404. *The Structure of the Carboxyl Group. A Quantitative Investigation of Oxalic Acid Dihydrate by Fourier Synthesis from the X-Ray Crystal Data.*

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A CAREFUL examination of the crystal lattice of oxalic acid dihydrate and the structure of the oxalate group has recently been made by Zachariasen (*Z. Krist.*, 1934, **89**, 442), based upon visual estimates of the intensities of the *X*-ray reflections from oscillation and Laue photographs; and Hendricks (*ibid.*, 1935, **91**, 48) has further studied the orientation of the oxalate group in the two forms of anhydrous oxalic acid and a number of its salts. In a later paper, Hendricks and Jefferson (*J. Chem. Physics*, 1936, **4**, 102) have reported a quantitative study of the structure of ammonium oxalate monohydrate, with absolute intensity measurements, and they derive values for the interatomic distances which they consider accurate to within ± 0·02 A.

Zachariasen and Hendricks and Jefferson obtain a value of about 1·58 A. for the length of the C—C bond in the oxalate group. This result is surprising because, for a C—C bond situated between two conjugated carboxyl groups, we might expect a length *less* than the normal single bond value of 1·54 A., owing to resonance. In an attempt to confirm this value and also to obtain a precise determination of the distances and valency angles for the carboxyl group, we have now carried out a series of absolute intensity measurements on the two principal zones of reflections from crystals of the dihydrate. Zachariasen's preliminary structure has proved sufficiently accurate to enable us to calculate the phase constants for practically all these reflections. A double Fourier synthesis of the results can thus be made, which gives a fairly sharp resolution of all the atoms in one projection of the structure, and of four of the atoms in another projection, enabling the positions of their centres to be determined with an accuracy which we would estimate at from 0·01 to 0·04 A.

Our results, which are discussed below, differ considerably from those of the above authors in regard to the length of the C—C bond, for which we obtain the value 1·43—1·45 A. It should be emphasised that this measurement is difficult to make, because the two carbon atoms are surrounded by four oxygen atoms which have considerably greater scattering power for *X*-rays. But we believe our result is correct to within 0·04 A. In other respects, our structure agrees reasonably well with the previous determinations. The suggestion of Hendricks and Jefferson that their abnormally large value of 1·58 A. for the C—C bond in ammonium oxalate is a result of repulsion between negatively charged parts of the oxalate group (—CO_2^-) may account for a certain difference in the C—C bond distances in the acid and its salts, but we should not expect this difference to be nearly so great as 0·15 A.

The projection along the *b* axis in the form of a contour map is shown in Fig. 1, the area covered being that of two unit cells, showing one complete oxalic acid molecule with its surrounding water molecules and parts of six other molecules. The atoms of the oxalic acid molecule lie nearly in one plane, as shown in the next section, but this plane makes an angle of about 29° with the plane of the projection, the (010). The six surrounding water

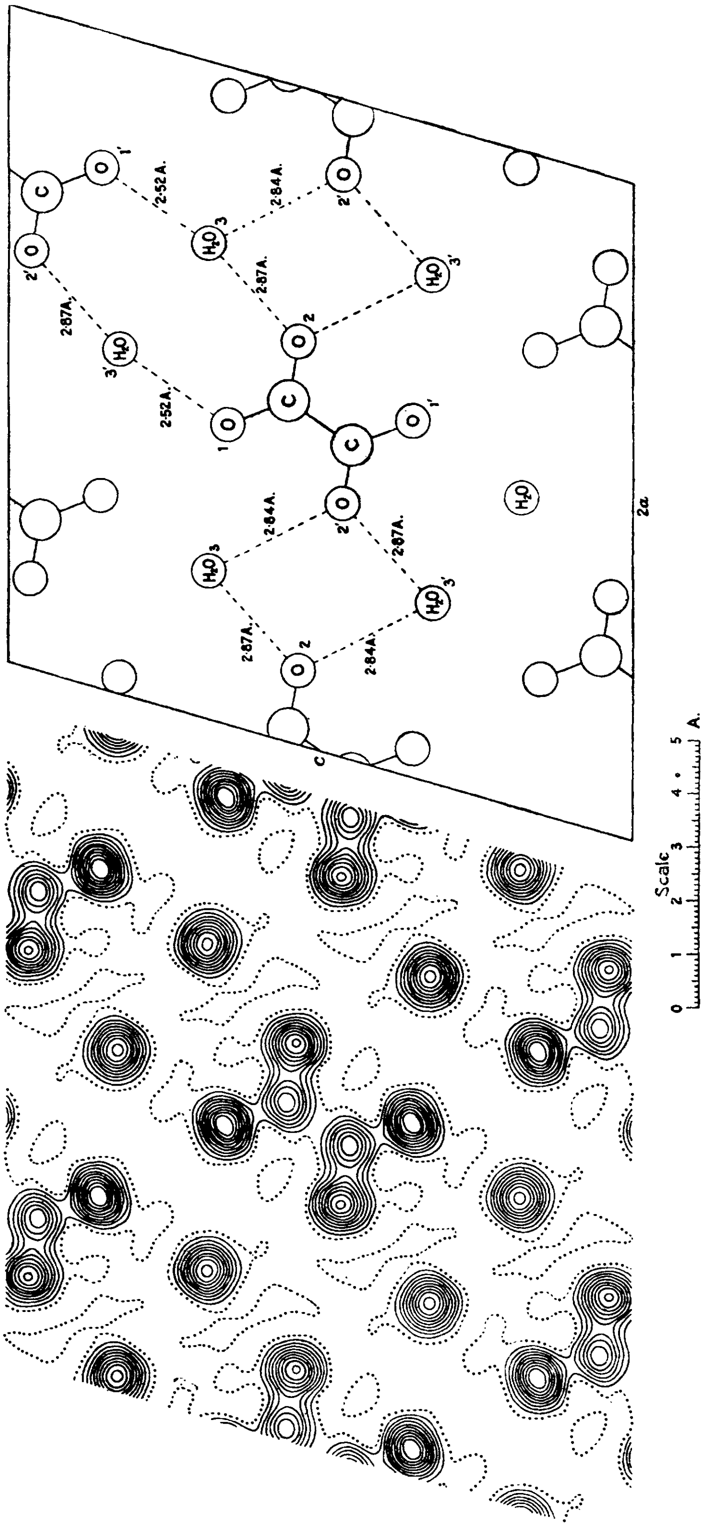


FIG. 1.

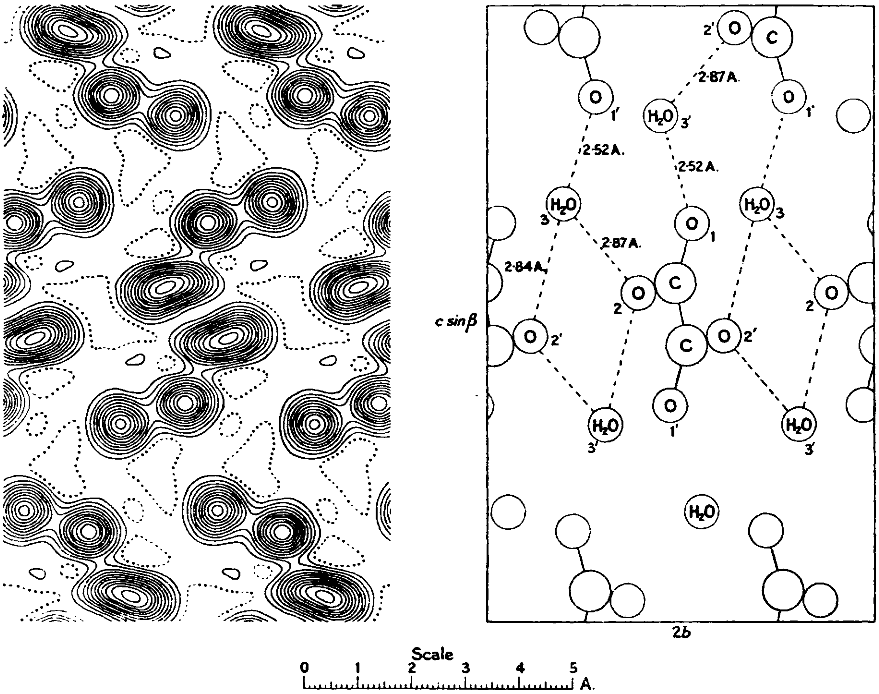
Projection along the b *axis, covering two unit cells. Each contour line represents a density increment of one electron per* A.², *the one-electron line being dotted.*

molecules also lie at various heights above and below this plane, as will be seen from Fig. 2. The density of the scattering matter rises to uniform peak values of nearly 11 electrons per A.^{2} on the oxygen atoms, and to over 7 electrons per A.^{2} on the carbon atoms, comparable to the values previously obtained in structures of this type (*Proc. Roy. Soc., A*, 1936, **157**, 79). The large intervening spaces between the molecules are very flat, and the value for the density here varies between + 0·5 and − 0·5 electron per A.^{2}, a result which constitutes a practical test for the satisfactory convergence of the Fourier series.

The projection along the *a* axis is given in a similar manner in Fig. 2, but owing to the high inclination of the molecular plane, only the water molecules and two of the oxygen atoms (1 and 1′) are separately resolved. The carbon atoms and the second oxygen atoms (2 and 2′) form a pair of well-defined ovals near the origin, the outer portions of which are obviously distended by the greater density of the oxygen atoms. The explanatory diagrams on the right of the contour maps are plotted from the co-ordinates given below, the atoms being drawn half size.

FIG. 2.

Projection along the a *axis, covering two unit cells. Each contour line represents a density increment of one electron per* A.^{2}, *the one-electron line being dotted.*



Co-ordinates of Atoms.—The *x* and *z* co-ordinates of all the atoms can be measured directly from the *b* projection (Fig. 1) with an accuracy of 0·02—0·03 A. The best resolution is obtained with the water molecules and the oxygen atoms 1 and 1′, and for these the accuracy is probably higher. In a similar manner the *y* co-ordinates are obtained from the *a* projection (Fig. 2) together with an independent check on the *z* co-ordinates. The centres of the unresolved pairs of carbon and oxygen atoms in this projection were assigned by trial. Two peaks, representing a carbon and an oxygen atom, were moved towards one another until the resulting contour lines gave the form of the oval in Fig. 2, and the positions of the centres were then taken as the positions of the atoms in Fig. 2. In this case the accuracy is probably about 0·04 A. These results are collected in Table I, the co-ordinates of the separately resolved atoms being given in Clarendon type. Only the four atoms in the asymmetric unit, half the oxalic acid molecule and one water molecule, are listed, as the co-ordinates of the others follow from the symmetry relations of the space group.

Crystal Data.—Oxalic acid dihydrate, $C_2H_2O_4,2H_2O$. The cell dimensions were checked by plane plate rotation photographs. The crystal is monoclinic prismatic, space group $P2_1/n$ (C_{2h}^5), $a = 6{\cdot}12 \pm 0{\cdot}02$, $b = 3{\cdot}60 \pm 0{\cdot}01$, $c = 12{\cdot}03 \pm 0{\cdot}03$ A., $\beta = 106{\cdot}2°$, with two centrosymmetric molecules per unit cell of volume 254·5 A.^{3}; d (found) = 1·63—1·65, (calc.) = 1·63, $M = 126$, $F(000) = 132$. Zachariasen's values for the cell dimensions are thus confirmed by our measurements.

TABLE I.

Co-ordinates referred to monoclinic crystal axes. Centre of symmetry as origin.

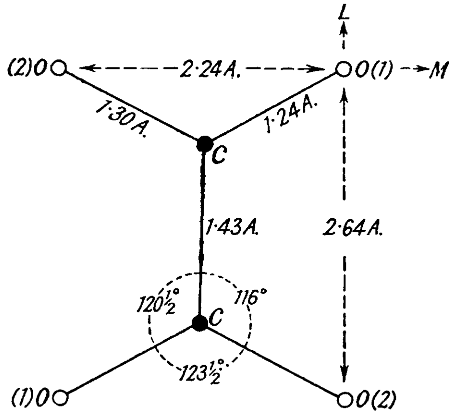
Atom (cf. Fig. 1).	x, A.	$2\pi x/a$.	y, A.	$2\pi y/b$.	z, A.	$2\pi z/c$.
C	$-\mathbf{0{\cdot}22}_5$	$-\mathbf{13{\cdot}2}°$	0·12	12·0°	**0·61**	**18·3°**
O(1)	$\mathbf{0{\cdot}52}_5$	**30·9**	$-\mathbf{0{\cdot}20}_5$	$-\mathbf{20{\cdot}5}$	**1·78**	**53·2**
O(2)	$-\mathbf{1{\cdot}39}_5$	$-\mathbf{82{\cdot}1}$	0·77	77·0	**0·42**	**12·6**
$H_2O(3)$	$-\mathbf{2{\cdot}76}_5$	$-\mathbf{162{\cdot}7}$	$-\mathbf{1{\cdot}41}$	$-\mathbf{141{\cdot}0}$	**2·15**	**64·4**

Discussion of the Structure.

The interatomic distances and the valency angles calculated from the co-ordinates are shown in Fig. 3, and the three distances of closest approach between the water molecules and the surrounding acid molecules are shown in Fig. 1. The distances between the carbon atom and the two oxygen atoms of the carboxyl group prove to be 1·24 A. for C—O (1) and 1·30 A. for C—O (2). The difference between these distances, *viz.*, 0·06 A., is not much greater than the probable experimental error, which we would estimate at 0·02—0·03 A., and in the absence of other asymmetry in the structure it would be difficult to attach much significance to this result. But it is supported by the position we find for the oxygen atom of the water molecule. The distance between the water oxygen and O(1) is only 2·52 ± 0·02 A., a value which indicates the formation of a true hydrogen bond between these atoms. The distances between the water oxygen and the O(2) atoms of adjoining molecules are 2·87 and 2·84 A., indicating intermolecular attractions of an intermediate type, called " hydroxyl bonds " by Bernal and Megaw (*Proc. Roy. Soc.*, *A*, 1935, **151**, 384). The formation of hydrogen and hydroxyl bonds in oxalic acid has already been discussed by Zachariasen and by Bernal and Megaw, but our revised result shows that a fairly sharp distinction can be drawn between the two types in this structure.

FIG. 3.

Dimensions of oxalic acid molecule.



In view of these results, it seems possible to make a rather definite correlation between the oxygen atom O(1) and the carbonyl oxygen, and between the oxygen atom O(2) and the hydroxyl oxygen. Resonance between single and double bonds in the carboxyl group undoubtedly occurs, although this may not lead to complete equalisation of the distances. The mean value for the C—O distance which we find, 1·27 A., is very close to that previously reported by Zachariasen (*loc. cit.*) and in good agreement with the value found by Pauling and his collaborators (*Proc. Nat. Acad. Sci.*, 1934, **20**, 336, 340) for the carboxyl group in formic acid and in basic beryllium acetate. It is also just above the mean value of 1·24 A. reported by Hendricks and Jefferson (*loc. cit.*) for ammonium oxalate monohydrate.

It should be especially noted that the molecules are not bound together in sheets by the hydrogen and hydroxyl bonds, as might be inferred from the projection shown in Fig. 1. Thus, the octagon formed by the atoms C, O(1), $H_2O(3)'$, O(2)′, C′, O(1)′, $H_2O(3)$, and O(2), indicated by the dotted lines in Fig. 1, is not a closed circuit, but leads back to a molecule one translation further along the *b* axis (normal to the projection plane) above the original molecule, a relation which cannot be distinguished in this projection, but will be clear from Fig. 2. The quadrilateral formed by the atoms $H_2O(3)$, O(2)′, $H_2O(3)'$, and O(2), shown by the dotted lines in Fig. 1 and Fig. 2, does, however, form a closed circuit.

As the present *X*-ray analysis does not reveal the positions of the hydrogen atoms directly, the question as to whether the structure can be regarded as "hydroxonium oxalate" $(H_3O)_2{}^{++}(C_2O_4)^{--}$ remains speculative. It seems likely, however, that the water molecules are connected by hydrogen bonds to the carbonyl oxygen atoms, and that the remaining hydroxyl groups are also interconnected by hydroxyl bond formation.

The "single-bond" C—C distance of 1·43 A. is at considerable variance with Zachariasen's value of 1·59 ± 0·07 A., and also with the value of 1·58 ± 0·01 A. given by Hendricks and Jefferson for ammonium oxalate monohydrate. On examining our result critically, we find that this distance might be increased to a possible maximum of about 1·48 A. by increasing the *y* co-ordinates of the carbon atoms in the *a* axis projection (Fig. 2), or decreased to about 1·42 A. by making allowance for a possible overlapping effect of the oxygen atoms in the *b* axis projection (Fig. 1). But the distance is in any case definitely below the normal C—C single-bond distance of 1·54 A., as in diamond, and it may be nearly as low as the C—C distance in graphite (1·42 A.). The most probable result of 1·43—1·45 A. indicates from 23% to 30% of double-bond property in the C—C link, if we make use of the empirical function given by Pauling, Brockway, and Beach (*J. Amer. Chem. Soc.*, 1935, **57**, 2706). The C—C link in oxalic acid is thus not a true single bond, presumably because it provides conjugation between double bonds in two adjacent carboxyl groups. It is interesting to note that for this reason Pauling and Brockway (*Proc. Nat. Acad. Sci.*, 1934, **20**, 340) thought that Zachariasen's value for the C—C distance in oxalic acid was too great. The presence of such double-bond properties in the link immediately explains the invariance of structure of the oxalate group, not only in the different crystalline modifications of the acid itself, but in many of the oxalates (compare Hendricks, *Z. Krist.*, 1935, **91**, 48) which display a planar or nearly planar configuration of the radical. Rotation about the C—C link is evidently restricted. On the purely chemical side, the quantitative oxidation of the acid with potassium permanganate is perhaps more easily understood in view of these results.

The four oxygen atoms of the acid molecule necessarily lie in a plane which contains the centre of symmetry. From the co-ordinates given in Table I the carbon atom is found to lie at 0·025 A. above this plane (and the other carbon atom at an equal distance below it). This figure, however, is subject to an uncertainty of 0·03—0·04 A., chiefly in the *y* co-ordinate of the carbon atom, and in the true structure all the atoms quite probably lie strictly in one plane. The orientation of the molecule in the crystal may be described by giving the direction cosines of the line *L* joining the oxygen atoms (cf. Fig. 3), the line *M* taken perpendicular to *L* and in the plane of the oxygen atoms, and their normal *N*. χ, ψ, and ω are the angles these lines make with the *a* and *b* crystal axes, and their perpendicular. Then

$$\begin{array}{lll}
\chi_L = 124{\cdot}2^\circ,\ \cos\chi_L = -\,0{\cdot}5615 & \chi_M = 47{\cdot}2^\circ,\ \cos\chi_M = 0{\cdot}6795 & \chi_N = 61{\cdot}8^\circ,\ \cos\chi_N = 0{\cdot}4722 \\
\psi_L = 77{\cdot}6^\circ,\ \cos\psi_L = 0{\cdot}2140 & \psi_M = 115{\cdot}6^\circ,\ \cos\psi_M = -\,0{\cdot}4320 & \psi_N = 28{\cdot}8^\circ,\ \cos\psi_N = 0{\cdot}8761 \\
\omega_L = 37{\cdot}0^\circ,\ \cos\omega_L = 0{\cdot}7989 & \omega_M = 53{\cdot}6^\circ,\ \cos\omega_M = 0{\cdot}5937 & \omega_N = 84{\cdot}4^\circ,\ \cos\omega_N = 0{\cdot}0971
\end{array}$$

EXPERIMENTAL.

Oxalic acid dihydrate was crystallised from water in the form of slender prisms elongated along the *b* axis. Most of the (*h*0*l*) reflections were recorded from a specimen cut to 0·5 mm.

in length and of roughly square cross-section, side 0·22 mm., weighing 0·038 mg. It was mounted on a thin glass fibre and completely immersed in a beam of uniform Cu-K_α radiation, the reflections being recorded photographically with a moving-film camera. The films, calibrated with continuous wedges giving linear increments of *X*-ray intensity, were measured on the integrating photometer described by Robinson (*J. Sci. Instr.*, **1933**, **10**, **233**). The calculated absorption coefficient for oxalic acid dihydrate for $\lambda = 1{\cdot}54$ A. is $\mu = 1{\cdot}755$ per mm., but as care was taken to employ specimens which presented very similar paths to the incident *X*-ray beam for the different reflections occurring during rotation, no separate absorption correction factors were applied to the relative intensity measurements.

For the absolute intensity measurements, the two-crystal moving-film spectrometer (Robertson, *Phil. Mag.*, **1934**, **18**, 729) was employed to calibrate the films with reflections of known absolute value. As the absorption corrections are large and important in the case of the absolute measurements, a further check was made by measuring the value of *F* for a few reflections in monochromatic molybdenum rays on the ionisation spectrometer. The different determinations agreed to within 5% in terms of *F*. The structure factors, *F*, were calculated from the measured intensities by the usual formula for a mosaic crystal (compare this vol., p. 1197), and the results are given in Table II under " *F* meas.".

Fourier Synthesis.—The measured values of *F* for the (*h*0*l*) and the (0*kl*) reflections given in Table II are the coefficients in the Bragg double series for the density of scattering matter,

$$\rho(x, z) = \frac{1}{ac \sin \beta} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F(h0l) \cos 2\pi(hx/a + lz/c)$$

with a similar expression for the (0*kl*) zone. The structure has a centre of symmetry, hence the phase constant of each term is represented by the sign of *F* given in the last two columns of Table II, under " F calc.".

In making the projection along the *b* axis, corresponding to the (*h*0*l*) zone of reflections, the series was summed at 450 points on the asymmetric unit (one quarter of the unit cell), the *a* axis being subdivided into 30 parts (intervals of 0·204 A.), and the *c* axis into 60 parts (intervals of 0·200 A.). For the *a* axis projection, corresponding to the (0*kl*) zone, the series was again summed at 450 points, the *b* axis being subdivided into 30 parts (intervals of 0·120 A.), and the $c \sin \beta$ translation into 60 parts (intervals of 0·193 A.). From these arrays of summation totals the contour maps were prepared by drawing sectional graphs of each row and each column of figures, and plotting the course of the contour lines by interpolation, on a scale of 5 cm. to 1 A.

Calculation of Structure Factors.—To determine the phase constants, the structure factors were first calculated from Zachariasen's co-ordinates with the results shown in the fifth column of Table II. All the measured reflections were included in the Fourier synthesis with the exception of the four marked * for which the signs were considered doubtful. These amount to such a small fraction of the total *F* values that they can have very little effect on the final results. After completing the synthesis, all the structure factors were recalculated from the final values of the co-ordinates given in Table I, and the results are given in col. 4 of Table II. It will be seen that none of the signs of the terms employed in the Fourier synthesis have changed, showing that Zachariasen's structure was an extremely good approximation. The way in which the calculated values of the structure factors have improved as a result of the Fourier synthesis is shown by the following comparison, which gives the total discrepancies between the measured and calculated values expressed as a percentage of the total measured *F* values, for Zachariasen's structure and for our final co-ordinates.

	(0*kl*) reflections.	(*h*0*l*) reflections.	All reflections.
Zachariasen's co-ordinates	20·6%	15·6%	17·0%
Co-ordinates of Table II	13·1%	11·7%	12·0%

The calculated *F* values are obtained from the relation $F = Sf$, where f is the atomic structure factor, and *S* the geometrical structure factor which assumes the form

$$16S = \Sigma 4 \cos 2\pi(hx/a + lz/c) \cos 2\pi ky/b \text{ when } (h + k + l) \text{ is even}$$
$$16S = -\Sigma 4 \sin 2\pi(hx/a + lz/c) \sin 2\pi ky/b \text{ when } (h + k + l) \text{ is odd}$$

for the space group $P2_1/n$, the summations being taken over the four atoms in the asymmetric unit. The factor 16 has been introduced because it is convenient to make the maximum value of *S* equal to unity. For the atomic factor *f* we have for the present employed a purely empirical

TABLE II.

Measured and Calculated Values of the Structure Factor.

hkl.	sin *θ* ($\lambda = 1·54$).	*F*, meas.	*F*, calc.	*F*, calc. (Z.).†	*hkl.*	sin *θ* ($\lambda = 1·54$).	*F*, meas.	*F*, calc.	*F*, calc. (Z.).†
200	0·262	22·5	+ 18·5	+ 15·5	$10\bar{3}$	0·207	4 *	+ 2	− 1·5
400	0·524	11	+ 12	+ 7·5	$10\bar{5}$	0·323	32·5	− 39·5	− 38·5
600	0·786	6·5	− 9	− 9·5	$10\bar{7}$	0·449	13·5	− 11·5	− 15·5
020	0·428	9·5	+ 9	+ 4·5	$10\bar{9}$	0·577	8·5	− 6·5	− 5
040	0·856	< 3	+ 1	0	$10\bar{1}\bar{1}$	0·709	21	− 20·5	− 15·5
002	0·134	10·5	+ 13	+ 12·5	$10\bar{1}\bar{3}$	0·840	< 5·5	+ 0·5	+ 1·5
004	0·267	8	− 5·5	− 11·5	2010	0·784	< 6	+ 2	+ 2·5
006	0·400	27	+ 27	+ 23·5	208	0·659	10·5	− 11·5	− 10·5
008	0·533	16	− 14	− 17·5	206	0·536	20	+ 17	+ 20·5
0010	0·667	17·5	− 15	− 19·5	204	0·421	12·5	+ 7	+ 11
0012	0·800	5	− 2·5	− 1	202	0·325	38	− 39	− 36·5
					$20\bar{2}$	0·259	5 *	− 1·5	+ 0·5
011	0·224	21·5	+ 23	+ 21·5	$20\bar{4}$	0·318	43	− 48	− 52
012	0·252	8·5	− 7·5	− 7·5	$20\bar{6}$	0·413	3	− 2·5	− 2
013	0·293	8	+ 8	+ 5	$20\bar{8}$	0·525	< 4·5	− 2	+ 4·5
014	0·342	30·5	+ 30·5	+ 34·5	$20\bar{1}\bar{0}$	0·645	8·5	− 7·5	− 7·5
015	0·396	9·5	− 9·5	− 8·5	$20\bar{1}\bar{2}$	0·770	< 6	+ 3	+ 6·5
016	0·454	17	+ 14·5	+ 16	309	0·806	8	− 8	− 5·5
017	0·514	7·5	+ 7	+ 3	307	0·691	< 5	− 2·5	− 3
018	0·575	6	+ 4·5	+ 1	305	0·583	< 5	− 7	− 6
019	0·637	6	− 4·5	− 5	303	0·488	3·5 *	− 2	− 3
0110	0·700	10	+ 9·5	+ 8	301	0·416	11	− 6·5	− 7·5
0111	0·764	13	− 11·5	− 9·5	$30\bar{1}$	0·379	4	− 1·5	− 4·5
0112	0·828	< 3	+ 1	− 0·5	$30\bar{3}$	0·390	18	+ 22	+ 18
021	0·433	8·5	+ 8	+ 7·5	$30\bar{5}$	0·439	14	− 11	− 7
022	0·448	11·5	− 10	− 9	$30\bar{7}$	0·520	5·5	− 4	− 4·5
023	0·473	< 3	+ 0·5	+ 2	$30\bar{9}$	0·620	21	+ 21	+ 20
024	0·504	12	− 13·5	− 12	$30\bar{1}\bar{1}$	0·730	< 5	− 3	− 0·5
025	0·543	9·5	+ 8	+ 7	$30\bar{1}\bar{3}$	0·847	< 5·5	− 1	+ 2·5
026	0·586	5 *	+ 3·5	+ 3	408	0·849	7·5	− 8	− 9
027	0·633	11	+ 12·5	+ 11	406	0·744	< 5	+ 0	− 2·5
028	0·684	< 3·5	− 1	+ 1·5	404	0·650	19	+ 20	+ 18
029	0·737	6	− 4·5	− 4·5	402	0·575	6·5	− 5	− 6
0210	0·792	4	− 3·5	− 2	$40\bar{2}$	0·504	27·5	+ 32	+ 31·5
0211	0·849	< 3	+ 1·5	0	$40\bar{4}$	0·518	5	− 4·5	− 5·5
031	0·645	4	+ 3	+ 4	$40\bar{6}$	0·565	< 5	− 1	− 5·5
032	0·655	8·5	− 13·5	− 13	$40\bar{8}$	0·636	< 5	+ 3	+ 6·5
033	0·672	6	− 8·5	− 9	$40\bar{1}\bar{0}$	0·725	< 5	− 3·5	− 5
034	0·695	8	+ 7·5	+ 6	$40\bar{1}\bar{2}$	0·825	< 5·5	− 1·5	− 3
035	0·723	< 3·5	+ 0·5	+ 2	505	0·813	5	+ 5·5	+ 4·5
036	0·756	< 3·5	− 1·5	− 0·5	503	0·736	11	+ 12·5	+ 12·5
037	0·795	< 3·5	+ 0·5	+ 1·5	501	0·676	8·5	+ 9	+ 10·5
038	0·833	4·5	− 6·5	− 7·5	$50\bar{1}$	0·639	< 5	− 5·5	− 5
039	0·880	1·5	− 2	− 2·5	$50\bar{3}$	0·631	9	+ 8·5	+ 5·5
041	0·858	< 3	− 1·5	− 2·5	$50\bar{5}$	0·648	6	− 6·5	− 4·5
042	0·866	2	+ 4	+ 4	$50\bar{7}$	0·691	22	− 22	− 21·5
1011	0·783	8·5	− 6·5	− 7·5	$50\bar{9}$	0·755	< 6	+ 1	− 0·5
109	0·650	< 5	0	− 1·5	$50\bar{1}\bar{1}$	0·838	< 5·5	− 1·5	+ 1
107	0·520	21·5	+ 21·5	+ 16	602	0·832	< 5·5	− 0·5	+ 1·5
105	0·391	13	+ 9·5	+ 11	$60\bar{2}$	0·761	< 6	− 0·5	− 1
103	0·268	25	+ 22	+ 24·5	$60\bar{4}$	0·756	8·5	− 8·5	− 7·5
101	0·162	23	+ 23	+ 25	$60\bar{6}$	0·778	8·5	− 9·5	− 11·5
$10\bar{1}$	0·129	16·5	+ 18·5	+ 16·5	$60\bar{8}$	0·818	< 5·5	− 3·5	− 1

* See p. 1822. † See p. 1822.

function found suitable for an organic compound of this type, consisting chiefly of oxygen atoms. The *f*-values used are as follows :

sin θ (λ = 1·54)	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8
f	106	86	70	57	45	34	25	16

The maximum value of f, at sin θ = 0, may be taken as $F(000)$ = 132, the total number of electrons in the unit cell. In making use of this composite *f*-curve, the carbon and oxygen atoms have been weighted in the ratio of 6 to 10, instead of in the ratio of their atomic numbers, 6 to 8. This weighting is suggested by the heights of the peaks in the electron-density maps. Such an approximate method of using a single composite *f*-curve, with an adjustment on the weighting of the different atoms, is not entirely satisfactory, but we have found it sufficiently accurate for practical purposes, and convenient for lengthy computations (compare *Nature*, 1936, **138**, 683). The composite curve given above is much below the theoretical *f*-curve for oxygen, as might be expected from the comparatively large thermal movements of the atoms.

SUMMARY.

The structure of oxalic acid dihydrate has been determined by a Fourier synthesis from the *X*-ray crystal data, absolute measurements of intensity for two zones of reflections being employed. Zachariasen's preliminary structure is confirmed, and more accurate values are given for the 12 parameters of the structure. A small difference in the C—O distances of the carboxyl group is indicated (1·24 and 1·30 A.), and the presence of the water oxygen atom at 2·52 A. from one of the carboxyl oxygens indicates the formation of a true hydrogen bond. The other carboxyl oxygen atom (probably the hydroxyl) is almost equidistant, at 2·87 and 2·84 A., from two other water oxygens, distances which in this case indicate hydroxyl bonds. The C—C distance in the oxalic acid molecule is only 1·43—1·45 A., indicating the presence of certain double-bond properties in this link, presumably due to conjugation of double bonds in adjacent carboxyl groups. This result offers an explanation of the invariance of the coplanar structure of the oxalate radical in the different crystalline modifications of the acid and its salts.

In conclusion, we wish to thank Professor Zachariasen for supplying us with numerical details of his work, and we are indebted to Sir William Bragg for the interest he has taken in the investigation.

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