The Structure of Anthracene-d_{10} at 16 K using Neutron Diffraction

By S. L. Chaplot*

Department of Physics, Edinburgh University, King's Buildings, Edinburgh EH9 3JZ, Scotland

N. Lehner

Institut Laue–Langevin, avenue des Martyrs, Grenoble 38042, France

and G. S. Pawley

Department of Physics, Edinburgh University, King's Buildings, Edinburgh EH9 3JZ, Scotland

Abstract

The crystal structure of anthracene-d_{10} at 16 K has been refined using neutron diffraction measurements [$C_{14}D_{10}$, $P2_1/a$, $a = 8.37 (3)$, $b = 6.00 (2)$, $c = 11.12 (4)$ Å, $\beta = 125.4 (1)°$]. Using 1105 structure factors, an R factor of 6.0% was obtained, which reduced to 3.2% when a simple one-parameter correction was made for multiple Bragg scattering, although this correction is not correlated to the crystal structure result. Constrained refinements have also been carried out which indicate significant distortions in the crystalline state from the free-molecule symmetry of *mmm*. The thermal-parameter analysis shows that the **T** tensor is reduced most on reducing the temperature from 298 to 16 K, whereas the thermal motion of the D nuclei is hardly affected. A comparison with the room-temperature result confirms the accuracy of the molecular-geometry measurement, and shows a molecular reorientation of over 1° between 16 and 298 K.

Introduction

Recently detailed measurements of the phonon-dispersion relation have been carried out on naphthalene-d_8 (Natkaniec *et al.*, 1980) and anthracene-d_{10} (Dorner *et al.*, 1981) at low temperature. These measurements are sufficiently accurate to require the knowledge of accurate crystal structures for the lattice-dynamical analyses. The room-temperature structure of anthracene has already been studied using X-ray (Mason, 1964) and neutron diffraction (Lehmann & Pawley, 1972) from anthracene-h_{10} and anthracene-d_{10} respectively. The present paper reports a short-wavelength neutron diffraction result on the crystal structure of anthracene-d_{10} at 16 K. Some interesting results are also presented on the molecular distortions by the crystalline forces from the free-state molecular-symmetry *mmm*, and on the associated internal vibrations of the molecule which may be expected to occur at low frequencies. The importance of multiple Bragg scattering is also discussed, as this is a severe problem in neutron diffraction from crystals with large unit cells especially if the crystal sample is large, the neutron wavelength small, and the experiment is done at low temperatures. A simple one-parameter correction for the multiple scattering was found to reduce the R factor from 6.0 to 3.2%, which is a most significant improvement, and this parameter was not found to have any significant correlation with the parameters of the crystal structure. This correction is identical in philosophy to that suggested by Le Page & Gabe (1979), but is much simpler because it is based on one parameter only.

Experimental

The neutron diffraction measurements were carried out at the Institut Laue–Langevin, Grenoble (France), using the four-circle diffractometer D15. The single crystal used was the same as that used earlier at room temperature by Lehmann & Pawley (1972). The spherical crystal of 9 mm diameter was centred in a neutron beam of cross-section 14 × 14 mm. Noses with openings of this latter size were placed before and after the sample and a larger aperture of 30 mm diameter was placed before the detector. The crystal was slowly cooled in a closed-cycle refrigerator, and the final temperature was kept steady at 16.00 ($\pm$ 0.03) K. The crystal was oriented such that the c^* axis was about 3° from the cylindrical axis of the refrigerator, in the hope of reducing the multiple Bragg scattering to some extent. The ω-scan mode, in which the crystal moves

---

* On leave from: Nuclear Physics Division, Bhabha Atomic Research Centre, Bombay 400085, India.

and the detector is fixed, was employed with a neutron wavelength of 0·8567 (5) Å using a Cu (442) monochromator crystal in transmission, and with $0° < 2\theta < 70°$. As the wavelength corresponds to neutron energies well in excess of the reactor Maxwellian distribution peak, contamination from higher-order reflections from the monochromator was quite negligible. A total of 1121 symmetry-independent Bragg reflections were measured, of which nearly 300 were repeated at equivalent positions. Another 119 forbidden reflections were also measured, in order to look for the effects of multiple scattering. A standard reflection was measured after every 25 scans.

Out of the 1121 reflections, the 16 strongest reflections were excluded from all the refinements, as these were affected by extinction. The reflection profiles were reduced to structure factors and their standard errors were estimated using the computer program *COLL* 5 (Lehmann & Wilson, 1974) at the Institut Laue–Langevin. These estimated errors were used as weights in all the refinements. The usual corrections for dead-time losses were applied with this program, though no correction was required for the variations in experimental conditions.*

The space group, $P2_1/a$, is known to be the same as at room temperature. The unit cell (see *Abstract*) was obtained by using a few selected Bragg reflections. The accuracy of this result was limited by the large size of the crystal necessary for the diffraction measurements and also by certain instrumental limitations in the χ, ω and 2θ movements. However, it is unlikely that these limitations affected the intensity measurements as a sufficiently large aperture was used in front of the detector. All estimated errors given later on parameters determined from the refinements do not take the unit-cell error into account as it should be possible to remove this systematic error after finding an accurate unit cell from powder diffraction work.

Refinements

The completely unconstrained refinement on 1105 different structure factors, F_i^{obs}, resulted in an R factor of 6% where $R = 100 \times \sum_i |F_i^{obs} - F_i^{calc}|/\sum_i |F_i^{obs}|$. The final refined atomic positions and thermal parameters are presented in Table 1. The refined parameters also include an extinction-correction parameter, c, for the spherical crystal (Zachariasen, 1967) such that the calculated structure factor was multiplied by $[(1 + x^2)^{\frac{1}{2}} - x]^{\frac{1}{2}}$, where $x = c(F^{obs})^2$ cosec $2\theta_{Bragg}$. Atomic positions are presented as orthogonal coordinates with respect to the crystal primitive-cell coordinate axes as described below.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36251 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *The final unconstrained atomic positions and thermal parameters for anthracene-d_{10} at 16K*

The parameter c is an extinction parameter. The orthogonal coordinates X_c, Y_c, Z_c are defined in the text, $X_c = \mathbf{A}x_f$. The Debye–Waller factor is given by $\exp(-2\pi^2 \sum_i \sum_j U_{ij} H_i H_j)$ where $H = h \cdot \mathbf{A}^{-1}$.

		Coordinates (Å)			Mean-square displacements (Å² × 1000)					
Number	Atom	X_c	Y_c	Z_c	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
1	D	−2·749	−1·742	3·513	21	19	19	3	7	−6
2	C	2·094	−1·128	2·889	7	8	7	−1	1	−1
3	C	−1·687	−1·598	1·659	6	6	6	−1	1	−1
4	D	2·008	−2·573	1·304	20	14	20	−1	2	−7
5	C	−0·836	−0·812	0·812	6	6	5	0	0	0
6	C	−0·408	−1·288	−0·448	6	6	5	−1	1	0
7	D	−0·739	−2·259	−0·800	19	13	18	−3	1	−4
8	D	−1·982	0·511	4·338	24	19	14	2	5	−2
9	C	−1·666	0·156	3·354	8	7	8	0	0	0
10	C	−0·846	0·937	2·569	7	6	6	−2	0	−1
11	D	−0·519	1·917	2·917	23	14	19	−5	1	−5
12	C	−0·415	0·491	1·274	5	5	6	0	0	0

$c = 0.0000145$ (11), scale factor = 9·84 (7).

Average error in X, Y or $Z = 0.002$ Å, in U's = 0·001 Å².

Two constrained refinements are reported here, and their results are given in Table 2. In the first, the atomic positions are constrained such that the molecule retains its free-state *mmm* symmetry. No constraints are applied to the thermal parameters in this refinement. In the second refinement, the atomic positions are not constrained but the atomic thermal parameters are constrained such that they are governed by the rigid-molecule translational and librational motion plus an extra internal isotropic thermal motion for the deuterium atoms. The statistical F tests (Hamilton, 1965) were applied to examine whether the two constrained refinements were significantly different from the unconstrained one. In these tests, the ratio $R_{c/u} = R_w(\text{constrained})/R_w(\text{unconstrained})$ is compared against the standard value of the quantity

$$S_{c/u} = [1 + \frac{N - n}{M - N} F_{(N-n, M-N)}]^{1/2},$$

obtained at some chosen confidence probability level, where

$$R_w^2 = \frac{\sum_i (F_i^{obs} - F_i^{calc})^2/\sigma_i^2}{\sum_i (F_i^{obs})^2/\sigma_i^2},$$

$F_{(N-n, M-N)}$ is the standard value of the F distribution with $(N-n)$ and $(M-N)$ degrees of freedom, M is the number of observations used, and N and n are respectively the number of parameters in the unconstrained and in the constrained refinement. The values of $S_{c/u}$ at the 99% confidence level are given in Table 2. Evidently, the constrained refinements both indicate significant deviations from the unconstrained refinement, thus suggesting that (i) the molecule suffers significant distortions in the crystalline state as com-

Table 2. *The reliability factors* (R *and* R_w) *for the various refinements, the number of variable parameters* (n) *and the ratios* $S_{c/u}$

The number of observations used (M) is 1105.

Refinement	n	R	R_w	$R_{c/u}$	$S_{c/u}$
(I) *mmm*	89	7·1	6·5	1·14	1·02
(II) TL + B(D)	51	6·7	6·2	1·09	1·05
(III) No constraints	110	6·0	5·7	–	–

pared to its free-state symmetry of *mmm* and (ii) the atomic thermal motions are not completely described in terms of the rigid-body vibrations of the molecule plus an isotropic internal motion for the deuterium atoms. These conclusions are similar to but more definitive than those arrived at in the room-temperature study of Lehmann & Pawley (1972). In this paper we attempt to analyse the internal distortions of the molecule.

The atomic coordinates may be expressed in three different coordinate systems, namely,

(1) as fractional coordinates x_f with respect to the three primitive cell axes a, b and c,

(2) as orthogonal coordinates X_c with respect to three Cartesian axes respectively along the crystallographic a, b and c^*,

(3) as orthogonal coordinates X_m with respect to the three principal axes of the molecule.

These coordinates, where X_c and X_m are in ångströms, are related by

$$X_c = A\, x_f \quad \text{and} \quad X_c = M\, X_m,$$

where

$$A = \begin{pmatrix} 8\cdot37 & 0 & -6\cdot442 \\ 0 & 6\cdot00 & 0 \\ 0 & 0 & 9\cdot064 \end{pmatrix},$$

$$A^{-1} = \begin{pmatrix} 0\cdot1195 & 0 & 0\cdot0849 \\ 0 & 0\cdot1667 & 0 \\ 0 & 0 & 0\cdot1103 \end{pmatrix}$$

and the orthogonal matrix

$$M = \begin{pmatrix} -0\cdot5110 & -0\cdot2974 & 0\cdot8065 \\ -0\cdot1329 & -0\cdot8996 & -0\cdot4160 \\ 0\cdot8493 & -0\cdot3198 & 0\cdot4201 \end{pmatrix}.$$

The matrix **M** depends on the orientation of the molecule in the unit cell and is determined by three Euler angles given in radians:

$$(\varphi, \theta, \psi) = [1\cdot2107\ (3),\ 1\cdot1372\ (3),\ 2\cdot0470\ (5)].$$

The definition of the Euler angles is given by Goldstein (1959) and is used by Pawley (1972) in constrained refinements. The values of the Euler angles given above are obtained from the first constrained refinement. The

atomic coordinates, X_m, in the principal-axes frame, for the *mmm* symmetry-constrained molecule are given in Table 3, and are not corrected for librational motion, which is small at such low temperatures. The atomic numbering used is shown in Fig. 1.

The difference between the symmetry-constrained and the unconstrained refinement indicates the molecular distortion. The differences in atomic positions expressed in the principal-axes frame are given in Table 3 and are shown in Fig. 2.

In the second constrained refinement where only the thermal parameters were constrained, the rigid-body translational and librational tensors were found to be

$$T = \begin{pmatrix} 0\cdot31\ (5) & -0\cdot01\ (3) & -0\cdot12\ (3) \\ & 0\cdot37\ (4) & -0\cdot03\ (2) \\ \text{sym.} & & 0\cdot54\ (4) \end{pmatrix} 10^{-2}\ \text{Å}^2$$

and

$$L = \begin{pmatrix} 2\cdot0\ (2) & 0\cdot5\ (1) & -2\cdot0\ (2) \\ & 1\cdot6\ (1) & -0\cdot5\ (1) \\ \text{sym.} & & 4\cdot6\ (4) \end{pmatrix} \text{deg}^2.$$

Table 3. *The atomic positions* X_m *for the constrained molecule* (Å), *and the differences* $\Delta X_m = M^{-1}.X_c - X_m$ *showing distortion, where* X_c *are unconstrained parameters from Table 1*

X_m	Y_m	Z_m	No.	Atom	ΔX_m	ΔY_m	ΔZ_m
4·625 (2)	1·258 (2)	0	1	D	−0·005	0·002	−0·016
3·676 (2)	0·716 (2)	0	2	C	−0·003	−0·001	−0·006
2·486 (2)	1·411 (2)	0	3	C	−0·003	−0·003	0·001
2·481 (2)	2·498 (2)	0	4	D	−0·005	−0·003	−0·001
1·226 (2)	0·722 (2)	0	5	C	−0·001	−0·003	0·004
0	1·413 (2)	0	6	C	−0·002	0·000	0·014
0	2·510 (3)	0	7	D	−0·001	−0·002	0·008
			8	D	0·004	0·001	0·011
Molecular			9	C	0·003	−0·002	0·001
symmetry			10	C	0·003	−0·002	0·007
related			11	D	0·007	−0·005	0·009
			12	C	0·003	−0·003	−0·003

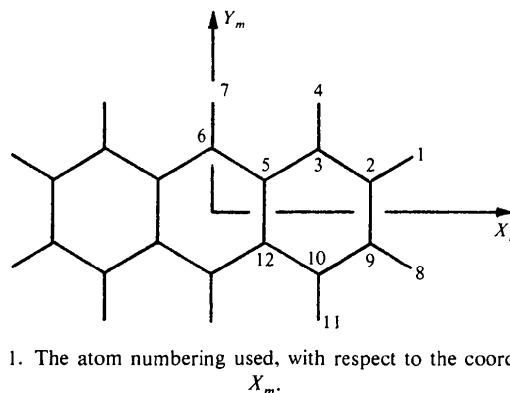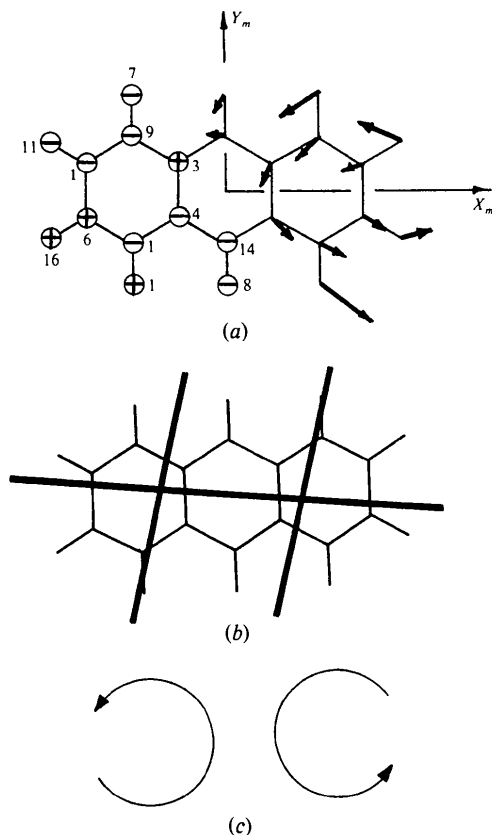Fig. 1. The atom numbering used, with respect to the coordinates X_m.

Fig. 2. The molecular distortion. (a) In-plane distortions (magnified 200×) and out-of-plane distortions in units of 10^{-3} Å. (b) Nodal lines for out-of-plane distortion. (c) The directions of angular distortions corresponding to in-plane shearing. Note that the out-of-plane distortion signs correspond to atoms related to those of Table 3 by inversion.

This refinement also included an extra isotropic thermal parameter for the deuterium atoms which was found to be 0·0084 (4) Å², the units being the same as for **T**. The above thermal parameters are expressed in the crystal Cartesian coordinate system used for the atomic positions X_c, as used by Pawley (1972).

Multiple-scattering correction

The intensities of the 119 forbidden reflections were found to have the distribution shown in Fig. 3. This distribution clearly suggests the existence of a significant contribution from multiple Bragg scattering. The intensities of these forbidden reflections did not show any $|Q|$ dependence and so it may be assumed that the effect is essentially random, although the distribution is not Gaussian. The average and the standard deviation of the distribution are respectively 62·0 and 4·0, in units where the intensity of a typical reflection 400 is 2400 and the maximum intensity observed is 19 000 for 409. We attempted a simple correction in which the
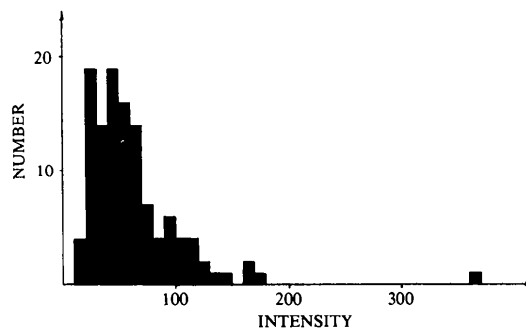

Fig. 3. Histogram of the intensities measured at forbidden reflections.

observed intensities were fitted to (F^2_{calc} + MSP) with MSP fixed at 62·0. The R factor for the unconstrained refinement on the structure factors reduced from 6·0 to 3·5%. This major improvement in the R factor, however, did not involve a significant change in any of the atomic positions or the thermal parameters.

We then allowed MSP to vary as an extra parameter in the least-squares refinement and the R factor further reduced to 3·2% with MSP = 53·8 (1·4). Thus the value refined for the MSP is nearly the same as that obtained from an average of the forbidden-reflection intensities. The magnitude of the estimated correlation of MSP with the various atomic position parameters was below 0·04 and with the various thermal parameters was below 0·08. This is not significant at the 98% confidence level. The actual change in these structural parameters was usually within the estimated errors when MSP was introduced, and thus may not be considered significant.

Discussion

The structure analysis presented above involves 10% more reflections than used by Lehmann & Pawley (1972) in their room-temperature analysis, and was originally planned to achieve a considerable resolution improvement by the use of a shorter wavelength. However, it is clear that the conditions of the present experiment led to a marked multiple-scattering contamination, giving results not significantly more accurate than those at room temperature.

Two structural results are presented above, the best fit of a symmetrical molecule and the distortion of this molecule due to the crystal forces. The first result, being from a constrained refinement, is statistically more acceptable than any symmetry averaging of unconstrained results, and leads to the bond lengths and angles given in Fig. 4. The accuracy of the bond lengths depends on the accuracy of the unit-cell determination, and therefore a more accurate determination of the latter could modify the bond lengths accordingly.
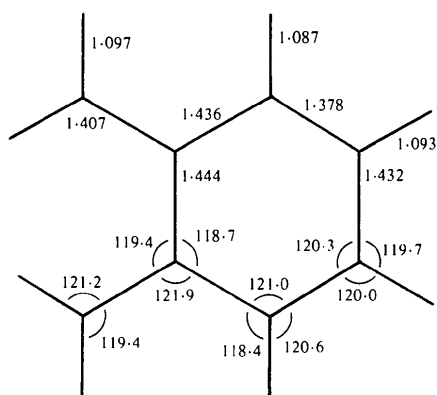
Fig. 4. Bond lengths (Å) and angles (°) for the symmetry-constrained molecule, not corrected for librational motion (but see text). Errors are approximately 0·003 Å and 0·1° respectively.

Fig. 2 shows the distortion of the molecule from the ideal *mmm* symmetry when in a crystal environment. The only distortions that can be found from crystal diffraction methods are those which break the free molecular symmetry but not the molecule crystal-site symmetry (Kurittu & Pawley, 1973). Thus some distortion will be present but undetectable in the coordinates X_m of Table 3 and the bond lengths of Fig. 4. The simplest distortions observable from these results are shown in Fig. 2. Fig. 2(b) shows nodal lines for an out-of-plane distortion, drawn so that all the atoms in any one region are displaced out of the plane in the same sense, the sense being opposite to that in all the adjacent regions. As the molecule can be distorted measurably in this manner, it is to be expected that an internal vibration with these nodal lines would be excited easily. Any such mode of vibration would be of the symmetry species Γ_1 or Γ_3, but such modes would not have the lowest frequency of all the internal modes. The 'butterfly' and 'twisting' modes of symmetry Γ_2 and Γ_4, already identified by the neutron coherent inelastic scattering work of Chaplot et al. (1981), must have lower frequencies as the vibrational patterns contain fewer nodal lines.

The other pattern of distortion indicated by the present work is shown in Fig. 2(c). This is an in-plane shearing in which the ring systems at the opposite ends of the molecule are twisted about the plane normal through equal angles.

The constrained refinement (II) was significantly poorer than the unconstrained refinement, most probably due to the improvement gained by allowing anisotropic motion for the deuterium nuclei. The mean-square displacements of these nuclei are very

close to the values at 298 K, indicating that even at the higher temperature the behaviour is far from classical. This contrasts with the rigid-body mean-square librational and translational displacements which increase by factors of 5 and 7 respectively between 16 and 298 K, though the classical ratio is almost 19. With this result in mind, it is clearly necessary to make a riding-motion correction (Cruickshank, 1956) for the C—D bond lengths, increasing the value from that shown in Fig. 4 by 0·014 Å.

It is worth comparing the molecular-geometry results with those of Lehmann & Pawley (1972). Both studies yield a mean value for C—D of 1·106 (1) Å. The present analysis gives C—C bonds about 0·005 Å longer than the room-temperature result, this being about 2 standard deviations. This may result from insufficient librational correction to the room-temperature result or from inaccuracies in the low-temperature unit cell. The librational correction does not have a direct effect on the bond angles, and these agree between the two analyses to within a standard deviation of 0·1°. A final comparison of the results shows that the molecule undergoes a reorientation in excess of 1° between 16 and 298 K, such movements being intimately related to the intermolecular forces.

References

Chaplot, S. L., Pawley, G. S., Bokhenkov, E. L., Sheka, E. F., Dorner, B., Kalus, J., Jindal, V. K. & Natkaniec, I. (1981). Chem. Phys. 57, 407–414.

Cruickshank, D. W. J. (1956). Acta Cryst. 9, 757–758.

Dorner, B., Bokhenkov, E. L., Chaplot, S. L., Jindal, V. K., Kalus, J., Natkaniec, I., Pawley, G. S., Schmelzer, U. & Sheka, E. F. (1981). In preparation.

Goldstein, H. (1959). Classical Mechanics. Reading, Mass.: Addison–Wesley (or in a later edition).

Hamilton, W. C. (1965). Acta Cryst. 18, 502–510.

Kurittu, J. & Pawley, G. S. (1973). Acta Cryst. A29, 615–618.

Lehmann, M. S. & Pawley, G. S. (1972). Acta Chem. Scand. 26, 1996–2004.

Lehmann, M. S. & Wilson, S. (1974). COLL 5. College 5 Data Reduction System. ILL report 74L 111T.

Le Page, Y. & Gabe, E. J. (1979). Acta Cryst. A35, 73–78.

Mason, R. (1964). Acta Cryst. 17, 547–555.

Natkaniec, I., Bokhenkov, E. L., Dorner, B., Kalus, J., Mackenzie, G. A., Pawley, G. S., Schmelzer, U. & Sheka, E. F. (1980). J. Phys. C, 13, 4265–4283.

Pawley, G. S. (1972). Advances in Structure Research by Diffraction Methods, Vol. 4, edited by W. Hoppe & R. Mason, pp. 1–64. Oxford: Pergamon.

Zachariasen, W. H. (1967). Acta Cryst. 23, 558–564.