164. *The Crystal Structure of Coronene: A Quantitative X-Ray Investigation.*

By J. Monteath Robertson and J. G. White.

A detailed *X*-ray investigation has led to a complete determination of the coronene structure. The monoclinic crystals, space group $P2_1/a$, have two planar, centro-symmetrical molecules of $C_{24}H_{12}$ per unit cell, and the molecular planes are inclined at about 44° to the (010) plane. The distance between the molecular planes is 3·40 A. The carbon–carbon bond length varies in different parts of the molecule. For the central ring and the " spokes " connecting it to the outer edges this distance is 1·43 A. The outer bonds are of two types, measuring $1{\cdot}38_5$ A. and $1{\cdot}41_5$ A., severally. The accuracy of these determinations is estimated to lie between $\pm 0{\cdot}01$ and $\pm 0{\cdot}02$ A., and they represent the first definite measurements of variable carbon–carbon bond length for any condensed ring aromatic hydrocarbon. Reference is made to molecular orbital calculations on this problem, and it is also discussed in terms of the 20 stable valency bond structures for coronene. This treatment provides a rough qualitative account of the bond length variations which have been observed.

A preliminary study of the crystal structure of coronene (Robertson and White, *Nature*, 1944, **154**, 605) has shown it to be of a relatively simple type. The two centro-symmetrical molecules are so disposed in the crystal as to afford clear-cut projections of high resolution, from which it is possible to obtain measurements of bond length and other structural details with considerable accuracy. At the same time the extremely high symmetry of the coronene molecule lends itself to a rather refined theoretical investigation of bond lengths and other properties by the method of molecular orbitals. In this connection, Coulson (*ibid.*, p. 797) has recently given a preliminary account of such calculations and has made comparisons with benzene and graphite. We have now completed a very detailed *X*-ray investigation of the coronene structure, chiefly with the object of testing experimentally the molecular orbital calculations which can be made for an aromatic structure of this type.

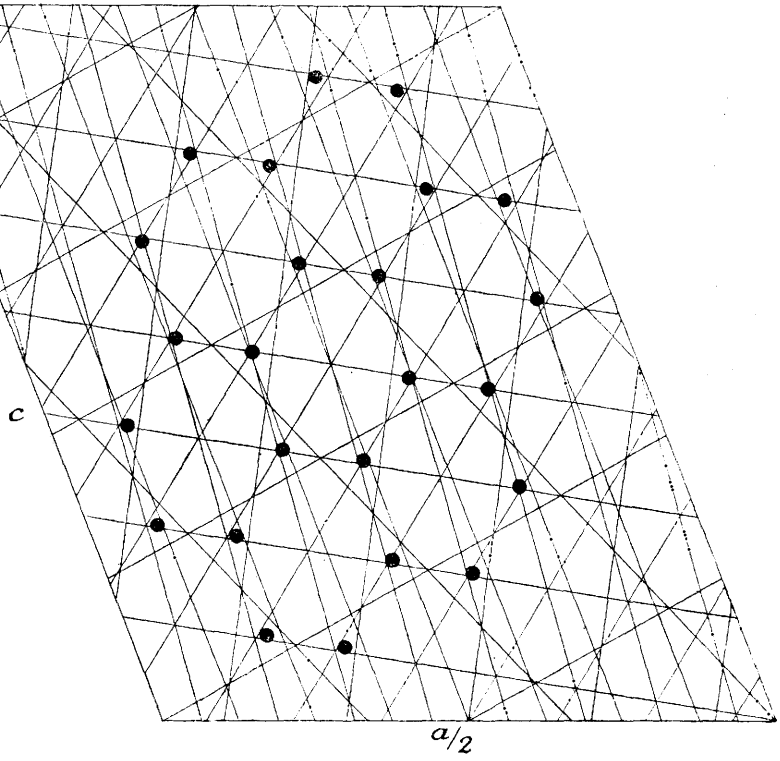
Earlier *X*-ray studies of anthracene (Robertson, *Proc. Roy. Soc.*, 1933, *A*, **140**, 79) and naphthalene (*idem*, *ibid.*, 1933, *A*, **142**, 674) have shown that to a good approximation these molecules consist of regular planar hexagons of carbon atoms, the average bond length being 1·41 A. in both cases. This mean value lies between the accepted values for benzene (1·39 A.) and graphite (1·42 A.) and is in good agreement with theoretical predictions (see Penney, *ibid.*, 1937, *A*, **158**, 306; Pauling, " The Nature of the Chemical Bond," Cornell, 1940). For the individual bonds, small variations from this mean value, of the order 0·01—0·03 A., would be difficult to detect experimentally in naphthalene and anthracene owing to various uncertainties, and particularly to lack of resolution in the two-dimensional Fourier methods of analysis employed. Nevertheless, the *X*-ray work on naphthalene gave some indication that the central carbon–carbon bond length might be slightly greater than the others, and this conclusion agreed with Penney's later, more detailed calculations of bond orders and bond lengths (*loc. cit.*). The finer details of his model, however, and especially the contraction of the 1 : 2-bond, still await any direct experimental confirmation.

The first definite measurements of variable carbon–carbon bond lengths in any condensed-ring aromatic hydrocarbon have now been obtained for coronene. The bonds are found to vary in length in different parts of the molecule over a range of 0·04 A., from about 1·43 A. in the central parts to about 1·39 A. on the outer edges. These variations are of fairly small order and are difficult to assess for each bond separately, the experimental uncertainty probably lying between ±0·01 and ±0·02 A. They are, however, sufficient to cause an appreciable displacement from hexagonal symmetry which is visible on the contoured maps of the structure (compare Fig. 7). The variations in bond length agree rather closely with the theoretical calculations and conform to a fairly definite pattern, which is discussed more fully below.

Description of the Structure.—Crystal data. Coronene, $C_{24}H_{12}$; *M*, 300·3; m. p. 434—436°; *d*, calc. 1·381, found 1·377; monoclinic prismatic, $a = 16{\cdot}10 \pm 0{\cdot}05$, $b = 4{\cdot}695 \pm 0{\cdot}005$, $c = 10{\cdot}15 \pm 0{\cdot}05$ A., $\beta = 110{\cdot}8^\circ \pm 0{\cdot}2^\circ$. Absent spectra, $(h0l)$ when h is odd; $(0k0)$ when k is odd. Space group, $C_{2h}^5(P2_1/a)$. Two molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell, 717·1 A.^{3}. Absorption coefficient for X-rays, $\lambda = 1{\cdot}54$, $\mu = 7{\cdot}30$ per cm. Total number of electrons per unit cell $= F(000) = 312$.

FIG. 1.

Prominent $(h0l)$ reflections for coronene.



The crystal habit is a familiar one, the long needle-like or lath-shaped crystals growing in the direction of the b axis. The crystals are usually very thin with only the (001) face prominently developed, but with care and slow crystallisation from tetrahydronaphthalene, good thick specimens can sometimes be obtained, displaying the (100), (101), and $(20\bar{1})$ faces in addition to the (001). No end faces could be definitely identified.

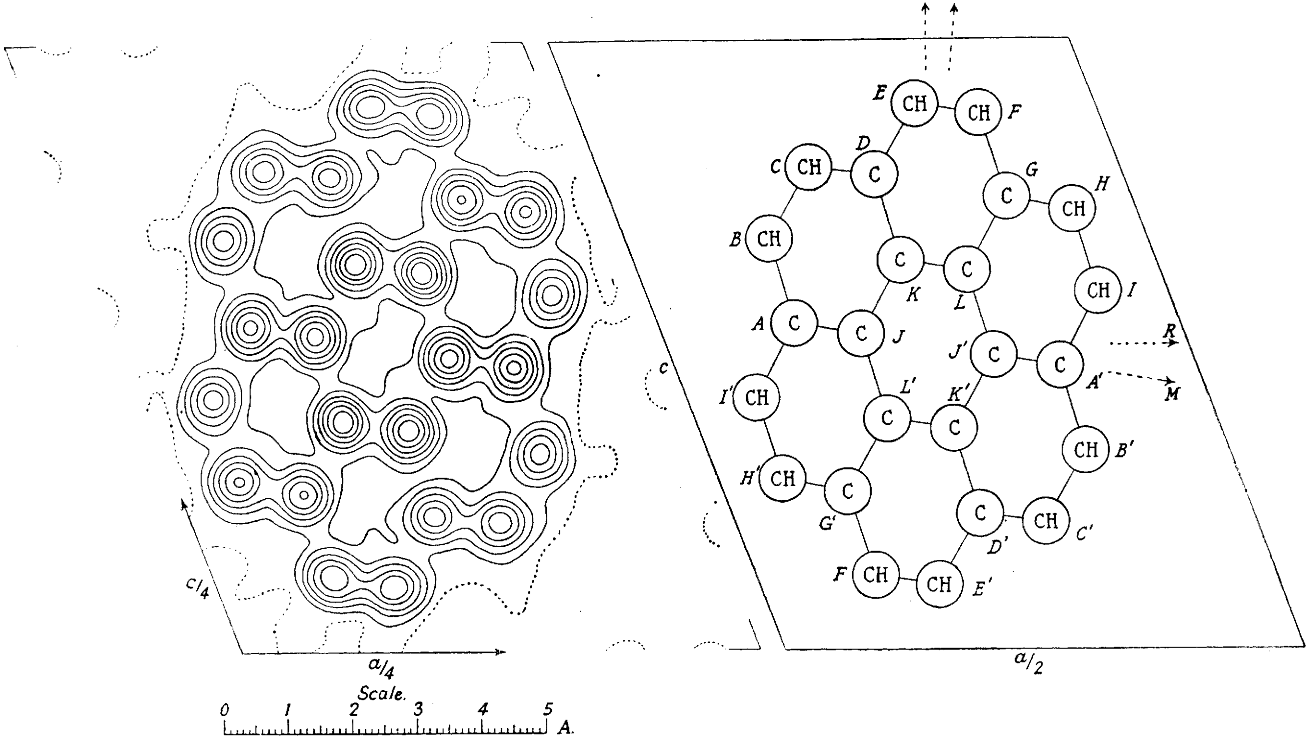
Analysis of the structure. The most prominent feature of the crystal structure is the relatively short b axis of 4·695 A. Now this periodicity, and also the crystal habit, are closely similar to those of phthalocyanine and many of its metal derivatives (Robertson, J., 1935, 615; Linstead and Robertson, J., 1936, 1736). Although coronene and phthalocyanine are compounds of widely different type, they are both large, planar molecules, and the data suggest that the arrangement in the crystal, especially the inclination of the molecular plane to the (010) crystal plane, may be similar in the two cases.

For coronene no direct analysis comparable to that carried out with the phthalocyanines is possible. It is necessary to proceed by trial and error methods in the first instance, but the problem is greatly simplified by the considerations outlined above. It is reasonable to assume that, as in the phthalocyanine structures, the molecular plane is inclined at about 45° to the (010) crystal plane. To specify the orientation of the molecule completely, two degrees of freedom remain to be settled. To determine these, a survey of the $(h0l)$ zone was made by moving-film methods, and it was found that the following small spacing planes gave outstandingly strong reflections: (16,00), $(16,0\bar{1})$, $(14,0\bar{8})$, $(10,0\bar{3})$, (602), $(40\bar{5})$, and (207). After several trials, one position of the molecule was found which could account satisfactorily for the enhancement of these reflections. This was done graphically without any detailed calculations in the first instance, by making projections of the coronene structure on the (010) plane and adjusting the atomic positions to coincide as nearly as possible with the traces of the prominent reflecting planes mentioned above. The final result is shown in Fig. 1, from which it is seen that the atoms can be made to group themselves very closely about the traces of these planes.

From this point, the work of refining the atomic positions proceeded by a straightforward application of double Fourier series methods. The projection of the structure obtained after the first refinement has already been reproduced (Robertson and White, *loc. cit.*). The Fourier series used contained 78 terms, and every carbon atom in the molecule was clearly resolved. The co-ordinates obtained from that synthesis enabled the phase constants of more reflections to be determined, and finally it was possible to set up a series of 129 terms which included all the reflections from the (*h*0*l*) zone that could be observed with copper radiation, with the exception of one very weak trace from the (2,0,11) plane, whose phase constant still remains doubtful. Most of the reflections were measured photometrically, and the results correlated with visual estimates for some of the weaker reflections. Details of absorption corrections, etc., are given below. The corrected F values employed in the final synthesis, with their phase constants (+ 1 or − 1), are collected in Table I.

FIG. 2.

Projection along the b *axis, showing one coronene molecule. The plane of the molecule is inclined at about* 44° *to the projection plane,* (010). *Each contour line represents a density increment of approximately one electron per* A.^{2}, *the one-electron line being dotted.*



(*a*) (*b*)

The results of this latest synthesis are given in Fig. 2, which shows the projection of one complete molecule (half the unit cell) on the (010) plane. Fig. 3 shows on a smaller scale how a group of six coronene molecules are arranged in the crystal, with a comparatively large gap of low density around each molecule. The reason for the prominent development of the (001) plane in the crystal is also clear from this figure, which shows that the molecular alinement in this direction involves very little interlocking.

Orientation and arrangement of molecules in the crystal. The projections of the structure shown in Figs. 2 and 3 allow two co-ordinates for each carbon atom to be determined with considerable accuracy, but of course they can give no direct information about the third co-ordinate (along the *b* axis). However, a detailed study of these maps (see Experimental) makes it clear that they represent a projection of the expected coronene structure, built from approximately regular planar hexagons of carbon atoms. The central hexagon is particularly regular, each pair of opposite sides being parallel to, and one half the length of, the line through the centre joining the other two corners. On the assumption that this ring is actually a regular planar hexagon,

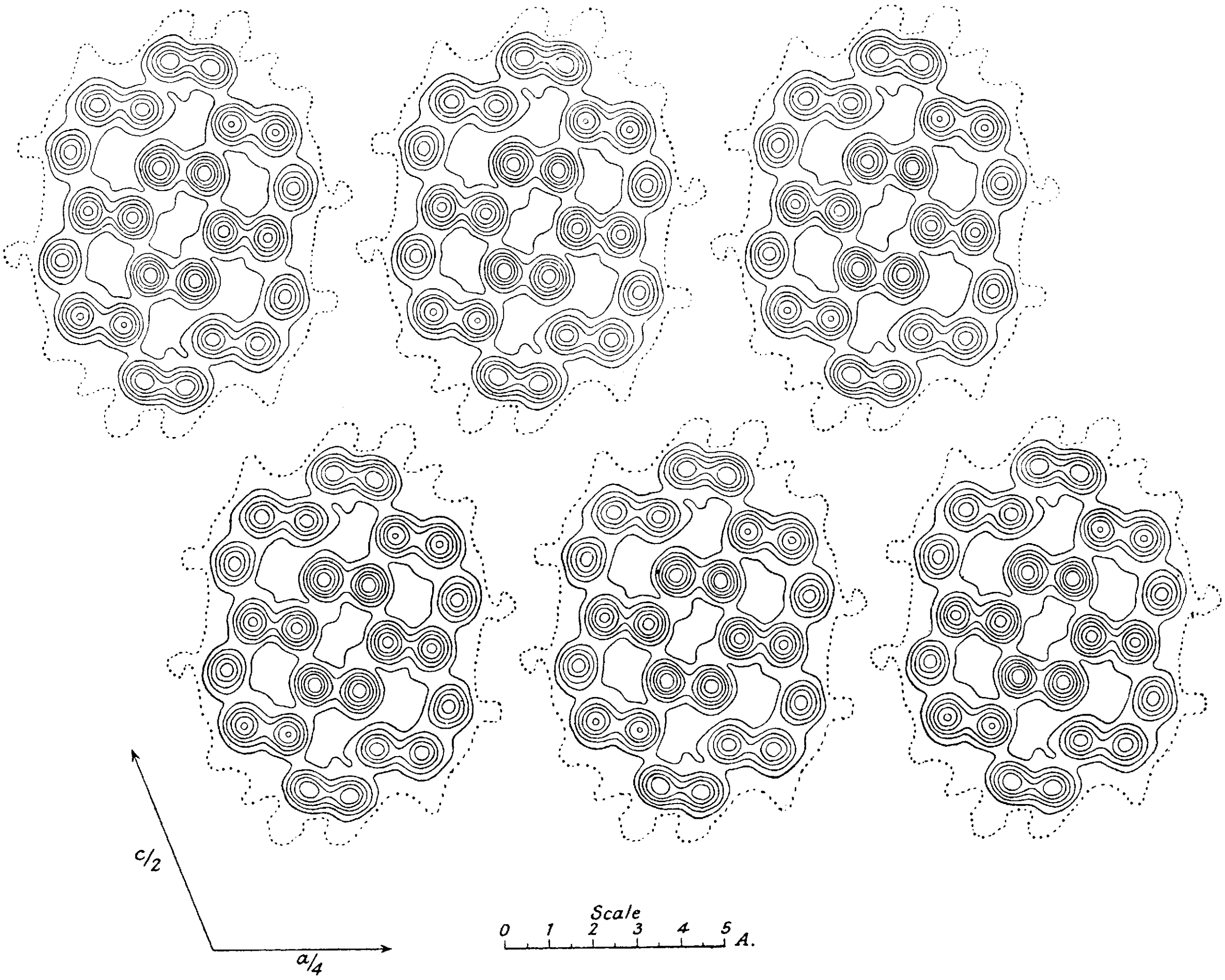
TABLE I.

Values and signs of F($h0l$).

h.	l = 0.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
20	—	—	—	—	—	—	—	—	—	—	—	—	—
18	—	—	—	—	—	—	—	—	—	—	—	—	—
16	+ 17	—	—	—	—	—	—	—	—	—	—	—	—
14	+ 6	—	—	—	− 6	—	—	—	—	—	—	—	—
12	− 5	+ 5	—	—	−10	− 8	—	—	—	—	—	—	—
10	+ 5	+ 7	+ 6	—	− 2	—	—	—	− 2	—	—	—	—
8	—	−10	−17	—	—	+ 2	—	—	—	−7	—	—	—
6	+ 7	− 6	−48	−18	+ 6	− 6	—	− 6	—	—	− 5	—	—
4	− 30	+23	+ 4	−16	+10	− 7	+11	+20	− 5	—	—	—	—
2	+ 65	−32	+12	+ 2	+ 5	− 5	+ 5	+46	+16	−7	+ 2	—	—
0	+312	+60	−29	+ 8	− 2	+ 8	− 8	+ 7	+13	−6	+ 4	−2	− 6
$\bar{2}$	+ 65	+58	−28	+27	−18	−14	+ 9	− 6	− 2	−4	—	—	−10
$\bar{4}$	− 30	−30	−24	+14	−16	−55	−11	+ 6	—	+3	—	—	− 3
$\bar{6}$	+ 7	+13	+21	+ 5	− 3	−15	− 8	—	—	−3	− 6	—	—
$\bar{8}$	—	—	− 8	− 9	—	+ 6	+ 7	+ 6	—	−5	−15	−3	+ 2
$\bar{10}$	+ 5	—	−21	−39	− 3	+ 3	− 6	− 6	− 3	+2	− 4	−3	+ 2
$\bar{12}$	− 5	—	+ 5	−14	− 5	+ 3	− 6	+ 7	− 6	—	—	—	—
$\bar{14}$	+ 6	—	− 3	+ 4	− 2	—	− 3	+15	+28	+5	− 3	—	—
$\bar{16}$	+ 17	+23	—	—	—	—	—	—	+12	+4	− 2	—	—
$\bar{18}$	—	+13	+ 6	—	+ 2	—	—	− 2	—	−3	—	—	—
$\bar{20}$	—	—	—	—	—	− 4	− 6	—	—	—	—	—	—

FIG. 3.

A group of six coronene molecules in the b-*axis projection.*



and further, that the molecular axes L and M (Fig. 2) are actually at right angles to each other (in the projection they are inclined at 94·2°) the complete orientation and dimensions of the molecule can be deduced. It was also assumed that the whole molecule is planar, but no other regularity was required for the remaining hexagons. These various assumptions were subsequently tested in detail by the calculation of structure factors for other zones of reflections, involving the third co-ordinate, with satisfactory results.

The orientation of the molecule in the crystal is given in Table II, where χ_L, ψ_L, ω_L; χ_M, ψ_M, ω_M; and χ_N, ψ_N, ω_N, are the angles which the molecular axes L, M (see Fig. 2) and their perpendicular N make with the a and b crystal axes, and their perpendicular, c'. The figures are probably accurate to within 0·5°.

These results show that the angle between the plane of the molecule and the (010) plane, which is expressed by ψ_N, the angle between the normal to the molecular plane and the b axis, is 43·7°. For metal-free phthalocyanine and also for nickel phthalocyanine this angle was 44·2° (Robertson, *loc. cit.*). The perpendicular distance between the molecular planes in coronene, $b \cos \psi_N$, is 3·40 A., almost identical with the interplanar distance in graphite. In Fig. 2, R represents the line of maximum inclination of the molecular plane to the projection plane, (010), and the molecular axis S lies in the (010) plane. Consequently, when the structure is viewed along the c' axis, we obtain an end view of the molecules, as depicted roughly in Fig. 4. Successive molecules in the direction of the a axis, although identical in the projection of Fig. 3, are inclined in opposite directions and may be derived by the operation of the glide plane of symmetry a. The planes of adjacent molecules in the a direction are nearly perpendicular.

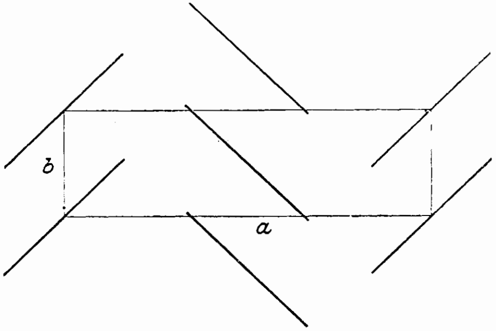
TABLE II.

Orientation of the molecule in the crystal.

$\chi_L = 84{\cdot}8°$ $\cos \chi_L = 0{\cdot}0912$
$\psi_L = 85{\cdot}6°$ $\cos \psi_L = 0{\cdot}0765$
$\omega_L = 6{\cdot}9°$ $\cos \omega_L = 0{\cdot}9928$
$\chi_M = 44{\cdot}2°$ $\cos \chi_M = 0{\cdot}7174$
$\psi_M = 46{\cdot}7°$ $\cos \psi_M = 0{\cdot}6865$
$\omega_M = 96{\cdot}8°$ $\cos \omega_M = -0{\cdot}1188$
$\chi_N = 133{\cdot}7°$ $\cos \chi_N = -0{\cdot}6905$
$\psi_N = 43{\cdot}7°$ $\cos \psi_N = 0{\cdot}7233$
$\omega_N = 89{\cdot}6°$ $\cos \omega_N = 0{\cdot}0078$

FIG. 4.

End view of molecules.



Co-ordinates and dimensions. The co-ordinates of the atoms can be measured directly from the contoured map in Fig. 2. These results, referred to the crystal axes, are collected in Table III. As the molecule has an exact centre of symmetry, only half the atoms, those of the asymmetric crystallographic unit, are listed. All the other atoms in the unit cell may be derived from these by the operations

TABLE III.

Co-ordinates with Respect to Monoclinic Crystal Axes : Centre of Symmetry as Origin.

Atom (cf. Fig. 2).	x, A. (*a*)	x, A. (*b*)	$\frac{2\pi x}{a}$. (*a*)	y, A. (*a*)	$\frac{2\pi y}{b}$. (*a*)	z, A. (*a*)	z, A. (*b*)	$\frac{2\pi z}{c}$. (*a*)
A	−1·922	−1·922	−43·0°	−1·967	−150·8°	0·364	0·352	12·9°
B	−1·800	−1·804	−40·3	−2·337	−179·3	1·770	1·794	62·4
C	−0·768	−0·752	−17·2	−1·769	−135·6	2·956	2·960	104·8
D	0·198	0·198	4·4	−0·794	− 60·9	2·806	2·818	99·7
E	1·258	1·256	28·2	−0·194	− 14·9	4·000	3·996	141·9
F	2·188	2·190	49·0	0·758	58·1	3·826	3·824	135·7
G	2·118	2·118	47·4	1·172	89·9	2·448	2·448	86·8
H	3·054	3·046	68·3	2·141	164·2	2·232	2·220	79·2
I	2·958	2·954	65·9	2·527	193·7	0·870	0·858	30·9
J	−0·962	−0·962	−21·5	−0·983	− 75·4	0·182	0·184	6·5
K	0·098	0·084	2·2	−0·397	− 30·4	1·402	1·402	49·9
L	1·060	1·062	23·7	0·587	44·9	1·224	1·226	43·4

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

It is clear, however, that the molecule approximates closely and probably exactly to a higher symmetry than that required by the centre of inversion. The outer bond distances are measurably shorter than the corresponding inner bonds of the central hexagon, and these outer bonds group themselves into two kinds. *BC*, *EF*, and *HI* show contractions of 3·2±0·4% compared with the inner bonds, while the remaining outer bonds show a smaller average contraction of about half that amount. In Table III the individual estimates of the atomic positions, without averaging, are shown in the columns headed (*b*). The co-ordinates finally adopted as the most probable are those which average the outer bonds into the two classes mentioned above, and these are given under the columns headed (*a*).

To express the results in terms of actual bond distances within the molecule, allowance must be made for the orientations of the molecular axes *L* and *M*, given in Table II. The dimensions so obtained are shown graphically in Fig. 5, and the atomic co-ordinates with respect to the molecular axes *L* and *M* are given in Table IV. For comparison, Table IV also gives the *L* and *M* co-ordinates which would result from a completely regular model of hexagons with a uniform interatomic distance of 1·39 A. The deviations from such a model are seen to be considerable.

FIG. 5.

Dimensions of the coronene molecule.

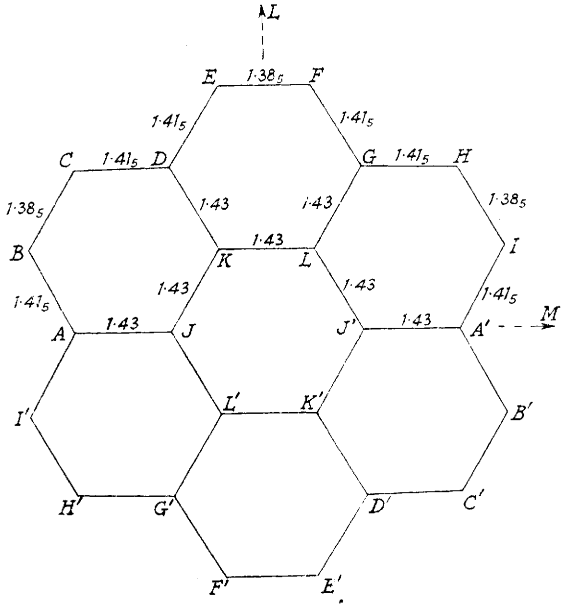


TABLE IV.

Co-ordinates with respect to molecular axes.

Atoms.	Fig. 5. *L*, A.	Fig. 5. *M*, A.	Regular model, 1·39 A. *L*, A.	Regular model, 1·39 A. *M*, A.
A and *A'*	0	±2·860	0	±2·780
B and *I*	1·243	±3·536	1·204	±3·475
C and *H*	2·441	±2·844	2·407	±2·780
D and *G*	2·476	±1·430	2·407	±1·390
E and *F*	3·684	±0·692	3·611	±0·695
J and *J'*	0	±1·430	0	±1·390
K and *L*	1·238	±0·715	1·204	±0·695

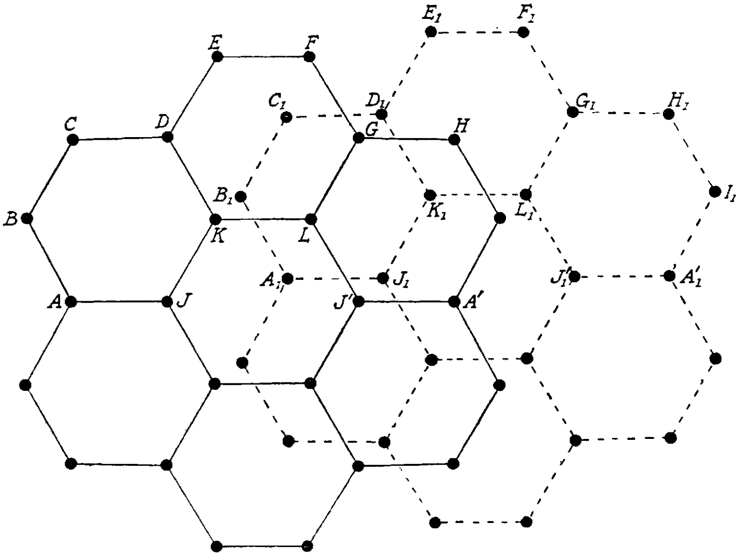
Intermolecular distances. The shortest distances between carbon atoms of adjacent molecules occur between those at either end of the *b* axis. The perpendicular distance between their planes is only 3·40 A., but the individual atoms do not occur vertically over each other. Indeed, there is a pronounced tendency to avoid such overlap, as can be seen from Fig. 6, which gives the normal projection of two parallel molecules separated by the translation *b*. The closest approaches are between atoms *J'* and J_1, and between *G* and D_1, where the distance is 3·43 A.; between *K* and B_1, and between *I* and L_1, it is 3·44 A. The other pairs of atoms are separated by 3·5 A. or more. Between other molecules, the separation is greater. From atom *E* on the standard molecule to *E'* on the molecule one translation along the *c* axis (Figs. 2 and 3) the distance is 3·87 A., and from *E* to *C'* on the same pair of molecules the distance is 3·93 A. From atom *I* on the standard molecule to *B* on the reflected molecule at ($\frac{1}{2}a$, $\frac{1}{2}b$) the distance is 3·77 A., and from *I* to *I'* on this same pair, 3·97 A. All other distances between atoms on neighbouring molecules appear to be greater than 4 A.

Discussion of Results.—The most striking result of this analysis is the comparatively large variation of bond length found within the coronene molecule. For the central hexagon and the " spokes " the average value obtained (Fig. 5) is 1·43 A., with a variation of ±0·01 A. The six outermost bonds, *BC*, *EF*, *HI*, etc., are definitely shorter, the average length being $1{\cdot}38_5 \pm 0{\cdot}00_5$ A., while the remaining twelve outer bonds, *AB*, *CD*, *DE*, *FG*, *GH*, etc., are intermediate in length, the average value being $1{\cdot}41_5$ A., with a somewhat larger variation of ±0·02 A.

The first question to be decided is whether these different groups of bond lengths are experimentally significant. The minor variations within the groups, which have been averaged, are almost certainly due to errors. The larger variations, however, appear to be real, and they have a substantial effect on the symmetry of the molecule in its outer parts, as can be seen from Fig. 7, which is an enlargement of the upper part of the electron-density map, showing atoms *C*, *D*, *G*, *H*, and parts of others. In any projection of a structure built from regular planar hexagons, all of the same size, these four atoms would lie in a straight line. The deviation from such a straight line can be seen very clearly in the diagram.

FIG. 6.

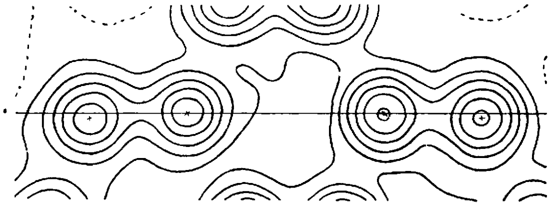
Normal projection of two parallel molecules.



A rigorous discussion of the accuracy obtainable by Fourier series methods is difficult, because it depends on many factors, such as the range and accuracy of the intensities, the size and perfection of the crystal specimens, and the various methods of computation and interpolation employed. One indirect method of approach is by comparing molecular dimensions obtained by *X*-ray analysis and Fourier series methods with independent measurements of the same dimensions by other methods. For example, in acetylene, spectroscopic measurements give 1·20 A. as the carbon–carbon triple-bond length, whereas *X*-ray measurements and Fourier series methods give 1·19 A. for this bond length in tolan (Robertson and Woodward, *Proc. Roy. Soc.*, 1938, *A*, **164**, 436). Agreement to within 0·01 or 0·02 A. has also been obtained between *X*-ray and electron-diffraction measurements in several cases.

FIG. 7.

Enlargement of upper part of the coronene molecule, showing distortion.

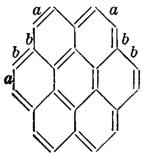


We have attempted a more direct approach in the present case by conducting a parallel investigation on a hypothetical structure with 10 carbon atoms placed asymmetrically to form a double ring, with bond distances comparable to those of the coronene projection. Structure factors were calculated from the coordinates and used to form a double Fourier synthesis, the range of terms employed being similar to those used for coronene. The results of this investigation will be reported more fully elsewhere, but it is noteworthy that the original atomic positions were reproduced as a result of this synthesis to within 0·014 A. on the average, and the maximum shift for any one atom was 0·020 A. In terms of bond lengths the average discrepancy was 0·013 A., and the maximum for any one bond was 0·024 A. When the bond lengths were averaged in groups of six, the differences between the given and the reproduced values were 0·006 A. and 0·007 A. for the two groups. Errors in intensity measurements would increase these discrepancies, but if the errors were small and random they would not have much effect, and probably very little effect on group averages.

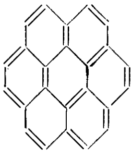
The general conclusion is that in the coronene investigation the errors in the bond-length determinations, after averaging as in Fig. 5, are probably about ±0·01 A. The positions of individual atoms may have maximum errors of between 0·02 and 0·03 A.

With regard to the theoretical significance of these results, Coulson (*loc. cit.*) has carried out some rather detailed calculations for the coronene molecule by the method of molecular orbitals. He has computed the energies of the mobile electrons in terms of the fundamental resonance integral β, and from this has deduced the bond orders and bond lengths. For the central bonds he obtains a length of 1·418 A., and as a mean length for all the bonds, 1·406 A. Our measured values are 1·43 and 1·41$_5$ A., respectively, and are thus in agreement with the theoretical values to within 0·012 A.

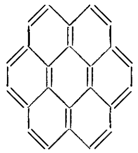
A very simple treatment of the problem can be given in terms of the stable valency bond structures for coronene, with results in remarkable agreement with our measurements. For a fixed position of the carbon atoms the bonds can be arranged in 20 distinct ways. These may be divided into the groups of structures (I)—(V), each containing the number of individuals shown. 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. Taking the number of individual structures to be as indicated in (I)—(V), we find the double-bond character for the outer bonds *a* (cf. I) to be 70%, for the other outer bonds *b*, 30%, for the six "spokes" 40%, and for the inner ring 30%. This gives a rough qualitative explanation of our measured results, the *a* bonds at 1·38$_5$ A. being rather shorter than in benzene, which has 50% double-bond character on the basis of the Kekulé structures. The other bond lengths in coronene, *b* at 1·415, and the inner bonds at 1·43 A., are all very close to the graphite bond length of 1·42 A., which corresponds to 33% double-bond character on the basis of its average valency bond structure. If the contributions of the first group of structures (I) to the normal state of the molecule are doubled relatively to the other contributions, we get a rather better explanation of the observed bond lengths. The *a* bonds then have 67% double-bond character, and all the others, 33%. On the basis of Pauling and Brockway's empirical curve relating double-bond character and distance (*J. Amer. Chem. Soc.*, 1937, **59**, 1223), these figures correspond to bond lengths of 1·37 A. and 1·42 A., as compared with our measured values of 1·38$_5$ A. for the *a* bonds and 1·42$_3$ A. for the mean of the *b* bonds and all the inner bonds. It may be noted that no combination of the structures (I)—(V) seems capable of differentiating the *b* bonds from the bonds of the inner ring.



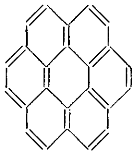
(I.)
4 Structures.



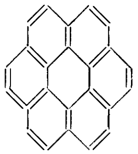
(II.)
6 Structures.



(III.)
3 Structures.



(IV.)
6 Structures.



(V.)
1 Structure.

It may be that the above agreements are partly fortuitous. Indeed, it would be surprising if a treatment which neglects even the first excited structures were found to be generally applicable in predicting bond lengths for complicated molecules. However, the situation is still largely unexplored, because measurements of small variations in individual bond lengths have not yet been made for any other condensed-ring aromatic hydrocarbon.

EXPERIMENTAL.

Determination of Crystal Data.—Copper *Ka* radiation, λ = 1·54, was employed in all the measurements. Rotation, oscillation, and moving-film photographs were used, the latter chiefly for intensity records. Of the (0*k*0) reflections, only the (020) could be observed, and to confirm the halving, long-exposure oscillation photographs were taken, but neither the (010) nor the (030) reflection appeared. There was no exception to the (*h*0*l*) halving with *h* odd, and the space group $P2_1/a$ was therefore assumed.

Density measurements were made by flotation in concentrated solutions of calcium chloride at 25° and the highest value obtained was 1·377 in good agreement with the calculated value of 1·381 for two molecules per unit cell.

Measurement of Intensities.—The (*h*0*l*) and (*hk*0) zones were explored in detail by moving-film exposures of the equatorial layer lines for crystals rotated about the *b* and *c* axes. The multiple-film technique (Robertson, *J. Sci. Instr.*, 1943, **20**, 175) was used to correlate the very strong and very weak reflections, and the total range of intensities covered was about 10,000 to 1. Measurements of the integrated intensities were made on the Dawton Scan Photometer (Robertson and Dawton, *ibid.*, 1941, **18**, 126) for most of the reflections, a few of the weaker ones being estimated visually. The absolute scale of the F values was not determined directly, but obtained by correlation with the calculated F values. As these involve an average atomic scattering factor based mainly on absolute measurements obtained from anthracene (Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 110), the coronene scale may not be quite accurate owing to a possible difference in temperature factor. This uncertainty does not in any way affect the conclusions regarding atomic positions, but may have some effect on the vertical scale of the contour maps (electron-density increment per contour line).

Small crystal specimens were employed, and completely bathed in a uniform *X*-ray beam. The two specimens mainly used for the (*h*0*l*) zone were cut to just over 1 mm. in length (along *b*) and had cross sections of 0·16 mm. by 0·32 mm. and 0·15 mm. by 0·24 mm., severally. Absorption corrections were worked out graphically by drawing and measuring a mean path for the *X*-ray beam through the crystal for each reflection. This method is only approximate, but should be fairly accurate for the (*h*0*l*) zone in view of the small crystal dimensions involved. The calculated correction factors varied from 1·10 to 1·24.

In the (*hk*0) zone, the crystal specimen had the rather more extreme cross-section of 0·13 mm. by 0·63 mm. and the absorption corrections varied from 1·10 to 1·51.

In general, these crystals appeared to be of a rather perfect mosaic type and there was not much evidence of extinction. The intensities obtained for the three strongest reflections, the 200, 001, and 20$\bar{1}$, varied a little in different crystal specimens, and the highest values were adopted as most likely to be correct.

Fourier Analysis.—The electron density on the *ac* plane, (010), was computed at 900 points on the asymmetric unit from the series

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

Both the *a* and the *c* axis were subdivided into 60 parts, the intervals along *a* being 0·268 A., and along *c*, 0·169 A., and the summation was carried out by means of three-figure strips (Robertson, *Phil. Mag.*, 1936, **21**, 176). The positions of the contour lines were obtained by graphical interpolation from the summation totals, by making sections of the rows and columns. The resulting contour map is shown in Fig. 2. The whole molecule, or twice the asymmetric unit, was drawn from the same sections, and the centres of all the atoms were assigned independently.

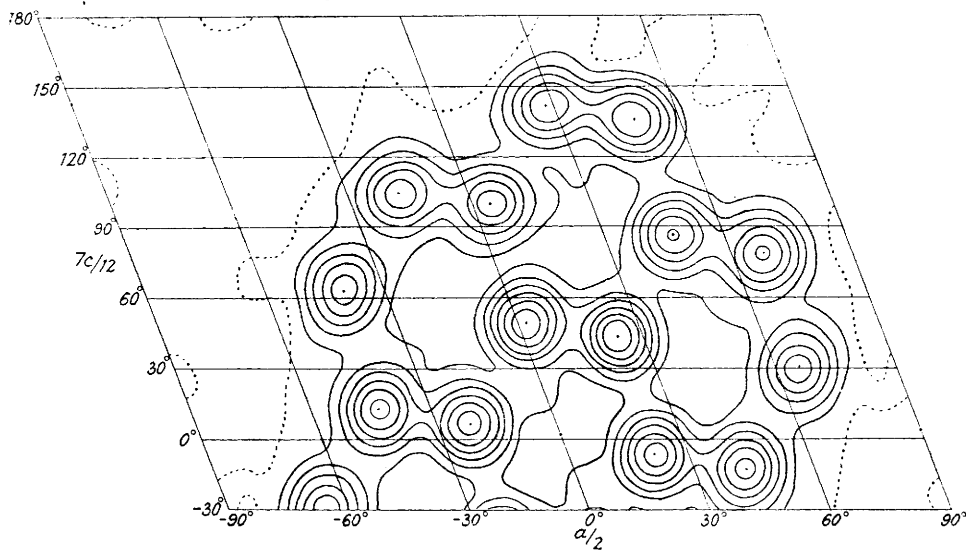
Calculation of Orientation.—It was found that the central ring of coronene fulfilled the conditions necessary for it to be the projection of a regular, planar hexagon, and on this basis it was possible to derive the orientation of the molecule without assumed regularity for the other rings.

One diameter of this central hexagon will actually lie in the projection plane. This is indicated by the direction *S* in Fig. 2, and the measured dimensions in this direction and near to it correspond to a hexagon radius of 1·43 A. The tilt of the axis *M* to *b*, or ψ_M, is now given by the relation $\sin \psi_M = r/R$, where *r* is the measured length of line in the *M* direction and *R* its real length. Taking *r* as the mean of *KL* and one half of *JJ'* (Fig. 2), and *R* as 1·43 A., we find $\psi_M = 46{\cdot}7°$.

This method cannot be applied to find ψ_L, for this angle is close to 90° and consequently too sensitive to small errors in the distance ratio; ψ_L may, however, be calculated from the observed angle between *L* and *M* in the projection (94·2°), and the assumption that these axes are actually perpendicular in the molecule. Let η_L and η_M be the angles which *L* and *M* make with the *a* axis in the projection. Then η_L is found to be $84{\cdot}75° \pm 0{\cdot}15°$, by taking the mean directions of the lines *DJG'*, *GJ'D'*, and the line joining the mid-points of *EF* and *KL* to the origin. Similarly, η_M is found to be $-9{\cdot}4°$, the angle which the line *AJJ'A'* makes with *a*. The complete orientation of the molecule may then be obtained from the relations

FIG. 8.

Co-ordinates assigned to the atoms in the asymmetric crystal unit.



(1) $\cos^2 \chi_L + \cos^2 \psi_L + \cos^2 \omega_L = 1$
(2) $\cos^2 \chi_M + \cos^2 \psi_M + \cos^2 \omega_M = 1$
(3) $\cos^2 \chi_N + \cos^2 \psi_N + \cos^2 \omega_N = 1$
(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) $\cos \chi_M \cos \chi_N + \cos \psi_M \cos \psi_N + \cos \omega_M \cos \omega_N = 0$
(7) $\cos \omega_L = \cos \chi_L \tan \eta_L$
(8) $\cos \omega_M = \cos \chi_M \tan \eta_M$
(9) $\psi_M = 46{\cdot}7°$

The results of this calculation are given in Table II.

Co-ordinates of Atoms, Molecular Dimensions, and Structure Factors.—If all the hexagons in coronene were regular and of the same size, we should expect that all parallel lines connecting similar pairs of atoms in the projection should be equal in length, but this is not the case. The "spokes," *KD*, *LG*, etc., are not significantly different from the corresponding parallel inner bonds, but the outermost bonds *BC*, *EF*, and *HI*, when compared with *JK*, *KL*, and *LJ'*, respectively, show a shortening of 3·2±0·4%, while the other outer bonds are also fairly consistently decreased, but to a smaller extent, *viz.*, *A'I*, 2·0%; *HG*, 0·8%; *GF*, 1·7%; *ED*, 2·2%; *DC*, 2·7%; and *BA*, − 1·3% (expansion).

Starting with the central regular hexagon of radius 1·43 A., these observations lead to the molecular model shown in Fig. 5, with co-ordinates relative to the molecular axes as given in Table IV. 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 (*x*, *y*, *z*). The latter are collected in Table III under the columns headed (*a*), and are plotted on the contour map in Fig. 8. It can be seen that they represent what are probably the best average positions of the atomic centres. Independently estimated centres, without reference to any molecular model, are given in Table III under the columns headed (*b*), and the deviations are small.

TABLE V. *Measured and calculated values of the structure factor.*

	Sin θ (λ = 1·54).	F.			Sin θ (λ = 1·54).	F.			Sin θ (λ = 1·54).	F.	
hkl.		Meas.	Calc.	*hkl.*		Meas.	Calc.	*hkl.*		Meas.	Calc.
200	0·103	65	+65	10,04	0·695	2	− 3	609	0·893	< 2	+ 2
400	0·205	30	−31	804	0·609	< 2	2	409	0·828	< 2	− 1
600	0·307	7	+ 7	604	0·520	6	+ 8	209	0·779	7	− 6
800	0·409	< 2	0	404	0·442	10	+12	$20\bar{9}$	0·706	4	− 6
10,00	0·512	5	+ 5	204	0·375	5	+ 5	$40\bar{9}$	0·740	3	+ 5
12,00	0·614	5	− 6	$20\bar{4}$	0·306	18	−16	$60\bar{9}$	0·689	3	− 3
14,00	0·716	6	+ 5	$40\bar{4}$	0·317	16	−12	$80\bar{9}$	0·703	5	− 7
16,00	0·818	17	+18	$60\bar{4}$	0·359	3	− 2	$10,0\bar{9}$	0·731	2	+ 5
18,00	0·921	< 2	+ 2	$80\bar{4}$	0·422	< 2	0	$12,0\bar{9}$	0·773	< 2	− 3
020	0·328	16	+19	$10,0\bar{4}$	0·499	3	− 4	$14,0\bar{9}$	0·827	5	+ 1
040	0·656	< 8	0	$12,0\bar{4}$	0·581	5	− 5	$16,0\bar{9}$	0·887	4	+ 7
001	0·082	60	+60	$14,0\bar{4}$	0·671	2	− 1	$18,0\bar{9}$	0·951	3	− 2
002	0·163	29	−31	$16,0\bar{4}$	0·764	< 2	+ 1	60,10	0·970	5	− 4
003	0·245	8	+10	$18,0\bar{4}$	0·858	2	+ 3	40,10	0·909	< 2	+ 1
004	0·326	2	− 2	$20,0\bar{4}$	0·955	< 1	+ 3	20,10	0·859	2	+ 1
005	0·408	8	+ 8	14,05	0·938	< 2	+ 1	$20,\overline{10}$	0·788	< 2	0
006	0·489	8	− 9	12,05	0·848	8	− 9	$40,\overline{10}$	0·770	< 2	+ 3
007	0·571	7	+ 8	10,05	0·759	< 2	0	$60,\overline{10}$	0·764	6	− 3
008	0·652	13	+13	805	0·673	2	+ 4	$80,\overline{10}$	0·774	15	−16
009	0·734	6	− 6	605	0·590	6	− 8	$10,0,\overline{10}$	0·796	4	− 4
00,10	0·815	4	+ 3	405	0·517	7	− 7	$12,0,\overline{10}$	0·830	< 2	+ 3
00,11	0·897	2	− 1	205	0·454	5	− 6	$14,0,\overline{10}$	0·873	3	− 3
00,12	0·978	6	− 5	$20\bar{5}$	0·382	14	−12	$16,0,\overline{10}$	0·926	2	− 3
14,01	0·747	< 2	− 4	$40\bar{5}$	0·386	55	−53	40,11	0·849	< 2	+ 1
12,01	0·646	5	+ 3	$60\bar{5}$	0·414	15	−18	20,11	0·939	2	− 1
10,01	0·545	7	+ 9	$80\bar{5}$	0·463	6	+ 7	$20,\overline{11}$	0·869	< 2	0
801	0·444	10	−10	$10,0\bar{5}$	0·528	3	+ 4	$40,\overline{11}$	0·849	< 2	0
601	0·344	6	− 4	$12,0\bar{5}$	0·603	3	+ 7	$60,\overline{11}$	0·844	< 2	0
401	0·244	23	+19	$14,0\bar{5}$	0·683	< 2	+ 4	$80,\overline{11}$	0·848	3	− 4
201	0·152	32	−28	$16,0\bar{5}$	0·771	< 2	− 1	$10,0,\overline{11}$	0·865	3	− 4
$20\bar{1}$	0·106	58	+55	$18,0\bar{5}$	0·860	< 2	− 4	$12,0,\overline{11}$	0·894	< 2	+ 1
$40\bar{1}$	0·191	30	−27	$20,0\bar{5}$	0·955	4	− 6	$14,0,\overline{11}$	0·929	< 2	+ 1
$60\bar{1}$	0·288	13	+ 8	12,06	0·908	< 2	0	$20,\overline{12}$	0·949	10	−10
$80\bar{1}$	0·389	< 2	0	10,06	0·821	< 2	+ 2	$40,\overline{12}$	0·928	3	− 4
$10,0\bar{1}$	0·487	< 2	+ 3	806	0·743	< 2	+ 3	$60,\overline{12}$	0·920	< 2	+ 1
$12,0\bar{1}$	0·588	< 2	− 1	606	0·663	< 2	− 5	$80,\overline{12}$	0·913	2	+ 2
$14,0\bar{1}$	0·688	< 2	− 2	406	0·594	11	+10	$10,0,\overline{12}$	0·934	2	+ 3
$16,0\bar{1}$	0·790	23	+24	206	0·532	5	+ 5	110	0·172	10	+ 9
$18,0\bar{1}$	0·890	13	+17	$20\bar{6}$	0·461	9	+12	210	0·193	57	−56
18,02	0·988	< 1	+ 1	$40\bar{6}$	0·457	11	−10	310	0·225	56	+53
16,02	0·887	< 2	+ 2	$60\bar{6}$	0·475	8	−10	410	0·262	19	−16
14,02	0·788	< 2	+ 2	$80\bar{6}$	0·514	7	+10	510	0·304	< 5	− 3
12,02	0·687	< 2	0	$10,0\bar{6}$	0·565	6	− 6	610	0·348	8	+ 7
10,02	0·588	6	+ 6	$12,0\bar{6}$	0·631	6	− 7	710	0·395	< 6	+ 3
802	0·489	17	−19	$14,0\bar{6}$	0·706	3	− 6	810	0·441	< 7	− 4
602	0·395	48	−48	$16,0\bar{6}$	0·763	< 2	− 1	910	0·489	< 7	− 1
402	0·304	4	0	$18,0\bar{6}$	0·870	< 2	+ 2	10,10	0·536	< 7	− 3
202	0·219	12	+ 9	$20,0\bar{6}$	0·961	6	− 8	11,10	0·586	< 8	0
$20\bar{2}$	0·158	28	−27	12,07	0·973	< 1	− 1	12,10	0·628	13	+15
$40\bar{2}$	0·211	24	−27	10,07	0·892	< 2	0	13,10	0·685	20	+24
$60\bar{2}$	0·290	21	+17	807	0·813	< 2	+ 1	14,10	0·735	13	+14
$80\bar{2}$	0·382	8	− 3	607	0·739	6	− 7	15,10	0·790	< 8	+ 7
$10,0\bar{2}$	0·476	21	−21	407	0·673	20	+19	120	0·332	< 5	0
$12,0\bar{2}$	0·574	5	+ 6	207	0·615	46	+51	220	0·344	9	−10
$14,0\bar{2}$	0·672	3	− 1	$20\bar{7}$	0·545	6	− 8	320	0·363	5	+ 3
$16,0\bar{2}$	0·772	< 2	− 3	$40\bar{7}$	0·535	6	+ 6	420	0·385	< 6	− 5
$18,0\bar{2}$	0·872	6	+ 4	$60\bar{7}$	0·543	< 2	0	520	0·416	6	+ 7
$20,0\bar{2}$	0·973	< 1	+ 1	$80\bar{7}$	0·572	6	+ 6	620	0·449	5	0
16,03	0·928	< 2	0	$10,0\bar{7}$	0·615	6	− 6	720	0·486	< 7	+ 2
14,03	0·831	< 1	+ 1	$12,0\bar{7}$	0·672	7	+ 6	820	0·525	7	− 9
12,03	0·733	< 2	0	$14,0\bar{7}$	0·739	15	+15	920	0·565	< 7	+ 4
10,03	0·637	< 2	+ 1	$16,0\bar{7}$	0·810	< 2	− 2	10,20	0·607	16	+17
803	0·545	< 2	− 2	$18,0\bar{7}$	0·890	2	0	11,20	0·651	14	+12
603	0·454	18	−17	10,08	0·965	2	− 3	12,20	0·696	< 9	+ 4
403	0·370	16	−18	808	0·885	< 2	+ 1	13,20	0·741	8	+ 7
203	0·296	2	+ 1	608	0·815	< 2	+ 1	14,20	0·794	8	− 8
$20\bar{3}$	0·229	27	+24	408	0·752	5	− 4	15,20	0·839	< 7	0
$40\bar{3}$	0·258	14	+14	208	0·696	16	+19	130	0·495	15	−19
$60\bar{3}$	0·317	5	+ 7	$20\bar{8}$	0·624	2	− 7	230	0·502	< 6	+ 6
$80\bar{3}$	0·395	9	− 7	$40\bar{8}$	0·610	< 2	+ 3	330	0·516	8	+10
$10,0\bar{3}$	0·481	39	−39	$60\bar{8}$	0·614	< 2	− 1	430	0·546	< 7	+ 1
$12,0\bar{3}$	0·571	14	−17	$80\bar{8}$	0·635	< 2	+ 2	14,30	0·876	< 7	+ 5
$14,0\bar{3}$	0·667	4	+ 4	$10,0\bar{8}$	0·671	3	− 3	15,30	0·910	7	− 5
$16,0\bar{3}$	0·763	< 2	+ 2	$12,0\bar{8}$	0·717	6	+ 1	140	0·659	8	+ 8
$18,0\bar{3}$	0·860	< 2	+ 2	$14,0\bar{8}$	0·778	28	+29	240	0·665	9	− 9
16,04	0·979	< 1	0	$16,0\bar{8}$	0·844	12	+16	340	0·674	9	+10
14,04	0·884	6	− 8	$18,0\bar{8}$	0·920	< 2	−2	440	0·687	8	− 8
12,04	0·788	10	−12	809	0·963	7	−8				

The co-ordinates of Fig. 8 and Table III, (*a*), were used for a final calculation of the structure factors of all the planes. The results are collected in Table V under "F, calc." An average atomic scattering curve, found suitable for carbon atoms in aromatic hydrocarbons of the anthracene type, was used (Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 110). The agreement between the observed and the calculated values of F, expressed in the usual way as a sum of all the discrepancies divided by the total of the measured structure factors, is 14·0% for the (*h*0*l*) reflections, and 13·1% for all the reflections. This discrepancy is of about the order usually encountered in such investigations, and there is little doubt that some of it is due to the distribution of electron density between the atoms, which is not allowed for in the scattering curves employed.

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CHEMISTRY DEPARTMENT, UNIVERSITY OF GLASGOW.

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