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### References

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

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

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

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

### Introduction

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

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

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showed that least-squares refinement with spherical form factors leads, for the hypothetical structure, to atomic positions which are displaced by *ca.* 0.02 Å from the true locations of the nuclei. Calculations with crude Slater-type wave functions showed that for a terminal oxygen atom in a nitro group the centroid of the electronic charge density may indeed be displaced by a few hundredths of an Ångström, the exact figure depending on the hybridization of the oxygen atom (Coppens & Coulson, 1967). In principle it is therefore possible to extract information from the X-ray data on the atomic hybridization and, more generally, on the electronic charge distribution in the crystal.

X-ray powder data on diamond and silicon have been analyzed by Dawson (1967) and Dawson & Sanger (1967) and significant information on the electron distribution was obtained. X-ray data on more complicated structures are at present of lower accuracy, but O'Connell, Ray & Maslen (1966) have shown through inspection of a large number of structures and averaging over chemically equivalent bonds within one structure, that bonding features generally occur in electron density maps.

A combination of X-ray and neutron diffraction was first applied by Calder, Cochran, Griffiths & Lowde (1962). They concluded that in the crystals of LiH the hydrogen ion suffers a pronounced contraction as compared with the free ion. Similarly, it was shown by Sabine & Dawson (1963) that a combination of the two techniques would permit a direct determination of the atomic scattering curves in BeO.

Comparative X-ray and neutron diffraction was applied to an organic molecule by Coppens (1967), who obtained evidence for appreciable deviations from atomic spherical symmetry in *sym*-triazine through the use of Fourier difference syntheses.

The present study is a continuation of such investigations. Unlike *sym*-triazine, oxalic acid dihydrate is intermolecularly hydrogen bonded. Its electronic structure may therefore be perturbed by intermolecular forces, though perhaps not within the accuracy of our experiments. On the other hand the stronger forces lead to smaller thermal displacements of the scattering centers, an obvious advantage in accurate studies.

In the preceding three papers of this series (Delaplane & Ibers, 1969; Sabine, Cox & Craven, 1969; Coppens & Sabine, 1969) detailed studies of the crystal structures of  $\alpha$ -protooxalic acid dihydrate ( $\alpha$ -POX) and the  $\alpha$  and  $\beta$  modifications of deuteriooxalic acid dideuterate ( $\alpha$ -DOX and  $\beta$ -DOX respectively) have been reported. In this paper the neutron and X-ray atomic positional and thermal parameters of  $\alpha$ -POX and in particular  $\alpha$ -DOX are analyzed in terms of the electronic charge distribution.

### Theory and assumptions

The general time-averaged expression for the scattering of an incident wave by an assemblage of scatterers is given, in the kinematic approximation, by

$$I(\mathbf{S}) \sim \sum_{j=1}^N \sum_{j'=1}^N f_j(\mathbf{S}) f_{j'}^*(\mathbf{S}) \exp 2\pi i \mathbf{S} \cdot (\mathbf{r}_j - \mathbf{r}_{j'}) T_j(\mathbf{S}) \cdot T_{j'}^*(\mathbf{S});$$

$N$  is the number of atoms in the crystal,  $f_j$  is the scattering amplitude of the  $j$ th atom and  $\mathbf{r}_j$  is the position vector of the  $j$ th atom,  $T$  is the Debye-Waller factor, and the double sum is carried out over all atoms in the crystal.  $\mathbf{S}$  is the scattering vector  $2\pi/\lambda (\mathbf{s} - \mathbf{s}_0)$  where  $\mathbf{s}_0$  and  $\mathbf{s}$  are unit vectors along the directions of the incident and diffracted beams.

In the present work it is assumed that:

(1) The kinematic approximation holds. This is either true because extinction, multiple reflection and

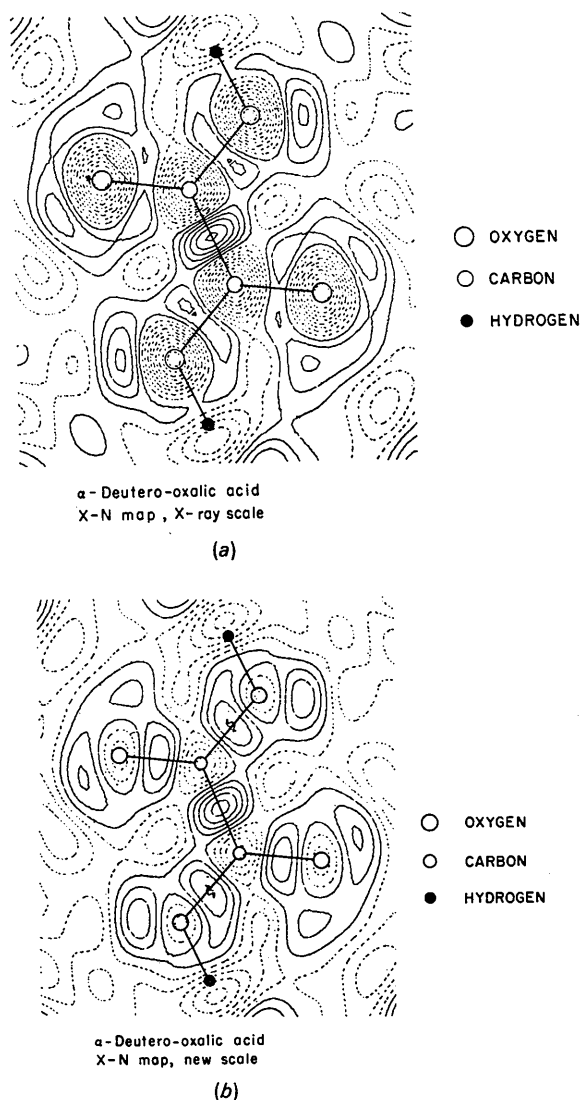


Fig. 1. X-N map through the molecular plane of the oxalic acid molecule in  $\alpha$ -DOX. Contours at  $0.05 \text{ e.}\text{\AA}^{-3}$ . Zero and negative contours dashed. (a) with X-ray scale factor (b) with scale factor obtained after additional refinement. See text.

absorption effects are low, or because the experimental data have been corrected for these effects.

(2) The adiabatic approximation holds. This implies that the atomic electrons have the same coordinates relative to the nucleus at any nuclear position. This is a quite accurate approximation (Born & Huang, 1954).

(3) The harmonic approximation holds ( $T_j$  real). This may not be accurately the case; however, it is not believed to introduce errors in the present comparison since the nucleus and electron distribution are affected equally.

(4) The relative contribution of thermal diffuse scattering (TDS) is the same for the two techniques since the inelastic one-phonon cross section for acoustic

modes (which is the dominant contributor to TDS at room temperature) contains the structure factor for the reflection (Cochran, 1963). The directional terms in the cross-section expression are also the same for X-rays and neutrons. Only when the neutron velocity is below the velocity of sound in the crystal is the TDS less for neutrons than for X-rays. This is unlikely in our experiment since the velocity of the thermal neutrons used is about 3300 m sec<sup>-1</sup>.

The two formulae for X-ray and neutron intensities are then

$$I_X(\mathbf{k}) \sim \sum_j \sum_{j'} f_j(\mathbf{S}) f_{j'}^*(\mathbf{S}) \exp 2\pi i \mathbf{S} \cdot (\mathbf{r}_j - \mathbf{r}_{j'}) T_j T_{j'}$$

$$I_N(\mathbf{k}) \sim \sum_j \sum_{j'} b_j b_{j'}^* \exp 2\pi i \mathbf{S} \cdot (\mathbf{r}_j - \mathbf{r}_{j'}) T_j T_{j'}$$

Since 1 Å wavelength neutrons are used and magnetic ions are absent, the nucleus alone is the scattering center and  $b$  is independent of both  $\mathbf{S}$  and the atomic environment.

It is commonly assumed in conventional structure analysis that the X-ray scattering factor  $f_j(\mathbf{S})$  is also independent of the atomic environment in the crystal. It is this assumption that is challenged in the work summarized above and in the present article.

#### *X-ray minus neutron Fourier sections*

A pictorial view of the distortions of atomic spherical symmetry can be obtained with an  $X-N$  difference Fourier (Coppens, 1967). Such a map is a Fourier summation with coefficients  $F_X - F_N$ , in which  $F_X$  are the observed X-ray structure factors with the calculated sign and the  $F_N$  are the corresponding structure factors calculated with the spherically symmetric free-atom X-ray scattering factors  $f(\mathbf{S})$  and neutron positional and temperature parameters. As discussed below the X-ray parameters differ from the neutron parameters because of the use of free-atom scattering factors and the  $X-N$  difference map (Fig. 1) therefore contains much larger features than the difference map calculated with the final X-ray parameters (Fig. 2). In the absence of an experimental determination of the scale factor the set  $F_N$  can be scaled to  $F_X$  using the X-ray scale factor as determined by least-squares. However, this scale factor is also affected by the incorrect choice of scattering factors. In the case of  $\alpha$ -DOX an additional cycle on the scale factor  $k$  alone, using the neutron least-squares parameters and X-ray observations, led to a 3.9% reduction of  $k$  (defined by  $kF_{\text{calc}} = F_{\text{obs}}$ ). Quantitatively the effect on the difference maps (Fig. 1) is quite pronounced, indicating the desirability of an experimental determination of the scale factor in future work. Qualitatively the two maps in Fig. 1 are similar. The qualitative features in these maps correspond to elementary theoretical-chemical concepts, such as overlap density and lone-pair density, as was the case for *sym*-triazine (Coppens, 1967) and the more recent low-temperature study on cyanuric acid (Coppens & Vos, 1969). Thus, overlap density is observed in the C-C

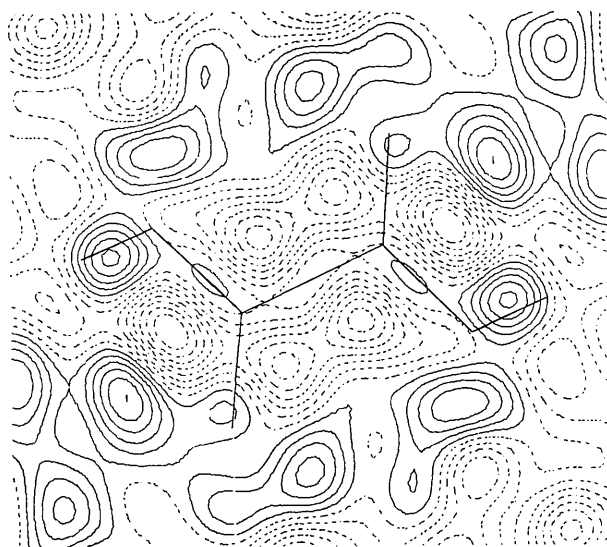


Fig. 2. Conventional X-ray difference map. Contours at 0.0125 e.Å<sup>-3</sup>. Note the difference in contour interval between Figs. 1 and 2.

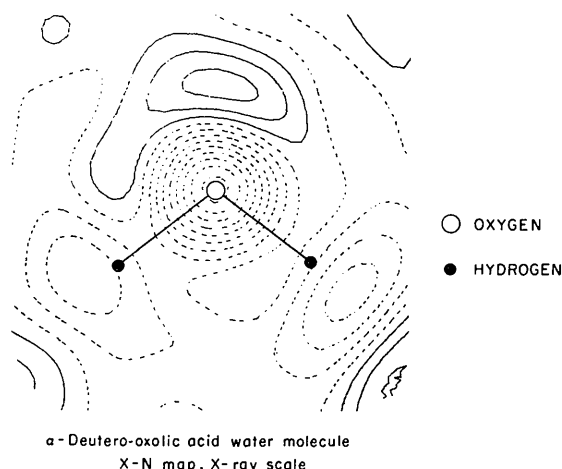


Fig. 3.  $X-N$  map through plane of water molecule. Scale factor and contours as in Fig. 1(a).

bond and in both C-O bonds. There are two lone pairs around the carbonyl oxygen atom and one lone pair at the back of the hydroxyl oxygen atom.

The electronic structures of these two oxygen atoms can be described as  $(1s)^2 (2sp^2)^1 (2sp^2)^2 (2sp^2)^2 (2p\pi)^1$  and  $(1s)^2 (2sp^2)^1 (2sp^2)^1 (2sp^2)^2 (2p\pi)^2$  respectively. This simple hybridization scheme therefore predicts two lone pairs in the molecular plane around the terminal carbonyl-oxygen atom and one lone pair in the molecular plane at the back of the hydroxyl oxygen atom, in good agreement with the observed difference density.

Similarly, the extra density observed at the back of the oxygen atom in the water molecule (Fig. 3) is attributed to the oxygen lone-pair orbitals.

It is of interest to examine sections perpendicular to the molecular plane through the overlap peaks at the midpoint of the bonds. The sections through the midpoints of C-C, C-O(1) and C=O(2) are given in Fig. 4. It is striking that all these peaks are elongated in the direction perpendicular to the molecular plane. It might be argued that the elongation represents the extra thermal motion in this direction. The root mean square displacements for the carbon atom and the two oxygen atoms are respectively 14% and 60% larger perpendicular to the molecular plane. Taking into account that the rigid-body motions of the molecule are translations and one libration around the inertial axis in the direction of the C-C bond (Coppens & Sabine, 1969), we find that the displacements of the C-C and C-O bond-midpoints are about 14% and 26% higher in the direction perpendicular to the plane. However, it may be pointed out that such a difference in r.m.s. amplitude corresponds to a very small elongation of the bond peak, since the valence electron density, unlike the 1s core density, is fairly diffuse (Coppens, 1969). The extension of the bond peak is therefore attributed to the partial  $\pi$ -character of the bond involved. A similar feature was observed in the *X-N* map of the aromatic *sym*-triazine molecule (Coppens, 1967).

The extension is most pronounced for the C-C bond, which at first sight is somewhat surprising since its bond length of 1.539 (2) Å is larger than usually observed for  $sp^2-sp^2$  C-C bonds. In hexaphenylbenzene the exocyclic bond, which is not shortened by conjugation as the rings are almost perpendicular, is 1.515 Å according to the electron diffraction results (Almenningen, Bastiansen & Skancke, 1958) and 1.499 Å according to the solid state X-ray determination (Bart, 1968). Thus the bond length alone would certainly not suggest conjugation between the carboxyl groups of the molecule. Calculations by Harcourt (1965) have suggested that the bond in the oxalate anion has in fact partial  $\pi$ -character, its lengthening being a result of delocalization of the oxygen lone-pair electrons into the antibonding  $\sigma$ -orbital of the C-C bond, leading to a  $\sigma$ -bond-order less than 1. Trueblood, Goldish & Donohue (1961) on the other hand, have attributed the anomalous length of the C-C bond in carboxylic acids and

the C-N bond in nitro compounds to non-bonded C---O repulsions. The present evidence, which indicates that the C-C bond in oxalic acid does indeed have  $\pi$ -character, would be compatible with either explana-

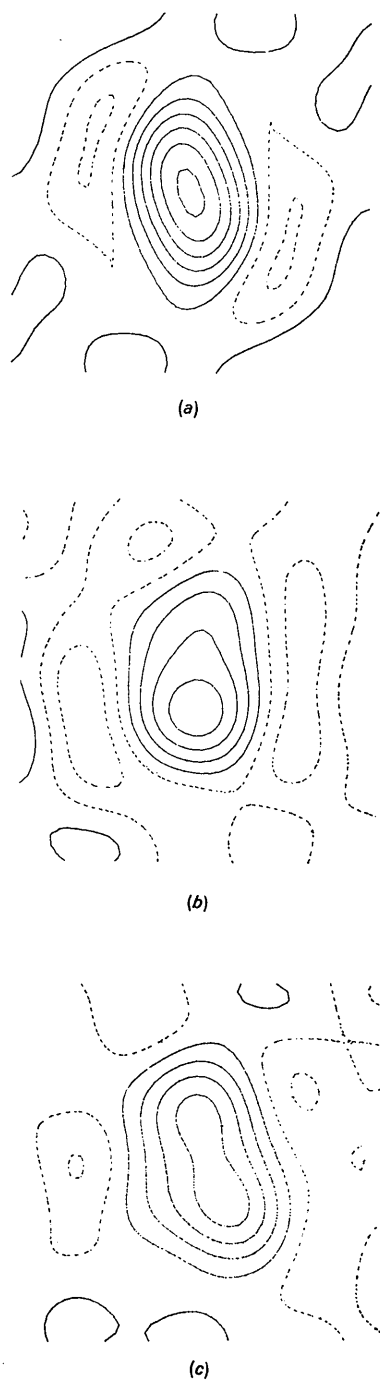


Fig. 4. *X-N* sections through the midpoint of the bonds. Scale factor and contours as in Fig. 1(b). The normal to the molecular plane is vertical in all three figures. (a) C-C bond (b) C-O (1) (c) C=O (2).

tion. Both mechanisms may in fact contribute to the lengthening of the bond.

It is clear that curves relating bond length to  $\pi$ -bond order are not valid in such a case.

*Comparison of X-ray and neutron positional parameters.*

Table 1 shows the X-ray and neutron positional parameters for the heavy atoms in both the  $\alpha$ -DOX and  $\alpha$ -POX structures. The agreement is in general excellent. The only significant difference, observed in both structures, is in the  $z$  parameter of the hydroxylic oxygen atom O(1). In the X-ray refinement this atom is shifted away from the O-H bond. Examination of

the  $X-N$  difference map (Fig. 1) shows that extra density (as compared with the spherical atom) is found both in the C-O bond and in the oxygen lone-pair region, very little density being found in the weaker O-H bond. Accordingly, the center of gravity of the charge cloud of O(1) is shifted away from the O-H bond as is the X-ray position. Such asphericity shifts were predicted earlier (Coppens & Hirshfeld, 1964; Coppens & Coulson, 1967), and have been found in a number of other compounds investigated both with X-rays and neutrons. Some of these shifts are summarized in Table 2. Their magnitude is generally 0.01 Å or less. It is important that the values are small (though significant)

Table 1. *Heavy atom positional parameters*

Fractional coordinates  $\times 10^4$

		$\alpha$ -DOX			$\alpha$ -POX		
		$x$	$y$	$z$	$x$	$y$	$z$
C(1)	X-rays	-452 (2)	545 (3)	507 (1)	-454 (2)	548 (3)	511 (1)
	Neutrons	-447 (2)	551 (3)	509 (1)	-452 (2)	547 (4)	510 (1)
O(1)	X-rays	855 (1)	-610 (3)	1477 (1)	848 (1)	-600 (3)	1481 (1)
	Neutrons	854 (2)	-609 (4)	1484 (1)	847 (4)	-599 (6)	1488 (2)
O(2)	X-rays	-2186 (1)	2297 (2)	360 (1)	-2201 (1)	2305 (2)	361 (1)
	Neutrons	-2183 (2)	2296 (4)	360 (1)	-2197 (3)	2310 (6)	360 (2)
O(3)	X-rays	-4496 (2)	6147 (4)	1808 (1)	-4512 (2)	6151 (4)	1800 (1)
	Neutrons	-4499 (2)	6139 (5)	1806 (1)	-4509 (4)	6136 (6)	1799 (2)

Table 2. *Asphericity shifts in some organic molecules (Å)*

The asphericity shift is defined as the shift of the X-ray position with respect to the position of the nucleus as determined with neutrons.

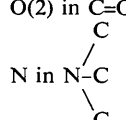
Compound	Atom	Shift	Direction	Reference
<i>sym</i> -Triazine	C in ring	0.015 (8)	Away from C-H bond	Coppens, 1967
Cyanuric acid (100°K)	N in ring	0.009 (6)	Towards lone pair	Coppens & Vos, 1969
	O(1) in C=O	0.006 (1)	Towards lone pairs	
	O(2) in C=O	0.003 (1)	Towards lone pairs	
Hexamethylene-tetramine	N in 	0.021 (7)	Towards lone pair	Duckworth, Willis & Pawley, 1969
$\alpha$ -DOX	O(1) in COD	0.008 (2)	Away from OH bond	This study
	O(2) in C=O	about $1\sigma$		
	O(3) in D <sub>2</sub> O	about $1\sigma$		
$\alpha$ -DOX	O(1) in COH	0.008 (2)	Away from OH bond	This study
	O(2) in C=O	about $1\sigma$		
	O(3) in H <sub>2</sub> O	0.005 (3)	About 45° from O(1)---O(3)	

Table 3. *Comparison of neutron and X-ray values for XH bond lengths (Å)\**

Compound	Bond	Neutron value	X-ray value	Difference	Reference
$\alpha$ -POX	O(1)-H(1)	1.026 (7)	0.89 (2)	0.14 (2)	This study
	O(3)-H(2)	0.964 (7)	0.84 (2)	0.12 (2)	
	O(3)-H(3)	0.956 (9)	0.79 (3)	0.17 (3)	
$\alpha$ -DOX	O(1)-H(1)	1.031 (2)	0.86 (2)	0.17 (2)	This study
	O(3)-H(2)	0.954 (2)	0.83 (2)	0.12 (2)	
	O(3)-H(3)	0.954 (2)	0.78 (2)	0.17 (3)	
<i>sym</i> -Triazine	C-H	1.045 (16)	0.92 (4)	0.13 (4)	Coppens, 1967
Cyanuric acid	N(1)-H(1)	1.026 (2)	0.79 (3)	0.24 (3)	Coppens & Vos, 1969
	N(2)-H(2)	1.037 (1)	0.87 (1)	0.17 (2)	

\* The bond lengths in this Table have not been corrected for apparent shortening due to thermal motion.

for the cyanuric acid low-temperature study. When this structure was refined with only the low-order X-ray data ( $\sin \theta/\lambda < 0.6 \text{ \AA}^{-1}$ ), the shifts actually increased, indicating that at higher angles a better balance is obtained between the lone-pair and overlap scattering (Coppens & Vos, 1969). It is therefore not obvious why no discrepancy is observed for the O(2) and O(3) atoms in oxalic acid, as the X-ray data for this compound include only Cu  $K\alpha$  reflections. The O(2) atom would seem to be electronically similar to the oxygen atoms in cyanuric acid which showed a discrepancy. Similarly the difference map for the water molecule (Fig. 3), shows density at the back of the oxygen atom, but a small shift of very doubtful significance is observed only in  $\alpha$ -POX. *A priori* we had expected a large discrepancy for the water molecule reflecting the lone-pair contribution to the dipole moment of  $\text{H}_2\text{O}$  (1.84 D, which if attributed to the lone pairs alone would shift the atomic centroid by about 0.04  $\text{\AA}$ ). We believe that such questions should be investigated further by collection of more accurate data at lower temperatures. It should be noted that the bonding features around all three oxygen atoms are reflected in the systematic changes in the X-ray temperature parameters to be discussed in the next section.

As is well known X-ray hydrogen atom positions are generally displaced towards the atom to which the hydrogen is bonded. This is in fact an extreme case of the asphericity shift discussed above for heavier atoms. The displacements for some of the compounds included in Table 2 are given in Table 3. In these compounds the discrepancy varies between 0.12 and 0.24  $\text{\AA}$ . This is considerably larger than the value of 0.07  $\text{\AA}$  predicted by Stewart, Davidson & Simpson (1965) from hydrogen-molecule wave functions even though the contracted

hydrogen-atom scattering curves based on these calculations were used in the present least-squares refinements. It seems to indicate an increased withdrawal of electrons from the hydrogen atom into the X-H bonds (X = C, N or O). Such a migration of charge is not unreasonable. *Ab initio* SCF calculations by Clementi and co-workers on pyridine-type molecules show for example that hydrogen in a C-H bond acts as a  $\sigma$ -donor: the population of the H 1s orbital is typically 0.7-0.8 electrons (Clementi, Clementi & Davis, 1967). In the homonuclear H-H molecule, for which the shift of 0.07  $\text{\AA}$  was calculated, no such charge migration would occur.

#### Comparison of X-ray and neutron thermal parameters

In an earlier publication some of the results of the present study were presented together with other structural results as evidence that X-ray thermal parameters are effected by bonding effects (Coppens, 1968). Here, we shall contrast the differences between the X-ray and neutron thermal parameters for  $\alpha$ -DOX with the difference-density maps of Fig. 1 and 3. The X-ray and neutron mean-square displacements of the heavy atoms in  $\alpha$ -DOX are summarized in Table 4. Significant differences are observed especially in the diagonal tensor elements, which are always larger in the X-ray case. This effect is also observed in  $\alpha$ -POX and  $\beta$ -DOX. However, the neutron data of the former were not corrected for extinction and probably are of somewhat lower accuracy than the  $\alpha$ -DOX data. For  $\beta$ -DOX the X-ray data were obtained by photographic methods. These two sets will therefore not be analyzed further.

Since the apparent X-ray motion is larger than the thermal displacements from the neutron data it is possible to plot the difference between the mean-square

Table 4. X-ray and neutron heavy atom thermal parameters  $U_{ij}$  ( $\text{\AA}^2 \times 10^4$ )

		$\alpha$ -DOX			
		X-rays	Neutrons	$\Delta$	$\Delta/\sigma$
C	11	322 (5)	288 (5)	34 (7)	+4.9
	22	389 (7)	331 (6)	58 (9)	+6.4
	33	300 (7)	246 (5)	54 (9)	+6.0
	12	-6 (5)	48 (4)	54 (6)	
	13	80 (3)	81 (4)	1 (5)	
	23	-6 (4)	-3 (4)	-3 (6)	
O(1)	11	452 (5)	392 (7)	60 (8)	+7.5
	22	688 (7)	605 (10)	83 (12)	+6.9
	33	259 (7)	232 (6)	27 (9)	+3.0
	12	161 (4)	154 (6)	7 (7)	
	13	97 (3)	73 (5)	24 (6)	
	23	23 (4)	16 (5)	7 (7)	
O(2)	11	411 (5)	383 (7)	28 (9)	+3.1
	22	657 (7)	591 (10)	66 (12)	+5.5
	33	341 (7)	291 (6)	50 (9)	+5.6
	12	175 (4)	182 (6)	-7 (7)	
	13	138 (3)	121 (5)	17 (6)	
	23	27 (4)	12 (5)	15 (6)	
O(3)	11	418 (7)	391 (7)	27 (10)	+2.7
	22	678 (11)	588 (10)	90 (15)	+6.0
	33	334 (7)	286 (7)	48 (10)	+4.8
	12	110 (5)	96 (6)	14 (7)	
	13	128 (3)	119 (6)	9 (7)	
	23	44 (6)	42 (6)	2 (6)	

displacements in the same way that thermal ellipsoids are plotted (Johnson, 1965). The difference ellipsoids are reproduced in Fig.5. Comparison with the X-N difference maps shows that for all atoms the apparent extra X-ray motion is such as to compensate for the overlap and lone-pair densities. This is, of course, not an unexpected result, as the difference map is derived from the same experimental information as the parameters. But, since the features in the difference map are chemically meaningful, it supports the thesis that the discrepancies between the X-ray and neutron thermal parameters are due to bonding effects. Thus, the apparent extra motion of the carbon atom is in the direction of the overlap density in the C-C bond; the hydroxylic oxygen atom vibrates in the direction of the lone pair and the overlap density in the C-O bond; the extra vibration of the carbonyl oxygen atom is fairly symmetric as its two lone pairs and the C=O bond charge form a ring of density in the difference map, while the oxygen atom of the water molecule shows extra apparent vibration in the direction of the lone-pair electrons.

Finally we would like to emphasize again the importance of a proper correction for extinction, if present. The neutron temperature parameters generally increased by about 7% when extinction was allowed for

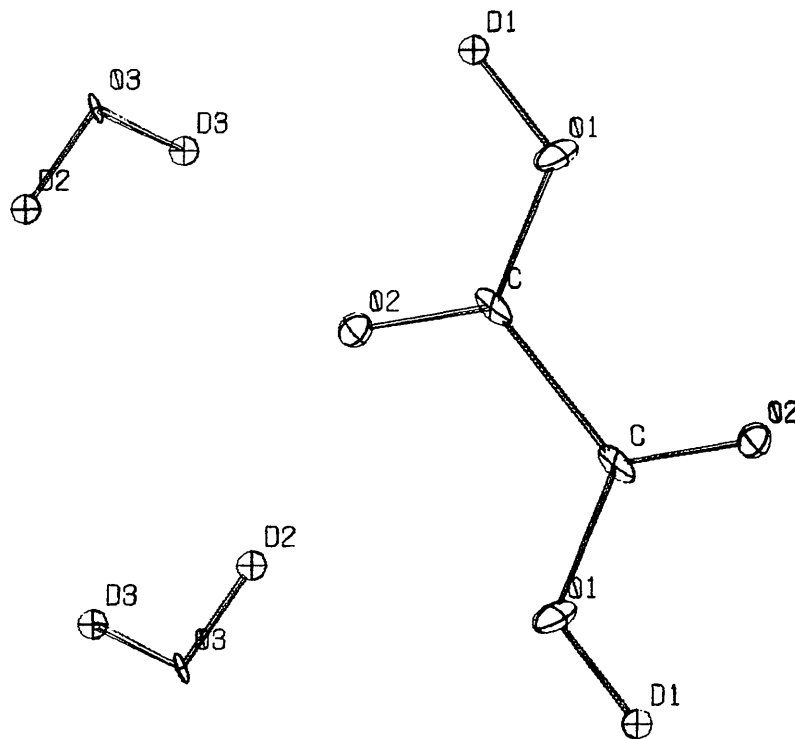
(Coppens & Sabine, 1969) and the X-ray parameters are similarly sensitive. Since in the present study extinction is stronger in the neutron case the discrepancies would have been larger without the extinction treatment. Similarly, we have argued that thermal diffuse scattering is not very different in the two cases. The fact that the observed features are chemically meaningful here, and in comparable studies of other compounds, supports our procedures and assumptions.

### Conclusion

The comparison of the X-ray and neutron studies indicate that the molecular environment should be reflected in X-ray scattering factors to prevent small systematic errors in positional parameters and fairly large systematic errors in temperature parameters. Refinement procedures with aspherical scattering factors are now in the programming stage.

### References

- ALMENNINGEN, A., BASTIANSEN, O. & SKANCKE, P. N. (1958). *Acta Chem. Scand.* **12**, 1215.  
BART, J. C. J. (1968). *Acta Cryst.* **B24**, 1277.



### A-DEUTERO OXALIC ACID X-N ELLIPSOIDS

Fig.5. X-N difference ellipsoids for  $\alpha$ -DOX viewed along  $b$ . The hydrogen atoms are indicated by circles. 80% probability ellipsoids.

- BORN, M. & HUANG, K. (1954). *Dynamical Theory of Crystal Lattices*, p.171. Oxford: Clarendon Press.
- CALDER, R. S., COCHRAN, W., GRIFFITH, D. & LOWDE, R. D. (1962). *J. Phys. Chem. Solids*, **23**, 621.
- CLEMENTI, E., CLEMENTI, H. & DAVIS, D. R. (1967). *J. Chem. Phys.* **46**, 4725.
- COCHRAN, W. (1963). *Rep. Progr. Phys.* **26**, 1.
- COPPENS, P. (1967). *Science*, **158**, 1577.
- COPPENS, P. (1968). *Acta Cryst.* **B24**, 1272.
- COPPENS, P. (1969). *Acta Cryst.* **A25**, 180.
- COPPENS, P. & COULSON, C. A. (1967). *Acta Cryst.* **27**, 18.
- COPPENS, P. & HIRSHFELD, F. L. (1964). *Isr. J. Chem.* **2**, 117.
- COPPENS, P. & SABINE, T. M. (1969). *Acta Cryst.* **B25**, 2442.
- COPPENS, P. & VOS, A. (1969). To be published.
- DAWSON, B. (1964). *Acta Cryst.* **17**, 990.
- DAWSON, B. (1967). *Proc. Roy. Soc. A* **298**, 264.
- DAWSON, B. & SANGER, P. L. (1967). *Proc. Roy. Soc. A* **301**, 195.
- DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2423.
- DUCKWORTH, J. A. K., WILLIS, B. T. M. & PAWLEY, G. S. (1969). *Acta Cryst.* **A25**, 482.
- HARCOURT, R. D. (1965). *Theor. Chim. Acta*, **3**, 194.
- JOHNSON, C. K. (1965). *A Fortran Thermal Ellipsoid Plot Program*, ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- MCWEENY, R. (1952). *Acta Cryst.* **5**, 463.
- MCWEENY, R. (1953). *Acta Cryst.* **6**, 631.
- MCWEENY, R. (1954). *Acta Cryst.* **7**, 180.
- O'CONNELL, A. M., RAE, A. & MASLEN, E. N. (1966). *Acta Cryst.* **21**, 208.
- SABINE, T. M., COX, S. W. & CRAVEN, B. M. (1969). *Acta Cryst.* **B25**, 2437.
- SABINE, T. M. & DAWSON, B. (1963). International Conference on Beryllium Oxide, p.34. Australian A.E.C., Sydney, Australia.
- STEWART R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
- TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961). *Acta Cryst.* **14**, 1009.

*Acta Cryst.* (1969). **B25**, 2458

## The Dislocation Arrangement in $\alpha$ -Oxalic Acid Dihydrate

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Crystals of  $\alpha$ -oxalic acid dihydrate have been examined by Lang topography. Both edge and screw dislocations are found with Burgers vectors parallel to the  $b$  axis. The dislocation density varies from zero to  $10^4$  lines  $\text{cm}^{-2}$  and the apparent mosaic spread varies between 10 and 50 seconds of arc. The implications of these observations for accurate structure factor determinations in molecular crystals are discussed.

### Introduction

Recent crystal structure investigations with X-rays and neutrons (Coppens, 1967; Sabine, Cox & Craven, 1969; Coppens & Sabine, 1969; Delaplane & Ibers, 1969) have had as their objective the determination of physically meaningful thermal parameters from which a determination of the asphericity of electron distribution around an atom in a crystal may be obtained. Since the calculations of X-ray structure factors are carried out for spherical atoms, and since the asphericity results from a distortion of the electron distribution along a chemical bond, the apparent X-ray temperature factor is increased. Inversion of the difference between neutron and X-ray thermal parameters enables the component of displacement of the electron density to be derived.

One of the major obstacles to the accurate determination of structure factors is extinction. Zachariasen (1967) has used a model of a real crystal as one which

consists of an aggregation of perfect crystal domains separated by boundaries which interrupt the periodicity and he distinguishes between two types of crystal. In Type I the secondary extinction is controlled by the mosaic spread parameter, that is, the degree of misorientation of these domains; in Type II crystals the secondary extinction is controlled by the size of the domains. He assumes that in most real crystals this size is less than  $10^{-4}$  cm so that primary extinction can be neglected.

Coppens & Hamilton (1969) have used a tensor form of Zachariasen's equations and from a least-squares analysis of the measured intensities have shown that extinction can be characterized by anisotropic parameters which have the physical meaning of mosaic block size and angular spread.

It is the purpose of the present work to determine, by direct observation, the arrangement of dislocations in oxalic acid dihydrate and to ascertain whether these defects provide a physical explanation for the extinc-