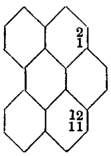
285. *The Crystal Structure of* 1 : 12-*Benzperylene : A Quantitative X-Ray Investigation.*

By J. G. White.

The crystal and molecular structure of 1 : 12-benzperylene has been determined by quantitative *X*-ray analysis. There are four molecules in the unit cell, and the structure resembles that of pyrene, but involves a considerably larger tilt of the plane of the molecule to the (010) plane. The accuracy of the analysis is limited by overlapping of adjoining molecules. In the most favourable Fourier projection, 11 of the 22 carbon atoms in the molecule are resolved and the measured bond distances between these atoms vary from 1·38 to 1·43 A. The variations in bond distances in different parts of the molecule are very similar to the corresponding variations noted in the case of coronene and are discussed in terms of the 14 non-excited valency-bond structures applicable to 1 : 12-benzperylene.

In recent investigations on the aromatic hydrocarbons coronene, pyrene, and 1 : 2 : 5 : 6-dibenzanthracene (Robertson and White, *J.*, 1945, 607; 1947, 358, 1001) small variations in carbon–carbon bond lengths in different parts of the molecules have been detected. In coronene and pyrene these variations are in qualitative agreement with calculations of the bond distances from the non-excited valency-bond structures alone. In the case of dibenzanthracene the agreement between the observed bond distances and those calculated on this basis is not quite so satisfactory, although the experimental data for this compound are rather less certain than for the other two. As has been pointed out in connection with coronene (Robertson and White, *loc. cit.*) the apparent agreements may be fortuitous, for in such complex molecules the excited structures must play a considerable part. Coulson's rigorous molecular orbital calculations on coronene (*Nature*, 1944, **154**, 797), however, are also supported by the *X*-ray measurements. The structure of 1 : 12-benzperylene (I), now described, is of interest in that this molecule differs by only two carbon atoms from that of coronene, and the *X*-ray measurements on coronene are the most accurate of those mentioned above. Unfortunately, the crystal structure of benzperylene is much less favourable for *X*-ray analysis than that of coronene. There are four molecules instead of two in the unit cell and in this respect the structure is similar to that of pyrene (Robertson and White, *loc. cit.*). Because of the overlapping of adjoining molecules only 11 of the 22 crystallographically independent atoms are resolved even in the most favourable Fourier projection, and accurate molecular dimensions are consequently incomplete. Although some interesting variations in carbon–carbon bond distances have been observed, complete and accurate data can be obtained only from a full three-dimensional analysis of the structure, and, as was the case with pyrene and 1 : 2 : 5 : 6-dibenzanthracene, one of the principal objects of the present investigation has been to refine the atomic parameters to the point where such a three-dimensional analysis can be undertaken.



(I.)

Description of the Structure.

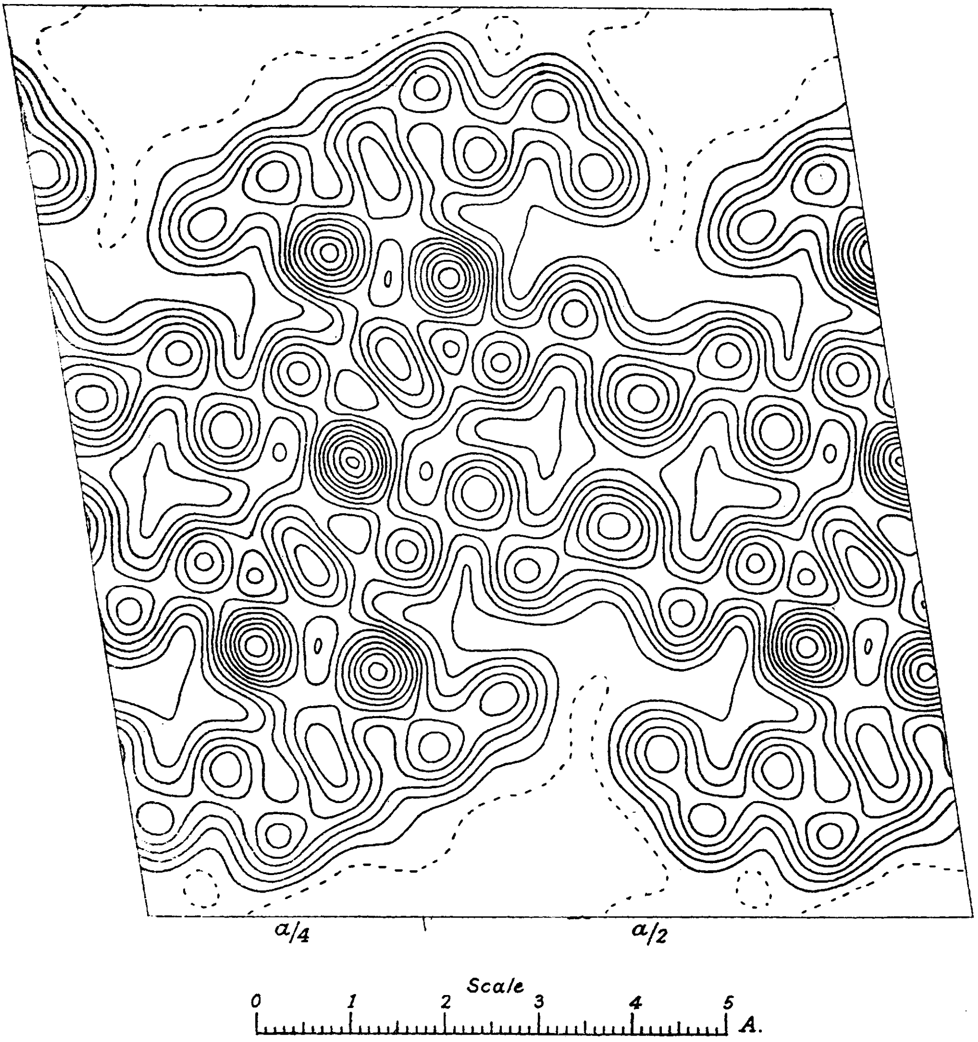
Crystal Data.—1 : 12-Benzperylene, $C_{22}H_{12}$; *M*, 276·3; m. p. 273°; *d*, calc. 1·338, found 1·349; monoclinic prismatic, $a = 11{\cdot}72 \pm 0{\cdot}05$, $b = 11{\cdot}88 \pm 0{\cdot}05$, $c = 9{\cdot}89 \pm 0{\cdot}03$ A., $\beta = 98{\cdot}5^\circ \pm 0{\cdot}2^\circ$. Absent spectra, (*h*0*l*) when *h* is odd; (0*k*0) when *k* is odd. Space-group $C_{2h}^5(P2_1/a)$. Four molecules per unit cell. No molecular symmetry. Volume of the unit cell, 1362 A.^{3}. Absorption coefficient for *X*-rays ($\lambda = 1{\cdot}54$), $\mu = 7{\cdot}01$ per cm. Total number of electrons per unit cell = F(000) = 576.

The crystals are in the form of prisms, the most prominent faces being (001) and (110). The (010) face was observed in only one crystal specimen.

Analysis of the Structure.—The asymmetric crystal unit consists of one complete molecule, and as a first approximation a regular, planar, hexagonal, model may be assumed in accordance with the usual chemical formula. Now the *b*-axis in benzperylene is appreciably larger than that of pyrene, *viz.*, 9·24 A. (Robertson and White, *loc. cit.*). This suggests that in benzperylene also there are two molecules accommodated in one *b*-axis translation, but tilted rather more steeply to (010) than in the pyrene or coronene structures.

A tilt of the molecular plane to (010) of about 55° being assumed, there remain five more degrees of freedom to be fixed, *viz.*, two more orientation angles and the free translations, x_p, y_p, z_p, of the molecular centre (taken as the centre of the central benzene ring) along the three crystal axes from the origin. The approximate orientation of the molecule can be readily found by an inspection of the X-ray reflections from the small-spacing ($h0l$) planes 204, 10,04, 800, 60$\bar{9}$, 80$\bar{4}$, and 80$\bar{5}$. These reflections are all very strong and hence the contributions from most of the atoms must be in phase. By means of a diagram similar to that constructed for coronene (Robertson and White, *loc. cit.*) it is found that only one orientation of the molecular model can account for the enhancement of all these reflections.

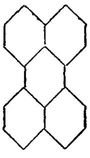
FIG. 1(*a*).



Projection along the b *axis on the* (010) *plane. The overlapping molecules are inclined at about* 58° *to the projection plane. Each contour line corresponds to one electron per* A.^{2}, *the two-electron line being dotted.*

From a general consideration of the axial sets of reflections ($h00$) and ($00l$) it would appear that there is only a small *c*-axis translation of the molecular centre involved, but a comparatively large translation along *a*. The asymmetry of the molecule, however, makes it difficult to distinguish between possible alternative positions for the molecular centre without very detailed calculations.

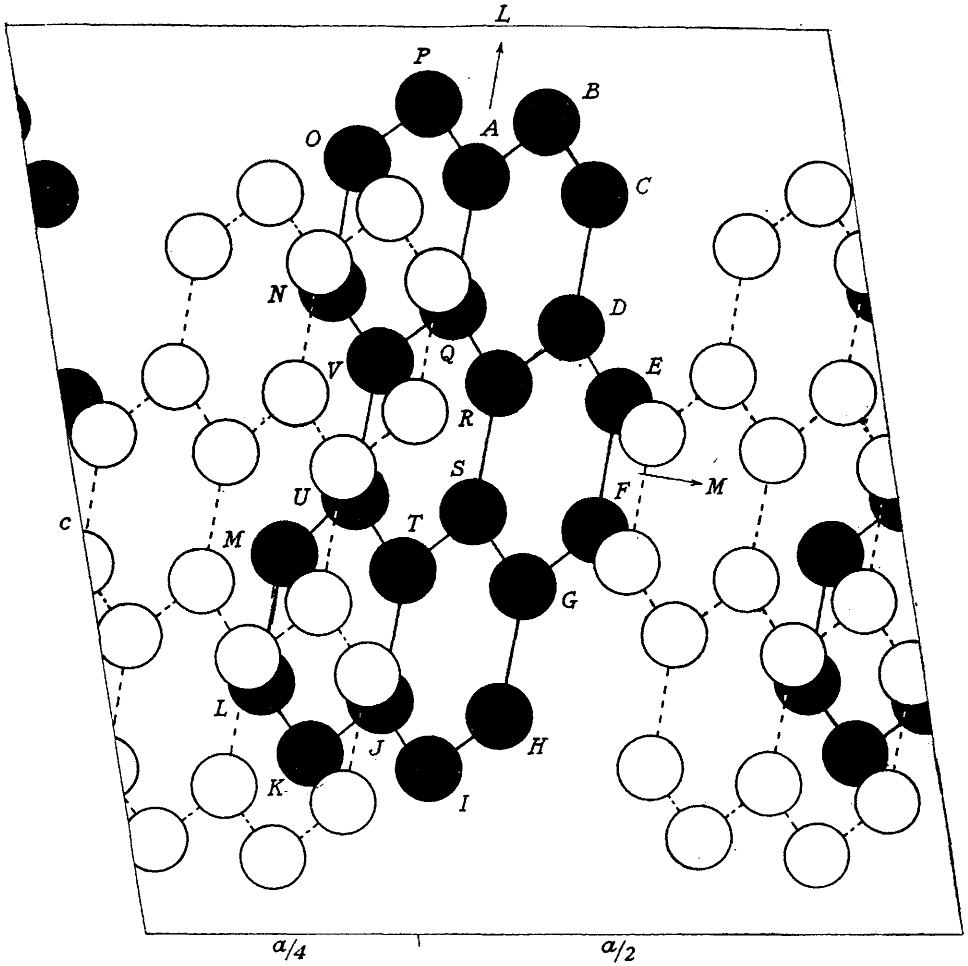
This work is shortened considerably by a comparison of benzperylene with perylene, $C_{20}H_{12}$ (II), on which a parallel investigation is in progress. The cell dimensions and space-group of perylene have been recorded by Hertel and Bergk (*Z. physikal. Chem.*, **1936**, **33**, 319) and are very closely related to those of benzperylene. Rotation photographs taken about corresponding axes for the two compounds show a remarkable similarity in intensity distribution, and this can only be due to a very close, three-dimensional similarity in structure.



(II.)

Now, with perylene, the reflection from the large-spacing (201) planes is too weak to be visible, and as this molecule probably contains an inherent centre of symmetry, it appears that the molecular centre lies on a line one-quarter of the way between the (201) planes. In benzperylene, the (201) reflection is recorded, since the two additional carbon atoms make appreciable contributions to this reflection, but we can assume from the general structural similarity noted above that the molecular centre of benzperylene lies in approximately the same relative position as that of perylene. When this deduction is considered in conjunction with the earlier observations on the structure of benzperylene, it becomes clear that there is only one reasonable position for the molecular centre, the free translation along the *a* axis (x_p) being approximately 0·9 A. and that along *c* 0·45 A.

Fig. 1(*b*).

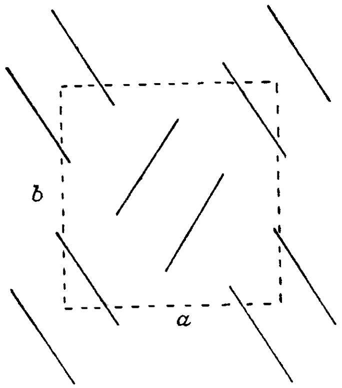


Calculations of the $(h0l)$ structure factors on the above basis led to good agreements with the observed values and it was possible to refine the atomic parameters from this stage by double Fourier series methods. Three successive Fourier analyses of the $(h0l)$ zone were carried out. In the final refinement 128 terms were included in the series, representing all the reflections which could be observed with copper-K_α radiation. The results are shown in the contour map of Fig. 1(*a*). Only 11 out of the 22 crystallographically independent atoms are separately resolved, the others being obscured by overlapping effects of adjoining molecules as shown in Fig. 1(*b*).

By assuming that the molecule is symmetrical about the axis *M* (Fig. 1*b*), it is possible to calculate the *x* and *z* co-ordinates of three more atoms, *J*, *K*, and *Q*, but the remaining eight atoms have been assigned " regularised " co-ordinates as described on p. 1406. These positions are in accordance with the appearance of the observed double peaks in Fig. 1(*a*), but it would not be possible to detect small displacements from these positions.

The *y* co-ordinates of all the atoms are calculated on the assumptions that the molecule is planar and that *L* and *M* are at right angles. These assumptions are confirmed by the satisfactory agreements between the calculated and observed values of the $(hk0)$ structure factors. The free translation along the *b*-axis must lie within fairly narrow limits from packing considerations, and it has been accurately determined by trial calculations using the observed values of the $(hk0)$ structure factors.

FIG. 2.



End view of molecules.

A complete picture of the crystal structure can be built up from Figs. 1 and 2. Fig. 2 shows the approximate appearance of the structure when viewed in a direction perpendicular to the *a*- and the *b*-axis.

Orientation, co-ordinates, and dimensions. By assuming a planar molecule with axes *L* and *M* [Fig. 1(*b*)] at right angles, and averaging certain distances as described more fully on p. 1404, it is possible to calculate precisely the orientation of the molecule with regard to the crystal axes. The results are collected in Table I, where χ, ψ, and ω are the angles which the molecular axes *L* and *M* and their perpendicular *N* make with the crystallographic axes *a*, *b*, and *c'* (*c'* is perpendicular to *a* and *b*). The tilt of the molecular plane to the (010) plane (expressed by ψ_N) is 58·2°, very close to the value found for naphthalene (Robertson, *Proc. Roy. Soc.*, 1933, *A*, **142**, 674) but considerably greater than that in the other hydrocarbons mentioned above. The perpendicular distance between two parallel, overlapping molecules is 3·38 A., not significantly different from the values found for coronene (3·41 A.) and graphite (3·40 A.).

TABLE I.

Orientation of the molecule in the crystal.

$\chi_L = 79{\cdot}7^\circ$	$\cos\chi_L = 0{\cdot}1787$	$\chi_M = 58{\cdot}6^\circ$	$\cos\chi_M = 0{\cdot}5216$	$\chi_N = 147{\cdot}4^\circ$	$\cos\chi_N = 0{\cdot}8345$
$\psi_L = 91{\cdot}2$	$\cos\psi_L = -0{\cdot}0216$	$\psi_M = 31{\cdot}8$	$\cos\psi_M = 0{\cdot}8500$	$\psi_N = 58{\cdot}2$	$\cos\psi_N = 0{\cdot}5265$
$\omega_L = 10{\cdot}3$	$\cos\omega_L = 0{\cdot}9837$	$\omega_M = 94{\cdot}4$	$\cos\omega_M = -0{\cdot}0761$	$\omega_N = 80{\cdot}7$	$\cos\omega_N = 0{\cdot}1622$

The co-ordinates with respect to the crystal axes are collected in Table II. The measured *x* and *z* co-ordinates of the 11 atoms separately resolved in the contour map of Fig. 1 are given in the columns headed (*b*), while the co-ordinates finally adopted are listed under (*a*).

The molecular dimensions and bond distances can be calculated from the observed crystal co-ordinates by combination with the orientation angles of Table I and the results are shown in Fig. 3. The ringed atoms *A*, *B*, *C*, *D*, *G*, *H*, *I*, *P*, *R*, *S*, and *T* are those which are separately resolved in Fig. 1(*a*), and bond distances between these atoms alone can be measured directly. The three atoms *J*, *K*, and *Q*, however, can be assigned accurate co-ordinates on the assumption that the molecule is symmetrical about the axis *M*. This assumption can be tested by a comparison of corresponding pairs of bond lengths on either side of *M*. The results are :

RD = 1·43 A.	*SG* = 1·42 A.	Mean value = 1·42 A.
RQ = 1·43 A.	*ST* = 1·43 A.	,, = 1·43 A.
AB = 1·43 A.	*JI* = 1·39 A.	,, = 1·41 A.
BC = 1·39 A.	*IH* = 1·37 A.	,, = 1·38 A.
CD = 1·45 A.	*HG* = 1·41 A.	,, = 1·43 A.

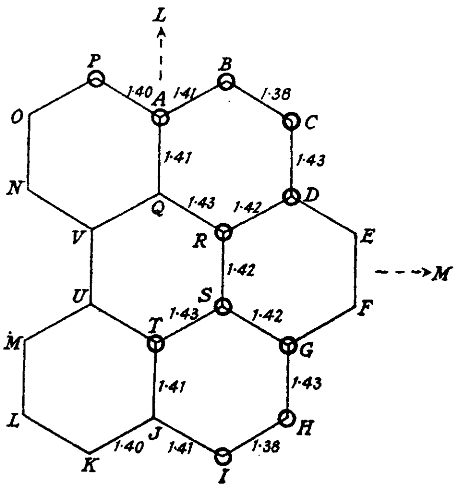
TABLE II.

Co-ordinates with respect to monoclinic crystal axes : centre of symmetry as origin.

Atom [cf. Fig. 1(*b*)].	*x*, A. (*a*).	*x*, A. (*b*).	$2\pi x/a$ (*a*).	*y*, A. (*a*).	$2\pi y/b$ (*a*).	*z*, A. (*a*).	*z*, A. (*b*).	$2\pi z/c$ (*a*).
A	1·832	1·832	56·3°	−2·085	−63·2°	3·300	3·300	120·1°
B	2·682	2·699	82·3	−1·051	−31·8	3·880	3·898	141·2
C	3·071	3·077	94·3	−0·017	− 0·5	3·105	3·096	113·1
D	2·617	2·617	80·3	0·034	1·0	1·684	1·655	61·3
E	2·999	—	92·1	1·072	32·5	0·883	—	32·2
F	2·540	—	78·0	1·102	33·4	−0·519	—	− 18·9
G	1·695	1·675	52·1	0·096	2·9	−1·136	−1·164	− 41·4
H	1·219	1·208	37·5	0·107	3·2	−2·553	−2·558	− 92·9
I	0·380	0·375	11·7	−0·897	− 27·1	−3·134	−3·122	−114·1
J	−0·028	—	− 0·9	−1·961	− 59·4	−2·376	—	− 86·5
K	−0·870	—	−26·7	−2·979	− 90·3	−2·963	—	−107·8
L	−1·272	—	−39·1	−4·036	−122·2	−2·186	—	− 79·6
M	−0·812	—	−24·9	−4·067	−123·2	−0·786	—	− 28·6
N	0·128	—	4·0	−4·129	−125·1	2·086	—	76·0
O	0·586	—	18·0	−4·160	−126·0	3·486	—	126·9
P	1·435	1·435	44·1	−3·133	− 94·9	4·075	4·075	148·4
Q	1·371	—	42·1	−2·060	− 62·4	1·899	—	69·1
R	1·756	1·755	53·9	−1·000	− 30·3	1·073	1·076	39·1
S	1·294	1·295	39·8	−0·970	− 29·4	−0·335	−0·338	− 12·2
T	0·430	0·430	13·2	−1·996	− 60·5	−0·974	−0·974	− 35·4
U	0·038	—	1·2	−3·045	− 92·3	−0·178	—	− 6·5
V	0·520	—	16·0	−3·075	− 93·2	1·292	—	47·0
Molecular centre	0·907	0·907	27·9	−2·015	− 61·0	0·462	0·462	16·8

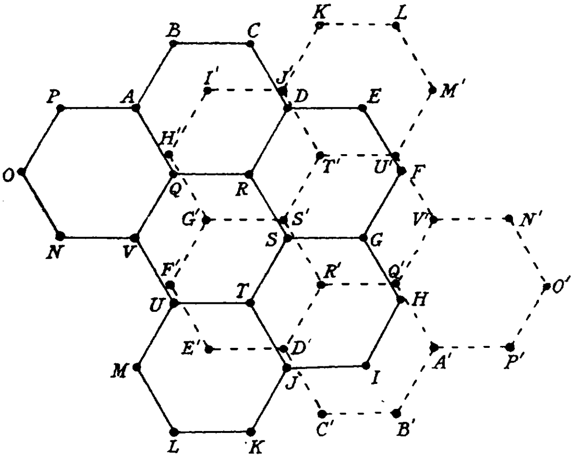
The deviations from the mean values are nowhere greater than ±0·02 A. and these differences are probably due to experimental error. The mean values have been employed in Fig. 3, and the corresponding crystal co-ordinates adopted in Table II under (*a*).

FIG. 3.



Dimensions of the benzperylene molecule.

FIG. 4.



Normal projection of two parallel molecules.

The bond distances shown in Fig. 3 vary over a range of 0·05 A. In this compound, however, the tilt of the molecule to the projection plane is considerably steeper than in any of the structures previously discussed, with consequent greater uncertainty in the *y* co-ordinates, and errors in bond length estimates may amount to ±0·03 A. Nevertheless, it seems probable that the more extreme variations noted above, *e.g.*, between *BC* and *HI*, on the one hand, and the bonds *QR*, *RS*, and *ST* in the central ring, on the other, are real. The smaller variations, however, may be spurious.

The molecular structure is summarised in Table III, where the co-ordinates with respect to the molecular axes *L*, *M*, and *N* are listed. These co-ordinates can be combined with the crystal co-ordinates of the molecular centre and the orientation angles of Table I according to the relations :

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

to give the final crystal co-ordinates of Table II.

TABLE III.

Co-ordinates with respect to molecular axes.

Atoms.	L, A.	M, A.	N, A.	Atoms.	L, A.	M, A.	N, A.	Atoms.	L, A.	M, A.	N, A.
A, J	±2·857	−0·009	0	E, F	±0·705	3·650	0	U, V	±0·740	−1·230	0
B, I	±3·535	1·225	0	K, P	±3·542	−1·225	0	Q, T	±1·445	−0·014	0
C, H	±2·847	2·424	0	L, O	±2·855	−2·450	0	R, S	±0·712	1·211	0
D, G	±1·419	2·447	0	M, N	±1·445	−2·450	0				

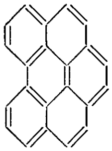
Intermolecular distances. The closest approach of adjacent molecules occurs along the b-axis where there is a perpendicular distance of 3·38 A. between the two molecules related by the centre of symmetry at the origin. Fig. 4 shows the normal projection of one of these molecules in the plane of the other. This diagram is very like the corresponding projection for coronene (Robertson and White, *loc. cit.*), with a similar staggered arrangement of the atoms of the two molecules. The closest approach in this direction between atoms of different molecules is from S on the standard molecule to S', the corresponding atom on the inverted molecule, where the distance is 3·38 A. The three pairs of atoms DJ', FU', and QH' are 3·39 A. apart.

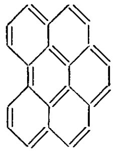
In other directions the distances are greater. Along the a-axis, from D on the standard molecule to O, the molecule at $x - \frac{1}{2}$, $-y - \frac{1}{2}$, z, the distance is 3·91 A. From N on the standard molecule to F', on the molecule at $\frac{1}{2} - x$, $\frac{1}{2} + y$, $-z$, the distance is 3·84 A., to E_1' it is 3·52 A., and to S_1' 3·74 A. On this same pair of molecules O is 3·72 A. from E_1', 3·49 A. from F_1', and 3·76 A. from I_1'. In the c-axis translation, P on the standard molecule is 3·74 A. from I_2 on the molecule at x, y, $z + 1$, and 4·00 A. from J_2 on the same molecule. These intermolecular distances are of about the same magnitude as is usually found in hydrocarbon structures.

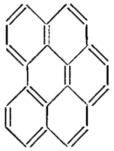
DISCUSSION OF RESULTS.

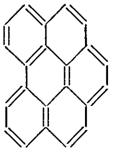
For the reasons explained above, the accuracy of the present analysis cannot be as high as in the coronene analysis. Nevertheless, the small differences between independently estimated values for corresponding lengths in different parts of the molecule suggest that the errors are not excessive, and as described below (see p. 1407), the molecular model of Fig. 3 gives better agreement with the observed F values than does a regular, hexagonal model in the same orientation. The possibility of errors amounting to ±0·03 A. for any individual bond distance cannot be excluded, but the evidence is fairly strong that the molecular co-ordinates given in Table III are, on the whole, more correct than those derived from a completely regular model. In particular, the bonds BC and HI are independently estimated to be 1·38±0·01 A., and it seems very probable that these two bonds are, in fact, distinctly shorter than the other bonds observed.

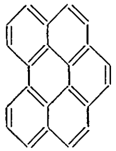
A rough calculation of the bond distances can be made from the 14 non-excited valency bond structures for 1 : 12-benzperylene (III—XVI). By the same method as described for coronene, pyrene, and 1 : 2-5 : 6-dibenzanthracene (Robertson and White, *loc. cit.*) the percentage double-bond character can be calculated for each bond in the molecule, and these values are shown in (XVII).

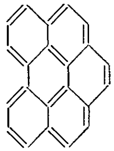

(III.)

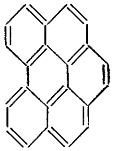

(IV.)

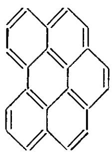

(V.)

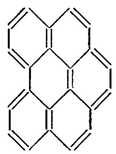

(VI.)

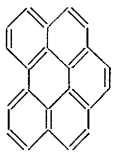

(VII.)

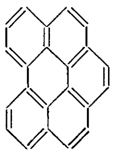

(VIII.)

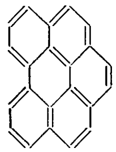

(IX.)

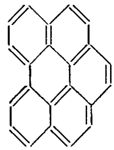

(X.)

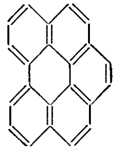

(XI.)


(XII.)

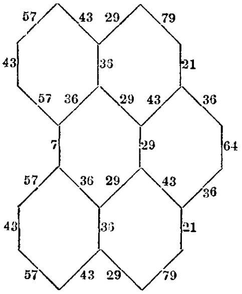

(XIII.)


(XIV.)


(XV.)

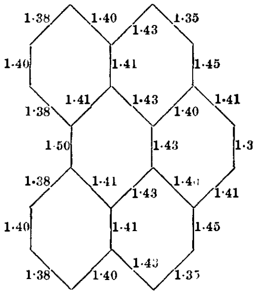

(XVI.)

The corresponding bond distances obtained from Pauling and Brockway's curve (*J. Amer. Chem. Soc.*, 1937, **59**, 1223) are given in (XVIII), and the observed distances in (XIX).



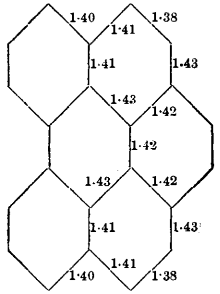
Bond orders.

(XVII.)



Distances calculated.

(XVIII.)



Distances found.

(XIX.)

There is a distinct qualitative resemblance between the observed and the calculated values, and the average value of the calculated bond distances (1·408 A.) is in excellent agreement with the observed average (1·412 A.). It should be noted that in the above calculation the 14 stable valency bond structures have been assigned equal weight, which is probably incorrect, and even more important, no account has been taken of the excited structures.

At this stage it is perhaps more noteworthy that the bond distances measured in benzperylene are very similar to those found between corresponding atoms in coronene (Robertson and White, *loc. cit.*). For instance, the shortest bonds in benzperylene are 1·38 A., while the corresponding bonds in coronene measure $1{\cdot}38_5$ A. The central ring of coronene is regular with bond lengths 1·43 A., and in benzperylene *QR* and *ST* measure 1·43 A. and *RS* 1·42 A. Other bond distances in both compounds vary between the extreme values of the two groups compared above. It would appear that this pattern of variations in carbon–carbon bond distances is characteristic of this complex type of condensed-ring aromatic hydrocarbon, and in this connection it is unfortunate that in the present investigation it has not been possible to measure bond distances on the " open " side of the molecule, *i.e.*, bonds involving the atoms *M, U, V,* and *N*, for here we should expect to find the largest differences between the coronene and the benzperylene structure. Further theoretical discussion is hardly justified until more accurate and complete measurements have been made on benzperylene or similar molecules.

EXPERIMENTAL.

Determination of Crystal Data and Intensities.—The *X*-ray work was carried out photographically by means of rotation, oscillation, and moving-film methods, Cu-K_α radiation being employed throughout. The axial lengths given above were checked by rotation about the diagonal of the *ab* face and agreement was obtained to 0·2%. The density was found by flotation of small crystals in a solution of silver nitrate at 20°, and the highest value obtained was 1·349 in good agreement with the value of 1·338 calculated for four molecules in the unit cell.

The estimates of intensity were made visually on moving-film photographs taken about the *b* and *c* crystal axes. For correlation of the strongest and the weakest reflections the multiple-film technique was used (Robertson, *J. Sci. Instr.*, 1943, **20**, 175). For the main part of the work crystal specimens were employed which were small and uniform enough to make absorption error negligible. The specimen used for most of the (*h*0*l*) measurements had a mean cross-section of 0·24 mm. × 0·28 mm. To check extinction effects, photographs were taken of small crystals which had been quenched in liquid air. The only evidence of extinction was in the strong (001) reflection, and for this reflection the highest intensity recorded was adopted as being the most probable. Considerably larger crystals were used in recording the very weakest reflections, and the final scale of intensity had the very large range of 60,000 : 1. An approximately absolute scale was obtained by correlation with the calculated F values.

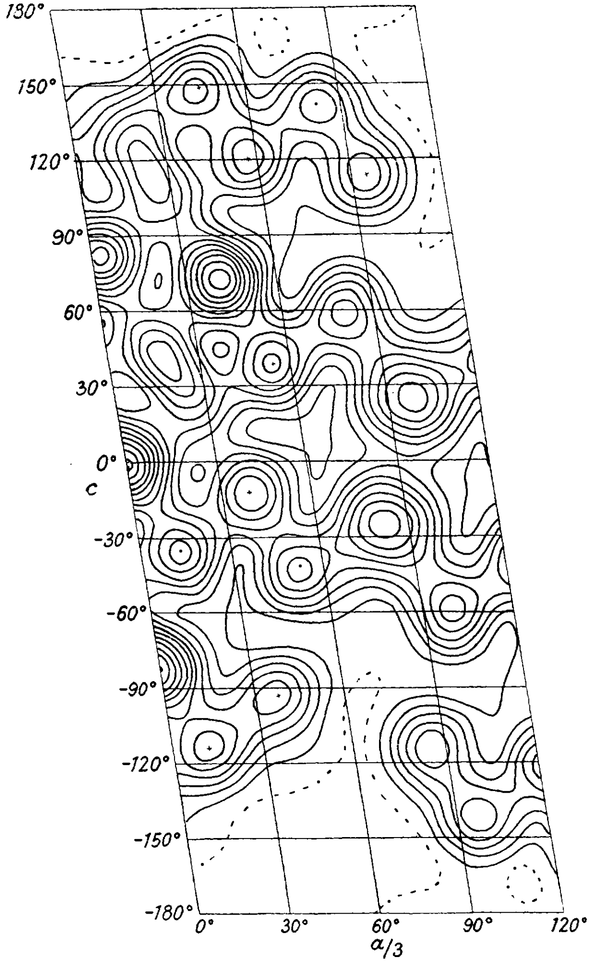
Fourier Analysis.—Using the measured values of F and the phase constants obtained from the trial structures, double Fourier series were set up according to the usual formulæ. The electron density was computed at 900 points on the asymmetric unit, the *a*-axis being divided into 60 parts (intervals of 0·195 A.) and the *c*-axis into 60 parts (intervals of 0·165 A.). 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 of the summation totals, by making sections of both the rows and columns. The contour map resulting from the final refinement is shown in Fig. 1, three-quarters of the unit cell being included.

Calculation of Molecular Orientation and Co-ordinates.—From the observed projection distances of lines parallel to *AQ*, which can be only very slightly tilted to the projection plane, it was found that the best average radius of the hexagons is 1·41 A. The observed projection distances of *PB*, *AC*, and

TG measure 1·286 ± 0·025 A. In a regular hexagonal structure of radius 1·41 A. the real distance considered would be 2·44 A. and so ψ_M, the angle between *M* and the *b* crystal axis, is obtained as 31·8°; ψ_L cannot be derived by the same method as it is so close to 90°, but can be obtained indirectly from the apparent angle which *L* makes with *M* in projection.

The projected lines *CDGH*, *BRSI*, and *AI* make an average angle of 79·7° ± 0·2° (η_L) with *a*, and the lines *PB*, *AC*, and *TG* make an average angle with *a* of −8·3° ± 0·4° (η_M). With these data and the nine trigonometrical relations given in the coronene analysis (Robertson and White, *loc. cit.*) the complete orientation of the molecule can be calculated with respect to the crystallographic axes *a*, *b*, and *c′* (*c′* is perpendicular to *a* and *b*) and is given in Table I. The above calculation assumes that the molecule is planar and that the axes *L* and *M* are at right angles.

FIG. 5.



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

The next step is to calculate the molecular co-ordinates in terms of the axes *L* and *M*. If we take a regular, planar model of hexagonal radius 1·41 A. and combine the molecular co-ordinates with the orientation angles of Table I, we obtain the crystal co-ordinates which this regular model would have if its centre coincided with the origin. By subtracting these co-ordinates from the *a* and *c* co-ordinates actually observed and averaging the eleven independent values, the free translations of the molecule along the *a* and *c* crystal axes are found to be 0·907 A. and 0·462 A., respectively.

The molecular co-ordinates can now be directly calculated from the relations :

$$x'' = x - x_P + z'' \cot \beta$$
$$z'' = (z - z_P) \sin \beta$$

$$L = (z'' \cos \chi_M - x'' \cos \omega_M)/(\cos \chi_M \cos \omega_L - \cos \omega_M \cos \chi_L)$$
$$M = (x'' \cos \omega_L - z'' \cos \chi_L)/(\cos \chi_M \cos \omega_L - \cos \omega_M \cos \chi_L)$$

where $x_P = 0{\cdot}907$ A. and $z_P = 0{\cdot}462$ A.

The unresolved atoms were assigned co-ordinates by regularising the hexagons *RSGFED* and *AQVNOP* as far as is consistent with the observed centres of the resolved atoms in these hexagons. The final x and z co-ordinates of the eleven resolved atoms are plotted in Fig. 5.

TABLE IV.

Measured and calculated values of the structure factor.

hkl.	sin θ ($\lambda = 1{\cdot}54$).	F, meas.	F, calc.
001	0·079	103	+104
002	0·158	53	− 53
003	0·237	34	+ 31
004	0·316	34	− 29
005	0·395	15	− 16
006	0·473	12	− 12
007	0·552	8	− 12
008	0·630	<1	− 3
009	0·709	13	+ 14
00, 10	0·789	8	+ 10
00, 11	0·866	6	− 5
00, 12	0·945	2	+ 1
020	0·130	14	− 14
040	0·259	6	+ 2
060	0·389	8	+ 16
080	0·519	14	+ 15
0, 10, 0	0·649	8	− 5
0, 12, 0	0·778	48	+ 46
0, 14, 0	0·907	<7	+ 1
200	0·133	50	+ 50
400	0·266	25	+ 22
600	0·400	17	− 17
800	0·534	36	+ 36
10, 00	0·665	10	− 6
12, 00	0·800	2	− 2
14, 00	0·931	<1	+ 1
20, 11	0·894	<1	− 1
20, 10	0·819	2	− 1
209	0·740	24	+ 24
208	0·664	15	+ 19
207	0·588	<1	− 1
206	0·510	16	− 8
205	0·435	29	+ 23
204	0·360	62	+ 53
203	0·290	3	+ 1
202	0·222	15	− 14
201	0·165	41	− 41
20$\bar{1}$	0·165	83	+ 83
20$\bar{2}$	0·193	59	− 50
20$\bar{3}$	0·255	19	+ 10
20$\bar{4}$	0·325	<1	− 2
20$\bar{5}$	0·398	13	− 21
20$\bar{6}$	0·471	6	+ 7
20$\bar{7}$	0·495	<1	− 1
20$\bar{8}$	0·624	2	+ 1
20$\bar{9}$	0·700	2	+ 1
20, $\bar{1}\bar{0}$	0·779	<1	− 1
20, $\bar{1}\bar{1}$	0·858	1	− 1
40, 11	0·942	2	0
40, 10	0·869	2	+ 1
409	0·794	<1	+ 2
408	0·720	5	+ 1
407	0·647	2	− 5
406	0·579	2	+ 5
405	0·508	7	− 7
404	0·444	1	− 8
403	0·383	11	+ 11
402	0·331	9	− 10
401	0·290	4	− 5
40$\bar{1}$	0·268	27	+ 25
40$\bar{2}$	0·290	18	+ 16
40$\bar{3}$	0·331	26	+ 24
40$\bar{4}$	0·384	4	+ 7
40$\bar{5}$	0·443	3	+ 2
40$\bar{6}$	0·509	10	+ 11
40$\bar{7}$	0·576	5	− 4
40$\bar{8}$	0·650	4	− 5
40$\bar{9}$	0·718	3	− 4
40, $\bar{1}\bar{0}$	0·796	3	+ 1
40, $\bar{1}\bar{1}$	0·870	<1	0
609	0·869	1	− 1
608	0·795	<1	+ 2
607	0·727	4	+ 5
606	0·666	4	+ 7
605	0·603	11	+ 13
604	0·545	6	+ 7
603	0·495	7	− 6
602	0·453	1	− 1
601	0·421	6	+ 4
60$\bar{1}$	0·398	2	+ 3
60$\bar{2}$	0·410	5	+ 6
60$\bar{3}$	0·436	12	− 11
60$\bar{4}$	0·473	2	0
60$\bar{5}$	0·521	2	− 2
60$\bar{6}$	0·574	1	+ 6
60$\bar{7}$	0·633	2	− 5
60$\bar{8}$	0·697	23	+ 21
60$\bar{9}$	0·763	32	+ 30
60, $\bar{1}\bar{0}$	0·830	2	− 5
60, $\bar{1}\bar{1}$	0·900	2	− 2
809	0·948	3	− 3
808	0·888	2	+ 2
807	0·823	1	− 2
806	0·766	1	− 6
805	0·709	15	+ 12
804	0·659	1	0
803	0·616	6	− 6
802	0·580	<1	− 5
801	0·562	10	+ 10
80$\bar{1}$	0·524	10	+ 10
80$\bar{2}$	0·530	7	− 8
80$\bar{3}$	0·549	3	− 5
80$\bar{4}$	0·575	32	+ 30
80$\bar{5}$	0·613	30	+ 30
80$\bar{6}$	0·661	4	− 4
80$\bar{7}$	0·618	1	+ 3
80$\bar{8}$	0·767	6	0
80$\bar{9}$	0·826	16	+ 14
80, $\bar{1}\bar{0}$	0·885	7	+ 8
80, $\bar{1}\bar{1}$	0·950	4	− 5
10, 08	0·976	2	− 2
10, 07	0·926	2	+ 3
10, 06	0·872	6	− 8
10, 05	0·824	22	+ 21
10, 04	0·778	50	+ 50
10, 03	0·729	5	+ 2
10, 02	0·707	5	− 3
10, 01	0·682	5	+ 4

TABLE IV (*contd.*)

hkl.	sin θ ($\lambda = 1{\cdot}54$).	F, meas.	F, calc.
10, 0$\bar{1}$	0·655	3	+ 1
10, 0$\bar{2}$	0·657	3	− 6
10, 0$\bar{3}$	0·669	5	− 9
10, 0$\bar{4}$	0·689	4	0
10, 0$\bar{5}$	0·719	20	+ 21
10, 0$\bar{6}$	0·753	4	+ 7
10, 0$\bar{7}$	0·795	2	− 6
10, 0$\bar{8}$	0·844	2	+ 3
10, 0$\bar{9}$	0·899	7	− 5
10, 0, $\bar{1}\bar{0}$	0·954	6	− 4
12, 05	0·943	<1	− 1
12, 04	0·900	11	+ 10
12, 03	0·868	14	+ 8
12, 02	0·839	2	− 5
12, 01	0·815	2	+ 4
12, 0$\bar{1}$	0·789	10	− 5
12, 0$\bar{2}$	0·795	<1	+ 2
12, 0$\bar{3}$	0·803	1	− 1
12, 0$\bar{4}$	0·820	1	0
12, 0$\bar{5}$	0·833	<1	− 1
12, 0$\bar{6}$	0·871	<1	0
12, 0$\bar{7}$	0·899	1	− 1
14, 0$\bar{1}$	0·919	2	+ 1
14, 0$\bar{2}$	0·918	2	+ 2
14, 0$\bar{3}$	0·924	<1	− 1
110	0·093	66	+ 64
120	0·145	49	+ 39
130	0·205	47	+ 35
140	0·268	18	− 19
150	0·330	5	− 2
160	0·389	<6	+ 1
170	0·459	<7	− 12
180	0·522	<8	+ 8
190	0·587	<8	− 1
1, 10, 0	0·651	15	− 18
1, 11, 0	0·743	33	+ 24
1, 12, 0	0·781	<9	− 2
1, 13, 0	0·847	<8	− 1
1, 14, 0	0·913	<6	0
210	0·147	57	+ 52
220	0·187	112	−108
230	0·236	8	+ 11
240	0·290	8	− 9
250	0·349	8	+ 6
260	0·410	12	+ 12
270	0·471	<7	− 6
280	0·535	<8	− 1
290	0·598	18	− 17
2, 10, 0	0·659	28	− 39
2, 11, 0	0·723	<9	− 7
2, 12, 0	0·778	<9	− 4
2, 13, 0	0·855	<8	+ 1
2, 14, 0	0·918	<6	− 2
310	0·208	57	− 52
320	0·239	64	+ 57
330	0·279	<5	− 3
340	0·327	<6	+ 1
350	0·380	<6	− 3
360	0·435	<7	− 6
370	0·495	<7	0
380	0·558	<8	0
390	0·614	11	− 9
3, 10, 0	0·678	16	− 18
3, 11, 0	0·739	<9	− 7
3, 12, 0	0·803	<9	0
3, 13, 0	0·868	12	− 4
3, 14, 0	0·932	<6	+ 2
410	0·275	<5	+ 5
420	0·293	<5	+ 7
430	0·330	<6	+ 6
440	0·372	8	− 12
450	0·419	<7	+ 4
460	0·472	10	− 10
470	0·527	<8	− 1
480	0·580	<8	+ 7
510	0·341	6	+ 6
520	0·358	19	− 21
530	0·387	22	− 20
540	0·423	<7	+ 5
550	0·465	<7	− 6
610	0·404	<6	+ 3
620	0·416	24	− 20
630	0·440	<7	+ 3
640	0·477	<7	− 6
710	0·421	12	+ 12
720	0·485	<7	0
730	0·507	16	− 12
740	0·534	<8	+ 7
810	0·540	30	+ 28
820	0·550	10	+ 10
830	0·570	<8	0
910	0·607	11	+ 14
920	0·617	<9	+ 3
10, 10	0·671	20	+ 19
10, 20	0·681	<9	− 5

The co-ordinates of Table II(*a*) were used for a final calculation of the structure factors of the (*h*0*l*) and (*hk*0) reflections and the results are collected in Table IV under "F_1 calc." It was found that on the basis of the usual hydrocarbon scattering curve (Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 110) the calculated structure factors for small-spacing planes were consistently higher than the observed values and the empirical scattering curve adopted for high sin θ values is given below (max. $f_G = 100$).

sin θ($\lambda = 1{\cdot}54$)	0·7	0·8	0·9
f_G	12·6	8·4	5·2

For the (*h*0*l*) zone, the mean discrepancy, expressed as

$$\frac{\Sigma(|\,\text{F, meas.}\,| - |\,\text{F, calc.}\,|)}{\Sigma\,|\,\text{F, meas.}\,|}$$

was found to be 16·6%, for the *hk*0 zone 10·9%, and for all the reflections together, 14·1%.

If instead of the co-ordinates of Table II, co-ordinates derived from a regular, hexagonal model in the orientation of Table I are employed for calculation of the (*h*0*l*) structure factors, the mean discrepancy increases to 18·5%, indicating that the given co-ordinates are preferable.

The author wishes to thank Professor J. Monteath Robertson, F.R.S., for his continued interest in this problem and for helpful discussion, Professor J. W. Cook, F.R.S., for some beautiful crystal specimens of 1 : 12-benzperylene and perylene, and the Carnegie Trustees for a scholarship held during the earlier part of this work.

THE UNIVERSITY, GLASGOW.

[*Received, September 5th,* **1947.**]