

## 72. The Crystal Structure of Pyrene. A Quantitative X-Ray Investigation.

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

The crystal and molecular structure of pyrene has been determined by quantitative X-ray analysis. The molecular arrangement is more complicated than in anthracene or coronene because the unit cell contains four molecules and these do not coincide with any crystallographic element of symmetry. Nevertheless, the final results show that the molecule does contain an inherent centre of symmetry, in conformity with the chemical evidence, although this centre is not used in building the crystal structure. In the final analysis, direct measurements of the positions of 9 out of the 16 carbon atoms can be made from the Fourier maps, and the positions of the others can be estimated with a good deal of certainty. The bond-length measurements are not so accurate as in the coronene analysis, owing to less favourable resolution, and the possible errors may be as much as  $\pm 0.03$  or  $\pm 0.04$  Å. However, the most probable atomic positions indicate bond-length variations in different parts of the molecule, the distances varying from 1.39 to 1.45 Å. Details are given in Fig. 4. A rough qualitative explanation of these variations can be given in terms of the 6 stable valency bond structures applicable to pyrene, and the usual Pauling-Brockway bond character-distance curve.

WE recently made definite measurements of variable carbon-carbon bond lengths in the aromatic hydrocarbon coronene (*J.*, 1945, 607) and these variations can be given at least a rough qualitative explanation in terms of the 20 non-excited valency bond structures applicable to coronene. A more rigorous treatment of the problem by the molecular orbital method has been attempted by Coulson (*Nature*, 1944, 154, 797) and these results also receive some support from the X-ray measurements.

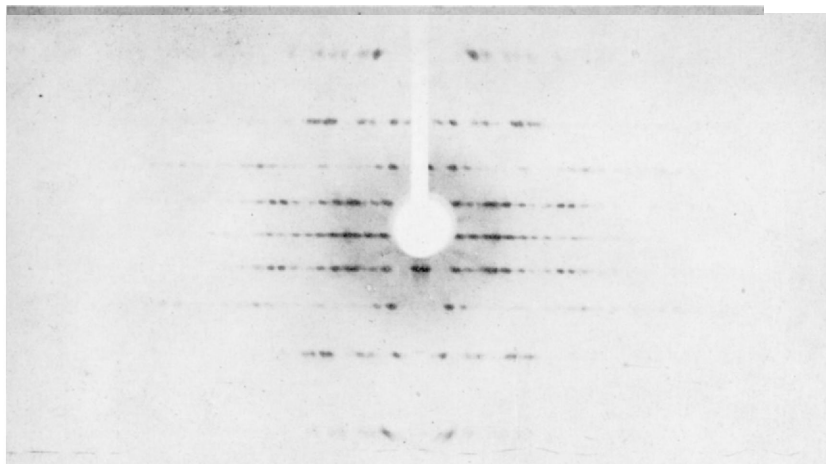
The extension of such measurements to other condensed-ring aromatic hydrocarbons is obviously a matter of importance, but the work is beset with considerable difficulties. The expected bond-length variations (0.01—0.05 Å.) are of just about the same order as the errors which frequently arise even in careful and reasonably quantitative X-ray work. Further, the coronene crystal structure is of a type which yields a particularly clear two-dimensional resolution of all the atoms in the molecule by Fourier series methods, and so it represents a specially favourable case for accurate bond-length determination. In the general case we must expect less sharply defined results, unless full three-dimensional Fourier methods are employed. For complicated structures the use of such methods is a formidable task, and in any case they must be preceded by some preliminary analysis, carried out with as much accuracy as possible.

In the present paper we describe such a preliminary analysis, by two-dimensional Fourier series methods, of the crystal structure of pyrene. The arrangement in the crystal is much more complicated than that of coronene, because the unit cell contains four molecules and these do not contain any symmetry element. On general chemical grounds one expects the pyrene molecule to contain a centre of symmetry, and this is very likely true; but the molecular centre is found to occupy a general position which does not coincide with any of the crystallographic centres of symmetry. In other words, it is not used in building the crystal structure. With regard to the orientation of the molecule in the crystal, we find that the inclination of the molecular plane to the symmetry axis is not very different from what it is in coronene or in the phthalocyanines. Nevertheless, in our principal Fourier projection (Fig. 2) only 9 out of the 16 carbon atoms are separately resolved, owing to the overlapping effects of adjoining molecules. This greatly limits the amount of accurate information which can be derived in a direct manner from the present analysis, but in spite of this some significant bond-length variations can be detected, and a reasonable model for the whole molecule can be constructed.

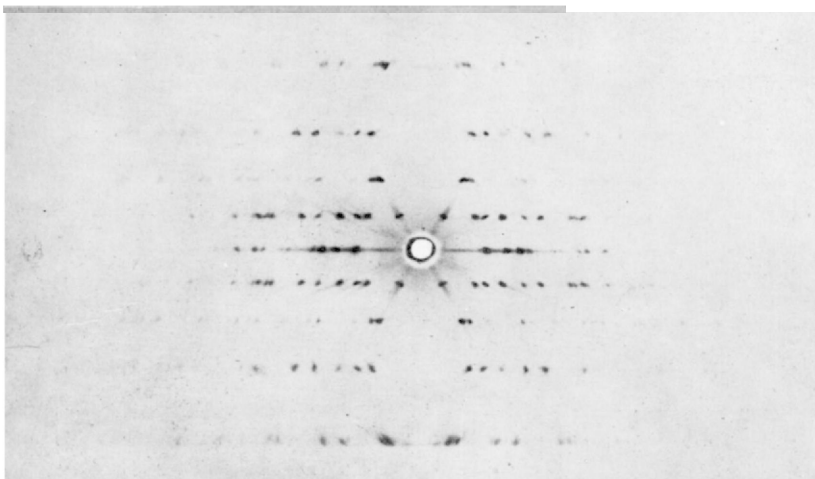
*Description of the Structure.—Crystal data.* Pyrene,  $C_{16}H_{10}$ ; *M*, 202.2; m. p. 150°; *d*, calc. 1.288, found (Dhar and Guha) 1.27; monoclinic prismatic,  $a = 13.60 \pm 0.05$ ,  $b = 9.24 \pm 0.03$ ,  $c = 8.37 \pm 0.10$  Å.,  $\beta = 100.2^\circ \pm 0.2^\circ$ . Absent spectra, ( $h0l$ ) when  $h$  is odd; ( $0k0$ ) 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, 1035 Å.<sup>3</sup>. Absorption coefficient for X-rays,  $\lambda = 1.54$ ,  $\mu = 6.76$  per cm.;  $\lambda = 0.71$ ,  $\mu = 0.86$  per cm. Total number of electrons per unit cell =  $F(000) = 424$ .

Further goniometric and optical crystal data are given by Groth ("Chemische Krystallographie", 1919, 5, 437), and the crystal structure has been investigated by Dhar and Guha (*Z. Krist.*, 1935, 91, 123). The lattice contents given by Dhar and Guha, particularly  $a$  and  $\beta$ , differ appreciably from ours. Their X-ray work was carried out by means of rotation and oscillation photographs, and leads to a determination of the space-group. They suggest

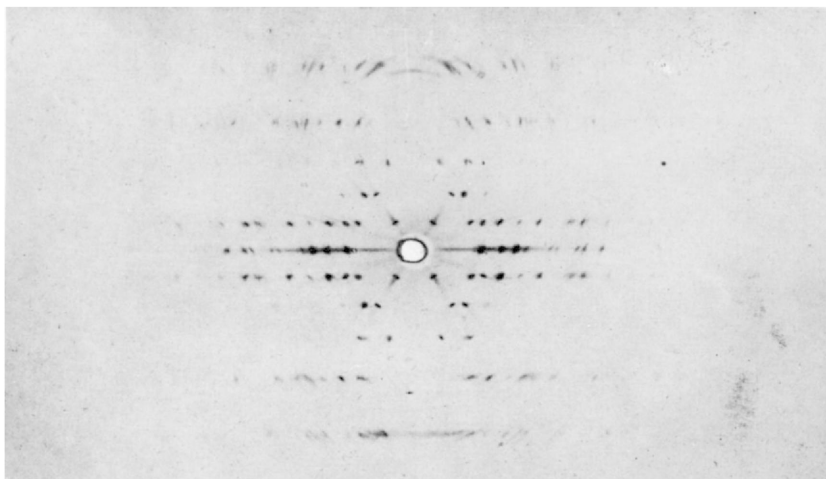
*Pyrene.*



*Naphthalene.*



*Anthracene.*



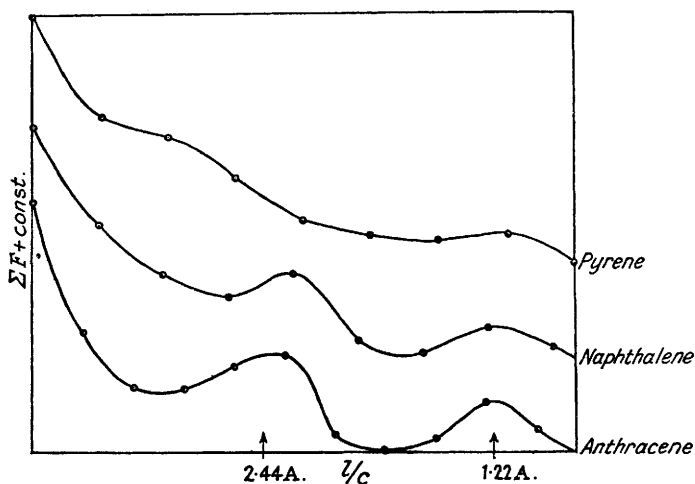
probable arrangements for the molecules in the crystal, but the work does not lead to the determination of any atomic positions.

*Analysis of the structure.* We may consider the asymmetric crystal unit to consist of one complete molecule, and it is reasonable to assume as a first approximation a regular planar structure in conformity with the chemical evidence. Now, the length of the  $b$  axis in pyrene is 9.24 Å., which is very nearly twice that of coronene (Robertson and White, *loc. cit.*) and of phthalocyanine (Robertson, *J.*, 1935, 615). Both these structures belong to the same space-group, but have only two molecules per unit cell. It therefore seemed a reasonable assumption that in pyrene the molecular planes might have a similar tilt to the  $b$  axis (about 45°) but with two molecules instead of one accommodated in each  $b$  translation. These two molecules would be grouped about one crystallographic centre of symmetry.

This enables one orientation angle to be estimated; but to specify completely the position of our molecular model in the crystal, five degrees of freedom remain, *viz.*, two other orientation angles and the co-ordinates ( $x_p, y_p, z_p$ ) of its centre with respect to the crystallographic origin (centre of symmetry).

Another clue to the molecular arrangement is provided by the characteristic appearance of the  $c$  axis rotation photograph (see Plate) and by comparison with naphthalene and anthracene

FIG. 1.



Periodicities in the anthracene, naphthalene, and pyrene structures.

(Robertson, *Proc. Roy. Soc.*, 1933, *A*, 140, 79; 142, 674). In pyrene there is a tendency for the third and the fourth layer line ( $l = 3$  and  $l = 4$ ) to be enhanced. The naphthalene photograph is similar, while in anthracene the fourth and the fifth layer line ( $l = 4$  and  $l = 5$ ) are enhanced. The analysis may be carried further by a study of the general reflections from planes beyond the limits of these photographs, when it is found that in pyrene and in naphthalene planes with  $l = 7$ , and in anthracene planes with  $l = 9$ , give enhanced reflections. These results are given more quantitatively in Fig. 1, where  $\Sigma F$  for a selection of planes are plotted against  $1/c$  for each crystal. There is clearly an important periodicity at about 1.22 Å. on this reciprocal scale in each crystal, and a further periodicity at about 2.44 Å. in naphthalene and anthracene, but this latter periodicity is much less defined in pyrene.

Now, the width of a benzene ring of radius 1.41 Å. is 2.44 Å., and the half width is 1.22 Å. It may therefore be inferred that the arrangement of the rings in these crystals is such that the above periodicities coincide at least approximately with the direction of the  $c$  axis in each case, as indicated in (I).

This correlation has been confirmed in the case of naphthalene and anthracene by detailed structure analysis (Robertson, *loc. cit.*). In pyrene we may expect a less exact alinement, and the condensed four-membered ring system will further suppress the 2.44 Å. periodicity.

The remaining degrees of freedom can be determined with considerable precision from a survey of certain ( $h0l$ ) structure factors for small spacing planes. Absolute measurements show

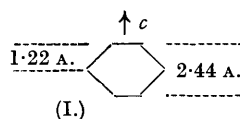


FIG. 2a.

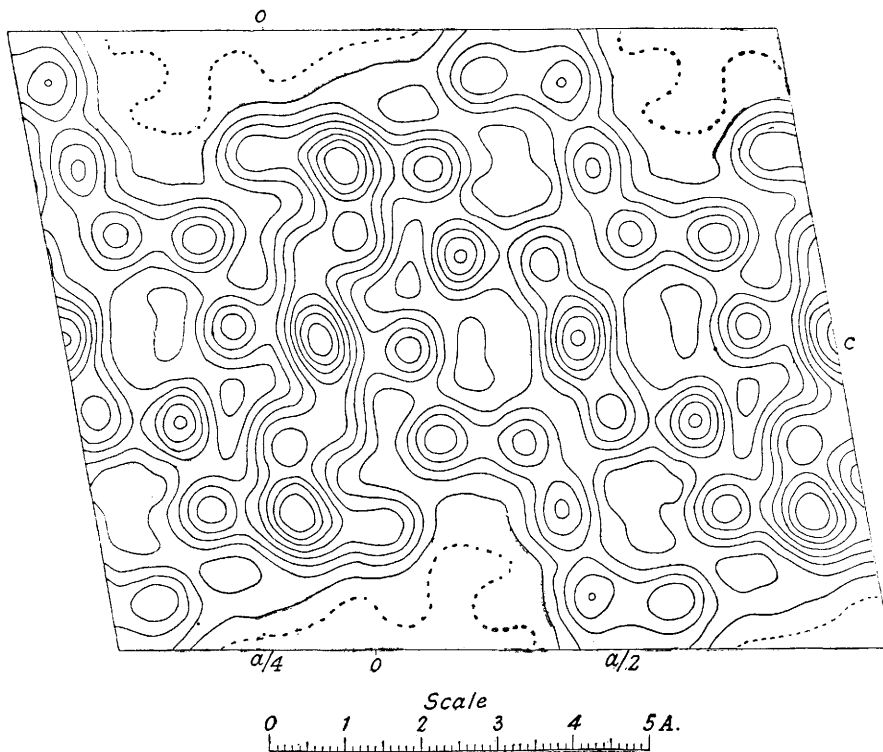
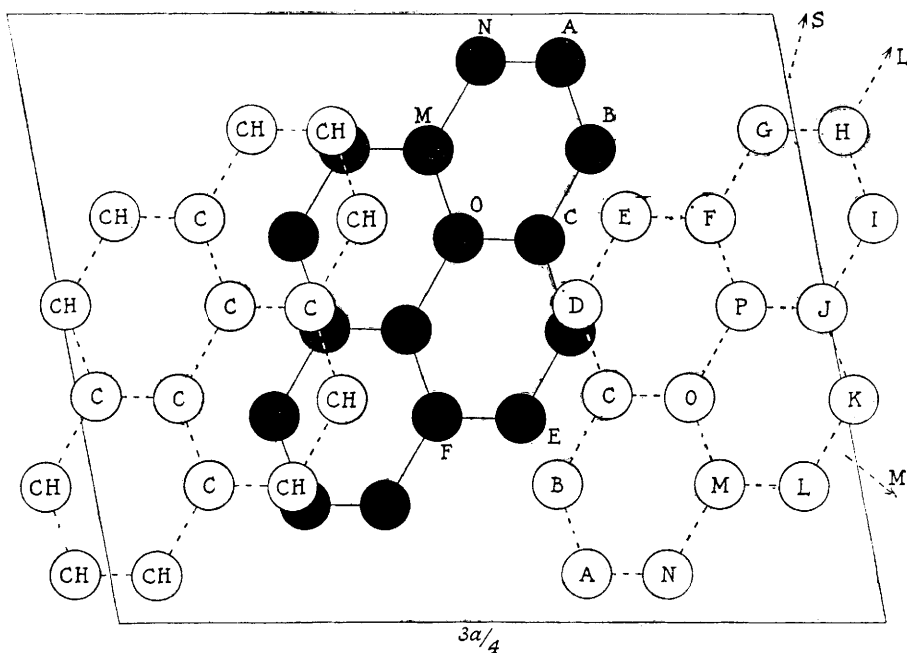


FIG. 2b.



Projection along the  $b$  axis, on the (010) plane. The overlapping molecules are inclined at about  $40^\circ$  to the projection plane, the molecular direction  $S$  lying in the projection plane. Each contour line corresponds to one electron per  $\text{\AA}^2$ , the one-electron line being dotted.

FIG. 3a.

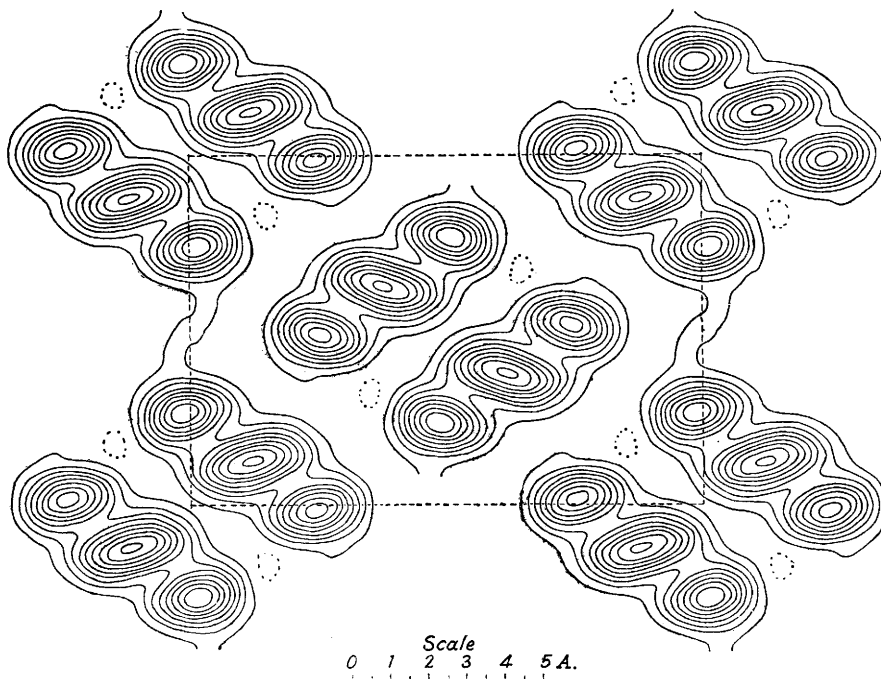
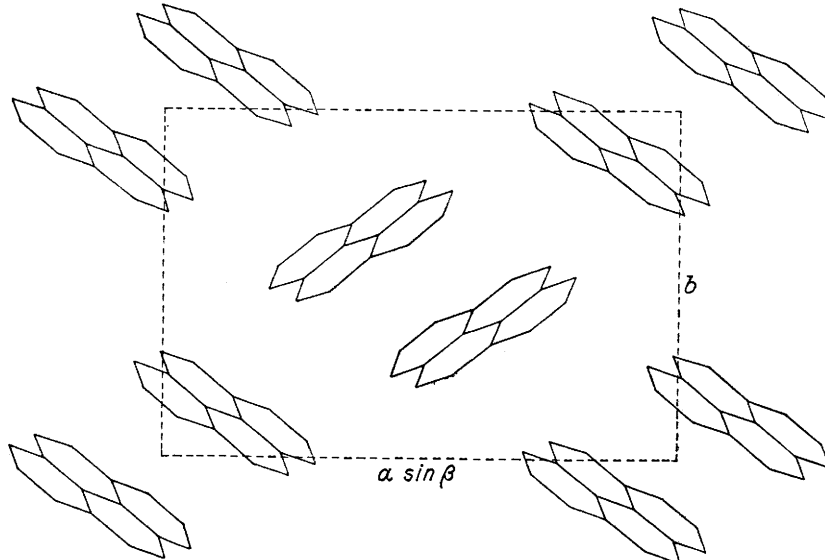


FIG. 3b.



Normal projection along the  $c$  axis, showing the relative positions of 10 molecules.  
Contour scale as in Fig. 1.

that for the (007), (206), (403), (80 $\bar{1}$ ), (12,0 $\bar{6}$ ), and (12,01) and (12,02) planes the contributions of many of the atoms must be in phase. A diagram similar to that given for coronene (Robertson and White, *loc. cit.*, Fig. 1) can be constructed, from which it is found that only one orientation of the proposed model will satisfy the conditions.

Other outstanding features of the spectra are the almost complete quarterings of the ( $h00$ )

and  $(0k0)$  series of reflections. This serves to fix the molecular centres at approximately  $\frac{a}{8}, \frac{b}{8}$  ( $x_p = 1.70$  A.,  $y_p = 1.16$  A.) from the centre of symmetry. Further calculations show that a small translation along the  $c$  axis of about 0.5 A. ( $z_p$ ) is also necessary.

Trial calculations based on the above considerations led to excellent agreements between the measured and the calculated values of the structure factor, and it was possible to proceed immediately to further refinement of the atomic positions by Fourier series methods. For the principal projection, along the  $b$  axis, 50 terms were included, representing separately measured values of the  $(hk0)$  structure factors (Table IV). The results are given by the contour map of Fig. 2(a), from which it can be seen that 9 out of the 16 crystallographically independent atoms are separately resolved. The other atoms are obscured by the overlapping effects of the adjoining molecules, as will be clear from Fig. 2(b).

The  $y$  co-ordinates of all the atoms and the  $x$  and  $z$  co-ordinates of the 7 unresolved atoms cannot be obtained directly from Fig. 2, but may be calculated on the assumption that the molecule is planar, that the  $L$  and  $M$  axes [Fig. 2(b)] are at right angles, and that the molecule is symmetrical about these axes. These assumptions are in conformity with the chemical evidence, but they receive direct and fairly detailed support from the agreements found between the measured and the calculated values of the structure factor (Table IV) and also from a second Fourier projection of the structure along the  $c$  axis, which is shown in Fig. 3. For this projection the 36 measured values of the  $(hk0)$  structure factors were employed. While no individual atoms are resolved in this projection, the separate molecules can be very clearly distinguished, and the positions of their centres can be fixed with some accuracy. The general shape of the contours gives very strong support to the assumption that the molecule contains an inherent centre of symmetry, even although such a centre is not utilised crystallographically.

*Orientation, co-ordinates and dimensions.* By assuming a planar centrosymmetrical model and averaging certain distances, as described more fully in the Experimental section, it is possible to calculate the orientation of the molecule precisely. The result are given in Table I, where  $\chi$ ,  $\psi$ , and  $\omega$  are the angles which the molecular axes  $L$  and  $M$  [Fig. 2(b)] and their perpendicular,  $N$ , make with the  $a$ ,  $b$ , and  $c'$  crystallographic axes ( $c'$  is the perpendicular to  $a$  and  $b$ ). These results show that the inclination of the molecular plane to the  $(010)$  plane, expressed by  $\psi_N$ , is  $40.2^\circ$ . This is rather less than the corresponding angle in coronene ( $43.7^\circ$ ) or in the phthalocyanines ( $44.2^\circ$ ). The perpendicular distance between successive molecular planes is given by  $\frac{1}{2}b \cos \psi_N = 3.53$  A., a value rather larger than the interplanar spacing in graphite ( $3.41$  A.), coronene ( $3.40$  A.), or phthalocyanine ( $3.38$  A.).

TABLE I.  
*Orientation of the molecule in the crystal.*

$\chi_L = 61.1^\circ$	$\cos \chi_L = 0.4834$	$\chi_M = 52.2^\circ$	$\cos \chi_M = 0.6130$	$\chi_N = 128.7^\circ$	$\cos \chi_N = -0.6248$
$\psi_L = 77.7^\circ$	$\cos \psi_L = 0.2130$	$\psi_M = 52.4^\circ$	$\cos \psi_M = 0.6101$	$\psi_N = 40.2^\circ$	$\cos \psi_N = 0.7630$
$\omega_L = 31.9^\circ$	$\cos \omega_L = 0.8487$	$\omega_M = 120.1^\circ$	$\cos \omega_M = -0.5017$	$\omega_N = 80.5^\circ$	$\cos \omega_N = 0.1648$

The co-ordinates with respect to the crystal axes are collected in Table II. The  $x$  and  $z$  co-ordinates of the nine resolved atoms can be measured directly from the projection in Fig. 2, and these values are given in bold type. The other crystal co-ordinates follow from the assumption of a planar molecule with symmetry about the  $L$  and  $M$  molecular axes. The figures in Table II give the co-ordinates of all the carbon atoms ( $A$ — $P$ ) in one pyrene molecule. The other three molecules in the unit cell can be derived from the one given by the usual symmetry operations and translations applicable to the space-group  $P2_1/a$ .

The molecular dimensions and bond lengths may be calculated from these co-ordinates, and the results are shown graphically in Fig. 4. The ringed atoms  $A, B, C, E, F, M, N, O, P$  are separately resolved in Fig. 2, and the bond distances between these atoms may be obtained by direct measurements combined with the orientation angles of Table I. The other bond lengths can only be derived by assuming exact symmetry about the  $L$  and  $M$  axes. This symmetry may be confirmed by comparing the original direct bond-length measurements of symmetrically placed pairs of resolved atoms. The results are

$AN = 1.40$	$AB = 1.38$	Assumed mean value, 1.39 A.
$NM = 1.43$	$BC = 1.42$	" " " 1.42 A.
$MO = 1.38$	$CO = 1.42$	" " " 1.39 A.
$PF = 1.38$	$CO = 1.42$	" " " 1.39 A.

The deviations from the mean values are nowhere greater than 0.03 A., and we do not feel that

TABLE II.

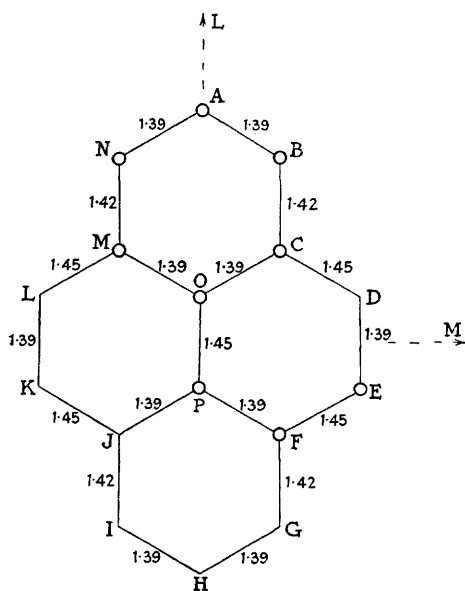
Co-ordinates. Centre of symmetry as origin.  $x, y, z$ , are referred to the monoclinic crystal axes.  $x', y, z'$ , are rectangular co-ordinates referred to the  $a$  and  $b$  crystal axes, and their perpendicular,  $c'$ .

$$x = x' - z' \cot \beta; \quad z = z' \operatorname{cosec} \beta.$$

Atoms (cf. Figs. 2 and 4).	$x$ , A.	$y$ , A.	$z$ , A.	$x'$ , A.	$z'$ , A.	$2\pi x/a$ .	$2\pi y/b$ .	$2\pi z/c$ .
A .....	<b>3.85</b>	-0.41	<b>3.51</b>	3.229	3.463	101.9°	- 16.0°	151.0°
B .....	<b>4.04</b>	0.18	<b>2.31</b>	3.630	2.271	106.9	7.1	99.4
C .....	<b>3.14</b>	-0.12	<b>1.08</b>	2.943	1.065	83.1	- 4.6	46.5
D .....	<b>3.33</b>	0.49	-0.18	3.364	-0.181	88.1	19.3	- 7.9
E .....	<b>2.45</b>	0.19	- <b>1.38</b>	2.692	-1.361	64.9	7.7	- 59.4
F .....	<b>1.33</b>	-0.73	- <b>1.37</b>	1.571	-1.345	35.2	- 28.5	- 59.0
G .....	0.43	-1.03	-2.59	0.884	-2.551	11.4	- 40.2	-111.4
H .....	-0.65	-1.91	-2.58	-0.189	-2.537	-17.2	- 74.8	-111.0
I .....	-0.83	-2.50	-1.37	-0.590	-1.345	-22.0	- 97.8	- 59.0
J .....	0.07	-2.20	-0.14	0.097	-0.139	1.9	- 86.0	- 6.0
K .....	-0.12	-2.81	1.12	-0.324	1.107	- 3.2	-109.9	48.2
L .....	0.76	-2.51	2.32	0.348	2.287	20.1	- 98.3	99.8
M .....	<b>1.88</b>	-1.59	<b>2.31</b>	1.469	2.271	49.8	- 62.1	99.4
N .....	<b>2.78</b>	-1.29	<b>3.53</b>	2.156	3.477	73.6	- 50.5	151.8
O .....	<b>2.06</b>	-1.01	<b>1.09</b>	1.870	1.078	54.5	- 39.5	46.9
P .....	<b>1.14</b>	-1.31	- <b>0.15</b>	1.170	-0.152	30.2	- 51.2	- 6.5
Centre of mol. ....	1.604	-1.160	0.470	1.520	0.463	42.5	- 45.3	19.9

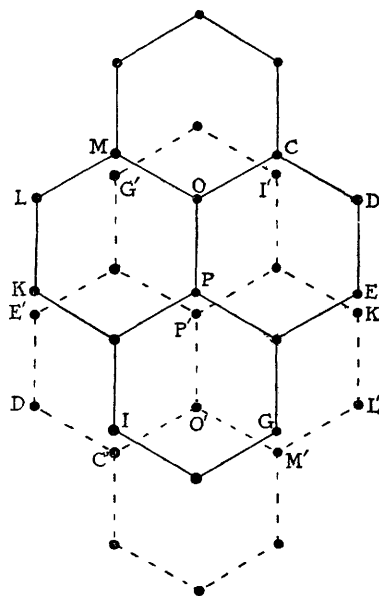
any significance can be attached to these deviations. The mean values have therefore been used in Fig. 4.

FIG. 4.



Dimensions of the pyrene molecule.

FIG. 5.



Normal projection of two parallel molecules.

For the bond lengths  $OP$  and  $EF$  we obtain the value of 1.45 Å. It is unfortunate that these unusually large values cannot be further confirmed by direct measurements on the bonds  $CD$ ,  $JK$ , or  $LM$ . From the nature of the projection it is clear that the possible error in the bond lengths is fairly large, and it may easily amount to  $\pm 0.03$  Å. However, the balance of the evidence is fairly strong that the bonds  $OP$  and  $EF$  (directly measured), and probably  $CD$ ,  $JK$ , and  $LM$  as well, are distinctly longer than any of the other bonds within the molecule.

With regard to the hexagon angles, there is no evidence that any of these differ appreciably from  $120^\circ$ .

It is convenient to summarise the molecular structure by giving the co-ordinates of the atoms

with reference to the molecular axes  $L$ ,  $M$ , and  $N$ . These are collected in Table III. When these figures are combined with the crystal co-ordinates of the molecular centre ( $x_p'$ ,  $y_p$ ,  $z_p'$ ) and the orientation angles, according to the relations

$$\begin{aligned}x' &= L \cos \chi_L + M \cos \chi_M + N \cos \chi_N + x_p' \\y &= L \cos \psi_L + M \cos \psi_M + N \cos \psi_N + y_p \\z' &= L \cos \omega_L + M \cos \omega_M + N \cos \omega_N + z_p'\end{aligned}$$

where  $x_p' = 1.520$ ,  $y_p = -1.160$ ,  $z_p' = 0.463$  Å., the crystal co-ordinates of Table II are reproduced.

TABLE III.

*Co-ordinates with respect to molecular axes.*

Atoms.	$L$ , Å.	$M$ , Å.	$N$ , Å.	Atoms.	$L$ , Å.	$M$ , Å.	$N$ , Å.
$A, H$ .....	$\pm 3.535$	0	0	$D, E, K, L$ .....	$\pm 0.695$	$\pm 2.459$	0
$B, G, I, N$ .....	$\pm 2.840$	$\pm 1.203$	0	$O, P$ .....	$\pm 0.725$	0	0
$C, F, J, M$ .....	$\pm 1.420$	$\pm 1.203$	0				

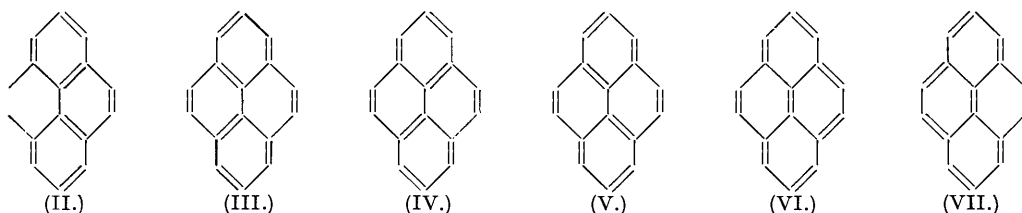
*Intermolecular distances.* The closest approach of adjacent pyrene molecules occurs along the  $b$  axis where the interplanar distance is 3.53 Å. Here the molecules are grouped in pairs about the symmetry centres, and the normal projection of one of them in the plane of the other is shown in Fig. 5. The hexagons are clearly arranged so as to avoid any direct overlap. Four pairs of atoms,  $PP'$ ,  $MG'$ ,  $CI'$ , and  $KE'$ , are nearly over each other, and for these the approach distance is 3.54 Å. The other pairs are in staggered positions at rather greater distances.

From atom  $D$  on the standard molecule to atom  $O'$  (inverted) on the reflected molecule half a translation along the  $a$  axis the distance is 3.61 Å., and from  $D$  to  $P'$  it is 3.64 Å. From  $A$  on the standard molecule to  $N'$  (inverted) on the reflected molecule half a translation along  $a$  and one translation along  $c$  the distance is 3.96 Å. All other intermolecular distances appear to be greater than 4 Å.

*Discussion of Results.*—The bond-length variations in the pyrene molecule, as depicted in Fig. 4, are even greater than those found for coronene. On the other hand, we cannot expect as high an accuracy from the present analysis as from the coronene analysis, for reasons which have been explained. The data given in Fig. 4 represent the most probable values for the bond lengths, after averaging. But as the possible error in individual bond-length measurements may be as high as  $\pm 0.03$  or  $\pm 0.04$  Å., the results must obviously be accepted with caution.

It should, however, be emphasised that the bond-length variations shown in Fig. 4 for the resolved atoms (circled) are based entirely on X-ray measurements, and are not in any way derived from chemical theory. The initial trial model which was set up in order to determine the phase constants consisted of perfectly regular planar hexagons of radius 1.39 Å. The final shifts from these initial positions are considerable, and they arise from the measured values of the structure factors which were employed as coefficients in the Fourier series.

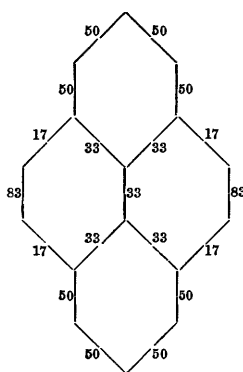
In view of this, the results receive a rather striking qualitative confirmation from a study of the simple valency bond structures which are applicable to pyrene. For a fixed position of the carbon atoms there are six different ways of drawing the bonds, (II)—(VII), and these may perhaps be considered as the structures which make the most important contributions to the normal state of the molecule.



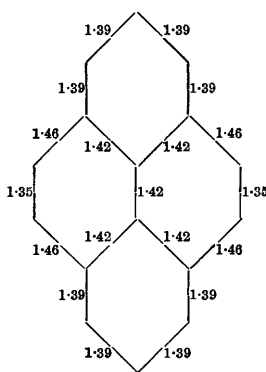
Assuming in the first instance that these structures make equal contributions (this is unlikely to be true), it is easy to compute the average double-bond character for each link in the molecule. This is shown in (VIII) as percentage double-bond character, and in (IX) these figures are translated into distances on the basis of Pauling and Brockway's empirical curve relating double-bond character and distance (*J. Amer. Chem. Soc.*, 1937, 59, 1223). In (X) the measured values of Fig. 4 are repeated for convenient comparison.



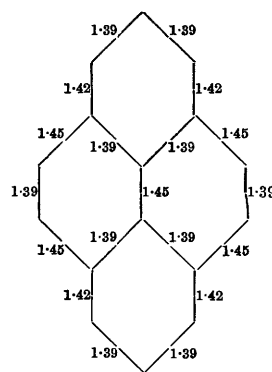
There is a distinct general resemblance between the measured values and those predicted on the basis mentioned above. The largest deviations occur in the central bonds where the



Bond orders.  
(VIII.)



Distances calculated.  
(IX.)



Distances found.  
(X.)

measured values vary from 1.38 to 1.45 Å., while the predicted values are constant at 1.42 Å. In the upper and the lower ring the predicted values are again more constant than the measured values. The average bond length over the whole molecule is in excellent agreement, the predicted value being 1.408 Å. and the measured value 1.412 Å.

Chemical evidence appears to suggest that the structures (II)—(V) are those most consistent with the reactivity of pyrene (see, for example, Cook, *Ann. Reports*, 1942, 39, 163). If the contributions of these structures are increased relatively to the others the main effect on the above calculations is to increase the length of the central bond, in agreement with the observations.

More detailed discussion of the bond distances is probably not justified until more reliable measurements can be made, or until other similar ring structures have been measured.

#### EXPERIMENTAL.

*X-Ray Measurements.*—Small tabular crystals, displaying the (001) and (110) faces, were employed. They were mounted for rotations about the  $a$ ,  $b$ , and  $c$  crystallographic axes, the weights of the principal specimens employed for intensity measurements being 0.077, 0.048, and 0.147 mg. The dimensions of the specimens were such as to make relative absorption corrections for different reflections in the same zone unnecessary. Absorption corrections were applied, however, in calculating the scale of absolute values of  $F$ .

All the X-ray work was carried out with copper- $K\alpha$  radiation,  $\lambda = 1.54$ . Rotation, oscillation, and moving-film photographs were taken, the latter mainly for intensity records. The observed halving led to the space group  $P2_1/a$  without ambiguity. The intensity measurements were carried out on a number of calibrated moving-film exposures by means of a photometer of the type described by Robinson (*J. Sci. Instr.*, 1933, 10, 233), and the different sets were correlated through the common axial reflections. Very strong reflections were reduced by a factor of 12 by means of automatic shutters in order to give accurate comparisons with the weaker reflections.

Absolute measurements were made by comparisons with standard crystals on the two-crystal moving-film spectrometer (Robertson, *Phil. Mag.*, 1934, 18, 729). In one experiment a small crystal of  $i$ -erythritol, and in another experiment a small crystal of oxalic acid, were used as standards. (Direct absolute measurements had previously been made on these standards with an ionisation spectrometer.) Good agreements were obtained in the two experiments. The absolute values of  $F$  were calculated by the usual formulæ applicable to mosaic-type crystals, and the results are collected in Table IV under "F meas."

*Fourier Analysis.*—Using the phase constants determined from the trial structures and the measured values of  $F$ , a double Fourier series was set up according to the usual formulæ. For the projection along the  $b$  crystal axis on the (010) plane, the electron density was computed at 450 points on the asymmetric unit, the  $a$  axis being divided into 60 parts (intervals of 0.227 Å.) and the  $c$  axis into 30 parts (intervals of 0.279 Å.). The summations were carried out by means of 3-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 the columns. The resulting contour map is shown in Fig. 2, three-quarters of the unit cell being included.

The projection along the  $c$  axis (Fig. 3) was computed in a similar manner. In this case each axis was divided into 60 parts, the intervals being 0.154 Å. along  $b$  and 0.223 Å. along  $a \sin \beta$ .

*Orientation of the Molecule, and Co-ordinates.*—From a consideration of the observed lengths in projection of  $ON$  and parallel distances [Fig. 2(b)], which can be only slightly tilted, it was found that the best average radius of the hexagon was 1.41 Å. With this average value and the assumption that the molecule is flat and the axes  $L$  and  $M$  are at right angles, it was possible to calculate the orientation of the molecule with regard to the crystallographic axes.

The distances  $NB$ ,  $MC$ , and  $PE$  are  $1.938 \pm 0.030$  A. in the projection, hence  $\psi_M$ , the angle which  $M$  makes with the  $b$  axis, is  $52.4^\circ$ . This method cannot be used to find the tilt of  $L$  as the line lies so nearly in the projection plane that a small discrepancy in the observed value would lead to a large difference in the angle calculated.

The calculation can be made, however, from the observed angle between  $L$  and  $M$  in the projection. Let  $\eta_L$  and  $\eta_M$  be the angles which  $L$  and  $M$  make with the  $a$  axis in projection.  $\eta_L$  is taken as the mean of the angles which  $BCF$ ,  $AOP$ , and  $NM$  make with  $a$ , which are  $60.2^\circ$ ,  $60.0^\circ$ , and  $61.3^\circ$ . The last is probably less reliable than the others as it is drawn through only two atoms and hence it was given only half the weight of the first two angles in deriving the mean value of  $60.34^\circ$ .  $\eta_M$  is the mean of the angles which  $NB$ ,  $MC$ , and  $PE$  make with  $a$ , and is observed as  $-39.3^\circ \pm 0.4^\circ$ . From these observations the complete orientation of the molecule may then be derived by making use of the nine relations which were given in the coronene analysis (Robertson and White, *J.*, 1945, 607, 615).

From the orientation of the molecule thus deduced it is possible to obtain the actual bond lengths connecting the best estimated centres of the various atoms by reducing each line for its calculated tilt. In this way the bond-length determinations already discussed were reached. The finally accepted centres for the resolved atoms are plotted on the contour map in Fig. 6.

FIG. 6.

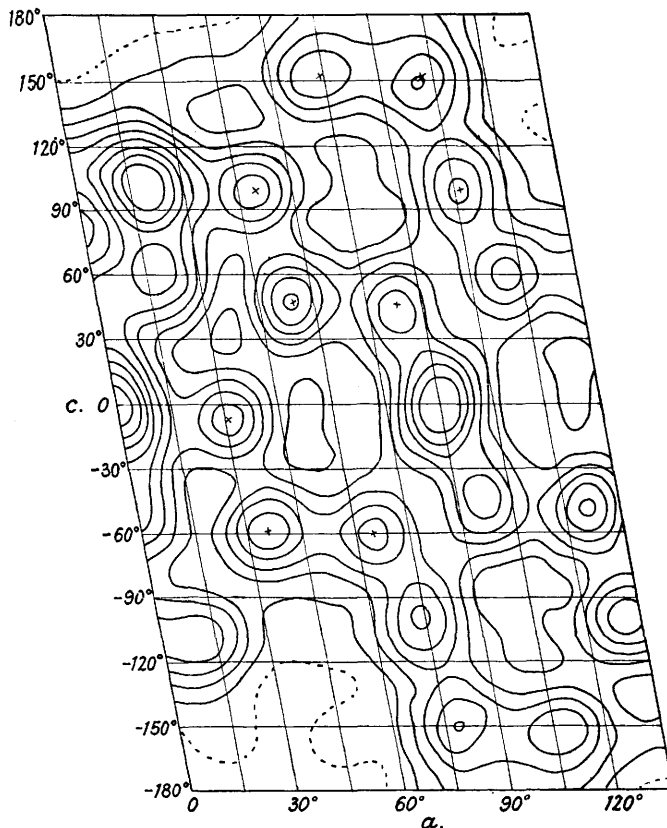
Co-ordinates assigned to the resolved atoms in the pyrene  $b$  axis projection.

Table II gives the finally accepted co-ordinates for the atoms, and includes the co-ordinates of the centre of the molecule ( $x_p, y_p, z_p$ ). The latter position can be estimated with considerable accuracy from the  $b$  axis projection (Fig. 2) and with rather less certainty from the  $c$  axis projection (Fig. 3). Even on the assumption of a strictly planar molecule, the  $b$  axis projection gives no information concerning the value of  $y_p$ , as the molecules may be translated up or down the  $b$  axis. The best value of  $y_p$  was therefore found by calculations of the  $(hk0)$  structure-factors, and confirmed from the  $c$  axis projection (Fig. 3).

On the basis of the final co-ordinates the structure factors were re-calculated and the results are given in Table IV under "F calc.". The scattering curve formerly given for hydrocarbons (Robertson, *Proc. Roy. Soc., A*, 1935, **150**, 110) was found rather unsuitable for pyrene, and the  $f_c$  values given below (max.  $f_c = 100$ ) were used instead.

$\sin \theta$ ( $\lambda = 1.54$ ) .....	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$f_c$ .....	70	56	43	30	19	12.5	8.5	5	3.5

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.
200	0.115	7.5	+ 7	205	0.462	2.5	- 12
400	0.230	47	+ 46	204	0.370	19.5	+ 21
600	0.345	< 2	- 4	203	0.285	15.5	+ 16
800	0.460	3	- 6	202	0.202	40.5	- 35
10,00	0.575	< 3	- 1	201	0.135	48	+ 43
12,00	0.690	< 3	- 1	201	0.160	6.5	+ 6
14,00	0.805	4.5	+ 2	202	0.235	18	- 15
020	0.167	< 1.5	+ 2	203	0.320	22	+ 25
040	0.333	19	+ 23	204	0.409	7	+ 1
060	0.500	< 3	+ 1	205	0.500	10.5	- 12
080	0.667	3.5	+ 5	206	0.591	21.5	+ 24
0,10,0	0.833	< 3	0	207	0.683	6.5	+ 6
001	0.094	65	+ 66	208	0.775	< 3	+ 1
002	0.187	32.5	- 31	209	0.868	< 3	0
003	0.281	5	+ 6	408	0.743	< 3	+ 3
004	0.374	< 2	- 2	407	0.657	< 3	+ 8
005	0.468	< 2.5	- 3	406	0.567	< 3	+ 2
006	0.561	9.5	+ 14	405	0.484	6.5	+ 4
007	0.654	33	+ 33	404	0.403	< 3	- 2
008	0.748	4.5	+ 1	403	0.330	3	- 7
009	0.841	4	- 4	402	0.270	12.5	+ 19
				401	0.233	38	+ 32
011	0.125	13	+ 12	401	0.264	20.5	- 16
012	0.205	< 5	- 4	402	0.320	27.5	+ 29
013	0.293	9	+ 9	403	0.393	40.5	+ 40
014	0.383	10.5	- 11	404	0.472	< 3	+ 1
015	0.475	< 8	+ 7	405	0.555	< 3	0
016	0.567	< 9	- 9	406	0.641	< 3	+ 3
017	0.660	11	- 13	407	0.729	< 3	+ 3
018	0.752	< 10	+ 1	408	0.820	< 3	- 2
021	0.191	< 5	- 2	608	0.767	< 3	0
022	0.251	8.5	+ 7	607	0.685	< 3	+ 2
023	0.326	26.5	- 25	606	0.605	< 3	+ 4
024	0.409	24	- 14	605	0.531	17	- 14
025	0.496	< 8	+ 7	604	0.461	17	- 14
026	0.585	< 9	- 3	603	0.405	< 3	- 1
027	0.675	< 10	- 1	602	0.362	3.5	- 5
031	0.267	< 6	- 1	601	0.342	9.5	- 11
032	0.312	11.5	+ 10	601	0.373	< 2	- 1
033	0.376	35	+ 30	602	0.421	17.5	- 13
034	0.450	12	- 12	603	0.482	9	- 9
035	0.530	< 9	0	604	0.550	< 3	+ 1
036	0.614	< 10	+ 4	605	0.625	< 3	- 3
037	0.701	< 10	+ 2	606	0.707	< 3	- 3
041	0.346	9	+ 14	607	0.790	< 3	- 1
042	0.382	13.5	- 15	608	0.875	< 3	+ 1
043	0.436	6.5	- 6	809	0.885	4	+ 4
044	0.501	< 9	- 3	808	0.806	5	+ 10
045	0.574	< 9	+ 2	807	0.732	< 3	+ 1
046	0.652	< 10	+ 2	806	0.660	< 3	+ 3
047	0.734	< 10	+ 4	805	0.595	< 3	+ 6
051	0.427	10.5	- 7	804	0.540	< 3	+ 2
052	0.457	< 8	- 4	803	0.494	< 3	+ 3
053	0.502	< 9	+ 3	802	0.466	23.5	+ 20
054	0.560	< 9	- 7	801	0.455	35	+ 31
055	0.626	< 10	+ 3	801	0.486	< 3	+ 4
056	0.698	< 10	+ 3	802	0.528	9	+ 12
061	0.509	7.5	- 5	803	0.580	5.5	+ 6
062	0.534	< 9	- 3	804	0.641	< 3	0
063	0.574	< 9	- 5	805	0.710	< 3	- 2
071	0.591	9	+ 9	806	0.785	< 3	+ 2
072	0.613	< 10	+ 2	10,06	0.730	< 3	- 1
073	0.647	< 10	+ 6	10,05	0.675	3	+ 10
				10,04	0.630	< 3	- 2
209	0.830	< 3	- 2	10,03	0.593	< 3	- 6
208	0.737	< 3	- 1	10,02	0.574	22	+ 17
207	0.647	7	- 7	10,01	0.569	< 3	- 2
206	0.552	< 3	+ 5	10,01	0.600	< 3	0.

TABLE IV.—continued.

Measured and calculated values of the structure factor.

$hkl$ .	$\sin \theta$ ( $\lambda = 1.54$ ).	F, meas.	F, calc.	$hkl$ .	$\sin \theta$ ( $\lambda = 1.54$ ).	F, meas.	F, calc.
10,02	0.637	< 3	+ 3	360	0.529	2.5	- 4
10,03	0.683	< 3	- 3	370	0.608	< 3	- 3
10,04	0.738	< 3	0	380	0.689	< 3	0
10,05	0.802	< 5.5	+ 7	410	0.245	11	- 10
10,06	0.870	< 3	- 3	420	0.284	< 3	+ 5
12,07	0.865	< 3	- 3	430	0.340	20	+ 20
12,06	0.809	14	+ 14	440	0.405	30.5	+ 30
12,05	0.764	10.5	+ 13	450	0.476	9	+ 7
12,04	0.725	< 3	- 2	460	0.551	< 3	- 1
12,03	0.698	< 3	0	470	0.627	< 3	- 2
12,02	0.682	< 3	0	480	0.705	< 3	+ 2
12,01	0.682	< 3	- 2	510	0.300	10	- 11
12,01	0.715	27	+ 28	520	0.333	7.5	- 6
12,02	0.749	18	+ 16	530	0.381	< 3	+ 1
12,03	0.792	< 3	- 4	540	0.440	10.5	+ 8
12,04	0.840	< 3	0	550	0.506	< 3	0
12,05	0.885	< 2	0	560	0.577	< 3	- 4
14,07	0.944	< 2	0	570	0.650	< 3	+ 3
14,06	0.897	4.5	- 4	610	0.355	10	- 11
14,05	0.856	4	- 1	620	0.383	15	- 14
14,04	0.828	< 3	- 1	630	0.426	< 3	+ 3
14,03	0.806	< 3	- 1	640	0.480	< 3	- 1
14,02	0.795	< 3	+ 3	650	0.541	5	- 5
14,01	0.798	< 3	- 4	660	0.607	< 3	+ 3
14,01	0.830	< 4	+ 3	710	0.411	< 3	+ 4
14,02	0.861	< 3	0	720	0.436	< 3	+ 4
14,03	0.898	< 2.5	0	730	0.474	< 3	+ 4
14,04	0.943	< 2	- 1	740	0.523	< 3	- 1
				750	0.580	< 3	+ 2
110	0.102	43	+ 46	760	0.642	4	- 7
120	0.176	42	+ 45	770	0.709	< 3	- 4
130	0.257	12.5	- 21	780	0.778	< 3	- 2
140	0.338	14.5	- 10	810	0.468	< 3	- 2
150	0.421	21.5	- 22	820	0.490	< 3	+ 1
160	0.503	15	- 14	830	0.524	< 3	+ 2
170	0.586	6	+ 6	840	0.568	< 3	- 4
180	0.669	< 3	0	850	0.621	< 3	+ 1
210	0.142	42	+ 43	860	0.679	< 3	- 1
220	0.203	83	- 107	910	0.524	< 3	- 3
230	0.275	32.5	+ 33	920	0.544	< 3	- 1
240	0.353	2	- 3	930	0.575	< 3	- 1
250	0.432	17	- 18	940	0.616	< 3	- 4
260	0.513	17	- 18	950	0.665	< 3	0
270	0.594	3.5	- 4	10,10	0.581	< 3	+ 1
280	0.677	< 3	0	10,20	0.599	3	+ 6
310	0.192	26.5	- 22	10,30	0.627	< 3	- 1
320	0.240	35.5	+ 32	10,40	0.665	< 3	- 1
330	0.304	22	+ 23	11,10	0.638	< 3	0
340	0.375	17.5	+ 13	11,20	0.654	< 3	+ 4
350	0.451	6.5	- 6	11,30	0.680	< 3	+ 3

These are generally smaller than the previous values. This may be due in part to errors in the absolute scale, but in addition there is a definite tendency for pyrene reflections of high order to fall off in intensity more rapidly than in anthracene and other hydrocarbons. This points to a curious difference in temperature factor, or possibly to some randomness in the structure, but further measurements are required before definite conclusions can be drawn.

The general agreements are very good, the average discrepancies, expressed as a sum of all the discrepancies divided by the sum of the measured F values, being 14.3% for the ( $h0l$ ), 12.9% for the ( $hk0$ ), and 8.8% for the ( $0kl$ ) structure factors, and 12.6% for all the structure factors together.