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A Neutron Powder Diffraction Study of Deuterated α-Resorcinol: a Test of Profile Refinement Using TLS Constraints

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Abstract

Constrained **TL**, **TLX** and **TLS** refinements have been used, with the powder-profile method, in the analysis of accurate neutron powder data for deuterated α-resorcinol at room temperature. There is good agreement between the translational and librational parameters derived from the **TL** refinement and those obtained from an equivalent analysis of accurate single-crystal neutron measurements. The fine details of the benzene ring are lost in the powder analysis, but the molecular orientation and the OH bond angles are in good agreement with the single-crystal values. No significant improvement could be found in the powder fit by applying the full **TLS** theory and, therefore, the approximate **TLX** model appears to be adequate for powder data.

1. Introduction

The application of rigid-body constraints to the study of thermal motion in molecular materials by single-crystal X-ray and neutron diffraction is a well established technique. The molecular vibrations are expressed in terms of two tensors, **T** and **L**, defining the translational and librational parts, respectively. In the approximate **TLX** model (Pawley, 1963), the centre of libration **X** is refined directly but in the general approach of Schomaker & Trueblood (1968) a further tensor **S** is introduced to take into account correlations between translational and librational vibrations.

The rigid-body analysis usually involves the fitting to a **TLS** model of anisotropic **B** factors (B_{ij}) previously determined from an unconstrained refinement. The agreement between the 'unconstrained' and **TLS B** factors can then be used to estimate the rigidity of the molecule. An alternative approach (Pawley, 1964, 1968) involves constraining the least-squares analysis of the data to refine the **T**, **L** and **X** (or **S**) matrices directly. This technique is particularly useful when limited data are available since the number of variable least-squares parameters may be reduced considerably. This is precisely the problem usually faced in neutron powder-profile refinements (Rietveld, 1969), where the number of reflections measured may be drastically limited by overlap due to instrument resolution.

In the case of room-temperature data from organic compounds, this problem is complicated by the high **B** factors associated with the light atoms in the structure, since these tend to reduce the peak/background ratios at high values of θ. A full unconstrained refinement involving 100 or more parameters will often be impracticable in these cases and the application of both structural and thermal constraints may be necessary to obtain a stable refinement.

In the field of powder-profile refinement, some work has been published on the application of exact structural constraints (Pawley, Mackenzie & Dietrich, 1977) but, as yet, there have been no attempts to apply thermal constraints. An evaluation of the direct application of the **TLS** method is therefore desirable and, to achieve this object, a series of rigid-body analyses has been undertaken on accurate room-temperature neutron data from a powder sample of fully-deuterated α-resorcinol. This compound was chosen since it had been the subject of an accurate single-crystal neutron study by Bacon & Jude (1973) (hereafter BJ), and reliable **T** and **L** values are thus available for comparison. However, an exact comparison of single-crystal and powder data has not been possible since, in order to obtain high precision in the powder measurements, it has been necessary to use fully deuterated material to avoid the large incoherent scattering from H. Unfortunately, no data are available for a deuterated single crystal.

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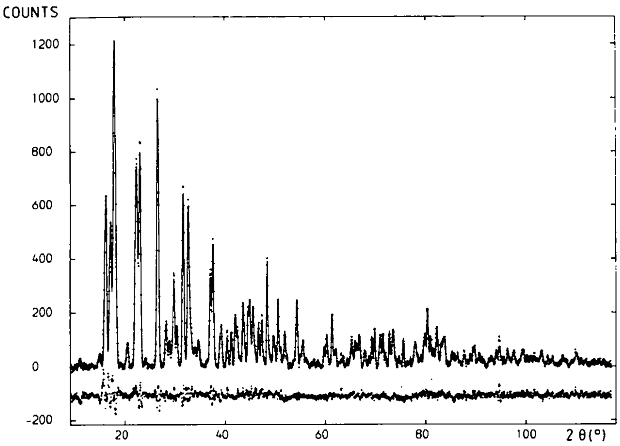

Fig. 1. The observed and calculated neutron powder diffraction profile of α-resorcinol at room temperature. The full line corresponds to the best fit using model (*C*). The points are the observed pattern after subtraction of an eye-estimated background of approximately 200 counts per point. The difference profile is also shown on an arbitrary scale.

The powder-profile refinements described below were carried out using the program *EDINP* (Pawley *et al.*, 1977) in which the constraints are programmed by the user.

2. Experimental

The neutron diffraction measurements were made on the DIA spectrometer at the ILL, Grenoble, using neutrons of wavelength 1·38 Å. The angular range recorded was $9° < 2\theta < 117°$ and the step width was 0·05° in 2θ with a counting time of 30 s per point. The sample was contained in a vanadium can of diameter 16 mm at room temperature and the resulting pattern is shown in Fig. 1.

3. The structure

α-Resorcinol crystallizes in the orthorhombic space group $Pna2_1$ with four molecules per unit cell. BJ have measured the unit-cell parameters of a hydrogenated sample at room temperature to be a = 10·527, b = 9·532, c = 5·660 Å. The benzene ring and the two O atoms were found to be coplanar within experimental error, with the possible exception of one benzene H atom. The two bonding H(*G*) and H(*J*) atoms (using the nomenclature of BJ), deviate from the plane by 0·111 and 0·060 Å, respectively. The essential parameters of the benzene ring and the OHO bonds are summarized in the first column of Table 1, and the molecule and the short OHO bonds are shown in Fig. 2.

Table 1. *Summary of structural parameters derived from the single-crystal and the constrained powder refinements*

For the single crystal and model (*A*) for the powder, the values of C—C and C—H given are the averages over the values in Table 3. The e.s.d.'s on the last significant digit are given in parentheses.

	Single crystal (Bacon & Jude, 1973)	Model (*A*)	Model (*B*)	Model (*C*)
Bond lengths* (Å)				
C–C	1·390 (4)	1·386 (11)	1·386 (10)	1·387 (10)
C–H	1·079 (7)	1·071 (14)	1·083 (13)	1·087 (14)
C(*D*)–O(*J*)	1·364 (4)	1·357 (10)	1·325 (10)	1·315 (10)
C(*F*)–O(*G*)	1·353 (5)	1·279 (12)	1·306 (11)	1·314 (12)
O(*J*)–H(*J*)	0·987 (7)	0·932 (13)	0·965 (13)	0·965 (13)
O(*G*)–H(*G*)	0·985 (5)	0·988 (12)	0·966 (11)	0·971 (12)
H(*J*)–O″(*G*)	1·765 (12)	1·842 (25)	1·816 (24)	1·808 (25)
H(*G*)–O″(*J*)	1·734 (13)	1·803 (24)	1·818 (24)	1·812 (24)
Bond angles (°)				
C(*E*)–C(*D*)–O(*J*)	116·3 (4)	116·6 (9)	118·0 (9)	117·9 (9)
C(*E*)–C(*F*)–O(*G*)	116·9 (5)	118·3 (8)	117·4 (9)	117·5 (9)
C(*D*)–O(*J*)–H(*J*)	111·9 (4)	117·3 (9)	115·4 (8)	116·8 (9)
C(*F*)–O(*G*)–H(*G*)	112·9 (4)	115·8 (9)	114·4 (9)	113·6 (9)
O(*J*)–H(*J*)–O″(*G*)	165·7 (5)	170·3 (10)	169·6 (10)	168·0 (10)
O(*G*)–H(*G*)–O″(*J*)	175·9 (5)	179·2 (10)	177·0 (10)	176·2 (10)
Euler angles (rad)				
ψ	4·482	4·496 (2)	4·484 (2)	4·482 (2)
θ	2·052	2·053 (1)	2·053 (1)	2·053 (1)
φ	−2·458	−2·459 (2)	−2·460 (2)	−2·457 (2)
Distance from plane of C_6H_4 (Å)				
O(*J*)	−0·015	−0·007 (10)	0·014 (11)	−0·009 (10)
O(*G*)	−0·004	0·003 (11)	−0·012 (11)	−0·011 (11)
H(*J*)	−0·067	−0·072 (12)	−0·061 (12)	−0·061 (12)
H(*G*)	−0·113	−0·119 (11)	−0·117 (11)	−0·103 (11)
Number of parameters	125	53	31	34
R (%)		10·2	10·5	10·4
Unit-cell dimensions (Å)				
a	10·527 (2)	10·516 (1)	10·518 (1)	10·517 (1)
b	9·532 (2)	9·541 (1)	9·541 (1)	9·541 (1)
c	5·660 (1)	5·660 (1)	5·660 (1)	5·660 (1)

Half-width parameters from the powder refinements (deg²):

$$U = 0{\cdot}59\ (2),\ V = -0{\cdot}79\ (2),\ W = 0{\cdot}34\ (1)$$

* Bond lengths are not corrected for shortening resulting from librational motion.

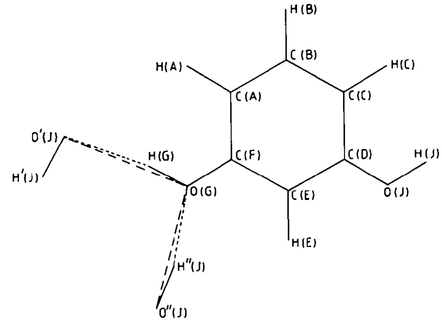

Fig. 2. The α-resorcinol molecule showing the hydrogen bonds.

4. The TL refinements

Two refinements were undertaken in which the thermal motion of the molecule was constrained by the **TL** method. In the first of these, model (*A*), the positional coordinates of the atoms were left unconstrained, and the molecular centre of libration was assumed to coincide with the centre of gravity and was held constant during the refinement. This model required 41 structural and 12 thermal parameters. An *R* value of 10·2% was obtained. In model (*B*), the benzene ring was constrained to be a perfect planar hexagon and the associated H atoms were constrained to be planar and to be in symmetrical positions. The benzene ring could be described by three Euler angles defining molecular orientation (Goldstein, 1959), two coordinates X_1 Y_1 defining its centre (Z_1 is indeterminate due to the space group), and two mean bond lengths C—C and C—H. The remaining O and H atoms comprising the hydroxyl groups were left to refine freely. In this case, 19 structural and 12 thermal parameters were refined, *R* being 10·5%. The structural parameters derived from models (*A*) and (*B*) are presented in the second and third columns, respectively, of Table 1, and the corresponding **T** and **L** matrices are shown in the second and third columns of Table 2. The tensors refer to the inertial axes defined by BJ.

A comparison of the structural parameters given in Table 1 for the two models shows that the agreement is good for the parameters relating to the benzene ring, but poorer for those defining the hydrogen bonds. The largest variations occur for the O—H and H—O″ intermolecular bond lengths. The good agreement between the two sets of values for **T** and **L** (Table 2) indicates that the thermal parameters are well defined from the powder pattern and that they are independent of the constraints applied to the structural parameters. Considering the amount of information on the anisotropic vibrations that must be lost due to reflection overlap for the powder, the agreement with the **T** and **L** results from the single-crystal measurements is surprisingly good. The diagonal elements of both **T** and **L** from the powder and single crystal agree to within three standard deviations. The agreement between the off-diagonal elements of **T** and **L** from the two techniques is poor, but these parameters are of less importance in the interpretation of the physical significance of the rigid-body analyses. A discussion of the structural parameters obtained from the powder and single-crystal refinements will be given in §7.

Table 2. *α-Resorcinol*: **T** ($\times 10^{-2}$ Å^2) *and* **L** (deg^2) *tensors from the single-crystal and the constrained powder refinements*

	Single crystal (Bacon & Jude, 1973)	Model (*A*)	Model (*B*)	Model (*C*)
T_{11}	3·69 (6)	3·9 (1)	4·0 (1)	3·8 (1)
T_{22}	2·71 (10)	3·2 (2)	2·9 (2)	3·9 (2)
T_{33}	2·84 (7)	2·4 (1)	2·6 (1)	1·9 (1)
T_{23}	0·33 (5)	−0·2 (1)	−0·3 (1)	0·0 (1)
T_{13}	−0·05 (4)	−0·3 (1)	−0·3 (1)	−0·2 (1)
T_{12}	−0·13 (4)	−0·5 (1)	−0·5 (1)	−0·4 (1)
L_{11}	19·1 (9)	20 (1)	22 (1)	17 (1)
L_{22}	5·2 (3)	7 (1)	6 (1)	7 (1)
L_{33}	7·2 (5)	6 (1)	8 (1)	5 (1)
L_{23}	−1·6 (3)	−1·0 (6)	−1·3 (7)	−2·3 (7)
L_{13}	−1·1 (4)	2·4 (5)	1·6 (5)	1·9 (5)
L_{12}	0·1 (4)	−0·8 (9)	−1·3 (8)	−0·8 (7)

5. The unconstrained refinement

A totally unconstrained refinement, varying 41 structural and 84 thermal parameters, proved to be unstable and the result was strongly dependent on the initial values of B_{ij}. The best *R* value obtained was 9·0%. Although the final B_{ij} matrix for each atom was positive definite, there was poor agreement with the single-crystal anisotropic temperature factors given by BJ.

Because of the uncertainty of the total number of independent reflections (*N*) contained in the powder pattern, it is difficult to perform a Hamilton significance test on the *R* values. However, if the unconstrained refinement (125 variables, $R = 9{\cdot}0\%$) is compared with the results of the refinement using model (*B*) (31 variables, $R = 10{\cdot}5\%$), the Hamilton test may be used in reverse to derive the minimum value of *N* for the unconstrained refinement to be a significant improvement over model (*B*). At the 1% significance level, $N > 275$ for this to be the case. From considerations of the mean angular half width per reflection, however, it is unlikely that *N* exceeds 200 for the powder pattern shown in Fig. 1. Hence it would appear that the 31 parameters of model (*B*) provide an adequate fit and, consequently, the fine details of the anisotropic vibrations are lost.

6. TLX and TLS refinements

Unfortunately the single-crystal work of BJ did not include full **TLX** or **TLS** analyses and thus a direct comparison of single-crystal and powder results is not possible in these cases. However, both **TLX** and **TLS** refinements were undertaken on the powder data with the structural parameters constrained as in model (*B*). The *R* values were 10·4 and 10·1%, respectively, and the results of the **TLX** refinement, model (*C*), are presented in the fourth columns of Tables 1 and 2. The centre of libration moved 0·71 Å from the molecular centre of gravity to (1·09, 0·94, −0·76) but the small drop of 0·1% in *R* on going from **TL** to **TLX** indicates that the coordinates of **X** are not well defined by the powder-profile refinement. Comparison of these results with the values derived using model (*B*) shows that the main effect of varying the centre of libration appears in the diagonal elements of **T**, as is well understood. Both the structural and the librational parameters are in good agreement with the model (*B*) results.

The application of the full **TLS** theory (Schomaker & Trueblood, 1968) yielded a stable refinement, but the resulting **S** matrix had off-diagonal elements that were within two standard deviations of zero. Pawley (1970) has shown, for single-crystal data, that the **S** matrix may be determined to a reasonable degree of accuracy only if R is less than 7%. However, room-temperature powder measurements on molecular compounds are unlikely to contain sufficient information and it seems most likely that the full **TLS** analysis is beyond the accuracy of the technique.

7. Discussion

A comparison of the structural parameters derived from the single-crystal and powder measurements shows that the Euler angles, C—C and C—H bond lengths, and the displacement of both H(*G*) and H(*J*) from the molecular plane, are accurately reproduced by the powder analysis. The intermolecular angles O—H—O″ also show reasonable agreement and consistency. The principal discrepancies are to be found for the hydroxyl groups, notably the C—O, O—H and H—O″ bond lengths and the C—O—H angle. On the basis of the results and analyses described above, it is not possible to determine whether these discrepancies are due to the effect of deuteration, in the case of the powder, or if they are the result of limitations and correlations inherent in the powder-profile technique. However, our recent neutron powder measurements on partially deuterated acetanilide, $C_6D_5HONCCH_3$, have shown that at 4·2 K there are two distinct bond lengths for C—H (~1·06 Å) and C—D (~1·10 Å). (The full results of this work will be published later.) On this evidence it is probable that the C—H, O—H and possibly the intermolecular distances in α-resorcinol are affected by the deuteration, but the discrepancies in the C—O bonds are probably due to correlations between structural and thermal parameters.

The importance of applying constraints in the powder-profile refinement is illustrated by the poor agreement between the single-crystal and powder results for the fine details of the thermal and structural parameters relating to the benzene ring. The individual C—C and C—H distances as derived from model (*A*) show no resemblance to the single-crystal results (see Table 3), and it seems apparent that small structural distortions are effectively lost in the powder analysis because of the reflection overlap. Once the benzene ring is constrained, as in model (*B*), the mean C—C and C—H parameters compare favourably with the single-crystal values.

Table 3. *The individual* C—C *and* C—H *bond lengths from the single crystal and model* (*A*) *for the powder*

The e.s.d.'s on the last significant digit are given in parentheses.

	Single crystal (Å)	Powder model (*A*) (Å)
C(*A*)—C(*B*)	1·391 (3)	1·387 (12)
C(*B*)—C(*C*)	1·391 (4)	1·385 (12)
C(*C*)—C(*D*)	1·388 (5)	1·384 (10)
C(*D*)—C(*E*)	1·385 (4)	1·353 (11)
C(*E*)—C(*F*)	1·393 (3)	1·387 (11)
C(*F*)—C(*A*)	1·390 (4)	1·419 (12)
C(*A*)—H(*A*)	1·081 (7)	1·058 (13)
C(*B*)—H(*B*)	1·085 (7)	1·086 (14)
C(*C*)—H(*C*)	1·077 (8)	1·086 (14)
C(*E*)—H(*E*)	1·073 (8)	1·052 (13)

It may be concluded, therefore, that the powder-profile refinement method can yield a surprisingly large amount of structural and thermal information provided that suitable constraints are applied to the least-squares analysis. The powerful **TLX** constraint, especially, is likely to prove a very useful tool in future powder-profile analyses of organic materials, as we are now able to determine the gross thermal features so important in certain phase transitions.

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