

## A Neutron Powder Diffraction Study of Deuterated $\alpha$ - and $\beta$ -Resorcinol

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### Abstract

The structure of  $\beta$ -resorcinol has been determined from neutron diffraction measurements on powder samples at 4.2 K and room temperature. The configuration of the hydroxyl groups is different from that found in  $\alpha$ -resorcinol and the intermolecular bond lengths are increased, indicating a weakening of the OH bonds. Translational and librational parameters have been determined from the room-temperature data, and they are similar to those measured in  $\alpha$ -resorcinol. Finally, studies of the internal consistency of the profile-refinement technique have been carried out for 4.2 K powder data on  $\alpha$ -resorcinol.

### 1. Introduction

$\alpha$ -Resorcinol,  $C_6H_4(OH)_2$ , space group  $Pna2_1$ , was the subject of the earliest diffraction studies of organic materials by X-rays (Robertson, 1936) and by neutrons (Bacon & Curry, 1956). More recently, a very accurate neutron single-crystal study was undertaken by Bacon & Jude (1973) (hereafter B&J), and the results were considered to be near the limit of accuracy possible from medium-flux reactors. There are 14 independent atoms in the asymmetric unit, each requiring three coordinates and six thermal parameters, and thus totalling 126 parameters.

In contrast, no recent work has been published on the high-temperature  $\beta$ -phase of resorcinol, particularly because of the difficulty in growing single crystals suitable for neutron diffraction. The phase transition occurs at 347 K and an early X-ray study by Robertson & Ubbelohde (1938a) [hereafter R&U(a)] showed that the two phases have the same orthorhombic space group  $Pna2_1$ . For  $\beta$ -resorcinol the unit-cell dimensions were found to be  $a = 7.91$ ,  $b = 12.57$ ,  $c = 5.50$  Å and  $Z = 4$ . This early work was not of sufficient accuracy to permit the location of the H atoms, but it did show that at least one O atom is displaced out of the plane of the benzene ring.

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The majority of compounds studied, to date, by the Rietveld profile-refinement method are inorganic materials requiring less than ten structural parameters (Cheetham & Taylor, 1977). Recently, however, the method has been extended to small organic molecules by means of constraints applied to the refinement process (Thomas & Bendall, 1978; Pawley, Mackenzie & Dietrich, 1977; Bacon, Lisher & Pawley, 1979). The program *EDINP*, written by Dr G. S. Pawley, has been used throughout the present analyses. Broadly based on *ORFLS* (Busing, Martin & Levy, 1962), this program allows the constraints to be programmed directly by the user.

The present neutron diffraction study is part of a general investigation being carried out in this laboratory into the application of neutron powder diffraction to the study of small organic molecules, and it may be considered in two parts. Firstly, various constrained refinements have been carried out on low-temperature  $\alpha$ -resorcinol data to ascertain which parameters of the structure can be determined accurately. This work has also investigated the internal consistency of the technique, especially concerning the dependence of the results of the refinement on the maximum  $2\theta$  angle and the step width of the powder pattern. The second part of the project involves the measurement of the deuterium positions for  $\beta$ -resorcinol, along with translational and librational parameters from the 4.2 K and room-temperature data respectively. The accuracy of these results is discussed in the light of the  $\alpha$ -resorcinol refinements, and the structures of the two phases are compared.

### 2. $\alpha$ -Resorcinol

#### 2.1. Experimental

Measurements have been carried out at 4.2 K and room temperature on a powder sample of deuterated  $\alpha$ -resorcinol. With neutrons of wavelength 1.3894 (5) Å the data were collected on the D1A spectrometer at the Institut Laue-Langevin (ILL), Grenoble. For each of the powder patterns described in this paper, the neutron wavelength was calibrated using a standard Ni powder. The results obtained from the room-

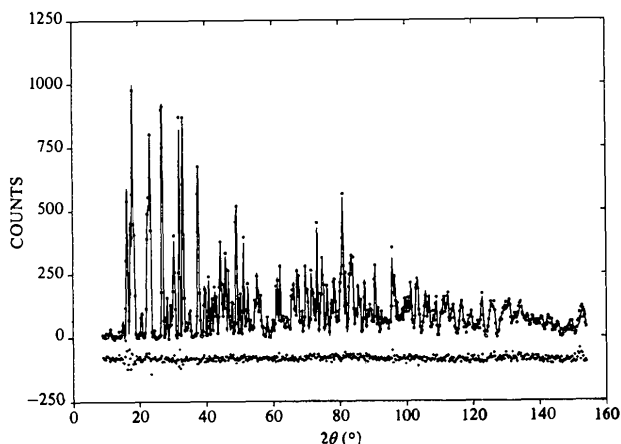


Fig. 1. The observed and calculated neutron powder diffraction profile of  $\alpha$ -resorcinol at 4.2 K. The full line corresponds to the best fit with model *A*. The points are the observed pattern after subtraction of a visually estimated background of approximately 150 counts per point. The difference profile is also shown on an arbitrary scale.

temperature data have been reported elsewhere (Bacon, Lisher & Pawley, 1979). With the sample contained in a vanadium can of diameter 16 mm, the 4.2 K powder pattern was recorded in the range  $9^\circ < 2\theta < 154^\circ$  in steps of  $0.05^\circ$  in  $2\theta$  (see Fig. 1).

## 2.2. The profile refinements

The  $\alpha$ -resorcinol molecule is illustrated in Fig. 4(a). The single-crystal results of B&J show that, within experimental error, the six C atoms of the benzene ring, three of the associated H atoms and the two O atoms are coplanar. The hydroxyl-group atoms H(*G*) and H(*J*) were found to deviate significantly from this plane and so also, to a lesser extent, did H(*E*). The single-crystal results also indicated that the benzene ring was slightly distorted from a hexagon.

In the light of these results, several constrained refinements were undertaken on the neutron powder data. In the first of these, model *A*, the benzene ring was constrained to be a perfect planar hexagon with the four associated deuterium atoms D(*A*), D(*B*), D(*C*) and D(*E*) in symmetrical positions coplanar with the ring. The section of the molecule could be described by three Euler angles  $\phi$ ,  $\theta$ ,  $\psi$  (Goldstein, 1959), two coordinates  $X_1$ ,  $Y_1$  defining the centre of the ring ( $Z_1$  is indeterminate) and the two mean bond lengths C—C and C—D. The  $x, y, z$  coordinates of each of the four OD-group atoms were also refined, bringing the total number of variable parameters to 19 for this model ( $R = 9.4\%$ ). In model *B*, the six benzene C atoms were again constrained as a perfect hexagon, but in this case the  $x, y, z$  coordinates of all the D atoms were refined. O(*G*) and O(*J*) were held coplanar with the ring and their positions were defined by a mean C—O distance

and the two bond angles C(*E*)C(*F*)O(*G*) and C(*E*)C(*D*)O(*J*). This model has 27 variable structural parameters ( $R = 9.3\%$ ). When all the atoms were allowed to refine freely without constraints, as in model *C*, there was a total of 41  $x, y, z$  coordinates ( $R = 9.1\%$ ). In each refinement, the peak-shape parameters and the unit-cell dimensions were varied along with an overall scale factor and two isotropic Debye-Waller factors: one of the latter was applied to the C and O atoms and the other to all the D atoms. The deuterium scattering length applied to the four benzene D atoms,

Table 1.  $\alpha$ -Resorcinol: summary of structural parameters derived from the refinements of the 4.2 K powder data

The single-crystal results of Bacon & Jude are shown for comparison. Only the principal parameters of models *A* and *B* are shown and these are marked with asterisks (the full set of structural parameters from model *A* are shown in Table 3). The remaining bond lengths and angles have been calculated from these parameters and their e.s.d.'s estimated. The values of C—C and C—D shown for model *C* and the single crystal are the averages over the values in Table 2. This also applies to model *B* in the case of C—D only. The e.s.d.'s on the last significant digit are given in parentheses.

	Model <i>A</i>	Model <i>B</i>	Model <i>C</i>	Single crystal (Bacon & Jude, 1973)
Bond lengths <sup>†</sup> (Å)				
C—C (mean)	1.392 (2)*	1.391 (2)*	1.393 (8)	1.390 (4)
C—D (mean)	1.102 (2)*	1.104 (7)	1.101 (8)	1.079 (7)
C( <i>D</i> )O( <i>J</i> )	1.366 (8)	1.353 (4)*	1.367 (9)	1.364 (4)
C( <i>F</i> )O( <i>G</i> )	1.341 (7)	1.353 (4)	1.344 (9)	1.353 (5)
O( <i>J</i> )D( <i>J</i> )	1.005 (9)	1.011 (7)	1.006 (10)	0.987 (7)
O( <i>G</i> )D( <i>G</i> )	1.005 (8)	1.009 (8)	1.012 (10)	0.985 (5)
D( <i>J</i> )O''( <i>G</i> )	1.719 (9)	1.723 (7)	1.725 (11)	1.765 (12)
D( <i>G</i> )O''( <i>J</i> )	1.700 (8)	1.697 (7)	1.680 (10)	1.734 (13)
Bond angles (°)				
C( <i>E</i> )C( <i>D</i> )O( <i>J</i> )	117.0 (4)	116.6 (3)*	117.3 (7)	116.3 (4)
C( <i>E</i> )C( <i>F</i> )O( <i>G</i> )	117.2 (5)	117.0 (3)*	117.2 (7)	116.9 (5)
C( <i>D</i> )O( <i>J</i> )D( <i>J</i> )	110.6 (6)	110.5 (6)	110.7 (9)	111.9 (6)
C( <i>F</i> )O( <i>G</i> )D( <i>G</i> )	112.0 (6)	110.9 (7)	112.0 (9)	112.9 (8)
O( <i>J</i> )D( <i>J</i> )O''( <i>G</i> )	166.3 (9)	166.4 (8)	165.9 (11)	165.7 (5)
O( <i>G</i> )D( <i>G</i> )O''( <i>J</i> )	174.5 (9)	173.7 (7)	175.0 (12)	175.9 (5)
Euler angles (radians)				
$\phi$	4.478 (1)*	4.480 (1)*	4.480 (1)	4.482
$\theta$	2.027 (1)*	2.029 (1)*	2.026 (1)	2.052
$\psi$	-2.470 (1)*	-2.469 (1)*	-2.468 (1)	-2.458
$X_1$ (Å)	1.313 (1)*	1.321 (2)*	—	—
$Y_1$ (Å)	1.259 (1)*	1.262 (2)*	—	—
Distance from plane of $C_6H_4$ (Å)				
O( <i>J</i> )	-0.007 (6)*	0.0	-0.024 (6)	-0.015
O( <i>G</i> )	-0.022 (6)*	0.0	-0.022 (6)	-0.004
D( <i>J</i> )	-0.087 (6)*	-0.082 (6)*	-0.090 (7)	-0.067
D( <i>G</i> )	-0.173 (7)*	-0.157 (6)*	-0.177 (6)	-0.113
Unit-cell parameters (Å)				
<i>a</i>	10.447 (1)*	10.447 (1)*	10.447 (1)	10.527 (2)
<i>b</i>	9.356 (1)*	9.357 (1)*	9.356 (1)	9.532 (2)
<i>c</i>	5.665 (1)*	5.665 (1)*	5.665 (1)	5.660 (1)
Debye-Waller factors (Å <sup>2</sup> )				
B(O + C)	0.56 (3)*	0.55 (2)*	0.56 (3)	—
B(D)	1.44 (4)*	1.43 (4)*	1.44 (4)	—
<i>R</i> (%)	9.4	9.3	9.1	—
Number of parameters				
	19	27	41	125
Half-width parameters from the powder refinements (deg <sup>2</sup> )				
	$U = 0.308 (7)$	$V = -0.417 (9)$	$W = 0.256 (3)$	

<sup>†</sup> Bond lengths are not corrected for shortening due to librational motion.

and another applied to  $D(G)$  and  $D(J)$ , were also varied. Table 1 contains a summary of the results of these three refinements. For models  $A$  and  $B$  only the principal parameters of the model are presented, and these are marked with an asterisk to differentiate them from the derived parameters. In the case of the unconstrained refinement (model  $C$ ) and the single-crystal results, all the bond lengths and bond angles shown were deduced from the final  $x, y, z$  values obtained, and the Euler angles represent the best plane through the six C atoms and four D atoms of the benzene group.

From Table 1 it can be seen that the Euler angles, the mean C—C and C—D distances, the hydroxyl-group bond lengths and bond angles and the unit-cell parameters are virtually independent of the model used in the refinement. A small error has been introduced into the results of model  $B$  by the constraint that the two C—O distances should be equal. Nevertheless, this does not appear to have introduced significant errors in any of the other major parameters, with the possible exception of the deviation of  $D(G)$  from the benzene plane. In each case, the values obtained for the deuterium scattering lengths were found to be within two e.s.d.'s of the accepted value: 6.67 fm.

Direct comparisons of the single-crystal and powder results are complicated by the possible effects of deuteration, and by the fact that the two sets of measurements correspond to different temperatures. The analysis of the room-temperature data (Bacon, Lisher & Pawley, 1979) showed that there was broad agreement between the 'bulk' structural parameters, such as the Euler angles and the C—C and C—D distances, obtained from the single-crystal and powder studies. The powder results also showed that reliable values could be obtained for the deviations of  $D(G)$  and  $D(J)$  from the benzene plane. It may be deduced, therefore, that the increases in the values of these two distances, found in the present study, are the effects of distortions within the molecule at 4.2 K. The principal discrepancies evident from the room-temperature results concerned the C—O distances and the CCO angles. These differences can be interpreted as evidence of correlations between structural and thermal parameters in the powder refinement. In the present refinements, the danger of such correlations is reduced owing to the smaller number of thermal parameters. In fact, the C—O bond parameters are now in excellent agreement with the single-crystal values. Nevertheless, refinements with different angular ranges of profile data (see § 2.3) do show that certain bond lengths are dependent on the value of  $2\theta_{\max}$ , an indication that thermal-structural correlations may still be significant.

Although the C—D and O—D distances obtained from the powder refinements are possibly affected in this way, the shortening of the intermolecular approach at 4.2 K is an unambiguous result. The D—O''

distances are reduced from 1.765 and 1.734 Å at room temperature to 1.719 and 1.700 Å, respectively, at 4.2 K. This result is expected since the thermal vibrations of the molecules at 4.2 K will be sufficiently reduced to allow a closer approach between adjacent molecules.

The single-crystal results of B&J indicated a small distortion of the benzene ring from the perfect hexagon. In the present work it was found that there was only a small drop in the  $R$  value on going from model  $A$  to model  $C$ , on releasing the hexagonal constraints applied to the benzene group, and hence the powder profile refinement is not sensitive to these small distortions. Table 2 contains values of the individual C—C and C—D distances as derived from models  $B$  and  $C$  and the single-crystal study. The two sets of C—C values, from model  $C$  and the single crystal, are generally in poor agreement and, furthermore, the agreement between the C—D distances from models  $B$  and  $C$  is also very poor, thus indicating that these parameters are strongly dependent on the constraints applied to the C atoms. B&J found evidence to suggest that  $D(E)$  is displaced out of the benzene plane since this displacement was 0.011 Å (from the best plane through  $C_6D_4$ ), which is three e.s.d.'s. The equivalent values derived from the powder refinements using models  $B$  and  $C$  were  $0.042 \pm 0.006$  Å and  $0.024 \pm 0.007$  Å, respectively. In both refinements,  $D(E)$  showed the largest planar deviation of all the four benzene D atoms; but the dependence of the values on the constraints applied to the benzene ring illustrates the difficulty in determining fine details of the structure from the powder data.

The profile-refinement method, therefore, appears to lack the accuracy necessary to determine small distortions within the benzene ring and, consequently, model  $A$  with just 19 structural parameters offers the most reliable results.

Table 2.  $\alpha$ -Resorcinol: individual C—C and C—D bond lengths from the single crystal, and models  $B$  and  $C$  for the powder (Å)

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

	Model $B$	Model $C$	Single-crystal (Bacon & Jude, 1973)
C(A)C(B)		1.403 (7)	1.391 (3)
C(B)C(C)		1.380 (8)	1.391 (4)
C(C)C(D)	} 1.391 (2)	1.411 (9)	1.388 (5)
C(D)C(E)		1.375 (8)	1.385 (4)
C(E)C(F)		1.392 (8)	1.393 (3)
C(A)C(F)		1.394 (9)	1.390 (4)
C(A)D(A)	1.104 (7)	1.074 (8)	1.081 (7)
C(B)D(B)	1.096 (7)	1.117 (8)	1.085 (7)
C(C)D(C)	1.108 (7)	1.096 (8)	1.077 (8)
C(E)D(E)	1.109 (7)	1.117 (9)	1.073 (8)

Table 3.  $\alpha$ -Resorcinol: structural parameters obtained from the refinements with differing amounts of profile data

Model *A* is used throughout and only those parameters refined directly are given. [The coordinates of D(*A*), D(*B*), D(*C*) and D(*E*) have been omitted.] The e.s.d.'s on the last significant digit are given in parentheses.

	Run (1) $\delta = 0.05^\circ$ $2\theta_m = 154^\circ$	Run (2) $\delta = 0.05^\circ$ $2\theta_m = 100^\circ$	Run (3) $\delta = 0.10^\circ$ $2\theta_m = 100^\circ$	Run (4) $\delta = 0.20^\circ$ $2\theta_m = 100^\circ$	Run (5) $\delta = 0.30^\circ$ $2\theta_m = 100^\circ$
C-C (mean) (Å)	1.392 (1)	1.395 (2)	1.396 (2)	1.396 (4)	1.395 (4)
C-D (mean) (Å)	1.102 (2)	1.094 (3)	1.092 (4)	1.092 (6)	1.097 (7)
$\varphi$ (rad)	4.478 (1)	4.482 (1)	4.482 (1)	4.482 (2)	4.484 (3)
$\theta$ (rad)	2.027 (1)	2.030 (1)	2.030 (1)	2.030 (2)	2.032 (2)
$\psi$ (rad)	-2.470 (1)	-2.467 (1)	-2.467 (2)	-2.466 (3)	-2.465 (4)
$X_1$ (Å)	1.313 (1)	1.313 (1)	1.313 (2)	1.314 (3)	1.313 (3)
$Y_1$ (Å)	1.258 (1)	1.261 (2)	1.261 (2)	1.262 (3)	1.262 (4)
$X_p$ (Å)	1.440 (5)	1.427 (6)	1.431 (8)	1.433 (12)	1.425 (14)
$Y_p$ (Å)	2.351 (5)	2.357 (5)	2.358 (7)	2.359 (11)	2.370 (13)
$Z_p$ (Å)	-0.007 (6)	-0.018 (7)	-0.021 (10)	-0.023 (15)	-0.023 (19)
$X_p$ (Å)	1.423 (4)	1.431 (5)	1.433 (7)	1.433 (10)	1.437 (13)
$Y_p$ (Å)	-2.332 (5)	-2.326 (5)	-2.327 (8)	-2.324 (11)	-2.316 (14)
$Z_p$ (Å)	-0.022 (6)	-0.015 (6)	-0.013 (9)	-0.011 (14)	-0.003 (17)
$X_p$ (Å)	0.847 (5)	0.837 (5)	0.836 (8)	0.832 (12)	0.834 (14)
$Y_p$ (Å)	3.158 (5)	3.148 (6)	3.150 (8)	3.149 (12)	3.145 (15)
$Z_p$ (Å)	-0.087 (6)	-0.098 (7)	-0.102 (10)	-0.099 (15)	-0.112 (18)
$X_p$ (Å)	0.852 (5)	0.863 (5)	0.863 (8)	0.862 (11)	0.857 (14)
$Y_p$ (Å)	-3.146 (5)	-3.133 (6)	-3.131 (8)	-3.130 (12)	-3.120 (15)
$Z_p$ (Å)	-0.172 (7)	-0.144 (8)	-0.141 (11)	-0.136 (16)	-0.131 (20)
Unit-cell parameters (Å)					
<i>a</i>	10.447 (1)	10.446 (1)	10.446 (1)	10.446 (1)	10.446 (1)
<i>b</i>	9.356 (1)	9.355 (1)	9.355 (1)	9.355 (1)	9.356 (1)
<i>c</i>	5.665 (1)	5.663 (1)	5.663 (1)	5.663 (1)	5.664 (1)
Debye-Waller factors (Å <sup>2</sup> )					
B(O + C)	0.56 (3)	0.34 (4)	0.33 (6)	0.34 (8)	0.26 (10)
B(D)	1.44 (4)	1.37 (4)	1.37 (5)	1.36 (8)	1.44 (10)
Number of points in profile	2910	1820	910	455	304
R (%)	9.4	7.2	7.3	7.4	7.4

### 2.3. Dependence on $2\theta_{\max}$ and step width

Much of the future work involving neutron powder diffraction on molecular materials is likely to be concerned with phase transitions, and the experiments will involve the collection of data at a number of temperatures. To minimize the amount of time spent in measuring at each temperature, it is important to determine the optimum values of the maximum  $2\theta$  angle ( $2\theta_{\max}$ ) and the angular separation, or step width, between the points ( $\delta$ ) in order to obtain the necessary accuracy in the final structural parameters.

The present measurements on  $\alpha$ -resorcinol afforded an excellent opportunity to study the structural parameters as functions of  $2\theta_{\max}$  and  $\delta$  for the case of a small organic molecule. Consequently, several refinements were undertaken, using model *A*, with varying amounts of the profile data and the results are presented in Table 3. In run (1) all the available data were incorporated in the refinement ( $\delta = 0.05^\circ$  and  $2\theta_{\max} = 154^\circ$ ). All the data for which  $2\theta > 100^\circ$  were omitted in the second refinement, run (2), although  $\delta =$

$0.05^\circ$  as before. In run (3),  $2\theta_{\max}$  was kept at  $100^\circ$ , but every alternate point was omitted so that  $\delta = 0.10^\circ$ . For runs (4) and (5),  $2\theta_{\max}$  was maintained at  $100^\circ$  but  $\delta$  was increased to  $0.20^\circ$  and  $0.30^\circ$ , respectively, by leaving out further points. The total number of profile points *N* included in each refinement is shown in Table 3.

An examination of the results from runs (2), (3), (4) and (5) shows that there is little variation in the values of the refined parameters for step widths up to  $0.20^\circ$ . Even with  $\delta = 0.30^\circ$  (run 5) the 'bulk' structural parameters are consistent with the more accurate results obtained from the other refinements. In this case, however, the use of only 304 profile points has resulted in some discrepancies in the values of the O and D coordinates, and hence this would appear to be the lower limit for *N* in the present study. As *N* decreases on going from run (2) to run (5), the e.s.d.'s on the parameters increase roughly in proportion to  $\sqrt{N}$ , as expected. However, certain worrying features emerge if one compares the results of runs (1) and (2),

where the effects of varying  $2\theta_{\max}$  are shown. Although the values of the bond lengths, Euler angles and unit-cell parameters agree well, there are differences in the O and D coordinates which are in some cases as large as one e.s.d. These discrepancies may be due to angular-dependent correlations involving, for example, the temperature factors or they may be caused by errors in the level of background subtracted over certain sections of the profile. On this evidence it is advisable, in any study involving profile refinement, to undertake more than one refinement with differing angular ranges in the data, in order to determine the internal consistency of the results.

### 3. $\beta$ -Resorcinol

#### 3.1. Experimental

It proved very difficult to obtain a pure sample of deuterated  $\beta$ -resorcinol by heating  $\alpha$ -resorcinol above the transition temperature and subsequently cooling in air to room temperature. A significant portion of the material reverted to the  $\alpha$  form within 2 h of cooling, as shown by room-temperature measurements on the HRPD powder spectrometer at AERE Harwell. This phase reversion in the deuterated salt had been reported by Robertson & Ubbelohde (1938*b*) [hereafter R&U(*b*)] in their early X-ray work. They found that the partially deuterated compound  $\beta$ -C<sub>6</sub>H<sub>4</sub>(OD)<sub>2</sub> tended to revert to the  $\alpha$  phase within 12 h at 293 K, whereas the hydrogenated material was stable in the  $\beta$  phase for several days.

In the present study, it was felt that the time spent in cooling the material past the transition temperature was the critical factor in determining the amount of phase reversion. To reduce this time, therefore, the deuterated

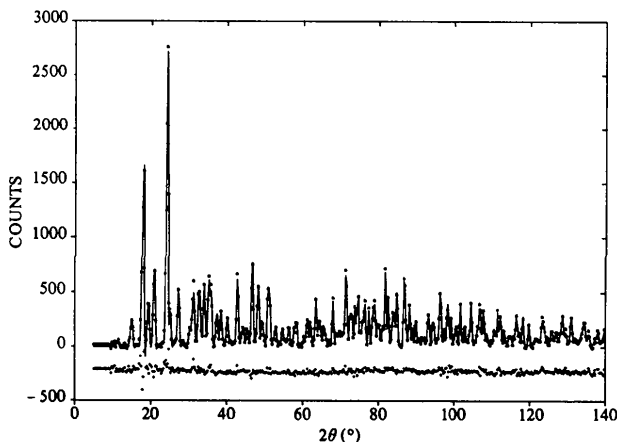


Fig. 2. The observed and calculated neutron powder diffraction profile of  $\beta$ -resorcinol at 4.2 K. The full line corresponds to the best fit with model A. A visually estimated background of approximately 350 counts per point has been subtracted to give the observed points. The neutron wavelength is 1.3842 (5) Å.

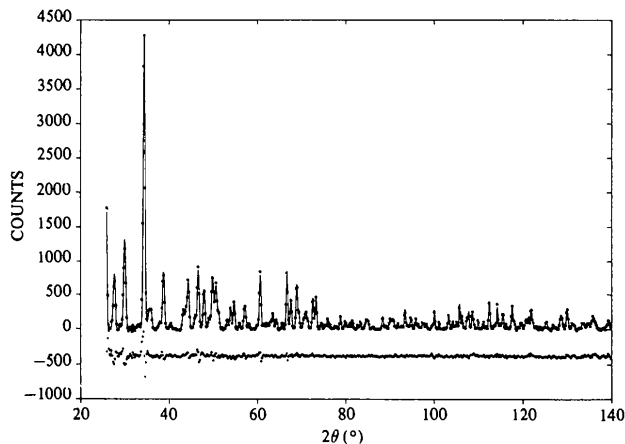


Fig. 3. The observed and calculated neutron powder diffraction profile of  $\beta$ -resorcinol at room temperature. The full line corresponds to the best fit obtained from the TLX refinement. A visually estimated background of approximately 550 counts per point has been subtracted to give the observed points. The neutron wavelength is 1.9063 (7) Å and  $\delta = 0.05^\circ$ .

powder was heated to 373 K for 30 min and was then plunged immediately into liquid nitrogen. Unfortunately, low-temperature neutron measurements could not be made on this sample directly since it showed considerable preferred orientation – the crystallites having grown into the thin plates characteristic of the  $\beta$  form. The sample was therefore brought up to room temperature, quickly ground and then cooled to 4.2 K – a process which took approximately 30 min. Neutron powder data were then collected in the range  $6^\circ < 2\theta < 140^\circ$  using the D1A spectrometer at the ILL, Grenoble, with neutrons of wavelength 1.3842 (5) Å. Several checks were made during these measurements for  $\alpha$ -resorcinol peaks in the low-angle part of the pattern, but there was no evidence to suggest significant contamination by this phase. The final pattern of  $\beta$ -resorcinol at 4.2 K is shown in Fig. 2.

After two days at 4.2 K, the sample was removed from the cryostat and remounted at room temperature on the D1A spectrometer. With neutrons of wavelength 1.9063 (7) Å, data were collected in the range  $26^\circ < 2\theta < 144^\circ$  with a total run time of approximately 36 h. During this period tests were made once more for  $\alpha$  contamination, but again none was found. The  $\beta$ -resorcinol pattern at room temperature is shown in Fig. 3. During both neutron diffraction experiments the powder sample was contained in a vanadium can of diameter 16 mm, and in each case the step width used was  $0.05^\circ$  in  $2\theta$ .

#### 3.2. Structure

The early work of R&U(*a*) had failed to locate the H atoms in  $\beta$ -resorcinol and, consequently, in the present

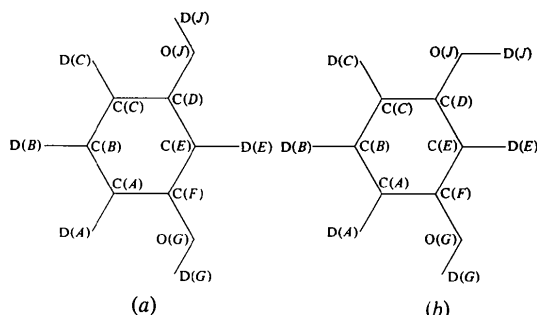


Fig. 4. The configurations of the resorcinol molecules: (a)  $\alpha$ -resorcinol, (b)  $\beta$ -resorcinol.

study it was necessary, initially, to estimate their positions from a knowledge of the C and O atoms.

It was assumed that the four D atoms of the benzene group lie in symmetrical positions coplanar with the C atoms, as in  $\alpha$ -resorcinol. The problem was then reduced to determining the positions of D(G) and D(J). From an investigation of the projection of the structure on (001), and a calculation of the OD-group intermolecular bond lengths, it was ascertained that the configuration of the hydroxyl groups is different from that found in the  $\alpha$  form. With the D atoms constrained to lie close to the benzene plane, it was determined that the only configuration minimizing the D—O'' intermolecular approaches and making the ODO'' angles approximately  $180^\circ$  is that shown in Fig. 4(b). This structure was further confirmed from initial profile refinements using the 4.2 K data in which several OD configurations were taken as starting points. It was found that the structure shown in Fig. 4(b) yielded by far the smallest *R* value.

The main difference in the  $\alpha$ - and  $\beta$ -resorcinol molecular geometries is, therefore, the breakdown in the symmetry of the O—D bonds. In  $\beta$ -resorcinol, O(J)D(J) is bent forwards from the line C(D)O(J), that is, in the opposite sense to O(G)D(G). A further discussion of the two phases is given in § 4.

### 3.3. The 4.2 K refinements

The constrained refinement was undertaken using model *A* (see § 2.2). Model *B* was omitted since the X-ray results had shown that at least one O atom was not coplanar with the benzene ring. The final atom coordinates are given in Table 4, and data on the bond lengths and bond angles are shown in the first column of Table 6. It should be noted that in Table 4 (and Table 5) e.s.d.'s are only quoted for those parameters which were varied directly in the refinement. These results were obtained using all the available data, but an additional refinement was also undertaken with  $2\theta_{\max} = 100^\circ$ . The results obtained were in good agreement with the full-data refinement, only the C(F)O(G) bond

Table 4.  $\beta$ -Resorcinol: the final coordinates of the atoms derived from the 4.2 K data set

Using model *A*, the parameters refined comprise the C—C and C—D bond lengths, the coordinates of the atoms in the hydroxyl group, the Euler angles ( $\varphi, \theta, \psi$ ) and the molecular centre ( $X_1, Y_1$ ). The benzene group is constrained to be hexagonal and planar, with D atoms in symmetrical positions. For the variable parameters, the e.s.d.'s on the last significant digit are shown in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
C(A)	0.1655	-0.0002	0.1673
C(B)	0.1330	0.1081	0.1860
C(C)	0.2069	0.1783	0.0187
C(D)	0.3134	0.1402	-0.1673
C(E)	0.3459	0.0318	-0.1860
C(F)	0.2720	-0.0384	-0.0187
D(A)	0.1074	-0.0554	0.2989
D(B)	0.0492	0.1381	0.3323
D(C)	0.1813	0.2635	0.0334
D(E)	0.4297	0.0018	-0.3323
O(G)	0.3181 (7)	-0.1404 (5)	-0.0404 (11)
O(J)	0.3841 (8)	0.2140 (4)	-0.3225 (11)
D(G)	0.2345 (10)	-0.1881 (6)	0.0455 (15)
D(J)	0.4792 (10)	0.1814 (5)	-0.4199 (14)

Euler angles of the  $C_6D_4$  group

$$\varphi = 5.145 (1) \text{ rad} \quad \theta = 0.923 (1) \text{ rad} \quad \psi = 1.442 (1) \text{ rad}$$

$$X_1 = 1.870 (2) \text{ \AA} \quad Y_1 = 0.883 (2) \text{ \AA}$$

length differing by more than two e.s.d.'s. It appears, therefore, that structural/thermal correlations were not important in the low-temperature  $\beta$ -resorcinol results.

In order to investigate possible distortions within the benzene ring, an unconstrained refinement was also performed. The use of 41 structural parameters only resulted in a drop of 0.3% in the *R* value, indicating that, as in the case of  $\alpha$ -resorcinol, any such distortions are too small to be detected reliably by the powder-profile method. Hence model *A* once again gives an adequate description of the structure, within the limitations imposed by the technique.

In  $\alpha$ -resorcinol, C(D)O(J) > C(F)O(G), but this inequality is reversed in the case of  $\beta$ -resorcinol if the labelling of R&U(*a*) is used. For reasons of consistency, therefore, the molecule has been re-labelled in the present paper so that the *H* and *G* groups of R&U(*a*) become, respectively, the *G* and *J* groups here. The remaining C and O atoms are similarly re-named to be consistent with Fig. 6 of B&J, and the new molecule is shown in Fig. 4(b).

For the important structural parameters, the agreement between the present neutron results and those from the early X-ray work of R&U(*a*) is surprisingly good considering the limited resolution of the final X-ray Fourier map. R&U(*a*) found that the benzene C atoms are coplanar, within their experimental error, but that the C—O bonds were both displaced slightly from the symmetrical positions. The values they obtained for the C(E)C(F)O(G) and C(E)C(D)O(J) angles were

Table 5.  $\beta$ -Resorcinol: the final coordinates of the atoms as derived from the room-temperature data set

For the variable parameters, the e.s.d.'s on the last significant digit are shown in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
C(A)	0.1660	-0.0021	0.1626
C(B)	0.1312	0.1059	0.1794
C(C)	0.2048	0.1765	0.0167
C(D)	0.3132	0.1392	-0.1626
C(E)	0.3480	0.0313	-0.1794
C(F)	0.2744	-0.0394	-0.0167
D(A)	0.1089	-0.0570	0.2890
D(B)	0.0470	0.1348	0.3187
D(C)	0.1778	0.2604	0.0298
D(E)	0.4322	0.0023	-0.3187
O(G)	0.3198 (9)	-0.1404 (6)	-0.0344 (14)
O(J)	0.3748 (11)	0.2110 (5)	-0.3205 (14)
D(G)	0.2420 (10)	-0.1892 (6)	0.0525 (16)
D(J)	0.4690 (12)	0.1829 (6)	-0.4150 (18)

Euler angles of the  $C_6D_4$  group

$$\varphi = 5.151 (2) \text{ rad} \quad \theta = 0.902 (1) \text{ rad} \quad \psi = 1.423 (2) \text{ rad}$$

$$X_1 = 1.901 (3) \text{ \AA} \quad Y_1 = 0.864 (2) \text{ \AA}$$

117.0 and 122.4°, respectively – in good agreement with the neutron values of 116.2 (7) and 123.2 (8)°. In addition, the X-ray results indicated that O(G) is situated at  $0.08 \pm 0.04$  Å above the plane of the benzene ring, whereas the present neutron data give a value of  $0.082 \pm 0.006$  Å.

The deuterium scattering lengths in Table 6 show that the production of  $\beta$ -resorcinol has resulted in a small loss of deuterium in the specimen. The  $\alpha$ -resorcinol refinements indicated that, within experimental error, all the H sites were fully deuterated, but the present  $\beta$ -resorcinol analysis shows that the deuterium levels have fallen to an average of  $97 \pm 1\%$  for the four benzene sites and to  $90 \pm 1\%$  for D(G) and D(J). These results show that hydrogen–deuterium exchange is more likely to occur at the bonding atoms rather than at the chemically inert benzene sites.

### 3.4. The room-temperature refinements

The analysis of the room-temperature data (Bacon *et al.*, 1979) had shown that meaningful results could be obtained from room-temperature powder data by the profile-refinement technique, providing suitable constraints are applied to the structural parameters and the anisotropic temperature factors,  $B_{ij}$ , are calculated from the TL or TLX rigid-body models (Pawley, 1963). Earlier studies involving the refinement of unconstrained  $B_{ij}$  (Ahtee, Ahtee, Glazer & Hewat, 1976; Albinati, Rouse & Thomas, 1978*a,b*) had produced non-positive-definite  $B_{ij}$  matrices for some atoms. Bacon *et al.* (1979) showed that the use of TLX constraints prevented the temperature factors from becoming physically unrealistic, and they also obtained

Table 6.  $\beta$ -Resorcinol: summary of structural and peak-shape parameters obtained from the 4.2 K and room-temperature powder refinements

Only the principal parameters of model A are shown and these directly refined variables are marked with asterisks. The remaining bond lengths and angles have been calculated and their e.s.d.'s estimated. The e.s.d.'s on the last significant digit are shown in parentheses.

	4.2 K	Room temperature
Bond lengths (Å)†		
C–C (mean)	1.394 (2)*	1.392 (2)*
C–D (mean)	1.096 (3)*	1.082 (3)*
C(D)O(J)	1.372 (8)	1.347 (11)
C(F)O(G)	1.342 (8)	1.327 (11)
O(J)D(J)	1.000 (8)	0.978 (12)
O(G)D(G)	1.003 (10)	0.994 (11)
D(J)O''(G)	1.789 (10)	1.878 (13)
D(G)O''(J)	1.702 (10)	1.712 (13)
Bond angles (°)		
C(E)C(D)O(J)	123.2 (6)	122.8 (13)
C(E)C(F)O(G)	116.2 (5)	116.9 (14)
C(D)O(J)D(J)	110.1 (7)	112.2 (12)
C(F)O(G)D(G)	111.1 (7)	112.9 (12)
O(J)D(J)O''(G)	165.8 (11)	166.5 (17)
O(G)D(G)O''(J)	170.2 (10)	170.8 (18)
Distance from plane of $C_6D_4$ (Å)		
O(J)	0.024 (6)*	-0.056 (9)*
O(G)	0.082 (6)*	0.072 (8)*
D(J)	0.251 (8)*	0.160 (11)*
D(G)	-0.215 (7)*	-0.181 (8)*
Unit-cell dimensions (Å)		
<i>a</i>	7.811 (1)*	7.934 (2)*
<i>b</i>	12.615 (1)*	12.606 (2)*
<i>c</i>	5.427 (1)*	5.511 (1)*
Deuterium scattering lengths (fm)		
D(A, B, C, E)	6.39 (6)*	6.04 (7)*
D(G, J)	5.61 (8)*	5.44 (8)*
Peak-shape parameters (deg <sup>2</sup> )		
<i>U</i>	0.198 (5)*	0.191 (6)*
<i>V</i>	-0.502 (10)*	-0.492 (11)*
<i>W</i>	0.430 (5)*	0.413 (5)*
Number of parameters	19	34
<i>R</i> (%)	10.1	11.9

For the 4.2 K data the final Debye–Waller factors were

$$B(O + C) = 0.67 (3) \text{ \AA}^2, \text{ and } B(D) = 1.63 (5) \text{ \AA}^2.$$

† Bond lengths are not corrected for shortening due to librational motion.

good agreement, for the T and L tensors, between the neutron results and those from the single-crystal study of B&J. Although some discrepancies were found in the bond lengths relating to the hydroxyl groups, the success of the  $\alpha$ -resorcinol room-temperature work in providing consistent results for the 'bulk' thermal and structural parameters gave us confidence to analyse the  $\beta$ -resorcinol powder data in a similar manner.

Table 7.  $\beta$ -Resorcinol: T, L and X tensors from the room-temperature refinement

The coordinates of X are relative to the crystallographic axes, and the T and L tensors are relative to the inertial axes described in § 3.4.

T ( $10^{-2} \text{ \AA}^2$ )	3.8 (1)	-0.07 (9) 4.3 (1)	0.1 (1) -0.5 (1) 3.9 (1)
L ( $\text{deg}^2$ )	19.7 (8)	-0.5 (5) 9.1 (9)	0.7 (4) -2.3 (6) 1.6 (8)
X ( $\text{\AA}$ )	2.13 (6)	0.52 (6)	-0.73 (6)

In the present refinements, the atoms were constrained using model *A*, described in § 2.2. This model had proved the most realistic in the 4.2 K work, and Bacon *et al.* (1979) adjudged it to give the most physically sensible results for  $\alpha$ -resorcinol. The results of the TLX refinement are presented in Tables 5, 6 and 7. Altogether, 34 structural and thermal parameters were varied and  $R = 11.9\%$ .

The T and L tensors in Table 7 are relative to the inertial axes *L*, *M*, *N* of the molecule, which are similar to those shown in Fig. 6 of B&J. These three axes are orthogonal: *L* is at right-angles to C(*A*)C(*F*) in the plane of the molecule; *M* is perpendicular to this plane; and *N* is defined by C(*B*)C(*E*). (Owing to the asymmetry of the molecule, the actual inertial axes deviate very slightly from the above definitions.) The final value for the centre of libration, *X*, is 0.51 Å from the molecular centre of gravity, but Bacon *et al.* (1979) concluded that this point was not well defined in the powder refinement.

A full TLS refinement (Schomaker & Trueblood, 1968) was also undertaken. The refinement was stable but the e.s.d.'s on the off-diagonal elements of the **S** matrix were large. This would appear to confirm the findings of Bacon *et al.* (1979) that the determination of the **S** matrix is beyond the accuracy of the technique.

The T and L tensors in Table 7 produce a positive-definite  $B_{ij}$  matrix for each atom. Further evidence of the physical realism of the present results can be seen in the consistency of the OD bond angles from 4.2 K to room temperature (Table 6) although it is probable that, at room temperature, the CO bond lengths may be in error, as was found to be the case in  $\alpha$ -resorcinol by Bacon *et al.* (1979).

#### 4. Discussion

The present work, taken along with that of Bacon *et al.* (1979), provides a comprehensive set of neutron powder measurements at 4.2 K and room temperature for both  $\alpha$ - and  $\beta$ -resorcinol, from which it is possible to

gain further insight into the differences between the two phases. Two factors which can facilitate an understanding of these differences are the relative thermal expansions of the two structures and the vibrational data.

The results indicate that both structures undergo strongly anisotropic expansion, with the largest increases occurring in the intermolecular bonds. In contrast, the internal dimensions of the molecules are relatively unchanged with the CD and OD bonds undergoing small contractions. The unit-cell dimensions are, therefore, greatly affected by the intermolecular approach which is, in turn, determined by the rigid-body molecular vibrations. The thermal-expansion coefficients of the  $\alpha$  phase are  $\Delta a/a = 23$ ,  $\Delta b/b = 68$ ,  $\Delta c/c = -3 \times 10^{-6} \text{ K}^{-1}$  and these are consistent with the changes in the unit cell after the phase transition. In the low-temperature form the line O(*G*)O(*J*) of the molecule is inclined at  $46.7^\circ$  to (010), whereas this angle is reduced to  $19.9^\circ$  in the  $\beta$  phase. The large expansion along the *b* axis in  $\alpha$ -resorcinol is evidence of the instability in the alignment of the molecule with a tendency to realign parallel to (010) on heating. The coefficients of thermal expansion in  $\beta$ -resorcinol are  $\Delta a/a = 54$ ,  $\Delta b/b = -2$ ,  $\Delta c/c = 53 \times 10^{-6} \text{ K}^{-1}$ , which shows that the molecule is now stabilized in the (010) orientation. The volume of the cell is reduced by 3% in the  $\beta$  phase at room temperature in comparison with  $\alpha$ -resorcinol, but the coefficient of volume expansion is larger:  $\Delta V/V = 106 \times 10^{-6} \text{ K}^{-1}$ , compared with  $88 \times 10^{-6} \text{ K}^{-1}$  in  $\alpha$ -resorcinol.

At room temperature the translational amplitudes along the inertial axes *L*, *M*, *N* are, respectively, 0.19, 0.20, 0.14 Å in  $\alpha$ -resorcinol and 0.19, 0.21, 0.20 Å in  $\beta$ -resorcinol. The corresponding librational amplitudes are 4.1, 2.6,  $2.2^\circ$  ( $\alpha$ -resorcinol) and 4.4, 3.0,  $1.3^\circ$  ( $\beta$ -resorcinol). The main difference in the rigid-body vibrations in the two phases is that in  $\beta$ -resorcinol there is an increase in the translational amplitude along the *N* axis of the molecule, and a corresponding reduction in the librational amplitude along this direction. However, the outstanding feature of the librational motion is preserved in the  $\beta$  form, namely the largest amplitude occurs about the *L* axis, about which the moment of inertia is smallest. Thus, as in the  $\alpha$  phase, the C atoms closest to the *L* axis, that is C(*D*), C(*E*) and C(*F*), have smaller vibrational amplitudes than C(*B*) which lies furthest from this axis.

$\beta$ -Resorcinol approximates to the typical layered structure of a hydrocarbon, as can be seen from the *b*-axis projection of the structure shown in Fig. 5. In  $\alpha$ -resorcinol, at 4.2 K, the intermolecular bond lengths are similar: 1.719 Å for D(*J*)O''(*G*) and 1.700 Å for D(*G*)O''(*J*). There is, however, a considerable lengthening of D(*J*)O''(*G*) to 1.789 Å in  $\beta$ -resorcinol and this is evidence, along with the breakdown in the



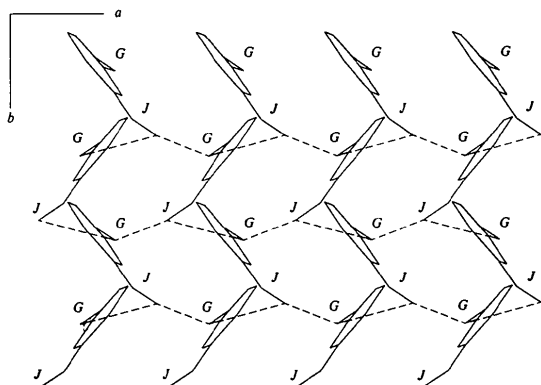


Fig. 5.  $\beta$ -Resorcinol:  $b$ -axis projection. For reasons of clarity the benzene deuterium atoms have been omitted.

symmetry of the hydroxyl groups, that the influence of the OD bonds is considerably weaker in this phase. The layered structure has been seen by R&U( $b$ ) as an attempt to minimize the van der Waals potential following the breakdown of the strong OD bonds in  $\alpha$ -resorcinol. Two important features follow the phase transition: the decrease in the planarity of the molecule and a distortion of the O—O'' bond angles. In  $\alpha$ -resorcinol these angles are  $105.5$  and  $102.9^\circ$ , very close to the tetrahedral value of  $109.5^\circ$  [see Fig. 8 of Robertson (1936)]. R&U( $b$ ) point out that such an open structure will not, in general, have a minimum van der Waals energy, but this fact may be outweighed by the influence of the OD bonds. The fact that all but the two bonding D atoms lie close to the molecular plane in  $\alpha$ -resorcinol is also an indication of instability in the structure. In  $\beta$ -resorcinol, the atoms of the hydroxyl group lie further from the molecular plane and the corresponding values of the O—O'' bond angles are now  $122.2$  and  $94.4^\circ$  respectively. Since the rigid-body thermal vibrations of the two phases are not drastically different, it seems likely that the breakdown of the  $\alpha$  structure is attributable to the instability of the OD bonds and the planarity of the O atoms rather than to any direct effect of the thermal motion.

### 5. Conclusions

The method of strict constraints has been applied successfully to the study of  $\alpha$ - and  $\beta$ -resorcinol, and the results throw some light on the mechanism of the phase transition. Studies of the internal consistency of the technique of constrained profile refinement indicate that

inconsistencies may be revealed if data from different angular ranges within the profile are used in the refinement. Consequently, it is recommended that the possibility of angle-related errors should be investigated in a particular case. The number of points measured within a particular angular range of the diffraction pattern is important in determining the accuracy of the final parameters, but the actual values appear to be independent of  $\delta$  for values of  $\delta$  up to  $0.20^\circ$ .

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