1956), and here it will suffice to summarize the conclusions:

(*a*) Simonsen's chemical constitution is confirmed and HDE is, as it stands, a violator of the 'isoprene rule'.

(*b*) The rings are *cis*-fused, and HDE is, therefore, based on *cis*-decalin together with the substituents in the equatorial positions. This is despite the fact that *trans*-fusion is the more stable configuration when the rings are unsubstituted.

(*c*) From optical rotation considerations Klyne (1954) has established the absolute configuration of part of eremophilone, and this in turn determines the absolute configuration of HDE, as illustrated in the paper by Grant & Rogers mentioned above. However, recent work by Djerassi (private communication) on the dispersion of the optical rotation has shown that Klyne's conclusions are probably incorrect. The absolute configuration of HDE is that based on Djerassi's work, and is shown in Fig. 6.

6·2. *Crystallographic conclusions*

(*a*) The structure of HDE was primarily determined through the application to the plane group *pgg* of a new method of using sign relations. The signs of a number of terms were determined without any previous knowledge of the signs of any other terms or of the stereochemistry of the molecule.

(*b*) The method failed to give a satisfactory set of signs for the (010) projection, probably because of the relatively small number of independent products available for consideration. It is interesting to note that, if the correct set of signs is put back into the products considered, then these are also a self-consistent set. That is, the correct set is another solution that might have been converged upon.

(*c*) Taylor's Fourier-transform method seems to be very useful when the location of a molecule in one projection is to be found from its known position in another projection, especially when packing considerations or heavy-atom positions are not available.

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A Detailed Refinement of the Crystal and Molecular Structure of Naphthalene

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A detailed refinement of Abrahams, Robertson & White's data for naphthalene has been carried out. The many calculations needed were performed on the Manchester University electronic computer. As for anthracene, the difference map indicates some channelling of the electrons along the lines of the bonds. The anisotropic vibrations of the carbon atoms can be interpreted in terms of anisotropic translational and rotational oscillations of the molecules. The magnitudes of the angular oscillations (~ 4°) agree well with those inferred from Raman spectra. C–C bond lengths with e.s.d.'s of about 0·005 Å are obtained.

1. Introduction

A very considerable extension of Ahmed & Cruickshank's (1952) refinement of Mathieson, Robertson & Sinclair's (1950) data for anthracene was recently described (Cruickshank, 1956*a*, 1957*a*). The present paper describes a similar extension of Ahmed & Cruickshank's refinement of Abrahams, Robertson & White's (1949*a*) data for naphthalene.

The experience gained in the work on anthracene has enabled the analysis of naphthalene to be carried through with appreciably less effort, though, as before, very large calculations were involved. These were performed on the Manchester University electronic computer. The work on naphthalene may be described quite briefly as the methods and results are very similar to those for anthracene.

The space group for naphthalene is $P2_1/a$, with two molecules in a unit cell of dimensions (Abrahams *et al.*, 1949*a*)

$$a = 8{\cdot}235,\ b = 6{\cdot}003,\ c = 8{\cdot}658\ \text{Å},\ \beta = 122^\circ\ 55'.$$

2. Refinement of the co-ordinates and thermal parameters

The refinement of the structure was carried out in a manner similar to that for anthracene, but fewer stages were required. Starting from Ahmed & Cruickshank's results, only two cycles of isotropic and three cycles of anisotropic refinement were needed. In the second isotropic cycle R was 14·4% with temperature factors of $B = 4{\cdot}6$ Å^2 (atoms A and E), 4·0 Å^2 (B and D) and 3·4 Å^2 (C) applied to the McWeeny (1951) carbon f curve; the hydrogens were inserted at assumed positions, with temperature factors of 6·0 Å^2 for those attached to A and E and 5·0 Å^2 for those attached to B and D. No difference maps were computed at the end of the isotropic refinement, as the work on anthracene had shown them to be eventually redundant.

In the anisotropic refinement the six thermal parameters b_{ij} for each atom were determined from the curvature differences computed using only the 411 reflexions with $\sin\theta > 0{\cdot}65$. The Hoerni & Ibers (1954) scattering curve was used for carbon, and the hydrogens were inserted at the positions of Table 1, corresponding to C–H distances of 1·09 Å, with isotropic temperature factors of 6·0 Å^2 and 5·0 Å^2, as above. In the third and last anisotropic cycle R was 11·95% for all the planes and 14·4% for the high-order planes. As for anthracene, the absolute scale of the experimental data was checked by comparison of the observed and calculated peak heights computed with the high-order planes. The final mean ratio of the observed and calculated curvatures of the carbons for the high-order planes was 0·995, the greatest individual error being only 1·2%. The refinement was therefore almost complete. The mean density ratio, which should be 1·000 if both the experimental scale and the derived thermal motion are correct, was in fact 1·002, so that the scaling seems satisfactory for the high-order planes.

Table 1. *Assumed hydrogen fractional co-ordinates*

Atom	x	y	z
H-A	0·1375	0·0657	0·4663
H-E	0·0345	0·2999	−0·3394
H-B	0·1888	0·3176	0·2752
H-D	0·1490	0·4056	−0·0233

3. Difference maps

A difference map in the plane of the molecule is shown in Fig. 1. For this all the observed reflexions were used and the F_c's were those calculated in the third anisotropic cycle, with the hydrogens included. The difference-map in the plane $\frac{1}{2}$ Å above the molecular plane showed no significant features and has not been reproduced. The estimated standard deviation of the difference-map density calculated by Cruickshank's (1949) formula is 0·11 e.Å^{-3}. In the corresponding molecular-plane difference map of anthracene there were three main features: negative regions with minima of approximately −0·45 e.Å^{-3} enclosed by the six-membered rings; negative regions between neighbouring C–H lines; and slightly positive regions around the lines joining adjacent atoms. The present naphthalene molecular-plane difference map shows the first feature distinctly, the second feature rather less definitely, and the third hardly at all. As in anthracene, the difference synthesis integrates to a slightly negative value in a reasonable molecular volume. This seems to indicate that the scaling of a proportion of the low-order F_o's is not quite accurate. While it would be thus unwise to be dogmatic about conclusions drawn from the present data, it is interesting to note that the difference maps for naphthalene and anthracene are both consistent with the idea of a lateral contraction of the σ-electrons on the formation of the bonds.

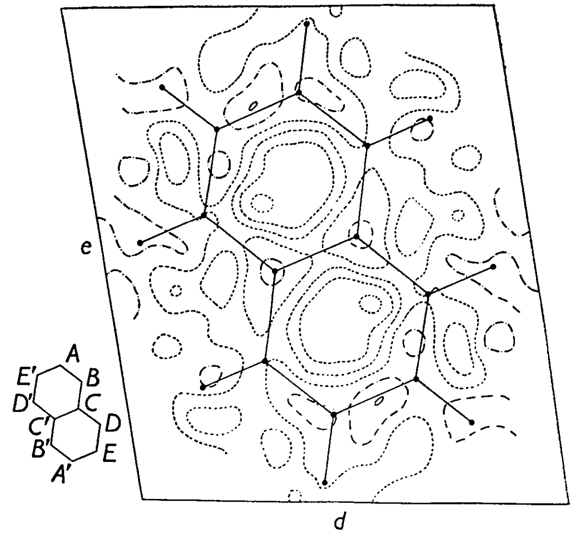

Fig. 1. Difference map in central plane of molecule. Contour intervals 0·1 e.Å^{-3}. Full lines: positive; chain lines: zero; broken lines: negative.

4. Description of the anisotropic thermal motion

The final set of anisotropic thermal parameters b_{ij} for the carbon atoms were determined after the third anisotropic cycle. The b_{ij}'s for each atom were then transformed to symmetric tensors **U** such that

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

Table 2. *Observed and calculated* U_{ij}

(Values in 10^{-2} Å^2)

	U_{11}		U_{12}		U_{13}		U_{22}		U_{23}		U_{33}	
Atom	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
A	5·84	5·28	0·41	0·62	0·10	0·02	6·84	7·12	−0·19	−0·32	6·34	6·42
E	5·20	5·28	−1·51	−1·22	−0·11	0·10	7·57	7·15	−0·19	−0·05	6·08	5·98
B	5·48	6·06	0·82	0·63	−0·28	−0·09	4·79	4·83	−0·29	−0·22	5·63	5·48
D	5·98	6·06	−1·01	−1·24	0·01	−0·01	4·86	4·83	0·10	0·05	4·89	5·02
C	5·47	5·28	−0·22	−0·30	0·37	0·06	3·84	4·00	−0·01	−0·05	3·73	3·73

is the value of the mean square oscillation in Å^2 in a direction $\mathbf{l} = (l_1, l_2, l_3)$ (Cruickshank, 1956*b*). These tensors were referred to the natural molecular axes: axis 1 passing through the centre and the mid-point of *AE′*, axis 2 through *C′*, and axis 3 perpendicular to the plane. The values of the six independent U_{ij}'s for each carbon atom are shown in Table 2 in the columns headed 'Obs.'.

The anisotropic thermal motion may be analysed in terms of the rigid-body vibrations of the molecule (Cruickshank, 1956*c*). These vibrations can be expressed in terms of the symmetric tensors **T**, giving the translational vibrations of the mass centre, and **ω**, the angular oscillations about axes through the centre. The **T** and **ω** tensors for naphthalene, determined by least squares from the five **U** tensors, are shown in Table 3. The r.m.s. amplitudes of translational oscillation in the directions of the molecular axes, obtained from the square-roots of the diagonal elements of **T**, are 0·22, 0·20 and 0·19 Å respectively. The corresponding r.m.s. amplitudes of angular oscillation obtained from **ω** are 4·4, 3·7 and 4·2°.

Table 3. *Values of* T_{ij} *and* ω_{ij}

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

$$\mathbf{T} = \begin{pmatrix} 5{\cdot}01 & -0{\cdot}30 & 0{\cdot}10 \\ & 4{\cdot}00 & -0{\cdot}05 \\ & & 3{\cdot}44 \end{pmatrix} \qquad \boldsymbol{\omega} = \begin{pmatrix} 19{\cdot}50 & 2{\cdot}25 & 2{\cdot}56 \\ & 13{\cdot}95 & 0{\cdot}76 \\ & & 17{\cdot}73 \end{pmatrix}$$

Conversely, given the **T** and **ω** tensors, the **U** tensors for each atom may be calculated. The resulting values of U_{ij} are shown in Table 2 in the columns headed 'Calc.'. The r.m.s. difference between the $U_{ij}^{\text{obs.}}$ and the $U_{ij}^{\text{calc.}}$ is 0·0022 Å^2. This corresponds to an e.s.d. for $U_{ij}^{\text{obs.}}$ of $0{\cdot}0022 \times (30/18)^{\frac{1}{2}} = 0{\cdot}0028$ Å^2, allowing for the fact that 12 parameters have been determined from 30 $U_{ij}^{\text{obs.}}$. The resulting e.s.d.'s of the elements of **T** and **ω**, given by least-squares formulae, are shown in Table 4.

Table 4. *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})

$$\sigma(\mathbf{T}) = \begin{pmatrix} 0{\cdot}13 & 0{\cdot}13 & 0{\cdot}15 \\ & 0{\cdot}18 & 0{\cdot}18 \\ & & 0{\cdot}36 \end{pmatrix} \qquad \sigma(\boldsymbol{\omega}) = \begin{pmatrix} 6{\cdot}57 & 1{\cdot}34 & 2{\cdot}43 \\ & 1{\cdot}94 & 1{\cdot}44 \\ & & 1{\cdot}40 \end{pmatrix}$$

The values of the **T** and **ω** tensors are rather similar to those for anthracene, except that their principal magnitudes are rather larger. Within experimental error the principal axes of **T** and **ω** coincide with the molecular axes. The greatest amplitude of translational vibration is again along the long axis of the molecule. The amplitude along the short axis is probably not significantly greater than that normal to the ring.

The amplitudes of angular oscillation about the molecular axes have already been predicted from two slightly differing sets of Raman frequencies (Cruickshank, 1956*d*) to be 3·2, 3·1 and 4·0°, or 3·3, 3·2 and 4·1°. Considering their e.s.d.'s, the X-ray values of 4·4, 3·7 and 4·2° are satisfactorily close. The X-ray values imply mean frequencies of 84, 62 and 47 cm.$^{-1}$ for the branches of lattice vibrations corresponding to oscillations about each of the molecular axes, as compared with the pairs of long-wave lattice frequencies of 109, 127; 74, 76; 46, 54 cm.$^{-1}$ determined by Kastler & Rousset (1941) from Raman shifts.

The spherically averaged mean square amplitudes of the atoms in naphthalene during the internal vibrations of the molecule at room temperature have been estimated theoretically by Higgs (1955) to be: *A*, $0{\cdot}17 \times 10^{-2}$ Å^2; *B*, $0{\cdot}20 \times 10^{-2}$ Å^2; *C*, $0{\cdot}13 \times 10^{-2}$ Å^2. The neglect of these internal vibrations has probably had a negligible effect on the determination of **ω** from the **U**'s, but Higgs' calculations suggest that the diagonal elements of **T** may be too large by $0{\cdot}10 - 0{\cdot}20 \times 10^{-2}$ Å^2. The average value of the diagonal elements of **T** is $4{\cdot}15 \times 10^{-2}$ Å^2; allowing for the subtraction of the internal vibrations, this is sufficiently close to the value of $(\overline{u^2})_{\text{trans.}} = 4{\cdot}03 \times 10^{-2}$ Å^2, assumed in the calculations of the variation of thermal motion with temperature (Cruickshank, 1956*d*) and of the entropy (Cruickshank, 1956*e*), for it to be unnecessary to revise these calculations.

5. Molecular dimensions, co-ordinates and orientation

The final carbon co-ordinates obtained from the differential syntheses of the third anisotropic cycle are given in Table 5. The bond lengths and angles derived from these are given in Tables 6 and 7, together with those obtained by Abrahams *et al.* (1949*b*) and Ahmed & Cruickshank (1952). The changes from the results obtained by Ahmed & Cruickshank are very small. The mean coordinate difference is only 0·005 Å and the maximum 0·012 Å. The largest change in a bond length is 0·016 Å. There are no significant differences

Table 5. *Final carbon fractional co-ordinates*

Atom	x	y	z
A	0·0856	0·0186	0·3251
E	0·0116	0·1869	−0·2541
B	0·1148	0·1588	0·2200
D	0·0749	0·2471	−0·0784
C	0·0472	0·1025	0·0351

Table 6. *Naphthalene bond lengths*

Bond	Present study	Ahmed & Cruickshank	Abrahams *et al.*
A–B	1·353 Å	1·369 Å	1·363 Å
D–E	1·361	1·362	1·354
B–C	1·421	1·426	1·421
C–D	1·419	1·424	1·420
A–E′	1·416	1·404	1·395
C–C′	1·405	1·393	1·395

Table 7. *Naphthalene bond angles*

Angle	Present study	Abrahams *et al.*
E′–A–B	121° 01′	121° 05′
D–E–A′	119 56	120 50
A–B–C	120 21	119 35
C–D–E	120 12	119 30
B–C–C′	118 46	118 55
C′–C–D	119 43	120 10
B–C–D	121 31	120 55

Table 8. *Mean bond lengths and angles*

Bond or angle	Mean without rotational correction	Mean with rotational correction	E.s.d.
A–B	1·357 Å	1·361 Å	0·004 Å
B–C	1·420	1·425	0·003
A–E′	1·416	1·421	0·006
C–C′	1·405	1·410	0·006
E′–A–B	120° 29′	120° 31′	10′
A–B–C	120 16	120 15	15
B–C–C′	119 14	119 14	10
B–C–D	121 31	121 32	19

between chemically equivalent bond lengths and angles, and the means of these are shown in the second column of Table 8.

Slight corrections are necessary to allow for the angular oscillations, which cause the atoms to appear too close to the centre of the molecule (Cruickshank, 1956*f*). Using the magnitudes of angular oscillation obtained from the Raman results referred to in § 4, the increases in the radial distances of the atoms are: atoms *A* and *E*, 0·0080 Å; *B* and *D*, 0·0065 Å; *C*, 0·0027 Å. The effect of these corrections is to increase all the bond lengths by about 0·005 Å, but to leave the angles virtually unaltered. The corrected mean bond lengths and angles are shown in the third column of Table 8 and also in Fig. 2.

The e.s.d.'s of the carbon co-ordinates, estimated using $|F_o-F_c|$ as an estimate of $\sigma(F)$, vary between 0·0044 Å for atom *A* and 0·0032 Å for atom *C*. The corresponding e.s.d.'s for the mean bond lengths and angles are shown in the fourth column of Table 8. The comparison of the experimental bond lengths for naphthalene and anthracene with those predicted by various theories is of such interest that it is being reported separately (Cruickshank, 1957*b*).

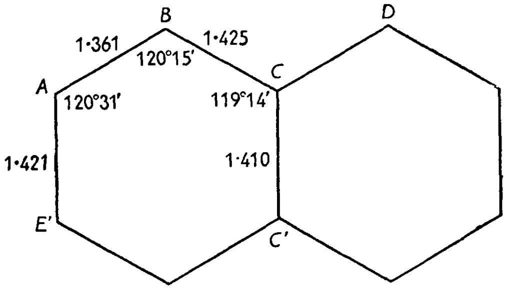

Fig. 2. Corrected mean bond lengths (Å) and angles.

The best plane through the carbon co-ordinates is

$$x-0\cdot5268y+0\cdot3742z' = 0\ ,$$

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

$$x-0\cdot527y+0\cdot369z' = 0\ .$$

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

Axis 1: −0·4379, −0·2103, −0·8741;
Axis 2: −0·3207, −0·8718, −0·3704;
Axis 3: 0·8399, −0·4425, 0·3143.

The corresponding direction angles differ by at most 0·6° from those given by Abrahams *et al.* (the precise definitions of the axes are similar to those used in anthracene).

The deviations of the final carbon co-ordinates from the best plane are

A, 0·000 Å *E*, 0·007 Å
B, +0·005 Å *D*, −0·007 Å
C, −0·004 Å.

The deviations, though small, are possibly significant (Weatherburn, 1947), for on three degrees of freedom

$$\chi^2 = \Sigma\Delta^2/\sigma^2 = 150\times10^{-6}/(0\cdot0039)^2 = 9\cdot9\ .$$

Fig. 3 (reproduced from Abrahams *et al.*, 1949*b*) shows the positions of the naphthalene molecules in the unit cell, the hydrogen atoms being omitted for clarity. The arrangement of the approximately close-packed structure is very similar to that of anthracene, each molecule having 12 near neighbours within 3 Å. Table 9 lists the various close approaches of atoms in neighbouring molecules to atoms of the molecule at (0, 0, 0). There are in all 28 short interatomic distances between one molecule and its neighbours, involving 7 crystallographically independent vectors. The only carbon atoms of the reference molecule which are

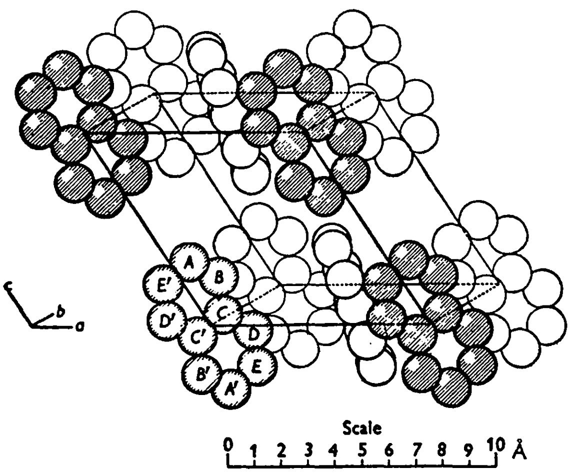

Fig. 3. Positions of the naphthalene molecules in the unit cell.

Table 9. *Close intermolecular approaches*

(Distances in Å)

Atom in reference molecule	Atom in neighbouring molecule
H–E'	2·66, H–A'(0, 0, 1); 2·86, H–A($\frac{1}{2}$, $-\frac{1}{2}$, 1); 3·07, H–B($\frac{1}{2}$, $-\frac{1}{2}$, 1)
H–A	2·66, H–E(0, 0, 1); 2·86, H–E'($\frac{1}{2}$, $\frac{1}{2}$, 1); 2·40, H–B($\frac{1}{2}$, $-\frac{1}{2}$, 1)
H–B	2·95, H–D'(0, 1, 0); 2·40, H–A($\frac{1}{2}$, $\frac{1}{2}$, 1), 3·07, H–E'($\frac{1}{2}$, $\frac{1}{2}$, 1)
C	2·82, H–D($\frac{1}{2}$, $-\frac{1}{2}$, 0)
D	2·82, H–D($\frac{1}{2}$, $-\frac{1}{2}$, 0)
H–D	2·95, H–B'(0, 1, 0); 2·82, C($\frac{1}{2}$, $\frac{1}{2}$, 0); 2·82, D($\frac{1}{2}$, $\frac{1}{2}$, 0)

approached directly are C and D, and C' and D'. C and D are both 2·82 Å from the hydrogen D of the molecule at ($\frac{1}{2}$, $-\frac{1}{2}$, 0), which lies almost immediately above C and D, so causing the negative deviations of these atoms from the mean molecular plane.

The shortest H–H distance which is presumed in naphthalene is 2·40 Å, as compared with 2·50 Å in anthracene. The explanation of this extra shortness seems to be that the next shortest in naphthalene, 2·66 Å, is considerably larger than the next shortest in anthracene, 2·54 Å, so that the total energies of molecular interaction are roughly comparable.

It is a pleasure to acknowledge the great help given by Miss Diana E. Pilling in running many of the calculations and drawing out the difference map; by Prof. J. M. Robertson in correspondence and discussion; and by the Manchester University Computing Machine Laboratory in making their Ferranti Mark I electronic computer available.

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On the Determination of Crystal and Counter Settings for a Single-Crystal X-ray Diffractometer

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A simple analogue computer is described with which crystal and counter settings for a three-circle single-crystal diffractometer can be determined. It is shown that the accuracy attainable is quite adequate for the measurement of integrated intensities by a rocking-crystal technique.

Introduction

Furnas & Harker (1955) have described two schemes of data-collection for use with three-circle single-crystal diffractometers in which the motion of the counter is restricted to a plane. The one referred to in this note is the so-called 'cone diffractometer' method,