947. *The Structure of the Oxalate Ion.*

By G. A. Jeffrey and G. S. Parry.

An *X*-ray analysis of the crystal structure of ammonium oxalate monohydrate confirms the earlier conclusion of Hendricks and Jefferson (*J. Chem. Phys.*, 1936, **4**, 102), that in contrast to the oxalic acid molecule, the oxalate ion is non-planar; the angle between the planes of the carboxyl groups is 28°. The bond lengths in the ion are C–C 1·56, C–O^1 1·23, C–O^2 1·25 Å, all ±0·05 Å, and the angle O–C–O is 125°±3°.

The recent *X*-ray analysis refinement of the crystal structures of oxalic acid dihydrate (Cruickshank and Ahmed, *Acta Cryst.*, in the press) and α-anhydrous oxalic acid (Cox, Dougill, and Jeffrey, *J.*, 1952, **4854**) has confirmed the original observations by Zachariasen (*Z. Krist.*, 1934, **89**, 442) and Hendricks (*ibid.*, 1935, **91**, 48) that the oxalic acid molecule although planar has a C–C bond which is indistinguishable in length from 1·54 Å, the value ascribed to a normal single bond. It was inferred that the carboxyl groups were separated by a pure σ-bond with no conjugation across the molecule, and that some other interpretation than resonance interaction between carboxyl groups was necessary to account for the planar configuration (Jeffrey and Parry, *Nature*, 1952, **169**, 1105). However, it might be argued that the central C–C bond has some degree of π-bonding character which restricts rotation, but is stretched as compared with the bonds in a non-polar molecule owing to the repulsion of the carbon atoms which tend to carry net positive charges by reason of the $\overset{\delta+}{\mathrm{C}}\!-\!\overset{\delta-}{\mathrm{O}}$ and $\overset{\delta+}{\mathrm{C}}\!=\!\overset{\delta-}{\mathrm{O}}$ polarity. There may indeed be a small effect of this kind, for there are theoretical and experimental reasons for using 0·75 Å rather than 0·77 Å for the standard radius for a trigonal hybridised carbon atom (Coulson, Victor Henri Memorial Vol., Desoeur, Liège, 1948, 15; *J. Phys. Chem.*, 1952, **56**, 311). In the oxalate ion where the C–O bonds are equivalent, the carboxyl group resonance is greater than in the acid, and any conjugation across the molecule should be more marked. It is of interest, therefore, to consider carefully the evidence relating to the crystal structure of ammonium oxalate hydrate, for which it is reported that the oxalate ion is non-planar in addition to having a C–C bond length of 1·58 Å (Hendricks and Jefferson, *J. Chem. Phys.*, 1936, **4**, 102).

Ammonium oxalate hydrate crystallises in the orthorhombic sphenoidal class with two molecules related by the space-group symmetry $P2_12_12$ in a unit cell of dimensions $a = 8{\cdot}04$, $b = 10{\cdot}27$, $c = 3{\cdot}82$ Å. As there are only two oxalate ions in the cell, the two-fold axis of symmetry normal to the C–C bond must be coincident with the crystallographic c-axis. Nine parameters then define the atomic positions of the ion. The water molecule lies in a special position determined by one unknown parameter, and the ammonium ions are in general positions. In Hendricks and Jefferson's structure analysis, careful experimental measurements were made of the intensities for the ($hk0$) zone, an ionisation spectrometer being used. An approximate structure was determined in which the oxalate centres were at ($00z$), ($\frac{1}{2}\frac{1}{2}\bar{z}$) and the oxygen atoms of the water molecules were at ($\frac{1}{2}0z'$, $0\frac{1}{2}\bar{z}'$), where $z = 0{\cdot}07$ and $z' = -0{\cdot}20$ in fractions of the c-axis. The x and y co-ordinates were refined by a well-resolved Fourier projection down the c-axis until the agreement index, $R =$

$(\Sigma|F_{\text{obs.}} - F_{\text{calc.}}|)/(\Sigma|F_{\text{obs.}}|)$, for the $(hk0)$ observations was 0·25. The C–C bond length, which depends only on the xz carbon co-ordinates, was 1·58 Å. It is not possible from this projection to ascertain whether the oxalate ion is planar. Hendricks and Jefferson therefore examined photographs of the $(0kl)$ zone and concluded that a coplanar oxalate ion was incompatible with the intensities of 004, 014, and 034. An angle of 28° between the planes of the carboxyl groups was found to give calculated intensities in good qualitative agreement with those observed. The C–O bond lengths were 1·25 and 1·23 Å and the O–C–O angle was 129°. Although there was no doubt that the $(hk0)$ projection was correct, it was difficult to assess the reliability of the z-co-ordinates in the absence of quantitative $(0kl)$ intensity measurements and because of the assumptions in respect to the atomic scattering factors (that $f_{\text{NH}_4^+} = f_{\text{O}} = f_{\text{H}_2\text{O}} = 2f_{\text{C}}$ over all values of sin θ).

Our new experimental data consisted of quantitative measurements of the intensities of the $(hk0)$ and $(0kl)$ zones, covering a wider range of sin θ than the previous structure analysis. Commencing with the $(hk0)$ projection, the structure factors were calculated from Hendricks and Jefferson's parameters, the more appropriate scattering factor curves discussed below (p. 4867) being used. The agreement with the observed values improved to $R = 0{\cdot}159$ with some particularly large discrepancies for four strong reflections. These appeared to be due to experimental error, for the comparison of the same calculated values with our intensity measurements gave better agreement with $R = 0{\cdot}107$ over the same range of 80 reflections and $R = 0{\cdot}115$ over the full range; the appreciable difference remained only for (110). A difference synthesis, computed with $(F_{\text{O}} - F_{\text{C}})$ as the Fourier coefficients, showed that the termination-of-series corrections were small. There was some indication of a shift of the carbon atoms towards the origin, but the resulting improvement in R was not significant. There was no "difference" electron density which could be unambiguously associated with the hydrogen electrons of the water molecules. The xy-co-ordinates derived by Hendricks and Jefferson were unquestionably more accurate than indicated by the agreement they had obtained between their observed and calculated structure factors, and with the possible exception of the carbon y-parameter there was no refinement of their values.

The y- and z-parameters were now investigated, our quantitative measurements for the $(0kl)$ zone being used. The structure factor phases were calculated from Hendricks and Jefferson's parameters and a Fourier projection was computed. As was expected the NH_4^+ and H_2O were the only resolved atomic peaks. The C and O^2 atoms completely overlapped and O^1 was partially resolved. However, the distribution of the electron density on the projection and the agreement index for the $(0kl)$'s of $R = 0{\cdot}127$ proved conclusively that the ion was not planar. The parameters were refined by successive difference syntheses which confirmed the suspected change in the carbon y-parameter and produced small shifts in the z-parameters, the largest of which was 0·03 Å. The final agreement index was $R = 0{\cdot}097$.

The atomic parameters are given in Table 1, and the corresponding dimensions of the oxalate ion in Table 2.

TABLE 1. *Atomic co-ordinates.*

	In unit cell fractions :			In Å :		
	x	y	z	x	y	z
C	0·092	0·025	0·066	0·739	0·257	0·252
O^1	0·200	$\overline{0{\cdot}056}$	0·140	1·608	$\overline{0{\cdot}575}$	0·535
O^2	0·118	0·142	0·001	0·949	1·458	0·004
NH_4	0·386	0·228	0·424	3·103	2·342	1·620
H_2O	0·500	0·0	$\overline{0{\cdot}192}$	4·020	0·0	$\overline{0{\cdot}733}$

TABLE 2. *Dimensions of the oxalate ion.*

C–C	1·56 Å	O^1–C–O_2	125·3°
C–O^1	1·23	O^1–C–C	116·3
C–O^2	1·25	O^2–C–C	118·5

Angle between the COO^- planes 28°.

O^1 . . . O^2 2·20 Å. O^1 . . . $O^{1\prime}$ 3·42 Å. O^1 . . . $O^{2\prime}$ 2·76 Å.

The standard deviation for the x- and y-co-ordinates of the carbon atom as calculated by Cruickshank's method (*Acta Cryst.*, 1949, **2**, 65) is 0·008 Å, which gives a standard deviation for the C–C bond of 0·022 Å; the probable limit of error on the C–C bond length is therefore $\pm$0·05 Å. The z-parameters of atoms unresolved in the a-axis projection are less accurately defined, so the probable limits for the C–O bonds are greater. The new co-ordinates do not differ significantly from the results of the earlier work, and greater accuracy could be obtained only by more precise experimental measurements of the principal zones or by measurement of the general (*hkl*) intensities. This was not considered necessary in this investigation, which has shown conclusively that the oxalate ion is non-planar in the crystals of ammonium oxalate monohydrate.

The C–C length of 1·56 Å is not significantly different from 1·54 or the 1·53 Å found in the structure analysis of the oxalic acid dihydrate. As in the α-anhydrous acid and the acid hydrate, the π-electronic systems of the carboxyl groups are separated by a single C–C bond. It is to be expected that the absence of conjugation would be associated with a non-planar structure, as is indeed found in the ion, in marked contrast to the planar acid molecules. The angle between the planes of the carboxyl groups is 28°, which, associated with the O^1–$O^{2\prime}$ distance of 2·76 Å, is smaller than might be expected for perfectly free rotation about the central bond. In an isolated oxalate ion, a 90° angle would correspond to minimum interaction between the oxygen atoms, but in the crystal the configuration will be modified by the potential field of neighbouring ions and water molecules. The observed angle of 28° is therefore a characteristic of the crystal structure rather than of the oxalate ion and may be different in other crystalline salts. There appear to be no other structural studies of the crystalline oxalates apart from Hendricks's early paper (*loc. cit.*), which gives the approximate structures of the neutral and acid potassium and rubidium salts. This work was not as detailed as in the ammonium salt analysis and it was assumed that all the ions were planar. However, there is no evidence that this is necessarily true, for, in reconsidering these results at the end of the later paper, Hendricks and Jefferson conclude that oxalate ions which are non-planar to the extent of $\pm$10° are compatible with their X-ray and optical data for the neutral salts.

The two C–O bond lengths in the oxalate ion do not differ significantly, and the mean is in good agreement with other data, *e.g.*, the formate ion in calcium formate in which the C–O lengths are 1·25, 1·25, 1·25, and 1·24 $\pm$ 0·03 Å, and the O–C–O angles are 125° and 124°$\pm$4° (Isamu and Kanji, "*X*-Rays," 1948, **5**, 37; Structure Reports, Vol. II, p. 556, Oosthoek, Utrecht, 1951).

The interionic distances and the co-ordination of the ions and water molecules are described in the earlier paper and are materially unaffected by the results of this analysis.

EXPERIMENTAL

Suitable crystals were obtained by evaporation of an aqueous solution in the form of small needles elongated about the a-axis. No corrections were made for absorption; these errors were minimised by using crystals of an approximately uniform cross-section of 0·02 cm. (μ = 13·14 cm.$^{-1}$). The intensities were measured by eye-estimation from Leeds–Weissenberg photographs of the zero layer line about the a- and c-axes, Cu-K_α radiation being used. In the (*hk*0) zone, 106 structure amplitudes were recorded as against 80 in the earlier work; 48 (0*kl*) structure amplitudes were measured.

In calculating the structure factors, the Hartree scattering factor curves were used for oxygen and carbon with a temperature factor of $B = 2{\cdot}46 \times 10^{-16}$, which was deduced from the slope of a plot of $\log_e \dfrac{\Sigma|F_o|}{\Sigma|F_o|}$, against $4 \sin^2 \theta$, the summation being over ranges of $4 \sin^2 \theta = 0{\cdot}6$. In deriving the $NH_4{}^+$ scattering factors it was assumed that the amplitude of oscillation of the N–H bonds was such that a good approximation could be made by treating the ion as a freely rotating group. The scattering factor curve was calculated from the following expression

$$f_{NH_4^+} = f_{N^+} + 4f_H \frac{\sin\,[4\pi r_H\,(\sin\theta)/\lambda]}{4\pi r_H\,(\sin\theta)/\lambda}$$

The N^+ scattering factors were obtained from a curve which was identical with the Hartree curve for neutral N when $(\sin\theta)/\lambda > 0{\cdot}3$ and tended smoothly to a value of 6·0 as $(\sin\theta)/\lambda$

approached zero. A Hartree f_H was used, and the length of the NH bond (r_H) was assumed to be 1·0 Å. As the use of this scattering function contributed more than any other single factor to the improved agreement between observed and calculated structure factors, it is given in the following Table, without a temperature factor.

$10^{-8}(\sin\theta)/\lambda$	0	0·1	0·2	0·3	0·4	0·5	0·6	0·7
$4f_H \cdot \frac{\sin[4\pi r_H(\sin\theta)/\lambda]}{4\pi r_H(\sin\theta)/\lambda}$	4·00	2·44	0·44	−0·16	−0·08	0·0	0·02	0·01
f_{N^+}	6·00	5·29	4·04	3·00	2·30	1·90	1·65	1·54
$f_{NH_4^+}$	10·00	7·73	4·48	2·84	2·22	1·90	1·67	1·55

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DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY,
THE UNIVERSITY OF LEEDS.

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