Figure 21(b).



Distances calculated.

The atomic co-ordinates with respect to the molecular axes L, M and N are given in Table 8. Also in Table 8 are the atomic co-ordinates with respect to another set of molecular axes L' and M'. For ease of working (as explained in the experimental section) it was found useful to imagine the molecule moved parallel to itself down the b-axis, until the plane of the molecule passed through the origin of the unit cell. Then molecular axes L' and M' were chosen parallel to L and M respectively, but meeting at the cell origin instead of at the molecular centre.

Table 8.

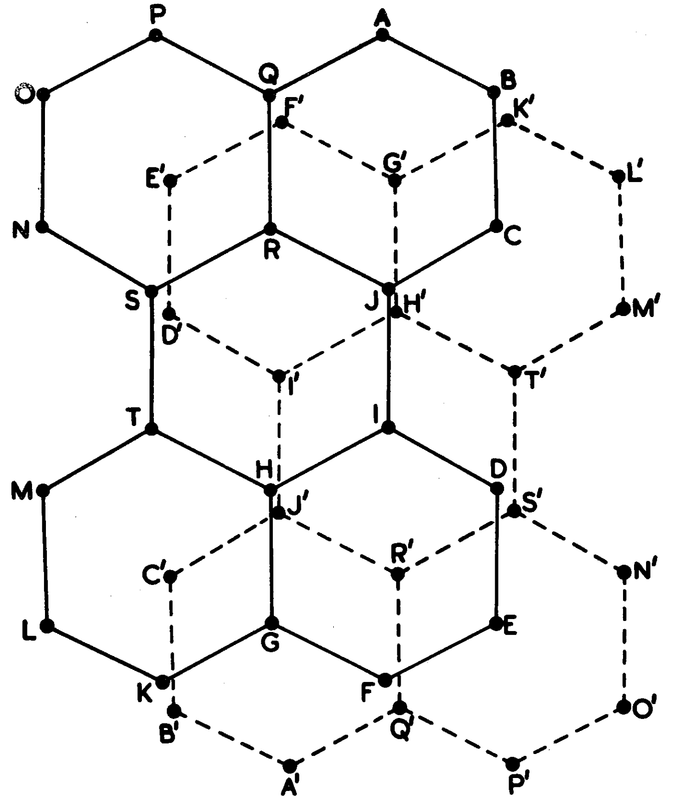
Atom	L,A.	M,A.	N,A.	L',A.	M',A.
A	3.518	1.218	0	4.085	3.020
B	2.891	2.448	0	3.458	4.250
C	1.439	2.476	0	2.006	4.278
D	-1.439	2.476	0	-0.872	4.278
E	-2.891	2.448	0	-2.324	4.250
F	-3.518	1.218	0	-2.951	3.020
G	-2.878	0	0	-2.311	1.802
H	-1.434	0	0	-0.867	1.802
I	-0.749	1.277	0	-0.182	3.079
J	0.749	1.277	0	1.316	3.079
K	-3.518	-1.218	0	-2.951	0.585
L	-2.891	-2.448	0	-2.324	-0.645
M	-1.439	-2.476	0	-0.872	-0.674
N	1.439	-2.476	0	2.006	-0.674
O	2.891	-2.448	0	3.458	- 0.645
P	3.518	-1.218	0	4.085	0.585
Q	2.878	0	0	3.445	1.802
R	1.434	0	0	2.001	1.802
S	0.749	-1.277	0	1.316	0.526
T	-0.749	-1.277	0	-0.182	0.526
U (molecular centre)	0	0	0	0.567	1.802

The molecular co-ordinates in the above Table are obtained from the averaged crystal co-ordinates, i.e. the co-ordinates under heading(a) in Table 7.

Intermolecular Distances

The closest approach of adjacent molecules occurs along the b-axis, where there is a perpendicular distance of 3.47A between the two molecules related by the centre of symmetry at the origin. Fig. 22 shows the normal projection of one of these molecules in the plane of the other.

Figure 22.



The normal projection of two parallel molecules.

This diagram has a similar staggered arrangement of the atoms as in the corresponding projections for other hydrocarbons such as coronene, ovalene and 1:12 benzperylene. The closest approaches between atoms of different molecules lie in this direction. The closest approaches are from atom D on the standard molecule to S' on the inverted molecule, and from H to J' where the distance is 3.49A. Between atoms F and Q', and between atoms K and B' the distance is 3.50A. All other pairs of atoms are separated by very much more than 3.5A.

In other directions the distances are greater. Along the a-axis, from L on the standard molecule to E_1 on the molecule at $(x - \frac{1}{2})$, $(-y - \frac{1}{2})$, z and from M on the standard molecule to D_1, the distances are 3.70A. From B on the standard molecule to K_2 on the molecule at $(\frac{1}{2} - x)$, $(\frac{1}{2} + y)$, $-z$ the distance is 3.71A. In the c-axis translation, P on the standard molecule is 3.86A from F_3 on the molecule at x, y, (z + 1). Some other intermolecular distances are tabulated below. All these distances are taken from the atom on the standard molecule to the atom on the translated molecule (denoted by subscript).

<u>Molecule at $(\frac{1}{2} - x)$; $(\frac{1}{2} + y)$; $- z$.</u>

B to L_2 = 3.85A
C to L_2 = 3.93A
C to M_2 = 3.85A
C to T_2 = 3.89A
D to N_2 = 3.88A
D to S_2 = 3.76A
E to O_2 = 3.91A
E to P_2 = 3.98A

<u>Molecule at $(x-\frac{1}{2})$; $(-y-\frac{1}{2})$; z.</u>

L to D_1 = 3.73A
L to F_1 = 3.75A
M to I_1 = 3.82A
N to B_1 = 3.77A
N to C_1 = 3.75A
O to A_1 = 3.82A
O to B_1 = 3.79A

Apart from these and a few other distances between atoms on the standard molecule and the molecule related by the centre of symmetry at the origin, all other intermolecular distances appear to be greater than 4A. These intermolecular distances are of about the same magnitude as is usually encountered in hydrocarbon structures

Discussion of Results.

There were discrepancies between the unit cell chosen by Hertel and Bergk (44) and the simpler unit cell chosen for this work. The c-axis previously chosen was measured as 13.65A. This axis corresponds to the $[10\bar{1}]$ diagonal in the simpler unit cell, and its length was measured as 13.84A (±0.03A). A summary of the axial lengths obtained are shown below.

Hertel and Bergk		Simpler Unit Cell	
a-axis	10.3A	c-axis	10.31A
b-axis	10.8A	b-axis	10.87A
c-axis	13.65A	$[10\bar{1}]$ -diagonal	13.84A.
[101] - diagonal	11.2A (calc.) 11.3A (found)	a-axis	11.35A.

A check on the simpler unit cell was made by measuring the [110] diagonal. This was found to be 15.73 ± 0.05A., and agreed very well with the a and b axial measurements, from which [110] calculates to 15.72A. The new values were those accepted.

There is a large variety of bond lengths found within this molecule, but the most striking result is the length of the bonds joining the two naphthalene groups, i.e. 1.50A. Unfortunately there is only one measurement available for this bond. Atoms I and J are completely resolved, but atoms S and T are concealed by the overlapping effects. However the resolution of atoms I and J is very good and the error in the estimation of this bond length is probably no more than ±0.03A.

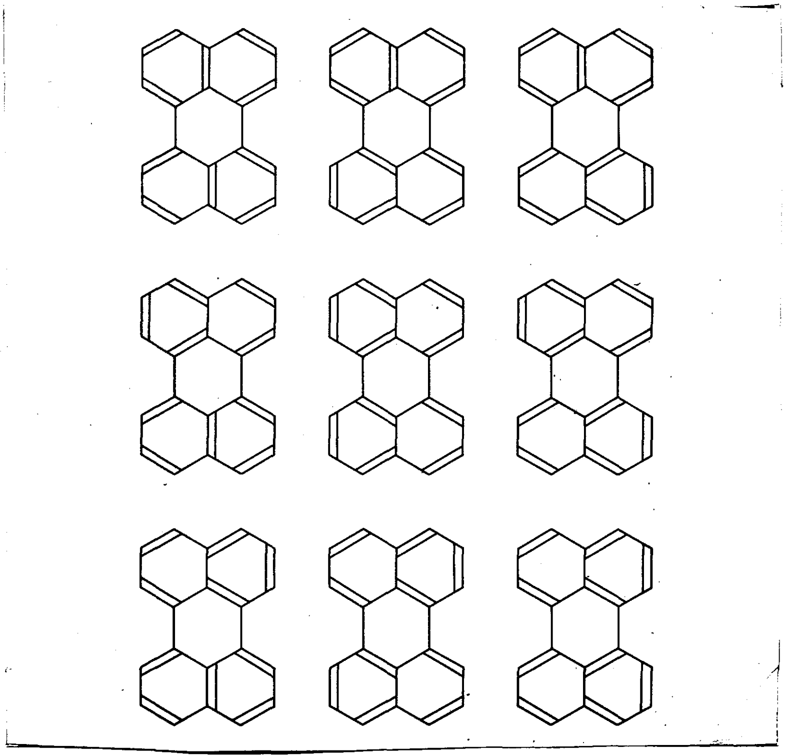
However due to the overlapping effects and subsequent bad resolution of the atoms, the accuracy of this analysis will not be as good as that of the ovalene analysis. Nevertheless the estimated values of the bond lengths can be averaged in various parts of the molecule, and although the apparent agreement is spurious, the errors in the finally accepted values of the bond lengths are probably no more than ±0.03A or ±0.04A.

The Booth correction has not been applied to this compound. Since the resolution was not very good it is doubtful if the Fourier synthesis on the calculated values of the structure factors would give resolution much better than this.

The results obtained in this investigation have been compared with those predicted by theory. The agreements in the case of perylene are not nearly as good as those obtained with previous hydrocarbons.

The bond distances have been calculated from the non-excited Kekulé structures (see Fig. 23).

Figure 23.



The 9 Kekulé structures of perylene.

There are nine of these stable valence-bond structures, and it is clearly seen that in no structure is the bond joining the naphthalene groups a double bond. Hence this bond has zero double bond character, i.e. it is a pure single bond (1.54A) This agrees remarkably well with the observed value of 1.50A. It is also obvious that the

Kekulé structures for perylene are simply a combination of the Kekulé structures for two naphthalene groups (since these groups are joined by an invariant single bond, the non-excited structures are independent). Thus the calculated bond lengths of perylene by this method are similar to those calculated for naphthalene with a pure single bond joining the two naphthalene groups. Fig 21 (b) shows the values obtained for the bond distances in perylene (calculated from a knowledge of the percentage double bond character, and the Pauling-Brockway curve). These may be compared with the measured values (Fig. 21a). The mean deviation of these predicted values from the experimental values is 0.028A. The maximum deviation of any one bond is 0.045A.

A comparison of the measured bond lengths in the naphthalene group of perylene with those obtained from the three-dimensional analysis of the naphthalen structure (15) is given below. Bonds which are chemically different in perylene are chemically equivalent in naphthalene, and so have the same value for the bond length in the latter case.

The agrement is very poor, and even though the accuracy in the perylene measurements is not very high, the magnitude of the discrepancies indicates that these differences are real.

Perylene	Naphthalene
AB = 1.38A	
CJ = 1.38A	1.354A or 1.363A.
AQ = 1.375A	
JR = 1.45A	1.420A or 1.421A.
BC = 1.45A	1.395A
QR = 1.445A	
	1.395A

The bond lengths of perylene have also been obtained theoretically by the method of molecular orbitals (Coulson, C.A. - unpublished communication). Once again the agreement is very poor. The results are shown below alongside the experimental values.

Bond	Molecular Orbitals	X-ray Results
AB	1.387A	1.38A
BC	1.401	1.45
CJ	1.398	1.38
JR	1.423	1.45
*QR	1.422	1.445
AQ	1.416	1.375
IJ	1.444	1.50

* bond which could not be directly measured

The mean deviation of these predicted values from the experimental values is 0.030A, and the maximum deviation of any one bond is 0.056A.

The diamagnetic susceptibility of perylene in powdered form has been measured (46). Two values were obtained, using the mass susceptibility of naphthalene and that of purified water as standards, and the two results gave the susceptibility per molecule of perylene as $-(171 \pm 1) \times 10^{-6}$. Now if the molecule of perylene is considered to consist of two naphthalene nuclei combined at both the peri-positions, the magnetic susceptibility of the perylene molecule may be calculated from that of naphthalene and hydrogen.

Thus:- $\chi_M(\text{Perylene}) = 2\chi_M(\text{Naphthalene}) - 4\chi(\text{Hydrogen})$

where χ_M = diamagnetic susceptibility per molecule

This value is then obtained as -171.8, which is in complete agreement with the measured value. This indicates that the perylene molecule consists of two naphthalene nuclei playing a predominant role, and the central ring formed by joining the peri-positions has a special structure for which no correction to the diamagnetic susceptibility has to be made. It seems probable then, that the bonds joining the peri-positions are longer than usually observed in polycyclic aromatic hydrocarbons. This latter point is in keeping with the results obtained from the X-ray investigation, and the results obtained from the diamagnetic susceptibility support the interpretation of the perylene molecule by the non-excited Kekulé structures.

Perylene has also been shown to have a small dipole moment (47) indicating that there is no true centre of symmetry. The absorption spectrum of perylene (48) also tends to indicate that the perylene molecule is not completely planar. No evidence has been obtained in the investigation of perylene by X-ray diffraction methods to support the idea of a non-planar structure. On the contrary, the very good agreement between the observed and calculated values of the structure factors in the (hk0) zone, supports the fact that the perylene molecule is planar, as far as the carbon atoms are concerned. No information can be obtained regarding positions of hydrogen atoms however, and it may well be that the hydrogen atoms adjacent to the bonds joining the two naphthalene groups are forced out of the plane. This could then explain the small dipole moment, and the results from the absorption spectra.

Experimental

Determination of Crystal Data and Intensities.

The X-ray work was carried out photographically by means of rotation, oscillation and moving-film methods, copper K_α radiation being employed throughout. The moving-film photographs were used to determine the space group, and for intensity purposes. The space group was established as $P_{2_1/a}$, since there was no exception to the (h0l) absences when h was odd. Of the (0k0) reflections, six were observed and there was no exception to the (0k0) absences when k was odd.

The density was found by flotation of small crystals in a solution of silver nitrate. The highest value obtained was 1.322, and was in good agreement with the value of 1.341 calculated for four molecules in the unit cell.

Two zones (h0l) and (hk0) were explored in detail by moving-film methods. Long exposures of the equatorial layer lines for crystals rotated about the b and c crystal axes were obtained. The estimates of the intensities were made visually and the multiple film technique (41) was used in the correlation of intensities. The total range of intensities covered was 5,000 to 1, which is just about the order usually encountered in the investigation of hydrocarbon structures. An approximately absolute scale of F values was obtained by correlation of the observed data with the calculated F values. Since this involves a scattering curve, the scale may not be quite accurate. This, however, will not affect the positions of the atomic centres since all the atoms are of the same kind, but only the vertical scale of the contour maps. The atomic scattering factor used was based mainly on absolute measurements obtained from anthracene (42).

The crystal specimen used in the investigation of the (h01) zone was small and uniform. It had a cross-section of 0.35 mm. by 0.38 mm. No absorption correction was applied. In the investigation of the (hk0) zone the crystal was in the form of a square plate - the cross-section was 0.85 mm. by 0.90 mm. Since the dimensions were uniform and the absorption coefficient was small (μ = 6.96 per cm.), no absoprtion correction was applied.

The observed values of the structure factors for the planes (001) and (002) are rather lower than the calculated values (10% and 20% lower respectively). This is probably due to extinction, and so in the final Fourier analysis, these planes were included as their calculated values. In the (hk0) zone one plane has probably an inaccurate measured F value. The (110) plane, which has a very small 2sinθ, was partially cut off the film used. Due to this and also to the fact that the intensity is strong, the measurement of the intensity is probably inaccurate.

Trial Analysis and Fourier Analysis

From a tracing of the small-spacing planes of high intensity and the absence of the (201) planes, an approximate estimate of the atomic positions was obtained. The orientation of the molecule and the free translation of the molecular centre from the origin in the ac plane (x_0 and z_0) were obtained. The first trial structure was obtained from these data and the assumption that the perylene molecule was planar and consisted of regular hexagons of side 1.41A. A refinement of the atomic positions obtained was carried out using the double Fourier Series methods.

The electron density on the ac plane was computed at 900 points on the asymmetric unit from the series

$$\rho(x,z) = \frac{1}{ac\sin\beta}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} F(h0l)\cos 2\pi\left(\frac{hx}{a}+\frac{lz}{c}\right)$$

The *a*-axis was divided into 60 parts (intervals of 0.189A) and the *c*-axis into 60 parts (intervals of 0.172A). The summations were carried out by means of three-figure strips (43). The positions of the contour lines were obtained by graphical interpolation of the summation totals by making sections of both rows and columns. The contour map resulting from the final refinement is shown in Fig. 18, three-quarters of the unit cell being included.

Calculation of Molecular Orientation and Co-ordinates.

In order to calculate the orientation it is necessary to assume some distance in space of the molecule. In this case it was assumed that the distances BO and CN were the same as in a regular hexagonal structure of side 1.41A. The mean projection distance of BO and CN was measured as 2.823A, and in space it would be 4.884A. Since BO and CN are parallel to the M molecular axis, sin $\psi_M = 2.823/4.884$ (ψ_M is the angle which the M molecular axis makes with the *b* crystal axis). Hence $\psi_M = 35.3^\circ$. It is also necessary to know the tangents of the angles which the L and M molecular axes make with the *a* crystal axis (tan η_L and tan η_M respectively). If the molecule has a centre of symmetry and is planar, it is unnecessary to measure these angles. The tangents of these angles can be calculated from the rectangular co-ordinates (see later) of certain pairs of atoms. The lines joining such atoms as AF, IJ, etc. should be parallel to the L molecular axis, and hence the tangent of the angle which these lines make with the *a*-axis should be the same as the tangent of the angle which the L molecular axis makes with the *a*-axis.

e.g. from atoms A and F, $\tan\eta_L = (z'_A - z'_F)/(x'_A - x'_F)$
Similarly for the $\tan\eta_M$, take atoms such as A and P, which when joined give a line parallel to the M molecular axis

Thus from atoms A and P, $\tan\eta_M = (z'_A - z'_P)/(x'_A - x'_P)$
In this way a series of values are obtained which can be averaged. Thus $\tan\eta_L$ is found to be 8.4646 ± 0.1181, and $\tan\eta_M$ to be -0.1382 ∓ 0.0024. With these dataand the

nine trigonometrical relations given in Part I (see page 45) the complete orientation of the molecule can be calculated with respect to the crystallographic axes a and b and their perpendicular c'.

The rectangular co-ordinates (x', y, z'), referred to the a and b crystal axes and their perpendicular c', of the resolved atoms can be obtained from the crystal co-ordinates using the equations

$$x = x' - z'\cot\beta \qquad \text{and} \qquad z = z'\operatorname{cosec}\beta$$

Using these rectangular co-ordinates in conjunction with the orientation, the co-ordinates of the atoms with respect to molecular axes L' and M' (previously defined), can be obtained from the following equations:-

$$x' = L' \cos\chi_L + M' \cos\chi_M$$

$$z' = L' \cos\omega_L + M' \cos\omega_M$$

The L' and M' co-ordinates of U (the molecular centre) can now be obtained by once again using the molecular symmetry. It is obvious from a study of the molecule that the following relationships will hold.

From atoms A and F :- $L'_U = (L'_A - L'_F)/2 + L'_F = (L'_A + L'_F)/2$

From atoms A and P :- $M'_U = (M'_A - M'_P)/2 + M'_P = (M'_A + M'_P)/2$

Also note than $M'_U = M'_G$; M'_H ; M'_Q ; M'_R .

Thus using only the co-ordinates of the resolved atoms, and obtaining first their rectangular co-ordinates and then their L' and M' molecular co-ordinates, a set of values can be obtained for L'_U and M'_U. Thus L'_U is found to be 0.567 ± 0.004A and M'_U to be 1.802 ± 0.010A. From these values the crystal co-ordinates of the molecular centre can be obtained. The values obtained are $x_U = 1.171$A and $z_U = 0.429$A.

By subtracting the values of L'_U and M'_U from the L' and M' co-ordinates of the resolved atoms, the L and M molecular co-ordinates of these atoms can be obtained (note that the L and M molecular co-ordinates of the molecular centre are zero). From a study of the molecule it can be seen that there is a distinct relationship between the molecular co-ordinates of some of the atoms. Thus $L_A = L_P = -L_F = -L_K$ and $M_A = M_F = -M_P = -M_K$. This can be repeated for several sets of atoms. The values obtained for the resolved atoms can be averaged, and values of the L and M molecular co-ordinates of unresolved atoms can be obtained from the use of the symmetry elements shown above. In this way the L and M molecular co-ordinates of all the atoms are obtained, and from them the crystal co-ordinates of all the atoms are obtained using the following equations.

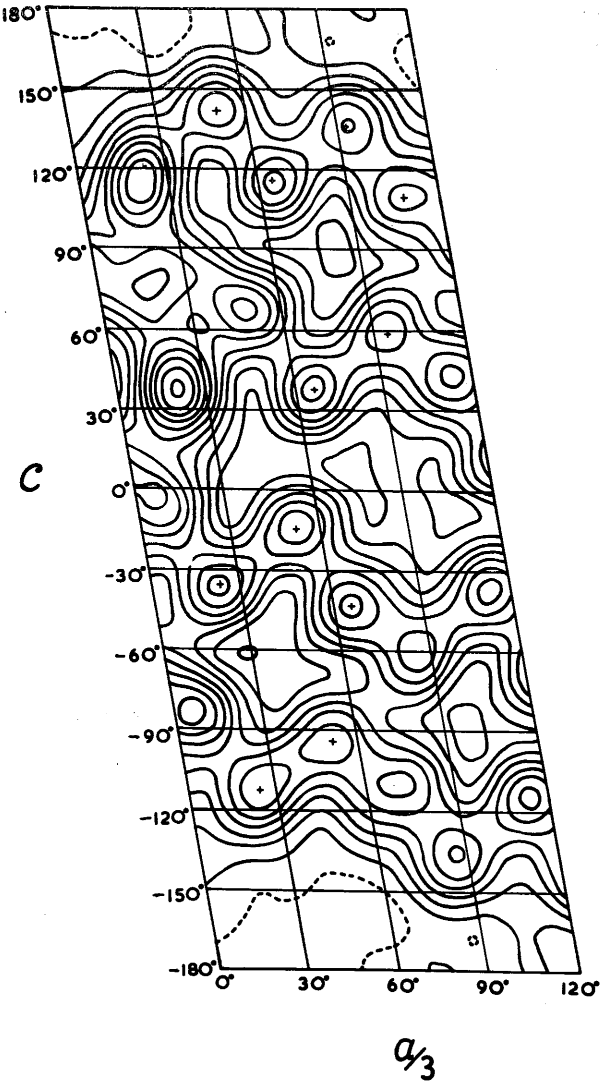
$$x' = L\cos\chi_L + M\cos\chi_M + N\cos\chi_N + x'_U \qquad x = x' - z'\cot\beta$$
$$y = L\cos\psi_L + M\cos\psi_M + N\cos\psi_N + y'_U \qquad z = z'\,\mathrm{cosec}\,\beta$$
$$z' = L\cos\omega_L + M\cos\omega_M + N\cos\omega_N + z'_U$$

Note that since the molecule is planar the N molecular co-ordinates are all zero. The free translation along the b-axis (i.e. y_U) was found by trial and error. The value finally adopted was $y_U = -1.564$A. The monoclinic crystal co-ordinates finally adopted are collected in Table 7 under column (a) and the positions of the resolved atoms are plotted in Fig. 24, the projection on the ac plane.

Structure Factors

The co-ordinates collected in Table 7 under column (a) were used in the final calculation of the structure factors, which are shown in the following pages under F calc. The agreement between the observed and calculated values of F, expressed in the usual way as a sum of all the discrepancies divided by the sum of the measured structure factors, is 16.9% for the (h0l) reflections and 14.1% for the (hk0) reflections. In the (h0l) zone 80 planes were observed out of a total possible of 150, and in the (hk0) zone 50 planes were observed out of a total possible of 160.

Figure 24.



Projection on the (010) plane showing co-ordinates assigned to the resolved atoms.

Measured and calculated values of F (Perylene).

(hkl)	2sinθ	F meas.	F calc.
200	0.277	34.4	+34.9
400	0.553	10.7	+ 5.8
600	0.830	7.3	+ 4.4
800	1.106	27.3	-21.8
10,00	1.383	20.0	-20.1
001	0.152	78.4	+77.5
002	0.305	87.7	-85.5
003	0.457	30.2	+28.0
004	0.609	34.0	-30.1
005	0.762	18.6	-21.8
007	1.066	4.5	- 3.9
009	1.371	9.1	+ 8.4
00,10	1.523	12.0	+11.9
00,11	1.675	4.0	- 3.6
209	1.449	18.2	+19.4
208	1.299	6.9	+ 8.9
207	1.151	4.4	- 8.0
206	1.004	17.4	-20.0
205	0.858	21.5	+20.4
204	0.715	60.0	+56.5
203	0.577	3.1	- 2.3
202	0.449	7.0	- 3.1
201	0.340	3.5	- 1.0
$20\bar{1}$	0.290	60.8	+64.6
$20\bar{2}$	0.372	18.2	-16.4
$20\bar{3}$	0.488	24.0	+17.9
$20\bar{4}$	0.620	2.9	+ 9.6
$20\bar{5}$	0.760	19.7	-24.8
$20\bar{7}$	1.050	9.9	-11.7
$20\bar{8}$	1.197	7.7	-14.2
406	1.154	6.5	+11.6
405	1.022	5.9	+ 3.5
404	0.896	3.7	- 5.2
403	0.782	2.5	+ 4.3
402	0.680	8.9	-11.3
401	0.600	26.8	-24.1
$40\bar{1}$	0.545	37.0	+35.4
$40\bar{2}$	0.580	16.5	+ 9.5
$40\bar{3}$	0.648	4.6	- 4.8
$40\bar{5}$	0.854	2.7	+ 2.0
$40\bar{6}$	0.976	8.8	+10.1
$40\bar{8}$	1.240	7.8	+ 6.5
$40\bar{9}$	1.379	10.8	+ 7.1
608	1.597	3.5	+ 4.3
606	1.347	7.0	+ 2.0

(hkl)	2sinθ	F meas.	F calc.
605	1.227	4.3	+ 2.0
601	0.871	11.5	+14.2
$60\bar{1}$	0.815	7.7	+ 7.6
$60\bar{2}$	0.829	9.7	+ 9.5
$60\bar{3}$	0.870	3.3	+ 4.6
$60\bar{4}$	0.933	39.4	+39.6
$60\bar{5}$	1.016	11.9	+12.2
$60\bar{6}$	1.116	9.0	- 8.6
$60\bar{7}$	1.222	5.5	+ 7.0
$60\bar{8}$	1.339	3.6	- 6.3
$60\bar{9}$	1.464	3.6	+ 2.1
$60\overline{11}$	1.724	3.8	- 5.8
806	1.564	3.5	+ 4.5
805	1.456	36.4	+50.4
804	1.360	20.0	+18.8
803	1.273	11.9	-15.6
802	1.200	9.4	+ 9.6
801	1.144	14.0	-14.8
$80\bar{3}$	1.115	3.3	- 4.1
$80\bar{4}$	1.160	14.6	+16.0
$80\bar{5}$	1.220	30.0	+27.2
$80\bar{6}$	1.296	4.4	- 6.5
$80\bar{7}$	1.385	3.6	+ 4.8
$80\bar{9}$	1.592	31.4	-35.9
$80\overline{10}$	1.708	13.1	-17.3
$80\overline{11}$	1.826	4.1	+ 7.2
10,04	1.612	8.5	+11.7
10,03	1.536	3.6	- 3.5
10,01	1.419	4.4	+ 4.7
$10,0\bar{1}$	1.363	15.2	- 8.0
$10,0\bar{5}$	1.450	7.7	- 3.2
$10,0\bar{6}$	1.508	4.7	- 1.0
12,04	1.872	5.7	- 2.9
12,03	1.800	3.3	+ 1.5
$14,0\bar{1}$	1.913	7.8	- 3.3
020	0.284	7.0	- 5.8
040	0.567	23.1	+22.7
060	0.851	10.8	+13.7
080	1.135	10.0	-13.0
0,10,0	1.419	48.8	-46.5
0,12,0	1.702	7.3	- 6.7
110	0.198	49.2	+54.8
120	0.316	44.2	+45.5
130	0.448	29.4	+24.3
140	0.584	29.4	-23.3
150	0.723	12.5	-13.2

(hkl)	2sinθ	F meas.	F calc.
160	0.862	12.6	- 14.9
190	1.284	9.5	+ 12.6
1,11,0	1.567	29.6	-27.3
1,12,0	1.708	10.2	- 8.8
1,13,0	1.850	5.8	+ 5.8
210	0.311	61.9	+ 60.7
220	0.396	101.0	-117.2
230	0.508	15.3	+ 15.7
240	0.632	12.2	- 14.1
260	0.896	13.0	+ 12.4
280	1.168	11.1	+ 12.8
290	1.307	17.3	+ 12.2
2,12,0	1.724	16.4	+ 19.2
310	0.439	46.2	-47.6
320	0.503	48.7	+ 42.2
350	0.823	7.9	- 9.0
380	1.208	6.5	+ 9.5
390	1.344	12.8	+ 10.8
3,12,0	1.752	8.8	- 9.0
530	0.813	22.6	- 14.9
540	0.895	7.5	+ 7.6
610	0.842	22.6	+ 16.3
620	0.878	8.2	+ 7.0
630	0.933	10.9	+ 13.2
670	1.295	8.3	+ 11.3
710	0.978	25.3	+ 20.5
720	1.009	10.4	+ 4.7
750	1.200	10.3	+ 8.6
760	1.289	6.8	-, 9.9
790	1.602	9.8	- 9.0
810	1.115	21.0	+ 20.1
820	1.142	8.9	+ 4.6
850	1.314	8.3	- 12.8
910	1.253	19.4	- 18.9
10,2,0	1.414	6.9	+ 4.5

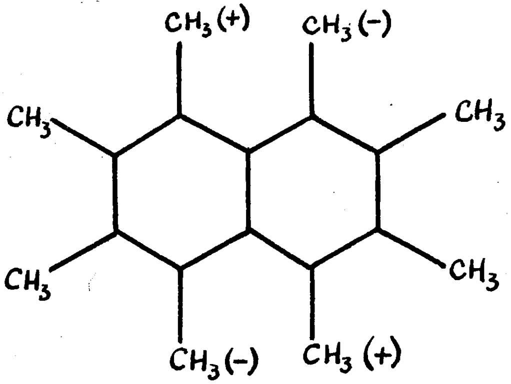
Part 3.

The Crystal Structure of Octamethylnaphthalene (A Quantitative X-ray Investigation)

Introduction.

Octamethylnaphthalene (Fig. 25), $C_{18}H_{24}$, has recently been synthesised by Abidir and Cook (unpublished). The structure of this compound was studied with a view to investigating the planarity of the molecule. Hexamethylbenzene has been shown to be planar by Lonsdale (27), and Brockway and Robertson (8).

Figure 25.



However the intramolecular distance between the methyl groups attached to the α-positions in octamethylnaphthalene is considerably less than the intramolecular distance between two adjacent methyl groups in the hexamethylbenzene molecule, and it is doubtful if these two methyl groups can be accommodated in the same plane as the naphthalene nucleus.

The molecule, presuming it to be completely planar, would have a centre of symmetry and three two-fold axes of symmetry at right angles. If however, the methyl groups in the α-positions are displaced from the plane, one up out of the plane and the other down out of the plane (see Fig. 25; (+) denotes up and (-) denotes down), the centre of symmetry is destroyed but the three twofold axes of symmetry remain. There is another possibility where two methyl groups directly opposite each other are both up out of the plane and the other two down, but the former proves to be the case.

Since the only difference between naphthalene and octamethylnaphthalene is in the substitution of all the hydrogen atoms by methyl groups, it will be of interest to compare the results obtained for the bond lengths in both cases.

The purpose of the investigation has already been mentioned, but it was also intended to refine the structure sufficiently by the usual two-dimensional methods of analysis to enable a possible analysis by the three-dimensional Fourier methods. In this case it has been shown that a full three-dimensional analysis will be necessary before the structure is completely known.

Crystal Data.

Octamethylnaphthalene, $C_{18}H_{24}$, M, 240.4. m.p. 174°

d, calc. 1.109 d, found 1.089

orthorhombic, a = 16.66 ± 0.03A, b = 11.31 ± 0.01A,

c = 7.64 ± 0.03A.

Absent Spectra - (hkl) when h + k is odd

(h0l) when h is odd and l is odd

(hk0) when h is odd and k is odd

(0kl) when k is odd and l is odd

Space Group - Ccca (D_{2h}^{22}).

Four molecules per unit cell.

Molecular symmetry - three twofold axes at right angles.

Volume of the unit cell, 1,439.6A^3

Absorption coefficient for X-rays, λ = 1.54A, μ = 5.44 per cm.

Total number of electrons per unit cell = F(000) = 528.

The crystals tend to be flat plates with no well-defined cleavage.

These were the better-developed crystals. The others were simply clusters of very small needles. One of the specimens used was a small, almost square plate, with the c-axial direction perpendicular to the plate. The only face which was well-developed and could be identified was the (001) face.

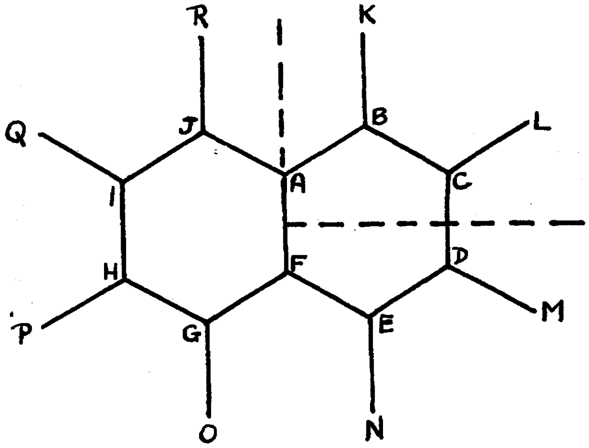
Crystal Structure

The most prominent feature of the crystal structure is the space group, $Ccca$, which has 16 asymmetric units. Since there are only 4 molecules in the unit cell, this means that the asymmetric unit is one-quarter of a molecule, i.e. $4\frac{1}{2}$ carbon atoms and 6 hydrogen atoms. In this space group if there are only 4 molecules per unit cell, then the molecules lie at special positions. The molecular centre of octamethylnaphthalene is the centre of the central bond in the naphthalene nucleus. This molecular centre must lie at the origin of the unit cell, i.e. at (000). Then to obtain the position of another molecular centre, the operation ($\frac{1}{2}\frac{1}{2}0$) is applied. Now to obtain the positions of the remaining two molecular centres, the operation ($0\frac{1}{2}\frac{1}{2}$) is applied to each of the first two.

Now for octamethylnaphthalene it is necessary to proceed by trial and error. If, as a first approximation, the molecule is assumed to be planar, then it is apparent from packing considerations that the molecular plane must lie in the (001) plane. The molecular plane cannot be tilted out of the crystal plane because of the space group symmetry, as will be shown, and since the length of the c-axis is only 7.64A, then it is obvious the molecule cannot be accommodated either in the (100) or in the (010) planes. If the symmetry of the space group around the origin is considered, then it is as shown $\overset{(-)\,|\,(+)}{\underset{(+)\,|\,(-)}{\oplus}}$, where (+) denotes up out of the plane and (-) down out of the plane. Now consider the molecule whose molecular centre lies at the origin. This supplies four asymmetric units. If that molecule was tilted in any way, the symmetry required by the space group could not be retained.

Having decided that the molecule probably lies in the (001) plane, then, in order to fulfil the requirements of the space group and have one-quarter of the molecule as the asymmetric unit, the central bond of the naphthalene nucleus must lie along either the a axis or the b axis (see Fig.(26) - the dotted lines represent the a and b crystal axes).

Figure 26.



This gives two possible positions of the molecule - one in which bond AF lies along the a crystal axis, and one in which bond AF lies along the b crystal axis. The asymmetric unit then consists of the four carbon atoms at B, C, K and L, one-half the carbon atom at A and the six hydrogen atoms from the methyl groups at K and L. Assuming regular hexagons of side 1.40A for the naphthalene nucleus and a length of 1.50A for the bonds BK and CL, a trial structure was obtained with bond AF lying along the b crystal axis. The co-ordinates of the carbon atoms were found, and structure factors calculated for the 8 axial planes (200) - (16,00). No good agreement was obtained between the observed and calculated values of F, but a line synthesis was done using these 8 planes and thus projecting the contents of the unit cell on to the a-axis. No peak was observed at the origin, as should have been the case.

The molecule was now turned through 90°, i.e. bond AF lay along the a-axis. Using the same dimensions for the molecule, structure factors for the 8 a-axial planes were again calculated. This time the agreement between the observed and calculated values of the structure factor was 22%. The atomic scattering curve used was that based mainly on absolute measurements obtained from anthracene (42). The line synthesis obtained is reproduced in Fig. 27 and the F values used are shown below. It was decided that this was the correct position for the molecule.

Planes included.	(200)	(400)	(600)	(800)	(10,00)	(12,00)	(14,00)	(16,00)
F calc.	+154.8	-41.9	-56.3	-105.3	-12.5	+33.4	-23.1	-21.4
F obs.	166.8	70.9	42.6	100.9	20.9	22.0	14.2	10.7

Figure 27.

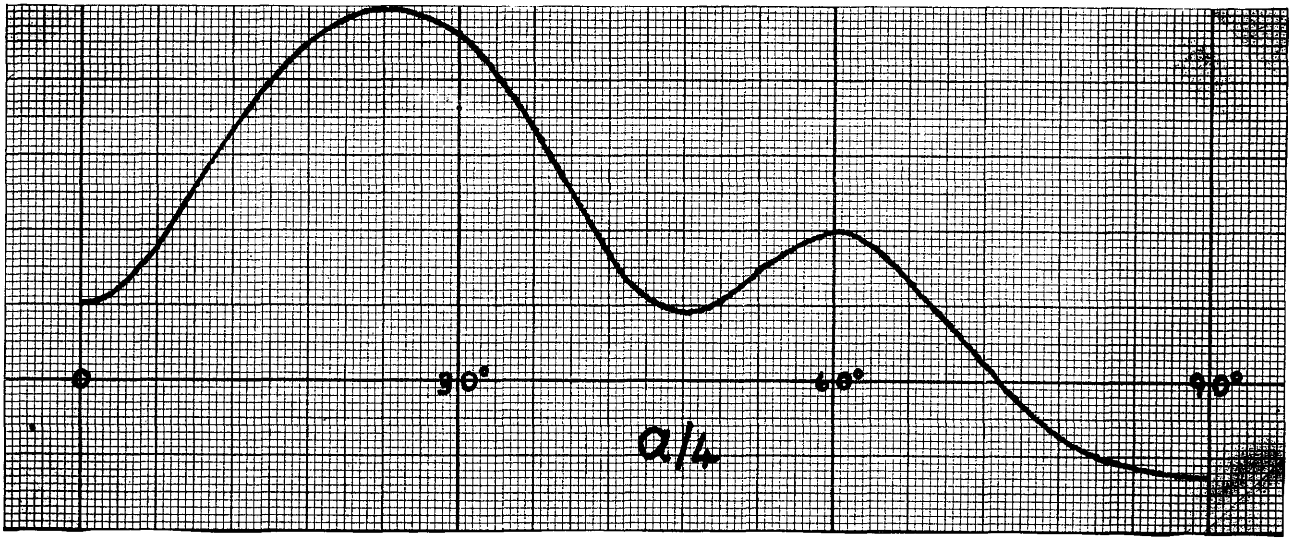
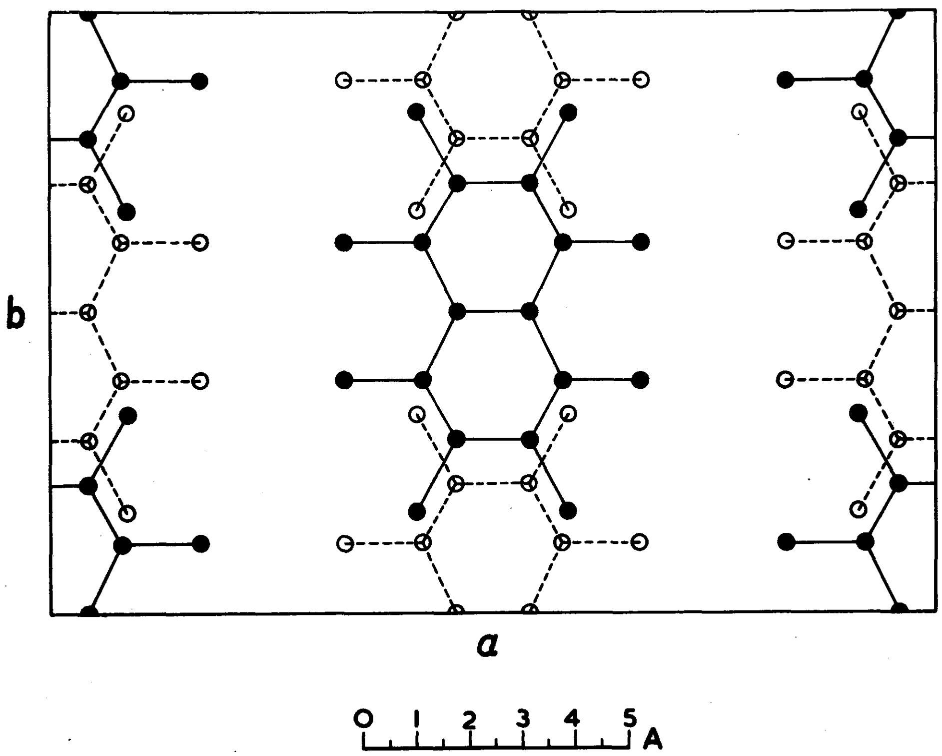


Figure 28 shows the projection of the contents of the unit cell on to the (001) plane; the molecules drawn with broken lines being out of the plane by a translation of c/2.

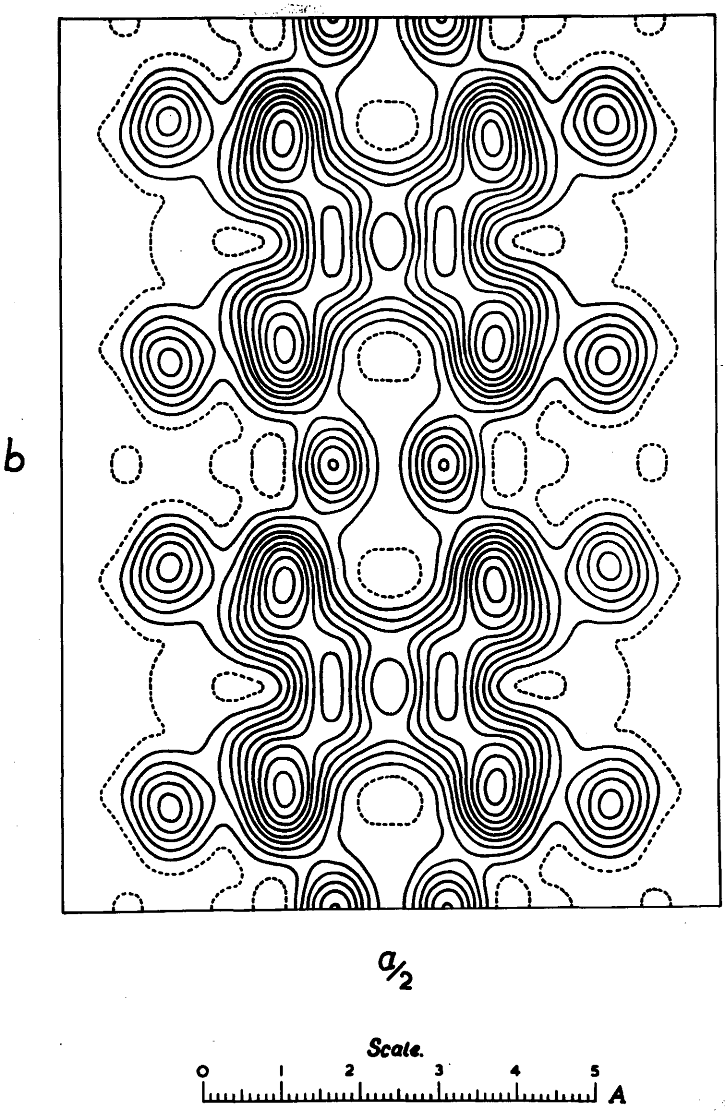
It is apparent from this diagram that all the atoms of the asymmetric unit will not be resolved in the electron density diagram due to overlapping effects of different molecules.

Figure 28.



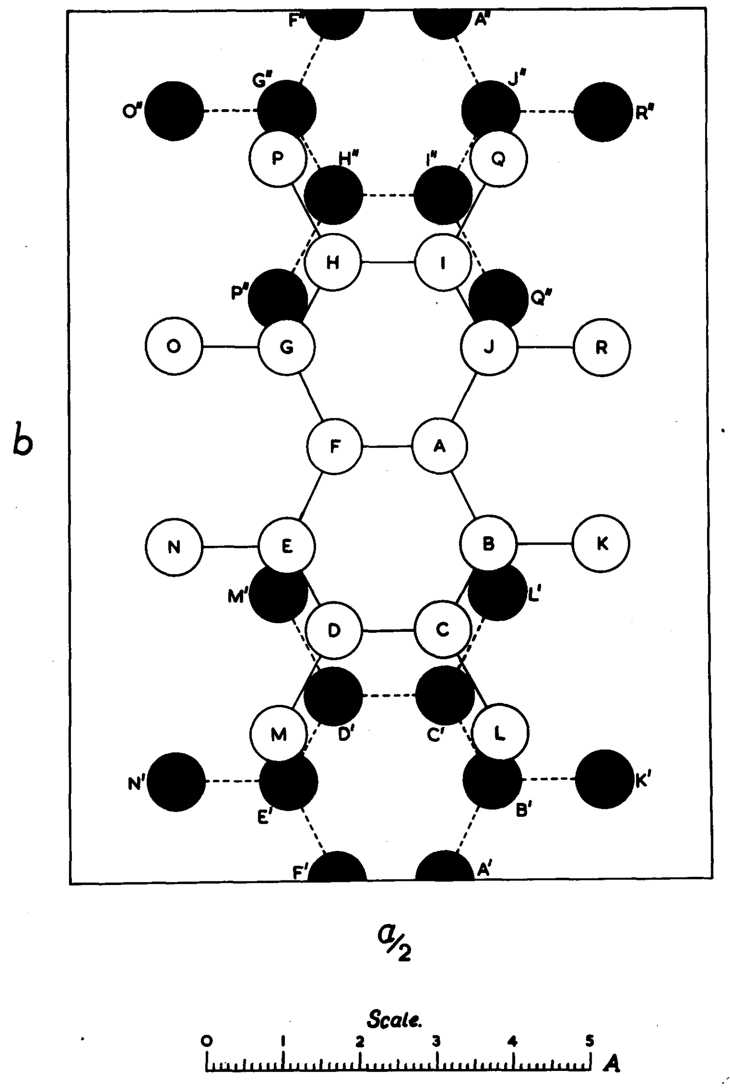
A Fourier Series in the (hk0) zone was now carried out. 35 reflections were included in this refinement, out of a total possible of 71. Since there are so few parameters to be found (two for each atom except A, whose y co-ordinate is zero, i.e. nine in all), the atoms were moved until the best agreement between the observed and calculated values of the structure factors was obtained. The discrepancy for the 35 planes included was 23.7%. The atomic scattering curve used was that used in the investigation of naphthalene (15). The projection of the structure obtained from this synthesis is reproduced in Fig. 29. This is the projection of one-half the unit cell. The key diagram to this projection is shown in Fig. 30. As was expected only two of the five carbon atoms were resolved. Note that the carbon atom at C, however, is blocked by C' - the equivalent atom on another molecule. Since the x-co-ordinates of these atoms are equal, a ridge is formed between them (see Fig. 29), from which the ridge peak can be accurately measured, thus giving the x-co-ordinate of C. The remaining co-ordinates were simply found by putting the atoms in various positions in accordance with the observed double peak, until the best agreement was obtained between the observed and calculated values of the structure factors. It was assumed however that bond BK would be parallel to the a-axis, i.e. the y-co-ordinates of atoms B and K are the same. The agreement between the observed and calculated F values was now 21%. There were two sign changes. The planes (420) and (460) changed sign. Further investigation of this zone was carried out, and will be

Figure 29.



Projection on to the (001) plane. The contents of half the unit cell are included. Contours at intervals of 1 electron per A^2. The one electron line is broken.

Figure 30.



Projection down the c-axis showing positions of atoms and overlapping effects.

described later under the heading "Difference Fourier Syntheses".

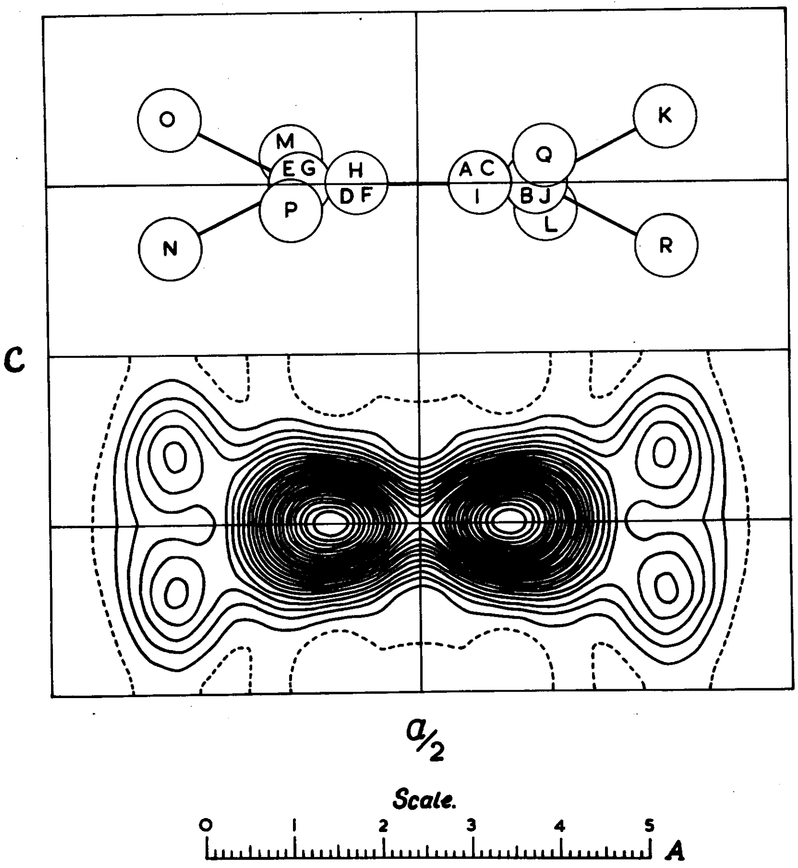
An investigation of the (h01) zone by the double Fourier Series methods was now carried out. If the molecule is completely planar, and lies in the (001) plane, then no resolution of any of the atoms may be expected, with the exception of the methyl group in the α-positions.

23 planes were included in the Fourier analysis of the (h01) zone, which has a maximum possible number of planes of 46 up to a $2\sin\theta = 2$. Assuming the molecule is completely planar, i.e. the z co-ordinates of all the atoms were zero, no good agreement could be obtained between the observed and calculated values of the structure factors for the 23 observed planes. Now, as was stated previously, there is a possibility that the methyl group in the α-position is displaced from the molecular plane. A trial structure, giving this methyl group a z co-ordinate of 32° but leaving the remainder of the structure planar, i.e. z co-ordinates zero, gave a discrepancy of 24% between F obs. and F calc. for the 23 observed planes. The signs of the terms for the synthesis in the (h01) zone were taken from these values. The projection of the structure obtained from this synthesis is shown in Fig. 31 - four

asymmetric units being shown. Directly above the electron density diagram is a key diagram showing how one complete molecule of octamethylnaphthalene is projected in this zone; the letters denoting the positions on which the various carbon atoms fall. It is quite apparent from this projection that the methyl group in the α-position is displaced from the molecular plane. In actual fact the z co-ordinate adopted for the carbon atom at K was 34.2°. Using this value for this co-ordinate, and not changing any of the others, the discrepancy between the observed and calculated values of the structure factors for the 23 planes observed in the (h0l) zone was reduced to 20.6%.

Considering the number of parameters involved in the calculation of the structure factors, and the number of planes over which the discrepancy was taken, the value quoted seems rather high. Attention was turned to the methyl group attached to the β-position of the naphthalene nucleus. This group was unresolved on both the electron density maps which have been reproduced. Trials were now made of moving this methyl group out of the molecular plane, and it was found that this movement considerably reduced the discrepancy between F obs. and F calc. in the (h0l) zone. Eventually, at a position where the z co-ordinate of this

Figure 31.



Projection down the b-axis showing one complete molecule of octamethylnaphthalene. Each contour line represents a density increment of approximately one electron per A^2, the one electron line being dotted. The diagram above the contour map shows the alternate displacement of the methyl groups, the naphthalene nucleus being assumed planar.

group (i.e. at L) was 18°, the discrepancy between the observed and calculated values of the structure factors for the 23 planes observed in the (h0l) zone dropped from 20.6% to 11.8% This undoubtedly suggests that this methyl group is displaced from the molecular plane also. So far the planarity of the naphthalene nucleus has been retained. This may not be so, however, and will be discussed later.

The electron density was computed at 225 points in the (0kl) zone by the usual Fourier methods. 17 reflections were observed in this zone, out of a total possible of 33. No good resolution of the atoms was obtained in this projection, except of the carbon atom at A. The remaining four atoms projected to give one large electron density mass. The y and z co-ordinates of the resolved atom A are zero, i.e. atom A lies at the origin in this zone. Hence no information was obtained from this projection, and it has not been reproduced.

Difference Fourier Syntheses and Effects of Hydrogen Atoms.

The discrepancy of 21% between the observed and calculated values of the structure factors in the (hk0) zone was considered to be rather high. So far only the carbon atoms have been positioned, but there are also six hydrogen atoms in the asymmetric unit. These hydrogens then constitute 18% of the scattering material, and will undoubtedly have some measureable effect on the structure factors.

It was decided then to do a difference or error synthesis on the (hk0) zone, i.e. a Fourier synthesis using as coefficients ($F_o - F_c$), where F_o is the measured value of the structure factor and F_c is the calculated value of the structure factor for all the carbon atoms. This is equivalent in effect to a Fourier synthesis on F_o (calculated the usual way) from which the electron density, ρ_o , is obtained at a number of points. From this, point for point has been subtracted ρ_c, the electron density obtained from a Fourier synthesis on F_c.

$$\text{i.e.}\ \sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}(F_o - F_c)\cos 2\pi\left(\frac{hx}{a}\right)\cos 2\pi\left(\frac{ky}{b}\right) = \rho_o - \rho_c$$

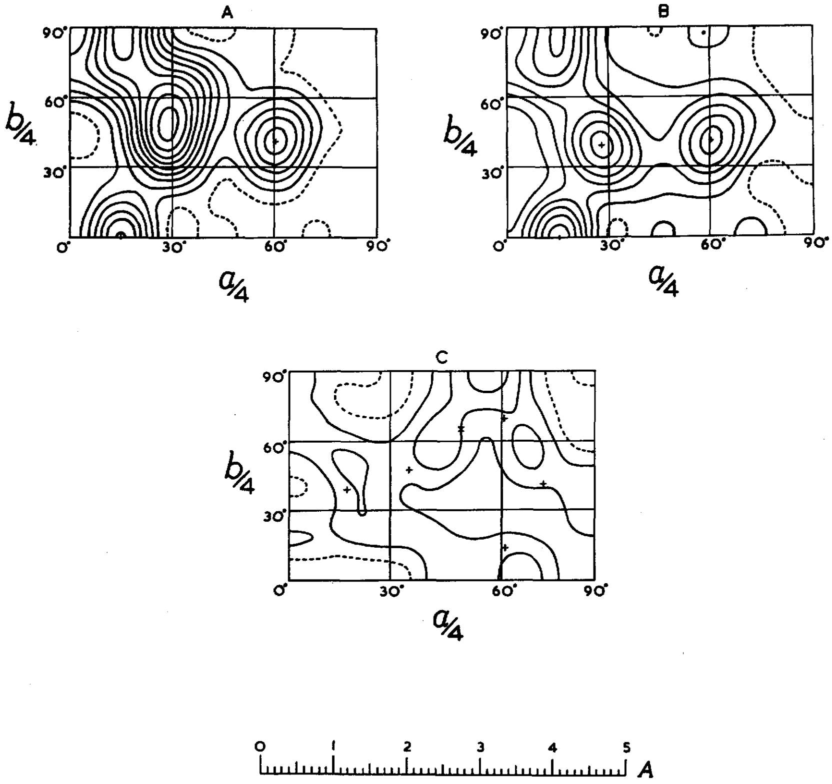
Thus from the electron densities at a number of points obtained from observed data has been subtracted the electron densities at these same points due to the contribution of the carbon atoms. Since no account has been taken of the hydrogen atoms, the resulting electron density diagram should be, in part, the result of their electron density distribution. This method has been employed by Cochran (49) in the refinement of adenine hydrochloride. Cochran (50) has also given an account of some properties of the ($F_o - F_c$)

synthesis.

It can also be shown that with a well resolved atom, whose chosen co-ordinates are in error, the difference synthesis will give two areas, one of positive and one of negative density. In order to minimize the difference between the measured and calculated values of the structure factors, the atomic co-ordinates must be moved away from the negative area toward the positive area. Thus the difference synthesis can also be used to refine atomic positions. The difference synthesis also has the property of giving co-ordinates corrected for the termination of series error. It should be noted however that wrong scaling or a wrong scattering curve will introduce spurious effects in a difference synthesis.

An (F_o - F_c) synthesis was done in the (hk0) zone of octamethylnaphthalene. The projection (of the asymmetric unit) obtained is reproduced in Fig. 32C. There are some fairly well-defined peaks at the 1 - 1.5 electron level which will probably be due to hydrogen atoms. Apart from these however, the electron density diagram is comparatively flat, indicating that there are no great errors in atomic co-ordinates. It is possible though, that some effects have been blocked by the effect of the hydrogen atoms.

Figure 32.



A The projection of the asymmetric unit on to the (001) plane, showing positions chosen for the resolved atoms.

B Projection on the (001) plane, with the contribution due to carbon atom at L removed. Positions chosen for resolved atoms are shown.

C Difference synthesis of (hk0) zone, showing positions chosen for hydrogen atoms. Contours at intervals of 0.5 electron per A^2.

No direct, accurate measurement could be obtained for the positions of the hydrogen atoms. However, approximate positions were obtained in the following manner. It was assumed that there would be no free rotation of the methyl groups, due to steric hindrance. It was also assumed that the C-H bonds of the methyl groups would be 1.08A long, and that the four bonds (i.e. 3 C-H bonds and 1 C-C bond) on the methyl group would adopt tetrahedral positions. These latter are probably not completely accurate, but are a sufficient approximation. The positions of the hydrogen atoms were now obtained, using these assumptions and at the same time attempting to fit the positions to be observed peaks on the electron density diagram. The positions adopted for the six hydrogen atoms are shown on Fig. 32 C.

The contributions of the hydrogen atoms to the structure factors were calculated in a similar manner to that adopted in the investigation of the structure of hexamethylenediamine (51) i.e. only reflections with a sinθ less than 0.6 were considered to have an appreciable contribution from the hydrogen atoms. For larger-angle reflections the contribution will be so near to zero, that it may be neglected. In these calculations a scattering curve for hydrogen was assumed of similar shape to the scattering curve used in considering the contributions of the carbon atoms, but of one-sixth the height.

The effect of including the hydrogen contributions in this manner produced two phase changes in the structure factors. These were in the planes (420) and (460). however, the structure factors of these two planes had changed sign after the Fourier series performed on the (hk0) zone, so that the effect of the hydrogen atoms was simply to change the sign back to the original. The effect of including the hydrogen atom contributions led to a very marked reduction in the discrepancies between the observed and calculated values of the structure factors in the (hk0) zone - a reduction of 5.3% over the 35 observed planes. This undoubtedly indicates that the hydrogen atoms do have a considerable effect on the structure factors, and this reduction of 5.3% would probably be even greater if more accurate positions were obtained.

In the projection on the (001) plane, the carbon atom at B was not resolved, due to the close approach of the methyl group, L', from another molecule (see Figs. 29 and 30). Now the discrepancy in this zone is 21% of which it has been shown that at least 5.3% is contributed by the hydrogen atoms. This low discrepancy means that the positions of the carbon atoms are placed fairly accurately. However, it had been assumed that the y-co-ordinates of B and K were the same. There is a possibility that the methyl groups in the α-positions are forced slightly outwards (as well as up and down), in which case the y co-ordinates of B and K would not be the same.

To investigate this possibility, it was assumed that the position selected for the methyl group at L was correct. Now in order to resolve the atom B, the atom L (or L') must be removed from the structure. If F_L is the contribution of atom L to the structure factor (calculated) and F_o is the measured value of the structure factor, then $(F_o - F_L)$ is the structure factor of a structure from which atom L has been removed. If a Fourier synthesis is now performed on $(F_o - F_L)$, then an electron density diagram should be obtained in which atom B is resolved. This diagram is reproduced in Fig. 32 B alongside the actual projection on the (hk0) zone 32 A.

This method is very similar to one used by Whittaker (52) in the investigation of the structure of Bolivian Crocidolite. In this case the contributions to the electron density of two oxygen atoms were removed in order to resolve two silicon atoms. The method employed here however, was to assign co-ordinates to the oxygen atoms, and then to assume that these atoms would have circular symmetry in projection, with a radial distribution of electron density similar to that of another resolved oxygen atom in the structure. The distribution of electron density due to these oxygen atoms was then subtracted from the projection point by point in the vicinity of the silicon atoms. This differs from the method adopted here in that, once the co-ordinates of L had been decided, the electron density at points due to L was obtained by performing a Fourier summation. This does involve a scattering curve however, and some errors may be introduced here. The scattering curve used however gave remarkably good agreements, and so these errors are probably small. Note that this is exactly the same as the difference synthesis technique. Thus:-

$$\rho_o = \sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} F_o \cos 2\pi \frac{hx}{a} \cos 2\pi \frac{ky}{b}$$

$$\rho_L = \sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} F_L \cos 2\pi \frac{hx}{a} \cos 2\pi \frac{ky}{b}$$

Hence $$\rho_o - \rho_L = \sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} (F_o - F_L) \cos 2\pi \frac{hx}{a} \cos 2\pi \frac{ky}{b}$$

The y co-ordinate obtained for atom B in this projection on the (001) face did show a shift (see Fig. 32B), which was of the order of 0.06A, i.e. the difference between the y co-ordinates of B and K, which had been assumed to be equal, was 0.06A. The co-ordinates of the resolved atoms A and K did not change by any more than 0.01A in the two projections (c.f. Figs. 32A and 32B) i.e. removing the contribution of atom L has not greatly affected the co-ordinates of the previously resolved atoms. This is to be expected however, since atom L is at a considerable distance from atoms A and K. The removal of the contribution of L will have more influence on the atom nearest it, i.e. atom B. However it is doubtful if as large an error as 0.06A would be introduced. One other point to note is that if the co-ordinates of L are accepted as being correct, then these new co-ordinates of B are more in accordance with the position of the double peak (Fig. 32A), than were the previous co-ordinates. If these new co-ordinates of B are adopted, then the discrepancy between the observed and calculated values of the structure factor for the 35 planes observed in the (hk0) zone falls from 21% to 20%.

Co-ordinates and Dimensions.

Fig. 32A (the projection on the (001) plane) allows of direct measurement of the x and y crystal co-ordinates of two of the atoms, viz. A and K. As previously mentioned, it also allowed of direct measurement of the x crystal co-ordinate of atom C. The x and y co-ordinates of atom B were those obtained from Fig. 32B - the remaining three parameters, i.e. the y co-ordinate of atom C and the x and y co-ordinates of atom L having been obtained by trial and error. These co-ordinates are tabulated below.

Atom	x, A.	$2\pi x/a$.	y, A.	$2\pi y/b$
A	0.690	14.9°	0	0
B	1.319	28.5°	1.241	39.5°
C	0.708	15.3°	2.400	76.4°
K	2.795	60.4°	1.301	41.4°
L	1.430	30.9°	3.745	119.2°

No direct measurement of the z co-ordinates of the atoms is possible, except in the cases of the carbon atoms at A and K, due to the lack of resolution in the projections on the (010) and (100) planes. The z co-ordinate of atom A must be zero due to the symmetry required by the space group. This atom was the only one resolved in the projection on the (100) plane (previously mentioned). The x and z co-ordinates of atom K may be directly measured from the projection on the (010) plane (see Fig. 31). The z co-ordinates of the remaining carbon atoms, i.e. B, C and L, can only be obtained by trial and error.

As has been mentioned already, the discrepancy between the observed and calculated values of the structure factors for the 23 planes observed in the (h0l) zone was

20.6%, when atom K was given a measured z co-ordinate of 34.2° and the remaining four carbon atoms were assumed to lie in the (001) plane, i.e. their z co-ordinates were zero. If the methyl group at L (i.e. attached to the β-position of the naphthalene ring) was moved out of the (001) plane, giving it a z co-ordinate of -18°, this discrepancy was reduced to 11.8%. Since the expression used for calculating structure factors in the three principal zones, i.e. (hk0), (0kl) and (h0l) is a product of cosines, it is impossible to differentiate between a co-ordinate of - 18° and +18° without using three-dimensional data. However, it seems more feasible for the methyl group in the β-position to be displaced in the opposite direction to that in the α-position thus giving an alternate up and down arrangement of methyl groups.

Further investigation into the z co-ordinates of the unresolved atoms using trial and error methods, showed that another situation was possible - one in which the naphthalene group is twisted. If the methyl group in the β-position is only displaced by an amount equivalent to -12.2°, and the naphthalene group is twisted in such a way that atom A remains in the (001) plane, atom B is moved up out of the plane by an amount equivalent to 12.2° and atom

C is moved down out of the plane by an amount equivalent to -4.5°, then this again leads to a reduction in the discrepancy between the observed and calculated values of the structure factors in the (h01) zone from 20.6% to 11.8%. This is equivalent to saying that the methyl group in the α-position is pulling the carbon atom to which it is attached, i.e. atom B, up out of the (001) plane with it; and that the methyl group in the β-position is pulling the carbon atom to which it is attached, i.e. atom C, down out of the (001) plane with it. In other words the strain due to the displacement of the methyl groups is being distributed throughout the naphthalene nucleus. This possibility is perfectly feasible, and more probable than that the strain is confined to the carbon-methyl bonds.

Another possibility, which was found to reduce the discrepancy between the observed and calculated values of the structure factors in the (h01) zone to 12.2%, was one in which the displacement of the naphthalene group was not so great. The z co-ordinates for these different positions are tabulated below under the headings structure 1, structure 2 and structure 3 and will be referred to as such from now on. The positions of the carbon atoms, in each of these structures, are completely defined by their z co-ordinates combined with the x and y co-ordinates previously tabulated.

	Structure 1.		Structure 2.		Structure 3.	
Atom	z, A.	$2\pi z/c$	z, A.	$2\pi z/c$	z, A.	$2\pi z/c$
A	0	0	0	0	0	0
B	0	0	0.259	12.2°	0.127	6.0°
C	0	0	-0.095	-4.5°	-0.049	-2.3°
K	0.726	34.2°	0.726	34.2°	0.726	34.2°
L	-0.382	-18.0°	-0.259	-12.2°	-0.318	-15.0°

On the basis of these co-ordinates, the bond lengths within the molecule were calculated. These are tabulated below, along with some intramolecular distances.

Bond (see Fig. 30)	Structure 1.	Structure 2.	Structure 3.
AF	1.38A	1.38A	1.38A
AB	1.39A	1.42A	1.40A
BC	1.31A	1.36A	1.32A
CD	1.42A	1.43A	1.42A
BK	1.65A	1.55A	1.59A
CL	1.57A	1.54A	1.55A
Intramolecular Distance			
KR (α-CH_3 to α-CH_3)	2.98A	2.98A	2.98A
KL (α-CH_3 to β-CH_3)	3.01A	2.97A	2.99A
LM (β-CH_3 to β-CH_3)	2.96A	2.91A	2.93A

The bond AF has the same length in all three structures, as has the intramolecular distance KR. This arises because the x, y and z co-ordinates of atoms A and K are directly measurable from the projections on the three main zones. The co-ordinates of atoms F and R (these atoms are simply in another asymmetric unit) may be derived from the space group symmetry. These distances are the only ones which can be accurately determined.

Since the z co-ordinates of the atoms are not completely fixed, no intermolecular distances have been calculated.

Positions of the Hydrogen Atoms.

The positions chosen for the hydrogen atoms are tabulated below. H_1, H_2 and H_3 are the hydrogen atoms on the methyl group at K, and H_4, H_5, H_6 are the hydrogen atoms on the methyl group at L.

Atom	x, A.	$2\pi x/a$	y, A.	$2\pi y/b$	z, A.	$2\pi z/c$.
H_1	2.971	64.2°	2.183	69.5°	1.362	64.2°
H_2	2.971	64.2°	0.418	13.3°	1.362	64.2°
H_3	3.466	74.9°	1.301	41.4°	-0.083	-3.9°
H_4	0.796	17.2°	4.427	140.9°	-0.804	-37.9°
H_5	2.351	50.8°	3.594	114.4°	-0.804	-37.9°
H_6	1.652	35.7°	4.156	132.3°	0.715	33.7°

These positions were obtained in the manner already explained. The contributions of the hydrogen atoms to the structure factors in the (0kl) and (h0l) zones have not been calculated.

Discussion of Results.

The most striking result of this analysis is the undoubted non-planarity of the octamethylnaphthalene structure. There is no doubt that the methyl groups, attached to the α-positions of the naphthalene nucleus, are displaced from the molecular plane. This displacement is considerable - the methyl group being displaced by 0.726A. If the naphthalene nucleus was planar, then the bond BK, i.e. the bond joining the methyl group to the α-position, would make an angle of about 28° with the molecular plane. It has also been shown that there is probably a slight strain outwards, i.e. the bonds joining the methyl groups to the carbon atoms in the α-positions are not parallel.

It is also highly probable that the methyl group, attached to the β-position of the naphthalene nucleus, is also displaced from the molecular plane. Co-ordinates for three possible positions of the molecule have been quoted, which reduce the discrepancy in the (h01) zone by about 9%. In each of these three structures the methyl group at the β-position is displaced by at least 0.26A.

No decision can be arrived at regarding the nature of the naphthalene nucleus. Structures 1, 2 and 3 give discrepancies of 11.8%, 11.8% and 12.2% respectively between observed and calculated values of the structure factors in the (h01) zone, and discrepancies of 10.5%, 13.9% and 12.2% respectively in the (0kl) zone. There were no changes in the phase angles of the structure factors between any of these three structures. A full three-dimensional analysis of this compound will be required before the structure is completely defined. Undoubtedly a comparison between the observed and calculated values of the structure factors for three-dimensional data will indicate which structure is the more probable, but the full three-dimensional analysis will be necessary to obtain accurate co-ordinates and bond lengths.

The bond lengths obtained from combining the three different sets of z co-ordinates with the x and y co-ordinates have been tabulated below. Alongside are the values obtained for the bond lengths in the three-dimensional analysis of the naphthalene structure (15). Also alongside are the bond lengths predicted for naphthalene using the percentage double bond character, i.e. obtained from the three Kekulé structures. The carbon-methyl group bonds have been assumed to be 1.54A, which is the usual value for a carbon-carbon single bond.

	Structure				
Bond	1	2	3	Naphthalene	Kekulé Structures
AF	1.38A	1.38A	1.38A	1.395A	1.42A
AB	1.39A	1.42A	1.40A	1.420A	1.42A
BC	1.31A	1.36A	1.32A	1.359A	1.37A
CD	1.42A	1.43A	1.42A	1.395A	1.42A
BK	1.65A	1.55A	1.59A		1.54A
CL	1.57A	1.54A	1.55A		1.54A

It can be seen that the agreement between the bond lengths obtained using the z co-ordinates assigned to structure 2, give remarkably good agreement between those measured for naphthalene, and those predicted by the Kekulé structures. This is the structure in which the ring has its maximum twist. The discrepancy between the observed and calculated values of the structure factors in the (Okl) zone is greatest using the z co-ordinates of structure 2, viz. 13.9%. However only 17 reflections out of a maximum possible of 33 were observed in this zone, and too much stress cannot be laid on this discrepancy.

An examination of structure 1, i.e. the structure in which the naphthalene nucleus is assumed planar, shows that the bond lengths which give extremely bad agreement are BC and BK - each bond involving atom B. In order to improve this agreement, i.e. to make the length of bond BC 1.36A and the corresponding length of bond BK 1.56A, the x co-ordinate of B would have to be increased by 0.1A. Such a shift is highly improbable, since the accuracy of the atomic co-ordinates should be well within this limit.

No corrections, such as the correction for termination of series, etc. have been applied as yet for obvious reasons and so no estimation of the accuracy of the co-ordinates and hence of the bond lengths can be made. The low discrepancy between observed and calculated values of the structure factor in the (hk0) zone probably means that there is a high degree of accuracy in the x and y co-ordinates. Since the z co-ordinates have not been determined positively, it is obvious that limits of error cannot be assigned to them.

The co-ordinates quoted for the hydrogen atoms are probably inaccurate. No attempt was made to obtain really accurate co-ordinates, since the purpose of positioning them has been attained, i.e. in showing that the contribution of the hydrogen atoms to the structure factors in the (hk0) zone was considerable.

Experimental

Determination of Crystal Data.

Copper K_α radiation, $\lambda = 1.54$A, was employed in all the measurements. Rotation, oscillation and moving-film photographs were used, the latter to determine the space group and for intensity purposes. The space group was established as Ccca. The general absences required, i.e. (hkl) absent when h + k is odd, were determined from moving-film photographs taken about the first layer lines of crystals rotated about the a and b crystal axes. Thus (h1l) is absent when h is even and (1kl) is absent when k is even.

The density was found by flotation of small crystals in a solution of silver nitrate at 20°C. The value of 1.089 found was in good agreement with that of 1.109 calculated for four molecules per unit cell.

Measurement of Intensities.

All three zones, i.e. (hk0), (h0l) and (0kl), were explored in detail by moving-film methods. Long exposures of the equatorial layer lines for crystals rotated about the a, b and c axes were obtained. The multiple film technique (41) was used in the correlation of the intensities, all of which were estimated visually. The total range of intensities covered was 7,500 to 1. If two planes, (200) and (002) are omitted however, this range falls to about 2,000 to 1.

An approximately absolute scale of F values was obtained by correlation of the observed values with the calculated values. Since this involves a scattering curve, the scale may not be quite accurate, but this will only affect the vertical scale of the contour maps. The atomic scattering factor used was that used in the three-dimensional analysis of the naphthalene structure (14).

An experimental scattering curve was made by dividing the observed F values by the geometric structure factors for the planes. This was found to be almost identical to that used for naphthalene, and so the latter was used.

Small crystal specimens were employed throughout. The specimen used in the (hk0) zone had a cross-section of 0.12 mm by 0.35 mm, and that used in the (h0l) zone a cross-section of 0.42 mm. by 0.46 mm. No absorption corrections were applied, since the value of the absorption coefficient was so small (=5.44 per cm.)

Trial Analysis and Fourier Analysis.

The trial analysis of octamethylnaphthalene has already been fully dealt with.

The electron density on the ab plane, (001) was computed at 450 points on the asymmetric unit from the series

$$\rho(x,y) = \frac{1}{ab}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} F(hk0)\cos 2\pi\frac{hx}{a}\cos 2\pi\frac{ky}{b}$$

The electron density on the ac plane,(010),was computed at 450 points on the asymmetric unit from the series.

$$\rho(x,z) = \frac{1}{ac}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} F(h0l)\cos 2\pi\frac{hx}{a}\cos 2\pi\frac{lz}{c}$$

The a-axis was divided into 120 parts, the b-axis into 60 parts and the c-axis into 60 parts. The intervals along a were 0.139A, those along b were 0.189A and those along c 0.127A. The summations were carried out by means of three-figure strips (43). The positions of the contour lines were obtained by graphical interpolation of the summation totals, by making sections of the rows and columns. The contour maps obtained have already been reproduced.

Co-ordinates of Atoms and Molecular Dimensions.

The co-ordinates of the resolved atoms were directly measured, and the remaining ones obtained by trial and error. Since the crystal axes are orthorhombic, the molecular dimensions can be calculated from the crystal co-ordinates by a straightforward application of the distance formula, i.e. if R is the distance between atoms A and B, whose crystal co-ordinates are known, then:-

$$R^2 = (x_A - x_B)^2 + (y_A - y_B)^2 + (z_A - z_B)^2$$

Structure Factors.

The x and y co-ordinates of the carbon atoms listed on page 113 were used in the final calculation of the structure factors. Considering the carbon atoms alone, the agreement between the observed and calculated values of F, expressed in the usual manner as a sum of all the discrepancies divided by the sum of the measured structure factors, is 20% for the (hk0) reflections. When the contribution from the hydrogen atoms, whose co-ordinates are listed on page 117., are included this discrepancy becomes 14.7%. The agreements between observed and calculated values of F for the (h0l) and (0kl) zones depend on the set of z co-ordinates (page 116) used in conjunction with the x and y co-ordinates chosen (page 113). These agreements are as shown.

Zone	Structure 1.	Structure 2.	Structure 3.
(h0l)	11.8%	11.8%	12.2%
(0kl)	10.5%	13.9%	12.2%

These calculated structure factors are listed in the following pages. The F values for the (hk0) zone are listed first. F(C) calc. means F calculated for carbon contributions alone, andF(C,H) calc. means F calculated for both carbon and hydrogen contributions. The values of F meas. quoted are scaled using F(C) calc. and are not absolutely correct for comparison with F(C,H) calc. The F values for the (0kl) and (h0l) zones are then listed as follows; F (1) calc. means F calculated using the z co-ordinates for structure 1, F(2) calc. means F calculated using the z co-ordinates for structure 2 and so on. The values of F meas. quoted are scaled using F(2) calc. and are not absolutely correct for comparison with F(1) calc. and F(3) calc.

Measured and calculated values of F (Octamethylnaphthalene)

(hkl)	2sinθ	F meas.	F(C) calc.	F(C,H) calc.
200	0.185	169.7	+177.1	+161.5
400	0.370	70.1	- 53.5	- 67.1
600	0.555	43.1	- 57.1	- 46.7
800	0.739	100.4	- 97.5	-109.3
10,00	0.924	22.6	- 25.3	- 23.5
12,00	1.109	21.9	+ 29.3	- 27.6
14,00	1.294	14.2	- 12.3	
16,00	1.479	10.8	- 20.2	
18,00	1.664	< 6.3	- 6.7	
20,00	1.849	< 4.8	- 4.2	
020	0.272	58.8	- 54.0	- 57.4
040	0.545	82.4	- 72.0	- 89.7
060	0.817	20.5	+ 15.9	+ 20.2
080	1.089	23.3	+ 24.7	+ 25.5
0,10,0	1.362	19.3	+ 31.6	
0,12,0	1.634	< 6.5	- 5.1	
0,14,0	1.906	< 4.1	- 4.3	
220	0.329	48.3	- 44.4	- 43.3
420	0.459	5.0	- 0.6	+ 6.5
620	0.618	10.7	+ 25.3	+ 23.8
820	0.787	7.0	+ 9.4	+ 5.3
10,2,0	0.963	< 5.7	+ 0.8	+ 2.2
12,2,0	1.142	< 6.4	+ 3.2	+ 3.1
14,2,0	1.322	< 7.0	+ 3.1	
16,2,0	1.504	< 6.9	+ 4.1	
18,2,0	1.686	< 6.2	+ 2.7	
20,2,0	1.869	< 4.6	- 2.1	
240	0.576	29.9	+ 40.2	+ 35.2
440	0.659	69.3	+ 76.4	+ 75.9
640	0.778	33.7	+ 14.8	+ 23.1
840	0.918	26.0	+ 22.7	+ 23.2
10,4,0	1.073	21.8	- 22.6	- 24.5
12,4,0	1.236	50.1	- 55.6	
14,4,0	1.404	13.8	- 14.5	
16,4,0	1.576	< 6.7	+ 2.4	
18,4,0	1.751	< 5.7	+ 1.8	
20,4,0	1.928	6.7	+ 7.4	
260	0.838	19.3	+ 23.6	+ 20.5
460	0.897	5.4	+ 0.6	- 5.8
660	0.988	15.9	- 21.0	- 17.5
860	1.102	< 6.3	0	+ 1.8
10,6,0	1.233	13.2	+ 5.6	

(hkl)	2sinθ	F meas.	F(C) calc.	F(C,H) calc.
12,6,0	1.377	13.7	- 3.4	
14,6,0	1.530	< 6.9	- 2.2	
16,6,0	1.690	< 6.2	- 5.3	
18,6,0	1.854	6.7	- 4.2	
280	1.106	11.8	- 3.7	- 0.6
480	1.150	< 6.5	- 5.2	- 2.4
680	1.222	< 6.7	+ 12.7	
880	1.316	13.9	- 11.3	
10,8,0	1.428	11.1	- 8.3	
12,8,0	1.554	< 6.8	+ 7.5	
14,8,0	1.691	< 6.2	- 2.3	
16,8,0	1.837	< 4.9	- 0.7	
18,8,0	1.989	< 1.3	+ 0.8	
2,10,0	1.374	9.3	+ 13.6	
4,10,0	1.411	< 7.0	+ 2.3	
6,10,0	1.471	< 7.0	+ 1.6	
8,10,0	1.550	< 6.8	- 12.6	
10,10,0	1.646	< 6.5	- 11.1	
12,10,0	1.756	< 5.7	- 1.2	
14,10,0	1.879	< 4.4	- 4.1	
2,12,0	1.644	< 6.5	+ 1.9	
4,12,0	1.675	< 6.3	- 2.1	
6,12,0	1.726	< 5.9	- 8.4	
8,12,0	1.793	< 5.3	+ 2.8	
10,12,0	1.877	< 4.5	+ 5.8	
12,12,0	1.975	< 2.0	+ 0.7	

(hkl)	2sinθ	F meas.	F(1) calc.	F(2) calc.	F(3) calc.
002	0.403	290.7	+265.9	+265.9	+268.8
004	0.806	76.1	+ 74.8	+ 73.4	+ 78.1
006	1.210	20.4	+ 21.9	+ 18.2	+ 23.4
008	1.613	< 9.0	+ 14.5	+ 9.0	+ 13.9
202	0.444	156.4	+137.1	+136.5	+138.6
402	0.547	10.7	- 16.4	- 17.7	- 18.2
602	0.686	64.5	- 65.7	- 66.1	- 67.5
802	0.842	60.6	- 66.7	- 65.3	- 67.0
10,02	1.008	16.2	- 17.5	- 16.3	- 16.8
12,02	1.180	< 9.0	+ 10.7	+ 11.1	+ 11.4
14,02	1.355	< 9.7	- 6.9	- 7.3	- 6.9
16,02	1.532	< 9.5	- 14.0	- 14.6	- 14.4
18,02	1.711	< 8.3	- 8.9	- 9.0	- 9.2
20,02	1.891	< 5.8	- 2.1	- 1.9	- 2.1

(hkl)	2sinθ	F meas.	F(1) calc.	F(2) calc.	F(3) calc.
204	0.827	77.5	+ 82.2	+ 80.0	+ 83.1
404	0.887	16.4	+ 15.5	+ 13.0	+ 13.4
604	0.979	42.1	- 52.9	- 53.1	- 55.4
804	1.094	17.1	- 24.7	- 22.1	- 24.9
10,04	1.226	< 9.7	- 8.9	- 6.1	- 7.1
12,04	1.371	9.7	- 13.1	- 12.0	- 11.6
14,04	1.524	< 7.7	- 0.1	- 1.0	+ 0.2
16,04	1.684	< 8.5	- 5.8	- 7.3	- 6.8
18,04	1.848	< 6.5	- 8.7	- 8.8	- 9.2
206	1.224	23.8	+ 35.5	+ 32.6	+ 35.8
406	1.265	14.3	+ 14.3	+ 12.9	+ 12.7
606	1.332	< 9.7	- 22.6	- 21.2	- 24.2
806	1.418	< 9.7	- 9.8	- 6.1	- 9.4
10,06	1.522	< 9.5	- 8.0	- 5.2	- 6.3
12,06	1.641	< 8.8	- 14.5	- 14.3	- 13.2
14,06	1.772	< 7.4	- 0.3	- 2.0	- 0.5
16,06	1.910	< 5.3	- 0.8	- 2.0	- 1.6
208	1.624	< 9.0	+ 11.7	+ 7.9	+ 11.0
408	1.654	< 8.8	+ 6.2	+ 6.3	+ 5.8
608	1.705	< 8.3	- 0.9	+ 2.4	- 0.8
808	1.774	< 7.4	- 6.7	+ 0.5	- 6.0
10,08	1.859	< 6.3	- 7.6	- 6.1	- 6.8
022	0.486	39.4	- 37.2	- 40.9	- 39.2
042	0.678	25.7	- 25.5	- 24.7	- 26.2
062	0.911	9.0	+ 14.6	+ 19.0	+ 16.6
082	1.161	17.2	+ 13.6	+ 11.4	+ 12.9
0,10,2	1.420	18.7	+ 23.1	+ 21.7	+ 22.6
0,12,2	1.683	< 10.1	- 2.8	- 1.6	- 2.2
0,14,2	1.948	< 5.1	- 1.1	- 1.0	- 1.1
024	0.851	14.4	- 15.0	- 22.1	- 19.1
044	0.973	24.6	+ 19.1	+ 22.5	+ 18.6
064	1.148	< 10.9	+ 7.5	+ 17.6	+ 11.9
084	1.355	< 11.7	+ 1.0	- 5.0	- 1.5
0,10,4	1.583	11.7	+ 12.3	+ 7.7	+ 11.0
0,12,4	1.822	< 8.6	- 0.2	+ 2.3	+ 0.9
026	1.240	< 11.3	- 2.8	- 8.1	- 5.3
046	1.327	15.6	+ 16.5	+ 21.2	+ 16.8
066	1.460	< 11.7	- 1.7	+ 10.0	+ 3.1
086	1.628	< 10.9	+ 2.3	- 4.4	- 0.3
0,10,6	1.822	< 8.6	+ 7.5	+ 3.4	+ 6.2
028	1.636	< 10.9	+ 2.0	- 1.4	+ 0.5
048	1.703	< 10.1	+ 3.2	+ 7.0	+ 4.3
068	1.808	< 8.6	- 4.8	+ 1.4	- 2.4
088	1.946	< 5.1	+ 5.0	+ 1.0	+ 3.7

Appendix.

The Unit Cell Dimensions and Space Group of Benzfurazane Oxide.

The structure of benzfurazane oxide, $C_6H_4N_2O_2$, is unknown. It is known that the nitrogen atoms are attached to the ortho positions of the benzene ring, but no other information was available. It was proposed to investigate the crystal structure using X-ray diffraction methods, with a view to obtaining the molecular structure.

Copper K_α radiation, $\lambda = 1.54$A, was employed in all the measurements. Rotation, oscillation and moving-film photographs were used, the latter to determine the space group, which was established as P1 or P$\bar{1}$. The density of the crystals was measured by flotation of small crystals in a solution of silver nitrate at 20°C. The density found, 1.466 was in extremely good agreement with that of 1.459 calculated for four molecules in the unit cell.

Crystal Data.

Benzfurazane Oxide, $C_6H_4N_2O_2$. M, 136.1 m.p. 69°- 70°

d, calc. 1.459 d, found 1.466

triclinic, $\underline{a} = 10.76 \pm 0.02$A $\alpha = 99.2°$

$\underline{b} = 7.83 \pm 0.03$A $\beta = 95.5°$

$\underline{c} = 7.51 \pm 0.01$A $\gamma = 94.0°$

Space Group - P1 or P$\bar{1}$

Four molecules per unit cell. Molecular symmetry, not known.
Volume of the unit cell, 619.5A^3
Total number of electrons per unit cell = F(000) = 280.
The values of the angles of the unit cell were obtained from a direct measurement of the ab, bc and ac diagonals of the unit cell. Rotation photographs were obtained about these three diagonals, from which their lengths were measured.

These were found to be:- [101] = 13.70 ± 0.03A
[110] = 13.74 ± 0.03A
[011] = 11.68 ± 0.04A

The values for the angles obtained using these values for the diagonals have already been listed. These were in good agreement with the reciprocal values obtained from the moving-film photographs. The reciprocal values for the unit cell are listed below.

$a^* = 0.0937$. $\alpha^* = 80.4°$
$b^* = 0.1298$ $\beta^* = 83.9°$
$c^* = 0.1357$ $\gamma^* = 85.1°$

Since there are four molecules per unit cell, and the crystal is triclinic, no further work has been attempted on this compound as yet.

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