

Oxalic Acid Dihydrate – an Accurate Low-Temperature Structural Study using High-Resolution Neutron Powder Diffraction

BY ALICE LEHMANN AND PETER LUGER

Institut für Kristallographie, Freie Universität Berlin, D-14195 Berlin 33, Takustrasse 6, Germany

CHRISTIAN W. LEHMANN*

School of Chemistry and Applied Chemistry, University of Wales Cardiff, PO Box 912, Cardiff CF1 3TB, Wales

AND RICHARD M. IBBERSON

ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, England

(Received 16 June 1993; accepted 21 October 1993)

Abstract

Deuterated oxalic acid dihydrate, $C_2D_2O_4 \cdot 2D_2O$, $M_r = 132.10$, monoclinic, $P2_1/n$, $Z = 2$. At 100 K, $a = 6.13338$ (6), $b = 3.50018$ (1), $c = 11.98334$ (3) Å, $\beta = 106.0599$ (2)°, $V = 247.218$ Å³, $D_x = 1.694$ g cm⁻³, $\chi^2 = 1.93$. At 15 K, $a = 6.13661$ (4), $b = 3.47501$ (1), $c = 11.97044$ (2) Å, $\beta = 105.9778$ (1)°, $V = 245.406$ Å³, $D_x = 1.706$ g cm⁻³, $\chi^2 = 2.59$. High-resolution neutron powder diffraction data have been recorded at temperatures of 15 and 100 K on fully deuterated oxalic acid dihydrate, which has been widely used as a crystallographic standard, in order to assess in particular the potential use of neutron powder diffraction data for charge-density studies. The accuracy and precision of the structural parameters obtained in the present powder study are found to be comparable to neutron and X-ray single-crystal results. The technique is therefore shown to have a useful role in providing reliable high-quality structural data in cases where single crystals are difficult to obtain.

Introduction

In structural investigations of small molecules, charge-density studies are becoming increasingly important in allowing characterization of molecular properties beyond the simple determination of bond lengths and angles. For example, the distribution of atomic charges and dipole moments may be described.

However, a major problem for such an analysis is the deconvolution of electron density and thermal motion. Insufficient accounting of the 'thermal

smearing' of electron density introduces systematic errors to atomic charges and properties calculated therefrom. This holds particularly for H atoms because their atomic parameters are difficult to determine with X-rays. A neutron diffraction experiment yields considerably more precise atomic parameters for H atoms, but also for heavier atoms (Coppens *et al.*, 1979).

For these reasons, the most precise charge-density studies reported utilize complementary neutron and high-resolution X-ray single-crystal diffraction experiments (Klooster, Swaminathan, Nanni & Craven, 1992). The major drawbacks of such neutron experiments are their time-consuming nature and the typical requirement for large single crystals that are frequently difficult to obtain. The use of neutron powder diffraction negates these difficulties. Unfortunately, the accuracy of the structural parameters thereby obtained has in the past been to some extent sacrificed because of the inherent peak overlap of a powder profile. However, the advent of a new generation of powder diffractometers at pulsed neutron sources, with resolution $\Delta d/d$ better than 10^{-3} , permits the recording of extremely impressive powder diffraction patterns with a high information content. Indeed high-resolution powder diffraction at a pulsed source has been applied successfully to a number of small organic compounds (see, for example, David, Ibberson, Jeffrey & Rubble, 1992; David & Ibberson, 1992; Ibberson, David & Prager, 1992). The structural results obtained in these studies are qualitatively comparable to equivalent single-crystal studies.

In order to test whether such powder diffraction data are of sufficient quality for charge-density studies, oxalic acid dihydrate has been chosen as a test sample. The crystal structure is well known

* Permanent address: Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England.

(Coppens & Sabine, 1969; Coppens, Sabine, Delaplane & Ibers, 1969; Delaplane & Ibers, 1969; Sabine, Cox & Craven, 1969). Furthermore, the International Union of Crystallography utilized oxalic acid dihydrate as one of the crystallographic standard samples in order to study the reproducibility of experimentally determined electron-density maps. Hence, a number of single-crystal experiments around 100 K have been performed (Coppens *et al.*, 1984) to enable the comparison of X-ray and neutron radiation experiments.

In the present study, powder diffraction data of deuterated oxalic acid dihydrate at 100 K were measured using a High-Resolution Powder Diffractometer (Ibberson, David & Knight, 1992) at the pulsed neutron spallation source ISIS, Rutherford Appleton Laboratory, England, and the results are compared with those from a 100 K single-crystal neutron experiment (Feld, 1980), namely the data set D81. Recent developments in routinely collecting X-ray single-crystal data sets at temperatures as low as 15 K (Hendriksen, Larsen & Rasmussen, 1986; Luger *et al.*, 1992) stimulated a further powder measurement at this temperature. In particular, the influence of H-atom parameters to charge-density studies at low temperatures is of interest and powder data at 15 K were recorded in order to determine accurate positions and especially anisotropic displacement parameters for the H atoms. A single-crystal data set at 15 K (Zobel, Luger, Dreissig & Koritsanszky, 1992) measured using laboratory X-rays was used for comparison.*

Experimental

The high incoherent scattering cross-section of hydrogen for neutrons makes it unsuitable for the most accurate studies and where possible, deuteration is preferable. Data collection was thus performed on fully deuterated oxalic acid dihydrate ($C_2D_2O_4 \cdot 2D_2O$, $M_r = 132.10$). To achieve a high degree of deuteration, the sample was recrystallized seven times from D_2O (99.8%, Merck). A crystalline powder with a small crystallite size was obtained from the hot solution by annealing very quickly with ice-cooled water whilst stirring vigorously. The sample was subsequently dried over $CaCl_2$.

Diffraction data were recorded at 15 and 100 K using the time-of-flight powder diffractometer HRPD at ISIS (Ibberson, David & Knight, 1992). A 15 mm-diameter cylindrical vanadium sample can

* The numbered intensity of each measured point on the profile has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71641 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0311]

Table 1. *Monoclinic cell constants, space group $P2_1/n$, at 15 and 100 K obtained from high-resolution powder and single-crystal experiments (e.s.d.'s in parentheses)*

	15 K		100 K	
	HRPD*	X-ray single crystal†	HRPD*	Neutron single crystal‡
<i>a</i> (Å)	6.13661 (4)	6.093 (2)	6.13338 (6)	6.101 (2)
<i>b</i> (Å)	3.47501 (1)	3.469 (1)	3.50018 (1)	3.498 (3)
<i>c</i> (Å)	11.97044 (2)	11.926 (2)	11.98334 (3)	11.985 (9)
β (°)	105.9778 (1)	105.69 (2)	106.0599 (2)	105.68 (4)

* HRPD = high-resolution neutron powder diffraction.

† Zobel, Luger, Dreissig & Koritsanszky (1992).

‡ Feld (1980).

was used loaded into a helium gas-flow cryostat. Data at both temperatures were recorded over the time-of-flight range 20–120 ms, corresponding to the *d*-spacing range 0.414–2.486 Å with a resolution of $8 \times 10^{-4} \Delta d/d$. The beam aperture was 15 mm in the horizontal and 20 mm in the vertical plane. The measuring times were 22.75 (445.9 μA h proton beam current) and 22.61 h (354.1 μA h proton beam current) for the 15 and 100 K data, respectively.

Data were normalized to the spectral distribution of the incident flux using a monitor spectrum recorded simultaneously with the diffraction data. A previously recorded vanadium spectrum was used to correct for detector efficiency effects. An empirical correction was applied for absorption of the vanadium can and cryostat tails. The resulting data sets for refinement included 1286 unique reflections for the 15 K data and 1296 unique reflections for the 100 K data in the time-of-flight range 28–110 ms (0.580–2.279 Å *d* spacing).

Results and discussion

Full profile refinements were performed using the Rietveld method (Rietveld, 1969), modified for the time-of-flight technique (David, Ibberson & Matthewman, 1992). For both data sets, the starting structural model was taken from the X-ray (15 K; Zobel, Luger, Dreissig & Koritsanszky, 1992) and neutron (100 K; Feld, 1980) single-crystal experiment. The cell dimensions determined in the current experiment are shown in Table 1. The data sets were refined over the time-of-flight range 28–110 ms using the standard peak-shape model of a Voigt function convoluted with a double exponential decay.

The regions 82.4–82.75 (15 K) and 82.4–83 ms (100 K) were excluded from the refinement as there was some evidence for severe extinction effects – these regions include the reflections $\bar{1}07$, $\bar{3}10$ and 115. Anisotropic extinction has been reported to be severe for oxalic acid dihydrate in previous single-crystal studies (Coppens & Sabine, 1969). Refinement of all parameters (scale factor, background parameters,

cell constants, peak-shape parameters, atomic positions, displacement and absorption parameters) gave a final χ^2 of 2.59 for 15 K and 1.93 for 100 K. The total number of refined parameters was 84 for both data sets.

The resulting agreement between the observed and calculated profiles for both data sets is shown in Fig. 1, with final positional and displacement parameters given in Table 2. Further analysis shows that the standard deviations obtained from the 100 K powder data set for positional and anisotropic displacement parameters are only up to five (on average three) times larger than those from the 100 K neutron single-crystal experiment.

In Table 3, the ratio of positional and anisotropic displacement parameters for the 100 K powder and the 100 K single-crystal data set is given. Taking the average of all ratios, a value of 1.07 (3) is obtained. However, the r.m.s. deviation* equals 0.17 and is approximately six times larger than the mean e.s.d. The agreement between the positional parameters is very good, except the y/y ratio for O1/H1 (0.82). This results in a much shorter bond length O1—D1 (Table 4) for the powder data [1.039 (1) Å] than for

$$* \text{ R.m.s. deviation} = [\sum(x - \bar{x})^2 / (n - 1)]^{1/2}.$$

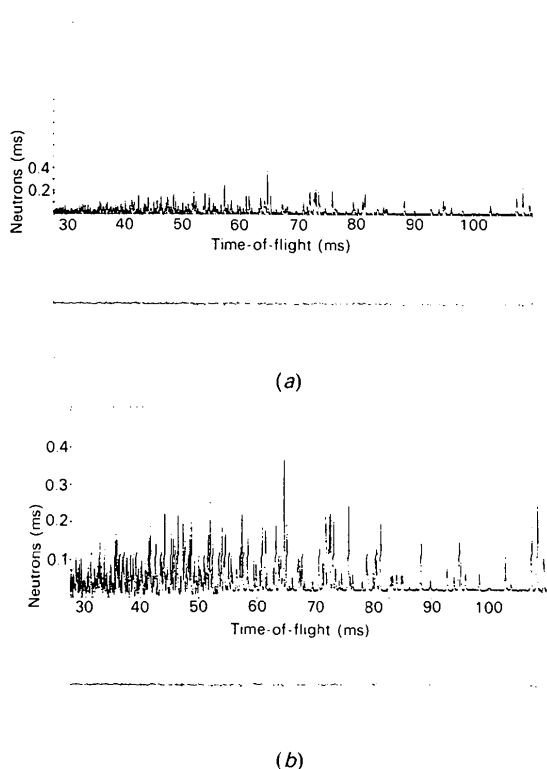


Fig. 1. Observed (dots), calculated (line) and difference (observed - calculated/e.s.d.'s) profiles of oxalic acid dihydrate (a) at 100 K and (b) at 15 K.

Table 2. Atomic positions and anisotropic displacement parameters (\AA^2) for the powder data sets (upper line 15 K, lower line 100 K; e.s.d.'s in parentheses)

The anisotropic displacement parameters are given by the expression:

$$T = \exp\{-2\pi^2[U_{11}(ha^*)^2 + U_{22}(kb^*)^2 + U_{33}(lc^*)^2 + 2(U_{12}hka^*b^* \times \cos \gamma^* + U_{13}hla^*c^* \cos \beta^* + U_{23}klb^*c^* \cos \alpha^*)]\}.$$

	x			y			z		
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{11}	U_{22}	U_{33}
C	-0.0434 (1)			0.0592 (2)			0.05217 (5)		
	0.0076 (4) 0.0018 (3)		0.0012 (3)	0.0022 (2)	0.0027 (2)	-0.0001 (2)			
	-0.0438 (1)			0.0574 (2)			0.05208 (6)		
	0.0143 (5) 0.0083 (4)		0.0068 (4)	0.0008 (3)	0.0048 (3)	-0.0003 (3)			
O1	0.0843 (1)			-0.0562 (2)			0.14982 (6)		
	0.0076 (4) 0.0079 (4)		0.0017 (4)	0.0019 (3)	0.0016 (3)	0.0001 (3)			
	0.0839 (1)			-0.0569 (3)			0.14940 (7)		
	0.0168 (6) 0.0178 (5)		0.0063 (4)	0.0035 (4)	0.0051 (4)	-0.0007 (4)			
O2	-0.2187 (1)			0.2453 (2)			0.03643 (6)		
	0.0034 (4) 0.0058 (4)		0.0034 (3)	0.0000 (3)	0.0017 (3)	-0.0007 (3)			
	-0.2194 (1)			0.2414 (2)			0.03622 (7)		
	0.0123 (5) 0.0163 (5)		0.0074 (4)	0.0035 (4)	0.0043 (3)	-0.0003 (3)			
O3	-0.0490 (2)			0.1354 (2)			0.32050 (7)		
	0.0074 (4) 0.0058 (4)		0.0023 (4)	-0.0029 (3)	0.0014 (4)	-0.0004 (3)			
	-0.0482 (2)			0.1322 (3)			0.32053 (8)		
	0.0129 (5) 0.0157 (5)		0.0081 (4)	-0.0043 (4)	0.0034 (4)	0.0001 (4)			
D1	0.0247 (1)			0.0216 (2)			0.22041 (7)		
	0.0271 (5) 0.0194 (5)		0.0178 (4)	0.0001 (3)	0.0099 (4)	-0.0000 (3)			
	0.0246 (2)			0.0177 (3)			0.21972 (8)		
	0.0336 (6) 0.0301 (6)		0.0227 (5)	0.0011 (4)	0.0096 (5)	0.0002 (4)			
D2	0.0745 (2)			0.1991 (2)			0.38656 (7)		
	0.0209 (5) 0.0237 (5)		0.0150 (4)	0.0016 (4)	0.0030 (4)	-0.0020 (3)			
	0.0741 (2)			0.1975 (3)			0.38616 (8)		
	0.0293 (6) 0.0303 (6)		0.0217 (5)	0.0003 (4)	0.0042 (5)	-0.0028 (4)			
D3	-0.1437 (1)			-0.0426 (3)			0.34872 (7)		
	0.0235 (5) 0.0246 (5)		0.0215 (5)	-0.0051 (4)	0.0121 (4)	-0.0007 (4)			
	-0.1428 (2)			-0.0449 (3)			0.34836 (8)		
	0.0333 (6) 0.0340 (6)		0.0300 (6)	-0.0080 (5)	0.0141 (4)	-0.0009 (4)			

the single-crystal data [O1—H1 1.0757 (7) Å]. The resulting bond angles (Table 5) differ only slightly.

The agreement for the anisotropic displacement parameters is less pronounced (Table 3), especially the U_{11} components for all the atoms which deviate considerably. To display the difference between the displacement parameters from the powder and the single-crystal data at 100 K, we used the program PEANUT (Hauser & Bürgi, 1991). This program has been written to display differences between mean-square-displacement (m.s.d.) tensors (Hummel, Raselli & Bürgi, 1990; Hummel, Hauser & Bürgi, 1990). The well known constant probability ellipsoids (ORTEP; Johnson, 1971) are not suitable to display differences between m.s.d.'s. Although individual m.s.d.'s are positive and definite and hence give a closed surface of constant probability, this does not hold for the difference between m.s.d.'s. By calculating the m.s.d. differences in all directions, a closed 'peanut'-shaped surface is obtained. To obtain

Table 3. Ratio between the atomic coordinates and the U_{ii} components for the 100 K powder and single-crystal data set (e.s.d.'s in parentheses)

	x/x	y/y	z/z	U_{11}/U_{11}	U_{22}/U_{22}	U_{33}/U_{33}
C	0.975 (3)	0.975 (4)	1.002 (1)	1.70 (6)	0.93 (4)	1.03 (6)
O1	0.988 (2)	1.018 (5)	0.9955 (5)	1.47 (5)	1.10 (3)	0.97 (6)
O2	0.9914 (7)	0.995 (1)	0.999 (2)	1.16 (5)	1.06 (3)	0.91 (5)
O3	1.006 (4)	1.006 (2)	0.9973 (3)	1.25 (5)	1.02 (4)	1.02 (6)
D1/H1	1.049 (9)	0.82 (2)	0.9862 (4)	1.53 (3)	1.13 (2)	1.29 (3)
D2/H2	0.945 (3)	1.004 (2)	0.9969 (3)	1.27 (3)	0.89 (2)	1.08 (3)
D3/H3	1.006 (2)	0.984 (9)	0.9942 (3)	1.27 (3)	1.05 (2)	1.00 (2)

Table 4. Bond lengths (Å) at 15 and 100 K, comparing the results from powder and single-crystal experiments (e.s.d.'s in parentheses)

	15 K		100 K	
	Powder	Single	Powder	Single
C—C	1.542 (1)	1.5425 (4)	1.543 (1)	1.5512 (3)
C—O1	1.2794 (9)	1.2884 (4)	1.276 (1)	1.2883 (3)
C—O2	1.225 (1)	1.2239 (5)	1.224 (1)	1.2273 (3)
O1—D1/H1	1.045 (1)	0.97 (3)	1.039 (1)	1.0757 (7)
O3—D2/H2	0.959 (1)	0.85 (1)	0.953 (1)	0.9712 (6)
O3—D3/H3	0.971 (1)	0.91 (1)	0.969 (2)	0.9697 (9)

Table 5. Bond angles (°) at 15 and 100 K obtained from powder and single-crystal experiments (e.s.d.'s in parentheses)

	15 K		100 K	
	Powder	Single	Powder	Single
O1—C—O2	126.70 (7)	127.00 (3)	126.80 (9)	126.80 (3)
O1—C—C	113.30 (6)	112.60 (3)	113.20 (7)	112.50 (2)
O2—C—C	120.00 (6)	120.40 (2)	120.00 (7)	120.70 (2)
D1/H1—O1—C	113.30 (8)	113 (1)	113.50 (9)	113.20 (4)
D2/H2—O3—D3/H3	105.9 (1)	103 (1)	106.2 (1)	106.20 (7)

comparable features to ellipsoids with constant probability surfaces, the r.m.s. displacements are calculated instead. In Fig. 2, the differences of powder r.m.s. displacements minus single-crystal r.m.s. displacements is shown.

The size of the lobes indicates the magnitude of the difference (scale factor 6.15), while the orientation describes the direction. The preferred orientation of the difference displacement parameters,

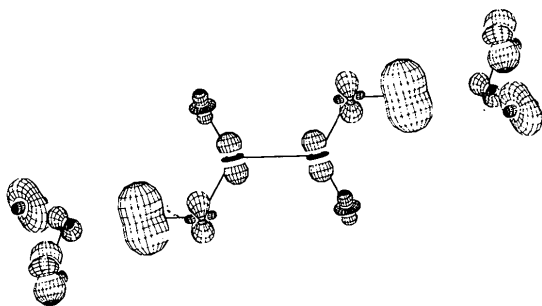


Fig. 2. Difference r.m.s. displacements (powder - single crystal) at 100 K. The shaded lobes indicate negative differences, while the non-shaded lobes indicate positive differences. Type: difference surface; r.m.s. deviation scale: 6.15; zoom: 1.30.

especially for the oxalic acid molecule itself, results from the already mentioned disagreement of the U_{11} components. Since the same effect is observed for the 15 K data, a systematic error such as the effect of anisotropic extinction cannot be excluded. However, the mean ratio of the displacement parameters is given by $U_{ii,powder}/U_{ii,single} = 1.15 (4)$, $i = 1-3$.

Comparison with the results of Coppens *et al.* (1984) shows that this ratio is slightly larger than the ratios of the reported neutron single-crystal experiments, where the ratios range from 1.03 to 1.08. With respect to the ratios of X-ray and neutron single-crystal experiments (1.03-1.33), the powder data are in very good agreement. Taking only the U_{22} and U_{33} components into account, a ratio of $U_{ii,powder}/U_{ii,single} = 1.04 (4)$, $i = 2, 3$, is calculated which is in excellent agreement.

Summary

Returning to the original question, the present study shows that neutron powder diffraction experiments offer a good alternative to neutron single-crystal experiments in order to obtain both accurate and precise positional and displacement parameters, which may then be appropriate for use in charge-density studies.

The e.s.d.'s obtained from the 100 K powder data are slightly higher than those from neutron single-crystal experiments, but compared with the agreement between neutron and X-ray single-crystal experiments, data from high-resolution neutron powder diffraction are of excellent quality. The second high-resolution neutron powder diffraction data set measured at 15 K produced meaningful atomic positions and anisotropic temperature factors, especially with regard to the D atoms. These parameters can now be used in the interpretation of charge-density distributions. As one would expect, the cell constants obtained are, in terms of their e.s.d.'s, about two orders of magnitude more precise than the X-ray parameters but show considerable discrepancies (Table 1). Given that the influence of cell constants on charge-density studies is a well known problem, this accurate determination is particularly relevant.

In conclusion, high-resolution neutron powder diffraction can provide high quality structural information on moderately sized organic structures. The technique requires only comparatively short data collection periods, without the need to grow large single crystals. This is particularly advantageous in cases of compounds that are liquids at room temperature, although care must be taken in order to avoid preferred orientation effects in powder samples. However, the quality of neutron powder

diffraction data is more seriously compromised by the use of protonated rather than deuterated samples.

This work was supported by the Gaduiertenkolleg 'Synthese und Strukturaufklärung niedermolekularer Verbindungen'. One of us (AL) is grateful to Professor M. B. Hursthouse, Cardiff, for being a most friendly host while part of this work was carried out. Beam-time allocation by ISIS under RB/2472 is gratefully acknowledged.

References

- COPPENS, P., DAM, J., HARKEMA, S., FEIL, D., FELD, R., LEHMANN, M. S., GODDARD, R., KRÜGER, C., HELLNER, E., JOHANSEN, H., LARSEN, F. K., KOETZLE, T. F., McMULLAN, R. K., MASLEN, E. N. & STEVENS, E. D. (1984). *Acta Cryst.* **A40**, 184–195.
- COPPENS, P., GURU ROW, T. N., LEUNG, P., STEVENS, E. D., BECKER, P. J. & YANG, Y. W. (1979). *Acta Cryst.* **A35**, 63–72.
- COPPENS, P. & SABINE, T. M. (1969). *Acta Cryst.* **B25**, 2442–2451.
- COPPENS, P., SABINE, T. M., DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2451–2458.
- DAVID, W. I. F. & IBBERSON, R. M. (1992). *Acta Cryst.* **C48**, 301–303.
- DAVID, W. I. F., IBBERSON, R. M., JEFFREY, G. A. & RUBBLE, J. R. (1992). *Physica B*, **180/181**, 597–600.
- DAVID, W. I. F., IBBERSON, R. M. & MATTHEWMAN, J. C. (1992). Report RAL-92-032. Rutherford Appleton Laboratory, Chilton, Didcot, England.
- DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2423–2437.
- FELD, R. (1980). Thesis, Phillips-Universität, Marburg/Lahn, Germany.
- HAUSER, J. & BÜRGI, H.-B. (1991). *PEANUT*. Universität Bern, Switzerland.
- HENDRIKSEN, K., LARSEN, F. K. & RASMUSSEN, S. E. (1986). *J. Appl. Cryst.* **19**, 350–354.
- HUMMEL, W., HAUSER, J. & BÜRGI, H.-B. (1990). *J. Mol. Graphics*, pp. 214–220.
- HUMMEL, W., RASELLI, A. & BÜRGI, H.-B. (1990). *Acta Cryst.* **B46**, 683–692.
- IBBERSON, R. M., DAVID, W. I. F. & KNIGHT, K. S. (1992). Report RAL-92-031. Rutherford Appleton Laboratory, Chilton, Didcot, England.
- IBBERSON, R. M., DAVID, W. I. F. & PRAGER, M. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1438–1439.
- JOHNSON, C. K. (1971). *ORTEPII*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- KLOOSTER, W. T., SWAMINATHAN, S., NANNI, R. & CRAVEN, B. M. (1992). *Acta Cryst.* **B48**, 217–227.
- LUGER, P., ANDRE, C., RUDERT, R., ZOBEL, D., KNÖCHEL, A. & KRAUSE, A. (1992). *Acta Cryst.* **B48**, 33–37.
- RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
- SABINE, T. M., COX, G. W. & CRAVEN, B. M. (1969). *Acta Cryst.* **B25**, 2437–2441.
- ZOBEL, D., LUGER, P., DREISSIG, W. & KORITSANSZKY, T. (1992). *Acta Cryst.* **B48**, 837–848.

Acta Cryst. (1994). **B50**, 348–357

Lengthening of the Covalent O—H Bond in O—H···O Hydrogen Bonds Re-examined from Low-Temperature Neutron Diffraction Data of Organic Compounds

BY TH. STEINER AND W. SAENGER

Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-14195 Berlin, Germany

(Received 11 May 1993; accepted 27 October 1993)

Abstract

The lengthening of the covalent O—H bond in O—H···O hydrogen bonds is re-examined from high-precision low-temperature neutron diffraction studies of organic molecules (32 crystal structures, 136 hydrogen bonds, $T < 130$ K, $R < 0.06$, H atoms on symmetry elements excluded). Accuracies are around or better than 0.002 Å. The dependencies of the covalent O—H bond length on the H···O and O···O separations are smooth with no sign of discontinuities. For all types of O—H and O—D hydrogen-bond donors and in combination with all types of O acceptors, the O—H bond length follows the same function of the H···O separation (within the experimental accuracy). For angles at H $> 150^\circ$, no depen-

dency of the O—H bond length on the hydrogen-bond angle can be detected for constant H···O. The bond-valence concept that is established in inorganic chemistry also proves to be a good model for O—H···O hydrogen bonds in organic compounds.

Introduction

It is well known that in $X-H\cdots Y$ hydrogen bonds, the covalent $X-H$ bond is lengthened because of the $H\cdots Y$ interaction, and that the lengthening increases with shortening hydrogen-bond distances $X\cdots Y$ and $H\cdots Y$. A quantitative empirical description of the relevant relations requires neutron diffraction data,