

Neutron Diffraction Study of Hydrogen Bonding and Thermal Motion in Deuterated α and β Oxalic Acid Dihydrate*

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A three-dimensional neutron diffraction study of the α and β modifications of deuterated oxalic acid dihydrate has been made. The two structures are compared with particular reference to the D–O–D angles in the water molecules, which are respectively $105.8 \pm 0.2^\circ$ and $108.8 \pm 0.2^\circ$ in the α and β forms. It is concluded that the electronic structure of the water molecule is dependent on the hydrogen bonding environment. Rigid-body motion analysis of the oxalic acid molecules shows a larger vibration around the long molecular axis and excess vibration of the hydroxylic deuteron in the direction of the short hydrogen bond. The excess root mean square amplitude is in quantitative agreement with earlier infrared data. A discussion of the deuterium scattering length is given, and it is shown that this quantity cannot be less than 6.51 ± 0.02 fermi.

Introduction

It has been supposed for some years that crystals of deuterated oxalic acid dihydrate are not isomorphous with crystals of the hydrated material (Fukushima, Iwasaki & Saito, 1964; Fukushima, Iwasaki, Saito, Sato & Hoshino, 1965; Iwasaki & Saito, 1967). However, Delaplane & Ibers (1969) found that the crystal structure did not change on deuteration, except for small changes in bond lengths and angles.

The present work was undertaken to determine the deuterium atom position in deuterated α -oxalic acid dihydrate (α -DOX) to complement the X-ray work of Delaplane & Ibers, and to use the atomic and thermal coordinates in a re-analysis of the X-ray data to determine the asphericity of the distribution of bonding electrons (Coppens, Sabine, Delaplane & Ibers, 1969). The structure of β -deuteriooxalic acid dihydrate (β -DOX) has been examined with neutrons by Iwasaki & Saito (1967), whose work came to our attention while these measurements were in progress, but as they had measured the integrated intensity of only 90 reflections in the $h0l$ and $hk0$ reciprocal lattice planes, it was decided to complete the experiment. Our measurements of lattice parameters agreed with those of Fukushima, Iwasaki & Saito (1964). When the more accurate X-ray lattice parameters of Iwasaki & Saito (1967) became available they were used in the data analysis.

Experimental

Crystal growth

The crystals were grown by repeated recrystallization of anhydrous oxalic acid in D_2O under a nitrogen at-

mosphere. Large crystals grew readily. The α and β forms appear to grow at random. Initially Dr B. M. Craven at the Crystallographic Laboratory of the University of Pittsburgh attempted to grow the α form. The first crystal from the solution was α and the second β . That α crystal was lost and subsequently only the β form would grow at Pittsburgh.

We repeated Craven's experiments at Brookhaven and obtained only the α form. No attempt was made to examine this effect further.

The crystals finally used had volumes of 3.3 and 4.0 mm³ for α -DOX and β -DOX respectively.

The unit-cell constants are as follows:

α -(COOD) ₂ ·2D ₂ O*	β -(COOD) ₂ ·2D ₂ O†
Space group $P2_1/n$ ($Z=2$)	Space group $P2_1/a$ ($Z=2$)
<i>a</i> 6.150 Å	<i>a</i> 10.021 Å
<i>b</i> 3.605	<i>b</i> 5.052
<i>c</i> 12.102	<i>c</i> 5.148
β 106.63°	β 99.27°

*from Delaplane & Ibers (1969)

†from Iwasaki & Saito (1967)

Data collection

The data for both crystals were collected at the Brookhaven High Flux Beam Reactor. The neutron intensity at the specimen was 1.5×10^6 n cm⁻² sec⁻¹ at a wavelength of 1.07 Å. Second-order contamination was avoided by using a Ge(331) monochromator. The α -DOX crystal was mounted with **b** along the ϕ axis of a four-circle diffractometer while the **c*** axis of the β -DOX crystal lay along the ϕ axis. On rotation of the crystals about the ϕ axis at $\chi = 90^\circ$ no multiple scattering effects (Coppens, 1968) were observed.

Under computer control (Bednowitz, Coppens & Hamilton, 1966) the integrated intensities of a total of 627 independent reflections from the α crystal ($\sin \theta/\lambda < 0.65 \text{ \AA}^{-1}$) and 682 from the β crystal ($\sin \theta/\lambda < 0.70 \text{ \AA}^{-1}$) were measured.

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Structure refinement

An absorption correction using an absorption coefficient of 0.13 cm⁻¹ computed from the true absorption cross sections and the incoherent scattering cross sec-

tions of the atomic species present, was applied to the α-DOX data. Since the maximum difference between the corrections applied to different reflections was 0.3%, no absorption correction was made for β-DOX.

Table 1. Observed and calculated structure factors for α-DOX (× 100)

Negative F_{obs} indicates an unobserved reflection. Column labelled EXT lists 100 · y, where y is the extinction correction to the intensity: I_{obs} = I_{calc} · y. The entry is deleted for y > 0.99. F_{obs} has been divided by y^{1/2}.

K = -4				K = -2				K = -1				K = 1				K = 3				
M	L	F _{obs}	F _{calc}	M	L	F _{obs}	F _{calc}	M	L	F _{obs}	F _{calc}	M	L	F _{obs}	F _{calc}	M	L	F _{obs}	F _{calc}	
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
1	2	1	1	1	2	1	1	1	2	1	1	1	2	1	1	1	1	2	1	1
1	3	1	1	1	3	1	1	1	3	1	1	1	3	1	1	1	1	3	1	1
1	4	1	1	1	4	1	1	1	4	1	1	1	4	1	1	1	1	4	1	1
1	5	1	1	1	5	1	1	1	5	1	1	1	5	1	1	1	1	5	1	1
1	6	1	1	1	6	1	1	1	6	1	1	1	6	1	1	1	1	6	1	1
1	7	1	1	1	7	1	1	1	7	1	1	1	7	1	1	1	1	7	1	1
1	8	1	1	1	8	1	1	1	8	1	1	1	8	1	1	1	1	8	1	1
1	9	1	1	1	9	1	1	1	9	1	1	1	9	1	1	1	1	9	1	1
1	10	1	1	1	10	1	1	1	10	1	1	1	10	1	1	1	1	10	1	1
1	11	1	1	1	11	1	1	1	11	1	1	1	11	1	1	1	1	11	1	1
1	12	1	1	1	12	1	1	1	12	1	1	1	12	1	1	1	1	12	1	1
1	13	1	1	1	13	1	1	1	13	1	1	1	13	1	1	1	1	13	1	1
1	14	1	1	1	14	1	1	1	14	1	1	1	14	1	1	1	1	14	1	1
1	15	1	1	1	15	1	1	1	15	1	1	1	15	1	1	1	1	15	1	1
1	16	1	1	1	16	1	1	1	16	1	1	1	16	1	1	1	1	16	1	1
1	17	1	1	1	17	1	1	1	17	1	1	1	17	1	1	1	1	17	1	1
1	18	1	1	1	18	1	1	1	18	1	1	1	18	1	1	1	1	18	1	1
1	19	1	1	1	19	1	1	1	19	1	1	1	19	1	1	1	1	19	1	1
1	20	1	1	1	20	1	1	1	20	1	1	1	20	1	1	1	1	20	1	1
1	21	1	1	1	21	1	1	1	21	1	1	1	21	1	1	1	1	21	1	1
1	22	1	1	1	22	1	1	1	22	1	1	1	22	1	1	1	1	22	1	1
1	23	1	1	1	23	1	1	1	23	1	1	1	23	1	1	1	1	23	1	1
1	24	1	1	1	24	1	1	1	24	1	1	1	24	1	1	1	1	24	1	1
1	25	1	1	1	25	1	1	1	25	1	1	1	25	1	1	1	1	25	1	1
1	26	1	1	1	26	1	1	1	26	1	1	1	26	1	1	1	1	26	1	1
1	27	1	1	1	27	1	1	1	27	1	1	1	27	1	1	1	1	27	1	1
1	28	1	1	1	28	1	1	1	28	1	1	1	28	1	1	1	1	28	1	1
1	29	1	1	1	29	1	1	1	29	1	1	1	29	1	1	1	1	29	1	1
1	30	1	1	1	30	1	1	1	30	1	1	1	30	1	1	1	1	30	1	1
1	31	1	1	1	31	1	1	1	31	1	1	1	31	1	1	1	1	31	1	1
1	32	1	1	1	32	1	1	1	32	1	1	1	32	1	1	1	1	32	1	1
1	33	1	1	1	33	1	1	1	33	1	1	1	33	1	1	1	1	33	1	1
1	34	1	1	1	34	1	1	1	34	1	1	1	34	1	1	1	1	34	1	1
1	35	1	1	1	35	1	1	1	35	1	1	1	35	1	1	1	1	35	1	1
1	36	1	1	1	36	1	1	1	36	1	1	1	36	1	1	1	1	36	1	1
1	37	1	1	1	37	1	1	1	37	1	1	1	37	1	1	1	1	37	1	1
1	38	1	1	1	38	1	1	1	38	1	1	1	38	1	1	1	1	38	1	1
1	39	1	1	1	39	1	1	1	39	1	1	1	39	1	1	1	1	39	1	1
1	40	1	1	1	40	1	1	1	40	1	1	1	40	1	1	1	1	40	1	1
1	41	1	1	1	41	1	1	1	41	1	1	1	41	1	1	1	1	41	1	1
1	42	1	1	1	42	1	1	1	42	1	1	1	42	1	1	1	1	42	1	1
1	43	1	1	1	43	1	1	1	43	1	1	1	43	1	1	1	1	43	1	1
1	44	1	1	1	44	1	1	1	44	1	1	1	44	1	1	1	1	44	1	1
1	45	1	1	1	45	1	1	1	45	1	1	1	45	1	1	1	1	45	1	1
1	46	1	1	1	46	1	1	1	46	1	1	1	46	1	1	1	1	46	1	1
1	47	1	1	1	47	1	1	1	47	1	1	1	47	1	1	1	1	47	1	1
1	48	1	1	1	48	1	1	1	48	1	1	1	48	1	1	1	1	48	1	1
1	49	1	1	1	49	1	1	1	49	1	1	1	49	1	1	1	1	49	1	1
1	50	1	1	1	50	1	1	1	50	1	1	1	50	1	1	1	1	50	1	1
1	51	1	1	1	51	1	1	1	51	1	1	1	51	1	1	1	1	51	1	1
1	52	1	1	1	52	1	1	1	52	1	1	1	52	1	1	1	1	52	1	1
1	53	1	1	1	53	1	1	1	53	1	1	1	53	1	1	1	1	53	1	1
1	54	1	1	1	54	1	1	1	54	1	1	1	54	1	1	1	1	54	1	1
1	55	1	1	1	55	1	1	1	55	1	1	1	55	1	1	1	1	55	1	1
1	56	1	1	1	56	1	1	1	56	1	1	1	56	1	1	1	1	56	1	1
1	57	1	1	1	57	1	1	1	57	1	1	1	57	1	1	1	1	57	1	1
1	58	1	1	1	58	1	1	1	58	1	1	1	58	1	1	1	1	58	1	1
1	59	1	1	1	59	1	1	1	59	1	1	1	59	1	1	1	1	59	1	1
1	60	1	1	1	60	1	1	1	60	1	1	1	60	1	1	1	1	60	1	1
1	61	1	1	1	61	1	1	1	61	1	1	1	61	1	1	1	1	61	1	1
1	62	1	1	1	62	1	1	1	62	1	1	1	62	1	1	1	1	62	1	1
1	63	1	1	1	63	1	1	1	63	1	1	1	63	1	1	1	1	63	1	1
1	64	1	1	1	64	1	1	1	64	1	1	1	64	1	1	1	1	64	1	1
1	65	1	1	1	65	1	1	1	65	1	1	1	65	1	1	1	1	65	1	1
1	66	1	1	1	66	1	1	1	66	1	1	1	66	1	1	1	1	66	1	1
1	67	1	1	1	67	1	1	1	67	1	1	1	67	1	1	1	1	67	1	1
1	68	1	1	1	68	1	1	1	68	1	1	1	68	1	1	1	1	68	1	1
1	69	1	1	1	69	1	1	1	69	1	1	1	69	1	1	1	1	69	1	1
1	70	1	1	1	70	1	1	1	70	1	1	1	70	1	1	1	1	70	1	1
1	71	1	1	1	71	1	1	1	71	1	1	1	71	1	1	1	1	71	1	1
1	72	1	1	1	72	1	1	1	72	1	1	1	72	1	1	1	1	72	1	1
1	73	1	1	1	73	1	1	1	73	1	1	1	73	1	1	1	1	73	1	1
1	74	1	1	1	74	1														

The resulting change in the positional parameters is small, and always less than 1.5 times the combined standard deviations. As anticipated, temperature parameters change significantly: the average increase in the diagonal tensor elements is about 7%. Clearly it is essential to correct for severe extinction if systematic errors in the temperature parameters are to be avoided.

Final extinction, positional and thermal parameters are given in Tables 3, 4 and 5.

Final R factors are as follows:

R = (sum |Fo - |Fc|| / sum Fo) 0.043(0.062) alpha-DOX 0.038(0.058) beta-DOX
Rw = (sum w|Fo - |Fc|^2 / sum wFo^2)^1/2 0.044(0.055) 0.038(0.062)

The numbers in parenthesis refer to final R factors before the extinction refinement. The R factors after ex-

Table 2. Observed and calculates structure factors for beta-DOX (x 100)

Table with columns for h, k, l, Fobs, Fcalc, Ext, K=0, K=1, K=2, K=3, K=4, K=5, K=6. It contains a large grid of numerical data representing structure factors and extinction coefficients for various hkl reflections.

Table 3.* Extinction parameters for α - and β -DOX

	α -DOX	R	R_w	g or G_{ij} (10^{-4})	Corresponding mosaic spread (sec)	Corresponding particle size ($\text{cm} \times 10^{-4}$)
	Isotropic	0.044	0.045	1.58 (6)	3.7	1.7
	Type I	0.043	0.044			
G_{11}				3.08 (44)	3.3	
G_{22}				2.25 (19)	3.9	
G_{33}				5.26 (88)	2.5	
G_{12}				-1.25 (39)		
G_{13}				-1.07 (91)		
G_{23}				0.84 (46)		
	Type II	0.043	0.044			
G_{11}				0.61 (6)		1.4
G_{22}				0.19 (3)		2.5
G_{33}				0.34 (4)		1.8
G_{12}				-0.10 (5)		
G_{13}				-0.28 (6)		
G_{23}				0.00 (4)		
	Isotropic	0.040	0.039	1.93 (9)	3.0	2.1
	Type I	0.038	0.038			
G_{11}				2.42 (53)	3.8	
G_{22}				4.82 (86)	2.7	
G_{33}				4.25 (43)	2.8	
G_{12}				1.12 (67)		
G_{13}				-0.16 (37)		
G_{23}				1.38 (42)		
	Type II	0.038	0.039			
G_{11}				0.24 (4)		2.2
G_{22}				0.19 (3)		2.5
G_{33}				0.35 (5)		1.8
G_{12}				-0.07 (3)		
G_{13}				-0.05 (3)		
G_{23}				-0.05 (2)		

* All tensor elements refer to the crystallographic axes a , b and c .

Table 4. Atomic parameters for α -DOX ($\times 10^3$)

Positional parameters are given as fractions of the cell edges.

Thermal parameters are in the form: $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	$x, \sigma(x)$	$y, \sigma(y)$	$z, \sigma(z)$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	-447 (2)	551 (3)	509 (1)	163 (3)	501 (9)	36 (1)	44 (4)	23 (1)	-2 (2)
O(1)	854 (2)	-609 (4)	1484 (1)	223 (4)	915 (15)	34 (1)	143 (5)	21 (1)	8 (2)
O(2)	-2183 (2)	2296 (4)	360 (1)	217 (4)	894 (15)	43 (1)	169 (5)	35 (1)	6 (2)
O(3)	-4499 (2)	6139 (5)	1806 (1)	222 (4)	889 (15)	42 (1)	88 (6)	35 (2)	20 (3)
D(1)	259 (2)	79 (4)	2171 (1)	260 (4)	895 (16)	47 (1)	60 (5)	30 (1)	4 (2)
D(2)	-5712 (2)	6849 (5)	1151 (1)	287 (5)	1026 (17)	55 (1)	92 (6)	24 (2)	-44 (3)
D(3)	-3591 (2)	4453 (5)	1522 (1)	294 (5)	1103 (19)	89 (1)	143 (7)	74 (2)	-15 (3)

Table 5. Atomic parameters for β -DOX ($\times 10^3$)

Positional parameters are given as fractions of the lattice parameters.

Thermal parameters are in the form: $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	$x, \sigma(x)$	$y, \sigma(y)$	$z, \sigma(z)$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	505 (1)	219 (2)	4045 (2)	58 (1)	241 (4)	291 (4)	4 (1)	48 (1)	35 (2)
O(1)	1463 (1)	-1518 (2)	4359 (2)	77 (1)	339 (6)	467 (5)	47 (2)	102 (2)	120 (4)
O(2)	377 (1)	1998 (3)	2470 (3)	79 (1)	339 (5)	375 (6)	31 (2)	85 (2)	117 (4)
O(3)	3278 (1)	-804 (3)	1516 (3)	100 (2)	503 (7)	487 (7)	-88 (3)	132 (3)	-219 (6)
D(1)	2148 (1)	-1196 (2)	3126 (2)	84 (1)	382 (6)	461 (6)	30 (2)	93 (3)	54 (4)
D(2)	3491 (1)	-1717 (3)	35 (3)	120 (2)	476 (7)	398 (6)	0 (2)	78 (2)	-121 (4)
D(3)	3937 (1)	527 (3)	2002 (3)	96 (1)	411 (6)	480 (6)	-44 (2)	70 (2)	-72 (4)

tion refinement include all reflections. The improvement is conspicuous.

Discussion

The crystal structures of α -POX and α -DOX are compared in the first paper of this series (Delaplane & Ibers, 1969).

The extinction parameters

The extinction parameters show significant anisotropy in the extinction (Table 3). The improvement in R on going from isotropic to anisotropic extinction refinement is small, though significant according to statistical tests (Hamilton, 1965). There is little difference between agreement factors obtained with Type I and Type II treatments. Both show that the anisotropy is less pronounced than in the specimen used for X-ray data collection, though the crystals used in the present study are more nearly perfect. Thus, particle size (Type II) varies between 1.4 and 3.9 μ here as against 0.3–1.2 μ in the smaller crystal of the X-ray study (Delaplane & Ibers, 1969).

The positional and temperature parameters are equal to within one standard deviation for the two treatments. It is therefore of no consequence for the

structural analyses whether Type I or Type II is closer to reality. In fact, extinction is probably affected both by mosaic spread and by particle size and neither extreme is entirely correct in this case.

The oxalic acid molecules

Bond lengths and bond angles are given in Tables 6 and 7 together with the X-ray values of Delaplane & Ibers (1969) and the X-ray and neutron values of Iwasaki & Saito (1967), and Fukushima *et al.* (1965).

Intramolecular distances and angles in the oxalic acid molecule are remarkably similar in the two polymorphs (Fig. 1). As indicated by nonbonded H...O distances the short hydrogen bond is somewhat stronger and the long hydrogen bonds are somewhat weaker in α -DOX. There is a correlation between the six H...O bond lengths in the two structures and the corresponding O-H...O angles, the shorter bonds being associated with the larger angles. A similar observation has been made by Hamilton (1962) in a survey of several structures. The comparison of the X-ray and neutron parameters will be discussed in a subsequent article.

The water molecule

Iwasaki, Iwasaki & Saito (1967) discussed the difference between the water-molecule angles in α -POX and β -

Table 6. Bond lengths for α and β -DOX

The notation for symmetry related atoms is as in Fig. 1 of this paper and Fig. 1 of Delaplane & Ibers (1969).

Bond	α -DOX		β -DOX	
	This investigation	Delaplane & Ibers (1969)	This investigation	Fukushima <i>et al.</i> (1965)
C(1)—C(1')	1.539 (2)	1.537 (2)	1.537 (2)	1.539 (5)
C(1)—O(1)	1.291 (2)	1.287 (1)	1.291 (2)	1.300 (4)
C(1)—O(2)	1.208 (2)	1.209 (1)	1.203 (2)	1.201 (4)
O(1)—D(1)	1.031 (2)	0.86 (2)	1.020 (2)	1.042 (8)
O(3)—D(2)	0.954 (2)	0.83 (2)	0.944 (2)	0.946 (10)
O(3)—D(3)	0.954 (2)	0.78 (2)	0.947 (2)	0.960 (10)
D(1)...O(3'')	1.493 (2)	1.67 (2)	1.520 (2)	1.500 (8)
D(2)...O(2''')	1.939 (2)	2.05 (2)	1.960 (2)	1.965 (9)
D(3)...O(2 ^{IV})	2.008 (2)	2.21 (2)	1.895 (2)	1.874 (10)
O(1)...O(3''')	2.524 (2)	2.531 (1)	2.538 (2)	2.540 (4)
O(3)...O(2''')	2.879 (2)	2.880 (2)	2.855 (2)	2.854 (5)
O(3)...O(2 ^{IV})	2.906 (2)	2.907 (1)	2.834 (3)	2.822 (4)

Table 7. Bond angles for α and β -DOX

Bond	α -DOX		β -DOX	
	This investigation	Delaplane & Ibers (1969)	This investigation	Fukushima <i>et al.</i> (1965)
O(1)—C(1)—O(2)	126.6 (1)	126.8 (1)	126.1 (1)	126.2 (3)
O(1)—C(1)—C(1')	112.2 (1)	111.8 (1)	112.0 (1)	111.5 (3)
O(2)—C(1)—C(1')	121.2 (1)	121.4 (1)	121.9 (1)	122.3 (3)
C(1)—O(1)—D(1)	112.8 (1)	113.8 (8)	112.0 (1)	112.3 (5)
D(2)—O(3)—D(3)	105.8 (2)	101.2 (17)	108.8 (2)	110.5 (9)
O(1)—D(1)...O(3'')	177.4 (1)	176.3 (15)	174.2 (2)	174.4 (6)
D(1)...O(3'')—D(2'')	113.7 (1)	113.7 (10)	131.4 (2)	130.0 (7)
D(1)...O(3'')—D(3'')	119.2 (1)	110.7 (7)	119.8 (2)	119.4 (7)
O(3)—D(2)...O(2''')	167.7 (2)	172.0 (13)	157.3 (2)	155.8 (7)
D(2)—O(2''')—C(1''')	123.1 (1)	125.2 (4)	132.8 (1)	
O(3)—D(3)...O(2 ^{IV})	156.0 (2)	148.9 (20)	170.3 (1)	169.1 (8)
D(3)...O(2 ^{IV})—C(1 ^{IV})	129.6 (1)	131.0 (4)	125.1 (1)	

DOX. The present investigation shows that the differences are somewhat smaller than found previously but still highly significant. The values are: α -POX, $105.9^\circ \pm 0.7^\circ$ (Sabine *et al.*, 1969); α -DOX, $105.8 \pm 0.2^\circ$; β -DOX, $108.8 \pm 0.2^\circ$. Iwasaki, Iwasaki & Saito have attributed this difference to a change in hybridization of the water molecule initiated by the arrangements of the hydrogen bonds in the crystal. Our results confirm that the difference is not an isotope effect since the bond angles are equal in α -DOX and α -POX. The water molecule in α -DOX is of type *K* of the classification of Chidamba-

ram, Sequeira & Sikka (1964), one of the lone-pair orbitals being directed towards an H-bond donor group while the other lone pair is not specifically directed to any neighboring group (Fig. 2). The water molecule in β -DOX, on the other hand, is of type *F* in which the bisector of the lone pairs is directed toward an H-bond donor group. It seems reasonable to assume that in this situation the angle between the lone pairs is decreased in order to increase the total interaction with the proton or deuteron of the donor group. In the orthogonal atomic-hybrid approximation (Coulson, 1961) this

Table 8. Components of molecular inertial axes *L*, *M* and *N* along dimensionless axes $\mathbf{a}_i = |\mathbf{a}^i| \mathbf{a}_i$

α -DOX	1	2	3	β -DOX	1	2	3	Direction
<i>L</i>	0.2368	-0.1948	-0.8442	0.7142	0.0392	-0.5747		Almost \parallel C-C bond
<i>M</i>	0.8202	-0.4851	0.5255	0.4392	-0.8025	0.4692		In plane of molecule approximately \perp C-C
<i>N</i>	0.5208	0.8525	0.1061	0.5450	0.5953	0.6705		\parallel molecular plane

Table 9. Contravariant components T^{ij} and covariant components ω_{ij} of molecular translation and libration tensors and their standard deviations with respect to dimensionless axes $\mathbf{a}_i = |\mathbf{a}^i| \mathbf{a}_i$

α -DOX	11	22	33	12	23	13
$10^4 T^{ij}$ (\AA^2)	282 (15)	343 (21)	241 (11)	50 (13)	-5 (9)	69 (9)
$10^4 \omega_{ij}$ (rad^2)	92 (10)	24 (4)	252 (29)	-18 (4)	57 (13)	-155 (23)
β -DOX	11	22	33	12	23	13
$10^4 T^{ij}$ (\AA^2)	291 (11)	315 (13)	384 (13)	19 (8)	48 (9)	124 (8)
$10^4 \omega_{ij}$ (rad^2)	167 (15)	6 (7)	147 (14)	44 (9)	-17 (4)	-151 (16)

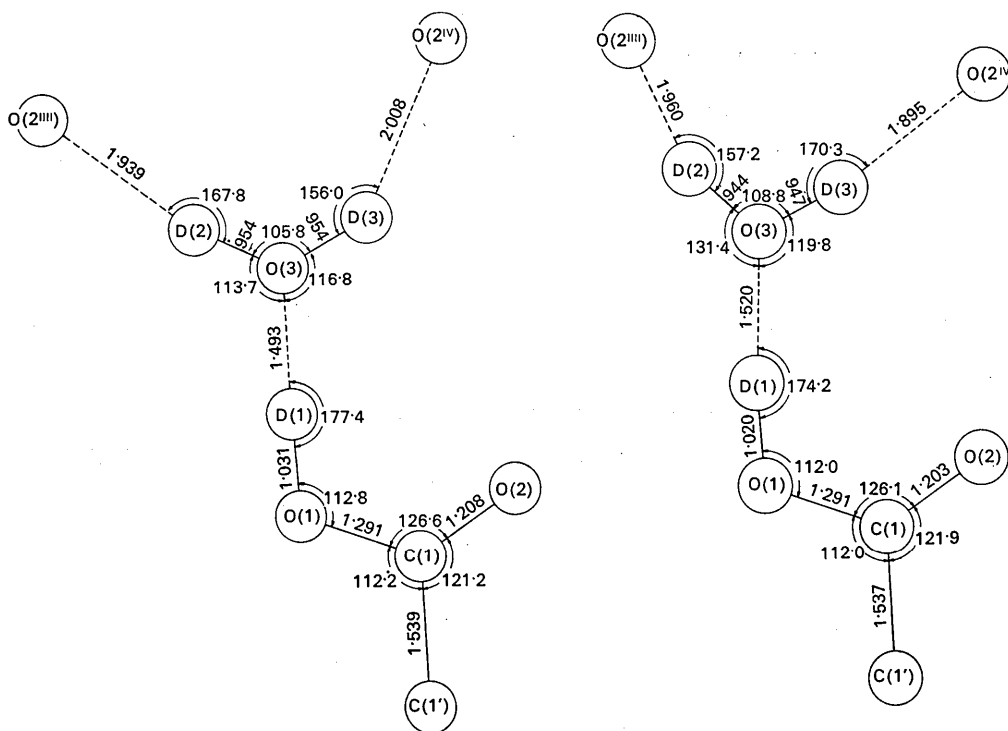


Fig. 1. Diagrammatic view of oxalic acid molecules in α -DOX and β -DOX.

implies that the p -character of the lone pairs and therefore the s -character of the oxygen bonding orbitals increases.

This increase in s -character of the bonding orbitals results in an opening up of the DOD angle and it should also lead to a slight strengthening of the OD bonds. The two OD bond lengths in the water molecule in β -DOX are observed to be slightly shorter than corresponding bond lengths in α -DOX, the averages being 0.954 and 0.946 Å respectively. The standard deviation of the difference is 0.002 Å. The difference is therefore just outside the experimental error.

Thermal parameters

Since it is to be expected that the carboxylic group would behave as a rigid body, a least-squares analysis was carried out to obtain the elements of the tensors \mathbf{T} and $\boldsymbol{\omega}$ describing respectively the translational vibrations and librations of a rigid body using a program written by Hirshfeld & Rabinovich (1966). The coordinates of the center of libration were fixed at the center of symmetry. Results are given in Tables 8, 9, 10 and 11. The rigid-body motions are strikingly similar in the two polymorphs. In both modifications translational vibrations are largest in the direction of the N axis which is perpendicular to the molecular plane, while librations are very large around L (approximately parallel to the C–C bond) and essentially zero around other axes of inertia. The librations around the principal axes parallel to L have r.m.s. amplitudes of 9.4 and 9.3° in α -DOX and β -DOX respectively. That hydrogen bonding does not prevent large librations of carboxylic groups has also been observed in structural studies of other carboxylic acids, such as fumaric acid (Brown, 1966) and terephthalic acid (Bailey & Brown, 1967). The observed atomic tensor elements U_{ij} agree well with corresponding values calculated with the rigid-body parameters for C(1), O(1) and O(2) (Table 10). However, in both structures $(U_{ij})_{\text{observed}}$ exceeds $(U_{ij})_{\text{calculated}}$ for the hydroxylic deuterium atom. The difference is especially pronounced in the direction of

the L axes (r.m.s. amplitudes 0.09 and 0.07 Å in α - and β -DOX respectively), indicating a vibration of the deuterium atom in the shallow potential well between oxygen atoms 1 and 3. A similar, but larger effect has been observed by Sequeira, Berkebile & Hamilton (1968) for the symmetrical hydrogen bond in potassium hydrogen diaspinate where the corresponding amplitude for the hydrogen atom is 0.19 Å. The observed stretching frequency of the short O–H bond in oxalic acid dihydrate is 1900 cm^{-1} (Lord & Merrifield, 1953). In the harmonic approximation this corresponds to an r.m.s. amplitude of 0.093 Å (see Fig. 3). The corresponding r.m.s. amplitude of the deuterium in the deuterated compound at the frequency of 1348 cm^{-1} is 0.079 Å. Thus, the observed r.m.s. amplitudes of the deuterium atoms are in good agreement with the infrared data.

Table 10. Magnitudes $\times 10^4$, and directions of principal components of molecular translation and libration tensors \mathbf{T} and $\boldsymbol{\omega}$

Magnitude	Direction cosines of principal tensor axes along inertial axes L , M and N defined in Table 7.			
	L	M	N	
α -DOX				
$T(1)$	375 Å ²	0.1128	0.0730	0.9909
$T(2)$	254	0.3549	0.9345	0.0284
$T(3)$	241	0.9281	0.3485	0.1313
$\omega(1)$	270 rad ²	0.9975	0.0666	0.0220
$\omega(2)$	23	0.0251	0.0454	0.9987
$\omega(3)$	–13	0.0655	0.9968	0.0469
β -DOX				
$T(1)$	432 Å ²	–0.1848	0.2196	0.9579
$T(2)$	296	–0.0239	–0.9754	0.2190
$T(3)$	239	–0.9825	–0.0176	0.1855
$\omega(1)$	265 rad ²	–0.9925	0.1168	0.0365
$\omega(2)$	23	–0.0421	–0.0461	0.9981
$\omega(3)$	–17	–0.1149	–0.9921	0.0506

No rigid-body analysis was attempted for the water molecules as the number of observations (18) only slightly exceeds the number of rigid-body parameters to be determined (15 if the three librational axes are assumed to intersect).

Table 11. Observed and calculated thermal vibration tensor elements U_{ij} (Å² $\times 10^4$) of atoms in the oxalic acid molecules referred to molecular axes of inertia L , M and N

	C		O(1)		O(2)		D(1)	
	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc
α -DOX								
U_{11}	239	244	258	268	256	278	346	262
U_{22}	260	266	294	298	295	288	414	387
U_{33}	363	365	687	682	698	690	615	601
U_{12}	–2	1	38	35	–25	–31	50	53
U_{13}	11	15	17	7	6	10	3	7
U_{23}	–1	–10	–30	–21	–14	–5	–31	–29
β -DOX								
U_{11}	242	245	259	278	260	269	311	263
U_{22}	305	315	339	338	343	347	458	434
U_{33}	407	409	677	674	764	760	694	690
U_{12}	–4	–5	20	28	–40	–39	–51	–55
U_{13}	–38	–34	–33	–42	–63	–48	–37	–48
U_{23}	30	30	17	20	57	47	51	57

Bond lengths in the oxalic acid molecules corrected for rigid-body motion are given in Table 12.

Table 12. *Bond distances in the oxalic acid molecule corrected for thermal motion*

Standard deviations contain an arbitrary contribution equaling $\frac{1}{3}$ of the thermal motion correction.

Bond	α -DOX	β -DOX
C—C	1.539 (2)	1.538 (2)
C—O(1)	1.306 (5)	1.307 (5)
C—O(2)	1.222 (5)	1.216 (5)
O(1)—D(1)	1.032 (2)	1.021 (2)

Distribution of hydrogen isotopes

Before extinction was properly included in the refinement the results showed a small preference of the protons for the weaker hydrogen bond. This preference seems to have been an artifact introduced by the severe extinction; it disappeared in the final treatment (Table 13). It is however quite possible that the protons and deuterons distribute differently over the strong and weak hydrogen bonds, which have different frequencies and therefore different zero-point energies. An unequal distribution does in fact exist in a crystal containing 34% deuterium. This composition has been chosen so that, if random replacement took place, there would be practically no coherent scattering density at the hydrogen sites (Coppens, to be published).

Table 13. *Scattering length of deuterium (f) as determined by least-squares refinement*

($1f = 10^{-13}$ cm)

	α -DOX	β -DOX
D(1)	6.42 (5)	6.51 (4)
D(2)	6.35 (5)	6.53 (4)
D(3)	6.35 (6)	6.49 (4)

The deuterium scattering length

The scattering length of deuterium has recently been redetermined by Bartolini, Donaldson & Groves (1967) from a mirror-reflection experiment. The new value of $6.18 \pm 0.04 f$ is considerably different from the older recommended value, which was $6.77 \pm 0.08 f$ (BNL 325, Supplement 2, 1964). Because of this controversy, and also because the deuterium percentage in the crystal was not accurately known,* the deuterium scattering lengths were considered parameters in the least-squares refinement. It may be emphasized that the results are relative to the less controversial values of the scattering lengths of C and O (6.61 and $5.77 f$ respectively). The final values for the refined scattering lengths, given in Table 13, show that the deuterium scattering length cannot be lower than $6.51 \pm 0.02 f$, which is the average over the three sites in β -DOX. This assumes a 100% deuterium substitution, so the true value is probably higher.

* Deuterium analysis of the sample crystals showed the deuterium content to be 95% or larger.

The discrepancy between our value and the recent mirror experiment is in marked contrast to the agreement between the mirror and crystal-structure analysis results for the scattering length of ^{11}B : Craven & Sabine (1966) obtained $6.4 \pm 0.1 f$ for the boron atoms in $\text{D}_3^{11}\text{BO}_3$, while Donaldson, Passell, Bartolini & Groves (1965) obtained $6.6 \pm 0.3 f$ from the mirror experiments.

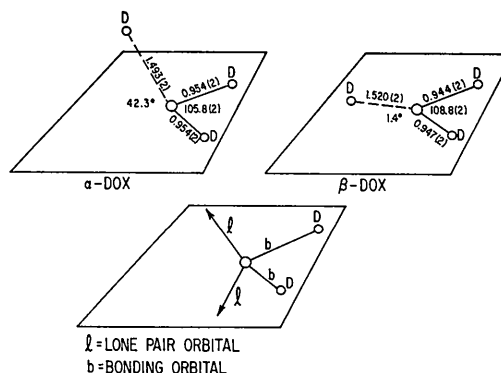


Fig. 2. Diagrammatic view of the water molecules in α -DOX and β -DOX. The numbers 42.3 and 1.4 indicate the angles between the $\text{O} \cdots \text{D}$ vector and the plane of the water molecule.

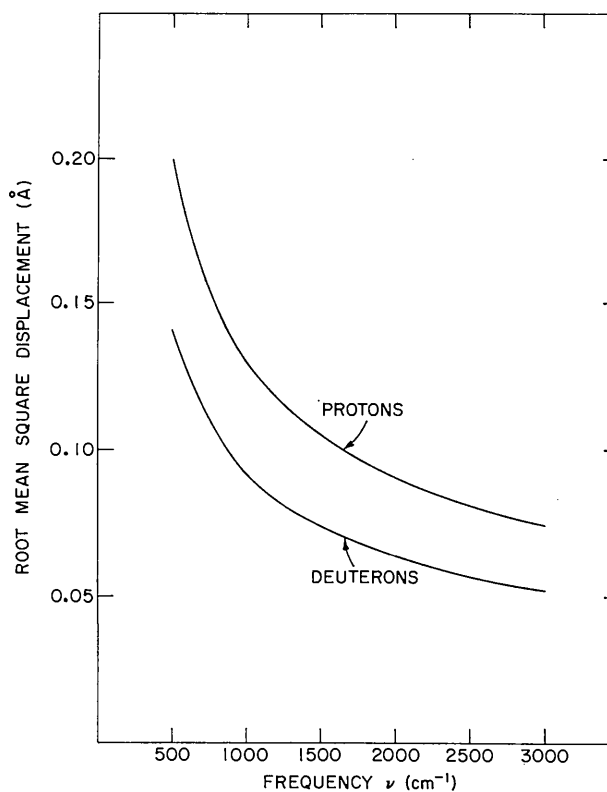


Fig. 3. R.m.s. displacement versus frequency for protons and deuterons in a harmonic potential at 300°K according to the expression

$$\langle u^2 \rangle = \frac{h}{4\pi^2 m_{\text{H,D}} \nu} \left\{ \frac{1}{2} + [\exp(h\nu/kT) - 1]^{-1} \right\}.$$

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References

- BAILEY, M. & BROWN, C. J. (1967). *Acta Cryst.* **22**, 387.
 BARTOLINI, W., DONALDSON, R. E. & GROVES, D. J. (1967). Univ. of California, Livermore, UCRL 70445.
 BEDNOWITZ, A. L., COPPENS, P. & HAMILTON, W. C. (1966). Abstracts of the Pittsburgh Diffraction Conference, November 1966.
 BROWN, C. J. (1966). *Acta Cryst.* **21**, 1.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
 CHIDAMBARAM, R., SEQUEIRA, A. & SIKKA, S. K. (1964). *J. Chem. Phys.* **41**, 3616.
 COPPENS, P. (1968). *Acta Cryst.* **A24**, 253.
 COPPENS, P. & HAMILTON, W. C. (1969). *Acta Cryst.* In the press.
 COPPENS, P., SABINE, T. M., DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2451.
 COULSON, C. A. (1961). *Valence*, 2nd. ed. p.203. Oxford Univ. Press.
 CRAVEN, B. M. & SABINE, T. M. (1966). *Acta Cryst.* **20**, 214.
 DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2423.
 DONALDSON, R. E., PASSELL, L., BARTOLINI, W. & GROVES, D. J. (1965). *Phys. Rev.* **138**, B1116.
 FUKUSHIMA, F., IWASAKI, H. & SAITO, Y. (1964). *Acta Cryst.* **17**, 1472.
 FUKUSHIMA, F., IWASAKI, H., SAITO, Y., SATO, S. & HOSHINO, S. (1965). *Bull. Chem. Soc. Japan*, **38**, 151.
 HAMILTON, W. C. (1962). *Ann. Rev. Phys. Chem.* **13**, 19.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
 HIRSHFELD, F. L. & RABINOVICH, D. (1966). *Acta Cryst.* **20**, 146.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 IWASAKI, F. F., IWASAKI, H. & SAITO, Y. (1967). *Acta Cryst.* **23**, 64.
 IWASAKI, F. F. & SAITO, Y. (1967). *Acta Cryst.* **23**, 56.
 LARSON, A. C. (1967). *Acta Cryst.* **23**, 664.
 LORD, R. C. & MERRIFIELD, R. E. (1953). *J. Chem. Phys.* **21**, 166.
 SABINE, T. M., COX, G. W. & CRAVEN, B. M. (1969). *Acta Cryst.* **B25**, 2437.
 SEQUEIRA, A., BERKEBILE, C. A. & HAMILTON, W. C. (1968). *J. Mol. Struct.* **1**, 283.
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.

Acta Cryst. (1969). **B25**, 2451

An Experimental Determination of the Asphericity of the Atomic Charge Distribution in Oxalic Acid Dihydrate*

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It is shown that a combination of X-ray and neutron diffraction methods will give meaningful information about the distribution of bonding electrons in a typical simple molecular crystal (oxalic acid dihydrate). Difference maps combining X-ray and neutron diffraction information show bond and lone-pair densities in analogy with an earlier study of *sym*-triazine. Discrepancies between X-ray and neutron positional and thermal parameters are discussed and compared with similar differences in some other compounds. It is concluded that molecular environment should be reflected in X-ray scattering factors if small systematic errors in some of the positional parameters and fairly large systematic errors in the temperature parameters are to be eliminated.

Introduction

McWeeny (1952, 1953, 1954) in a series of articles emphasized that X-ray diffraction data contain informa-

tion about the asphericity of the atomic charge distribution. Model calculations by Dawson (1964) on a hypothetical structure consisting of two non-spherically symmetric nitrogen atoms in the unit cell confirmed that the effect may be appreciable for first-row atoms. Dawson found, for example, that the *R* factor between the structure factors calculated with spherical nitrogen atoms and those calculated with the proper form factors for the prepared state may be as high as 8%. He also

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