

187. *The Crystal Structure of the Orthorhombic Modification of 1 : 2 : 5 : 6-Dibenzanthracene. A Quantitative X-Ray Investigation.*

By J. MONTEATH ROBERTSON and J. G. WHITE.

The crystal and molecular structure of the orthorhombic modification of 1 : 2 : 5 : 6-dibenzanthracene has been determined by quantitative X-ray analysis. The molecular arrangement in the crystal is quite different from that found for other aromatic hydrocarbons (*e.g.*, anthracene, coronene, or pyrene). There are four molecules in the unit cell and these each possess an exact centre of symmetry (space-group *Pcab*). The molecules lie approximately in layers along the 200 planes, to which they are tilted at an angle of about 31°; 9 out of the 11 carbon atoms are separately resolved in the Fourier maps, and the bond lengths connecting these atoms can be directly measured. These vary from 1.38 to 1.45 Å.

An approximate calculation of the bond distances from the 12 stable valency-bond structures for dibenzanthracene is given, but there is less agreement with the observed values than was found in coronene and pyrene.

Unfortunately, the accuracy is not likely to be quite as high as in the other structures mentioned above. In the central ring of the molecule the resolution is good and here the error should not exceed ± 0.02 Å. In the outer parts of the molecule the bond-length variations (Fig. 3) must be considered rather doubtful. It is shown, however, that the co-ordinates given lead to better structure factor agreements than can be obtained from any regularised model.

RECENT X-ray measurements on coronene and pyrene (Robertson and White, *J.*, 1945, 607; this vol., p. 358) have established that the carbon-carbon bond lengths vary slightly in different parts of these molecules. These variations are small, in fact, not much greater than the possible experimental error under present conditions; nevertheless, the variations do seem to conform to a fairly definite pattern which is capable of at least partial explanation in terms of the more important structures which contribute to the normal states of these molecules.

We have now extended our measurements to 1 : 2 : 5 : 6-dibenzanthracene. This hydrocarbon exists in two distinct crystalline modifications, monoclinic and orthorhombic. Preliminary data for the monoclinic form have been given by Iball and Robertson (*Nature*, 1933, 132, 750). The orthorhombic form, with which we are concerned in the present paper, was first described by Krishnan and Banerjee (*Z. Krist.*, 1935, 91, 170, 173), who studied the magnetic anisotropy of the crystal and from their measurements of the magnetic susceptibilities were able to deduce the approximate orientation of the molecules. Accurate values for the cell dimensions, and a determination of the space-group have been given by Iball (*Nature*, 1936, 137, 361), but detailed atomic positions have not been given by any of these authors.

The crystal structure and molecular arrangement in orthorhombic dibenzanthracene differs from that of both the coronene and the pyrene structures. Like coronene, the molecules are found to display an exact centre of symmetry and to this extent the analysis is simplified. However, the unit cell contains four complete molecules and their mutual arrangement (see Figs. 1 and 2) makes it impossible to obtain resolution of all the atoms in any projection of the structures. In this respect the results obtained from the present two-dimensional analysis resemble the pyrene results, and they should similarly be regarded as a preliminary analysis, carried out with as much accuracy as possible, which must be undertaken before any further refinement by more elaborate three-dimensional methods can be attempted. In the present case the most favourable Fourier projection of the structure (Fig. 1) shows separate resolution of nine out of the eleven crystallographically independent carbon atoms, and direct measurements of these positions can be made. The results indicate certain bond-length variations, as shown in Fig. 3. These figures represent the most probable values, but they are unfortunately subject to certain errors. The accuracy in the central ring should be reasonably high, the errors here probably not exceeding ± 0.02 Å. In the other parts of the molecule the observed bond-length variations must be considered rather doubtful.

Description of the Structure.—Crystal data. 1 : 2 : 5 : 6-Dibenzanthracene, $C_{22}H_{14}$; *M*, 278.3; *m. p.* 267.5°; *d*, calc. 1.294, found 1.282; orthorhombic bipyramidal, *a* = 8.22, *b* = 11.39, *c* = 15.14 Å. (Iball). Absent spectra, (*0kl*) when *l* is odd, (*h0l*) when *h* is odd, (*hk0*) when *h* is odd. Space-group D_{2h}^{16} (or Q_h^{16}) (*Pcab*). Four molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell, 1418 Å.³. Absorption coefficient for X-rays, $\lambda = 1.54$ Å., $\mu = 6.78$ cm.⁻¹; $\lambda = 0.71$ Å., $\mu = 0.86$ cm.⁻¹. Total number of electrons per unit cell = F(000) = 584.

Structure analysis. The space-group *Pcab* with only four molecules in the unit cell requires that the molecules must possess centres of symmetry which coincide with the crystallographic centres of symmetry. The asymmetric unit may therefore be taken as one half of the chemical

FIG. 1(a).

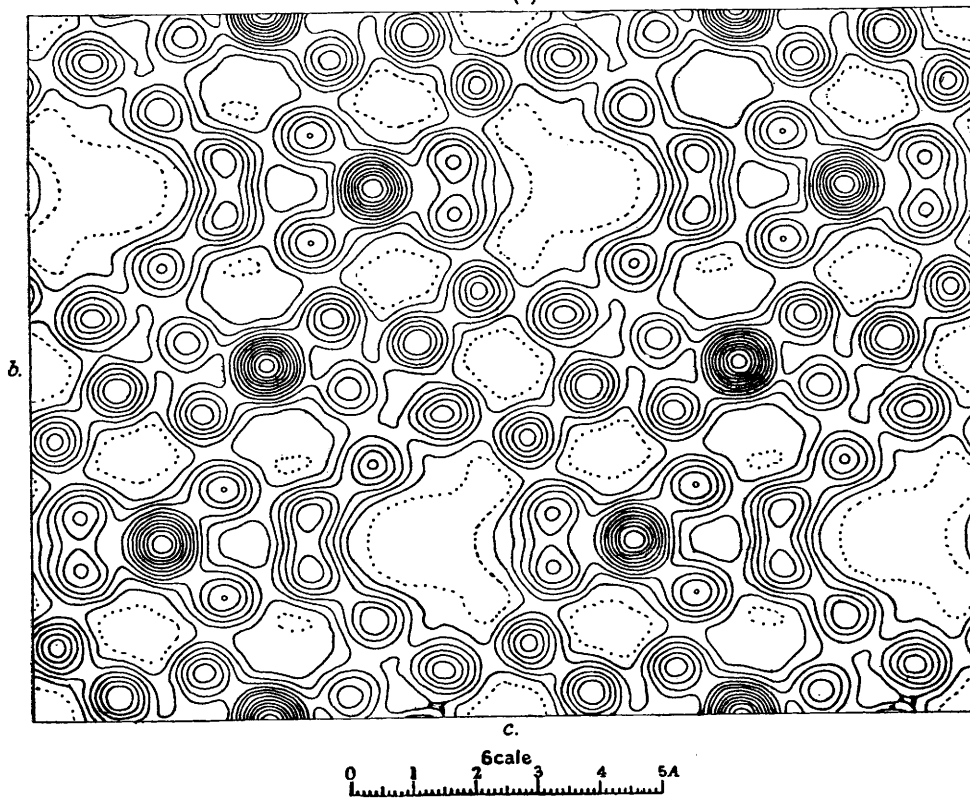
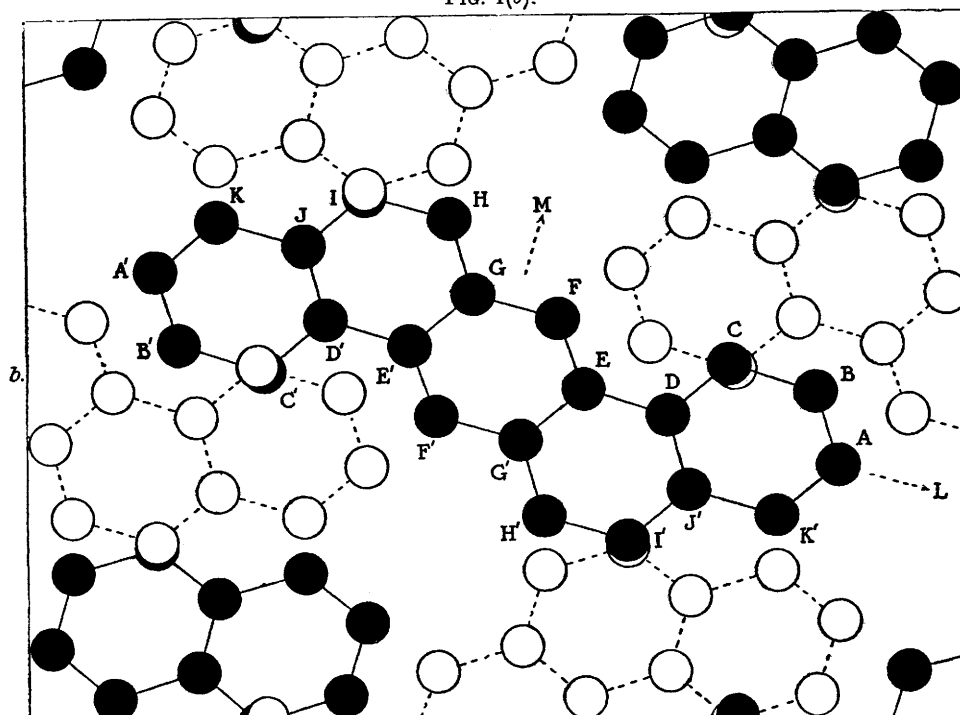


FIG. 1(b).



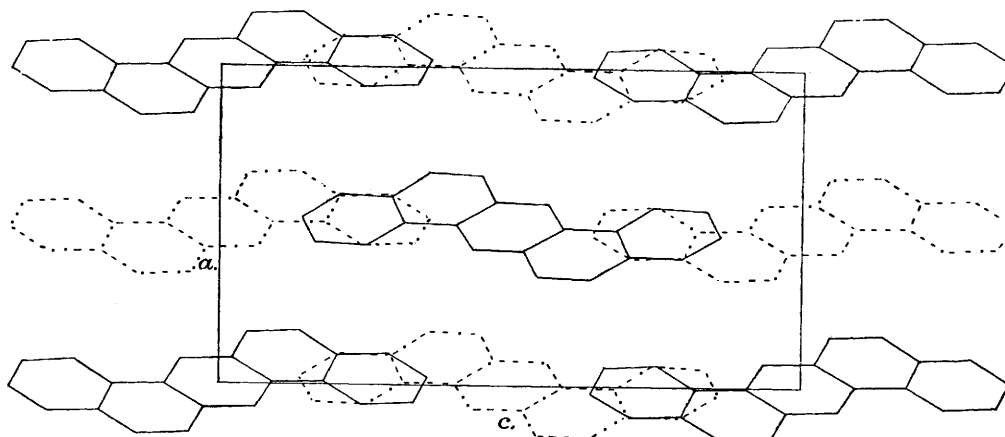
Projection along the *a* axis on the (100) or *bc* plane. The molecules are inclined at about 31° to the projection plane. Each contour line corresponds to a density increment of one electron per \AA^2 , the one-electron line being dotted.

molecule, or eleven carbon atoms, if we neglect the hydrogen atoms. As a first approximation a regular planar structure was assumed, according to the usual chemical formula.

The magnetic measurements of Krishnan and Banerjee (*loc. cit.*) give the tilt of the molecular plane to the bc plane as 29° , and these authors predict that the long axis of the molecule (L in Fig. 1*b*) probably lies along the c axis of the crystal. The first of these observations is probably fairly accurate, but the second can only be an approximation. Now, the strength of the (200) reflection ($F = 153$) suggests that if the molecular plane is inclined at about 30° to the bc plane, as the magnetic measurements suggest, then the line of zero tilt in the molecule must be its longest axis, that is, the molecular axis L must lie in, or very nearly in, the bc plane.

Bearing these factors in mind, only one degree of freedom remains to be fixed, the angle which L makes in the bc projections with the crystal axis c (or b). A suitably drawn projection of the molecules may then be pivoted about the centre of symmetry in the bc plane and the effect of various positions on the $(0kl)$ structure factors may be tested by inspection or simple calculation. In practice the (020) structure factor was used as an index, as its low value ($F = 24$) makes it extremely sensitive. When the molecular axis L is made to coincide with the crystal axis c the calculated value of this structure factor is much too large, but it can be brought to the correct value by a rotation of about 16° away from the c direction. A further small rotation would make

FIG. 2.



View of the molecular arrangement projected on the 010 plane. The dotted molecules are situated half a translation along the b axis.

this structure factor pass through zero and assume a negative value, but this possibility can be ruled out by the calculation of certain other structure factors.

Detailed calculations on this basis gave reasonably good agreements between the measured and the calculated values of all the structure factors, and it was possible to proceed immediately to further refinement of the atomic positions by Fourier series methods. Two successive Fourier syntheses of the $(0kl)$ zone were carried out, 50 terms being included in the first, and 56, all the reflections which could be observed in this zone, in the second. The results of this final synthesis are given by the contour map of Fig. 1*a*), from which it can be seen that nine out of the eleven crystallographically independent atoms are resolved. The other two atoms, C and I , are obscured by the overlapping of related atoms in adjoining molecules as indicated in Fig. 1*b*).

The y and z co-ordinates finally adopted were obtained from those actually measured on this map after a correction for incompleteness of the Fourier series due to Booth (*Nature*, 1945, 156, 51). In this method a Fourier synthesis of the same zone is carried out using the calculated instead of the observed values of the structure factors and omitting all terms which are omitted in the final Fourier synthesis. The resulting map was found to give certain small changes in the atomic positions and these shifts were added to the observed co-ordinates but with opposite sign. This led to a slight improvement in the agreements between the measured and the calculated values of the structure factors, as described below. (Experimental Section).

The x co-ordinates of the atoms cannot be obtained directly, as the other possible projections would give little information because of overlapping effects. These co-ordinates can only be calculated on the assumption that the molecule is planar, but this assumption is well supported

by the agreements obtained between the calculated and the observed values of the structure factors for the other two zones.

A complete picture of the crystal symmetry may be obtained by considering Fig. 1 in conjunction with Fig. 2, which shows diagrammatically the projection along the b axis.

Orientation, co-ordinates, and dimensions. By assuming a planar molecule and averaging certain distances as described more fully in the Experimental Section, it is possible to calculate the orientation of the molecule. The results are given in Table I, where χ , ψ , and ω are the angles which the molecular axes L and M [Fig. 1 (b)] and their perpendicular, N , make with the a , b , and c crystallographic axes. These results give the inclination of the molecular plane to the (100) plane, expressed by χ_N , as 31.3° in reasonably good agreement with the value of 29° predicted by Krishnan and Banerjee (*loc. cit.*).

TABLE I.

Orientation of the molecule in the crystal.

$\chi_L = 92.1^\circ$	$\cos \chi_L = -0.0374$	$\chi_M = 58.8^\circ$	$\cos \chi_M = 0.5180$
$\psi_L = 106.1^\circ$	$\cos \psi_L = -0.2771$	$\psi_M = 35.3^\circ$	$\cos \psi_M = 0.8162$
$\omega_L = -16.2^\circ$	$\cos \omega_L = 0.9601$	$\omega_M = 75.2^\circ$	$\cos \omega_M = 0.2558$
	$\chi_N = 31.3^\circ$	$\cos \chi_N = 0.8545$	
	$\psi_N = 120.5^\circ$	$\cos \psi_N = -0.5069$	
	$\omega_N = 96.5^\circ$	$\cos \omega_N = -0.1130$	

The co-ordinates with respect to the crystal axes are collected in Table II; y_1 and z_1 are the co-ordinates of the resolved atoms measured directly from the Fourier projection, while y_2 and z_2 are the values finally adopted after correction for the incompleteness of the Fourier series. It will be seen that the difference is small. The co-ordinates of the two atoms C and I which cannot be directly measured are those which the atoms would have in a regular hexagonal molecule in the above orientation. These positions are in agreement with the appearance of the double peaks shown in Fig. 1(a) but the centres cannot be assigned with any great certainty.

Table II lists the co-ordinates (x, y, z) for the eleven carbon atoms in the asymmetric crystal unit; the co-ordinates of all the other atoms in the unit cell may be obtained from these by the relations appropriate to the space-group $Pcab$, *viz.*,

$$\pm (x, y, z; 1/2 + x, 1/2 - y, z; x, 1/2 + y, 1/2 - z; 1/2 - x, y, 1/2 + z)$$

TABLE II.

Co-ordinates. Centre of symmetry as origin; y_1 and z_1 are co-ordinates measured directly, y_2 and z_2 co-ordinates adopted after correction.

Atoms [cf. Fig. 1(b)].	x , A.	y_1 , A.	y_2 , A.	z_1 , A.	z_2 , A.	$2\pi x/a$.	$2\pi y_2/b$.	$2\pi z_2/c$.
A	-0.215	-1.580	-1.584	5.465	5.476	-9.4°	-50.1°	130.3°
B	0.444	-0.380	-0.392	5.094	5.108	19.4	-12.4	121.4
C	0.504	0.020	0.020	3.723	3.723	22.1	0.6	88.5
D	-0.095	-0.776	-0.770	2.738	2.740	-4.2	-24.3	65.1
E	-0.028	-0.370	-0.354	1.382	1.392	-1.2	-11.2	33.2
F	0.600	0.786	0.794	0.992	0.978	26.2	25.0	23.3
G	0.647	1.198	1.172	-0.384	-0.376	28.3	37.1	-8.9
H	1.328	2.400	2.404	-0.760	-0.740	58.2	76.0	-17.6
I	1.381	2.794	2.794	-2.097	-2.097	60.5	88.3	-49.8
J	0.769	1.980	1.978	-3.076	-3.063	33.7	62.6	-73.0
K	0.827	2.380	2.388	-4.452	-4.448	36.2	75.3	-105.9

The molecular dimensions and bond lengths may be calculated from these co-ordinates and are shown graphically in Fig. 3. The ringed atoms are those separately resolved in Fig. 1, and the bond distances between these atoms are the only ones which can be obtained directly.

From the orientation of the molecule and the co-ordinates given in Table II the molecular co-ordinates of the atoms may be calculated and these are collected in Table III.

Intermolecular distances. The closest distance of approach between atoms of different molecules occurs between the standard molecule and the reflected molecule at $(1/2 - x, y, 1/2 + z)$. Between C on the standard molecule and J on this reflected molecule the distance is 3.54 Å., while between F and A' the atoms are 3.56 Å. apart. Other distances in this direction are CD' 3.76 Å., CK 3.71 Å., EB' 3.87 Å., and FK 3.78 Å. The distances are not quite so close between the first molecule and the reflected molecule at $1/2 + x, 1/2 - y, z$, where the atom I on the standard molecule is 3.59 Å. from D' on the reflected molecule, 3.75 Å. from J , and 3.82 Å.

TABLE III.

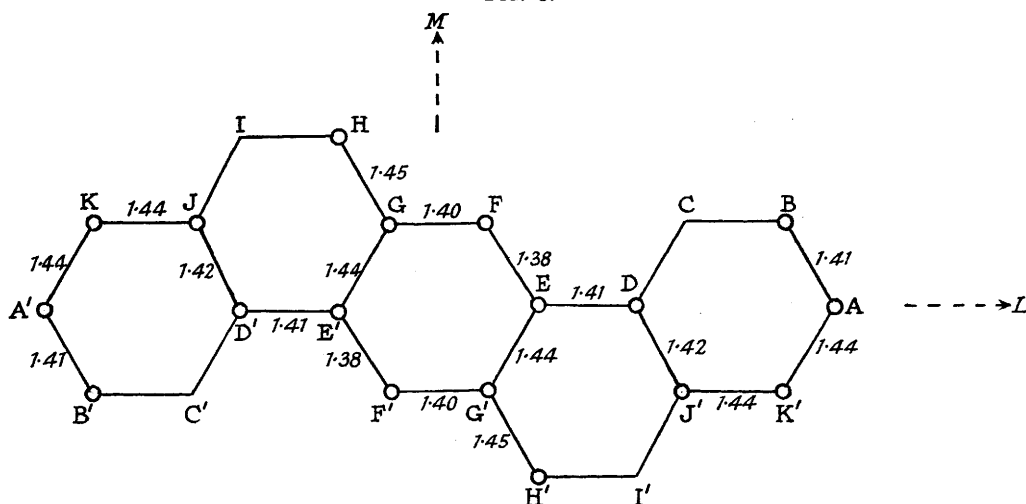
Co-ordinates with respect to molecular axes.

Atom.	L, Å.	M, Å.	N, Å.	Atom.	L, Å.	M, Å.	N, Å.
A	5.703	-0.003	0	G	-0.708	1.196	0
B	4.996	1.218	0	H	-1.427	2.460	0
C	3.550	1.230	0	I	-2.840	2.460	0
D	2.847	0.023	0	J	-3.520	1.229	0
E	1.435	0.050	0	K	-4.964	1.240	0
F	0.696	1.209	0				

from E'. All other pairs of atoms are more than 4 Å. apart, and the distances given above are just about the same as the usual intermolecular distances encountered in hydrocarbon structures.

It will be noted that in the dibenzanthracene structures all the primitive translations are greater than 8 Å., and we do not encounter pairs of molecules which directly overlie one another as in the phthalocyanine; coronene, or pyrene structures. It is therefore not profitable to discuss the normal projections of pairs of parallel molecules in this case, because they are widely separated and interleaved with parts of other differently oriented molecules.

FIG. 3.



Dimensions of the molecule of 1 : 2 : 5 : 6-dibenzanthracene.

Discussion of Results.—The bond-length measurements given in Fig. 3 vary from 1.38 to 1.45 Å., a slightly larger range than that found in coronene, and about the same as that found in pyrene (Robertson and White, *loc. cit.*). Unfortunately, the accuracy obtained in the present investigation is not likely to be quite as high as in these other structures. The unusually large values found for *GH*, *JK*, and *KA'* are very difficult to assess, as the atoms *H* and *K* are so distorted by their proximity to the corresponding atoms in the reflected molecule that their centres are rather more uncertain than those of the other resolved atoms. These bond lengths must therefore be considered as rather doubtful. The central ring, however, is quite free from any such distorting effects, and here the maximum error in the bond lengths should not be greater than ± 0.03 Å., and probably does not exceed ± 0.02 Å. The bond *GE* is, therefore, probably longer than the other two independent bonds in this ring, which are both very close to the benzene value of 1.39 Å.

Beyond this fairly definite conclusion little can be said with certainty. It will be noted that the dibenzanthracene molecule contains no symmetry element apart from the centre that can be used to average the bond lengths into any system of groups, as was done for coronene. However, the measurements recorded in Fig. 3 do receive a measure of general support from the very satisfactory agreements obtained between the observed and calculated values of the structure factors (Table IV). These agreements are better than can be obtained from any regular model placed in the same orientation.

For comparison with the results obtained for coronene and pyrene (Robertson and White,

is little agreement. The widest divergence is in the bond $K'A$, which is calculated as rather shorter than the benzene value and found experimentally longer than the graphite distance. As stated above, the position of K is rather uncertain, and under such conditions agreement could not be expected.

Structures (I) and (II) each contain four benzenoid rings, (III) and (IV) each contain three, and (V) and (VI) each contain only two, the remaining rings being quinonoid in type. If we attempt to apply the Fries rule, by preferring those structures which contain the largest number of benzenoid rings, the effect on the above calculations is disappointing. The bond lengths in the central ring tend to become equalised at the benzene value of 1.39 Å., and in the other parts of the molecule more extreme values are obtained, which are not in agreement with the observations.

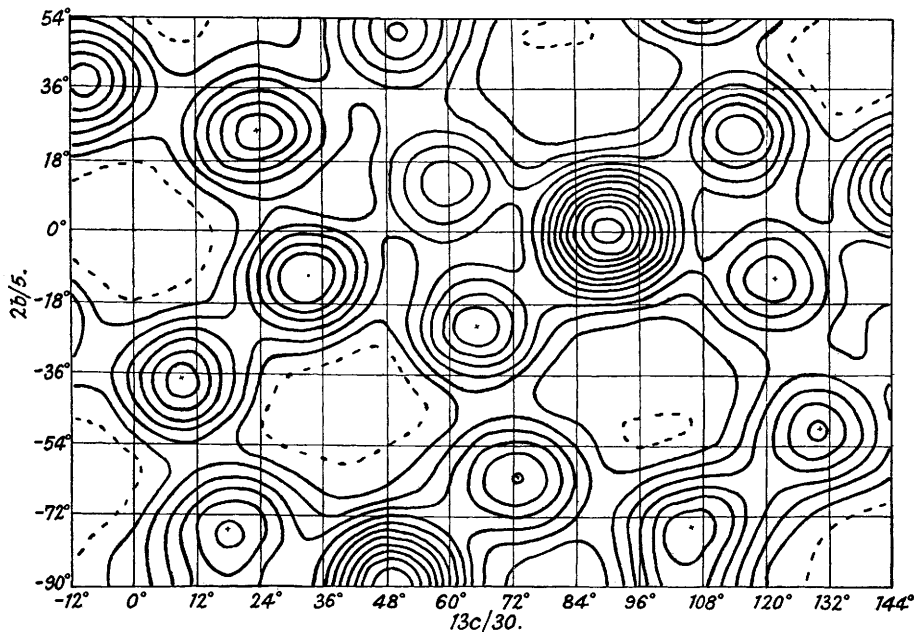
While lack of agreement in the outlying parts of the molecule may be due to experimental error to some extent, it should be noted that no rigorous theoretical derivation of bond lengths in a molecule of this shape has yet been made. It is possible that the excited structures (completely neglected in the above treatments) may play an appreciable part in such an asymmetric molecule, while in more symmetric molecules of the coronene type they may be relatively less important.

The calculated average value for the bond lengths in (VIII) is 1.41 Å., while the experimental average is 1.42 Å. The latter figure is, surprisingly, rather larger than that usually found in polycyclic aromatic hydrocarbons. It would, however, be necessary to determine the primitive translations of the crystal with greater accuracy before attaching undue importance to this average figure.

EXPERIMENTAL.

X-Ray Measurements.—Most of the X -ray work was carried out photographically with $\text{Cu-}K\alpha$ radiation ($\lambda = 1.54$), using rotation, oscillation, and moving-film methods. In addition, certain absolute measurements were made on the ionisation spectrometer, using monochromatic copper and molybdenum radiation.

FIG. 4.



Co-ordinates assigned to the resolved atoms in the bc projection of dibenzanthracene.

Some very beautifully formed specimens of the crystals were supplied by Dr. Iball, crystallised from ethyl acetate. These crystals appear to be remarkably stable and are little affected by exposure to X -rays; we have used some of them for many years as sub-standards for calibration purposes in absolute intensity work.

For the present investigation the intensity work was carried out mainly on three different specimens, which weighed 0.116, 0.081, and 0.0665 mg., respectively. These specimens were selected so that on rotation the path of the X -ray beam in the crystal did not vary by more than about 0.2 mm., and relative

TABLE IV.

Measured and calculated values of the structure factor.

<i>hkl.</i>	$\sin \theta$ ($\lambda = 1.54$).	F, meas.	F, calc.	<i>hkl.</i>	$\sin \theta$ ($\lambda = 1.54$).	F, meas.	F, calc.
002	0.102	50	-49	048	0.488	7	+4
004	0.203	13	-14	058	0.529	5	+8
006	0.303	10	+16	068	0.574	8	+12
008	0.407	30	-27	078	0.624	28	-27
00,10	0.508	16	-19	088	0.677	34	+31
00,12	0.610	< 5	- 6	098	0.731	13	-14
00,14	0.711	< 5	+ 3	0,10,8	0.789	< 5	0
00,16	0.812	< 4	+ 2	0,11,8	0.848	< 4	0
00,18	0.916	< 3	- 3	0,12,8	0.906	< 3	- 3
				0,13,8	0.968	< 2	- 2
020	0.135	24	+34	01,10	0.510	8	+7
040	0.270	55	+50	02,10	0.524	7	-6
060	0.406	10	-7	03,10	0.545	4	+2
080	0.541	15	-6	04,10	0.573	6	-11
0,10,0	0.676	< 5	0	05,10	0.608	< 5	+8
0,12,0	0.810	< 4	-1	06,10	0.648	< 5	+5
0,14,0	0.946	< 3	+2	07,10	0.693	6	-6
				08,10	0.740	9	-11
200	0.188	153	+170	09,10	0.793	< 5	0
400	0.375	7	-5	0,10,10	0.847	< 4	+1
600	0.562	< 5	-3	0,11,10	0.901	< 4	0
800	0.749	5	-8	0,12,10	0.957	< 3	-2
				01,12	0.611	8	+7
012	0.122	28	+35	02,12	0.623	31	+42
022	0.169	4	-2	03,12	0.641	27	+32
032	0.227	43	-36	04,12	0.665	9	+9
042	0.289	40	-38	05,12	0.696	< 5	+1
052	0.354	37	+30	06,12	0.731	4	+3
062	0.419	45	-43	07,12	0.712	< 5	+4
072	0.484	< 4	-7	08,12	0.815	< 4	+2
082	0.551	< 4	-1	09,12	0.861	< 4	-1
092	0.617	< 5	-2	0,10,12	0.910	< 3	-2
0,10,2	0.684	< 5	+2	0,11,12	0.962	< 3	-1
0,11,2	0.750	< 5	-3	01,14	0.712	< 5	-2
0,12,2	0.817	5	-5	02,14	0.721	13	-14
0,13,2	0.883	6	+6	03,14	0.738	8	+8
0,14,2	0.952	< 3	-3	04,14	0.760	< 5	-3
014	0.214	26	+22	05,14	0.787	< 5	0
024	0.244	4	+5	06,14	0.818	< 4	-1
034	0.287	34	-29	07,14	0.854	< 4	-4
044	0.338	4	-5				
054	0.394	6	+4	201	0.194	52	+54
064	0.454	7	+13	202	0.212	50	-41
074	0.515	4	+4	203	0.240	9	+11
084	0.578	< 4	-5	204	0.275	10	-13
094	0.642	11	+11	205	0.314	7	-5
0,10,4	0.707	24	+23	206	0.356	< 5	+5
0,11,4	0.772	26	+23	207	0.400	41	+36
0,12,4	0.835	< 4	+3	208	0.446	18	-12
0,13,4	0.901	< 4	-2	209	0.492	< 7	+3
0,14,4	0.968	< 2	+2	20,10	0.539	< 7	+5
016	0.311	19	+23	20,11	0.587	30	+37
026	0.333	35	-27	20,12	0.635	14	+14
036	0.366	36	+33	20,13	0.684	13	-14
046	0.407	29	-28	20,14	0.732	< 8	+4
056	0.456	40	-40	20,15	0.786	7	+5
066	0.508	19	-19	401	0.378	17	-18
076	0.563	5	+6	402	0.388	< 6	+4
086	0.621	< 5	-2	403	0.405	23	-20
096	0.681	6	-4	404	0.426	36	-37
0,10,6	0.740	4	-7	405	0.453	9	-12
0,11,6	0.795	< 5	-12	406	0.482	7	+2
0,12,6	0.867	< 4	-1	407	0.516	14	+10
0,13,6	0.930	< 3	-1	408	0.551	< 7	+8
0,14,6	0.994	< 2	-2	409	0.590	15	-13
018	0.410	20	+21	40,10	0.630	< 8	+1
028	0.427	< 3	+2	40,11	0.671	28	+29
038	0.454	21	-25	40,12	0.714	15	+16

TABLE IV.—continued.

Measured and calculated values of the structure factor.

<i>hkl.</i>	$\sin \theta$ ($\lambda = 1.54$).	F, meas.	F, calc.	<i>hkl.</i>	$\sin \theta$ ($\lambda = 1.54$).	F, meas.	F, calc.
40,13	0.760	< 8	+ 1	260	0.448	13	+ 15
40,14	0.800	< 8	- 6	280	0.574	13	- 7
40,15	0.853	10	+ 6	2,10,0	0.703	< 9	- 3
601	0.565	12	-14	320	0.312	76	- 76
602	0.570	10	+10	340	0.389	16	+ 15
603	0.582	9	+11	360	0.494	< 7	- 2
604	0.597	39	-31	380	0.610	19	+ 15
605	0.616	8	- 9	3,10,0	0.733	16	+ 7
606	0.638	< 8	+ 3	420	0.399	60	+ 60
607	0.664	< 8	- 2	440	0.463	10	- 9
608	0.691	< 8	+ 4	460	0.553	9	+ 5
609	0.722	< 8	+ 3	480	0.659	< 8	+ 2
801	0.753	< 8	0	4,10,0	0.773	15	- 9
802	0.760	< 8	- 2	520	0.487	20	- 19
803	0.766	16	+12	540	0.541	< 8	- 12
804	0.780	10	- 5	560	0.620	16	+ 16
				580	0.716	< 9	0
120	0.165	71	- 71	5,10,0	0.823	11	+ 7
140	0.287	36	+ 34	620	0.578	9	- 10
160	0.417	17	- 20	640	0.624	14	+ 11
180	0.549	21	+ 19	660	0.693	7	- 7
1,10,0	0.682	< 8	0	680	0.780	< 8	+ 4
220	0.232	108	+108	720	0.670	< 8	0
204	0.330	10	- 8	740	0.710	< 9	- 2

absorption corrections for different reflections in the same zone were neglected. Most of the intensities were measured from calibrated films, using an integrating photometer of the type described by Robinson (*J. Sci. Instr.*, 1933, 10, 233). Only a few of the weakest reflections were estimated visually.

The absolute measurements were made directly on the ionisation spectrometer, with monochromatic rays, and also by means of sub-standards, employing the photographic technique (Robertson, *ibid.*, 1943, 20, 175). The usual formulæ and correction factors for mosaic crystal specimens were employed.

Fourier Analysis.—Using the phase constants obtained initially from the trial structures and the measured values of F, a double Fourier series was set up according to the usual formulæ. The electron density was computed at 450 points on the asymmetric unit, the *b* axis being divided into 60 parts (intervals of 0.190 Å.) and the *c* axis into 60 parts (intervals of 0.252 Å.). The summations were 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 both the rows and columns. The resulting contour map is shown in Fig. 1, the whole unit cell being included.

Orientation of the molecule and co-ordinates. From an inspection of the observed lengths in projection of *ED* and parallel distances, which can be only very slightly tilted, it was found that the best average radius of the hexagons is 1.42 Å. With this average value and the assumptions that *L* and *M* are at right angles and that the molecule is planar, it was possible to calculate the orientation of the molecule with respect to the crystallographic axes.

The distances *FG'*, *EH'*, and *BK'* as measured from the projection given in Fig. 1 are 2.102 ± 0.040 Å., and from the assumed mean radius of the hexagons (1.42 Å.) the angle χ_M which *M* makes with the *a* crystal axis is obtained as 58.8° . The inclination of *L* cannot be derived in this way because it is very near to 90° . The calculation may, however, be made from the observed angle between *L* and *M* in the projection. The projected lines *ADE*, *BF*, and *K'J'G'* are inclined at a mean angle of $-16.1^\circ \pm 0.6^\circ$ to the *c* axis, and the lines *BK'*, *EH'*, and *FG'* make the mean angle of $72.6^\circ \pm 0.3^\circ$ with *c*. From these figures the complete orientation of the assumed regular planar molecule may be obtained by relations similar to those already given for the coronene analysis (Robertson and White, *loc. cit.*).

The next step consists of assigning the most probable positions to the centres of the resolved atoms, without the aid of any regularised model. The positions finally adopted after the Booth corrections for incompleteness of the Fourier series, etc., are shown by small crosses in Fig. 4. From these positions and the orientation now calculated, the actual molecular co-ordinates may be obtained (Table III), and the interatomic distances readily follow. The crystal co-ordinates are given in Table II.

The structure factors of the (*0kl*) zone have been recalculated on various assumptions, and the mean discrepancy, expressed as

$$\frac{\sum \{ |F_{\text{meas.}}| - |F_{\text{calc.}}| \}}{\sum F_{\text{meas.}}}$$

has been evaluated with the following results. For a regular hexagonal model with a constant carbon-carbon distance of 1.42 Å. placed in the best orientation, the discrepancy is 16.1%. For the co-ordinates obtained directly from the contour maps (Figs. 1 and 4) without any assumptions about regularity (y_1, z_1 in Table II), the discrepancy is reduced to 15.0%. After the Booth corrections, the final values for the co-ordinates, which are used for calculating the bond lengths (y_2, z_2 in Table II), give a discrepancy of 13.8%. The differences between these figures are small, and their significance is difficult to estimate, but they do seem to justify the use of our final co-ordinates as being preferable to any set of regularised co-ordinates.

In calculating the structure factors the scattering curve formerly used for hydrocarbons (Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 110) was found to be rather unsuitable, as the calculated values for small spacing planes were consistently higher than the observed values. For the large spacing planes the tendency was for the observed structure factors to be larger than the calculated. In order to keep the upper part of the scattering curve at the usual values, all the absolute F 's were multiplied by a scale correction factor of 0.84 and then an empirical scattering curve was drawn for $\sin \theta = 0.5-0.9$. The values used for this range are given below (max. $f_c = 100$).

$\sin \theta (\lambda = 1.54)$	0.5	0.6	0.7	0.8	0.9
f_c	23.5	15.0	9.5	7.0	4.5

The general agreements calculated from the final co-ordinates are quite as good as are usually found in this type of analysis. The discrepancies are 13.8% for the $(0kl)$ zone, 12.0% for the $(h\bar{h}0)$ zone, and 13.2% for the $(h0l)$ zone. For all structure factors the mean discrepancy is 12.6%. The measured and calculated values of the structure factors are collected in Table IV.

We thank Professor J. W. Cook, F.R.S., and Dr. J. Iball for pure specimens of material used in this work, and Dr. Iball for much valuable preliminary data. We are also indebted to the Royal Society for a grant which defrayed the cost of some of the apparatus employed.

UNIVERSITY OF GLASGOW.

[Received, November 4th, 1946.]