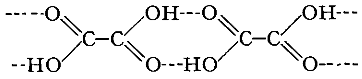
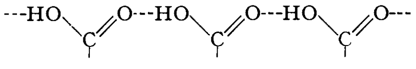
946. *The Structure of α-Oxalic Acid and of the Carboxyl Group.*

By E. G. Cox, (Miss) M. W. Dougill, and G. A. Jeffrey.

Three-dimensional *X*-ray intensity data have been used to refine the crystal structure analysis of α-oxalic acid, with corrections for termination-of-series errors. The dimensions of the centrosymmetrical molecule are as follows: C–C 1·560, C–O 1·289, C=O 1·194 Å, O–C=O 128·1°, C–C=O 122·7°, C–C–O 109·1°, with standard deviations of 0·010 Å, 0·007 Å, 0·6°, 0·5°, and 0·5°, respectively. The hydrogen bonding between molecules gives rise to a corrugated layer structure which is particularly compact, with the relatively high density of 1·91 g./c.c. There is only one crystallographically unique hydrogen bond which is associated with a C=O · · · H–O–C separation of 2·71 Å. From the length of the C–C bond it is inferred that there is no conjugation of the carboxyl groups across the molecule, and since therefore resonance stabilisation presumably cannot be invoked, other factors which could determine the planar configuration of the molecule are considered. The structure of the carboxyl group is discussed in relation to data from other acids. It is concluded that, in contrast to the amino-acid crystal structures, for the aliphatic carboxylic acids there is no evidence that the structure of the acid group varies with the environment of the oxygen atoms.

Anhydrous oxalic acid exists in two crystalline forms, both of which can be obtained at room temperature, although a study of its thermodynamic properties (Bradley and Cotson, to be published) has shown that the monoclinic β-form is unstable, with the transition point above the decomposition temperature. Both modifications were examined crystallographically by Hendricks (*Z. Krist.*, 1935, **91**, 48) who determined the unit-cell dimensions, space-groups, and the main structural features. He showed that the α- and the β-form differed in the intermolecular arrangement and in the distribution of the hydrogen bonds which were characterised by oxygen–oxygen distances of 2·7 Å between adjacent molecules. β-Oxalic acid possesses the cyclic type of carboxyl and hydrogen bond system (I) which is found in the simple monocarboxylic acid dimers and also in the crystal structure of potassium hydrogen carbonate (Nitta, Tomiie, and Koo, *Acta Cryst.*, 1952, **5**, 292). In the dicarboxylic acids this type of bonding links the molecules end-to-end in infinite chains. (The intermolecular oxygen–oxygen distances between chains, although shorter than the hydrocarbon van der Waals approach of 3·5 Å, only correspond to weak forces as compared with those linking the carboxyls to form the polymer-like chains.) A similar type of structure is found in the β-form of succinic acid and the higher members of the dicarboxylic acid series (Verweel and MacGillavry, *Z. Krist.*, 1939, **102**, 60; Morrison and Robertson, *J.*, 1949, 980, 987, 1001); in these cases, however, the β-form is the more stable. In α-oxalic acid the hydrogen bonds and carboxyl groups form an extended chain system, diagrammatically represented in (II), which links the molecules together to form a puckered layer structure throughout the crystal. This is somewhat similar to the hydrogen bonding in the structures of sodium and ammonium hydrogen carbonates (Zachariasen, *J. Chem. Phys.*, 1933, **1**, 634; Brooks and Alcock, *Nature*, 1950, **166**, 435). These two systems of hydrogen bonding are analogous to the two common forms of association in liquids, *viz.*, (i) dimerisation as in monocarboxylic acids and (ii) polymerisation as in alochols. The crystallographic data recorded for α-forms of succinic and higher members of the acids (Caspari, *J.*, 1928, 32; Rieck, *Rec. Trav. chim.*, 1944, **63**, 4) are insufficient to show whether a similar arrangement occurs in them.


(I)


(II)

Hendricks found that the molecular dimensions in both forms of oxalic acid were approximately the same, *viz.*, C–C = 1·57, C–O^{1} 1·22, C–O^{2} 1·29 Å, and O^{1}–C–O^{2} = 127°. The atomic parameters on which these molecular dimensions were based were determined by trial, and Hendricks estimated that they were reliable to about a hundredth of the cell dimensions, *i.e.*, to about 0·07 Å, so there is an uncertainty of about 0·1 Å in his interatomic distances. It is impossible, therefore, to draw any detailed conclusions relating to the character of the C–C and C–O bonds from these results, and the object of our re-investigation of the α-form has been to determine the molecular dimensions with sufficient precision to do this. In particular, we set out to determine first the degree of conjugation between the two carboxyl groups as observed in the length of the intervening C–C link, and secondly the stereochemistry of the carboxyl group.

Cell Dimensions and Intensity Measurements.—The α-crystals are orthorhombic, space-group *Pcab*, with four centrosymmetrical molecules in the unit cell; the crystal structure is defined, with the exception of the hydrogen atoms, by the parameters of one carbon atom and two oxygen atoms. Our measurements of the cell dimensions by the Straumanis method gave $a = 6{\cdot}546 \pm 0{\cdot}005$, $b = 7{\cdot}847 \pm 0{\cdot}005$, $c = 6{\cdot}086 \pm 0{\cdot}005$ Å, differing somewhat from the earlier values and removing a discrepancy between observed and calculated density. With $M = 90$, $V = 312{\cdot}6$ Å^{3}, the calcuated density is 1·916 in agreement with the observed value of 1·90 g./cm.^{2}. Of the 354 reflections possibly observable with copper radiation, 50 were too weak to be distinguished from the background and two [(545) and (555)] were not recorded; calculated intensities for these two were subsequently found to be quite small and the error introduced by their omission is considered to be negligible.

Method of Structure Refinement.—It was confirmed that the structure factors calculated from the approximate atomic positions determined by Hendricks (Table 1, column A) gave satisfactory agreement with the quantitative measurements for the (*hk*0) and (0*kl*) reflections, and they were therefore used as the starting point for the structure refinement. Two Fourier projections on (100) and (001) gave new co-ordinates which differed from the original by not more than 0·25 Å. After refinement for phase changes, the signs were calculated for the 352 general *hkl* reflections which had been measured, and these structure factors were used for a three-dimensional refinement. This was carried out in three stages, with corrections for sign changes when necessary, as follows: (1) Sectional syntheses at $x = 0{\cdot}030$ and 0·14 and $z = 0{\cdot}935$ and 0·75 evaluated at 60ths of the cell edges in the vicinity of the atomic peaks. (2) A complete three-dimensional synthesis at 60ths throughout the whole unit cell (a section of this is shown in Fig. 1). (3) Differential syntheses evaluated at the positions of the maxima interpolated from (2). The shifts in Å from these syntheses are given in column Δ^{1}, Table 2, and show that the co-ordinates at which the differential syntheses were calculated were in no case greater than 0·005 Å away from the true maxima.

TABLE 1. *Atomic parameters in fractional co-ordinates.*

		A	B	C			A	B	C			A	B	C
C	X	0·05	0·0603	0·0600	O^1	X	0·13	0·1555	0·1553	O^2	X	0·02	0·0284	0·0283
	Y	0·06	0·0569	0·0551		Y	0·99	0·9957	0·9941		Y	0·22	0·2135	0·2141
	Z	0·91	0·9127	0·9150		Z	0·75	0·7670	0·7674		Z	0·95	0·9553	0·9561

A, Hendricks' parameters (change of origin from published values).
B, Final co-ordinates from $F_{obs.}$ syntheses.
C, Final co-ordinates corrected for termination-of-series errors.

The termination-of-series corrections were obtained from differential syntheses with $F_{calc.}$ as coefficients (cf. Cox, Gillot, and Jeffrey, *Acta Cryst.*, 1949, **2**, 356); they are given in column Δ_2, Table 2. The mean value of the corrections is 0·006 Å, and the maximum 0·015 Å.

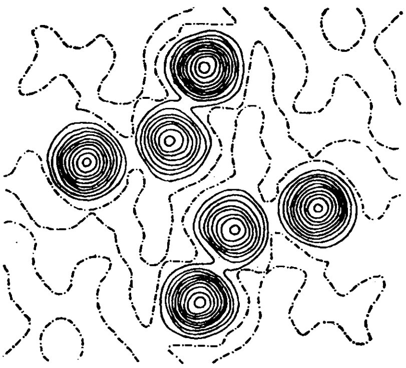
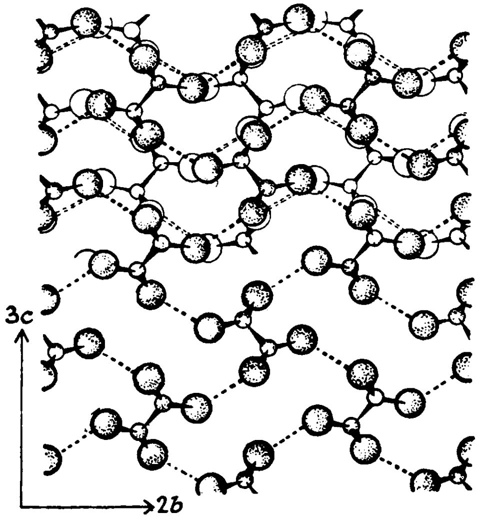


FIG. 1. *Electron-density distribution for an oxalic acid molecule in the section parallel to* (302).

Contour interval 2·0 eÅ^{-3}.
— · — · — · — 0·0 eÅ^{-3}.

FIG. 2. *Structure of α-oxalic acid projected on* (100) *showing* (*above*) *the two hydrogen-bonded layers and* (*below*) *a single layer.*



The *X*-ray intensities have appreciable values at the limiting spacing for Cu-K_α radiation and consequently the Fourier series is quite sharply terminated. This leads to diffraction ripples and variations in the background of the three-dimensional Fourier synthesis as high as 1·5 $e/\text{Å}^3$. However, the effect on the atomic parameters is offset by the sharp curvature of the atomic peaks (cf. Fig. 1) and the termination-of-series corrections are no greater than in other organic structure analyses in which there is a more rapid decline of intensities with sin θ.

TABLE 2. *Atomic parameters* (*in* Å).

		Δ^1	A	Δ^2	B			Δ^1	A	Δ^2	B
C	X	0·0022	0·3947	$\overline{0\cdot 0019}$	0·3928	O^2	X	$\overline{0\cdot 0037}$	0·1859	$\overline{0\cdot 0006}$	0·1853
	Y	$\overline{0\cdot 0004}$	0·4465	$\overline{0\cdot 0141}$	0·4324		Y	$\overline{0\cdot 0035}$	1·6753	0·0047	1·6800
	Z	$\overline{0\cdot 0015}$	$\overline{0\cdot 5313}$	$\overline{0\cdot 0140}$	$\overline{0\cdot 5173}$		Z	$\overline{0\cdot 0041}$	$\overline{0\cdot 2720}$	0·0048	$\overline{0\cdot 2672}$
O^1	X	0·0032	1·0179	$\overline{0\cdot 0013}$	1·0166						
	Y	$\overline{0\cdot 0022}$	$\overline{0\cdot 0337}$	$\overline{0\cdot 0126}$	$\overline{0\cdot 0463}$						
	Z	0·0000	$\overline{1\cdot 4180}$	0·0024	$\overline{1\cdot 4156}$						

Δ^1 Shifts in the differential synthesis, with $F_{obs.}$
A Final co-ordinates from observed data.
Δ^2 Termination-of-series corrections.
B Corrected final co-ordinates.

The three-dimensional Fourier syntheses and the differential syntheses were computed with B.T.M. Hollerith equipment by methods described elsewhere (Cox, Gross, and Jeffrey, *Acta Cryst.*, 1949, **2**, 351; Greenhalgh and Jeffrey, *ibid.*, 1950, **3**, 311; Greenhalgh, *Proc. Leeds Phil. Soc.*, 1950, **5**, 301).

The final atomic co-ordinates are given in unit-cell fractions in Table 1, and in Å in Table 2. The molecular dimensions and principal intermolecular distances are given in Table 3.

TABLE 3.—*Intramolecular dimensions* (*in* Å).

C–C′	1·560	O^1 · · · · · O^2	2·23	O^1 · · · · · O$^{1\prime}$	3·49	C′–C–O^1	122° 40′
C–O^1 ·	1·194	O^1 · · · · · O$^{2\prime}$	2·63	O^2 · · · · · O$^{2\prime}$	3·42	C′–C–O^2	109° 3′
C–O^2	1·289					O^1–C–O^2	128° 9′

The list of observed and calculated structure factors is given in Table 7; the agreement between these two sets of values expressed as $\Sigma|F_{obs.} - F_{calc.}|/\Sigma|F_{obs.}|$ is 0·145. In the earlier stages of the structure refinement, the James and Brindley scattering factor curves for C and O^- with no temperature factor were used. Later, these were replaced by experimental *f*-curves which were used for the $F_{calc.}$ in Table 7; they approximate very closely to the Hartree curves for carbon with a temperature factor of $B = 0{\cdot}6 \times 10^{-16}$, and oxygen with $B = 0{\cdot}8 \times 10^{-16}$. No contribution from the two hydrogen atoms was included in the calculations. A difference synthesis with $F_{obs.} - F_{calc.}$ as coefficients was evaluated in the form of a bounded projection between the limits $x = 0$ and $\frac{1}{2}$ to separate overlapping molecules, but it showed no features which were significant and which could be associated with the hydrogen electrons.

TABLE 4. *Intermolecular distances* (*in* Å).

O^1 · · · · · O^2	2·71 (I—II)	O^1 · · · · · O^1	3·29 (I—IV)	O^2 · · · · · O^2	3·11 (I—II′)
	3·21 (I—II′)		3·28 (I—IV′)		3·32 (I—III)
	3·54 (I—III)		3·28 (I—IV′a)		3·32 (I—IIIa)
	3·46 (I—III′)				3·11 (I—II′a)
	3·29 (I—IV)				
	3·24 (I—IV′)				

Roman numerals refer to the half-molecules in the following general positions:

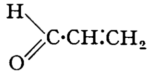
I	$x, y, z.$	III	$\frac{1}{2} + x, \frac{1}{2} - y, z.$	IV	$\frac{1}{2} - x, y, z - \frac{1}{2}.$
II	$x, -\frac{1}{2} + y, -\frac{1}{2} - z.$	III′	$\frac{1}{2} - x, -\frac{1}{2} + y, -z.$	IV′	$\frac{1}{2} + x, -y, -\frac{1}{2} - z.$
II′	$-x, \frac{1}{2} - y, z - \frac{1}{2}.$	IIIa	$x - \frac{1}{2}, \frac{1}{2} - y, z.$	IV′a	$x - \frac{1}{2}, -y, -z - \frac{1}{2}.$
II′a	$-x, \frac{1}{2} - y, \frac{1}{2} + z.$			IVa	$\frac{1}{2} - x, y, \frac{1}{2} + z.$

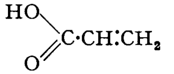
The R.M.S. standard deviation for the atomic positions calculated by Cruickshank's method (*Acta Cryst.*, 1949, **2**, 65) from $|F_{obs.} - F_{calc.}|$ and the curvature of the atomic maxima are for C 0·0052, for O^1 0·0042, and for O^2 0·0045 Å. The corresponding standard deviations of the bond lengths are C–C 0·0103, C–O^1 0·0067, C–O^2 0·0063 Å, and for the valency angles C′CO^1 36′, C′CO^2 33′, O^{1}CO^2 31′.

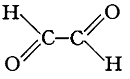
Discussion of the Structure.—It is convenient to discuss the results under three headings: (i) the character of the central C–C bond and the structure of the carboxyl group; (ii) the stereochemistry of the oxalic acid molecule as a whole; and (iii) the molecular arrangement in the crystal lattice.

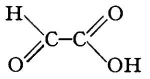
(i) *The* C–C *bond and the carboxyl group.* The observed value of 1·560 Å for the C–C bond length is 0·015 Å longer than the "standard" C–C single bond length of 1·5445 Å in diamond. To discover whether this difference represents anything more than experimental error we apply the significance test $P = 1 - \text{erf}\,(\Delta/\sqrt{2}\sigma)$ to the difference, Δ (0·015 Å), and the standard deviation, σ (0·0103 Å), of the measured length; this gives a value of $P = 0{\cdot}071$ which is in the "possibly significant" range so that the difference in bond length cannot be accepted as real without independent support. A parallel investigation of oxalic acid dihydrate (Ahmed and Cruickshank, *Acta Cryst.*, in the press) gives a value of 1·529 Å for the C–C bond whch is 0·015 Å shorter than the standard but not significantly different from it. We conclude therefore that the central bond in the oxalic acid molecule has a length which is the same as the diamond bond within probable limits (defined as 2·58σ) of ±0·025 Å. The theory of bond order–length relationships in conjugated organic molecules indicates that the length of the carbon–carbon bond is most sensitive to changes in π-bonding in the region of the single bond, and it can therefore be inferred with some certainty that in oxalic acid there is no appreciable degree of conjugation between the two carboxyl groups across the central bond. Although the geometry of the molecule and the trigonal hybridisation of the carbon valencies would appear at first sight to be as favourable to conjugation in this molecule as in, say, 1 : 3-butadiene, the strongly electronegative oxygen atoms evidently prevent any appreciable π-bonding across the C–C link. Oxalic acid and butadiene can be regarded as the extreme members of a series butadiene (III), acraldehyde (IV), acrylic acid (V), glyoxal (VI), glyoxylic acid (VII), oxalic acid (VIII), in which a sequence of increasing C–C bond lengths might be expected, ranging from the 1·46 Å in butadiene to the 1·54 Å in oxalic acid. So far only the two extreme molecules have been studied with sufficient detail to give reliable data.

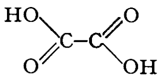
$H_2C{:}CH{\cdot}CH{:}CH_2$ (III)


(IV)


(V)


(VI)


(VII)

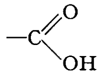

(VIII)

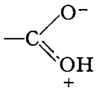
The dimensions of the carboxyl group reveal a significant distinction between the two C–O bonds both in interatomic distances and in valency angles. The probability (calculated from the standard deviations) that the difference of 0·10 Å in the bond lengths is due to experimental error is quite negligible. This is in agreement with the results from oxalic acid dihydrate (Ahmed and Cruickshank, *loc. cit.*) and from *N*-acetylglycine (Carpenter and Donohue, *J. Amer. Chem. Soc.*, 1950, **72**, 2315), the one case in the recent series of accurate structure analyses of amino-acids where there is no possibility of any intermolecular influence by zwitterion formation in the crystal; as shown in Table 5, these three substances contrast sharply with threonine and hydroxyproline in which zwitterion formation leads to a symmetrical resonance configuration (Shoemaker, Donohue, Schomaker, and Corey, *ibid.*, p. 2328; Donohue and Trueblood, *Acta Cryst.*, 1952, **5**, 419).

TABLE 5. *Dimensions of the carboxyl group from some recent precision structure analyses.*

	$C-O_1$	$C-O_2$	O_1-C-O_2	O_1-C-C'	O_2-C-C'
α-Oxalic acid	1·19	1·29	128°	123°	109°
Oxalic acid dihydrate	1·19	1·28	126°	122°	112°
N-Acetylglycine	1·19	1·31	124°	124°	112°
L_s-Threonine	1·24	1·25	127°	116°	117°
Hydroxyproline	1·25	1·27	126°	119°	115°

The difference between the two C–O bond lengths is substantially less than we should expect between pure single and double bonds. Although the C=O bond is very close to the mean of a number of observations on aldehydes and ketones, the C–OH bond is much shorter than the C–O single bond length of 1·44 Å found in alcohols and ethers (see, *e.g.*, Cox and Jeffrey, *Proc. Roy. Soc.*, 1951, *A*, **207**, 110). In terms of valence bond resonance these results correspond to a structure for the un-ionised carboxyl group in which (IX) is more important than (X).


(IX)


(X)

Apart from the special case of zwitterion formation in amino-acids, it is not certain to what degree the structure of the carboxyl group is dependent on the molecular environment and hydrogen-bond system; it has been suggested (Vaughan and Donohue, *Acta Cryst.*, 1952, **5**, 534) that the relative contributions of the two resonance forms, (IX) and (X), depend upon the situation of the two oxygen atoms in the crystal structure, *i.e.*, upon the number and strength of the hydrogen bonds. But the correlation of the results from the anhydrous oxalic acid and the dihydrate, which differ significantly only by 3° in the O^2–C–C angle, is evidence that the acid group will have very nearly the same structure in all carboxylic acids regardless of environment. For in the anhydrous acid there is only one hydrogen bond between the two different oxygens, whereas in the dihydrate the situation is very different: there is no direct hydrogen bonding between carboxyl groups and there are two different kinds of hydrogen bonds from the carboxyl oxygens to the water molecules. We think therefore that the results for oxalic acid can be critically compared with measurements on other carboxylic acids, and not only in the solid state.

Although formic acid has been studied in some detail, the results (Table 6) appear to be inconclusive. In their electron-diffraction analysis of the monomer, Karle and Brockway considered 19 models with C=O between 1·22 and 1·29 Å, C–O between 1·29 and 1·45, and O–C=O between 115° and 130°. Schomaker and O'Gorman, with more extensive experimental measurements, considered 17 models in which the distances varied from 1·33 to 1·25, and 1·41 to 1·17, the mean being kept at 1·29 Å. The results of the infra-red spectrum analyses of the acid and its deuterated forms, although favouring the earlier electron-diffraction work are not decisive (see Schomaker and O'Gorman, *loc. cit.*). The formic acid dimer was also examined by electron diffraction (Karle and Brockway, *loc. cit.*), with the conclusion that a model with equal C–O bonds was unacceptable. As in the work on the monomer, the model which would now appear to be the most likely from our results was not included in the trials. The same uncertainty applies to the electron-diffraction work on acetic acid monomer and dimer (Karle and Brockway, *loc. cit.*).

TABLE 6. *Molecular dimensions of formic acid.*

C-O	C=O	O-C=O	Method *	Ref.
Monomer				
1·42 Å	1·24 Å	117°	E.D.	Karle and Brockway, *J. Amer. Chem. Soc.*, 1944, **66**, 574.
1·368	1·213	123·5°	E.D.	Schomaker and O'Gorman, *ibid.*, 1947, **69**, 2638.
1·41	1·225	125°	Spec.	Williams, *J. Chem. Phys.*, 1947, **15**, 232.
Dimer				
1·36	1·25	121°	E.D.	Karle and Brockway, *loc. cit.*

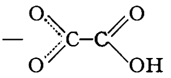
* E.D. = Electron diffraction. Spec. = spectroscopic.

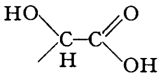
In the higher members of the dicarboxylic acid series (Morrison and Robertson, *loc. cit.*) there is a tendency for the C–O lengths to be distinguished; for β-succinic, adipic, sebacic, and β-glutaric acids, the shorter bonds are 1·25, 1·23, 1·24, and 1·23 Å, and the longer 1·30, 1·29, 1·27, and 1·30 Å. These results are from two-dimensional Fourier syntheses of the *X*-ray data with no termination-of-series corrections, and in no case is there any evidence that the dimensions of the carboxylic acid group are significantly different from those found in oxalic acid. The same applies to the *X*-ray analyses of other carboxylic acids (*e.g.*, the acetylenedicarboxylic acids, Dunitz and Robertson, *J.*, 1947, 148; tartaric acid, Stern and Beevers, *Acta Cryst.*, 1950, **3**, 341; racemic acid hydrate, Parry, *ibid.*, 1951, **4**, 131).

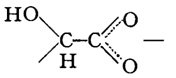
There is therefore at present no evidence which contradicts the supposition from the results of the two oxalic acid analyses that, in the aliphatic carboxylic acids in contrast to the amino-acids, the structure of the acid group will differ only by small changes in valency angles with different hydrogen-bond environment.

(ii) *The stereochemistry of the molecule as a whole.* In both anhydrous forms and in the dihydrate it is a space-group requirement that the oxalic acid molecule be centrosymmetric, and with the established planar distribution of carbon valencies in the carboxyl group, it follows that the whole molecule is planar. This stereochemistry was determined in the first investigations (Hendricks, *loc. cit.*; Zachariasen, *Z. Krist.*, 1934, **89**, 442) and no discrepancies have appeared in the refinements of the anhydrous form (or the dihydrate) to contradict this expectation. The planarity of the molecule together with the value of 1·43 Å for the C–C bond reported from the dihydrate structure (Robertson and Woodward, *J.*, 1936, 1817; Dunitz and Robertson, *J.*, 1947, 142) was originally considered to be evidence for conjugation between the carbonyl groups. Since it now appears that the C–C is a single bond in length and by inference also a single bond in character, the significance of the planar configuration must be reconsidered. In the absence of the stabilising resonance energy associated with double-bond character it is difficult to account for the planarity of the molecule without the hypothesis of some special attractive force between the carbonyl and hydroxyl groups. Normally, since all the oxygen atoms tend to have excess negative charge, repulsive forces would favour a staggered configuration which increases the $O^1 \cdots O^{2\prime}$ distances more than it diminishes the $O^1 \cdots O^{1\prime}$ and $O^2 \cdots O^{2\prime}$ distances. Indeed a re-examination of the crystal structure of ammonium oxalate hydrate (following paper), confirms the earlier observation of Hendricks and Jefferson (*J. Chem. Phys.*, 1936, **4**, 102) that the oxalate ion is not planar and that the carboxyl groups are inclined to each other at an angle of about 30°; it further shows that the central C–C bond is not significantly different from 1·54 Å, showing that this is a single bond in the ion as well as in the acid.

In an isolated case a planar configuration might be attributed to restraint imposed on the molecules in order to achieve the most energetically favourable system of intermolecular hydrogen bonds and van der Waals forces. That this cannot be the explanation is clearly shown by the fact that the oxalic acid molecule is flat in the dihydrate and in both anhydrous forms in which the hydrogen bond systems and molecular environments are entirely different. In the α-structure it appears rather that with some deviation from planarity in the molecule a more regular and even more compact crystal structure might be possible. Dipole-moment data indicate that in both C–OH and C=O the negative end of the dipole lies at the oxygen atom, and if it is assumed that the C=O dipole is substantially greater in magnitude than the C–OH dipole, it might be thought that the molecule would be caused to assume a planar *trans*-configuration by repulsion of the $\overset{\delta+}{\mathrm{C}}{=}\overset{\delta-}{\mathrm{O}}$ dipoles. Approximate calculations of the energy of repulsion are not conclusive, however, and it is doubtful whether the available information about the distribution of charge in the molecule is accurate enough to sustain a detailed calculation. An experimental approach to the problem is to determine the configurations of the hydrogen oxalate ion (XI); this is reported to be planar in potassium hydrogen oxalate (Hendricks, *Z. Krist.*, 1935, **91**, 57) but the analysis is not conclusive by modern standards, and we are making new experimental measurements on this substance.


(XI)


(XII)

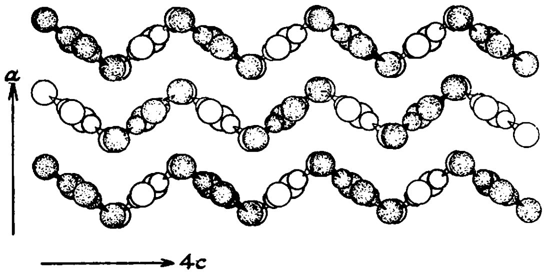

(XIII)

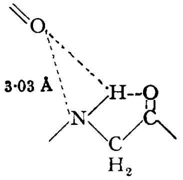
It has been pointed out elsewhere (Jeffrey and Parry, *Nature*, 1952, **169**, 1105) that there appears to be a correlation between the stereochemistry of the oxalic acid molecule and that of the α-hydroxy-acids. The crystal structures of two of these acids, tartaric acid (Stern and Beevers, *Acta Cryst.*, *loc. cit.*) and racemic acid hydrate (Parry, *ibid.*, *loc. cit.*), have been studied in some detail and it is a remarkable feature of the results that the $C(OH)\cdot CO_2H$ group is planar in both. In both cases a *trans*-configuration (XII) is indicated. The same planar arrangement is also found for each half of the tartrate ion (XIII) in Rochelle salt (Beevers and Hughes, *Proc. Roy. Soc.*, 1941, *A*, **177**, 251), and in $KNaC_4H_4O_6,4H_2O$ (Sadanaga, *Acta Cryst.*, 1950, **3**, 416).

These experimental results all suggest very strongly that the coplanar orientation of the C–OH and C=O bonds in these molecules is determined by some additional intramolecular force. While the presence of hydrogen atoms may well be essential to the operation of this force, it does not seem to be intramolecular hydrogen bonding of the normal kind found, for example, in salicylic acid, since in the structures under consideration all the hydrogen atoms are accounted for by intermolecular hydrogen bonds, although it should be noted that the hydrogen atoms have not been located in our analysis. The additional force seems to be associated with the strongly polar carbonyl group, which may exert an attractive force on an OH group in the same molecule even though its hydrogen atom is engaged in hydrogen-bond formation in another direction. There is in fact evidence to show that there is a similar situation around the NH group in the case of *N*-acetylglycine. As Elliott (*J. Chem. Phys.*, 1952, **20**, 756) has pointed out in another connection, Carpenter and Donohue's *X*-ray analysis (*loc. cit.*) combined with Newman and Badger's infra-red studies (*ibid.*, 1951, **19**, 1147) shows that the N–H $\cdots$ O intermolecular bonds are not linear; the H atom is displaced towards a carbonyl oxygen atom in the same molecule as shown in (XIV) so that it is roughly equidistant from both oxygen atoms, and the whole O:C·C·NH system in the molecule is planar. But it does not seem possible to invoke the same mechanism to account for the planarity of the oxalic acid molecules, for in both the anhydrous and the dihydrate structures the intermolecular $O^2 \cdots O^1$ and the intramolecular $O^2 \cdots O^{1'}$ directions are almost at 180° to each other, as in (XV).

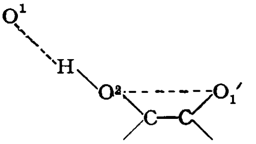
(iii) *The intermolecular arrangement.* The oxalic acid molecules in the α-form are linked by the hydrogen bonds to form a corrugated layer type of structure as shown in Figs. 2, 3, and 4. There is one hydrogen bond only from each oxygen linking a $C=O \cdots H-O-C$ pair with an oxygen–oxygen separation of 2·71 Å. All other intermolecular oxygen–oxygen distances are greater than 3·1 Å, and there are nine of these ranging from 3·1 to 3·55 Å.

FIG. 3. *Structure of α-oxalic acid projected on* (010). *There are no hydrogen bonds between the corrugated layers which are viewed edgewise.*





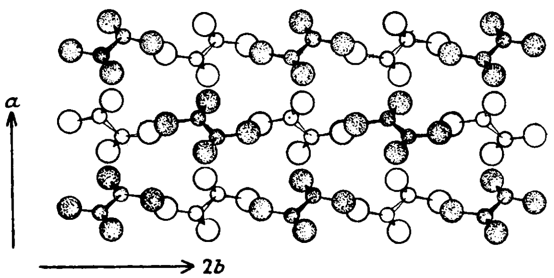
(XIV)



(XV)

It is well known that the oxygen–oxygen separation for hydrogen bonding depends on the crystal structure. The value of 2·71 Å is intermediate between the two distances in the dihydrate, where 2·49 Å probably corresponds to $C-OH \cdots OH_2$ and 2·88 Å to $C=O \cdots HOH$ (Ahmed and Cruickshank, *loc. cit.*). The single $C=O \cdots HO{\cdot}C$ hydrogen-bond distance in the β-anhydrous form is also reported as 2·71 Å (Hendricks, *loc. cit.*) but this is liable to be amended by as much as ±0·2 Å on refinement of the crystal-structure analysis.

FIG. 4. *Structure of α-oxalic acid projected on* (001).



Apart from the neighbour at 2·71 Å, each oxygen atom is surrounded by nine others in adjacent molecules at distances varying between 3·1 and 3·55 Å. Figs. 2, 3, and 4 show the relationship between the two different hydrogen-bonded layers. The centres of the molecules in alternate layers are staggered by $\frac{1}{2}(a + b + c)$, and the symmetry and cell dimensions are such that in projection down the *a*-axis the oxygen atoms nearly overlap. For each O^1 there are two near neighbours in the same layer, seven in the layer below, and one in the layer above; for $O^{1'}$ the number of nearest neighbours above and below is reversed. For O^2 there are four near neighbours in the same layer, five above and one below. This

TABLE 7. *Observed and calculated structure factors for α-oxalic acid.*

Plane	$F_{\text{calc.}}$	$F_{\text{obs.}}$	Plane	$F_{\text{calc.}}$	$F_{\text{obs.}}$	Plane	$F_{\text{calc.}}$	$F_{\text{obs.}}$	Plane	$F_{\text{calc.}}$	$F_{\text{obs.}}$
002	8·4	8·9	811	−11·1	7·6	236	−9·4	8·7	644	11·5	11·8
4	28·5	25·7	2	−1·7	1·7	7	2·3	4·8	740	5·3	<3·0
6	−25·3	24·5	020	30·9	29·5	331	−15·3	13·2	1	−6·4	6·6
200	50·4	39·3	2	−62·4	47·9	2	3·3	5·3	2	4·6	<3·0
1	57·1	45·4	4	6·0	7·9	3	−1·4	2·5	3	−8·1	8·0
2	54·0	44·0	6	−19·2	18·9	4	−2·0	<3·0	052	18·0	18·2
3	−6·4	7·8	120	−8·1	8·7	5	−11·2	11·8	4	18·4	17·7
4	−3·7	6·2	1	12·3	12·9	6	−2·5	4·6	6	3·1	3·5
5	25·3	22·8	2	−8·2	8·5	7	8·5	2·5	151	22·4	21·8
6	−5·1	7·8	3	23·1	21·6	431	0·2	<3·0	2	5·4	5·7
7	−7·7	9·4	4	2·5	<3·0	2	−5·6	5·7	3	9·0	10·8
400	2·0	2·6	5	10·7	12·4	3	7·4	9·0	4	−4·1	5·3
1	−5·3	5·4	6	2·0	<3·0	4	−8·2	8·4	5	8·1	8·2
2	36·0	30·9	7	2·0	<3·0	5	9·0	10·1	6	7·9	9·3
3	39·2	35·2	220	−36·3	36·4	6	−6·4	7·0	251	−11·5	12·8
4	−6·1	9·2	1	40·4	35·0	531	−8·6	7·1	2	13·6	14·7
5	5·9	6·9	2	−6·8	6·9	2	−2·9	2·8	3	−2·6	3·6
6	5·6	5·4	3	−22·4	21·8	3	−4·9	5·6	4	12·2	12·5
600	16·2	14·3	4	−21·2	18·4	4	4·0	5·5	5	7·0	7·2
1	1·7	3·7	5	11·4	12·6	5	1·3	5·5	6	4·7	7·3
2	−11·0	12·1	6	−1·2	2·7	631	3·1	1·5	351	12·8	13·0
3	23·4	20·6	7	−14·0	13·6	2	−8·3	8·2	2	3·7	<3·0
4	16·2	15·9	320	−19·7	18·7	3	6·3	6·1	3	14·3	14·9
5	8·9	8·6	1	8·7	9·6	4	−7·7	8·8	4	3·1	4·8
800	−6·3	9·1	2	−11·2	11·6	5	6·4	5·5	5	−3·5	5·3
1	15·4	11·6	3	9·4	11·5	731	−4·8	4·6	6	7·0	5·9
2	−3·4	4·6	4	2·6	<3·0	2	−0·4	2·4	451	−15·8	16·8
012	31·4	30·4	5	8·2	8·8	3	−4·7	2·3	2	4·0	5·5
4	28·9	25·8	6	6·0	6·3	831	7·9	2·5	3	−1·8	<3·0
6	14·2	14·9	7	2·1	<3·0	040	60·4	50·4	4	3·5	5·4
111	39·6	31·8	420	−37·9	29·7	2	−11·7	10·3	5	6·6	8·6
2	16·9	17·5	1	−15·7	15·6	4	22·6	18·7	551	9·0	8·8
3	−1·7	<3·0	2	3·5	6·6	6	−12·2	10·3	2	0·5	<3·0
4	−3·6	5·2	3	14·9	16·6	140	1·3	<3·0	3	4·3	<3·0
5	−3·9	5·8	4	−16·6	17·2	1	0·1	3·0	4	10·9	11·6
6	7·9	10·2	5	−12·1	10·9	2	−3·2	3·1	651	−11·1	11·5
7	−12·5	13·6	6	7·0	8·9	3	2·2	4·1	2	−4·4	4·5
211	−19·9	20·5	520	−17·5	17·4	4	6·1	7·7	3	−2·4	<3·0
2	22·9	22·3	1	−0·1	<3·0	5	−8·1	7·6	751	5·6	4·1
3	−7·3	8·3	2	−8·0	8·3	6	2·3	3·9	2	5·8	3·7
4	22·8	20·6	3	1·1	<3·0	7	−12·3	11·1	060	10·1	8·1
5	1·8	<3·0	4	0·5	<3·0	240	8·9	12·9	2	−26·1	23·9
6	12·8	12·2	5	2·3	<3·0	1	29·9	26·1	4	14·9	12·7
7	2·9	2·7	6	6·2	6·4	2	23·6	22·3	6	−4·4	3·6
311	10·4	11·6	620	1·6	4·4	3	−14·5	14·1	160	−4·4	5·9
2	18·0	16·7	1	−6·5	5·4	4	−2·0	3·8	1	8·8	10·2
3	11·6	13·4	2	−21·4	16·5	5	15·3	13·5	2	−8·5	9·4
4	10·3	13·5	3	4·1	7·8	6	1·8	2·9	3	24·1	21·7
5	−12·1	14·1	4	10·0	12·0	7	−5·9	3·5	4	3·2	4·4
6	2·6	<3·0	5	−11·0	7·7	340	−3·2	6·5	5	13·9	13·3
7	4·2	3·8	720	−7·9	7·5	1	2·5	3·4	6	1·2	2·5
411	−22·5	22·3	1	−3·2	3·0	2	0·8	<3·0	260	−16·5	17·9
2	10·4	10·8	2	−6·1	5·1	3	−6·6	6·3	1	15·2	14·5
3	−9·1	9·7	3	−3·1	3·8	4	9·4	11·9	2	1·0	<3·0
4	11·6	12·9	4	−0·4	<3·0	5	−5·2	5·4	3	−18·9	16·4
5	1·4	<3·0	820	−7·5	7·7	6	7·5	11·1	4	−3·5	4·6
6	9·0	9·8	1	9·2	7·3	440	−5·4	5·6	5	7·0	15·9
511	−0·1	<3·0	032	1·7	2·6	1	−10·7	11·0	6	6·6	5·8
2	8·2	10·3	4	−4·0	3·9	2	21·3	19·6	360	−18·2	18·1
3	1·0	<3·0	6	−12·2	11·7	3	17·6	17·5	1	10·2	11·4
4	17·1	16·8	131	−11·2	10·6	4	−6·4	7·2	2	−12·3	13·0
5	3·9	6·1	2	7·6	10·5	5	−1·5	<3·0	3	10·2	12·1
6	−5·6	5·0	3	−17·3	16·9	6	6·1	6·2	4	2·0	<3·0
611	−16·5	14·9	4	−7·8	9·5	540	−3·9	7·5	5	13·4	14·6
2	1·4	<3·0	5	−2·3	3·5	1	−4·5	6·3	460	−14·0	14·7
3	−7·9	8·3	6	5·1	6·0	2	5·1	3·8	1	−13·8	13·5
4	3·5	3·4	7	−5·4	6·1	3	−8·1	8·3	2	7·9	6·8
5	0·0	<3·0	231	−1·6	1·8	4	6·9	8·5	3	1·5	<3·0
711	−5·2	6·5	2	−0·8	2·2	640	15·4	14·2	4	−8·4	11·1
2	6·8	8·2	3	4·5	5·4	1	−3·1	3·5	5	−10·1	9·7
3	−2·5	<3·0	4	−6·4	7·5	2	−8·5	8·4	560	−21·8	18·5
4	3·1	1·8	5	8·2	10·0	3	10·9	11·3	1	0·3	<3·0

TABLE 7.—*continued.*

Plane	$F_{\text{calc.}}$	$F_{\text{obs.}}$	Plane	$F_{\text{calc.}}$	$F_{\text{obs.}}$	Plane	$F_{\text{calc.}}$	$F_{\text{obs.}}$	Plane	$F_{\text{calc.}}$	$F_{\text{obs.}}$
562	−9·3	9·3	274	3·5	3·0	082	−20·2	14·9	480	−11·0	10·8
3	3·4	<3·0	5	4·8	6·6	4	13·5	15·8	1	−12·6	13·5
660	12·2	11·9	371	−17·0	17·0	180	4·6	4·8	2	5·9	7·0
1	−7·4	7·8	2	−9·7	10·0	1	−4·2	4·0	3	−2·2	3·7
2	−9·7	8·4	3	−3·4	4·7	2	−1·8	<3·0	580	2·6	<3·0
3	−0·3	<3·0	4	−11·8	12·8	3	−3·6	4·4	1	−2·9	3·4
072	6·1	5·5	5	−5·2	<3·0	4	4·1	5·9	092	−3·5	2·6
4	7·1	6·5	471	−6·2	6·4	280	−15·3	12·5	191	3·3	4·8
171	−23·0	22·3	2	1·0	<3·0	1	7·9	7·8	2	0·0	<3·0
2	−1·7	<3·0	3	0·8	<3·0	2	−1·5	4·4	3	5·3	8·2
3	−11·9	13·2	4	−0·5	<3·0	3	−16·8	17·6	291	2·2	<3·0
4	−8·6	9·3	571	−5·1	4·8	4	−1·7	4·6	2	−1·0	<3·0
5	6·8	7·9	2	−13·0	12·0	380	3·9	3·8	3	0·1	<3·0
271	−4·2	4·1	3	−5·6	5·9	1	1·5	<3·0	391	4·1	5·4
2	5·0	5·6	671	−3·9	3·9	2	2·9	4·4	2	−3·5	5·0
3	−1·0	<3·0	080	−0·3	<3·0	3	−9·2	10·3	0100	10·2	6·9

close packing leads to the density of 1·91 g./c.c. which is exceptionally high for a crystal containing only carbon, oxygen, and hydrogen. It is noteworthy that a completely flat layer structure with a square hydrogen-bonding system similar to that in pentaerythritol or racemic acid hydrate is not possible in this case because only one proton is available for each pair of oxygen atoms. Accordingly, one pair of sides of the quadrilateral O^1 (I) O^2 (II) O$^{1'}$ (I) O$^{2'}$ (II) is extended to 3·2 Å, and the planar molecules are tilted to form the buckled layers. The equilibrium distance between oxygens not linked by hydrogen bonds must be close to 3·2 Å, significantly less than the van der Waals diameter commonly ascribed to methylene and methyl groups. In this structure there is no distinction between the intermolecular separation of carbonyl and hydroxyl oxygens.

The β-anhydrous form also has a high density, but that of the dihydrate is only 1·64 g./c.c., and higher members of the dicarboxylic acid series range from 1·55 g./c.c. downwards with increase in the number of carbon atoms. In the hydroxy-acids, tartaric and racemic hydrate, there are also many oxygen–oxygen distances of 3·1—3·5 Å, but in these structures the additional hydrogen bonding places a restraint on the intermolecular arrangement. Because of the directional property of the hydrogen bond, the molecular packing is less efficient than in the anhydrous oxalic acids from the point of view of space filling, and the densities are less (1·76 and 1·70, respectively).

Concomitantly with the close packing and high density, the potential field due to intermolecular forces is greater and the thermal atomic vibration at room temperature is less in anhydrous oxalic acid crystals than in most organic molecular structures of similar constitution. This is manifested in the crystal-structure analysis in the relatively small value for the thermal vibration factor ($e^{-B(\sin^2\theta)/\lambda^2}$) associated with the atomic scattering factors, and more strikingly in the exceptionally high values of the electron density at the atomic maxima in the Fourier synthesis (Fig. 1). For the C, O^1, and O^2, $\rho_{\text{max.}}$ is 17·2, 21·2, and 20·8 eÅ^{-3} respectively (uncorrected for termination-of-series errors which are about 1 eÅ^{-3}). It was confirmed by approximate integration from the electron-density maps that the number of electrons associated with each atom was of the correct order (5·9, 7·7, and 8·3 e, for C, O^1, and O^2, respectively).

EXPERIMENTAL

The anhydrous oxalic acid was prepared from the dihydrate by heating it at 100° to remove the water and by sublimation at 130°. Decomposition starts at about 150°. Crystallisation by cooling a saturated solution in fuming nitric acid at 60° gave crystals of the α-form which were too large for *X*-ray intensity measurements. Smaller and more suitable crystals were obtained from acetone solution. They absorb water rapidly to form the dihydrate on the surface, and single crystals stored over phosphoric oxide were quickly transferred to Lindemann glass tubes for the *X*-ray measurements.

The crystal used for the intensity measurements had dimensions 0·06 × 0·08 × 0·06 cm. across opposite corners of a bipyramid. With the absorption coefficient of 17·4 cm.$^{-1}$ for Cu-K_α this gives a probable error due to absorption of about 5% in the observed structure factors. The *X*-ray intensities were estimated by eye from photographs taken on a Leeds–Weissenberg camera, a multiple film technique being used. All planes within the reflecting sphere for Cu-K_α radiation with the exception of (545) and (555) could be recorded on 4, 3, and 4 equi-inclination layer line photographs about the *a*, *b*, and *c* axes, respectively.

We are grateful to the Brotherton Committee for the award of a Brotherton Research Scholarship, and to the West Riding Education Authority for the award of a County Technological Scholarship to one of us (M. W. D.). We wish also gratefully to acknowledge grants from the Royal Society and the Department of Scientific and Industrial Research and the loan of apparatus by Imperial Chemical Industries Limited.

Department of Inorganic and Physical Chemistry,
The University of Leeds.

[*Received, August 8th,* 1952.]