

## The Structure of Perdeuterioanthracene by Neutron Diffraction

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Neutron diffraction measurements have been obtained for perdeuterioanthracene at room temperature. The conventional *R*-factor after refinement of 1001 structure amplitudes is 0.034. Refinements were done in which the molecule was constrained to its free state symmetry, but this indicated considerable distortion. A rigid-body motion constraint indicated that most of the thermal motion can be accounted for by the external modes of vibration, but that the internal modes should be considered for an optimum fit.

The crystal structures of naphthalene and anthracene have gained considerable attention and will continue to do so because of their fundamental importance. In this paper we present work on fully deuterated anthracene,  $C_{14}D_{10}$ , whose crystal structure is the same as hydrogenous anthracene. References to all earlier work can be found in the paper by Mason,<sup>1</sup> who investigated anthracene at 95 K and 290 K. The present work has been done only at room temperature, but we hope to make measurements at other temperatures, giving more definitive information on the variation of the structure parameters with temperature than is presently available.

### EXPERIMENTAL

Three-dimensional intensity data from a single crystal grown by Dr. J. Sherwood of Strathclyde University were collected on a Hilger and Ferranti automatic four circle diffractometer at the Danish Atomic Energy Establishment, Risø. The moving crystal, fixed detector technique ( $\omega$  scan) was used in the measurements with a neutron wavelength of 1.025 Å. The crystal was mounted with the *b* axis along the  $\varphi$  axis of the instrument. In measuring the reflections, the crystal was rotated  $\pm 5^\circ$  alternately about the diffraction vector from the calculated position<sup>2</sup> thereby at least avoiding simultaneous reflection from *0k0* and *h0l*, when *hkl* was recorded.

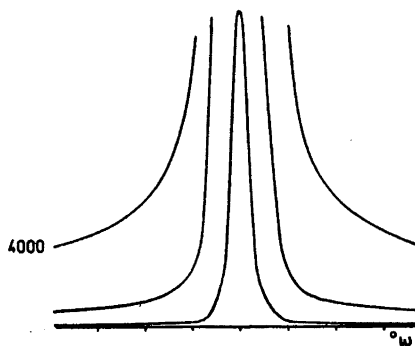
The crystal was spherical with a diameter of 8.7 mm. The monochromatic neutron beam was uniform within  $\pm 5\%$  over a circle of 8.5 mm diameter, and as a test the intensity of the 020 reflection was found to be constant within 2 standard deviations

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when the crystal was moved  $\pm 1$  mm in the vertical and horizontal directions from the instrument centre.

1145 reflections with  $k, l \geq 0$  were measured in sequence of increasing  $\sin \theta/\lambda$  up to  $\sin \theta/\lambda = 0.65 \text{ \AA}^{-1}$ . A standard reflection, 004, was measured after every 10 reflections. Step scan measurements were used and counts for each step of  $0.08^\circ$  were recorded. The total scan interval was  $7.68^\circ$ . As the wings of the reflection profile were not horizontal, it was difficult to determine the point of division between the peak and the background. Fig. 1 gives the profile of the standard reflection on three scales. The peak width was chosen from this to be  $2.72^\circ$  and each background  $1.36^\circ$ . The outer part of the profile,  $1.12^\circ$  on each side, was excluded from the data reduction as overlapping from other reflections occurred in this region for high  $\sin \theta/\lambda$  values. Structure factors and standard deviations based on counting statistics,  $\sigma(F^2)$ , were calculated and corrected for dead time losses. The structure factors were further corrected for drift in the experimental conditions as reflected in the time variation of the standard reflection. This was of the order of 2 % within the total measuring period.

Fig. 1. The average of many  $\omega$  scans of the standard reflection 004. The scan is presented on three scales, the smallest scale, then  $\times 10$ , and  $\times 50$ . The lowest reading in the background corresponds to 4000 counts. The divisions for  $\omega$  are degrees.



After averaging over symmetry the number of structure factors was 1093. Of these, 92 had  $F^2 < 3 \times \sigma(F^2)$  and were excluded from all the refinements, and the remainder are given in Table 1.

Absorption corrections were made for a spherical crystal, but extinction was not taken into account until the refinement stage. The thermal diffuse scattering correction<sup>3</sup> was not attempted, although Fig. 1 shows the extent of its importance. It was thought that any attempt to make an approximate correction would fail owing to the anisotropic nature of the acoustic modes which are the dominant scatterers.

#### CRYSTAL DATA

Unit cell dimensions were determined from measurements on the neutron diffractometer:

$$\begin{array}{ll} a = 8.542 \text{ \AA} & \sigma = 0.005 \text{ \AA} \\ b = 6.016 \text{ \AA} & \sigma = 0.006 \text{ \AA} \\ c = 11.163 \text{ \AA} & \sigma = 0.005 \text{ \AA} \\ \beta = 124.59^\circ & \sigma = 0.06^\circ \end{array}$$

The space group is  $P2_1/a$ , with two molecules per unit cell. Absorption coefficient,  $\mu = 0.09 \text{ cm}^{-1}$ . The measurements were done at room temperature, 298 K.



## EXPERIMENTS

No structure determination was necessary in the present case, so refinements were started immediately from the parameter values of the X-ray determination. All refinements were done with a programme designed to facilitate the use of constraints.<sup>4</sup> All positional and thermal parameters were referred to a unit orthogonal coordinate system. For an atomic position

$$x (\text{\AA}) = Ax \text{ (fractional)},$$

$$A = \begin{pmatrix} 8.542 & 0 & -6.3372 \\ 0 & 6.016 & 0 \\ 0 & 0 & 9.1898 \end{pmatrix}$$

$$A^{-1} = \begin{pmatrix} 0.11707 & 0 & 0.08073 \\ 0 & 0.16622 & 0 \\ 0 & 0 & 0.10882 \end{pmatrix}$$

A refinable extinction correction parameter for the spherical crystal was introduced as follows.<sup>5</sup> The calculated structure factor  $F'_h$  is given by

$$F'_h = F'_h((1+x^2)^{\frac{1}{2}} - x)^{\frac{1}{2}}$$

$$x = c(F_h^{\text{obs}})^2 \operatorname{cosec} 2\theta_{\text{Bragg}}$$

$F'_h$  is the usual form of the calculated structure factor. The value of the parameter  $c$  from the unconstrained refinement was  $3.9(5) \times 10^{-7}$ , and if a comparison is to be made with other structure refinements then we need the scale factor  $s = 51.1(3)$  where  $F_h^{\text{calc}} = s F_h^{\text{calc}}$  (absolute), given that the absolute values use the scattering lengths 0.65 for carbon and 0.63 for deuterium. In a number of constrained refinements the extinction parameter did not vary more than  $\frac{1}{2}\sigma$  from the value just given, and this is one indication of negligible correlation between this parameter and the various model parameters.

The unconstrained refinement reached an  $R$ -factor of 0.034, where

$$R = \sum |F_{\text{obs}} - F_{\text{calc}}| / \sum F_{\text{obs}}$$

The parameters of this refinement are given in Table 2.

In the case of flat molecules it has become customary, when refinement is completed, to fit the best plane through the molecule and to fit rigid-body translational and librational mean-square displacement tensors  $T$  and  $L$  to the anisotropic temperature factors. It then becomes very difficult to assess whether the deviations from planarity or rigidity are significant. This can be made more realistic by performing constrained refinements and by comparing the results with the unconstrained result using the statistical test suggested by Hamilton.<sup>6</sup>

Three constrained refinements will be reported. In the first, I, the molecules are restricted in such a way that the only shifts allowed for the atoms are such that the free state molecular symmetry,  $mmm$ , is retained. No constraint is applied to the anisotropic temperature factors. The  $R$ -factor,

Table 2. Structural parameters from the unconstrained refinement. The positional parameters are in Å, with average errors 0.0014 Å for carbon atoms and 0.0021 Å for deuterium atoms. The temperature factor has the form  $\exp(-\sum b_{ij}h_ih_j)$  so that  $b_{ij}$  when divided by  $2\pi^2$  are in Å<sup>2</sup>. The average errors in these units are 0.012 for carbon components and 0.021 for deuterium components.

Atom	$x$	$y$	$z$	$b_{11}$	$b_{22}$	$b_{33}$	$b_{23}$	$b_{31}$	$b_{12}$
C(1)	2.042	1.088	-2.908	0.98	1.29	0.92	0.20	0.11	-0.11
C(2)	1.672	1.559	-1.682	0.79	0.87	0.92	0.13	-0.01	-0.15
C(3)	0.830	0.791	-0.822	0.61	0.59	0.75	0.00	-0.09	-0.03
C(4)	0.444	1.258	0.439	0.71	0.54	0.82	-0.06	-0.12	-0.05
C(5)	-0.375	0.490	1.275	0.63	0.61	0.73	-0.07	-0.09	0.02
C(6)	-0.763	0.939	2.572	0.96	0.91	0.79	-0.17	-0.03	0.03
C(7)	-1.575	0.177	3.361	1.10	1.32	0.82	-0.04	0.13	0.07
D(1)	2.687	1.684	-3.551	1.53	1.94	1.42	0.31	0.43	-0.40
D(2)	2.022	2.525	-1.335	1.31	1.03	1.43	0.08	0.00	-0.50
D(4)	0.806	2.228	0.784	1.26	0.73	1.21	-0.18	-0.07	-0.24
D(6)	-0.405	1.905	2.917	1.82	1.17	1.19	-0.44	0.05	-0.12
D(7)	-1.857	0.531	4.353	1.89	2.01	1.02	-0.23	0.40	-0.07

Table 3.  $R$  and  $R_w$  for the various constrained refinements.

	Constraints	$R$	$R_w$	Number of parameters
I	$mmm$	0.041	9600	89
II	$mmm, T L, \text{iso. D}$	0.051	13900	30
III	$T L, \text{aniso. D}$	0.040	9300	53
IV	Unconstrained	0.034	6980	110

and the weighted sum of squared deviations  $R_w$  are given in Table 3. The parameters of this model give the best symmetry averaged molecule determinable from the diffraction data.

The bond lengths and angles are given in Fig. 2, where the bond lengths have been corrected for librational effects<sup>7</sup> and for the deuterium riding

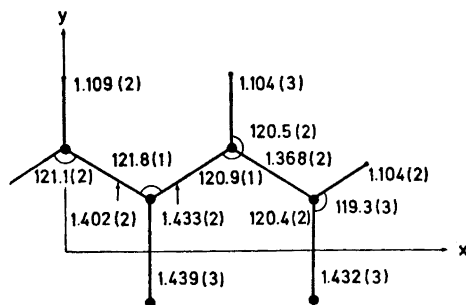


Fig. 2. The best symmetry averaged molecular geometry, corrected for librational and riding motion effects.

motion,<sup>8</sup> using the thermal parameters from model III. This molecule is positioned in the crystal by the matrix  $M$  ( $\varphi, \theta, \psi$ ),

$$x \text{ (crystal orthogonal)} = Mx \text{ (molecular),}$$

$$M = \begin{pmatrix} -0.494434 & -0.322639 & 0.807118 \\ -0.125268 & -0.892417 & -0.433475 \\ 0.860141 & -0.315431 & 0.400825 \end{pmatrix}$$

where the three Euler angles (see Ref. 4 for the definition used) are

$$\varphi = 1.2193 \text{ (3) radians}$$

$$\theta = 1.1584 \text{ (3)}$$

$$\psi = 2.0637 \text{ (5)}$$

How significant is the distortion of the molecule, suggested by the difference between models I and IV? Hamilton's test requires

$$\mathcal{R} = \frac{R(\text{constrained})}{R(\text{unconstrained})}$$

or more rigorously

$$\left\{ \frac{R_w(\text{constrained})}{R_w(\text{unconstrained})} \right\}^{\frac{1}{2}}$$

Now let us define

$$\mathcal{R}^{mmm} = \left\{ \frac{R_w(\text{I})}{R_w(\text{IV})} \right\}^{\frac{1}{2}} = 1.173$$

for the constraint we are testing, and then this value must be compared with the  $\mathcal{R}$ -distribution points. The 10 %, 1 %, and 0.1 % points give values 1.018, 1.023 and 1.028, respectively, all much lower than  $\mathcal{R}^{mmm}$ . The difference is thus highly significant, and the model should be rejected. However, if we were to adopt this procedure at all times we would never get any idea as to how near the result is to the fully symmetric geometry. To give us more physical insight Pawley<sup>4</sup> has suggested calculating

$$\mathcal{S}^{mmm} = \frac{\mathcal{R}^{mmm} - 1}{\mathcal{R}(1\%) - 1} = \frac{0.173}{0.023} = 7.5$$

Comparison with similar results from other structure refinements then puts each case in perspective. Four examples already analysed gave the following results:

	$\mathcal{R}^{mmm}$	$\mathcal{R}(1\%)$	$\mathcal{S}^{mmm}$
Anthracene	1.173	1.023	7.5
Naphthalene	1.079	1.062	1.3
Pyrene	1.184	1.047	3.9
Ovalene	1.141	1.021	6.7

The comparison is somewhat surprising, suggesting that the molecular distortion due to the crystalline forces is considerably greater for anthracene than for naphthalene or pyrene.

The first constraint of thermal parameters that was attempted was such that they conformed to a rigid-body translational and librational motion of the molecule as a whole, plus an extra isotropic motion of the deuterium atoms due to the internal modes. At the same time the molecule was constrained to *mmm* symmetry. This was model II. Subsequently the symmetry constraint was removed, as model I had indicated a significant molecular distortion, and the extra thermal motion of the deuterium was considered anisotropic. This last constraint has proved to be successful in a number of refinements<sup>9</sup> and the three extra parameters required refined to the following values.

Extra mean-square displacement along the C–D bond = 0.0024(5) Å<sup>2</sup>

Extra mean-square displacement perpendicular to the C–D bond in the molecular plane = 0.0094(7) Å<sup>2</sup>

Extra mean-square displacement perpendicular to both the bond and the molecular plane = 0.0178(11) Å<sup>2</sup>

This is an average of the motions over the five independent C–D bonds, and is close to the values which are expected.<sup>9</sup>

From model III we also get the best estimates of  $T$  and  $L$ , namely

$$T = \begin{pmatrix} 2.54 & 0.08 & -0.67 \\ & 2.51 & -0.09 \\ & & 3.53 \end{pmatrix} \text{ or } \begin{pmatrix} 3.87 & -0.09 & 0.06 \\ & 2.47 & 0.09 \\ & & 2.23 \end{pmatrix} 10^{-2} \text{ \AA}^2$$

$$L = \begin{pmatrix} 10.75 & 1.39 & -2.59 \\ & 8.51 & -2.90 \\ & & 17.13 \end{pmatrix} \text{ or } \begin{pmatrix} 18.43 & 1.11 & 2.18 \\ & 8.24 & -0.85 \\ & & 9.72 \end{pmatrix} \text{ deg}^2$$

where the first tensor values are in the orthogonal system and the second are in the molecular system. Average errors are  $0.03 \times 10^{-2} \text{ \AA}^2$  and  $0.2 \text{ deg}^2$ . The second set compare favourably with those calculated by lattice dynamics, namely

$$T = \begin{pmatrix} 4.19 & 0.10 & -0.16 \\ & 3.25 & 0.03 \\ & & 2.72 \end{pmatrix} 10^{-2} \text{ \AA}^2$$

$$L = \begin{pmatrix} 15.09 & 1.08 & 2.78 \\ & 5.98 & 0.49 \\ & & 9.01 \end{pmatrix} \text{ deg}^2$$

However, it should be remembered that this calculation is appropriate to  $C_{14}H_{10}$ , not  $C_{14}D_{10}$ .

The question of significance must again be raised. In this case we have

$$\left\{ \frac{R_w(\text{III})}{R_w(\text{IV})} \right\}^{\frac{1}{2}} = \mathcal{R}^{\text{TL}^+} = 1.154$$

The 1% point of the  $R$ -distribution is 1.051 giving  $\mathcal{S}^{\text{TL}+} = 3.0$ , which makes anthracene one of the more rigid of molecules investigated by Pawley.<sup>4</sup> In all the examples compared, however, there is not one example where the difference has not proved statistically significant, though an example has recently been found<sup>11</sup> where the difference in the fits has not been statistically significant, namely 1,2,3-trichlorobenzene.

### CONCLUSION

The molecules of anthracene suffer some distortion in the crystal structure, though this is not apparent from Fig. 3. This diagram shows the Fourier function through the best plane of the molecule. This plane is defined by the matrix  $M$  and the Euler angles of model I. No attempt has been made to explain the distortion of the molecule which is therefore an open problem in lattice statics.

The thermal motion of the molecule as a rigid unit dominates the overall thermal motion, though a model which accounts in some ways for internal mode motion does differ significantly from the unconstrained model. It is our intention to study the temperature variation of the thermal motion by doing experiments at higher and at lower temperatures. This should also give us a more accurate picture of the variation of the structure parameters and thereby the anharmonicity in the lattice vibrations.

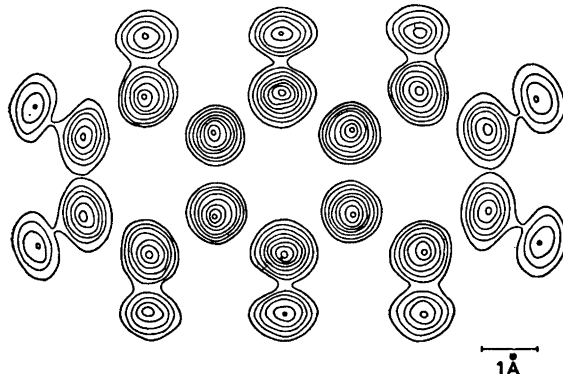


Fig. 3. The Fourier function in the best plane through the molecule.

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