

Neutron Powder Diffraction Analysis of Hydrogen-Bonded Solids. I. Refinement of the Structure of Deuterated Acetic Acid at 4.2 and 12.5 K

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The structure of deuterated acetic acid has been refined at two different temperatures [4.2 (± 1 .) and 12.5 (± 1 .) K] by the profile-analysis technique of neutron powder diffraction data, with both isotropic and anisotropic temperature factors. The results are compared with existing single-crystal data (neutron and X-ray) for the non-deuterated compound. The geometry of the molecule does not change with temperature, and the lengthening of the O...O distance (2.68 Å) may be attributed to the isotope effect.

Introduction

Recently there have been a number of structural determinations of hydrogen-bonded compounds using single-crystal neutron diffraction to determine with accuracy the geometry and the H positions (Speakman, 1974, 1975, 1976, 1977; Olovsson & Jönsson, 1976). The determinations of the structures of both deuterated and hydrogenous compounds have also been carried out with a view to studying the effect of the substitution of H by D on the geometry, the so-called 'isotope effect'.

We are currently investigating the possibility of using neutron powder diffraction (hereafter NPD) for obtaining structural information on molecular crystals and deuterated hydrogen-bonded molecules. NPD may present some advantages compared to the single-crystal method and may be an extremely useful complementary technique; because of the short data-collection time, it is easier to carry out temperature-dependent studies, or to investigate pressure dependences; NPD is obviously the natural choice in all those cases in which the growth of the large single crystals required for neutron diffraction may be difficult or impossible (*e.g.* compounds undergoing phase transitions, or liquids or gases at room temperature).

A major problem in using powder data is the presence in the powder pattern of many overlapping peaks that prevent an effective use of the information contained in the profile. The use of the Rietveld profile analysis (Rietveld, 1969) of neutron powder data overcomes this problem and makes possible the determination of precise geometries (for example, *cf.* Chowdhury, Wedgwood, Chadwick & Wilde, 1977; Cheetham & Taylor, 1977). We therefore decided to refine the structure of CD₃COOD at low temperature

[4.2 (± 1 .) and 12.5 (± 1 .) K] as a check of the validity of the method as applied to low-symmetry compounds, and to compare the geometry obtained by NPD with that obtained for CH₃COOH by an X-ray single-crystal determination (Nahringbauer, 1970) and by a neutron single-crystal study at 133 K (Jönsson, 1971).

Data collection

The data have been collected using the PANDA diffractometer on the PLUTO reactor at AERE, Harwell. This powder diffractometer is a conventional two-circle machine using an array of 3 × 3 BF₃ counters. The sample (approximately 5 g of acetic acid, with a deuteration >98%) was frozen, ground and loosely packed into a thin-walled cylindrical vanadium can at liquid-nitrogen temperature.

Two different sets of data were collected, using a liquid He cryostat, at 4.2 and 12.5 K with the temperature controlled within a range of ± 1 . K. The intensities have been obtained using three independent detectors with an angular separation of 5° ($\pm 0.02^\circ$) in the horizontal plane, moving in steps of 0.1°; the counting time for each position was determined by a fission counter monitoring the incident beam. The data for the three counters were subsequently averaged but no extinction or absorption corrections were considered to be necessary. The wavelength was determined using Ni powder for calibration; however, the relatively large variations of the cell constants between 4.2 and 12.5 K may be due, in part, to small inaccuracies in this calibration.

The details of the data collection together with the relevant crystallographic data are given in Table 1.

Table 1. *Crystal data and experimental details for C₂O₂D₄ (M_r = 64.076)*In the last column the X-ray data for CH₃COOH (Nahringbauer, 1970) are given.

	Neutrons	Neutrons	X-rays
Temperature of the data collection (K)	4.2 (±1.)	12.5 (±1.)	278
<i>a</i> (Å)	13.1269 (10)	13.2118 (14)	13.310 (1)
<i>b</i> (Å)	3.8497 (3)	3.8942 (4)	4.090 (1)
<i>c</i> (Å)	5.7226 (5)	5.7610 (7)	5.769 (1)
<i>V</i> (Å ³)	289.19	296.40 (5)	314.05
Space group	<i>Pna</i> 2 ₁	<i>Pna</i> 2 ₁	<i>Pna</i> 2 ₁
<i>D_c</i> (g cm ⁻³)	1.471	1.435	1.269
λ (Ni-calibrated) (Å)	1.3140	1.5375	—
Monochromator	Ge (511)	Ge (511)	—
Take-off angle (2 θ°)	82.5	90.0	—
Angular range (2 θ°)	8.0 ≤ 2 θ ≤ 98.0	6.5 ≤ 2 θ ≤ 115.0	—
Number of parameters refined	40 (Isotropic)		

Table 2. *Positional parameters, thermal parameters (Å²) and agreement factors for the refinements at two temperatures (e.s.d.'s on the last significant digit are given in parentheses)*

The anisotropic temperature factors have the form:

$$T = \exp[-\frac{1}{4}(h^2 a^{*2} B_{11} + k^2 b^{*2} B_{22} + l^2 c^{*2} B_{33} + 2hka^* b^* B_{12} + 2hla^* c^* B_{13} + 2klb^* c^* B_{23})].$$

Isotropic refinement (4.2 K)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
C(1)	0.1637 (6)	0.3037 (19)	0.1650 (27)	0.69 (14)	0.1647 (6)	0.2970 (20)	0.1645 (31)	0.31 (20)
C(2)	0.0904 (6)	0.3851 (20)	0.3496 (20)	0.24 (12)	0.0928 (8)	0.3957 (25)	0.3535 (25)	1.44 (24)
O(1)	0.1245 (6)	0.1142 (20)	0.0	0.30 (15)	0.1217 (10)	0.1115 (21)	0.0	0.73 (24)
O(2)	0.2527 (6)	0.3872 (20)	0.1675 (18)	0.28 (16)	0.2527 (7)	0.3937 (22)	0.1713 (23)	0.34 (29)
D(1)	0.1273 (7)	0.5212 (21)	0.4909 (22)	1.04 (16)	0.1278 (8)	0.5253 (28)	0.4953 (23)	2.12 (25)
D(2)	0.0534 (7)	0.1503 (26)	0.4120 (22)	2.24 (24)	0.0537 (8)	0.1589 (23)	0.4158 (25)	1.98 (25)
D(3)	0.0285 (8)	0.5398 (26)	0.2808 (24)	2.19 (20)	0.0280 (9)	0.5289 (30)	0.2832 (25)	2.75 (25)
D(4)	0.3202 (7)	0.5488 (22)	0.3845 (24)	2.06 (19)	0.3190 (9)	0.5588 (25)	0.3858 (22)	1.59 (24)
	<i>R_I</i> = 9.53%	<i>R_y</i> = 13.56%	<i>R_w</i> = 13.90%	<i>R_{exp}</i> = 7.25%	<i>R_I</i> = 7.83%	<i>R_y</i> = 11.37%	<i>R_w</i> = 11.54%	<i>R_{exp}</i> = 5.2%

Anisotropic refinement (12.5K)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B₁₁</i>	<i>B₂₂</i>	<i>B₃₃</i>	<i>B₁₂</i>	<i>B₁₃</i>	<i>B₂₃</i>
C(1)	0.1645 (9)	0.3024 (22)	0.1637 (42)	1.65 (48)	0.91 (46)	-0.65 (65)	1.21 (40)	1.20 (60)	4.22 (61)
C(2)	0.0894 (8)	0.3992 (25)	0.3484 (38)	2.76 (62)	1.26 (35)	5.25 (77)	-0.81 (40)	2.10 (60)	1.32 (61)
O(1)	0.1238 (8)	0.1102 (23)	0.0	-0.55 (76)	1.44 (50)	2.57 (63)	-1.41 (61)	-0.30 (90)	3.43 (61)
O(2)	0.2542 (9)	0.3917 (31)	0.1649 (32)	1.65 (62)	1.04 (67)	-0.89 (75)	-0.40 (40)	-2.10 (60)	1.32 (62)
D(1)	0.1284 (8)	0.5164 (30)	0.4892 (34)	1.45 (73)	3.28 (71)	4.47 (74)	-0.61 (60)	-1.80 (50)	-0.62 (42)
D(2)	0.0532 (8)	0.1567 (25)	0.4108 (42)	3.03 (76)	2.81 (68)	2.08 (98)	-0.40 (40)	0.60 (90)	-0.35 (52)
D(3)	0.0235 (9)	0.5363 (38)	0.2747 (37)	2.41 (69)	5.86 (61)	3.43 (89)	1.41 (40)	1.80 (90)	1.50 (53)
D(4)	0.3222 (10)	0.5530 (30)	0.3824 (32)	1.69 (69)	1.75 (54)	3.17 (73)	1.41 (61)	0.30 (60)	1.85 (62)
	<i>R_I</i> = 5.48%	<i>R_y</i> = 10.24%	<i>R_w</i> = 10.20%	<i>R_{exp}</i> = 5.27%					

Structure refinement

We assumed the space group to be *Pna*2₁ (*Z* = 4) as determined by X-rays (Jones & Templeton, 1958); Nahringbauer's coordinates for C and O atoms with D atoms in calculated positions were used as starting values for the refinement. These parameters have been refined by full-matrix least-squares analysis of the powder profile [data up to 99° (2 θ) for the experiment at 4.2 K, and up to 91° (2 θ) for that at 12.5 K] following the method described by Rietveld (1967, 1969) and using the modification of the original computer program by Hewat (1973), and Thomas & Clarke (1978).

In this method, a Gaussian shape being assumed for the diffraction peaks *h*, with full width at half maximum given by $H_h^2 = u \tan^2 \theta_h + v \tan \theta_h + w$ (where θ_h is the Bragg angle and *u, v, w* are parameters to be refined), the intensity at each point is calculated by summing the contributions of all the Bragg peaks contributing to that particular point. The program minimizes the sum of the squares of the differences between the calculated intensities $|y_c|$ and observed counts $|y_o|$ for each 2 θ point in the pattern. Other parameters refined are the cell constants, the scale factor and four instrumental parameters (the 2 θ zero error, angular misplacement of the instrument, and the parameters *u, v, w*, defining the Gaussian shape of the peaks).

The agreement factor on these quantities is defined as $R_y = 100 \sum (|y_o| - k|y_c|) / \sum |y_o|$. Another residual usually quoted relates to the observed and calculated integrated intensities (Hewat, 1973; and for the approximations involved see Rietveld, 1969): $R_I = 100 \sum (|I_o| - k|I_c|) / \sum |I_o|$.

These values are reported in Table 2 together with the weighted discrepancy index $R_w = 100 \sum w(|y_o| - k|y_c|)^2 / \sum w|y_o|^2$ (the weight w is determined from counting statistics) and an 'expected' agreement factor based on the number N of observations (y_o) and the number of parameters to be refined P : $R_{\text{exp}} = 100 [(N - P) / \sum w|y_o|^2]^{1/2}$.

However, it must be pointed out that no R factor from this profile-refinement procedure can be directly compared with those from single-crystal work. Therefore, the results of these two determinations may be used to see the differences that can be expected from repeated measurements.

The neutron-scattering lengths used in the refinement were 0.663×10^{-14} m for C, 0.575×10^{-14} m for O, and 0.667×10^{-14} m for D (*International Tables for X-ray Crystallography*, 1974).

The refinement of the data at 4.2 K converged quickly to $R_y = 13.56\%$ and $R_I = 9.53\%$, close to the expected value of $R_{\text{exp}} = 7.25\%$. The values of the final positional parameters, isotropic temperature factors and agreement factors are given in Table 2. The data collected at 12.5 K were refined with isotropic temperature factors to $R_I = 7.83\%$. In view of the low values of R_I and R_{exp} we decided to carry out a refinement with anisotropic temperature factors for all the atoms; the final R_I was 5.48%.

This further anisotropic refinement gave unreliable non-positive-definite values for three B_{ii} 's (see Table 2); nevertheless, the positional coordinates obtained by the isotropic and the anisotropic refinement are not significantly different.

The observed and calculated powder profile for CD_3COOD at 12.5 K is shown in Fig. 1.

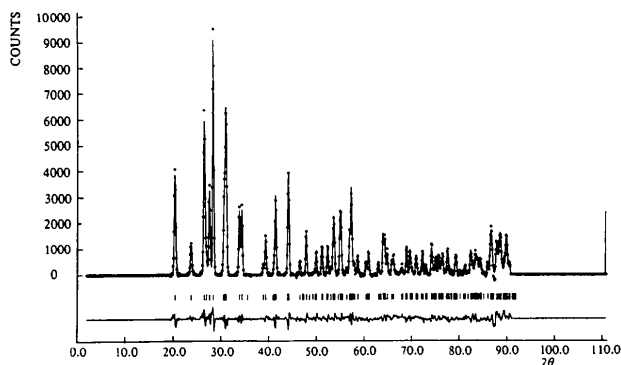


Fig. 1. The observed (•) and calculated (—) powder profile for CD_3COOD at 12.5 K. The difference profile and reflection positions are also shown.

Discussion

An overall view of two adjacent hydrogen-bonded molecules is given in Fig. 2, while the relevant bond distances and angles at the two different temperatures are given in Table 3 together with the values obtained by single-crystal neutron diffraction (Jönsson, 1971) at 133 K and the X-ray data at 83 K (Nahringbauer, 1970) for comparison.

The geometry of the molecule compares well with that obtained by the single-crystal diffraction studies although the bond lengths are less accurate in the powder case. The C—O distances of 1.23 (2) and 1.32 (2) Å are consistent at 4.2 and 12.5 K and compare well with the values of 1.229 (5) and 1.319 (6) Å at 83 K (X-ray values) and 1.206 (8) and 1.321 (7) Å at 133 K (neutron values). In fact, the molecular geometry does not significantly change with temperature, as is also shown by the constant C—C bond length [mean 1.49 (2) Å] and the comparison of

Table 3. Bond lengths (Å) and angles (°) for CD_3COOD at various temperatures

The e.s.d.'s on the last significant digit are given in parentheses. For comparison some values of X-ray* and neutron† single-crystal studies are given.

	4.2 K	12.5 K	83 K*	133 K†
C(1)—C(2)	1.48 (2)	1.50 (3)	1.478 (6)	1.501 (7)
C(1)—O(1)	1.32 (2)	1.32 (2)	1.319 (6)	1.321 (7)
C(1)—O(2)	1.23 (2)	1.23 (3)	1.229 (5)	1.206 (8)
C(2)—D(1)	1.09 (2)	1.06 (2)		1.01 (2)
C(2)—D(2)	1.11 (2)	1.12 (3)		1.08 (2)
C(2)—D(3)	1.10 (2)	1.08 (2)		1.05 (2)
O(1')—D(4)	1.02 (2)	1.04 (2)		1.05 (2)
O(2)—D(4)	1.67 (2)	1.64 (2)		1.64 (1)
O(2)—O(2)	2.24 (1)	2.27 (2)		
O(2)—O(1')	2.68 (1)	2.66 (2)		2.631 (8)
C(1)—C(2)—D(1)	110.6 (6)	112.0 (7)		
C(1)—C(2)—D(2)	110.5 (8)	108.5 (8)		
C(1)—C(2)—D(3)	110.5 (8)	109.0 (9)		
C(2)—C(1)—O(1)	112.7 (9)	113.5 (9)	113.8 (4)	
C(2)—C(1)—O(2)	124.6 (8)	124.9 (7)	124.2 (6)	
D(1)—C(1)—O(2)	122.6 (8)	120.6 (9)	122.0 (6)	
D(2)—D(4)—O(1')	165.6 (9)	169.8 (9)		

* X-ray study (Nahringbauer, 1970).

† Neutron study (Jönsson, 1971).

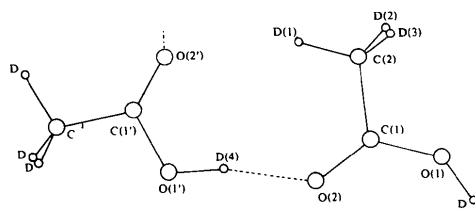


Fig. 2. Perspective view of two adjacent hydrogen-bonded molecules. The two molecules are related by the transformation $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$.

values of the C—C—O bond angles at various temperatures [112.7 (9) and 124.6 (8)° at 4.2 K; 113.5 (9) and 124.9 (7)° at 133 K; 113.8 and 124.2° at 83 K].

The substitution of H by D is expected to produce an increase in the distance between two adjacent hydrogen-bonded O atoms (Rundle, 1964; Hamilton & Ibers, 1968; Olovsson & Jönsson, 1976); we found an O...O distance of 2.76 (1) Å, compared with a value of 2.631 (8) Å obtained in the single-crystal neutron study of the undeuterated compound. This difference is in the expected range [for example, in α -oxalic acid dihydrate (Delaplane & Ibers, 1969) the lengthening due to the isotope effect is in the range 0.017 (5)–0.022 (5) Å] and does not change, within experimental accuracy, with temperature. The average value for the C—D distance is 1.10 (2) Å.

It may be interesting to note that the non-bonded distance between the carbonyl O and the D of the methyl group of the adjacent hydrogen-bonded molecule is 2.37 (1) Å.

This value is 0.23 Å shorter than the value of 2.6 Å for the sum of the van der Waals radii for H and O (Pauling, 1960). The hydrogen-bonded molecules form infinite chains packed in layers parallel to (100), and the interactions between the chains are due to van der Waals forces.

Conclusion

With this determination we have confirmed the suitability of the powder profile refinement technique for the refinement of molecular structures, acting as a technique complementary to single-crystal studies.

Further experience in the use of this technique on molecular crystals will help in assessing the range of applicability of the method; for example, the application of the constrained refinement (Pawley, Mackenzie & Dietrich, 1977) seems particularly promising for the study of complex crystals.

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