

Neutron Powder Diffraction Analysis of Hydrogen-Bonded Solids. II. Structural Study of Formic Acid at 4.5 K

BY A. ALBINATI

Istituto di Chimica del Politecnico, Piazza L. da Vinci 32, 20133 Milano, Italy

AND K. D. ROUSE AND M. W. THOMAS

Materials Physics Division, AERE Harwell, Didcot, Oxfordshire OX11 0RA, England

(Received 28 October 1977; accepted 26 November 1977)

The structure of deuterated formic acid has been refined using neutron powder diffraction data collected at $4.5 (\pm 1)$ K, with isotropic and anisotropic temperature factors. The resulting geometry is compared with that from a previous X-ray determination [Holtzberg, Post & Fankuchen, *Acta Cryst.* (1953), 6, 127–130]. In the present refinement the C–O bond lengths are different [1.36 (2), 1.23 (2) Å] and are in agreement with those of other carboxylic acids. The presence of deuterium causes an increase in the O...O bond length.

Introduction

The structure of formic acid has been extensively investigated both theoretically and experimentally. In the gas phase the geometry of the monomer (Karle & Brockway, 1944; Almennigen, Bastiansen & Motzfeld, 1969) has been determined by electron diffraction, as has that of the dimer (Almennigen, Bastiansen & Motzfeld, 1970); in the solid state it has been determined by X-ray diffraction (Holtzberg, Post & Fankuchen, 1953). The nature of the hydrogen bond has been studied by theoretical calculations of various degrees of sophistication (see, for example, Bosi, Zerbi & Clementi, 1977).

Because of the interest of this simple compound, during our studies of molecular solids by neutron powder diffraction (Albinati, Rouse & Thomas, 1978) we have refined the structure of deuterated formic acid at low temperature (4.5 ± 1 K) and have determined the geometry of the molecule with an accuracy greater than that obtained previously by X-ray diffraction (Holtzberg *et al.*, 1953).

Data collection

The neutron data have been collected with the PANDA diffractometer on the PLUTO reactor at AERE Harwell using an array of three BF₃ counters (with an angular separation in the 2θ plane of $5 \pm 0.02^\circ$) up to $2\theta = 97^\circ$, in steps of 0.1° .

The sample (approximately 3 g of formic acid with a deuterium content >99%) was frozen, ground and

packed in a vanadium can and cooled in a cryostat to liquid He temperature (4.5 ± 1 K) in order to minimize the thermal motion. The wavelength used ($\lambda = 1.4340$ Å) was obtained by reflection from the (511) plane of a Ge monochromator with a take-off angle of 82.5° ; the accurate value for λ was determined using Ni powder for calibration. The counting time for each counter position was determined by monitoring the incident beam with a fission counter. The intensities from the three counters were averaged but no absorption or extinction correction was applied.

Structure refinement

The space group, the positional parameters for the C and O atoms, and the cell constants were assumed to be those of Holtzberg *et al.* (1953); the two D atoms were placed in calculated positions.

The lattice parameters, fractional coordinates and both isotropic and anisotropic temperature factors were refined by least squares using the profile-analysis method of Rietveld (1969), as modified by Hewat (1973). The scale factor, the cell constants and four instrumental parameters (the instrumental zero point and the parameters u, v, w defining the Gaussian f.w.h.m.) were also refined during each cycle.

The refined cell parameters and other crystallographic data are given in Table 1.

The quantities minimized by the Rietveld technique are the differences between the observed (y_o) and calculated (y_c) intensities for each 2θ point of the profile. It is therefore possible to avoid the necessity of deconvoluting overlapping reflections using the profile up to high 2θ values.

The scattering lengths for C (0.663×10^{-14} m), O (0.575×10^{-14} m) and D (0.667×10^{-14} m) were

Table 1. *Crystal data and experimental details for DCOOD at 4.5 (± 1) K*

<i>a</i> (Å)	10.2361 (8)
<i>b</i> (Å)	3.5203 (2)
<i>c</i> (Å)	5.3572 (4)
<i>V</i> (Å ³)	193.04
Space group	<i>Pna2</i> ₁
<i>Z</i>	4
Deuteration (%)	99
Wavelength (Å)	1.4340
Monochromator	Ge (511)
Take-off angle ($2\theta^\circ$)	82.5
Angular range ($2\theta^\circ$)	16–97
Number of parameters refined	
isotropic	28
anisotropic	53

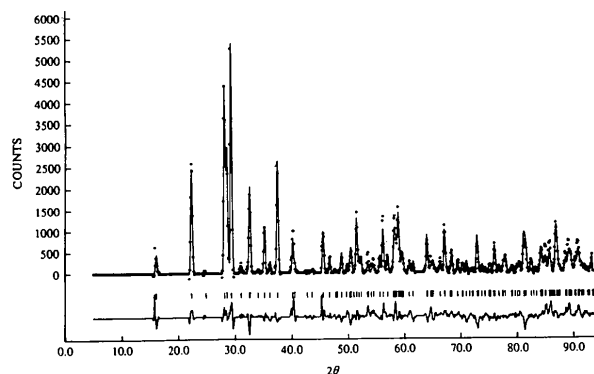


Fig. 1. The observed (•) and calculated (—) powder profile for DCOOD at 4.5 K. Reflection positions have been marked and the difference profile is also shown.

Table 2. *Positional parameters, thermal parameters (Å²) and agreement factors*

The anisotropic temperature factors have the form:

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

The agreement factors are defined as: $R_y = 100 \Sigma(|y_o| - k|y_c|) / \Sigma|y_o|$; $R_l = 100 \Sigma(|I_o| - k|I_c|) / \Sigma I_o$; $R_{\text{exp}} = 100[(N-P) / \Sigma w|y_o|^2]$; where I_o , I_c are intensities for each reflection; y_o , y_c are intensities for each 2θ point; N is the number of observations and P the number of parameters.

Isotropic refinement

	<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)	0.1568 (9)	0.3183 (28)	0.1700 (30)	0.56 (10)	D(1)	0.1041 (8)	0.4280 (29)	0.3279 (30)	1.16 (18)
O(1)	0.0759 (9)	0.1439 (37)	0.00	0.82 (15)	D(2)	0.3593 (9)	0.5436 (29)	0.3661 (34)	1.88 (20)
O(2)	0.2719 (10)	0.3512 (27)	0.1506 (30)	0.55 (10)					

$$R_x = 10.20\% \quad R_y = 18.36\% \quad R_{\text{exp}} = 7.82\%$$

Anisotropic refinement

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
C(1)	0.1554 (10)	0.3302 (28)	0.1778 (27)	3.35 (40)	1.14 (45)	1.15 (43)	0.86 (14)	0.66 (44)	-0.07 (25)
O(1)	0.0782 (12)	0.1523 (41)	0.00	2.09 (80)	1.00 (40)	1.87 (72)	0.72 (90)	0.88 (57)	2.11 (75)
O(2)	0.2742 (11)	0.3461 (24)	0.1433 (30)	3.35 (42)	1.00 (38)	-0.72 (56)	-1.01 (24)	0.44 (22)	-0.90 (30)
D(1)	0.1013 (9)	0.4239 (35)	0.3235 (30)	1.68 (42)	3.67 (59)	1.15 (72)	0.43 (14)	2.85 (46)	-0.15 (48)
D(2)	0.3604 (12)	0.5389 (23)	0.3612 (33)	4.02 (42)	0.40 (49)	1.15 (58)	0.43 (29)	-1.75 (44)	-0.60 (37)

$$R_x = 7.94\% \quad R_y = 14.05\% \quad R_{\text{exp}} = 7.64\%$$

taken from *International Tables for X-ray Crystallography* (1974).

The refinement converged smoothly to final agreement factors on the intensities of 10.2% with isotropic temperature factors and 7.9% with anisotropic B_{ij} 's.

The final atomic parameters and agreement factors are given in Table 2; the final observed and calculated profile is drawn in Fig. 1.

Discussion

An overall view of two hydrogen-bonded molecules is given in Fig. 2; the most relevant bond lengths and angles are in Table 3.

There is no significant difference (at the 3σ level) between the isotropically and anisotropically refined coordinates.

The overall geometry is in agreement with that found by X-rays but a few significant differences do exist. The two C—O distances are now significantly different: 1.36 (2) and 1.23 (2) Å, compared with 1.26 (3) and 1.23 (3) Å in the earlier determination (Holtzberg *et al.*, 1953). These values found at 4.5 K can be compared with those given by gas-phase electron diffraction [1.362 (3) and 1.218 (3) Å for the monomer, and 1.333 and 1.221 Å for the deuterated dimer (Almenningen *et al.*, 1969, 1970)], and also with those found in other carboxylic acids; for example, acetic acid 1.321 (7) and 1.206 (8) Å (Jönsson, 1971) from a single-crystal study, and 1.32 (2) and 1.23 (2) Å from powder refinement (Albinati *et al.*, 1978). Average values of 1.319 (3) and 1.202 (3) Å have been found in the addition compound formic acid—formamide (Nähringbauer & Larsson, 1968).

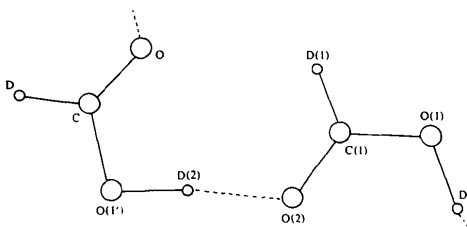


Fig. 2. Perspective view of two adjacent hydrogen-bonded molecules. The two molecules are related by the symmetry operation $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$.

Table 3. Bond lengths (Å) and angles (°)

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

C(1)—O(1)	1.36 (2)	O(1)—C(1)—O(2)	118.6 (8)
C(1)—O(2)	1.23 (2)	O(1)—C(1)—D(1)	111.7 (9)
C(1)—D(1)	1.02 (2)	O(2)—C(1)—D(1)	129.7 (9)
O(1)—O(2)	2.25 (1)	*O(1')—D(2)—O(2)	171.5 (9)
*O(1')—D(2)	1.04 (2)		
*O(1')—O(2)	2.65 (1)		
O(2)—D(2)	1.61 (2)		

* O(1') is related to O(1) by $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$.

The distance between the two O atoms of hydrogen-bonded molecules is 2.65 (1) Å, comparable with the 2.68 (1) Å found in deuterated acetic acid (Albinati *et al.*, 1978), but longer than the X-ray value of 2.58 (3) Å. Though the precision of the earlier value was low, it seems that in this case the deuterium gives rise to an appreciable 'isotope effect' at low temperature. It may be interesting to note a distortion of the two D—C—O bond angles [111.7 (9), 129.7 (9)°] as compared with the corresponding values in the formic acid-formamide adduct (average values 114.5 and 120.5°; Nahringsbauer & Larsson, 1968).

The formic acid molecules form infinite hydrogen-bonded chains tightly packed in layers, by van der Waals forces; a short non-bonding distance of 2.60 (2) Å is found between the D and the carboxylic O of the adjacent hydrogen-bonded molecule; all other distances are in the expected range.

The values of the refined isotropic thermal parameters (see Table 2) seem reasonable, but the refinement with anisotropic temperature factors caused four of the B_{ii} 's to become slightly negative.

This feature seems to occur with molecular crystals [see, for example, Ahtee, Ahtee, Glazer & Hewat (1976) and Albinati *et al.* (1978)] where the relative magnitude of the thermal ellipsoids may still be correct but not their absolute magnitudes. It seems that the unconstrained profile refinement is capable of giving reliable information on structure but not on molecular vibrations.

More work is still needed to explore fully the limits of the profile-analysis technique, and the possible improvements of the method to handle more complicated cases.

The authors wish to thank Dr B. T. M. Willis for helpful discussions and encouragement. One of us (AA) is grateful to the UKAEA for support at Harwell.

References

- AHTEE, A., AHTEE, M., GLAZER, A. M. & HEWAT, A. W. (1976). *Acta Cryst.* B32, 3243–3246.
- ALBINATI, A., ROUSE, K. D. & THOMAS, M. W. (1978). *Acta Cryst.* B34, 2184–2187.
- ALMENNINGEN, A., BASTIANSEN, O. & MOTZFELDT, T. (1969). *Acta Chem. Scand.* 23, 2848–2864.
- ALMENNINGEN, A., BASTIANSEN, O. & MOTZFELDT, T. (1970). *Acta Chem. Scand.* 24, 747–748.
- BOSI, P., ZERBI, G. & CLEMENTI, E. (1977). *J. Chem. Phys.* 66, 3376–3386.
- HEWAT, A. W. (1973). Report RRL/73/187. AERE Harwell, Oxfordshire.
- HOLTZBERG, F., POST, B. & FANKUCHEN, I. (1953). *Acta Cryst.* 6, 127–130.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JÖNSSON, P. G. (1971). *Acta Cryst.* B27, 893–898.
- KARLE, J. & BROCKWAY, L. O. (1944). *J. Am. Chem. Soc.* 66, 574–584.
- NAHRINGBAUER, I. & LARSSON, G. (1968). *Ark. Kemi*, 30, 127–130.
- RIETVELD, H. M. (1969). *J. Appl. Cryst.* 2, 65–71.