Many diffractometers do not operate on the constant count principle but a very close approximation can be obtained to this mode of operation by arranging the time spent on each reflexion to be such that near constant counts are obtained.

Conclusion

It is clearly desirable to design an experiment for which the subsequent least-squares technique is geometry-independent. This being so, the mode of operation to be preferred should be constant count, variable time.

It is of interest to note that this technique is the diffractometer analogue of the much used multiple-film photographic technique where the intensities are measured in a relatively small optical density range.

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The Crystal Structure of Deuterated Oxalic Acid Dihydrate, $(COOD)_2.2D_2O$, by X-ray Analysis

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Crystals of deuterated oxalic acid dihydrate, $(COOD)_2.2D_2O$, are monoclinic with $a=10{\cdot}021$, $b=5{\cdot}052$, $c=5{\cdot}148$ Å, $\beta=99{\cdot}27°$, $Z=2$, space group $P2_1/a$. They are not isomorphous with those of $(COOH)_2.2H_2O$. The structure was determined by Harker–Kasper inequalities and Fourier method using visually estimated Cu $K\alpha$ data. Positional and anisotropic thermal parameters were refined by the full-matrix least-squares method, the final R index being 0·073 for 506 observed reflexions. The oxalic acid molecules and the water molecules are linked with hydrogen bonds which make three-dimensional networks. The hydrogen bond distances O–D···O are 2·540, 2·854 and 2·822 Å.

Introduction

Ubbelohde and his coworkers have done extensive work on the isotope effect of deuterium substitution on structures of hydrogen bonded crystals (Robertson & Ubbelohde, 1939; Ubbelohde, 1939; Ubbelohde & Woodward, 1942; Dickson & Ubbelohde, 1950; Gallagher, Ubbelohde & Woodward, 1954). They reported that the maximum isotope effects were found to lie near the directions of the short hydrogen bonds and concluded that these short hydrogen bonds were subjected to a considerable expansion by the deuterium substitution, while for the long hydrogen bonds no appreciable effect was observed. These conclusions were derived, however, from the variations of the unit-cell dimensions alone, and no attempt was made to determine the positional parameters of the deuterated crystals.

It is widely known that the crystal structures of compounds containing hydrogen are not affected by the substitution of hydrogen by deuterium. However, in some exceptional cases the effect of substituting deuterium for hydrogen is so large as to give rise to the spontaneous crystallization of a different structure, as in the case of potassium dihydrogen phosphate (Ubbelohde & Woodward, 1939) or resorcinol (Robertson, 1936, 1938).

In the case of the crystals of oxalic acid dihydrate, $(COOH)_2.2H_2O$, an investigation of the isotope effect was also carried out by Robertson & Ubbelohde (1939). They reported that the crystals of deuterated oxalic acid dihydrate, $(COOD)_2.2D_2O$, are isomorphous with those of $(COOH)_2.2H_2O$ (Robertson & Woodward, 1936), and that the short hydrogen bonds are expanded by the substitution of deuterium. The crystal structure of $(COOH)_2.2H_2O$ was further refined (Ahmed & Cruickshank, 1953; Garrett, 1954) although the result was not essentially different from the structure previously reported (hereafter called the α form). Recently a nuclear magnetic resonance study was made for a single crystal of deuterated oxalic acid dihydrate (Chiba, 1964), and it was found that the O–D direction in this crystal could not be interpreted on the basis of the ordinary structure of $(COOH)_2.2H_2O$. By an X-ray study it was shown that the crystal of $(COOD)_2.2D_2O$ represents a new modification (hereafter called the β form) (Fukushima, Iwasaki & Saito, 1964; Fukushima, Iwasaki, Saito, Sato & Hoshino, 1965).

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In order to make clear the difference between these two forms, the determination of the crystal structure of deuterated oxalic acid dihydrate (β form) was undertaken by a three-dimensional X-ray analysis.

Experimental

10 g of anhydrous oxalic acid was dissolved in 40 ml warm heavy water (99·75 mole% D_2O) and the solvent was evaporated. This procedure, after three or four repetitions, was followed by recrystallization from D_2O. The crystals obtained were colorless and rhomboidal in form. A high concentration of D_2O was necessary for their formation. When the solutions were cooled rapidly, occasionally needle-like crystals grew which had the same habit as $(COOH)_2.2H_2O$ (α form). The rhomboidal crystals (β form) were always obtained when the concentration of D_2O was high and the crystallization was carried out slowly. We shall hereafter deal with this form of crystal.

The crystals exhibit dominant {100}, {110}, {001} and {111} faces. No distinct cleavage is observed. Morphological characteristics of this crystal are entirely different from those of $(COOH)_2.2H_2O$. Fig. 1 shows the crystal habits of these two kinds of crystal.

The crystals are monoclinic. The cell dimensions were determined with a single-crystal diffractometer and Cu $K\alpha$ radiation ($\lambda = 1·5418$ Å). The crystal data are listed in Table 1, together with those of $(COOH)_2.2H_2O$.

Approximately cylindrical crystals having an average radius of 0·1 mm were used for collecting intensity data. They were coated with Gryptal to prevent dehydration and isotope exchange. Even with these precautions, the crystals were not stable, and they had to be replaced several times during the whole course of collecting the intensity data. The intensity data were recorded on equi-inclination Weissenberg photographs by the multiple-film technique with Cu $K\alpha$ radiation.

Table 1. *Crystal data*

	$(COOD)_2.2D_2O$	$(COOH)_2.2H_2O$*
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$
a	10·021 ± 0·008 Å	11·88 Å
b	5·052 ± 0·008	3·60
c	5·148 ± 0·006	6·12
β	99·27° ± 0·07°	103·5°
Z	2	2
V	257 Å^3	254 Å^3

* The unit cell of the α form has been transformed in conformity with that of the new modification.

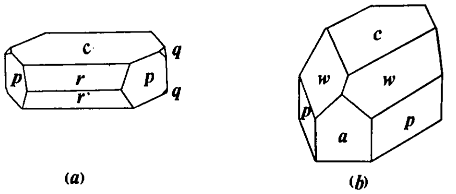


Fig. 1. The crystal habits of α- and β-oxalic acid dihydrate. (*a*) $(COOH)_2.2H_2O$ (α form). (*b*) $(COOD)_2.2D_2O$ (β form). $a = \{100\}$, $c = \{001\}$, $p = \{110\}$, $r = \{101\}$, $r' = \{10\bar{1}\}$, $w = \{111\}$. (The indices of the α form are given after Groth (1910). They are based on the space group $P2_1/n$, not $P2_1/a$.)

Four layers $hk0$–$hk3$ were collected about the c axis and five layers $h0l$–$h4l$ about the b axis. The intensities were estimated visually by comparison with a standard scale. Of the 579 independent reflexions within the effective copper limiting sphere ($\sin\theta = 0·993$), 506 non-zero reflexions were observed. The intensities covered a range of about 40000:1.

The usual Lorentz and polarization correction and the Phillips spot shape correction were applied. Absorption effect was so small (max. $\mu R = 0·16$) that it was neglected. It was found later that the extinction effect was also negligible. The structure factors obtained from various sets of layer line photographs were put on the same scale by the least-squares method. They were placed on an approximately absolute scale by Wilson's graphical method. At a later stage of refinement the scale factor was treated as a parameter.

Structure determination

A preliminary structure of $(COOD)_2.2D_2O$ was obtained by the two-dimensional Fourier method. Harker–Kasper inequalities,

$$\{U(hkl) \pm U(h'k'l')\}^2 \le \{1 \pm U(h+h', k+k', l+l')\} \times \{1 \pm U(h-h', k-k', l-l')\},$$

were used in solving both (001) and (010) projections, by employing the graphical method developed by Sakurai (1952).

For $hk0$ data signs of 23 out of the 60 observed reflexions were determined. A Fourier synthesis computed with these signs showed the molecules clearly. After the refinements only one of the signs was found to be incorrect. Calculation of the structure factors with the first trial atomic parameters obtained from this electron density projection gave a reliability index $R = 0·31$. A Fourier synthesis based on the calculated phases indicated small shifts of the atomic parameters, and recalculation taking account of these shifts reduced R to 0·23.

For the (010) projection, signs of 8 out of the 59 reflexions were determined uniquely and signs of 27 other reflexions were established with reasonable certainty in terms of the two sign symbols q and r. Using the result of the c-axis projection, $qr = S(10,0,0) = -1$. Fourier syntheses corresponding to the remaining two sign-combinations, $q = \pm 1$, were computed. The synthesis corresponding to $q = -1$ (hence $r = +1$) showed the molecule consistent with the model which had been deduced from the (001) projection. The calculation of the structure factors with the atomic parameters obtained from this electron density map gave a reliability index $R = 0·33$.

The positional parameters and individual isotropic temperature factors were refined by successive two-dimensional Fourier syntheses and by difference Fourier syntheses until the R index was reduced to 0·13 for both $hk0$ and $h0l$ reflexions. At this stage, all the deuterium atoms appeared, although not completely resolved, on the difference electron-density projections. Strong anisotropic thermal motions of the atoms were also indicated on these maps.

The three-dimensional refinement of the structure was carried out in the following two steps. First, 506 reflexions were used to refine the atomic coordinates and individual isotropic temperature factors of the carbon and oxygen atoms, and an overall scale factor by the diagonal least-squares method. After four cycles the R index was reduced from 0·198 to 0·181 for all hkl reflexions including unobserved ones. A further refinement was carried out by the full-matrix least-squares method with anisotropic temperature factors. In these cycles all the deuterium atoms, with their positional and isotropic thermal parameters which were determined by a neutron diffraction study (Iwasaki, Iwasaki & Saito, 1967), were included in the structure factor calculations. The deuterium parameter, however, was not refined. After two more cycles of refinements the R index was reduced to 0·080 including unobserved reflexions, and 0·073 with non-zero reflexions. The shifts in the final cycle were less than one-tenth of the e.s.d.

In Table 3 are given the final positional parameters and also the anisotropic temperature factors β_{ij} which are defined as the coefficients in the expression

$$\exp\left[-\left(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{23}kl+2\beta_{13}hl\right)\right].$$

A comparison of the observed and calculated structure factors is given in Table 4.

It must be added that two more cycles of least-squares refinement were tried with the hope of improving the positional parameters of deuterium atoms. The R index was then slightly improved (0·079 including unobserved reflexions and 0·072 omitting zeros), but the O–D bond lengths became too short. Therefore, these results were not adopted as the final parameters.

The final three-dimensional electron-density map is shown in Fig. 2. The three-dimensional difference Fourier synthesis based on the differences between the observed structure factors and those calculated from the positional parameters of carbon and oxygen atoms clearly showed the peaks for deuterium atoms near the positions expected (Fig. 3). A final three-dimensional difference Fourier synthesis, (C, O and D atoms subtracted), showed no significant spurious peak.

Table 2. *Unitary structure factors and signs determined by the inequalities*

*hk*0 data								*h*0*l* data							
h	*k*	|*U*|	*S*	*h*	*k*	|*U*|	*S*	*h*	*l*	|*U*|	*S*	*h*	*l*	|*U*|	*S*
2	0	0·17		2	3	0·09		2	0	0·17		6	5	0·14	
4	0	0·19	−	3	3	0·23	+	4	0	0·17	qr	0	6	0·36	q
6	0	0·57	+	4	3	0·24		6	0	0·46	+	2	6	0·34	r*
8	0	0·31		5	3	0·11	+*	8	0	0·32		−2	1	0·01	
10	0	0·75	−	6	3	0·02		10	0	0·63	qr	−4	1	0·47	+
12	0	0·26	−	7	3	0·31	−	12	0	0·27		−6	1	0·37	qr*
1	1	0·28	+	8	3	0·02		0	1	0·22	qr	−8	1	0·22	
2	1	0·05		9	3	0·08	+	2	1	0·25	q	−10	1	0·76	+
3	1	0·35		10	3	0·22		4	1	0·38	r*	−12	1	0·10	
4	1	0·30	+	11	3	0·03		6	1	0·29	qr	−2	2	0·61	q
5	1	0·13		0	4	0·05	−	8	1	0·34	q	−4	2	0·11	
6	1	0·52	+	1	4	0·05		10	1	0·09		−6	2	0·09	
7	1	0		2	4	0·36		12	1	0·32	r	−8	2	0·33	q
8	1	0·20		3	4	0·06		0	2	0·16		−10	2	0·20	qr*
9	1	0·13		4	4	0·36	+	2	2	0·30	r	−12	2	0·42	r
10	1	0		5	4	0·18		4	2	0·40	q	−2	3	0·37	r
11	1	0·33	−	6	4	0·37	−	6	2	0·15		−4	3	0·14	
12	1	0·24	+	7	4	0·34		8	2	0·43	r	−6	3	0·67	q
0	2	0		8	4	0·27		10	2	0·21	q	−8	3	0·17	
1	2	0·46	−	9	4	0·09		0	3	0·32	q	−10	3	0·09	
2	2	0·19		1	5	0·53		2	3	0·06		−12	3	0·80	q
3	2	0·10		2	5	0·41	+	4	3	0·24	r	−2	4	0·09	
4	2	0		3	5	0·15		6	3	0·06		−4	4	0·06	
5	2	0·77	+	4	5	0·06		8	3	0		−6	4	0	
6	2	0·02		5	5	0·08		10	3	0·10		−8	4	0·09	
7	2	0·03		6	5	0·09		0	4	0·09		−10	4	0·30	q
8	2	0·31		7	5	0·02		2	4	0·38	+	−2	5	0·63	+
9	2	0·03	−	0	6	0·30		4	4	0·30	qr*	−4	5	0·18	
10	2	0·02		1	6	0·18	+	6	4	0·09		−6	5	0·29	
11	2	0·38	+	2	6	0·22		8	4	0·43	+	−8	5	0·61	+
1	3	0·28	−	3	6	0·37		0	5	0·38		−2	6	0·39	qr
								2	5	0·24		−4	6	0·08	
								4	5	0·06		−6	6	0·40	+

* marks reflexions with incorrect signs.

Computing procedures

The reduction of the original data, the first attempts to get an approximate structure, and also all other calculations not mentioned in the following, were carried out on the FACOM 202 computer installed in this Institute.

Interlayer correlations were calculated by the least-squares equations of Rollett & Sparks (1960) programmed by T. Sakurai on the CDC 3600 computer at C. Ito Electronic Computing Service Co., Ltd. The three-dimensional Fourier summation was carried out on the FACOM 202 computer using the program written by H. Iwasaki. Diagonal least-squares refinement was carried out by use of the program written by Y. Iitaka.

The full-matrix least-squares refinement was carried out with the program ORFLS of Busing, Martin & Levy (1962) on the IBM 7090 computer under the University Contribution System of Japan IBM Co. Ltd. and in part on the same type of computer at Mitsubishi Atomic Power Industries, Inc.

These least-squares refinements were performed by minimizing the function,

$$R=\Sigma\, w(hkl)\{|F_o|-|F_c|\}^2\,,$$

where the sum is taken over all independent reflexions and $w(hkl)$ is the weight for each term. In the present work the weighting scheme is as follows:

$w=0\cdot01$ for $F_o=0$,
$w=0\cdot25$ for large $|F_o|$'s and those which have large e.s.d.'s from a calculation of the net scaling. They are marked by an asterisk in Table 4.
$w=1$ for all other $|F_o|$'s.

The atomic scattering factors used for these calculations are taken from *International Tables for X-ray Crystallography* (1962).

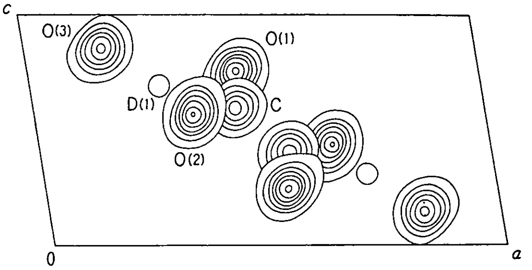


Fig. 2. Sections of the final three-dimensional electron density map through the atomic centers parallel to (010). The contours are at intervals of 2·0 e.Å^{-3}, starting with the 1·0 e.Å^{-3} contour.

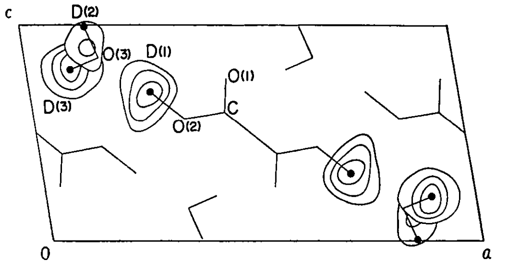


Fig. 3. Sections of the final three-dimensional difference Fourier map through the atomic centers parallel to (010). The contours are at intervals of 0·2 e.Å^{-3}, starting with the 0·2 e.Å^{-3} contour. Black circles indicate the positions of deuterium atoms obtained from a neutron diffraction study.

Results and discussion

The oxalic acid molecule has a center of symmetry coincident with that of the crystal. The acid molecule lies completely in one plane which makes an angle of 53·4° with the plane (010), whereas the corresponding angle in the α form is 29°. The equation of the molecular plane is

$$2\cdot931X+1\cdot988Y+2\cdot000Z=1$$

where X, Y and Z are the fractional coordinates referred to the crystal axes a, b and c. The deviations of the atoms from this plane are given in Table 5. The planarity of the $(COO)_2$ group was also found in anhydrous oxalic acid (Cox, Dougill & Jeffrey, 1952), α-oxalic acid dihydrate (Ahmed & Cruickshank, 1953), sodium oxalate (Jeffrey & Parry, 1952) and potassium oxalate monohydrate (Pedersen, 1964), whereas in ammonium oxalate monohydrate (Robertson, J. H., 1965) the two carboxyl groups are rotated by 26·6°.

The bond lengths and angles are listed in Table 6. The standard deviations of the bond distances are 0·004 Å and those of the angles are 0·3° on the average.

Two C–O distances of the carboxyl group are significantly different. The shorter bond (1·201 Å) which is typical of the double bond length is associated with a

Table 3. *The final parameters and their estimated standard deviations*

The anisotropic temperature factors are of the form:

$$\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{23}kl+2\beta_{13}hl)].$$

The values of the deuterium atoms are those obtained from the neutron diffraction study. Temperature factors are multiplied by 10^4. E.s.d.'s in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C	0·0503 (3)	0·0230 (7)	0·4040 (6)	68 (3)	263 (13)	281 (12)	0 (6)	54 (5)	4 (10)
O(1)	0·0371 (2)	0·2002 (5)	0·2464 (5)	94 (3)	331 (11)	375 (10)	34 (5)	100 (4)	117 (9)
O(2)	0·1466 (2)	−0·1519 (5)	0·4360 (5)	85 (3)	348 (11)	447 (11)	52 (5)	108 (4)	121 (9)
O(3)	0·3281 (3)	−0·0793 (6)	0·1511 (5)	108 (3)	477 (14)	452 (12)	−86 (5)	134 (5)	209 (11)
D(1)	0·217 (4)	−0·121 (8)	0·309 (7)	56	215	212	0	17	0
D(2)	0·152 (4)	0·328 (9)	−0·003 (8)	56	215	212	0	17	0
D(3)	0·106 (4)	0·556 (9)	0·798 (8)	64	244	241	0	20	0

Table 4. *Observed and calculated structure factors*

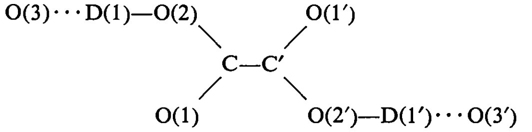
h	10Fo	10Fc
h	0	0
2	131	150
4	95	-103
6	176	185
8	66	-68
10	102	-105
12	22	-22
h	0	1
-12	6	8
-10	134	130
-8	43	49
-6	131	136
-4	344	380
-2	49	-49
0	227	-225
2	191	-197
4	191	-195
6	84	-88
8	65	-64
10*	9	7
12	25	30
h	0	2
-12	41	43
-10	21	18
-8	67	-72
-6	20	-18
-4	40	-47
-2	519	-513
0	96	-89
2	186	177
4	156	-163
6	26	27
8	77	71
10	18	-20
h	0	3
-12	87	-87
-10	7	5
-8	22	31
-6	207	-209
-4	35	35
-2	150	146
0	134	-125
2	0	-7
4	55	52
6	6	-8
8	0	-6
10*	6	6
h	0	4
-10	26	-29
-8	0	-8
-6	4	-12
-4	10	9
-2	15	15
0	15	-15
2	78	74
4	45	44
6	5	1
8	23	28
h	0	5
-8	73	76
-6	30	36
-4	20	-22
-2	118	119
0	50	55
2	26	-28
4	4	2
6	9	-11
h	0	6
-6	38	41
-4	5	-7
-2	38	-44
0	35	-39
2	27	-33
h	1	0
1	222	223
2	30	-32
3	196	208
4	144	-148
5	47	-45
6	162	-168
7	0	-5
8	40	-43
9	23	-25
10	0	-0
11	60	-60
12	21	-22
h	1	1
-12	14	13
-11	8	9
-10	12	10
-9	90	93
-8	81	83
-7	84	85
-6	11	-13
-5	62	-57
-4*	301	-305
-3*	275	270
-2	66	-65
-1	5	-7
0	64	-60
1	514	-515
2	454	-456
3	48	48
4	46	-41
5	30	-29
6	90	91
7	93	-96
8	22	-25
9	34	37
10*	4	5
11	24	27
12	23	30
h	1	2
-12	19	17
-11*	3	1
-10	14	-14
-9	77	-79
-8	151	-150
-7	51	47
-6	54	-58
-5	108	-108
-4	6	-2
-3*	214	-221
-2*	174	-179
-1	92	97
0	26	-30
1	10	13
2	142	143
3*	11	-6
4	67	63
5	58	54
6	30	26
7	16	14
8	30	28
9*	4	4
10	18	17
11	11	-11
h	1	3
-12	27	-31
-11	12	-13
-10	38	-39
-9	24	-21
-8	0	2
-7	31	35
-6	39	41
-5	13	12
-4	14	12
-3	15	-14
-2	51	55
-1	115	121
0	161	175
1	44	-43
2	63	58
3	75	-69
4	21	-23
5	22	22
6	36	35
7	32	-34
8	0	6
9	14	-16
10	15	-18
h	1	4
-11	49	56
-10	65	67
-9	31	-35
-8	17	22
-7	21	-30
-6*	4	-10
-5	62	64
-4	111	125
-3	92	-103
-2	47	52
-1	56	-60
0	53	-56
1	52	54
2	35	8
3	7	0
4	0	2
5	15	15
6	32	-33
7	28	32
8	12	-13
h	1	5
-8	31	31
-7	27	-25
-6	13	15
-5	19	25
-4	32	-34
-3	38	43
-2	34	-37
-1	29	33
0	26	-28
1	36	40
2	21	-21
3	0	3
4	18	-21
5	0	-5
6	6	-7
h	1	6
-6	46	-50
-5	22	23
-4	32	-34
-3	12	14
-2	7	10
-1	42	-48
0	9	-12
1	18	-21
2	0	-4
3*	7	-10
h	2	0
0	12	5
1	275	266
2	93	-83
3	44	-45
4	0	-6
5	245	-247
6*	7	-7
7	9	12
8	56	-58
9*	6	8
10	0	5
11	39	-38
12	6	7
h	2	1
-11	10	-10
-10	12	10
-9	89	77
-8	21	-17
-7	18	-17
-6	14	12
-5	143	-138
-4	62	-55
-3*	8	-7
-2	252	-227
-1	96	-84
0	24	18
1	184	-169
2*	8	3
3	65	-60
4	66	-62
5*	14	-4
6	71	67
7	24	20
8	52	50
9	0	2
10	25	24
11*	7	3
h	2	2
-12	26	-28
-11	7	-6
-10	0	-2
-9	20	-16
-8	69	-58
-7	108	-100
-6	105	-98
-5	48	-42
-4	77	69
-3	106	93
-2	75	65
-1	146	-139
0	107	99
1	41	-35
2	158	156
3	180	178
4	81	75
5	26	-29
6	58	52
7	25	-24
8	11	-6
9	44	40
10	30	-27
h	2	3
-11	66	-58
-10*	5	10
-9	10	-9
-8	61	56
-7	116	101
-6	87	80
-5	81	-73
-4	157	160
-3	24	-22
-2	55	53
-1	147	147
0	33	-31
1	0	-2
2	0	9
3	22	-19
4	90	-80
5	47	44
6	75	-72
7	13	10
8	19	-16
9	6	-4
h	2	4
-10	35	35
-9*	5	1
-8	59	53
-7	0	6
-6	58	-54
-5	32	28
-4	80	-79
-3	39	38
-2	47	-47
-1	32	31
0	92	-93
1*	20	-15
2	45	-41
3	13	12
4	0	4
5	0	12
6	17	15
7	22	-22
8	18	22
h	2	5
-8	46	-41
-7	49	44
-6	41	-39
-5	40	41
-4	16	-15
-3	67	-63
-2	25	31
-1*	4	-2
0	14	13
1*	9	11
2	29	29
3	42	-42
4	26	27
5	14	-14
h	2	6
-5	15	-16
-4	0	-4
-3	0	-7
-2	13	12
-1	22	-21
0	8	7
1	5	-4
h	3	0
1	92	-95
2	32	-30
3	68	62
4	66	67
5	28	-32
6	0	4
7	57	-56
8*	6	0
9*	6	-9
10	23	22
h	3	1
-11*	9	-11
-10	38	-34
-9	37	-33
-8*	11	-5
-7	50	51
-6	43	44
-5	16	-12
-4	76	-78
-3	141	-149
-2	52	48
-1	46	-44
0	136	133
1	43	40
2	67	-61
3	67	-60
4	73	69
5	31	-28
6	53	51
7	81	75
8	36	-37
9	44	42
h	3	2
-10	14	13
-9	0	-5
-8	32	-31
-7	75	-68
-6	83	82
-5	70	-69
-4	69	67
-3	93	88
-2	32	-29
-1	104	98
0	78	74
1	12	7
2	9	-8
3	129	122
4	74	-72
5	92	86
6	15	-11
7	12	-10
8	22	-19
10	3	-16
h	3	3
-10	46	37
-9	17	-13
-8	0	-3
-7	75	73
-6*	16	8
-5	127	127
-4	0	-1
-3	40	37
-2	96	-93
-1	34	31
0	35	-31
1	29	28
2	32	-28
3	35	-30
4	44	-45
5	72	-65
6	23	22
7	43	-36
8	13	12
h	3	4
-9	60	51
-8	49	-40
-7	21	18
-6	64	-70
-5	62	-66
-4	22	24
-3	60	-57
-2	21	-23
-1	19	-16
0	17	-12
1	76	-70
2	64	64
3	44	-40
4	19	17
5	32	28
6	4	1
h	3	5
-7	52	-49
-6	0	-1
-5	9	10
-4	24	24
-3	13	-13
-2	42	40
-1	9	-7
0	0	1
1	33	30
2	0	5
3	14	14
h	4	0
0	13	-16
1	12	14
2	79	78
3	14	-16
4	64	65
5	28	27
6	56	-57
7	43	48
8	31	-33
9	11	-10
10	2	1
h	4	1
-9*	8	-3
-8	46	43
-7	34	-35
-6	54	58
-5	21	22
-4	0	-1
-3	52	56
-2	19	-18
-1*	28	-39
0	0	2
1	70	76
2	68	-73
3	93	102
4	59	-60
5	12	-13
6	0	-1
7	17	16
8	0	0
9	15	20
h	4	2
-9	33	35
-8	0	3
-7	57	52
-6	64	-60
-5	0	-4
-4	50	-46
-3	74	75
-2	13	10
-1	67	65
0	20	-19
1	0	-6
2	13	-14
3	16	-11
4	60	59
5	44	-41
6	31	29
7	22	-23
8	9	-9
h	4	3
-9	22	25
-8	20	-21
-7	19	18
-6	55	49
-5	26	-26
-4	27	21
-3*	17	-4
-2	24	-19
-1	57	-55
0	47	49
1	92	-100
2	23	21
3	0	-5
4	39	-39
5*	8	-5
6	0	-0
7	16	-20
h	4	4
-7	15	-5
-6	23	-16
-5	47	-46
-4*	12	-5
-3	60	-59
-2	0	-2
-1	22	22
0	14	-13
1	14	13
2	0	-3
3	0	9
4	0	5
5	15	23
h	4	5
-4*	27	31
-3	16	17
-2	0	-2
-1	30	35
h	5	0
1	73	80
2	53	-62
3	20	23
4	9	11
5	9	10
6	9	-10
7	4	0
h	5	1
-5	51	63
-4*	12	-2
-3	16	17
-2	44	-52
-1	14	-17
0	18	-19
1	16	-15
2	20	23
3	49	-55
4	20	24
5	31	-36
6*	4	2
7*	4	-5
h	5	2
-6	12	11
-5	22	-20
-4	17	-16
-3	29	-29
-2	33	31
-1	57	-59
0	61	66
1*	3	-8
2	21	-19
3	18	18
4	0	-2
5	12	-14
6	18	21
h	5	3
-5	18	-17
-4	35	35
-3	15	13
-2	26	-24
-1	0	2
0	19	-26
1*	8	-7
2*	6	-5
3	0	8
4	8	-13
h	6	0
0	25	29
1	16	-20
2	17	23
3	26	-33
h	6	1
-4*	9	13
-3	20	-30
-2	16	25
-1	37	-50
0	25	-33
1*	9	-12
2	18	-24
h	6	2
-2	16	-16
-1	16	18
0	14	14
1	15	15

CCO angle of 111·5°. The difference Fourier map clearly shows that the deuterium atom is attached to the oxygen atom of the long C–O bond, which is shorter than the ordinary C–O single bond length (1·41 Å). This is probably due to the formation of a hydrogen bond. In α-oxalic acid dihydrate the oxygen atom of the longer C–O bond, 1·285 Å, is associated with a hydrogen bond of 2·491 Å.

Table 5. *Deviations of the atoms from the best plane through the carbon and oxygen atoms of the oxalic acid molecule*

$2{\cdot}931X+1{\cdot}988Y+2{\cdot}000Z=1$

Atom	Deviation	Atom	Deviation
C	0·0016 Å	C′	−0·0016 Å
O(1)	−0·0053	O(1′)	0·0048
O(2)	−0·0046	O(2′)	0·0040
D(1)	0·020	D(1′)	−0·020
O(3)	0·1609	O(3′)	−0·1609



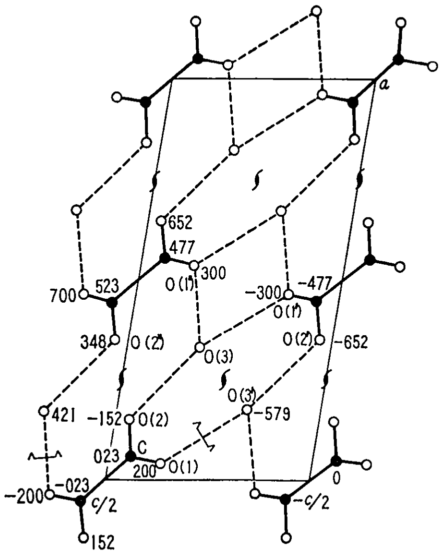


Fig. 4. Projection of the structure along the *b* axis. Black circles, C; open circles, O. The broken lines indicate the hydrogen bonds. The broken lines with _/___/_ indicate that an atom at one end displaced one unit cell along the *b* axis is linked with the atom at the other end of the broken line.

The oxalic acid molecules and the water molecules are linked together with hydrogen bonds forming a three-dimensional network as shown in Figs. 4 and 5 with broken lines. In Fig. 4, there exist a series of bonds starting from O(1) and going through O(2) and the water oxygen atom O(3), across the carboxyl group to O(2′) and back to O(3′). Thus one can see that the O(3′) is linked to O(1) of the carboxyl group displaced one unit cell along the *b* axis from the starting point and, therefore, a helical chain of hydrogen bonds is formed parallel to the *b* axis. Another type of hydrogen bond, for example O(3)···O(1″), connects the adjacent two helical chains of hydrogen bond.

The general features of this hydrogen bond network of the crystal are similar to those found for α-oxalic acid dihydrate. The hydrogen bond distances as obtained in this investigation are 2·540, 2·854 and 2·822 Å, while in α-oxalic acid dihydrate they are 2·491, 2·885 and 2·879 Å, respectively. The short hydrogen bond O(2)···O(3) connects the hydroxyl oxygen atom with the water oxygen atom. A detailed discussion of the hydrogen bond in this structure will be given in the following paper (Iwasaki, Iwasaki & Saito, 1967).

All other intermolecular approaches correspond to the normal van der Waals interactions. They are listed in Table 7.

Analysis of the thermal vibration

The anisotropic vibrational parameters are converted to the root mean square displacements, $(\overline{u_i^2})^{\frac{1}{2}}$, from the mean atomic position of each atom, in the directions of the three principal axes of the ellipsoid of vibration.

With the center of the C–C bond as origin, the molecular axes were chosen as follows; *L*, parallel to the C–C bond, *M*, perpendicular to *L* and in the plane of the oxalic acid molecule, and *N*, perpendicular to *L* and *M*. The anisotropic thermal paramcters β_{ij} listed in Table 3 were transformed to the thermal vibration tensor components U_{ij} (Å²) referred to the molecular axes *L*, *M* and *N*, which are shown in Table 8. For

Table 6. *Bond lengths and angles*

	$(COOD)_2.2D_2O$ Present work	$(COOH)_2.2H_2O$ X-rays (Ahmed *et al.*)	$(COOH)_2.2H_2O$ Neutrons (Garrett)
C–C	1·539 ± 0·005 Å	1·529 Å	1·533 Å
C–O(1)	1·201 ± 0·004	1·187	1·229
C–O(2)	1·300 ± 0·004	1·285	1·254
O(2)-[D(1)]···O(3)	2·540 ± 0·004	2·491	2·518
O(1)···[D(2)]-O(3)	2·854 ± 0·005	2·885	2·856
O(1)···[D(3)]-O(3)	2·822 ± 0·004	2·879	2·840
∠ O(1)CO(2)	126·23° ± 0·30°	125°48′	126°43′
∠ CCO(1)	122·31 ± 0·27	121 38	120 54
∠ CCO(2)	111·46 ± 0·32	112 34	112 22
∠ O(2)O(3)O(1)	145·41 ± 0·14		

Table 7. *Intermolecular distances between molecule* 1 *and neighboring molecules*

Molecule			
1 at	x,	y,	z
2	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$-z$
3	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z
4	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$1-z$
5	x,	$1+y$,	z
6	$\frac{1}{2}+x$,	$-\frac{1}{2}-y$,	z

Atom (in molecule 1)	to atom	in molecule	d
O(1)	O(3)	1	3·346 Å
O(3)	O(2)	2	3·756
O(3)	O(3)	2	3·235
O(3)	C	3	3·690
C	O(2)	4	3·434
C	O(3)	4	3·142
O(1)	O(2)	4	3·407
O(1)	O(3)	4	3·367
O(2)	O(2)	4	3·266
O(2)	O(3)	4	3·575
O(3)	O(2)	4	3·012
O(1)	O(2)	5	3·539
O(3)	C	6	3·278
O(3)	O(1)	6	3·760
O(3)	O(2)	6	3·561

The standard deviations are 0·005 Å on the average.

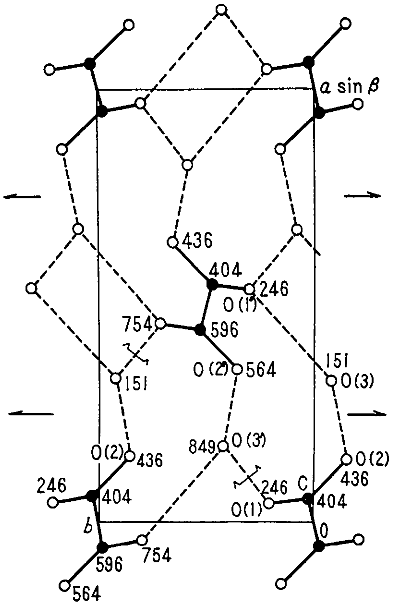


Fig. 5. Projection of the structure along the c axis. Black circles, C; open circles, O.

the sets of U_{ij}'s, principal axis transformations have been performed on the thermal ellipsoids of the four heavy atoms. The direction cosines relating the principal axes to the molecular axes (L, M, N), and the root mean square vibrational displacements along each principal axis are given in Table 9. A schematic representation is shown in Fig. 6, in which the root mean square displacement along each of the principal axis is plotted on the axis as it projects on the average plane of the molecule of oxalic acid. To help showing the axial directions, the ellipses have been drawn through the points representing the root mean square displacement.

Table 9. *The direction cosines* (l_1, l_2, l_3) *of the principal axes of anisotropic temperature factors relative to the molecular axes* (L, M, N) *and the root mean square vibrational displacements* (*r.m.s.d.*)

	r.m.s.d.	l_1	l_2	l_3
C	0·158 Å	0·993	−0·118	0·023
	0·184	0·097	0·838	0·552
	0·203	0·067	0·548	−0·834
O(1)	0·155	0·971	0·236	0·030
	0·188	0·237	−0·965	−0·115
	0·265	0·002	0·119	−0·993
O(2)	0·157	0·929	−0·366	0·032
	0·186	0·361	0·924	0·124
	0·278	0·075	0·103	−0·992
O(3)	0·160	0·949	−0·207	0·236
	0·318	0·147	0·957	0·251
	0·192	0·278	0·204	−0·939

As is clear from Fig. 6, the largest principal axes for C, O(1) and O(2) lie close to the normal of the molecular plane. The mean square displacements of O(1) and O(2) along the long principal axis are larger than that of C. Along the two other principal axes the mean square displacements are of the same order for each of the atoms, C, O(1) and O(2). These facts suggest that the librational motion of the whole molecule takes place about the C–C axis. On the other hand, for the oxygen atom O(3) of the water molecule the longest principal axis lies near to the M axis.

If the oxalic acid molecule is assumed as a rigid body, its thermal motion as a whole can be analyzed by the method of Cruickshank (1956). The rigid body

Table 8. *Anisotropic temperature factor coefficients referred to the molecular axes* (Å^2 × 10^{-2})

	C		O(1)		O(2)	
	obs.	calc.	obs.	calc.	obs.	calc.
U_{11}	2·51	2·37	2·47	2·60	2·62	2·70
U_{22}	3·61	3·36	3·54	3·68	3·36	3·58
U_{33}	3·91	3·91*	6·99	6·99*	7·68	7·68
U_{12}	0·13	0·08	−0·26	−0·25	0·37	0·42
U_{23}	−0·33	−0·33	−0·42	−0·39	−0·43	−0·48
U_{13}	−0·04	−0·10	−0·04	−0·01	−0·35	−0·31

* Based on the assumption of $\omega_{12}=0$

vibrations are expressed in terms of two symmetric tensors: T, the anisotropic translational vibrations of the center of mass, and ω, the anisotropic angular oscillations about axes through the center. For a planar molecule, four atoms at least are needed to determine these tensor components. Unfortunately, because there are only three independent heavy atoms in this case, it is not possible to determine all the T_{ij} and ω_{ij} uniquely. However, since the principal axes of all the ellipsoids lie not very far from the molecular axes (Fig. 6), it can be assumed that off-diagonal elements of these tensors are small. By assuming that one of the off-diagonal elements, ω_{12}, is negligibly small compared with the three parameters ω_{11}, ω_{22} and T_{33}, the approximate values of the tensor components were obtained as follows:

$$T=\begin{pmatrix} 2{\cdot}36 & 0{\cdot}08 & -0{\cdot}10 \\ & 3{\cdot}23 & -0{\cdot}27 \\ & & 3{\cdot}55^{*} \end{pmatrix} (\text{Å}^2\times 10^{-2}),$$

$$\omega=\begin{pmatrix} 2{\cdot}18^{*} & 0^{*} & 0{\cdot}04 \\ & 0{\cdot}61^{*} & 0{\cdot}09 \\ & & 0{\cdot}23 \end{pmatrix} (\text{rad}^2\times 10^{-2}).$$

(*Based on the assumption of $\omega_{12}=0$)

The calculated values of the thermal vibration tensor components U_{ij} referred to the molecular axes are listed in Table 8 together with the observed values.

These results show that the libration about the L axis and the translation along the N axis are quite large. This conclusion can be satisfactorily interpreted in terms of the crystal structure. Thus in the N direction, the acid molecules are in contact with each other with the van der Waals force alone. On the other hand the acid molecule is tightly connected to the water molecules by the hydrogen bonds in the L direction. Thus the libration of the acid molecule takes place most easily about the C–C axis.

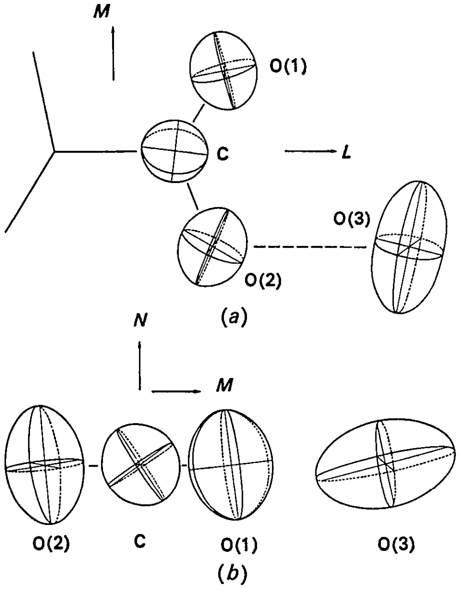


Fig. 6. The root mean square vibrational displacements in the principal axis directions projected (*a*) along the N axis, (*b*) along the L axis.

The water molecule is linked by the three hydrogen bonds O(2)···O(3), O(1′)···O(3) and O(1″)···O(3). The O(2)···O(3) and O(1′)···O(3) are nearly parallel to the L axis, and O(1′)···O(3) has a large component along the N axis. The direction of the largest vibration of the oxygen atom of water was found to lie near to the normal of the plane formed by these three hydrogen bonds. This shows that the water molecule is apt to move in the direction along which the intermolecular attraction is not very strong.

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