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The Crystal and Molecular Structure of Anthracene. II. Structure Investigation by the Triple Fourier Series Method

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A triple Fourier series investigation of the anthracene structure is described, utilizing the 667 structure factors and phase constants listed in Part I. The electron density has been evaluated at 54,000 points over the asymmetric unit (half the chemical molecule). Sections through the separate atoms are given, as well as an evaluation of the electron density in the plane of the molecule. The bond lengths can be determined by direct measurement with an accuracy estimated to be of the order of 0·01 A. They show considerable variation, from 1·36 A. for the $\alpha\beta$ bond, 1·39 for the $\beta\beta$ and the *om* bonds, 1·42 A. for the $o\alpha$ bond, to 1·44 A. for the *oo* bonds. These variations are in harmony with the chemical properties and with theoretical predictions. The molecule is planar to within about 0·01 A. The electron distribution is discussed. The hydrogen atoms are partially resolved on the electron-density maps and provide a direct measurement of the carbon–hydrogen distance at one position, where a value of 1·10 A. is obtained.

1. Introduction

The determination of 691 structure factors for the anthracene crystal has been described in the previous paper. We now apply these measurements to a full three-dimensional investigation of the structure by the triple Fourier series method. As the numerical evaluation of the results is closely similar to that already described in the corresponding investigation of the naphthalene structure (Abrahams, Robertson & White, 1949*a*, *b*), we give below only a brief account of the final results.

It has been noted in Part I that a final recalculation of the structure factors from the atomic co-ordinates now obtained (Table 3) shows that four small structure factors ($40\overline{8}$, $32\overline{3}$, $52\overline{9}$ and $27\overline{1}$) have changed sign, that is, they have been included in the present synthesis with incorrect sign. In addition, twenty-four observed structure factors (all small) were omitted from the synthesis because of uncertain sign. It can be shown that the total effect of these errors and omissions is everywhere small. (The maximum possible effect at any point, assuming all the omitted terms to be in phase, would be about 0·17 e.A.$^{-3}$. The probable effect at any point would be very much less than this.) Consequently no attempt has been made to apply corrections for these defects in the present analysis.

As in the case of naphthalene, the triple Fourier series has been evaluated at 54,000 points distributed over the asymmetric crystal unit (one-quarter of the unit cell, covering half a chemical molecule, or seven carbon atoms). A number of sections drawn through the various atoms are shown below, but the most detailed picture of the molecular structure is given in Fig. 3, where the electron density on a section drawn through the central plane of the molecule has been evaluated. On this diagram the bond lengths and electron distribution between the atoms can be measured directly.

2. Fourier synthesis

The axial subdivisions chosen were $a/60 = 0{\cdot}1427$ A., $b/60 = 0{\cdot}1006$ A., $c/60 = 0{\cdot}1861$ A., and the summation was carried out over the quarter unit cell from 0 to $\frac{30}{60}$ths along a, 0 to $\frac{30}{60}$ths along b, and 0 to $\frac{60}{60}$ths along c. Before commencing the summation the F values were multiplied by the factor $1000/V = 2{\cdot}114$ to give the final densities as electrons per A.$^3 \times 1000$. Three-figure numerical methods were used, the work being carried out on Hollerith machines under the supervision of Dr L. J. Comrie and Miss E. Gittus of the Scientific Computing Service Ltd., 23 Bedford Square, London, to whom we are again indebted for their careful handling and elaborate checking of this part of the work.

The summation totals showed the electron-density background in the regions between the molecules to be uniform, varying in general between zero and 0·2 e.A.$^{-3}$, with occasional negative regions which at no point exceeded $-0{\cdot}5$ e.A.$^{-3}$.

As in the case of naphthalene, these electron-density totals were first graphed along lines parallel to a, on a horizontal scale of about 10 cm. to 1 A. and a vertical scale of 1 cm. for a density of 0·5 e.A.$^{-3}$. From these graphs the positions of the contour levels, for sections parallel to (010) and (001), could be accurately determined. (Some additional interpolation graphs drawn parallel to b and c were also employed.) In this way eight sections passing near to the centres of each of the seven carbon atoms in the asymmetric crystal unit were constructed (fifty-six sections in all). The atomic coordinates were then measured from these sections and are collected in Table 1. One pair of sections, passing close to the centre of each atom, is reproduced in Fig. 1. The lettering of the atoms and their positions in the unit cell will be clear from Fig. 2.

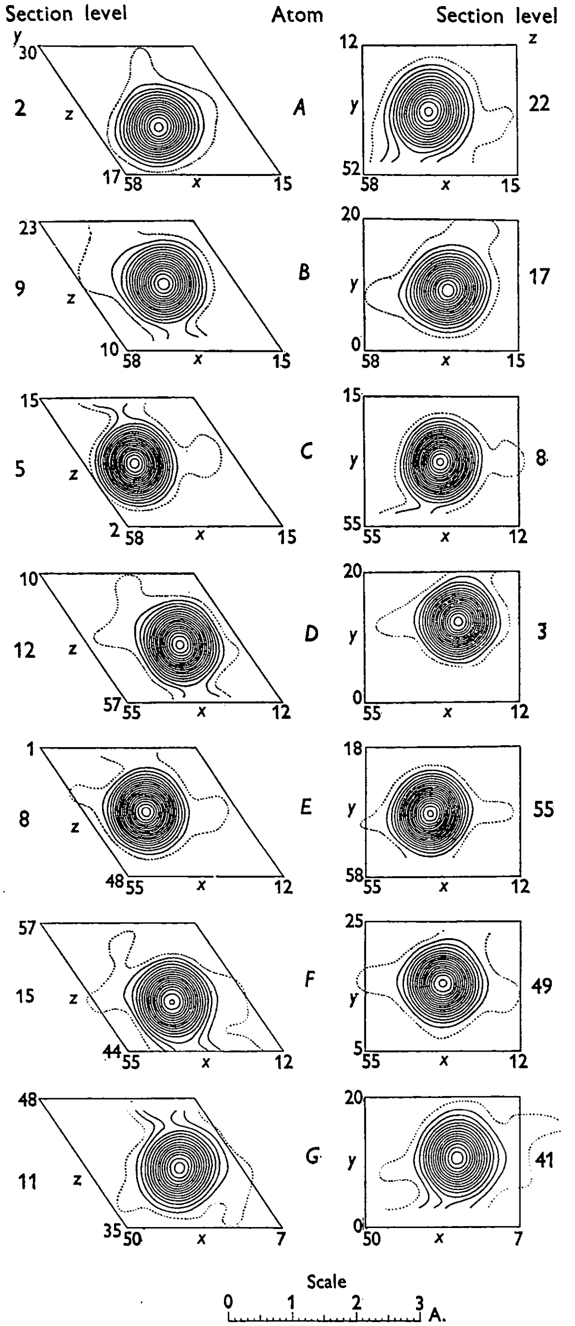


Fig. 1. Crystal sections parallel to (010) and (001) drawn near the centre of each of the seven carbon atoms in the anthracene asymmetric crystal unit. Each contour line represents a density increment of $\frac{1}{2}$ e.A.$^{-3}$, the half-electron line being dotted. Co-ordinates are given in 60ths.

It is evident from these sections as well as from the drift of values shown in some parts of Table 1 that the electron distributions are not truly spherical. The same considerations as have been mentioned in the case of the naphthalene structure probably apply here as well.

Section through the molecular plane

The averaged co-ordinates in Table 1 show that the carbon atoms lie very accurately on a plane whose equation is

$$x' - 0{\cdot}533y + 0{\cdot}500z' = 0,$$

where the co-ordinates x', y and z' are referred to orthogonal axes a, b and c', c' being taken perpendicular to the a and b crystal axes, so that

$$x' = x + z\cos\beta, \quad z' = z\sin\beta.$$

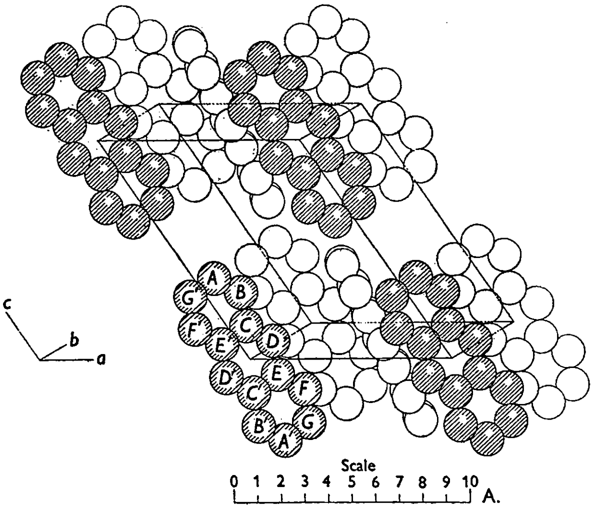


Fig. 2. Positions of the anthracene molecules in the unit cell.

The deviations of the various atoms from the plane defined above are small, and it seems unlikely that they have any real significance. The deviations are

A, +0·001 A., D −0·006 A.,
B, +0·012 A., E, −0·005 A.,
C, −0·003 A., F, +0·009 A.,
G, +0·009 A.

The electron density was next evaluated over the mean plane of the molecule, as defined by the above equation, in the same manner as has been described for naphthalene. The result is shown in Fig. 3 as a crystal section through the plane of the molecule. The bond lengths can be measured directly and with a high degree of precision from this diagram. The resolution is somewhat higher than in the case of naphthalene, and in particular the positions of the hydrogen atoms are more clearly defined. The one-electron line is seen to surround the positions of the *meso*-hydrogen atoms (attached to carbon atoms D and D'), while the hydrogen atoms attached to carbon atoms F and F' are separately resolved and indicate a carbon–hydrogen bond length of 1·10 A.

The relation of the boundary lines d and e in Fig. 3 with the crystal axes and the unit cell are shown in Fig. 4. The line d is the intersection of the molecular

Table 1. *Co-ordinates estimated from crystal sections*

Monoclinic crystal axes, centre of symmetry as origin. x and z are obtained from sections parallel to (010) and y from sections parallel to (001), at levels along the b and c axes as indicated.

	Level of sections					Average		
Atom	$b/60$	$c/60$	x (A.)	y (A.)	z (A.)	x (A.)	y (A.)	z (A.)
A	0	20	0·730	0·170	4·060	0·736 ± 0·006	0·171 ± 0·003	4·064 ± 0·004
	1	21	0·730	0·172	4·062			
	2	22	0·742	0·169	4·066			
	3	23	0·742	0·174	4·066			
B	8	15	1·005	0·953*	3·124	1·010 ± 0·005	0·939 ± 0·004	3·121 ± 0·006
	9	16	1·009	0·943	3·123			
	10	17	1·015	0·934	3·120			
	11	18	1·012	0·932*	3·115			
C	3	7	0·507	0·499	1·541	0·507 ± 0·006	0·499 ± 0·002	1·544 ± 0·004
	4	8	0·502	0·497	1·541			
	5	9	0·513	0·499	1·547			
	6	10	0·523*	0·500	1·548			
D	11	1	0·740	1·251	0·526	0·741 ± 0·001	1·246 ± 0·005	0·530 ± 0·004
	12	2	0·741	1·246	0·530			
	13	3	0·741	1·247	0·533			
	14	4	0·741	1·241	0·530			
E	6	53	0·254	0·792	−1·004	0·257 ± 0·005	0·791 ± 0·001	−1·001 ± 0·003
	7	54	0·254	0·792	−1·000			
	8	55	0·258	0·792	−1·001			
	9	56	0·262	0·790	−0·998			
F	14	48	0·513	1·540	−2·034	0·513 ± 0·001	1·546 ± 0·010	−2·032 ± 0·002
	15	49	0·513	1·544	−2·034			
	16	50	0·514	1·544	−2·030			
	17	51	0·513	1·556	−2·031			
G	9	39	0·020	1·049*	−3·534	0·021 ± 0·002	1·067 ± 0·005	−3·530 ± 0·004
	10	40	0·019	1·062	−3·532			
	11	41	0·023	1·072	−3·528			
	12	42	0·021	1·085*	−3·527			

* Omitted from average: section elliptical.

plane with the plane $z' = 0$ (or 001), and e is the intersection of the molecular plane with the plane $y = 0$ (or 010). From the equation of the molecular plane we have, for the line d,

$$x' = 0{\cdot}533y,$$

from which the angle between the b crystal axis and d is

$$\tan^{-1} 0{\cdot}533 = 28{\cdot}1^\circ.$$

Similarly, the angle between c' and e is

$$\tan^{-1}(-0{\cdot}500) = -26{\cdot}6^\circ.$$

The lengths of the lines d and e are

$$d = b/\cos 28{\cdot}1^\circ = 6{\cdot}840 \text{ A. (interval, } d/60 = 0{\cdot}114 \text{ A.)},$$
$$e = c'/\cos 26{\cdot}6^\circ = 10{\cdot}260 \text{ A. (interval, } e/60 = 0{\cdot}171 \text{ A.)}.$$

From these relations the angle θ between d and e is given by

$$\cos\theta = -\sin 28{\cdot}1^\circ \sin 26{\cdot}6^\circ,$$
$$\theta = 102{\cdot}1^\circ.$$

3. Molecular dimensions, co-ordinates and orientation

Direct measurement of the bond lengths and angles from Fig. 3 gives the results shown in Fig. 5 and Table 2. These results may also be obtained by calculation from the averaged co-ordinates in Table 1 and Table 3. The agreement obtained by these two methods is a good check on the accuracy of the graphical interpolation work, as the atom sections in Fig. 1 and Fig. 3 are drawn quite independently, and cut the atoms in quite different directions. The bond lengths calculated from the co-ordinates differ on the average by only 0·002 A. from those measured on Fig. 3, with a maximum deviation of 0·004 A., while the calculated angles differ on the average by 9′ from those measured, with a maximum deviation of 17′.

The co-ordinates referred to the monoclinic crystal axes and to the orthogonal axes are collected in Table 3, expressed in Ångström units and in angular measure.

The orientation of the molecule with respect to the orthogonal axes a, b and c' has been expressed in the same manner as for naphthalene, by giving the angles between these axes and the molecular axes L (long axis), M (short axis) and N (normal). The results are given in Table 4, and are compared with those obtained in the earlier (Robertson, 1933) investigation.

4. Discussion

Bond lengths

It is well known that the chemical structure of anthracene requires a much higher degree of molecular symmetry than is displayed by the molecule in the crystalline state. To satisfy the chemical requirements the bonds *AB* and *FG*, *BC* and *EF*, *CD* and *DE* (Fig. 5) should be identical. These bonds are, however, crystallographically independent, and their separate measurements are recorded in Fig. 5. The differences in the

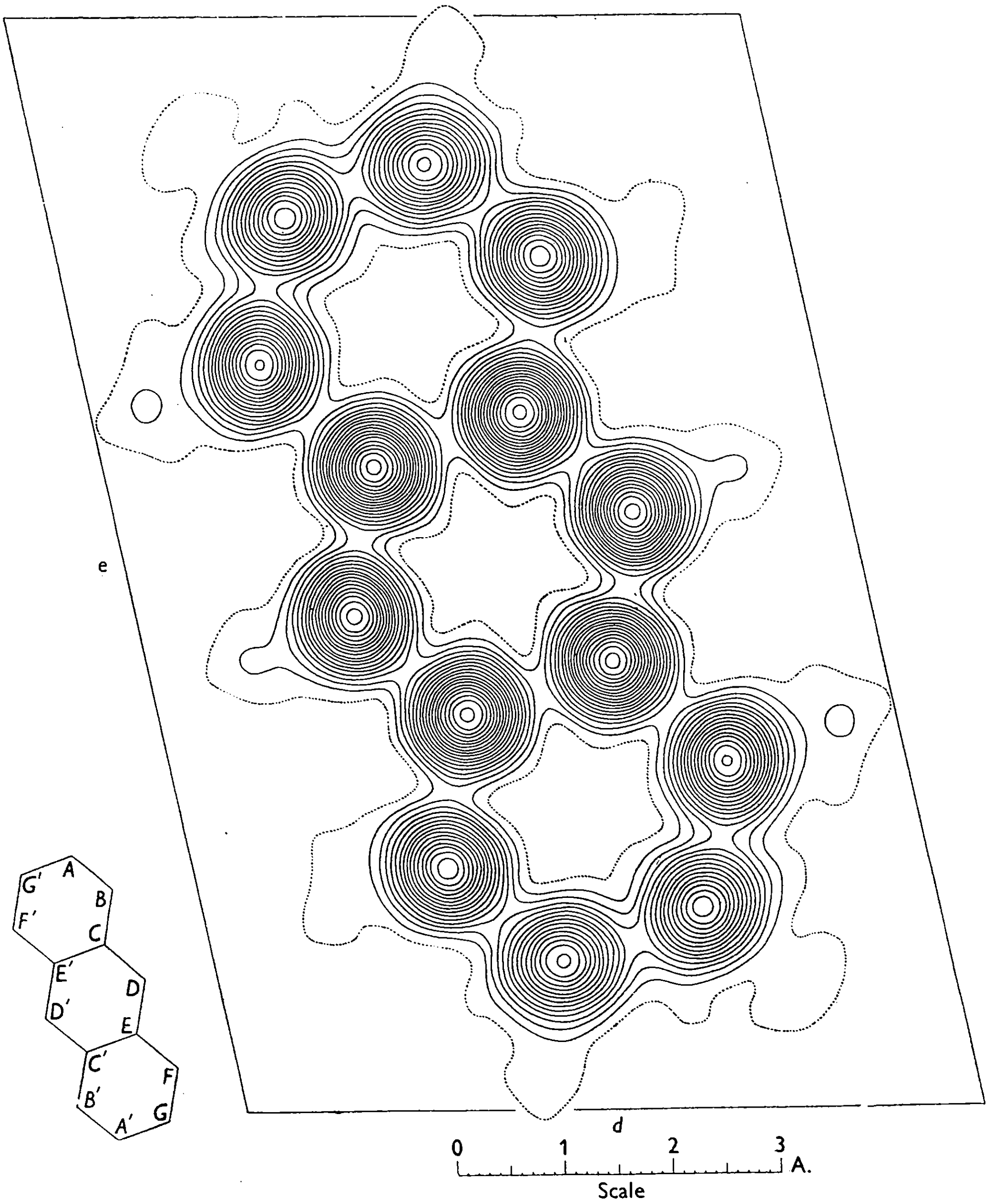


Fig. 3. A crystal section through the plane of the anthracene molecule. Each contour line represents a density increment of $\frac{1}{2}$ e.A.$^{-3}$, the half-electron line being dotted.

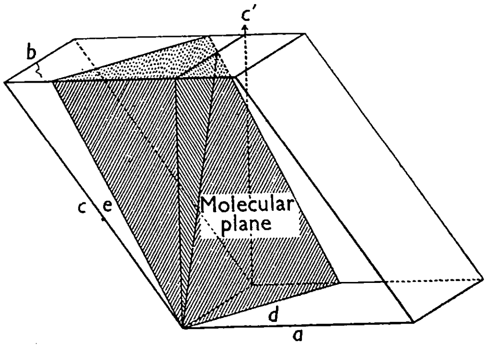


Fig. 4. Relation of molecular plane to the crystal axes and unit cell.

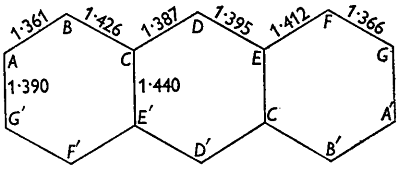


Fig. 5. Dimension of the anthracene molecule.

measurements of the separate members of these pairs amount to 0·005, 0·014 and 0·008 A., the mean difference being 0·009 A.

Table 2. *Dimensions of molecule*

(Measured from section through the mean plane.)

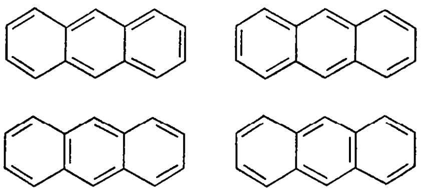
$AB = 1{\cdot}361$ A.
$BC = 1{\cdot}426$ A.
$CE' = 1{\cdot}440$ A.
$CD = 1{\cdot}387$ A.
$DE = 1{\cdot}395$ A.
$EF = 1{\cdot}412$ A.
$FG = 1{\cdot}366$ A.
$GA' = 1{\cdot}390$ A.

F-hydrogen = 1·102 A.

$G'AB = 121^\circ\ 10'$
$ABC = 120^\circ\ 45'$
$BCE' = 117^\circ\ 55'$
$E'CD = 119^\circ\ 0'$
$CDE = 122^\circ\ 10'$
$DEC' = 118^\circ\ 45'$
$C'EF = 119^\circ\ 0'$
$EFG = 120^\circ\ 40'$
$FGA' = 120^\circ\ 45'$

E–F-hydrogen = 119° 40′
G–F-hydrogen = 119° 40′

The non-excited (Kekulé) structures for anthracene are four in number, as shown below, and to some extent



these structures reflect the chemical properties, although the much more numerous excited structures are probably more important. A superposition of the simple Kekulé structures shown above, in conjunction with the empirical curve relating double-bond character to bond length (Pauling & Brockway, 1937), leads to a considerable measure of agreement with our measured values. This treatment, for example, predicts a distance of 1·36 A. for the shortest bond $\alpha\beta$, a distance of 1·44 A. for the bond oo, and a distance of 1·39 A. for the bond om, all in accurate agreement with our measurements. Our measurements on the other two bonds, however, differ considerably from the predicted values which are 1·44 A. in each case.

Table 3. *Co-ordinates referred to crystal axes*

(Origin at centre of symmetry.)

Atom	x (A.)	x' (A.)	$2\pi x/a$	y (A.)	$2\pi y/b$	z (A.)	z' (A.)	$2\pi z/c$
A	0·736	−1·577	31·0°	0·171	10·2°	4·064	3·341	131·2°
B	1·010	−0·767	42·5	0·939	56·1	3·121	2·565	100·8
C	0·507	−0·372	21·4	0·499	29·8	1·544	1·269	49·9
D	0·741	0·439	31·2	1·246	74·4	0·530	0·435	17·1
E	0·257	0·827	10·8	0·791	47·3	−1·001	−0·823	−32·3
F	0·513	1·670	21·6	1·546	92·3	−2·032	−1·671	−65·6
G	0·021	2·030	0·9	1·067	63·7	−3·530	−2·902	−114·0

Table 4. *Orientation*

		1933 values
$\cos\chi_L = -0{\cdot}4950$	$\chi_L = 119{\cdot}7^\circ$	$\chi_L = 119{\cdot}7^\circ$
$\cos\psi_L = -0{\cdot}1222$	$\psi_L = 97{\cdot}0$	$\psi_L = 96{\cdot}9$
$\cos\omega_L = +0{\cdot}8602$	$\omega_L = 30{\cdot}6$	$\omega_L = 30{\cdot}7$
$\cos\chi_M = +0{\cdot}3207$	$\chi_M = 71{\cdot}3$	$\chi_M = 69{\cdot}6$
$\cos\psi_M = +0{\cdot}8943$	$\psi_M = 26{\cdot}6$	$\psi_M = 28{\cdot}6$
$\cos\omega_M = +0{\cdot}3118$	$\omega_M = 71{\cdot}8$	$\omega_M = 70{\cdot}9$
$\cos\chi_N = +0{\cdot}8072$	$\chi_N = 36{\cdot}2$	$\chi_N = 37{\cdot}4$
$\cos\psi_N = -0{\cdot}4301$	$\psi_N = 115{\cdot}5$	$\psi_N = 117{\cdot}5$
$\cos\omega_N = +0{\cdot}4034$	$\omega_N = 66{\cdot}2$	$\omega_N = 66{\cdot}9$

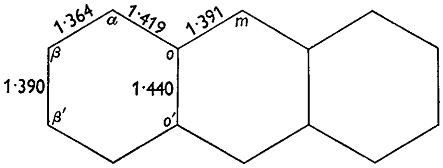


Fig. 6. Averaged values for the bond lengths in anthracene.

Although there may well be a real difference (of very small order) in these bond lengths, due to the manner in which the molecules are packed together to form the crystal lattice, the differences are only of the order of the probable experimental error in this work, and it will be better for the present purpose to average these values. This has been done in Fig. 6. Taking account of all the uncertainties in this work, it seems likely that these final averaged values for the bond lengths in anthracene should be accurate to within about 0·01 A. A similar conclusion was reached with regard to the accuracy of the bond-length measurements in the naphthalene structure (Abrahams *et al.* 1949*b*).

A more direct correlation with the chemical properties of anthracene may be obtained from our measurements by evaluating the corresponding bond orders and free valence numbers, according to the definitions of Coulson (1939, 1941). If this is done, it is found that the m position has the highest free valence, with the α position next, and then the β position. This sequence is in accord with the known chemical properties.

Extensive theoretical calculations have recently been carried out for the anthracene structure (for references see Abrahams *et al.* 1949*b*), but it is beyond the scope of the present paper to discuss these conclusions in detail. It may simply be noted here that our measurements show quite a promising agreement with the latest wave-mechanical treatments.

Electron distribution

In addition to bond-length measurements, the present investigation provides a very detailed picture of the electron distribution in the anthracene molecule. The peak values for the electron density on the different atoms are generally somewhat higher than those found in the naphthalene molecule. The general level of the peak values will depend on the absolute scale of the structure-factor measurements. Although absolute values are difficult to determine with precision, it is not likely that the naphthalene and anthracene measurements are in error by any large factor. The difference in the average level of peak values in the two crystals shows that the temperature factor is different in the two cases. This is to be expected in view of the higher melting point of anthracene (218° C. as against 80° C. for naphthalene) and the stronger binding forces which must exist between the molecules in the crystal.

The peak values of the density on the individual atoms in the anthracene molecule are found to fall off in a striking manner as we pass outwards from the centre of the molecule. This effect was noticed during the 1933 investigation on anthracene, and was also evident during our recent investigation of naphthalene (Abrahams *et al.* 1949*b*). It has been observed in a number of other organic crystal structures as well. The peak values on the different atoms in anthracene (Fig. 3), expressed as electrons per A.^{3}, are as follows

A, 7·5 G, 7·5
B, 8·0 F, 8·5
C, 9·5 D, 9·0 E, 9·0

Together with this effect there is the noticeable feature that for the atoms of the outer rings the electron-density contours are somewhat less circular than for the atoms of the central ring, and the bridge values of the electron density between the outermost pairs of atoms (AG', AB, $F'G'$) are higher than the average bridge values between the atoms of the central ring.

As has been suggested in the case of naphthalene, these features in the outer ring may be due to thermal agitation. If the molecule is oscillating about its centre, the effect would be most marked on the outlying atoms and consequently give rise to this slight blurring effect. Additional evidence in favour of this view is that the binding forces between the ends of the molecules appear to be relatively weaker than those between the sides of neighbouring molecules. This is demonstrated by the fact that the (001) plane is the most important natural face of the crystal and is also the cleavage plane.

Until these effects can be more accurately investigated and explained, it is difficult to attempt any correlation between the bridge values in the different bonds and the chemical properties of the compound.

Hydrogen atoms

The hydrogen atoms are more clearly defined than in the naphthalene structure, and their positions in Fig. 3 are indicated by electron-density maxima varying from just over $\frac{1}{2}$ e.A.$^{-3}$ for the hydrogen atoms attached to carbon atoms A, G, A' and G' to over 1 e.A.$^{-3}$ for those attached to carbon atoms D, F, D' and F'. This better definition is no doubt related to the lower temperature-factor effect described above, but in addition the fact that a greater electron density is associated with the hydrogens of the *meso*-carbon atoms may have some chemical significance. This part of the anthracene molecule displays more aliphatic character than do the positions in the other rings, and one might therefore expect the *meso*-hydrogen atoms to be relatively more negative than the others, i.e. to be associated with a somewhat greater share of the electron distribution.

The resolution of the hydrogen atom attached to carbon F is also very striking, and is sufficiently good to provide a reasonable estimation of the carbon–hydrogen distance. The value obtained, 1·10 A., is in good agreement with that generally assumed for this interatomic distance (Pauling, 1939, p. 158.).

In conclusion we wish to express our thanks to the Department of Scientific and Industrial Research for a Special Research Grant and for a Maintenance Allowance which enabled one of us (V.C.S.) to take part in this work. We are also indebted to the Carnegie Trustees for a Scholarship which enabled A.McL.M. to take his part in the work.

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