

Powder Neutron Diffraction Analysis of the Hydrogen Bonding in Deutero-Oxalic Acid Dihydrate at High Pressures

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Abstract

The structure of the title compound, $(\text{COOD})_2 \cdot 2\text{H}_2\text{O}$, has been studied as a function of pressure using the Rietveld refinement procedure with neutron powder data. The unit cell at ambient pressure has $a = 6.156$ (2), $b = 3.616$ (2), $c = 12.115$ (2), $\beta = 106.618$ (2)°, $V = 258.4$ Å³, space group $P2_1/n$. Final R_I values on the powder profile after constrained refinement are in the range 0.12 to 0.18. The only observable structural changes up to 0.5 GPa hydrostatic pressure are small changes in the hydrogen-bond arrangement. Of the three hydrogen bonds in the structure, the two longer bonds contract around 0.04 Å, whereas the shortest bond is unchanged. This is found to be in qualitative agreement with an estimate based on force constants from spectroscopic observations.

1. Introduction

Whenever hydrogen-bonding units are present in a material they will contribute considerably to the stability of its structure. Indeed, it is quite unusual to find a group that is potentially a hydrogen-bond donor or acceptor, and that is not involved in hydrogen bonding. Once a crystalline structure with hydrogen bonds is formed, the bonds are not easily modified. In a systematic study of hydrogen bonding with structural methods one will therefore commonly look at a series of different crystalline structures (Olovsson & Jönsson, 1976). Another less common approach is the variation of temperature (Takusagawa & Koetzle, 1979), and finally one could consider a variation of the pressure. For technical reasons this last method has been used least. In order to subject materials to pressure, they must be mounted between pistons or inside a pressure vessel. In a scattering experiment, this will cause serious absorption problems and, especially with X-rays, it will be preferable to study atoms with reasonable scattering power. In

neutron diffraction this is less critical, first because most materials have a low absorption power towards neutrons, and secondly because nearly all atoms have similar scattering power. It has thus been possible to study the behaviour of the hydrogen-atom motion near the phase transition in KH_2PO_4 when pressure was applied (Tibballs, Nelmes & McIntyre, 1982).

In this paper we report an investigation of the hydrogen bonds in α -oxalic acid dihydrate (Delaplane & Ibers, 1969) using pressures up to 0.5 GPa. Oxalic acid was chosen because it is a very small organic molecule which in the α modification has as many as three independent hydrogen bonds. The compound is packed in hydrogen-bonded layers, which are interlinked by hydrogen bonds and van der Waals contacts. Altogether the structure is held together by a three-dimensional network of hydrogen bonds, so one would expect most of the effect of pressure on the structure to be visible in the changes in the hydrogen bonds.

2. Measurement and structure refinement

The measurements were carried out on the high-resolution powder diffractometer DIA of the Institut Laue-Langevin (Hewat & Bailey, 1976) using a wavelength of 1.909 Å. Experiments were performed at room temperature. The full deuterated sample had a volume of 1 cm³. It was enclosed in a pressure cell made of high-strength aluminium alloy and hydrostatic pressures of up to 0.5 GPa could be obtained using He gas (Paureau & Vettier, 1975). Only a few lines from the cell were visible in the spectrum, so these parts of the spectrum were simply removed. This amounted on average to 12°. Measurements were made at ambient pressure, and at pressures of 0.2, 0.3, 0.4 and 0.5 GPa, respectively. The data were recorded in the range from $2\theta = 6$ to 160° in steps of 0.05°. The correction for detector efficiency and the visual estimation of the background were performed using the program *POWDER* (Hewat, 1976). Scan as a function of sample orientation showed no indication of preferred orientation.

Two kinds of structure refinements were carried out. First the profile-refinement program of Rietveld (1967), modified by Hewat (1974) was used.

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Individual atomic positions, temperature parameters, unit-cell parameters and halfwidth parameters for the peaks were adjusted. This led to agreement factors for the profile intensities in the range from 0.13 to 0.16. As the individual atomic positions were adjusted despite the fact that we do not expect any observable change in the covalent bond length, an intercomparison of bond lengths for the various pressures gave an estimate of the intramolecular distances and the associated sampling error. We found $l(\text{C}-\text{C}) = 1.59$ (3), $l(\text{C}=\text{O}) = 1.16$ (2) and $l(\text{C}-\text{O}) = 1.32$ (2) Å. The O-D lengths showed no systematic variation with pressure, and were in the range 0.92 to 1.00 Å. Errors in parentheses are in units of the last digit. Scattering lengths used were from Koester & Rauch (1981).

At this stage of the refinement we found a few peaks in the differences between observed and calculated intensities, which could not be accounted for. Calculation of intensities and positions of the strongest peaks in the various modifications clearly showed these peaks to come from a trace of β -oxalic acid dihydrate (Coppens & Sabine, 1969). Their position varied with pressure in a manner similar to α -oxalic acid dihydrate, but the peaks were too few and weak to allow us to register the variation of the unit cell of this compound as a function of pressure with any precision. Eventually, a little over 9° of the spectrum corresponding to the regions of the strongest peaks were removed. Even then there are obviously parts of the spectrum which are still affected. The observed and calculated spectra for the 0.3 GPa data are shown in Fig. 1 as an example of this. The agreement factors after this correction were in the range 0.11 to 0.15.

Further refinements were performed using techniques of constrained refinement (Pawley, 1972) and the program *EDINP* (Pawley, 1980). In this case the two molecules involved were fixed geometrically to

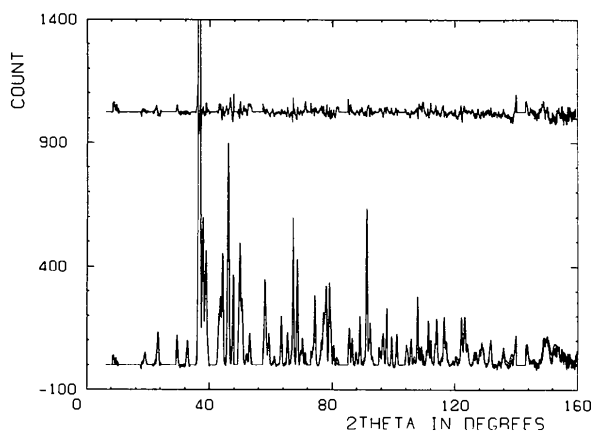


Fig. 1 Powder profile for data recorded at 0.3 GPa. The heavy line and superimposed lighter line represent the observed and calculated data respectively. The difference between observed and calculated values is given in the upper part of the plot.

Table 1. Variation of the hydrogen bonds with pressure, and agreement factor after constrained refinement

The agreement factor was defined as $R_i = \sum (I_{i,obs} - I_{i,calc}) / \sum I_{i,obs}$ where $I_{i,obs}$ and $I_{i,calc}$ are observed and calculated profile values at point i .

Bond	Pressure (GPa × 10)	O—D (Å)	D···O (Å)	∠O—D···O (°)	R (%)
O(1)—D(1)···O(3)	Ambient	1.002*	1.545	177.3	11.7
	2		1.551	178.0	16.5
	3		1.564	178.4	16.4
	4		1.560	178.7	16.2
	5		1.556	179.0	18.1
O(3)—D(2)···O(2)	Ambient	0.956*	1.939	162.0	
	2		1.928	162.2	
	3		1.915	162.2	
	4		1.908	162.3	
	5		1.896	163.6	
O(3)—D(3)···O(2)	Ambient	0.919*	2.029	154.6	
	2		2.008	153.2	
	3		1.991	153.5	
	4		1.989	153.6	
	5		2.004	150.5	

* Constrained value.

the mean value of the molecules determined in the previous refinements. The structural parameters were then the Eulerian angles describing the orientation of the two molecules and the position of the centre of gravity of the water molecule. As the oxalic acid molecule is located on a centre of inversion no positional parameter for this group is needed. In addition the two molecules were assumed to move as rigid bodies, and their motion was described by translation and libration tensors. Final R_i values on the profile were 0.12 to 0.18. The individual values are summarized in Table 1. The rather high values reflect both the relatively low intensities caused by small sample volumes and the effect of the trace of the β modification. (The powder profile data are in Table 2.* The size of the unit cell as a function of pressure and the atomic coordinates are found in Tables 3 and 4.*)

3. Results and discussion

The measurements show, as expected, a contraction of the unit cell as a function of pressure. This variation is given in Fig. 2. The most marked changes are along the two short axes, and this is in qualitative agreement with the structural arrangement. The molecular packing and their hydrogen-bond network are shown in Fig. 3. Two of the hydrogen bonds have their main components along the c axis, with a nearly equally large component along the a axis, and the third bond is nearly orthogonal to this. There are in a sense thus slightly more hydrogen bonds along c , and therefore the structure is more rigid in this direction. Moreover, one of the bonds along c involves the acid H atom

* Tables 2, 3 and 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39586 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of the oxalic acid. This bond is the shortest, and one can therefore expect some additional rigidity from this.

Recently the α and β modifications of oxalic acid have been studied by infrared and Raman spectroscopy (De Villipin, Novak & Bongear, 1982). In these compounds the O...O contacts are between 2.67 and 2.70 Å and are comparable with the two longest distances found in this study. For α -oxalic acid the force constant for the hydrogen bond is given as $0.19 \times 10^2 \text{ Nm}^{-1}$. From this we can estimate the expected changes in the bond length, if we assume that the crystal is entirely held together by hydrogen-bond forces, and if we moreover assume that the 'surface' held by each hydrogen bond is the section through the unit cell orthogonal to the bond, divided by the number of hydrogen bonds of a given type, i.e. 4. For a total of 0.5 GPa pressure we find the expected

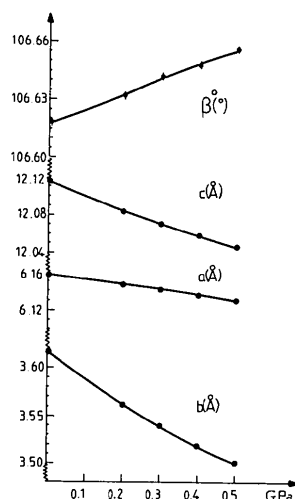


Fig. 2. The unit-cell dimensions as a function of pressure. Error bars are indicated for the β angle, for the axes they are smaller than the plotted points.

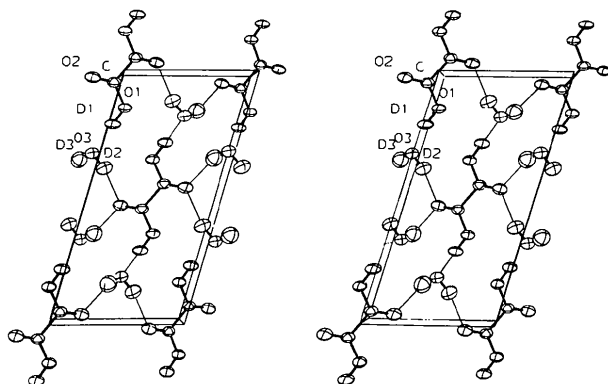


Fig. 3. Plot of the hydrogen-bond system viewed along b . The unit cell is outlined, with the c^* axis vertical and the a axis horizontal. Thin lines are hydrogen bonds, thick lines molecular bonds. The plot was produced using ORTEP II (Johnson, 1976).

contractions to be on average 0.037 Å for the three bonds. Table 1 gives the observed variations. Using a least-squares fit to the data to obtain the total change we observe contractions in the three bonds of -0.018 (8), 0.040 (10) and 0.044 (10) Å for $D(1)\cdots O(3)$, $D(2)\cdots O(2)$ and $D(3)\cdots O(2)$, respectively. The agreement with calculation is reasonable, especially when we keep in mind that the shortest bond $D(1)\cdots O(3)$ will have a force constant considerably larger than that quoted above. In this case the other longer bond with the main component in the c direction will take up most of the change, as observed.

A further effect of pressure would be a bending of the hydrogen bonds. In agreement with expectation, the longest bond has the largest change of about 4°, but in addition the bond angle of the shortest bond tends towards 180°.

The total change in structure is therefore a shift in the relative position of the water molecule followed by a rotation of the molecule mainly around the $O(3)$ - $D(2)$ axis. In all, the changes are small, as expected from the spectroscopic force constants. One might also have expected changes in the thermal-motion parameters. Because of the above-mentioned difficulties, however, we were unable to discern any systematic variations, even though the thermal motions, as seen in Fig. 2, are not unreasonable.

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