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An X-ray Study of α-Oxalic Acid Dihydrate, $(COOH)_2.2H_2O$, and of its Deuterium Analogue, $(COOD)_2.2D_2O$: Isotope Effect in Hydrogen Bonding and Anisotropic Extinction Effects

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A three-dimensional X-ray diffraction study of the α-modification of both $(COOH)_2.2H_2O$ and $(COOD)_2.2D_2O$ has been made. For each substance, intensity data were collected with Cu $K\alpha$ radiation out to 110° in 2θ on a Picker automatic diffractometer. Positional and anisotropic thermal parameters for all atoms were refined on F^2 by full-matrix least-squares techniques. A correction for anisotropic extinction effects was included in the least-squares refinement. The weighted R factors on F^2 are 3·9% (547 observed reflections) for α-$(COOH)_2.2H_2O$ and 3·9% (555 observed reflections) for α-$(COOD)_2.2D_2O$. The corresponding conventional R factors on F^2 are 2·8% and 2·8% respectively; on F they are 2·0% and 2·3%. The oxalic acid molecules and water molecules are linked together by a three-dimensional network of hydrogen bonds. All three crystallographically independent O–H···O bond lengths expand significantly with deuteration while the bond lengths within the oxalate fragment remain unchanged. In α-$(COOH)_2.2H_2O$, the O–H···O distances are 2·512 (1), 2·864 (2) and 2·883 (1) Å; the corresponding O–D···O distances in α-$(COOD)_2.2D_2O$ are 2·531 (1), 2·880 (2) and 2·907 (1) Å.

Introduction

Extensive studies have been made on the structural effects of deuterium substitution in hydrogen bonded solids. New polymorphs have been formed by deuterating potassium dihydrogen phosphate (Ubbelohde & Woodward, 1942), resorcinol (Robertson, 1936; Robertson & Ubbelohde, 1938) and oxalic acid dihydrate (Chiba, 1964; Iwasaki & Saito, 1967; Iwasaki, Iwasaki & Saito, 1967). Smaller effects have been found in investigations of isomorphous protonated and deuterated analogues of several compounds. A summary of these results shows several examples where the replacement of H by D produces a marked expansion of the crystal lattice (Ubbelohde & Gallagher, 1955; Ibers, 1965). From a knowledge of the protonated structure and the measured changes in the unit-cell dimensions on deuteration, Ubbelohde and co-workers found the directions of maximum expansion nearly to coincide with the directions of short hydrogen bonds in the lattice. By assuming the isotope effect to be localized in the hydrogen bonds, they calculated the differences in the corresponding O–H...O and O–D...O distances from the expansion coefficient in the direction of the bonds. They concluded that large isotope effects were observed only in short hydrogen bonds while deuteration had little or no effect on long hydrogen bonds. These conclusions are not unambiguous since many of the solids studied contain more than one crystallographically independent hydrogen bond. A determination of the atomic positions in the deuterated crystals was not attempted, as the precision obtainable at that time was too low to allow meaningful comparisons between the hydrogen and deuterium structures.

Crystals of deuterated oxalic acid dihydrate, $(COOD)_2.2D_2O$ (hereafter called α-DOX), were found by Robertson & Ubbelohde (1939) to be isomorphous with those of $(COOH)_2.2H_2O$ (hereafter called α-POX) (Robertson & Woodward, 1936; Ahmed & Cruickshank, 1953; Garrett, 1954) and to exhibit a large isotope effect. Recently the crystal structure of a new modification of $(COOD)_2.2D_2O$ was reported (hereafter called β-DOX) (Iwasaki & Saito, 1967; Iwasaki, Iwasaki & Saito, 1967) which is not isomorphous with that of α-DOX. In order to determine the exact nature of the isotope effect in α-DOX, a three-dimensional X-ray analysis was made of the crystal structures of both α-POX and α-DOX. A preliminary report of the present work has previously appeared (Delaplane & Ibers, 1966). The present paper is the first in a series of four papers. The next paper describes a neutron diffraction study of α-POX (Sabine, Cox & Craven, 1969); it is followed by a description of a neutron diffraction study of α-DOX and β-DOX (Coppens & Sabine, 1969) and in the final paper (Coppens, Sabine, Delaplane & Ibers, 1969) some comparisons are made between the X-ray and neutron results on oxalic acid dihydrate and their implications in terms of bonding effects are discussed.

Experimental

Crystals of α-POX were recrystallized from aqueous solution. About 0·35 g of anhydrous oxalic acid was dissolved in 2ml of 99·85 mole% D_2O with heating, and the water was evaporated in vacuo. After repeating the procedure three times, a final recrystallization yielded crystals of α-DOX. Crystals of both substances were colorless monoclinic needles with the needle axis coincident with the b axis. Recrystallization of oxalic acid dihydrate from D_2O has also been reported to produce rhomboidal crystals of β-DOX (Iwasaki & Saito, 1967; Iwasaki *et al.*, 1967; Coppens & Sabine, 1969). The pres-

ent work deals only with the α-form. The crystal data of both α-POX and α-DOX are listed in Table 1. The unit-cell dimensions were obtained at 26°C with the least-squares procedure described below [λ(Cu Kα_1) = 1·5405 Å].

Table 1. *Crystal data**

	α-$(COOH)_2.2H_2O$	α-$(COOD)_2.2D_2O$
Space group	$P2_1/n$	$P2_1/n$
a	6·119 (1) Å	6·150 (1) Å
b	3·607 (1)	3·612 (1)
c	12·057 (1)	12·102 (1)
β	106° 19 (1)′	106° 38 (1)′
Z	2	2
V	255·4 Å^3	257·6 Å^3

* Numbers in parentheses here and in succeeding Tables are the estimated standard deviations in the least significant digits.

Collection and reduction of data

α-DOX

A needle-shaped crystal with an average diameter of about 0·22 mm and a length of 0·45 mm was mounted in a thin glass capillary to prevent dehydration and deuterium-hydrogen exchange with the air. For subsequent absorption and extinction corrections, the crystal faces were indexed, and the crystal was measured. These measurements are given in Table 2. For data collection, the crystal was mounted about the b axis on a Picker four-circle automatic X-ray diffractometer. The arcs on the goniometer were then changed several degrees so that the crystal would not be oriented about the symmetry axis, thus minimizing the possibility of multiple reflections (Zachariasen, 1965). The mosaicity of the crystal was judged to be satisfactory upon checking ω scans of several strong reflections by the narrow-source, open-counter technique (Furnas, 1957). The average half-width was about 0·09°. A group of high-angle reflections was carefully centered using a narrow receiving slit and a narrow X-ray source as provided by a take-off angle of 0·5° for the X-ray tube. The lattice constants and the orientation angles were obtained from a least-squares refinement using the observed angle settings for each reflection as input data (Corfield, Doedens & Ibers, 1967).

Table 2. *Crystal dimensions*

α-DOX		α-POX	
*hkl**	*D*†	*hkl**	*D*†
001	0·113	001	0·133
00$\bar{1}$	0·113	00$\bar{1}$	0·133
101	0·138	101	0·124
$\bar{1}$0$\bar{1}$	0·138	$\bar{1}$0$\bar{1}$	0·124
10$\bar{1}$	0·103	10$\bar{1}$	0·087
$\bar{1}$01	0·103	$\bar{1}$01	0·087
1$\bar{2}$1	0·231	010	0·206
$\bar{1}$2$\bar{1}$	0·231	0$\bar{1}$0	0·206
Crystal volume‡	0·02297 mm^3		0·01856 mm^3

* Indices of each bounding plane.

† Perpendicular distance in millimeters of each plane from an origin at the center of the crystal.

‡ These values were calculated with the data processing and absorption correction program *DATAP* written by Coppens *et al.* (1965).

The intensity data were collected at a take-off angle of 1·2°. At this angle the intensity of a typical strong reflection was approximately 75% of the maximum value as a function of take-off angle. The scintillation counter was placed 21 cm from the crystal with a receiving aperture size of 5·0 mm wide and 4·0 mm high to minimize extraneous background radiation. The diffracted Cu $K\alpha$ beam was filtered through a 1·0 mil nickel foil. Integrated intensities were collected using the θ–2θ continuous scan technique. A symmetrical scan range of 2° in 2θ was used, and the scan rate was 2° min^{-1}. Stationary-counter background counts of 4 seconds were taken at each end of the scan range. Copper foil attenuators were automatically inserted when the intensity of the diffracted beam exceeded about 7000 counts sec^{-1} during the scan. The attenuator factors were about 2·3. The pulse height analyzer was set to accept about a 95% window centered on the Cu Kα peak.

The intensities of all four equivalent members (hkl, $\bar{h}\bar{k}\bar{l}$, $h\bar{k}l$, $\bar{h}k\bar{l}$) of the form $\{hkl\}$ were collected. Since in our procedure for data collection (Corfield, Doedens & Ibers, 1967) the reflections are ordered in an attempt to minimize slewing times of the drive motors, the equivalent members of a given form typically are collected at widely varying times during the period of data collection. The intensities of four standard reflections were checked periodically during the run to monitor diffractometer and crystal stability. No significant changes were observed in these standards. A total of 941 intensities were measured out to a 2θ value of 110° for Cu $K\alpha$ (hereafter called Data Set 1).

The procedure used in processing the data is similar to that previously described by Corfield, Doedens & Ibers (1967). The raw intensities were corrected for background, which was assumed to vary linearly throughout the scan range. Standard deviations were assigned to the corrected intensities through the expression

$$\sigma(I) = [CT + (t_p/2t_b)^2 (B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated peak count measured in time t_p, B_1 and B_2 are the background counts, each measured in time t_b, and $I = CT - (t_p/2t_b)(B_1 + B_2)$. The inclusion of the term $(pI)^2$ prevents intense reflections from being overweighted (Busing & Levy, 1957). An initial value of 0·03 was chosen for p, based on past experience with similar data sets. The values of I and $\sigma(I)$ were corrected for Lorentz–polarization and absorption effects. The absorption correction was effected by numerical methods. For a calculated absorption coefficient of 15·8 cm^{-1}, the transmission factor A^* varied from 0·77 to 0·68. The values of F^2 for each equivalent set of reflections were averaged to yield 323 independent reflections, of which 15 were less than their standard deviations. Standard deviations of F^2, $\sigma(F^2)$, were estimated from both the average of the individual standard deviations and from the range of F^2 values of the equivalent members of the form. The larger of

the two estimated values was chosen and was divided by $n^{1/2}$, where n is the number of equivalent members which were observed for that reflection (Robinson & Ibers, 1967). If $\sigma(F^2)$ is assumed to be a measure of $|F_o^2 - F_c^2|$, a predicted weighted R factor (R_2) may be computed from the F^2 and $\sigma(F^2)$ values. The predicted R_2 factor on F^2 of 3·8% indicates good agreement among equivalent members of the form $\{hkl\}$.

Because many of the most intense reflections in Data Set 1 were subsequently found to be severely attenuated by extinction effects, a supplementary data set was collected on a smaller crystal, a needle with an average diameter of 0·040 mm and a length of 0·16 mm. Following the above procedure, a symmetrical scan range of 1·8° was used with a scan rate of 1° min^{-1} and 10 sec background counts. During the period of data collection, which lasted 26 hours, the monitored intensities of the same four standard reflections used for Data Set 1, uniformly decreased by 15%. This was attributed to partial decomposition of the crystal. A total of 453 intensities consisting of all four members of the form $\{hkl\}$ were measured out to a 2θ value of 80° for Cu Kα_1 (hereafter called Data Set 2). Beyond this maximum 2θ value, there were very few reflections with $F^2 > \sigma(F^2)$.

The raw intensities in Data Set 2 were corrected for the effects of background, Lorentz–polarization, and absorption. The average decrease in the intensities of the four standard reflections as a function of time was used as the correction factor for the intensity loss during data collection. The individual F^2 values were averaged using the above procedure with a value of 0·01 for p. A total of 152 independent reflections was obtained of which 79 were less than their standard deviations.

α-POX

The procedure for collecting and processing the data parallels the one previously outlined for α-DOX, and only differences will be emphasized. A needle-shaped crystal with an average diameter of about 0·23 mm and a length of 0·41 mm was chosen for data collection. The measured dimensions of the crystal are given in Table 2. The average half-width of ω scans of several strong reflections was about 0·08°. Integrated intensities were collected using the θ-2θ continuous scan technique with a symmetrical scan range of 2° in 2θ and a scan rate of 2° min^{-1}. Stationary-counter background counts of 4 sec were taken at each end of the scan range. A total of 932 intensities consisting of all four members of the form $\{hkl\}$ were measured out to a 2θ value of 110° for Cu Kα_1 (hereafter called Data Set 1).

Four standard reflections were used to monitor the stability of both the crystal and the diffractometer. During the 45 hour period of data collection, the intensity of the standard 110 reflection was observed to increase by 15% with no significant drift in the intensities of the other three standards. After continuously irradiating the crystal with the X-ray beam for an additional 20 hours, the intensity of reflection 110 continued to increase and then leveled off at about 1·25 times its original value. Only very small increases were noted in the other three standards. No further observable intensity changes in any of the standard reflections were noted after dipping the crystal several times in liquid nitrogen. The reflection 110 is the most intense in the data set, while the other standards are only moderately strong. These intensity changes were interpreted as being due to extinction effects. In general, extinction effects are most prominent in the most intense reflections and depend upon the mosaic spread of the crystal. The continuous radiation damage to the crystal increased the mosaic spread as a function of time, thus increasing the observed intensities of the most intense reflections.

The raw intensities were corrected for background, Lorentz–polarization, and absorption effects and were then averaged. For a calculated absorption coefficient of 15·8 cm^{-1}, the transmission factor A^* ranged from 0·76 to 0·68. No attempt was made to correct for the intensity changes which occurred during data collection. For assigning the standard deviations, an initial value of 0·05 was used as the p factor. Of 321 independent F^2 values, 15 were less than their standard deviations. The predicted R_2 factor on F^2 was 5·9%.

A supplementary data set was collected on a smaller needle-shaped crystal with an average diameter of of 0·09 mm with a length of 0·21 mm. Following the above procedure, a symmetrical scan range of 1·8° was used with a scan rate of 2° min^{-1} and 4 sec stationary-counter background counts. No change was observed in the intensities of the monitored standard reflections during the period of data collection. A total of 440 intensities consisting of all four equivalent reflections of the form $\{hkl\}$ were measured out to a 2θ value of 80° for Cu $K\alpha_1$ (hereafter called Data Set 2).

The raw intensities in Data Set 2 were corrected for bakground, Lorentz–polarization, and absorption effects and were averaged. A value of 0·015 was used for the p factor in assigning $\sigma(F^2)$ values. Of 150 independent F^2 values, 19 were less than their standard deviations.

It is important to reiterate that in the data sets obtained here the intensities of members of a given form were collected at widely varying times during a given experiment and that the standard deviation of the average intensity was assigned on the basis of the agreement among the intensities of the individual members of the form. Thus resultant weighting scheme effectively allows for the effects of possible crystal decomposition during the experiment.

Initial refinements of the structures

α-DOX

Using only the F^2 values of Data Set 1, a least-squares refinement on F^2 was carried out. In all calculations of F_c^2, the atomic scattering factors tabulated by Ibers (1962) were used for C and O and those of Stewart, Davidson & Simpson (1965) were used for H (and D).

The initial parameters were those reported by Ahmed & Cruickshank (1953) for C and O and those of Garrett (1954) for H. Positional parameters and anisotropic thermal parameters for each atom and an overall scale factor were refined. The function $\Sigma w(F_o^2-F_c^2)^2$ was minimized with the weights w taken as $1/\sigma^2(F^2)$. After three cycles of least-squares refinement, carried out with a local modification of the Busing–Levy *ORFLS* program, the usual agreement indices $R_1=\Sigma(F_o^2-F_c^2)/\Sigma F_o^2$ and $R_2=[(\Sigma w(F_o^2-F_c^2)^2)/\Sigma wF_o^4]^{1/2}$ were 17·2 and 12·9% respectively. The predicted R_2 value of 3·8%, indicative of good agreement among equivalent members of the form $\{hkl\}$, suggested that the structure was still underrefined. For several intense reflections at low values of $\lambda^{-1}\sin\theta$, F_o^2 was consistently less than F_c^2 suggesting that these reflections may be severely attenuated by extinction.

An extinction correction of the form $(F_o^{corr})=y|F_o|$ where $y=\{C\beta(2\theta)I_{obs}+[1+C^2\beta^2(2\theta)I_{obs}^2]^{1/2}\}$ was applied (Zachariasen, 1968). I_{obs} is the observed intensity, C is the variable extinction coefficient, and $\beta(2\theta)$ is the function $2(1+\cos^4 2\theta)/(1+\cos^2 2\theta)^2$. The quantitity $\Sigma w(F_o^2-F_c^2/y^2)^2$ was minimized. This procedure is similar to the first-order secondary extinction correction given by Zachariasen (1963), only here the term $dA^*/d(\mu R)$ is assumed to have a constant value of 1·0. Three cycles of least-squares refinement yielded a value for C of $2\cdot78(13)\times10^{-4}$ (in absolute units) and values for R_1 and R_2 of 5·6 and 6·3% respectively.

The largest increase for any reflection due to the extinction correction was about 80% of the original F_o^2 value for the reflection 110. In general, most of the large corrected F_o^2 values for reflections of the form $\{hkl\}$ ($k\neq0$) appeared to be over-corrected while those of the form $\{h0l\}$ appeared to be under-corrected. A similar trend was subsequently found to exist in the F_o^2 and F_c^2 values for α-POX using the same method of correction. This anisotropic effect could possibly be explained by anisotropic extinction or by crystal-shape effects. The above approximate form of the extinction correction assumes the crystal to be spherical in shape and assumes that the misalignment of the crystal domains obeys an isotropic Gaussian distribution law.

Hamilton (1957) has found that secondary extinction coefficients can be very sensitive to the shape of the crystal and to the direction of the incident X-ray beam relative to the crystal faces. The program *GONO*9 of Hamilton can be used to apply an isotropic extinction correction by numerical integration procedures for crystals of any well-defined shape. The raw intensity data in Data Set 1 were reprocessed using a value for p of 0·01 as judged by the good agreement among the equivalent members of the forms in the previously averaged data set. The individual F^2 values were corrected for absorption and extinction effects with the program *GONO* 9, which had been modified to include the polarization term in the extinction correction for the X-ray case (Zachariasen, 1963). A value for the extinction parameter was estimated, and after averaging the symmetry-related values of F^2, a least-squares refinement of all the structural parameters was then made. The process was repeated until a value for the extinction parameter was found which would produce the lowest value for R_2. For an extinction coefficient of 0·0130 cm^{-1}, the values for R_1 and R_2 were 5·5 and 5·0% respectively. The agreement was slightly better than in the

Table 3. *Extinction parameters for* α-DOX

	Isotropic	Anisotropic crystal Type I	Anisotropic crystal Type II
Isotropic g or G_{11}*	0·400 (15)	0·010 (10)	4·08 (40)
G_{22}		0·242 (16)	15·96 (148)
G_{33}		0·041 (18)	4·32 (40)
G_{12}		0·002 (7)	−0·04 (74)
G_{13}		0·055 (14)	−1·91 (32)
G_{23}		0·007 (11)	−0·51 (67)

* The values of g and G_{ij} have been multiplied by 10^4.

Table 4. *Final positional and thermal parameters for* α-DOX*

	10^4x	10^4y	10^4z	$10^4\beta_{11}$†	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
C(1)	−452 (2)	545 (3)	507 (1)	183 (3)	588 (11)	44 (1)	−6 (5)	23 (1)	−3 (2)
O(1)	855 (1)	−610 (3)	1477 (1)	257 (3)	1041 (11)	38 (1)	149 (4)	28 (1)	11 (2)
O(2)	−2186 (1)	2297 (2)	360 (1)	234 (3)	994 (10)	50 (1)	162 (4)	40 (1)	13 (2)
O(3)	−4496 (2)	−3853 (4)	1808 (1)	238 (4)	1025 (16)	49 (1)	102 (5)	37 (1)	21 (3)
D(1)	4632 (20)	4894 (44)	2943 (13)	277 (54)	1434 (184)	63 (14)	33 (77)	−84 (21)	−82 (43)
D(2)	554 (23)	1564 (45)	3787 (16)	289 (60)	1681 (233)	93 (16)	−196 (84)	51 (26)	−6 (47)
D(3)	−3878 (35)	4510 (51)	1604 (19)	801 (108)	1043 (243)	151 (24)	326 (118)	−95 (39)	206 (6)

* The anisotropic crystal Type II extinction correction was applied in this refinement.

† The form of the anisotropic thermal ellipsoid is

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

previous refinement although a few intense reflections, such as 110, remained poorly corrected.

In order to improve the agreement between corresponding F_o^2 and F_c^2 values for reflections which were most severely affected by extinction, all reflections from Data Set 2 having $F^2 > 3\sigma(F^2)$ were used to replace the corresponding reflections in Data Set 1. The resulting merged data set consisted of a total of 323 reflections, of which 40 were from Data Set 2 and 283 from Data Set 1. Using the program *GONO* 9, an extinction parameter of 0·0170 cm^{-1} for the extinction correction of Data Set 1 was found to give the lowest value of R_2 for the merged data set. No extinction correction was needed for the F^2 values from Data Set 2. The final values of R_1 and R_2, after three cycles of refinement on F^2, were 4·7 and 4·8%, respectively. The agreement between corresponding values of F_o^2 and F_c^2 was only slightly better than in the previous refinement. Although

Table 5. *Observed and calculated structure amplitudes* (× 100) *in electrons for* α-DOX

F_{obs} has been corrected for extinction effects. A negative value of F_{obs} indicates an unobserved reflection.

K= -3

H	L	FOBS	FCALC
1	-8	164	176
1	-7	435	443
1	-6	135	131
1	-5	149	138
1	-4	87	71
1	-3	329	329
1	-2	368	368
1	-1	132	114
1	0	159	145
1	1	341	340
1	2	160	172
1	3	333	336
1	4	-31	73
1	5	548	554
1	6	69	77
2	-7	88	6
2	-6	755	747
2	-5	138	132
2	-4	572	568
2	-3	76	43
2	-2	300	289
2	0	476	477
2	1	174	175
2	2	118	108
2	3	126	138
2	4	1024	1011
2	5	431	431
3	-6	540	547
3	-5	212	200
3	-4	182	35
3	-3	478	481
3	-2	-66	16
3	-1	800	831
3	0	-63	35
3	1	266	284
3	2	261	279
3	3	-59	17
4	-3	131	115
4	-2	199	206
4	-1	-58	15

K= -2

H	L	FOBS	FCALC
1	-10	95	91
1	-9	256	254
1	-8	522	529
1	-7	713	732
1	-6	718	717
1	-5	132	120
1	-4	1521	1541
1	-3	315	315
1	-2	1145	1133
1	-1	1251	1232
1	0	1112	1118
1	1	181	175
1	2	1138	1172
1	3	813	837
1	4	1469	1487
1	5	401	398
1	6	87	92
1	7	402	413
1	8	91	133
1	9	734	734
2	-10	438	437
2	-9	579	578
2	-8	78	112
2	-7	800	799
2	-6	-59	37
2	-5	369	383
2	-4	-59	55
2	-3	-57	41
2	-2	1655	1634
2	-1	786	807
2	0	1771	1751
2	1	108	91
2	2	212	232
2	3	224	229
2	4	609	623
2	5	438	444
2	6	402	394
2	7	118	107
2	8	648	638
3	-10	80	66
3	-9	315	307
3	-8	433	423
3	-7	811	832
3	-6	707	695
3	-5	1114	1135
3	-4	150	115
3	-3	173	211
3	-2	804	806
3	-1	804	786
3	0	1071	1091
3	1	436	424
3	2	242	225
3	3	736	947
3	4	892	900
3	5	923	929
3	6	348	327
3	7	197	194
4	-9	112	111
4	-8	413	418
4	-7	608	600
4	-6	1031	1029
4	-5	394	390
4	-4	781	788
4	-3	534	530
4	-2	240	261
4	-1	558	584
4	0	365	375
4	1	81	46
4	2	89	99
4	3	-57	43
4	4	657	645
4	5	355	340
5	-7	284	299
5	-6	362	337
5	-5	305	291
5	-4	129	119
5	-3	60	10
5	-2	247	252
5	-1	496	515
5	0	896	884
5	1	402	389

K= -1

H	L	FOBS	FCALC
1	-12	129	164
1	-11	508	496
1	-10	999	988
1	-9	758	768
1	-8	488	489
1	-7	1218	1214
1	-6	845	831
1	-5	924	910
1	-4	2702	2670
1	-3	1797	1768
1	-2	472	476
1	-1	3413	3352
1	0	5159	5251
1	1	1331	1313
1	2	1643	1645
1	3	1386	1375
1	4	223	215
1	5	254	259
1	6	1793	1763
1	7	660	662
1	8	924	920
1	9	54	73
1	10	539	547
1	11	647	626
2	-12	467	451
2	-11	989	1006
2	-10	565	554
2	-9	566	574
2	-8	1515	1521
2	-7	489	479
2	-6	235	243
2	-5	2071	2055
2	-4	175	133
2	-3	870	864
2	-2	1559	1538
2	-1	931	946
2	0	2117	2079
2	1	284	296
2	2	1597	1592
2	3	336	329
2	4	103	106
2	5	397	370
2	6	1179	1206
2	7	440	421
2	8	365	380
2	9	633	638
2	10	127	112
3	-12	-51	98
3	-11	415	380
3	-10	287	302
3	-9	255	245
3	-8	168	105
3	-7	234	213
3	-6	372	359
3	-5	1662	1649
3	-4	1657	1686
3	-3	970	965
3	-2	1573	1541
3	-1	562	541
3	0	1118	1113
3	1	963	955
3	2	1204	1208
3	3	-30	65
3	4	1394	1409
3	5	277	293
3	6	502	506
3	7	246	257
3	8	837	825
4	-11	215	225
4	-10	411	419
4	-9	652	646
4	-8	174	206
4	-7	1228	1245
4	-6	991	998
4	-5	873	866
4	-4	-47	16
4	-3	888	901
4	-2	622	616
4	-1	86	132
4	0	384	390
4	1	186	175
4	2	960	969
4	3	738	750
4	4	836	846
4	5	507	500
4	6	64	14
5	-10	61	25
5	-9	425	420
5	-8	272	254
5	-7	585	578
5	-6	724	729
5	-5	112	144
5	-4	624	641
5	-3	1008	1001
5	-2	420	412
5	-1	599	609
5	0	346	354
5	1	185	187
5	2	-50	27
5	3	115	102
5	4	1053	1026
6	-7	855	837
6	-6	102	88
6	-5	87	76
6	-4	123	122
6	-3	-50	67
6	-2	409	422
6	-1	662	666
6	0	701	697

K= 0

H	L	FOBS	FCALC
0	2	1188	1177
0	4	707	736
0	6	2756	2753
0	8	1331	1357
0	10	1467	1444
0	12	410	413
1	-11	2072	2084
1	-9	623	647
1	-7	1213	1222
1	-5	4119	4081
1	-3	486	508
1	-1	2060	2058
1	1	2879	2837
1	3	2631	2651
1	5	1177	1192
1	7	1988	2015
1	9	208	211
1	11	780	780
2	-12	275	226
2	-10	692	686
2	-8	317	322
2	-6	367	350
2	-4	5538	5576
2	-2	428	413
2	0	2409	2499
2	2	4078	3995
2	4	1185	1170
2	6	1718	1696
2	8	913	933
2	10	220	181
3	-11	240	287
3	-9	1982	1983
3	-7	512	500
3	-5	1290	1282
3	-3	1782	1764
3	-1	440	438
3	1	787	800
3	3	349	366
3	5	234	256
3	7	-52	58
3	9	816	812
4	-10	170	176
4	-8	364	405
4	-6	-50	86
4	-4	519	534
4	-2	2499	2484
4	0	807	810
4	2	520	542
4	4	1700	1685
4	6	84	68
5	-9	211	164
5	-7	1864	1864
5	-5	493	452
5	-3	714	710
5	-1	257	282
5	1	755	771
5	3	1046	1027
5	5	646	646
6	-8	426	429
6	-6	940	962
6	-4	870	870
6	-2	118	109
6	0	717	720

K= 1

H	L	FOBS	FCALC
0	-11	1117	1117
0	-10	761	762
0	-9	429	434
0	-8	495	501
0	-7	592	585
0	-6	1485	1469
0	-5	839	834
0	-4	3275	3300
0	-3	749	758
0	-2	764	773
0	-1	2171	2196
0	1	2155	2196
0	2	773	773
0	3	752	758
0	4	3253	3300
0	5	839	834
0	6	1484	1469
0	7	587	585
0	8	498	501
0	9	428	434
0	10	758	762
0	11	1117	1117
1	-12	137	164
1	-11	507	496
1	-10	1000	988
1	-9	762	768
1	-8	490	489
1	-7	1213	1214
1	-6	840	831
1	-5	926	910
1	-4	2691	2670
1	-3	1789	1768
1	-2	483	476
1	-1	3401	3352
1	0	5116	5251
1	1	1331	1313
1	2	1664	1645
1	3	1384	1375
1	4	214	215
1	5	258	259
1	6	1778	1763
1	7	658	662
1	8	911	920
1	9	54	73
1	10	540	547
1	11	654	626
2	-12	468	451
2	-11	985	1006
2	-10	563	554
2	-9	557	574
2	-8	1518	1521
2	-7	491	479
2	-6	227	243
2	-5	2046	2055
2	-4	114	133
2	-3	864	864
2	-2	1552	1538
2	-1	934	946
2	0	2115	2079
2	1	285	296
2	2	1598	1592
2	3	334	329
2	4	105	106
2	5	379	370
2	6	1175	1206
2	7	441	421
2	8	359	380
2	9	633	638
2	10	124	112
3	-12	60	98
3	-11	408	380
3	-10	287	302
3	-9	253	245
3	-8	108	105
3	-7	237	213
3	-6	370	359
3	-5	1663	1649
3	-4	1657	1686
3	-3	969	965
3	-2	1574	1541
3	-1	564	541
3	0	1112	1113
3	1	976	955
3	2	1211	1208
3	3	-47	65
3	4	1403	1409
3	5	278	293
3	6	507	506
3	7	247	257
3	8	833	825
4	-11	233	225
4	-10	410	419
4	-9	657	646
4	-8	180	206
4	-7	1218	1245
4	-6	985	998
4	-5	867	866
4	-4	-49	16
4	-3	898	901
4	-2	615	616
4	-1	88	132
4	0	384	390
4	1	184	175
4	2	967	969
4	3	743	750
4	4	842	846
4	5	502	500
4	6	-47	14
5	-10	-47	25
5	-9	426	420
5	-8	262	254
5	-7	574	578
5	-6	713	729
5	-5	116	144
5	-4	635	641
5	-3	1004	1001
5	-2	416	412
5	-1	595	609
5	0	349	354
5	1	174	187
5	2	-50	27
5	3	127	102
5	4	1041	1026
6	-7	858	837
6	-6	106	88
6	-5	84	76
6	-4	125	122
6	-3	-48	67
6	-2	404	422
6	-1	661	666
6	0	699	697

K= 2

H	L	FOBS	FCALC
0	-10	331	338
0	-9	453	458
0	-8	115	78
0	-7	922	940
0	-6	287	265
0	-5	738	732
0	-4	1000	1032
0	-3	65	34
0	-2	904	906
0	-1	652	645
0	0	646	658
0	1	643	645
0	2	895	906
0	3	-53	34
0	4	1000	1032
0	5	739	732
0	6	294	265
0	7	922	940
0	8	123	78
0	9	445	458
0	10	327	338
1	-10	85	91
1	-9	249	254
1	-8	534	529
1	-7	729	732
1	-6	733	717
1	-5	134	120
1	-4	1535	1541
1	-3	319	315
1	-2	1142	1133
1	-1	1256	1232
1	1	1145	1118
1	2	1145	1172
1	3	821	837
1	4	1484	1487
1	5	413	398
1	6	78	92
1	7	399	413
1	8	115	133
1	9	736	734
2	-10	437	437
2	-9	594	578
2	-8	115	112
2	-7	807	799
2	-6	-59	37
2	-5	367	383
2	-4	-58	55
2	-3	-57	41
2	-2	1649	1634
2	-1	789	807
2	0	1774	1751
2	1	94	91
2	2	202	232
2	3	227	229
2	4	614	623
2	5	439	444
2	6	409	394
2	7	107	107
2	8	650	638
3	-10	81	66
3	-9	324	307
3	-8	645	623
3	-7	820	832
3	-6	709	695
3	-5	1121	1135
3	-4	130	115
3	-3	185	211
3	-2	816	806
3	-1	801	786
3	0	1090	1091
3	1	438	424
3	2	249	225
3	3	944	947
3	4	904	900
3	5	939	929
3	6	352	327
3	7	195	194
4	-9	113	111
4	-8	419	418
4	-7	615	600
4	-6	1036	1029
4	-5	399	390
4	-4	778	788
4	-3	551	530
4	-2	245	261
4	-1	570	584
4	0	365	375
4	1	83	46
4	2	93	99
4	3	60	43
4	4	656	645
4	5	359	340
5	-7	289	299
5	-6	367	337
5	-5	312	291
5	-4	117	119
5	-3	-47	10
5	-2	245	252
5	-1	489	515
5	0	886	884
5	1	408	389

K= 3

H	L	FOBS	FCALC
0	-7	64	41
0	-6	-58	45
0	-5	121	98
0	-4	549	547
0	-3	399	415
0	-2	632	650
0	-1	290	275
0	1	284	275
0	2	637	650
0	3	398	415
0	4	553	547
0	5	89	98
0	6	-58	45
0	7	-60	41
1	-8	160	176
1	-7	447	443
1	-6	126	131
1	-5	146	138
1	-4	-67	71
1	-3	323	329
1	-2	360	368
1	-1	144	114
1	0	171	145
1	1	341	340
1	2	178	172
1	3	337	336
1	4	-63	73
1	5	575	554
1	6	-64	77
2	-7	-64	6
2	-6	780	747
2	-5	135	132
2	-4	564	568
2	-3	89	43
2	-2	306	289
2	-1	665	679
2	0	482	477
2	1	161	175
2	2	123	108
2	3	145	138
2	4	1042	1011
2	5	438	431
3	-6	553	547
3	-5	212	200
3	-4	127	35
3	-3	483	481
3	-2	-63	16
3	-1	804	831
3	0	-66	35
3	1	273	288
3	2	274	279
3	3	57	17
4	-3	128	115
4	-2	209	206
4	-1	-58	15

the crystal used for the supplementary data collection was small enough to minimize extinction effects, the counting statistics for even the most intense reflections were very poor owing to the small reflecting power of the crystal.

α-POX

With the use of the α-DOX parameters as initial values, a least-squares refinement on F^2 was made for α-POX using only Data Set 1. The refinement procedure parallels the one previously outlined for α-DOX, and only differences will be emphasized. Positional parameters and anisotropic thermal parameters for each atom and an overall scale factor were refined for three cycles. The values for R_1 and R_2 were 19·5 and 14·8% respectively. A comparison with the predicted R_2 value of 5·9% suggested that the structure was still underrefined. The largest F_o^2 values at low angles were consistently less than the corresponding values for F_c^2. The F_o^2 values were corrected with the Zachariasen extinction correction previously described. Three cycles of least-squares refinement, which included the extinction coefficient as a variable, yielded a value for C of $3{\cdot}65(20) \times 10^{-4}$ (in absolute units) and values for R_1 and R_2 of 9·8% and 8·1% respectively.

A comparison of the corresponding F_c^2 and corrected F_o^2 values indicated that the same anisotropic extinction effects were present here as for the larger α-DOX crystal. For these reasons the raw intensity data were reprocessed ($p = 0{\cdot}015$), and the resulting F^2 values were corrected for absorption and extinction with the program *GONO* 9. An extinction parameter of 0·0155 cm^{-1} was found to give the lowest value for R_2.

The F^2 values corresponding to the four equivalent members of the form $\{hkl\}$ were averaged, and the structural parameters were refined by least-squares techniques. Three cycles of refinement led to values for R_1 and R_2 of 9·4 and 5·5% respectively.

The value for R_2 was still less than a predicted value of 2·7% derived from the new weighting scheme, and agreement between the most intense F_o^2 and F_c^2 values was still poor, perhaps because of the large magnitude of the correction. All F^2 values having $F^2 > 3\sigma(F^2)$ in Data Set 2 were used to replace the corresponding values in Data Set 1. The merged data set consisted of 321 independent reflections of which 114 were from Data Set 2 and 207 from Data Set 1. Several intense reflections in Data Set 2 were subsequently found to be slightly affected by extinction. Both data sets were separately corrected for extinction with the program *GONO*-9. Extinction coefficients of 0·0200 and 0·0093 cm^{-1} were chosen for Data Set 1 and Data Set 2 respectively, which gave the lowest value for R_2 for the merged data set. Three cycles of anisotropic least-squares refinement varying a separate overall scale factor for each data set gave the values for R_1 and R_2 of 4·2 and 4·4% respectively. The present experience of collecting supplementary data sets on small crystals is not wholly satisfactory. It is difficult, if not impossible, to find crystals of α-POX and α-DOX which are small enough for extinction to be negligible and yet reflecting power to be substantial.

Corrections for anisotropic extinction

Recently, Zachariasen's theory of extinction was extended to include the anisotropic case (Coppens & Hamilton, 1969) and an anisotropic extinction correction has been incorporated into the least-squares program. This technique has been applied to the present data sets.

α-DOX

The raw intensities of Data Set 1 were reprocessed as previously described. In assigning standard deviations, a value for p of 0·005 was used. This effectively increases the weights of the strongest reflections. This lower value was used since presumably the extinction present in the most intense reflections can now be corrected more effectively than before. The values of I and $\sigma(I)$ were corrected for Lorentz–polarization and absorption effects (Coppens, Leiserowitz, & Rabinovich, 1965). The intensities of only the two equivalent members (hkl) and $(\bar{h}\bar{k}\bar{l})$ of the form $\{hkl\}$ were averaged since anisotropic extinction effects may not necessarily conform to the symmetry operations of the space group. Since the crystal had a morphological center of symmetry, the extinction correction was assumed to be the same for the reflections (hkl) and $(\bar{h}\bar{k}\bar{l})$. The original 941 intensities were thus reduced to 581 independent reflections. The R_2 factor on F^2 for averaging was 1·4%. The structural parameters were again refined on F^2 using a least-squares technique similar to that previously described. The form factors of Hanson, Herman Lea & Skillman (1964) for C and O and of Stewart *et al.* (1965) for H(D) were used in all calculations of

Table 6. *Extinction parameters for* α-POX

	Isotropic	Anisotropic crystal Type I	Anisotropic crystal Type II
Isotropic g or G_{11}*	0·510 (23)	−0·077 (14)	2·22 (19)
G_{22}		0·447 (32)	21·34 (200)
G_{33}		0·013 (26)	1·68 (18)
G_{12}		−0·006 (8)	−1·49 (74)
G_{13}		0·073 (17)	0·10 (12)
G_{23}		0·005 (17)	−1·03 (77)

* The values of g and G_{ij} have been multiplied by 10^4.

F_c^2. A reflection was considered to be unobserved if $I_o < 1{\cdot}5\sigma(I_o)$. For such reflections, a term $\Delta(F^2) = 1{\cdot}5\ \sigma(F_o^2) - F_c^2$ was included in the refinement whenever $F_c^2 > 2{\cdot}0\ \sigma(F_o^2)$.

The applied extinction correction was of the form $(F_o^{\text{corr}}) = yF_o$ where here

$$y = \left[1 + \frac{2\bar{T}(p_2/p_1^2)F_c^2 g}{V \sin 2\theta}\right]^{1/2}.$$

$\bar{T}$ is the mean path length through the crystal for each reflection and has been modified for absorption effects through the approximation $\bar{T} \simeq (-\log A^*)/\mu$ where A^* is the transmission factor and μ is the linear absorption coefficient. For unpolarized X-rays, $p_n = (1 + \cos^{2n} 2\theta)/2$ and $(V = V_{\text{cell}}^2/\lambda^3) \times 10^{-4} \times 12{\cdot}593$ where the quantity 12·593 is $(mc^2/e^2)^2$. The extinction parameter g may be constant for all reflections in the isotropic case or may be derived from a tensor in the anisotropic case. This tensor may take two different forms since the extinction may be dominated by either the mosaic spread (Type I crystal) or the average domain size (Type II crystal). For Type I crystals, an anisotropic Gaussian mosaic spread distribution is assumed to be described by a tensor $\mathbf{G}_{ij}$: $g = (N'\mathbf{G}N)^{1/2}$ where N_i are the components of a unit vector normal to the plane containing the incident and diffracted beams. The components are defined relative to axes of unit length which are parallel to the real crystal axes. For Type II crystals, the average mosaic particle is ellipsoidal in shape and is described again by a tensor $\mathbf{G}_{ij}$: $g = (M'\mathbf{G}M)^{-1/2}$ where M_i are the components of a unit vector in the plane of the incident and diffracted beams and perpendicular to the incident beam. The components M_i are defined relative to a set of unit axes parallel to the real crystal axes.

Atomic positional and anisotropic thermal parameters for each atom, an overall scale factor, and the isotropic extinction coefficient g were refined for four cycles yielding values of 4·1 and 4·6% for R_1 and R_2 respectively. The final value for g is included in Table 3. The isotropic value for g was then converted to the six components G_{ij} of the tensor describing a three-dimensional Gaussian for a Type I crystal. These six components and the usual structural parameters were refined for 7 cycles. The values for R_1 and R_2 dropped to 2·5 and 4·0% respectively. The values for the components G_{ij} are given in Table 3. The isotropic value for g was then converted to the six components G_{ij} of the tensor describing the ellipsoidal shape of an average mosaic particle which characterizes the anisotropic extinction in a Type II crystal. These six components and the structural parameters were refined for 9 cycles yielding values of 2·8 and 3·9% for R_1 and R_2, respectively. The final values for the components G_{ij} are included in Table 3. In the final cycle of all of the three above refinements, no shift in any parameter was larger than a standard deviation. No attempts were made to carry out refinements on a merged data set which would include intensities from Data Set 2.

From a comparison of the various values for R_2, the structural parameters for the anisotropic Type II refinement were chosen as the best model which characterizes the extinction in this particular crystal. Clearly, there is very little difference in agreement between the models for Type I and Type II crystals. A proper description probably lies somewhere between these two models. The atomic positional and thermal parameters derived from the last cycle of the anisotropic Type II refinement are presented in Table 4, along with the corresponding standard deviations in these parameters as derived from the inverse matrix. These parameters correspond to values for R_1 and R_2 (based on F) of 2·3 and 2·0% respectively. The values for $100|F_o|$ (corrected for extinction) and $100|F_c|$ (in electrons) are given in Table 5.

The agreement in the atomic positional and thermal parameters among the latter three refinements is well within the combined standard deviations for each parameter. Among all of the refinements, corresponding positional parameters usually differ by no more than twice their combined standard deviations. Thermal parameters increase as much as five standard deviations in going from the uncorrected refinement to refinements where extinction corrections were made. Differences in the structural parameters among the various refinements are attributed to differences in extinction models and weighting scheme (different values for p). It is important to note that although corrections for extinction are necessary to obtain accurate thermal parameters positional parameters are rather insensitive to such corrections.

α-POX

In order to apply an anisotropic extinction correction, the raw intensities of Data Set 1 were reprocessed as previously described ($p = 0{\cdot}005$). The values of I and $\sigma(I)$ were corrected for Lorentz–polarization and absorption effects. The intensities of the two equiv-

Table 7. *Final positional and thermal parameters for* α-POX*

	10^4x	10^4y	10^4z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
C(1)	−454 (2)	548 (3)	511 (1)	180 (3)	575 (11)	42 (1)	−10 (5)	22 (1)	−1 (2)
O(1)	848 (1)	−600 (3)	1481 (1)	246 (3)	1019 (10)	37 (1)	141 (4)	26 (1)	9 (2)
O(2)	−2201 (1)	2305 (2)	361 (1)	226 (3)	974 (10)	49 (1)	158 (4)	39 (1)	13 (2)
O(3)	−4512 (2)	−3849 (4)	1800 (1)	230 (4)	1007 (15)	46 (1)	104 (5)	35 (1)	22 (2)
H(1)	4643 (20)	4953 (43)	2913 (12)	305 (54)	1463 (183)	70 (14)	12 (78)	−76 (22)	−76 (43)
H(2)	588 (23)	1587 (45)	3795 (16)	281 (59)	1868 (238)	96 (17)	−200 (86)	51 (27)	−15 (49)
H(3)	−3869 (31)	4508 (52)	1584 (18)	608 (91)	1134 (252)	172 (25)	227 (110)	−75 (37)	210 (63)

* The anisotropic crystal Type II extinction correction was applied in this refinement.

alent members (hkl) and $(\bar{h}\bar{k}\bar{l})$ of the $\{hkl\}$ form were averaged. The original 932 intensities were thus reduced to 575 independent reflections. The R_2 value on F^2 for averaging was 1·4%. The structural parameters were refined on F^2. A reflection was considered unobserved if $I_o < 1{\cdot}5\sigma(I_o)$. For such reflections, a term $\Delta(F^2) = 1{\cdot}5\sigma(F_o^2) - F_c^2$ was included in the refinement whenever $F_c^2 > 2{\cdot}0\sigma(F_o^2)$. Atomic positional and anisotropic thermal parameters for each atom, an overall scale factor, and the isotropic extinction coefficient g were refined for four cycles yielding values of 6·5% and 5·8% for R_1 and R_2 respectively. The final value for g is included in Table 6.

A second refinement was carried out which included the six components G_{ij} of the tensor describing a Gaussian for a Type I crystal as variable parameters. Since the anisotropic extinction effects in the α-POX and α-DOX crystals appeared to be similar, the values for the components G_{ij} corresponding to the α-DOX crystal were used as initial values. These six components, in

Table 8. *Observed and calculated strucure amplitudes* (×100) *in electrons for* α-POX

F_{obs} has been corrected for extinction effects. A negative value of F_{obs} indicates an unobserved reflection.

K= -3

H	L	FOBS	FCALC
	3	7	196	196
4	-9	86	90
4	-8	381	389
4	-7	612	597
4	-6	1049	1035
4	-5	406	396
4	-4	807	807
4	-3	540	530
4	-2	251	270
4	-1	593	611
4	0	376	392
4	1	83	55
4	2	127	128
4	3	-64	61
4	4	647	638
4	5	342	330
5	-7	267	275
5	-6	364	332
5	-5	306	288
5	-4	143	124
5	-3	-48	20
5	-2	225	227
5	-1	479	501
5	0	906	903
5	1	421	412

K= -2

H	L	FOBS	FCALC
1-10		106	103
1	-9	247	249
1	-8	576	566
1	-7	749	752
1	-6	731	716
1	-5	152	136
1	-4	1525	1552
1	-3	308	309
1	-2	1136	1132
1	-1	1274	1261
1	0	1094	1096
1	1	185	180
1	2	1158	1176
1	3	835	857
1	4	1494	1514
1	5	399	396
1	6	-65	90
1	7	423	429
1	8	143	161
1	9	750	756
2	-10	469	467
2	-9	592	582
2	-8	117	110
2	-7	806	793
2	-6	-60	27
2	-5	368	380
2	-4	-56	36
2	-3	-59	36
2	-2	1678	1642
2	-1	810	822
2	0	1806	1787
2	1	156	115
2	2	214	245
2	3	206	216
2	4	627	621
2	5	419	428
2	6	418	414
2	7	115	140
2	8	652	647
3	-10	62	69
3	-9	317	315
3	-8	468	448
3	-7	822	836
3	-6	717	702
3	-5	1168	1177
3	-4	152	143
3	-3	153	175
3	-2	816	808
3	-1	798	789
3	0	1387	1094
3	1	426	408
3	2	262	197
3	3	949	953
3	4	922	935
3	5	961	954
3	6	350	334

K= -1

H	L	FOBS	FCALC
1-12		92	130
1-11		537	525
1-10		1035	1025
1	-9	771	779
1	-8	484	487
1	-7	1192	1189
1	-6	856	843
1	-5	886	878
1	-4	2667	2677
1	-3	1790	1779
1	-2	449	453
1	-1	3467	3383
1	0	5176	5261
1	1	1328	1307
1	2	1635	1640
1	3	1373	1367
1	4	172	174
1	5	219	221
1	6	1807	1784
1	7	680	684
1	8	948	943
1	9	-51	66
1	10	569	581
1	11	642	622
2	-12	451	440
2	-11	986	1016
2	-10	558	550
2	-9	556	569
2	-8	1559	1563
2	-7	475	466
2	-6	257	270
2	-5	2047	2043
2	-4	110	120
2	-3	847	837
2	-2	1584	1567
2	-1	959	968
2	0	2039	2023
2	1	272	285
2	2	1604	1608
2	3	363	356
2	4	202	123
2	5	375	366
2	6	1192	1224
2	7	415	397
2	8	379	404
2	9	633	638
2	10	145	133
3	-12	50	88
3	-11	397	364
3	-10	318	330
3	-9	232	227
3	-8	113	122
3	-7	241	228
3	-6	369	354
3	-5	1648	1637
3	-4	1694	1708
3	-3	979	973
3	-2	1553	1526
3	-1	564	540
3	0	1154	1152
3	1	1010	1006
3	2	1220	1225
3	3	61	85
3	4	1394	1407
3	5	269	292
3	6	549	550
3	7	230	227
3	8	866	864
4	-11	223	239
4	-10	418	426
4	-9	690	661

K= 0

H	L	FOBS	FCALC
0	2	1172	1182
0	4	756	772
0	6	2781	2757
0	8	1367	1386
0	10	1525	1503
0	12	368	375
1	-11	2067	2091
1	-9	637	655
1	-7	1243	1260
1	-5	4061	4063
1	-3	429	447
1	-1	2024	2016
1	1	2743	2775
1	3	2641	2680
1	5	1205	1210
1	7	1990	1977
1	9	184	194
1	11	803	801
2	-12	328	281
2	-10	716	709
2	-8	276	283
2	-6	326	304
2	-4	5569	5566
2	-2	480	469
2	0	2442	2520
2	2	4060	4023
2	4	1132	1132
2	6	1792	1739
2	8	965	980
2	10	196	165
3	-11	266	298
3	-9	1996	1996
3	-7	462	446
3	-5	1273	1258
3	-3	1806	1784
3	-1	384	380
3	1	798	805
3	3	320	325
3	5	266	292
3	7	69	83
3	9	824	816
4	-10	213	220
4	-8	376	407
4	-6	-51	80
4	-4	531	554
4	-2	2554	2489
4	0	883	875
4	2	523	549
4	4	1738	1722
4	6	-51	25
5	-9	223	177
5	-7	1905	1886
5	-5	556	529
5	-3	716	705
5	-1	291	306
5	1	744	755
5	3	1094	1073
5	5	648	647
6	-8	402	406
6	-6	948	967

H	L	FOBS	FCALC
4	-8	172	209
4	-7	1212	1229
4	-6	1018	1030
4	-5	905	908
4	-4	59	39
4	-3	887	893
4	-2	610	604
4	-1	76	125
4	0	406	407
4	1	169	153
4	2	947	953
4	3	765	777
4	4	872	883
4	5	495	497
4	6	-51	13
5	-9	401	393
5	-8	251	232
5	-7	569	573
5	-6	733	733
5	-5	117	138
5	-4	651	659
5	-3	1021	1018
5	-2	412	411
5	-1	633	647
5	0	340	350
5	1	182	197
5	2	-51	56
5	3	158	136
5	4	1057	1046
6	-6	108	65
6	-5	110	89
6	-4	144	145
6	-3	53	37
6	-2	382	396
6	-1	682	684
6	0	721	716

H	L	FOBS	FCALC
6	-4	913	902
6	-2	129	126
6	0	743	743

K= 1

H	L	FOBS	FCALC
0-11		1135	1129
0-10		779	788
0	-9	428	438
0	-8	476	478
0	-7	558	558
0	-6	1506	1483
0	-5	820	817
0	-4	3350	3320
0	-3	726	735
0	-2	749	756
0	-1	2147	2176
0	1	2120	2176
0	2	752	756
0	3	726	735
0	4	3299	3320
0	5	819	817
0	6	1513	1483
0	7	559	558
0	8	485	478
0	9	434	438
0	10	782	788
0	11	1147	1129
1	-12	110	130
1	-11	536	525
1	-10	1041	1025
1	-9	769	779
1	-8	484	487
1	-7	1185	1189
1	-6	855	843
1	-5	885	878
1	-4	2726	2677
1	-3	1799	1779
1	-2	453	453
1	-1	3425	3383
1	0	5099	5261
1	1	1337	1307
1	2	1643	1640
1	3	1380	1367
1	4	177	174
1	5	222	221
1	6	1815	1784
1	7	694	684
1	8	939	943
1	9	-51	66
1	10	564	581
1	11	643	622
2	-12	457	440
2	-11	983	1016
2	-10	559	550
2	-9	555	569
2	-8	1560	1563
2	-7	470	466
2	-6	259	270
2	-5	2067	2043
2	-4	107	120
2	-3	853	837
2	-2	1584	1567
2	-1	958	968
2	0	2081	2023
2	1	272	285
2	2	1603	1608
2	3	362	356
2	4	111	123
2	5	374	366
2	6	1196	1224
2	7	421	397
2	8	391	404
2	9	633	638
2	10	132	133
3	-12	50	88
3	-11	398	364
3	-10	315	330
3	-9	227	227
3	-8	114	122
3	-7	248	228
3	-6	364	354
3	-5	1639	1637
3	-4	1688	1708
3	-3	982	973
3	-2	1567	1526
3	-1	569	540
3	0	1161	1152
3	1	1019	1006
3	2	1224	1225
3	3	62	85
3	4	1406	1407
3	5	268	292
3	6	549	550
3	7	227	227
3	8	873	864
4	-11	235	239
4	-10	410	426
4	-9	664	661

H	L	FOBS	FCALC
4	-8	163	209
4	-7	1213	1229
4	-6	1015	1030
4	-5	911	908
4	-4	59	39
4	-3	886	893
4	-2	603	604
4	-1	76	125
4	0	403	407
4	1	154	153
4	2	947	953
4	3	770	777
4	4	871	883
4	5	499	497
4	6	-55	13
5	-9	393	393
5	-8	250	232
5	-7	567	573
5	-6	727	733
5	-5	107	138
5	-4	645	659
5	-3	1019	1018
5	-2	411	411
5	-1	633	647
5	0	341	350
5	1	182	197
5	2	67	56
5	3	149	136
5	4	1055	1046
6	-6	90	65
6	-5	109	89
6	-4	152	145
6	-3	-49	37
6	-2	380	396
6	-1	679	684
6	0	719	716

K= 2

H	L	FOBS	FCALC
0-10		333	351
0	-9	457	458
0	-8	114	68
0	-7	930	943
0	-6	2793	2581
0	-5	717	708
0	-4	1015	1050
0	-3	76	49
0	-2	912	915
0	-1	655	657
0	0	644	657
0	1	654	657
0	2	908	915
0	3	64	49
0	4	1028	1050
0	5	716	708
0	6	297	268
0	7	929	943
0	8	90	58
0	9	449	458
0	10	340	351
1-10		113	103
1	-9	252	249
1	-8	562	566
1	-7	744	752
1	-6	718	715
1	-5	136	136
1	-4	1549	1552
1	-3	311	309
1	-2	1137	1132
1	-1	1268	1261
1	0	1093	1096
1	1	222	180
1	2	1162	1176
1	3	838	857
1	4	1501	1514
1	5	397	396
1	6	-65	90
1	7	429	429
1	8	136	151
1	9	754	756
2	-10	468	467
2	-9	592	582
2	-8	214	110
2	-7	797	793
2	-6	-60	27
2	-5	359	380
2	-4	73	36
2	-3	63	36
2	-2	1677	1642
2	-1	811	822
2	0	1824	1787
2	1	146	115
2	2	232	245
2	3	229	216
2	4	621	621
2	5	426	428
2	6	421	414
2	7	142	140
2	8	660	647

H	L	FOBS	FCALC
3-10		63	69
3	-9	341	315
3	-8	459	448
3	-7	813	836
3	-6	721	702
3	-5	1169	1177
3	-4	151	143
3	-3	140	175
3	-2	809	808
3	-1	806	789
3	0	1092	1094
3	1	425	408
3	2	218	197
3	3	951	953
3	4	927	935
3	5	958	954
3	6	344	334
3	7	199	196
4	-9	107	90
4	-8	384	389
4	-7	623	597
4	-6	1049	1035
4	-5	397	396
4	-4	803	807
4	-3	539	530
4	-2	243	270
4	-1	583	611
4	0	390	392
4	1	-65	55
4	2	144	128
4	3	72	61
4	4	645	638
4	5	346	330
5	-7	259	275
5	-6	363	332
5	-5	295	288
5	-4	120	124
5	-3	-50	20
5	-2	225	227
5	-1	474	501
5	0	909	903
5	1	420	412

K= 3

H	L	FOBS	FCALC
0	-7	-57	31
0	-6	-63	44
0	-5	123	103
0	-4	555	555
0	-3	402	430
0	-2	646	659
0	-1	302	289
0	1	301	289
0	2	644	659
0	3	417	430
0	4	557	555
0	5	117	103
0	6	-58	44
0	7	-61	31
1	-7	442	444
1	-6	147	137
1	-5	152	141
1	-4	112	63
1	-3	336	327
1	-2	370	371
1	-1	143	117
1	0	175	154
1	1	365	353
1	2	172	176
1	3	345	356
1	4	82	77
1	5	550	554
1	6	-62	78
2	-7	-62	1
2	-6	789	764
2	-5	155	143
2	-4	630	593
2	-3	86	57
2	-2	293	283
2	-1	696	691
2	0	493	483
2	1	155	172
2	2	127	97
2	3	120	123
2	4	1059	1040
2	5	453	448
3	-6	564	555
3	-5	213	204
3	-4	-64	42
3	-3	490	486
3	-2	-60	22
3	-1	823	858
3	0	-55	41
3	1	282	300
3	2	249	274
3	3	-64	10
4	-3	134	109
4	-2	176	188
4	-1	-59	4

addition to the usual structural parameters, were refined for 4 cycles. The values for R_1 and R_2 dropped to 3·6 and 4·4%, respectively. The final values for the components G_{ij} are given in Table 6.

A third refinement was carried out which included as variable parameters the six components G_{ij} of the tensor characterizing the anisotropic extinction in a Type II crystal. The initial values used were those derived for the α-DOX crystal. These six components, in addition to the usual structural parameters, were refined for 4 cycles yielding values of 2·8% and 3·9% for R_1 and R_2 respectively. The values for the components G_{ij} are included in Table 6. In the final cycle of all of the three above refinements, no shift in any parameter was larger than a standard deviation. No attempts were made to carry out refinements on a merged data set which would include intensities from Data Set 2.

A comparison of the R_2 values for the various models indicates that the anisotropic Type II refinement best characterizes the extinction in this particular crystal. The atomic positional and thermal parameters derived from the last cycle of the anisotropic Type II extinction are given in Table 7, along with the corresponding standard deviations in these parameters as derived from the inverse matrix. These parameters correspond to values for R_1 and R_2 (based on F) of 2·1% and 2·0% respectively. The values for $100|F_o|$ (corrected for extinction) and $100|F_c|$ (in electrons) are given in Table 8. The agreement in the positional parameters among all of the various refinements is comparable with that for α-DOX.

It is interesting to compare the extinction parameters given in Tables 3 and 6 for the α-DOX and α-POX crystals respectively. The form of the anisotropic extinction coefficient for a Type II crystal is $g=(M'\mathbf{G}M)^{-1/2}$. The anisotropy of the extinction appears to be very similar for both crystals, with the G_{22} component being the largest in both cases. The vector component is largest for those planes whose normals have a large component in the direction of the b axis. Therefore, the extinction coefficient will be largest for $h0l$ reflections. The mosaic spread and particle size corresponding to the diagonal elements of the non-diagonalized tensor **G** provide some idea of mosaic spread and particle size and their anisotropies. The values of $\bar{\mathbf{r}}$ (in direction **i**) $=10^{-4}\lambda G_{ii}^{1/2}$ are given in Table 9 for α-POX and α-DOX. The mean domain radius is much smaller near the b direction than in directions lying near the ac plane. This treatment should not be interpreted as giving a completely true picture of the mosaic structure because of the gross approximations made in this model. Nevertheless, these results do show that extinction can be anisotropic, and corrections for this anisotropy can be important.

Table 9. *Mean domain shapes for the* α-POX *and* α-DOX *crystals*

	α-POX	α-DOX
$\bar{r}$ (in direction 1)*	10·34	7·63
$\bar{r}$ (in direction 2)	3·34	3·86
$\bar{r}$ (in direction 3)	11·90	7·41

* The values of $\bar{r}$, in centimeters, have been multiplied by 10^5.

In difference maps computed after isotropic extinction corrections the highest features for both α-POX and α-DOX were about 0·16 e.A^{-3} in the centers of the C–C bonds. Maps computed after anisotropic extinction corrections no longer show these features, and show no density greater than about 0·1 e.A^{-3}. The disappearance of the residual density in the middle of the C–C bond may be due to a change in atomic scattering factors in going from the isotropic to anisotropic extinction correction or it may be due to this correction itself. Obviously the introduction of additional parameters in the anisotropic extinction model will tend to reduce the features of a residual density map. Nevertheless, as discussed in the last paper in this series, the differences between $|F_o|$ and $|F_c|$ after the anisotropic extinction correction are interpretable in terms of bonding effects.

Discussion

The results of this study confirm the general structural features of α-POX as described by previous investigators. The bond lengths and angles for both α-POX and α-DOX are given in Tables 10 and 11, respectively, along with the values obtained from the recent neutron diffraction studies of Sabine *et al.* (1969) and Coppens & Sabine (1969). The X-ray diffraction values for the O–H and O–D bond distances are consistently shorter than those found in the neutron diffraction studies. The corresponding X-ray and neutron diffraction values for bonds involving only the heavy atoms agree very well except for those which include the hydroxylic oxygen atom. Possible explanations for these differences will be offered later.

Perspective drawings of the structures of α-POX and α-DOX as viewed down the b axis are shown in Figs. 1 and 2 respectively. These Figures also display the labelling system for the various atoms. (These drawings were plotted with Johnson's program *ORTEP*. The scale represents a 50% probability contour for the thermal ellipsoids.) Discrete water molecules and oxalic acid molecules are linked together by a three-dimensional network of hydrogen bonds. The structures of α-POX and α-DOX are essentially identical except for differences in the corresponding OHO and ODO distances.

The oxalic acid molecule

The oxalate fragment is completely planar. The equation of the best least-squares plane through the carbon and oxygen atoms for each substance is given in Table 12. The deviation of each atom from the plane is also included. Including hydrogen (deuterium), the oxalic acid molecule has a crystallographic center of symmetry which lies between the two atoms. The distances of the hydrogen and deuterium atoms from the plane are

only 0·016 and 0·029 Å so that the whole acid molecule is essentially planar. The $(COO)_2$ group has also been found to be planar in β-deuterooxalic acid dideuterate (Iwasaki & Saito, 1967), α-anhydrous oxalic acid (Cox, Dougill, & Jeffrey, 1952), sodium oxalate (Jeffrey & Parry, 1952), lithium oxalate (Beagley & Small, 1964), and nearly planar in potassium oxalate monohydrate (Hodgson & Ibers, 1969). In contrast the two carboxyl

Table 10. *Final bond lengths for* α-POX *and* α-DOX

	α-POX		α-DOX	
Bond	X-ray*	Neutron†	X-ray‡	Neutron§
C(1)–C(1′)	1·538 (2) Å	1·536 (3) Å	1·537 (2) Å	1·539 (2) Å
C(1)–O(1)	1·285 (1)	1·291 (5)	1·287 (1)	1·291 (2)
C(1)–O(2)	1·212 (1)	1·212 (4)	1·209 (1)	1·208 (2)
O(1)–H(1)	0·89 (2)	1·026 (7)	0·86 (2)	1·031 (2)
O(3)–H(2)	0·84 (2)	0·964 (7)	0·83 (2)	0·954 (2)
O(3)–H(3)	0·79 (3)	0·956 (9)	0·78 (2)	0·954 (2)
H(1)···O(3″)	1·63 (2)	1·480 (7)	1·67 (2)	1·493 (2)
H(2)···O(2‴)	2·03 (2)	1·917 (8)	2·05 (2)	1·939 (2)
H(3)···O(2)	2·17 (2)	1·979 (9)	2·21 (2)	2·008 (2)
O(1)···O(3″)	2·512 (1)	2·506 (4)	2·531 (1)	2·524 (2)
O(3)···O(2‴)	2·864 (2)	2·864 (5)	2·880 (2)	2·879 (2)
O(3)···O(2)	2·883 (1)	2·881 (4)	2·907 (1)	2·906 (2)

* These values are derived from the parameters in Table 7.
† These values are those of Sabine *et al.* (1969).
‡ These values are derived from the parameters in Table 4.
§ These values are those of Coppens & Sabine (1969).

Table 11. *Final bond angles for* α-POX *and* α-DOX

	α-POX		α-DOX	
Bond	X-ray*	Neutron†	X-ray‡	Neutron§
O(1)–C(1)–O(2)	126·8 (1)°	126·6 (3)°	126·8 (1)°	126·6 (1)°
O(1)–C(1)–C(1′)	112·1 (1)	112·4 (3)	111·8 (1)	112·2 (1)
O(2)–C(1)–C(1′)	121·1 (1)	121·0 (3)	121·4 (1)	121·2 (1)
C(1)–O(1)–H(1)	114·3 (8)	114·4 (6)	113·8 (8)	112·8 (1)
H(2)–O(3)–H(3)	101·5 (15)	105·9 (7)	101·2 (17)	105·8 (2)
O(1)–H(1)···O(3″)	177·4 (15)	179·3 (6)	176·3 (15)	177·4 (1)
H(1)···O(3″)–H(2″)	113·6 (10)	112·8 (7)	113·7 (10)	113·7 (1)
H(1)···O(3″)–H(3″)	112·0 (7)	117·6 (4)	110·7 (7)	119·2 (1)
O(3)–H(2)···O(2‴)	171·0 (13)	166·9 (6)	172·0 (13)	167·7 (2)
H(2)···O(2‴)–C(1‴)	124·8 (4)	122·8 (6)	125·2 (4)	123·1 (1)
O(3)–H(3)···O(2)	150·2 (19)	156·6 (7)	148·9 (20)	156·0 (2)
H(3)···O(2)–C(1)	130·9 (4)	129·5 (7)	131·0 (4)	129·6 (1)

* These values are derived from the parameters in Table 7.
† These values are those of Sabine *et al.* (1969).
‡ These values are derived from the parameters in Table 4.
§ These values are those of Coppens & Sabine (1969).

Table 12. *Best weighted-least-squares plane through the oxalate fragment**

	Atoms	*A*	*B*	*C*
α-POX	C(1), O(1), O(2), C(1′), O(1′), O(2′)	3·132	3·077	−0·5445
α-DOX	C(1), O(1), O(2), C(1′), O(1′), O(2′)	3·144	3·081	−0·5439

Distances in Å, of atoms from the plane†

	α-POX	α-DOX
C(1)	−0·0013	−0·0018
O(1)	0·0004	0·0005
O(2)	0·0004	0·0006
H(1)	0·0163	0·0289
C(1′)	0·0013	0·0018
O(1′)	−0·0004	−0·0005
O(2′)	−0·0004	−0·0006
H(1′)	−0·0163	−0·0289

* Equations of planes are of the form: $AX+BY+CZ=0$ in monoclinic coordinates.
† The estimated average standard deviation is about 0·0010 Å.

groups are rotated by 26·6° about the carbon–carbon bond in ammonium oxalate monohydrate (Robertson, 1965). In both α-POX and α-DOX the two C–O distances in the carboxyl group are distinctly different. The bond between carbon and the oxygen atom not involved in hydrogen bonding [C(1)–O(2)] is shorter than the one between carbon and the hydrogen bonded oxygen atom [C(1)–O(1)] by an average value of 0·076 (1) Å. The neutron diffraction value for the hydroxyl O–D bond length of 1·031 (2) Å appears not to be significantly different from the corresponding O–H distance of 1·026 (7) Å.

The hydrogen bonding

In α-POX the oxygen atom of the water molecule is an acceptor for a strong hydrogen bond (O1)–H(1)...O(3′′) (2·512 Å) with the hydroxyl oxygen of the oxalic acid molecule. The hydrogen atom is completely associated with the hydroxyl oxygen atom as no evidence was found for any disordering of the hydrogen position or the existence of an H_3O^+ ion. The O(1)–H(1)...O(3′′) angle of 179·3° indicates that the hydrogen atom lies very close to the line joining O(1) and O(3). The weaker O(3)–H(2)...O(2′′′) (2·864 Å) and O(3)–H(3)...O(2) (2·883 Å) hydrogen bonds are far from linear (166·9 and

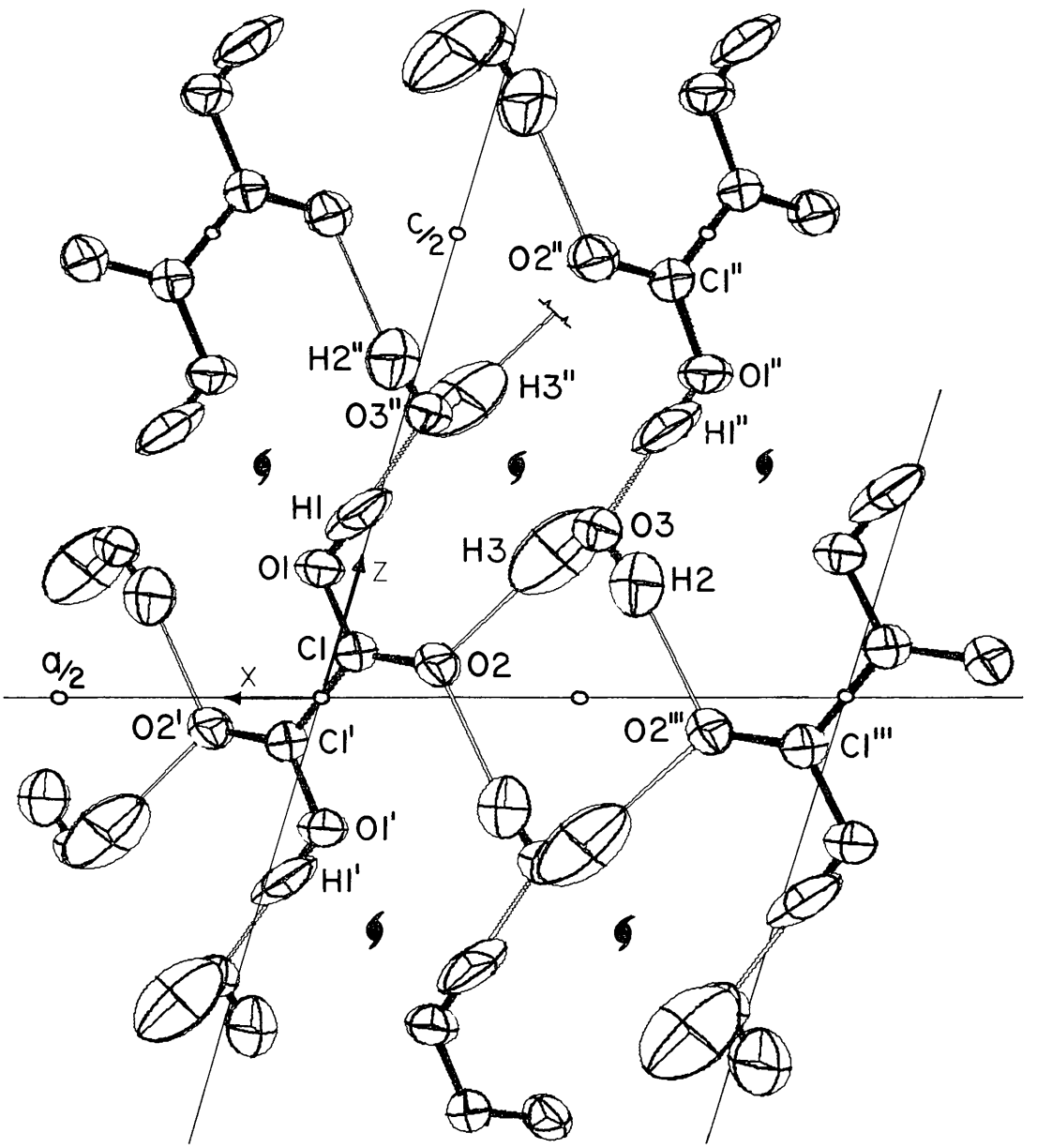

Fig. 1. Perspective view of α-POX along the *b* axis. The bond terminated indicates that the atom H(3′′) is hydrogen bonded to an oxygen atom that is displaced one unit-cell along the negative *b* axis from O(2′′).

156·6° respectively). These two hydrogen bonds form closed quadrilaterals which connect adjacent oxalic acid molecules. Infinite helical chains of hydrogen bonds extend up the *b* axis. The sequence of the chain is ...H(3″)–O(3″)...H(1)–O(1)–C(1)–O(2)...H(3)–O(3)...H(1′)–O(1′)–C(1′)–O(2″)... where O(2″) is hydrogen-bonded to a hydrogen atom displaced one unit-cell up the *b* axis from the starting point, H(3″).

The neutron values for the O–H bonds lengths in the water molecule (0·964 and 0·956 Å) are the same as those in gaseous water (0·96 Å). The H(2)–O(3)–H(1) angle of 105·9° is not significantly different from the value of 104·5° for water vapor.

Effects of extinction on bond lengths and bond angles

Selected bond lengths for some of the various extinction models are compared in Tables 13 and 15 for α-POX and α-DOX respectively. Corresponding selected bond angles are compared in Tables 14 and 16. Even though the agreement among the corresponding positional parameters for the various extinction models is good, small systematic differences in these parameters could introduce significant differences in bond lengths and angles. The largest differences that exist in corresponding values between any two sets are about twice the combined standard deviations. The values for the C(1)–C(1′) and C(1)–C(2) distances in α-POX

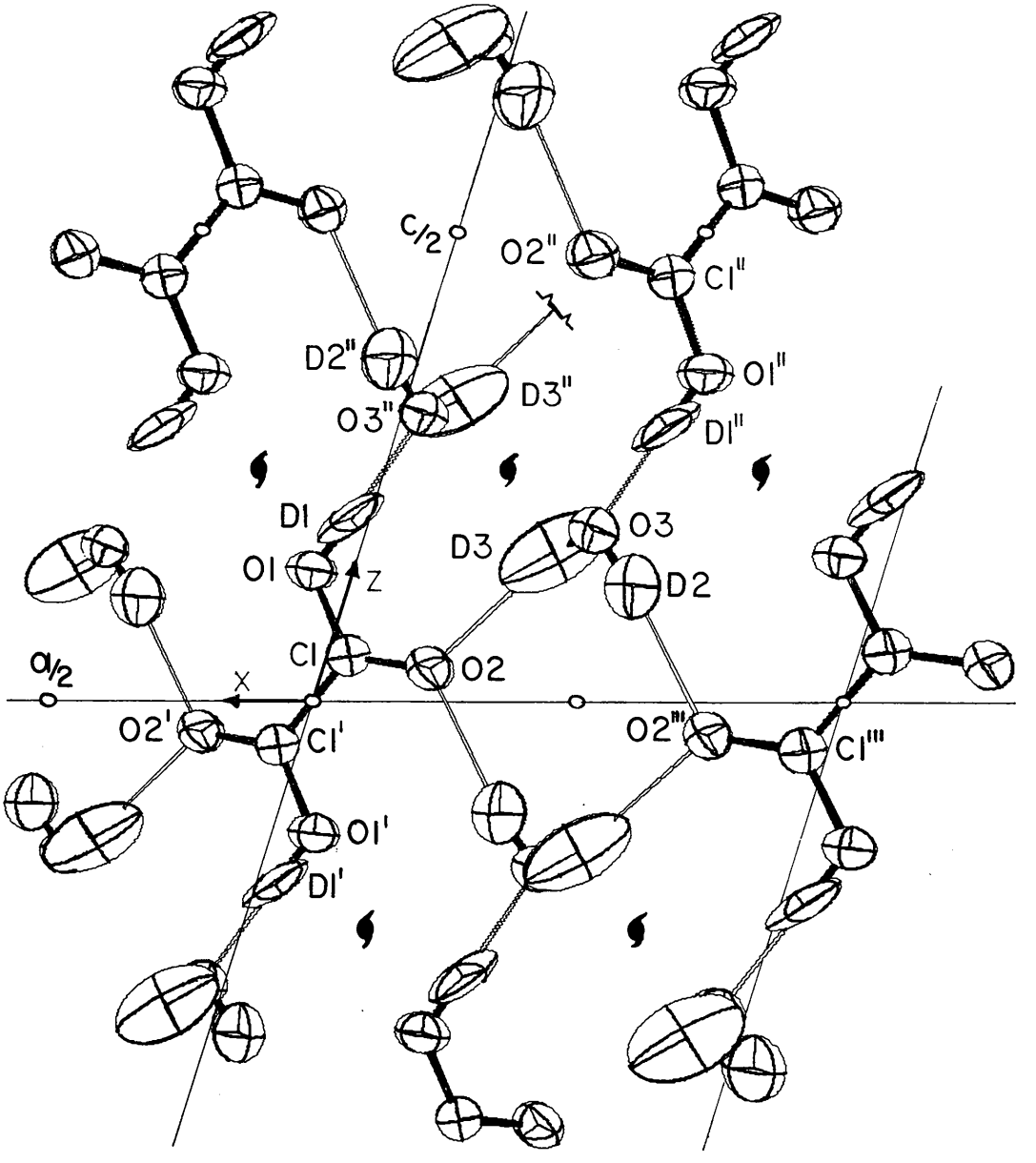

Fig. 2. Perspective view of α-DOX along the *b* axis.

for the merged data set are significantly different from those of the final anisotropic type II extinction refinement. They also differ somewhat from the values of the other refinements. The agreement among the corresponding values for α-DOX is much better. For the α-POX merged data set, the procedure of separately correcting two sets of data for extinction and then merging them is a possible source for systematic errors.

The corresponding X-ray and neutron values for the bond lengths involving only the heavy atoms agree very well. Exceptions are those bonds which involve the atom O(1). The X-ray and neutron values for the z coordinate of O(1) differ by 0·008 Å for both substances. This shortens the C(1)–O(1) bond and lengthens the O(1)...O(3″) distance relative to the corresponding neutron values. At present, these differences are poorly understood and are attributed to either systematic errors in some or all of the experiments or to bonding effects. This will be discussed in greater detail in the fourth paper in this series (Coppens *et al.*, 1969).

Table 13. *Comparison of bond lengths in* α-POX *for various extinction models*

Bond	No correction	Zachariasen correction	Merged data set	Anisotropic Type I correction	Anisotropic Type II correction
C(1)–O(1′)	1·543 (6) Å	1·545 (3) Å	1·546 (2) Å	1·539 (2) Å	1·538 (2) Å
C(1)–O(1)	1·284 (4)	1·284 (2)	1·281 (2)	1·285 (1)	1·285 (1)
C(1)–O(2)	1·210 (4)	1·208 (2)	1·207 (2)	1·212 (1)	1·212 (1)
O(1)–H(1)	0·98 (6)	0·94 (3)	0·82 (4)	0·89 (2)	0·89 (2)
O(3)–H(2)	0·93 (6)	0·83 (3)	0·81 (3)	0·82 (2)	0·84 (2)
O(3)–H(3)	0·74 (7)	0·82 (3)	0·80 (3)	0·80 (2)	0·79 (3)
O(1)···O(3″)	2·507 (4)	2·507 (2)	2·510 (2)	2·512 (2)	2·512 (1)
O(3)···O(2‴)	2·867 (4)	2·870 (2)	2·869 (2)	2·865 (2)	2·864 (2)
O(3)···O(2)	2·887 (3)	2·883 (2)	2·884 (2)	2·883 (1)	2·883 (1)

Table 14. *Comparison of bond angles in* α-POX *for various extinction models*

Bond	No correction	Zachariasen correction	Merged data set	Anisotropic Type I correction	Anisotropic Type II correction
O(1)–C(1)–O(2)	126·9 (3)°	126·9 (3)°	127·1 (1)°	126·8 (1)°	126·8 (1)°
O(1)–C(1)–C(1′)	112·1 (3)	112·0 (2)	111·9 (1)	112·0 (1)	112·1 (1)
O(2)–C(1)–C(1′)	121·0 (3)	121·1 (2)	121·0 (1)	121·1 (1)	121·1 (1)
O(1)–H(1)···O(3″)	176·0 (38)	178·3 (18)	175·7 (22)	176·4 (17)	177·4 (15)
O(3)–H(2)···O(2‴)	175·3 (38)	170·8 (24)	169·0 (19)	171·4 (15)	171·0 (13)
O(3)–H(3)···O(2)	159·0 (61)	160·2 (28)	153·9 (21)	150·4 (21)	150·2 (19)

Table 15. *Comparison of bond lengths in* α-DOX *for various extinction models*

Bond	No correction	Zachariasen correction	Merged data set	Anisotropic Type I correction	Anisotropic Type II correction
C(1)–C(1′)	1·540 (6) Å	1·543 (3) Å	1·541 (3) Å	1·538 (2) Å	1·537 (2) Å
C(1)–O(1)	1·285 (4)	1·286 (2)	1·283 (2)	1·287 (1)	1·287 (1)
C(1)–O(2)	1·210 (4)	1·207 (2)	1·209 (2)	1·209 (1)	1·209 (1)
O(1)–D(1)	0·89 (6)	0·91 (2)	0·88 (2)	0·85 (2)	0·86 (2)
O(3)–D(2)	0·91 (5)	0·82 (2)	0·84 (2)	0·83 (2)	0·83 (2)
O(3)–D(3)	0·70 (7)	0·79 (3)	0·70 (4)	0·77 (2)	0·78 (2)
O(1)···O(3″)	2·530 (5)	2·525 (2)	2·531 (2)	2·532 (1)	2·531 (1)
O(3)···O(2‴)	2·880 (5)	2·882 (2)	2·876 (2)	2·879 (1)	2·880 (2)
O(3)···O(2)	2·910 (3)	2·908 (2)	2·908 (1)	2·907 (1)	2·907 (1)

Table 16. *Comparison of bond angles in* α-DOX *for various extinction models*

Bond	No correction	Zachariasen correction	Merged data set	Anisotropic Type I correction	Anisotropic Type II correction
O(1)–C(1)–O(2)	126·9 (3)°	126·9 (2)°	126·9 (1)°	126·8 (1)°	126·8 (1)°
O(1)–C(1)–C(1′)	112·0 (3)	111·9 (2)	112·1 (2)	111·8 (1)	111·8 (1)
O(2)–C(1)–C(1′)	121·1 (3)	121·2 (2)	121·0 (1)	121·4 (1)	121·4 (1)
O(1)–D(1)···O(3″)	175·1 (41)	177·7 (18)	117·4 (25)	175·5 (16)	176·3 (15)
O(3)–D(2)···O(2‴)	175·6 (39)	170·3 (21)	171·7 (19)	171·5 (13)	172·0 (13)
O(3)–D(3)···O(2)	150·2 (19)	156·0 (22)	145·1 (31)	148·0 (21)	148·9 (20)

The isotope effect

All three crystallographically independent O–H...O bonds expand significantly with deuteration. The differences in the corresponding O–D...O and O–H...O distances are given in Table 17. The isotope effect is completely localized in the hydrogen bonds, as the bond lengths within the oxalate fragment remain invariant upon deuteration. The cell constants for both substances given previously in Table 1 agree with the directions and magnitudes of maximum and minimum expansion in the (010) projection of the unit cell originally found by Robertson & Ubbelohde (1939). Any changes in the *b* direction were not measured but were assumed to be small. They concluded that the changes in the lattice parameters were almost entirely due to an expansion of 0·041 Å in the strong O(1)–H(1)...O(3″) hydrogen bond since the direction of this bond is very near that of the maximum expansion. It was assumed that deuteration had little or no effect on the two weaker hydrogen bonds. even though the direction of the O(3)–H(3)...O(2) bond is essentially coincident with the direction of maximum expansion. The present results clearly indicate that this assumption is not valid as the largest expansion does in fact occur in this weak bond. There is also a significant expansion in the O(3)–H(2)...O(2‴) distance, which lies near the direction of minimum expansion. Ubbelohde & Roberson originally reported a small contraction of −0·0001 per unit length in this bond. Deuteration has no significant effect on the angles of the two weak hydrogen bonds. The O(1)–H(1)...O(3″) angle appears to bend 1·9(6)° with deuteration. This is accompanied by a slight decrease of 1·6(6)° in the C(1)–O(1)–H(1) angle.

Table 17. *Isotope effect on hydrogen bond distances*

	r_H	$r_D - r_H$	
Bond	X-ray	X-ray	Neutron
O(1)···O(3″)	2·512 Å	0·019 (1) Å	0·017 (5) Å
O(3)···O(2‴)	2·864	0·016 (3)	0·018 (6)
O(3)···O(2)	2·883	0·024 (1)	0·022 (5)

These results clearly show that correlations of specific bond-length changes with changes in cell constants alone are unreliable for complex crystals such as α-POX which contain more than one crystallographically independent hydrogen bond per unit cell. Consequently, most of the current data on isotope effects may be in error and should be carefully checked by single-crystal diffraction techniques.

The sensitivity of hydrogen bonds to isotopic substitution has been theoretically interpreted by Gallagher (1959) to be due to the differences in zero-point energy distributions of hydrogen and deuterium in the O...O potential field. The isotope effect was attributed to be a function of hydrogen bond length. Large expansions were predicted for strong bonds which diminished as the O...O distance increased. However, this ignores cooperative effects that appear to exist in systems such as α-POX, which contain complex networks of hydrogen bonds. Large isotope effects are not always localized in only the strongest hydrogen bonds, but may be spread throughout all of the hydrogen bonds in the crystal. Such effects are important and make it difficult to correlate directly the isotope effect with only hydrogen bond strengths in complex structures. Such considerations could alter conclusions that have been reached with regard to the structural effects of deuteration on the α-helix of proteins (Tomita, Rich, de Loze & Blout, 1962).

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A Neutron Diffraction Study of α-Oxalic Acid Dihydrate

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A determination of the crystal structure of α-oxalic acid dihydrate from three-dimensional neutron diffraction data has confirmed, with greater precision, the atomic parameters found previously from *h*0*l* and 0*kl* data. Assumptions concerning the vibration state of the molecule are shown to introduce uncertainties in bond lengths much greater than the standard deviations derived from least-squares refinement of atomic parameters. The extent to which data collection at low temperature would reduce the uncertainty is calculated.

Introduction

The crystal structure of α-oxalic acid dihydrate (here abbreviated α-POX) has been investigated several times by X-ray diffraction methods. Ahmed & Cruickshank (1953) obtained the positions of the carbon and oxygen atoms by a re-examination of earlier two-dimensional data of Robertson & Woodward (1936) and Brill, Hermann & Peters (1942). Garrett (1954) carried out a neutron diffraction investigation and located the hydrogen atoms from *h*0*l* and 0*kl* data.

The present three-dimensional neutron structure determination has been carried out in order to obtain more precise atomic parameters (particularly for the hydrogen atoms), to examine the effects of assumptions about the atomic anisotropic thermal motions on the observed bond lengths, and to enable a more complete comparison between X-ray and neutron diffraction studies of this material (α-POX, Delaplane & Ibers, 1969), and the two deuterated crystalline forms (α-DOX and β-DOX, Coppens & Sabine, 1969).

Experimental

The crystals of oxalic acid dihydrate were obtained from Dr A. McL. Mathieson of the Division of Chemical Physics, C.S.I.R.O., Melbourne.

The crystal data (from Delaplane & Ibers, 1969) are:

Space group $C_{2h}^5 - P2_1/n$,
$a = 6{\cdot}119$, $b = 3{\cdot}607$, $c = 12{\cdot}057$ Å, $\beta = 106°19'$, $Z = 2$.

Two crystals were used, one of mass 36·65 mg and one of mass 2·75 mg. Most of the data were obtained from the larger crystal which was pillar shaped with well developed {101}, {10$\bar{1}$} and {001} forms. The small crystal was cut to a rough cube.

Data collection

The data were collected on two single-crystal diffractometers installed on the reactor HIFAR. For these instruments the respective fluxes and wave lengths of the monochromatic neutron beam at the specimen are $2{\cdot}8 \times 10^5$ n cm^{-2} sec^{-1} at 1·10 Å, and 6×10^6 n cm^{-2} sec^{-1} at 1·09 Å.

The large crystal was mounted on a two-circle goniometer with **c*** along the φ axis so that a φ-rotation would present maximum and minimum path lengths for the incident and diffracted beams of 00*l* reflections and enable extinction and absorption effects to be detected. Both effects were apparent. However, the integrated intensities 00*l* observed at a φ-setting half way between the minimum and maximum neutron path length positions were 30 per cent larger than those