A Detailed Refinement of the Crystal and Molecular Structure of Anthracene

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A detailed refinement of Mathieson, Robertson & Sinclair's X-ray crystallographic data for anthracene is described. The many calculations needed were carried out on the Manchester University electronic computer. The difference maps indicate some channelling of the electrons along the lines of the bonds. The anisotropic vibrations of the carbon atoms are interpreted in terms of anisotropic translational and rotational oscillations of the molecules. The magnitudes of the angular oscillations agree well with those inferred from Raman spectra. C–C bond lengths with e.s.d.'s of about 0·004 Å and bond angles with e.s.d.'s of about 12′ are obtained. Close intermolecular approaches explain a very slight buckling of the molecules.

1. Introduction

The planar ring structures of the naphthalene and anthracene molecules were conclusively established by Robertson's (1933*a*, *b*) early applications of the double Fourier series method of X-ray crystal structure analysis. More recently Robertson and his co-workers have made very complete redeterminations of these structures by three-dimensional methods (naphthalene: Abrahams, Robertson & White, 1949*a*, *b*; anthracene: Mathieson, Robertson & Sinclair, 1950, and Sinclair, Robertson & Mathieson, 1950). In these investigations the carbon co-ordinates were determined by triple Fourier series of observed structure factors evaluated at points throughout the unit cell. These results have been corrected for finite-series effects by Ahmed & Cruickshank (1952), using Booth's (1945, 1946*a*) back-shift method. The corrections were made by computing differential syntheses (Booth, 1946*b*) with the observed and calculated structure factors given by Robertson and his co-workers. The finite-series corrections were not very large, averaging only 0·0058 Å per co-ordinate for each molecule, although in anthracene the bond AG' increased by 0·018 Å (see Figs. 1–3 for designation of carbon atoms).

The present paper describes a very considerable extension of Ahmed & Cruickshank's refinement of Mathieson, Robertson & Sinclair's data for anthracene. It has proved possible to obtain a detailed description of the anisotropic thermal motion of the anthracene molecules in the crystal, and in consequence to obtain some interesting results about the molecular electron density. The very large calculations necessary were carried out on the Manchester University electronic computer.

The space group for anthracene is $P2_1/a$, with two molecules in a unit cell of dimensions (Mathieson *et al.*, 1950)

$$a = 8\cdot561, \ b = 6\cdot036, \ c = 11\cdot163 \text{ Å and } \beta = 124° 42'.$$

2. Isotropic refinement

Though the present calculations were started with the intention of still further refining the anthracene bond lengths, the most interesting results concern the anisotropic thermal motion of the molecules. Sinclair *et al.* noticed that in the observed Fourier synthesis the peak heights fell off from 9·0–9·5 e.Å^{-3} for the carbon atoms C, D, E of the central ring to 7·5 e.Å^{-3} for the outer atoms A and G. They suggested that this might be due to thermal oscillations of the molecules about their centres (a suggestion also made by Robertson in his two-dimensional investigations of 1933). Ahmed & Cruickshank found that the spread of the peak heights, which they computed to be from 9·76 e.Å^{-3} (atom C) to 7·56 e.Å^{-3} (atom A), was much reduced when finite-series effects were considered. In their calculated differential syntheses, using F_c's for which each carbon had been given the same empirical scattering-factor curve, the peak heights varied from 9·10 e.Å^{-3} (atom C) to 7·94 e.Å^{-3} (atom A), so that the net differences ranged only from +0·66 e.Å^{-3} to −0·38 e.Å^{-3}. This suggested, falsely as it turned out, that the angular oscillations were of little importance.

The present refinement has consisted of a series of cycles on the Manchester computer, each cycle involving the calculation of a set of structure factors followed by observed and calculated differential syntheses (Ahmed & Cruickshank, 1953). For the first cycle the empirical scattering-factor curve for carbon was replaced by that of McWeeny (1951), with a temperature factor $B = 3\cdot17$ Å^2. With the hydrogens still omitted, the residual R dropped from the former 19·6% to 16·6%. It was then decided to vary individually the isotropic temperature factors of the chemically different carbon atoms so as to make the observed and calculated peak densities equal. For this Mathieson *et al.*'s experimental determination of the absolute scale of the $|F_o|$ was assumed correct. The temperature factor variations were made by trial and

error. By the fourth cycle R had dropped to 12·7%, the hydrogens being included at the assumed positions of Table 1, which gave C–H lengths of 1·09 Å. The

Table 1. *Assumed hydrogen fractional co-ordinates*

Atom	x	y	z
H–A	0·1327	0·0910	0·4726
H–G	0·0278	0·2790	−0·3852
H–B	0·1887	0·3168	0·3185
H–F	0·1307	0·4172	−0·1432
H–D	0·1554	0·3703	0·0841

temperature factors were then 4·00 Å² (atoms A and G), 3·45 Å² (B and E), 2·52 Å² (C and E) and 2·83 Å² (D); $B = 3·4$ Å² being assumed for all the hydrogens.

The variation of the B values was rather greater than had been expected from the variation in the peak heights. It implied that the rotational oscillations of the molecules about their centres were of appreciable magnitude. Examination of the observed and calculated peak curvatures showed that for all atoms, except C and E, the apparent directions of minimum vibration were approximately towards the centre of the molecule. This was a further indication of the angular oscillations. For C and E the directions of minimum vibration were perpendicular to the molecular plane. The interpretation of this did not become clear until much later in the analysis; it proved to be due to anisotropic translational vibrations of the molecule.

At this stage further refinement was delayed until the Manchester computer had been programmed to deal with anisotropic thermal motion and to compute difference maps directly in the (non-crystallographic) plane of the molecule (Cruickshank, Pilling, Ahmed & Bullough, 1957). The difference map then computed, using (F_o-F_c) as the Fourier coefficients, is shown in Fig. 1(a), the F_c's being those computed in the fourth isotropic cycle mentioned above, but with the hydrogen atoms omitted. The axes d and e are those defined by Sinclair *et al.* In Sinclair *et al.*'s map of the observed electron density only the hydrogen atoms attached to F and F' are separately resolved, the remainder appearing as bulges on the sides of the carbons. In the present difference map all the hydrogens appear as distinct peaks, though owing to random experimental errors the hydrogens attached to B and B' have double maxima. The apparent C–H distances vary from 0·87 Å to 1·10 Å, with a mean of 1·01 Å. The expected C–H distances of 1·09 Å are indicated as full lines in Fig. 1(a).

The other features of importance are the small peaks on the lines AG', CD, DE etc., and the depressions inside the rings. Discussion of the latter will be deferred. The former are due to anisotropic thermal motion. The peak between A and G' is due to the large movements of these atoms in the molecular oscillation about the axis perpendicular to the molecular plane. The interpretation of the peaks between C and

D, and D and E, did not become clear until the anisotropic thermal analysis was completed; they appear because the translational vibrations of the molecule are largest along its long axis. None of these peaks can be due to bonding effects as they are sharper than the peaks representing the hydrogen atoms.

Difference maps in planes $\frac{1}{4}$ Å, $\frac{1}{2}$ Å, $\frac{3}{4}$ Å, from the central plane of the molecule were also computed simultaneously. Fig. 1(b) shows the map $\frac{1}{2}$ Å above the central plane. Its features are less prominent than those of Fig. 1(a). The features of the map for $\frac{1}{4}$ Å are intermediate between those of Figs. 1(a) and 1(b), while the map for $\frac{3}{4}$ Å is almost flat. The difference maps thus show that the thermal motion is most anisotropic in the molecular plane.

3. Determination of the anisotropic thermal motion

While the computation of these differences maps was in progress, the separate determination of the anisotropic thermal motion was begun. For this each carbon atom was assumed to have its stationary scattering factor multiplied by a temperature term,

$$\exp -(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{23}kl+b_{13}hl) ,$$

depending on six parameters b_{ij}, different for each atom. One criterion for finding the six b_{ij}'s for an atom is to require that the six second derivatives ($\partial^2\varrho/\partial x^2$, $\partial^2\varrho/\partial x \partial y$, etc.) of the observed and calculated electron densities shall be equal at the atomic position (Cochran, 1951). The b_{ij}'s may be found by a process of successive refinement similar to that used for atomic co-ordinates. After calculating F_c's using given b_{ij}'s, observed and calculated differential syntheses are computed, and from the differences of the six observed and calculated second derivatives for each atom a new set of anisotropic parameters is derived. Sets of sixth-order linear equations connect the differences in the second derivatives with the alterations to the b_{ij}'s (Cruickshank, 1956a). These are readily set up and solved on the electronic computer.

After a first anisotropic refinement cycle in which R dropped to 11·0%, some doubt arose as to the validity of this method of determining anisotropic thermal motion. The objection is that the above criterion attributes all the differences between the observed and calculated peaks to the thermal motion, and does not allow for possible changes in the peak shapes due to the formation of bonds. One method (Jeffrey & Cruickshank, 1953) of minimizing this difficulty is to determine the temperature parameters from the high-order reflexions only. For these, the major part of the X-ray scattering is from the carbon inner-shell electrons, which are not involved in the bonding. Ideally the reflexions used would have a reciprocal radius approximately equal to or greater than that of the limiting sphere for Cu $K\alpha$ radiation. However, as Mathieson *et al.*'s data were obtained
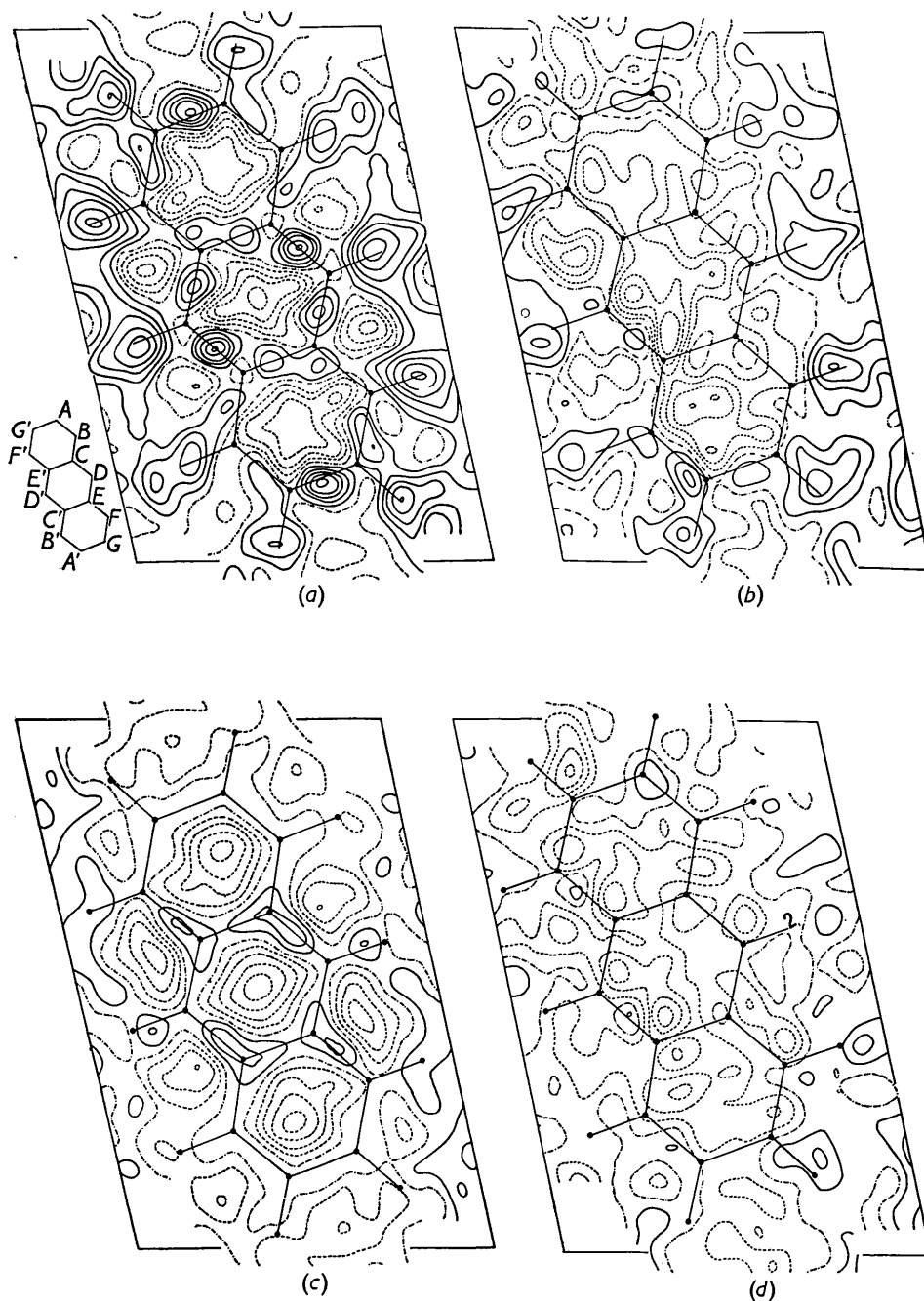
Fig. 1. (a, b) Difference map (a) in central plane of molecule, (b) ½ Å above central plane; isotropic carbons subtracted. (c, d) Difference map (c) in central plane, (d) ¾ Å above central plane; anisotropic carbons and isotropic hydrogens sub-tracted. Contour intervals 0·1 e.Å⁻³. Full lines: positive; chain lines: zero; broken lines: negative.

with Cu radiation, a compromise was necessary in the present work and planes with $\sin \theta > 0.65$ were considered as high-order planes. This reduced the number of independent planes used in the determination of the anisotropic thermal motion from the original 667 to 427 (64%). In differential syntheses computed using only high-order planes the peak densities were

approximately 45%, and the peak curvatures 75% of their original values.

The first anisotropic cycle was then extended by computing a set of differential syntheses using the high-order planes only. From the differences of the observed and calculated second derivatives a new set of thermal parameters was derived. Further cycles

were carried in a similar manner. Sufficient convergence was obtained by the end of the fourth anisotropic cycle. Table 2 shows the variation of the residual

Table 2. *Variation of R during the refinement*

	All planes (%)	High-order planes (%)
Mathieson *et al.* (empirical *f* curve)	19·6	—
4th isotropic cycle	12·7	14·8
1st anisotropic cycle	11·0	12·0
4th anisotropic cycle	10·8	11·2
6th anisotropic cycle (Hoerni & Ibers *f*)	10·9	11·5

R during the course of the refinement. As was to be expected, the inclusion of the anisotropic thermal motion resulted in a considerable improvement for the high-order planes. In each set of anisotropic structure factors it was assumed for simplicity that the hydrogens were vibrating isotropically, with temperature factors of 5·0, 4·0 and 3·4 $Å^2$ for those attached to A and G, B and F, and D, respectively. The hydrogen co-ordinates were those of Table 1.

The accurate determination of the thermal motion depends on the correctness of the absolute scale of Mathieson *et al.*'s experimental data. Throughout the refinement a careful watch was kept for any evidence that the scaling was proving unsatisfactory. A good check, both on the scaling and on the derived thermal parameters, can be obtained from the observed and calculated peak heights, which should be equal in the syntheses computed with the high-order planes. Table 3 shows the ratios of the high-order observed and calculated peak heights and curvatures in the fourth anisotropic cycle. The amounts to which the entries in the last four rows differ from unity are a measure of the extent to which the refinement is incomplete. The greatest unrefined curvature difference is 2·8% on $\partial^2 \varrho / \partial x^2$ of atom A. The mean of all the curvature ratios is out by only 0·4%. The entries in the first row should be 1·000 if the experimental scale and the derived thermal motion are correct. The largest error is only 1·4% and the mean is out only by 0·2%. The excellent agreement of the high-order observed and calculated peak densities is very satisfactory. It suggests that the McWeeny scattering factor curve

and the scaling of the experimental data are both very good for the high-order planes, or possibly have small complementary errors.

4. Final difference maps

The final difference map in the plane of the molecule is shown in Fig. 1(c). For this all the observed reflections were used and the F_c's were those calculated in the fourth anisotropic cycle, with the hydrogens included. Fig. 1(d) shows the map $\frac{3}{4}$ Å above the central plane, which was computed simultaneously. The estimated standard deviation of the difference map density calculated by Cruickshank's (1949) formula is 0·11 e.Å^{-3}. There are three main features of Fig. 1(c): the negative regions with minima of approximately $-0·45$ e.Å.$^{-3}$ enclosed by the six-membered rings; the negative regions between neighbouring C–H lines; and the slightly positive regions around the lines joining adjacent atoms. The differences between the densities at the various carbon positions, at the various hydrogen positions and at the mid-points of the bonds are not significant, though it is perhaps tempting to suggest that the densities at the carbons C and E may be higher than elsewhere. The features of Fig. 1(d) are less marked; the random behaviour of the contour lines is probably due to experimental errors and to incompletely refined thermal motion. The only general trend in this map is for the region above the carbon skeleton to be slightly negative. In summary, the difference maps show a slight concentration of the electrons along the lines of the bonds.

Caution is needed in interpreting these maps. They should represent the difference between the actual anthracene crystal electron density and that of the model used for the F_c's. The model consists of anisotropically vibrating 'molecules', each consisting of fourteen non-bonded (sp^3) carbon atoms, with Duncanson & Coulson (1944) analytical wave functions, and ten hydrogen atoms, the anisotropic motion having been determined from the high-order reflexions. The apparent interpretation of the difference maps is thus that the electrons are rather more channelled along the bonds in the actual molecules than they are in mere aggregates of atoms.

The difficulties of the present technique must be

Table 3. *Ratios of observed and calculated peak heights and curvatures for high-order planes in the 4th anisotropic cycle*

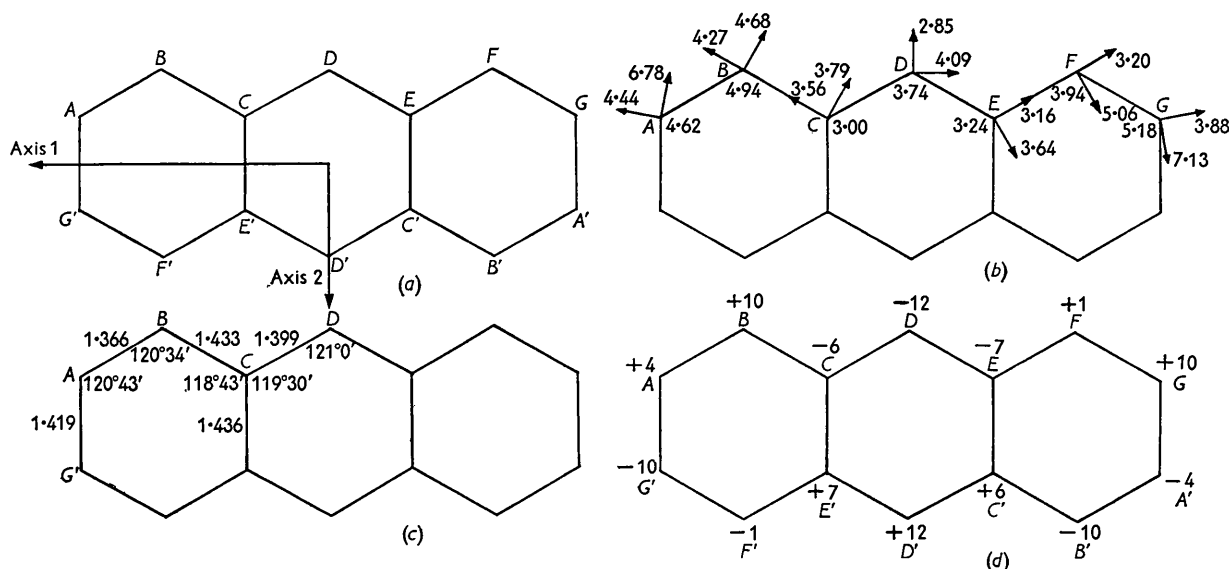| Atom	A	G	B	F	C	E	D	Mean
ϱ_0/ϱ_c	0·986	0·986	0·992	1·008	1·002	1·002	1·007	0·998
$\dfrac{\partial^2 \varrho_0}{\partial x^2} \Big/ \dfrac{\partial^2 \varrho_c}{\partial x^2}$	0·972	0·990	0·976	1·017	0·995	0·991	1·007	0·993
$\dfrac{\partial^2 \varrho_0}{\partial y^2} \Big/ \dfrac{\partial^2 \varrho_c}{\partial y^2}$	0·977	0·982	0·991	1·016	1·004	1·001	1·013	0·998
$\dfrac{\partial^2 \varrho_0}{\partial z^2} \Big/ \dfrac{\partial^2 \varrho_c}{\partial z^2}$	0·993	0·997	0·994	1·004	1·000	0·997	1·001	0·998
Mean curvature ratio	0·980	0·990	0·987	1·012	1·000	0·996	1·007	0·996

Fig. 2. (a) Natural molecular axes. (b) Values of $\overline{u^2}$ (in 10^{-2} Å^2) in the directions radial, tangential and perpendicular. (c) Corrected mean bond lengths (in Å) and angles. (d) Displacements (in 0·001 Å) of carbons from mean plane.

borne in mind. The first is the possibility of error in the absolute scale of the experimental data. One check on this has already been described; another is that the difference synthesis should integrate to zero in a reasonable molecular volume (the integral is identically zero for the whole unit cell). Examination of Figs. 1(c) and 1(d) suggests that the integral is about minus 2–3 electrons. As there are 94 electrons in an anthracene molecule, this may imply that the scale of the experimental F_o's should be raised by about 2–3%, an amount not precluded by the accuracy of the earlier check. A second difficulty is that, whatever the absolute scale, a systematic variation of the relative experimental scale with sin θ would invalidate the whole method, since the thermal motion is found from the high-order planes while the difference synthesis uses all the planes. Such an error might be the cause of the apparent 2–3% scaling error just mentioned. The error would undoubtedly have been greater if Mathieson et al. had not applied approximate corrections for absorption to the intensities. A final difficulty of the present technique is that the determination of the thermal motion depends on the correctness of the McWeeny scattering curve at high sin θ.

Some support for the technique may, however, be derived from the consistency of the different portions of Fig. 1(c). The molecule has only a crystallographic centre of symmetry, yet the left- and right-hand sides of the map are alike within random experimental error. Further, the negative regions within the carbon rings are similar.

As a check on the effects of using the McWeeny carbon f curve, two further cycles of anisotropic

refinement were run using the intrinsically more accurate Hoerni & Ibers (1954) scattering curve, derived from the self-consistent-field wave functions with exchange. The difference densities, evaluated at a number of key positions, were little changed, as the slightly sharper s.c.f. calculated peaks were compensated by the slightly larger ($\sim$ 3%) temperature factors required. The R values were also little affected and are shown in the last line of Table 2.

Rather similar difference maps have been obtained for benzene by Cox, Cruickshank & Smith (1957), though in that work the uncertainties were much greater. There are at present no theoretical calculations with which these results can be compared. Marsh (1952) has calculated the electron distribution in benzene by the molecular orbital method of linear combinations of atom orbitals. No comparison with his results can be made because of the effects of thermal motion and finite series. The first stage in an effective comparison with theory would be the calculation of theoretical difference maps, representing the difference between molecular orbital densities and the densities of aggregates of non-bonded atoms. The second stage would be the calculation of the effects of thermal motion and finite series on such difference maps. Rather rough calculations suggest that the negative regions in the centres of the six-membered rings are deeper than predicted by the simple l.c.a.o. theory. Detailed calculations will be needed to determine whether these holes can be explained simply by a change of the screening constants for the σ-orbitals or whether the l.c.a.o. method itself is particularly erroneous at the centre of a ring, as elementary considerations of electron repulsion would suggest.

Table 4. *Observed and calculated U_{ij}*

(Values in 10^{-2} Å^2)

Atom	U_{11}		U_{12}		U_{13}		U_{22}		U_{23}		U_{33}	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
A	4·68	3·94	0·81	0·63	−0·42	0·04	6·54	6·56	0·95	0·59	4·62	5·00
G	3·88	3·94	−0·31	−0·80	−0·52	−0·09	7·13	6·56	−0·26	−0·12	5·18	4·74
B	5·17	4·35	0·65	0·88	−0·11	0·26	3·78	4·57	0·31	0·53	4·94	4·67
F	3·91	4·35	−0·95	−1·05	0·26	0·09	4·35	4·56	−0·27	−0·41	3·94	4·33
C	3·59	3·94	0·08	0·15	0·54	0·00	3·76	3·28	−0·10	0·07	3·00	3·20
E	3·52	3·94	−0·34	−0·33	0·37	−0·05	3·28	3·28	−0·37	−0·17	3·24	3·11
D	4·09	4·35	−0·57	−0·09	0·30	0·17	2·85	2·87	0·15	−0·09	3·74	3·61

5. Description of the anisotropic thermal motion

The final set of anisotropic thermal parameters b_{ij} for the carbon atoms will be taken as those determined after the fourth anisotropic cycle, the last in which the McWeeny scattering curves were used. The b_{ij}'s for each atom were then transformed to symmetric tensors **U** such that

$$\overline{u^2} = \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} l_i l_j$$

is the value of the mean square oscillation in Å^2 in a direction $\mathbf{l} = (l_1, l_2, l_3)$ (Cruickshank, 1956a). (For isotropic motion the ordinary temperature parameter $B = 8\pi^2 \overline{u^2}$.) For convenience, these tensors were referred, not to the crystallographic axes, but to the natural molecular axes shown in Fig. 2(a). Axis 1 passes through the centre and the mid-point of AG', axis 2 through D', and axis 3 is perpendicular to the plane. The transformation of the b_{ij}'s to the U_{ij}'s was carried out in two stages: the b_{ij}'s were first transformed to **U** tensors referred to orthogonal axes defined by the crystal (Rollett & Davies, 1955) and ordinary orthonormal tensor transformations were then used for the change to the molecular axes. The values of the six independent U_{ij}'s for each carbon atom are shown in Table 4 in the columns headed 'Obs.'. The terms U_{11}, U_{22} and U_{33} give directly the values of $\overline{u^2}$ parallel to the molecular axes. Fig. 2(b) shows the values of $\overline{u^2}$ in the directions radial and tangential to the centre, and perpendicular to the molecular plane. The large tangential values of $\overline{u^2}$ for atoms A and G show the importance of the angular oscillations about the plane normal, while the values of $\overline{u^2}$ perpendicular to the plane for the outer atoms indicate an appreciable oscillation about axis 2.

Rather than attempt an interpretation of the oscillations by inspection of Table 4 a comprehensive description of the anisotropic thermal motion may be given in the manner suggested by Cruickshank (1956b). The internal vibrations of the molecule are sufficiently small for the motion to be analysed in terms of rigid-body vibrations. These can be expressed in terms of two symmetric tensors, **T** giving the anisotropic translational vibrations of the mass centre and **ω** the anisotropic angular oscillations about axes through the

centre. The value of $\overline{u^2}$ in a direction $\mathbf{l}$ at a point $\mathbf{r}$ in the molecule is then

$$\sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} l_i l_j = \sum_{i=1}^{3} \sum_{j=1}^{3} \{ T_{ij} l_i l_j + \omega_{ij} (\mathbf{l} \wedge \mathbf{r})_i \, (\mathbf{l} \wedge \mathbf{r})_j \}. \quad (1)$$

For the mass centre $U_{ij} = T_{ij}$, since $\mathbf{r} = 0$. Given the **U** tensors for a number of atoms, the **T** and **ω** tensors may be determined by the method of least squares. The resulting **T** and **ω** tensors for anthracene are given in Table 5. The r.m.s. amplitudes of translational

Table 5. *Values of T_{ij} and ω_{ij}*

(Values of T_{ij} in 10^{-2} Å^2 and of ω_{ij} in deg.^{2})

$$\mathbf{T} = \begin{pmatrix} 3\cdot80 & -0\cdot09 & -0\cdot09 \\ & 2\cdot85 & -0\cdot09 \\ & & 2\cdot70 \end{pmatrix} \quad \boldsymbol{\omega} = \begin{pmatrix} 15\cdot16 & 0\cdot79 & -4\cdot47 \\ & 4\cdot76 & -0\cdot79 \\ & & 9\cdot13 \end{pmatrix}$$

oscillation in the directions of the molecular axes, obtained from the square roots of the diagonal elements of **T**, are 0·20, 0·17 and 0·16 Å respectively. The corresponding r.m.s. amplitudes of angular oscillation obtained from **ω** are 3·9°, 2·2° and 3·0°.

Conversely, given the **T** and **ω** tensors, the **U** tensors for each atom may be calculated from (1). The resulting values of U_{ij} are shown in Table 4 in the column headed 'Calc.'. The r.m.s. difference between the $U_{ij}^{\text{obs.}}$ and the $U_{ij}^{\text{calc.}}$ is 0·0037 Å^2. This corresponds to an estimated standard deviation (e.s.d.) for $U_{ij}^{\text{obs.}}$ of $0\cdot0037 \times (42/30)^{\frac{1}{2}} = 0\cdot0043$ Å^2, allowing for the fact that 12 parameters have been determined from 42 $U_{ij}^{\text{obs.}}$. The e.s.d.'s of the elements of **T** and **ω**, given by least-squares formulae using the above e.s.d. of $U_{ij}^{\text{obs.}}$, are shown in Table 6 in positions corresponding to those of the elements in Table 5.

Table 6. *Values of $\sigma(T_{ij})$ and $\sigma(\omega_{ij})$*

(Values of $\sigma(T_{ij})$ in 10^{-2} Å^2 and of $\sigma(\omega_{ij})$ in deg.^{2})

$$\sigma(\mathbf{T}) = \begin{pmatrix} 0\cdot16 & 0\cdot16 & 0\cdot18 \\ & 0\cdot24 & 0\cdot24 \\ & & 0\cdot42 \end{pmatrix} \quad \sigma(\boldsymbol{\omega}) = \begin{pmatrix} 7\cdot82 & 1\cdot12 & 2\cdot17 \\ & 1\cdot12 & 0\cdot95 \\ & & 0\cdot95 \end{pmatrix}$$

An alternative, external, estimate of the e.s.d. of $U_{ij}^{\text{obs.}}$ may be obtained by the method described by Cruickshank (1956b), which uses $|F_o - F_c|$ as an estimate of $\sigma(F)$. This gives 0·0025 Å^2 as the average e.s.d. of the $U_{ij}^{\text{obs.}}$. Though this estimate agrees as to

order of magnitude with the first, internal, estimate, the difference is substantial. The discrepancy is only partially accounted for by the slight incompleteness of the refinement and by the effects of internal vibrations (Higgs, 1955).

The values of the **T** and ω tensors are of considerable interest. Within experimental error the principal axes of **T** coincide with the natural molecular axes. The greatest amplitude of translational vibration is along the long axis of the molecule, so that the molecule moves most easily in the direction in which it presents the least area of resistance. The amplitude along the short axis is not significantly greater than that normal to the ring.

Owing to the relatively small distances of the carbon atoms from axis 1, the values of ω_{11} and ω_{13} have considerable e.s.d.'s. Accordingly, despite the rather large value of ω_{13}, it may still be claimed that within experimental error the principal axes of ω coincide with the molecular axes.

In a manner similar to that shown for benzene (Cruickshank, 1957), the amplitudes of angular oscillation may be interpreted in terms of average frequencies of the rotational branches of the normal lattice vibrations. The analysis gives mean frequencies of 81, 65 and 43 cm.$^{-1}$ for the branches corresponding to oscillations about each of the molecular axes. Considering the e.s.d.'s of the amplitudes of oscillation, these compare satisfactorily with the long-wave lattice frequencies of 120 ± 8, 68 ± 5, 48 ± 4 cm.$^{-1}$ determined by Fruhling (1951) from Raman shifts in light scattered by anthracene crystals. The argument may be reversed and the Raman frequencies may be used to estimate the r.m.s. amplitudes of angular oscillation. This gives $2\cdot6°$, $2\cdot1°$ and $2\cdot7°$. The value of $2\cdot6°$ for the r.m.s. amplitude about axis 1 is almost certainly more accurate than the X-ray value of $3\cdot9°$ derived from ω_{11}, which had a large e.s.d. The values for the amplitudes about axes 2 and 3 are satisfactorily close to X-ray values of $2\cdot2°$ and $3\cdot0°$.

6. Molecular dimensions, co-ordinates and orientation

The final carbon co-ordinates obtained from the differential syntheses of the fourth anisotropic cycle are given in Table 7. The bond lengths and angles derived from these are given in Tables 8 and 9, together with those obtained by Sinclair et al. (1950) and Ahmed & Cruickshank (1952). The changes from the results

Table 7. *Final carbon fractional co-ordinates*

Atom	x	y	z
A	0·08754	0·02906	0·36585
G	0·00406	0·17922	−0·31611
B	0·11887	0·15548	0·28059
F	0·06061	0·25865	−0·18236
C	0·05902	0·08212	0·13816
E	0·03014	0·13086	−0·08984
D	0·08743	0·20847	0·04728

Table 8. *Anthracene bond lengths*

Bond	Present study	Ahmed & Cruickshank	Sinclair et al.
A–B	1·360 Å	1·365 Å	1·361 Å
F–G	1·368	1·375	1·366
B–C	1·435	1·428	1·426
E–F	1·427	1·418	1·412
C–D	1·397	1·393	1·387
D–E	1·396	1·398	1·395
A–G′	1·417	1·408	1·390
C–E′	1·434	1·436	1·440

Table 9. *Anthracene bond angles*

Angle	Present study	Sinclair et al.
G′–A–B	120° 36′	121° 10′
F–G–A′	120 47	120 45
A–B–C	120 55	120 45
E–F–G	120 15	120 40
B–C–E′	118 7	117 55
C′–E–F	119 19	119 0
E′–C–D	119 27	119 0
D–E–C′	119 31	118 45
C–D–E	121 2	122 10

obtained by Ahmed & Cruickshank are very small. The mean co-ordinate difference is only 0·004 Å and the maximum 0·012 Å. The largest change in a bond length is in AG', for which Sinclair et al. obtained 1·390 Å, Ahmed & Cruickshank 1·408 Å, and which is now 1·417 Å. There are no significant differences between chemically equivalent bond lengths and angles, and the means of these are shown in the second column of Table 10.

Table 10. *Mean bond lengths and angles*

Bond or angle	Mean without rotational correction	Mean with rotational correction	E.s.d.
A–B	1·364 Å	1·366 Å	0·004 Å
B–C	1·431	1·433	0·003
C–D	1·396	1·399	0·003
A–G′	1·417	1·419	0·006
C–E′	1·434	1·436	0·004
G′–A–B	120° 42′	120° 43′	10′
A–B–C	120 35	120 34	14
B–C–E′	118 43	118 43	8
E′–C–D	119 29	119 30	9
C–D–E	121 2	121 0	17

The arguments for the use of high-order planes in the determination of thermal motion seem equally applicable to the determination of co-ordinates (except perhaps that a true difference map might be expected to be centrosymmetrical near an atomic position). In fact, the co-ordinates obtained from the differential syntheses with high-order planes differed only by a mean of 0·0018 Å and a maximum of 0·0035 Å from those given in Table 7. These differences would seem to be only random, as a theoretical analysis of the errors of the two methods showed that an r.m.s. difference of 0·0024 Å between the results was to be expected if there were no systematic effects. As the

differences are so small, the co-ordinates obtained from the high-order planes have not been tabulated.

Slight corrections are necessary to allow for the angular oscillations causing the atoms to appear too close to the centre of the molecule (Cruickshank, 1956c). The radial error in the position of an atom is given by

$$\frac{1}{2r}\left(\frac{s^2}{1+s^2/q^2}+\frac{t^2}{1+t^2/q^2}\right),$$

where s^2 and t^2 are the two mean-square amplitudes of vibration of the atom in the angular oscillations, q^2 is the Gaussian peak-width parameter for an atomic peak without the angular oscillations and r is the distance from the centre. Using the magnitudes of angular oscillation obtained in § 5 from the Raman results, and an approximate value of q^2, the increases in the radial distances were: atoms A and G, 0·0054 Å; B and E, 0·0047 Å; C and E, 0·0025 Å; D, 0·0029 Å. The effect of these small corrections is to increase all the bond lengths slightly, their mean rising from 1·404 Å to 1·406 Å, but to leave the angles virtually unaltered. The corrected mean bond lengths and angles are shown in the third column of Table 10 and also in Fig. 2(c).

The e.s.d.'s of the carbon co-ordinates, estimated using $|F_o-F_c|$ as an estimate of $\sigma(F)$ (Cruickshank, 1949), vary between 0·0043 Å for atom A and 0·0030 Å for atoms C and E. The corresponding e.s.d.'s for the mean bond lengths and angles are shown in the fourth column of Table 10. They are perhaps slight underestimates of the true errors as no allowance has been made for errors in the estimation of the positional corrections required by the angular oscillations. It will be noticed that the angles are slightly but significantly different from 120°.

There has been considerable theoretical discussion in recent years of the bond lengths in naphthalene and anthracene (e.g. Pritchard & Sumner, 1955). It seems wise, however, to postpone any comparison with the theories until the similar revision of the experimental bond lengths for naphthalene has been completed, as to date the theories have had a tendency to agree with the results for one molecule but not for the other.

The best plane through the carbon co-ordinates is

$$x'-0\cdot5394y+0\cdot4988z' = 0, \tag{2}$$

where the co-ordinates are referred to orthogonal axes a, b, c' ($x' = x+z\cos\beta$, $z' = z\sin\beta$). Sinclair et al. gave

$$x'-0\cdot533y+0\cdot500z' = 0.$$

The direction cosines of the molecular axes referred to the orthogonal axes a, b, c' are

axis 1: −0·4960, −0·1248, +0·8593;
axis 2: −0·3234, −0·8919, −0·3162;
axis 3: +0·8059, −0·4347, +0·4020.

The corresponding direction angles differ by at most 0·3° from those given by Sinclair et al. As the observed

atomic positions do not conform exactly to the molecular symmetry, the actual axes used in the present work were: axis 3, normal to the mean plane (2); axis 1, through the projection of the mid-point of AG' on to the mean plane; axis 2, at right angles to the other two axes. (The present axis 2 is in the opposite direction to the corresponding axis M of Sinclair et al.; with this choice the axes 1, 2, 3 form a right-handed triad.)

The deviations of the final carbon co-ordinates from the mean plane (2) are

A, +0·004 Å, G, +0·010 Å,
B, +0·010 Å, F, +0·001 Å,
C, −0·006 Å, E, −0·007 Å,
D, −0·012 Å.

These deviations, though small, are highly significant (Weatherburn, 1947), for on four degrees of freedom

$$\chi^2 = \Sigma\Delta^2/\sigma^2 = 445\times10^{-6}/(0\cdot0035)^2 = 36\cdot3.$$

The deviations are shown in Fig. 2(d). They suggest that a molecule is being held in its equilibrium position by forces pushing down near D and up near D', up near A and B and down near A' and B', and up near G and down near G'. The following description of the crystal structure will show that this expectation is broadly correct.
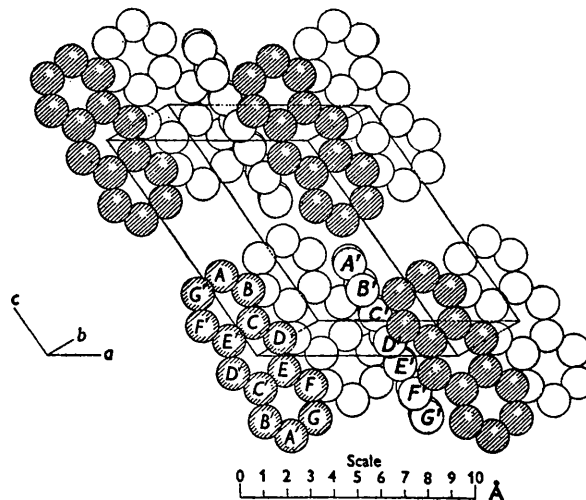
Fig. 3 (reproduced from Sinclair et al.) shows the

Fig. 3. Positions of the anthracene molecules in the unit cell.

positions of the anthracene molecules in the unit cell, the hydrogen atoms being omitted for clarity. The structure is approximately close-packed, for each molecule has 12 near neighbours. The molecule at $(0, 0, 0)$ is surrounded by six neighbours in the (001) plane whose centres are at $\pm(0, 1, 0)$, $\pm(\frac{1}{2}, \frac{1}{2}, 0)$, $\pm(\frac{1}{2}, -\frac{1}{2}, 0)$. Its upper end is wedged between the three molecules at $(0, 0, 1)$, $(\frac{1}{2}, \frac{1}{2}, 1)$ and $(\frac{1}{2}, -\frac{1}{2}, 1)$ and its lower is wedged between the corresponding molecules at $(0, 0, -1)$, $(-\frac{1}{2}, -\frac{1}{2}, -1)$ and $(-\frac{1}{2}, \frac{1}{2}, -1)$.

Table 11. *Close intermolecular approaches*

Distances in Å. Distances above or below molecular plane shown in brackets

Atom in reference molecule	Atom in neighbouring molecule
H–G'	2·50(−1·42)H–A'(0, 0, 1); 2·91(+2·85)H–A(½, −½, 1); 2·96(+1·65)H–B(½, −½, 1)
H–A	2·50(−1·42)H–G(0, 0, 1); 2·91(+2·18)H–G'(½, ½, 1); 2·54(+1·65)H–B(½, −½, 1)
H–B	2·79(−2·64)H–F'(0, 1, 0); 2·54(+0·23)H–A(½, ½, 1); 2·96(+2·18)H–G'(½, ½, 1)
H–D	2·72(−2·60)H–D'(0, 1, 0)
D	2·67(+2·56)H–F(½, −½, 0)
H–F	2·79(−2·64)H–B'(0, 1, 0); 2·67(+1·06)D(½, ½, 0)

The approaches to all these molecules, calculated from the carbon co-ordinates of Table 7 and the assumed hydrogen co-ordinates of Table 1, are less than 3 Å. With the exceptions of the molecules at ±(½, ½, 0) and ±(½, −½, 0) the close approaches are between one or more hydrogens of the molecule at (0, 0, 0) and one or more hydrogens of the neighbouring molecule. The contacts with the molecules at ±(½, ½, 0) and ±(½, −½, 0) are between a carbon D on one molecule to a hydrogen F on the other molecule.

Table 11 lists the various close approaches of atoms in neighbouring molecules to atoms of the molecule at (0, 0, 0). The distances of the neighbouring atoms above or below the molecular plane of the reference molecule are also shown. There are in all 26 short interatomic distances between one molecule and its neighbours, involving 7 crystallographically independent vectors. The only carbon atoms of the reference molecule which are approached directly are D and D'. These are 2·67 Å from the hydrogens F of the molecules at (½, −½, 0) and (−½, ½, 0), which lie almost directly above and below D and D' respectively. The pressures from these hydrogens are undoubtedly the reasons why the carbons D and D' deviate most from the molecular plane. Examination of Table 11 shows that the other forces on the various hydrogens of the reference molecule correspond reasonably well with the displacements of the adjacent carbon atoms from the mean plane. (The X-ray results, of course, are not sufficiently accurate to give the hydrogen displacements themselves.)

This analysis would have been virtually impossible without the aid of an electronic computer. The many calculations undertaken needed a total machine time of about 80 hr. on the Ferranti Mark I electronic computer at Manchester University. In future analyses of this kind only about half this work should be necessary, as a detailed isotropic refinement is eventually redundant and as faster convergence of the anisotropic refinement is now possible (Cruickshank, 1956a).

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