

sec-butyl and 5-ethyl-5-(1-methylbutyl) barbituric acids. Crystals of these compounds have been shown to have structures which closely resemble amobarbital II (Craven & Cusatis, unpublished). However, it is unlikely that barbiturates substituted with unbranched chains at C(5) could have a double ribbon structure because the chain packing would be very inefficient. A double ribbon structure is not found in barbital I, II or IV\* (Craven, Vizzini & Rodrigues, 1969). More work is needed to determine the extent to which chain length in a C(5) substituent affects the occurrence of double ribbons in barbiturate crystal structures. It is probable that length is a less critical factor than cross sectional area.

Solid solutions and molecular complex formation have been reported in many binary systems of 5,5'-dialkylbarbiturates (Brandstätter-Kuhnert & Vlachopoulos, 1967). This suggests the existence of hydrogen bonded frameworks in the solid state which are not greatly perturbed when one barbiturate is substituted for another. The double ribbon structure is well suited to this role, and in fact occurs in solid solutions in at least one such binary system (amobarbital/vinbarbital; Craven & Cusatis, unpublished).

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\* The crystal structure of barbital IV has not yet been determined, but the lattice translations are incompatible with a double ribbon structure.

assembled and modified by Dr R. Shiono, Crystallography Laboratory, University of Pittsburgh.

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## A Neutron-Diffraction Study of Perdeuteronaphthalene

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The crystal structure of perdeuteronaphthalene,  $C_{10}D_8$ , is very similar to that of  $C_{10}H_8$ . The space group is  $P2_1/a$  with  $a = 8.266 \pm 0.008$ ,  $b = 5.968 \pm 0.006$ ,  $c = 8.669 \pm 0.008$  Å;  $\beta = 122.92 \pm 0.02^\circ$ . 331 independent observations give an  $R$  value of 5.2% in a refinement where the anisotropic temperature factors were fixed at the best values obtained with the use of the rigid-body thermal-motion constraint, and the positional parameters were constrained to the  $mmm$  symmetry of the free molecule. Statistical tests showed that no significant improvement is possible on removing the constraints. Consequently, the molecular geometry resulting from the constrained refinements was better determined than it would have been from a conventional unconstrained refinement.

### Introduction

The present investigation of the crystal structure of perdeuteronaphthalene,  $C_{10}D_8$ , is part of the study of the lattice dynamics of molecular crystals. Measurement of phonon frequencies is best done with neutron

inelastic coherent scattering. Hydrogen is a very strong incoherent scatterer, and for this reason fully deuterated crystals are preferred.

Calculations have been made of phonon frequencies in naphthalene by Pawley (1967), with the use of the crystal structure of  $C_{10}H_8$  as determined by X-ray dif-



ment. A thermal diffuse scattering correction (Cooper & Rouse, 1968) was not applied as this requires a reliable lattice dynamical model. The present study is a necessary step towards this goal. All refinements were based on  $|F_{\text{obs}}|$  with unit weights.

The first refinements were carried out by the use of the rigid-body thermal-parameter constraint program (Pawley, 1964). With neutron scattering lengths of 0.66 and 0.65 for carbon and deuterium atoms the conventional  $R$  value reached 5.30%, dropping to 5.10% when the scattering lengths for the deuterium positions were reduced to 0.63 to take account of the 2% of hydrogen remaining in the crystal.

Removing the thermal-parameter constraints gave no significant improvement at the 2% level of the  $F$  distribution, assuming that  $\left(\frac{R_{\text{initial}}}{R_{\text{final}}}\right)^2$  is  $F$  distributed (Pawley, 1966).

We therefore list only the results of the constrained refinement. In Table 1 the calculated structure factors are listed as  $|F_{\text{calc}}^{\text{r.b.}}|$ . The mean square rigid-body translational and librational tensors are

$$\mathbf{T} = \begin{bmatrix} 4.84 & 0.20 & -0.09 \\ & 2.92 & -0.06 \\ & & 2.29 \end{bmatrix} \text{ \AA}^2 \times 10^{-2}$$

$$\sigma(\mathbf{T}) = \begin{bmatrix} 0.09 & 0.06 & 0.08 \\ & 0.08 & 0.08 \\ & & 0.15 \end{bmatrix} \text{ \AA}^2 \times 10^{-2}$$

$$\mathbf{L} = \begin{bmatrix} 31.59 & -3.49 & 0.11 \\ & 18.45 & -1.16 \\ & & 19.12 \end{bmatrix} \text{ deg}^2$$

$$\sigma(\mathbf{L}) = \begin{bmatrix} 1.98 & 0.78 & 1.05 \\ & 0.93 & 0.73 \\ & & 0.85 \end{bmatrix} \text{ deg}^2$$

[The use of  $\mathbf{L}$  instead of the  $\omega$  in the original paper (Cruickshank, 1956) seems now to be generally accepted]. The comparison of these tensors with the cal-

culations on  $\text{C}_{10}\text{H}_8$  can only be rough, so we must wait for phonon measurements and an improved model before a good comparison can be made.

The nuclear fractional coordinates found in this refinement are listed in Table 2 under the columns headed  $\bar{1}$  symmetry, the molecular site symmetry. The anisotropic temperature factors in this Table are those derived from  $\mathbf{T}$  and  $\mathbf{L}$  and the fractional coordinates just mentioned.

The nuclear positions in the coordinate system defined by the inertia axes of the molecule are given in Table 3. The  $z$  coordinates are deviations from the plane perpendicular to the axis of greatest inertia. This is the mean molecular plane weighted heavily by the carbon positions. The least-squares standard deviations are 0.0055 and 0.0079  $\text{\AA}$  for the carbon and deuterium atom positions respectively. The deviations from the mean molecular plane are no more than one standard deviation for the carbon atoms, but about two standard deviations for two of the deuterium atoms. We need to know whether this is evidence for molecular distortion or whether the deviations are insignificant.

To answer this question we should analyse the deviations from  $mmm$  symmetry, the symmetry of the molecule in the free state. Column 2 of Table 3 shows the  $x$  and  $y$  coordinates for the symmetry averaged molecule. We see that in three of the eight coordinate pairs averaged, namely  $C_x(A\&E)$ ,  $C_y(A\&E)$  and  $D_x(b\&d)$ , the individuals differ by about three standard deviations. The following analysis shows, however, that these deviations are insignificant.

The most valid test of molecular strain from  $mmm$  symmetry is given by comparing the results of refinements with and without the symmetry imposed. A new program was written to apply the molecular symmetry constraint throughout the SFLS refinement. The procedure which has been described by Pawley (1969) has been followed. A relatively small number of additions have been made to the usual basic least-squares program with the use of the *Editor* system, written by Dr J.G. Burns of Edinburgh. Unfortunately, the rigid-body thermal parameter constraint program is not

Table 2. Fractional coordinates of the molecule with and without the symmetry constraint, and the thermal parameters for the expression  $\exp[-10^{-4}(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2klb_{23} + 2lhb_{31} + 2kbb_{12})]$  obtained with the rigid body thermal parameter constraint.

	$mmm$ symmetry			$\bar{1}$ symmetry			Rigid body					
	$x/a$	$y/b$	$z/c$	$x/a$	$y/b$	$z/c$	$b_{11}$	$b_{22}$	$b_{33}$	$b_{23}$	$b_{31}$	$b_{12}$
C(C)	0.0482	0.1030	0.0359	0.0480	0.1035	0.0352	116	163	174	-10	69	0
C(B)	0.1149	0.1606	0.2205	0.1155	0.1591	0.2206	202	250	187	-50	87	-31
C(D)	0.0761	0.2476	-0.0782	0.0755	0.2487	-0.0777	190	200	235	15	118	-18
C(A)	0.0857	0.0174	0.3267	0.0857	0.0164	0.3260	262	357	181	-12	115	3
C(E)	0.0099	0.1869	-0.2555	0.0088	0.1876	-0.2566	251	311	228	52	145	16
D(b)	0.1883	0.3185	0.2733	0.1878	0.3178	0.2718	328	314	253	-119	126	-110
D(d)	0.1499	0.4043	-0.0213	0.1511	0.4053	-0.0219	307	232	338	-6	182	-89
D(a)	0.1368	0.0627	0.4665	0.1353	0.0630	0.4650	432	561	197	-42	163	-17
D(e)	0.0318	0.2978	-0.3408	0.0327	0.2972	-0.3414	402	448	311	113	238	14

written in the *Editor* system, so both constraints are not possible simultaneously at present.

The number of parameters needed to determine the nuclear positions for the full-symmetry molecule is 12, compared with 27 in the unconstrained case. Nine of these parameters are indicated in Fig. 1, the remaining three being the three Euler angles necessary to form the rotation matrix which puts the molecule in the correct orientation. This matrix is formed as described by Pawley (1969) and the rotated molecule is then transformed to crystal fractional coordinates by the matrix

$$\begin{pmatrix} \frac{1}{a} & 0 & -\cot \beta \\ 0 & \frac{1}{b} & 0 \\ 0 & 0 & \frac{\operatorname{cosec} \beta}{c} \end{pmatrix}$$

The best starting values for the Euler angles were

$$\begin{aligned} \varphi &= -1.1707^\circ \\ \theta &= 4.3952 \\ \psi &= 2.0597 \end{aligned}$$

Refinement was carried out by anisotropic temperature factors fixed at the values obtained from the rigid body thermal parameter constraint. The  $R$  value reached was  $R=5.15\%$ , with

$$\begin{aligned} \varphi &= -1.1707 \pm 0.0008^\circ \\ \theta &= 4.3946 \pm 0.0010 \\ \psi &= 2.0592 \pm 0.0012 \end{aligned}$$

The calculated structure factors are given in Table 1 under the heading  $|F_{\text{calc}}^{mmm}|$ .

The atomic coordinates are listed in Tables 2 and 3. This  $R$  value is not significantly worse than  $R=5.10\%$ , obtained with the thermal parameter constraint but no symmetry constraint.

When the thermal parameters were allowed to vary independently, the  $R$  value dropped to  $R=4.98\%$ . This improvement is not significant on the 25% level of the  $F$  distribution, and the results are therefore not given here.

We see in Fig. 1 the large difference between the lengths of the bonds  $C(C)-C(D)$  and  $C(D)-C(E)$ . Although this is in agreement with the X-ray result on  $C_{10}H_8$  (Cruickshank, 1957), it is instructive to test the significance of this variation with yet another constrained refinement. Let us take a model for the molecule determined by two parameters, the C-C and the C-D bond lengths. Assume that both rings are perfect hexagons with the C-D bonds pointing radially from the hexagon centres. All the atomic positions in the crystal are now determined by five parameters, the two bond lengths and the three Euler angles.

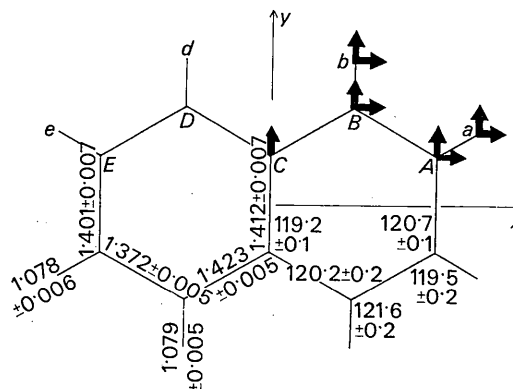


Fig. 1. The molecule of naphthalene. The capital letters denote the carbon atoms, the small letters the deuterium atoms. The bold arrows indicate the positional parameters consistent with the molecular symmetry. The bond lengths and angles and their errors come from the refinement incorporating the molecular symmetry and using the rigid-body thermal parameters, and are uncorrected for librational motion.

Table 3. *Coordinates of the molecule in Å*

The last columns contain unconstrained coordinates transformed into the inertia axes coordinate system.

Atom	Constrained <i>mmm</i> molecule	Best <i>mmm</i> molecule from next 2 columns	Centrosymmetric molecule, thermal parameter constraint	Atom
			-0.0088	X
			0.7076	Y coordinates
			-0.0015	Z
C(C)	0.7060	0.7060	1.2368 -1.2429	
			1.3982 1.3991	
C(B)	1.2420	1.2399	0.0055 -0.0055	C(D)
	1.3995	1.3987	2.4133 -2.4307	
			0.7046 0.6894	C(E)
C(A)	2.4219	2.4220	-0.0008 -0.0031	
	0.7004	0.6970	1.2043 -1.2461	
D(b)	1.2252	1.2252	2.4764 2.4800	D(d)
	2.4781	2.4782	-0.0005 0.0095	
			3.3453 -3.3700	
D(a)	3.3575	3.3577	1.2458 1.2205	D(e)
	1.2359	1.2332	-0.0154 0.0155	
C	0.0033	Standard	0.0055	
D	0.0046	deviations	0.0079	

A constrained refinement was carried out, giving  $C-C=1.4056 \pm 0.0015 \text{ \AA}$  and  $C-D=1.073 \pm 0.003 \text{ \AA}$ , but the  $R$  values obtained by the rigid-body thermal parameters and then by variable thermal parameters were 6.0 and 5.8% respectively. These are both significantly poorer than previous  $R$  values on the 2% level of the  $F$  distribution. We therefore conclude that the extra constraint is not realistic, and that the difference between the  $C(C)-C(D)$  and  $C(D)-C(E)$  bonds found earlier is highly significant.

### Conclusion

From our statistical tests we have found no evidence of deviation from either the rigid-body thermal motion model or the full-molecular-symmetry model. We have not attempted to fit the third or fourth cumulants introduced by Johnson (1969) but to the approximation of second cumulants (the usual approximation) we should have optimized our molecular geometry determination by applying these physically reasonable constraints. Indeed, we see that the standard deviations for the positional parameters are considerably diminished by the symmetry constraint, giving bond lengths and angles with errors as shown in Fig. 1. An attempt to simplify the model further gave a significantly poorer fit, indicating that the  $C-C$  bonds differ significantly in length.

We have presented three different constrained refinements specifically to answer three separate questions. The task of combining these constraint procedures in

one general program is great indeed, but a system where this is possible should be aimed at. In the present example the symmetry constraint gave the least change in the  $R$  value, the symmetry information being incorporated in the SFLS refinement. This is in contrast to the recent work of Maslen (1968) where this assumed symmetry information is used in 'phase refinement' after the fitting procedure is concluded. It will be of interest to investigate the 'phase refinement' by the use of the results of a symmetry constrained refinement.

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## The Structure of Bis- $\pi$ -cyclopentadienyl(toluene-3,4-dithiolato)molybdenum

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$(\pi-C_5H_5)_2MoS_2C_6H_3CH_3$  crystallizes in space group  $P2_1/n$  with  $a=14.97 \pm 0.01$ ,  $b=17.69 \pm 0.01$ ,  $c=12.63 \pm 0.01 \text{ \AA}$ ,  $\beta=115.5 \pm 0.2^\circ$  and  $Z=8$ . One of the two molecules is disordered as a result of the presence of both enantiomers in the same site. The least-squares refinement with isotropic temperature factors gave an  $R$  value of 0.098 for 3549 observed photographic data. The coordination symmetry about molybdenum approximates to  $C_{2v}$ ; the dithiol plane nearly bisects the  $132.5^\circ$  angle between normals to cyclopentadienyl rings, which have a staggered configuration. The average Mo-S distance in the ordered molecule is  $2.433 \pm 0.005 \text{ \AA}$ .

### Introduction

In a molecular orbital description of  $(\pi-C_5H_5)_2MX_2$  compounds Ballhausen & Dahl (1961) suggested that the lone pair of electrons lies between the two bonding

orbitals in a plane between the cyclopentadienyl rings. Their belief that the rings need not be parallel was verified by the structure determination of  $(\pi-C_5H_5)_2MoH_2$  (Gerloch & Mason, 1965), but the angle between Mo-H bonds was not firmly established (Abrahams & Ginsberg, 1966). To clarify the geometry of these compound we determined the structure of bis- $\pi$ -cyclopentadienyl-(toluene-3,4-dithiolato)molybdenum:

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