37. *The Crystal and Molecular Structure of Certain Dicarboxylic Acids. Part II. Acetylenedicarboxylic Acid Dihydrate.*

By J. D. Dunitz and J. Monteath Robertson.

The crystal and molecular structure of acetylenedicarboxylic acid dihydrate has been determined from the *X*-ray data. The structure is closely analogous to that of oxalic acid dihydrate, in which two water molecules (or probably oxonium ions) connect the carboxyl groups of adjoining molecules by means of strong hydrogen bridges, the whole forming a spiral arrangement which extends throughout the crystal. The molecular and intermolecular distances are indicated in Figs. 1 and 3. The results are strongly in favour of a symmetrical or nearly symmetrical coplanar structure for the molecule, with resonance effects extending throughout its structure. In locating the centres of the carboxyl group of atoms there are many possible sources of error, and uncertainties of about ± 0·04 A. may apply to the carbon–oxygen distances and to the formal single bond adjacent to the triple bond. The length of the triple bond itself (1·19 A.) should be considerably more accurate.

Crystal Data.—Acetylenedicarboxylic acid dihydrate, $C_4H_2O_4,2H_2O$; *M*, 150·1; m. p. (anhydrous) 175° (decomp.); *d*, calc. 1·469, found 1·470; monoclinic prismatic, $a = 11·05 \pm 0·03$, $b = 3·86 \pm 0·01$, $c = 7·98 \pm 0·02$ A., $\beta = 98·0° \pm 0·3°$. Absent spectra, ($h0l$) when h is odd; ($0k0$) when k is odd. Space-group, $C_{2h}^5(P2_1/a)$. Two molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell, 337·1 A.^{3} Absorption coefficient for *X*-rays ($\lambda = 1·54$ A.), $\mu = 14·5$ cm.$^{-1}$. Total number of electrons per unit cell = F(000) = 156.

Large, well-formed crystals were easily obtained from water as colourless laths or plates, elongated along the *b* axis, the largest face being (001). The (201) and $(20\bar{1})$ are usually developed, and the (100) appears occasionally. Other faces are generally absent.

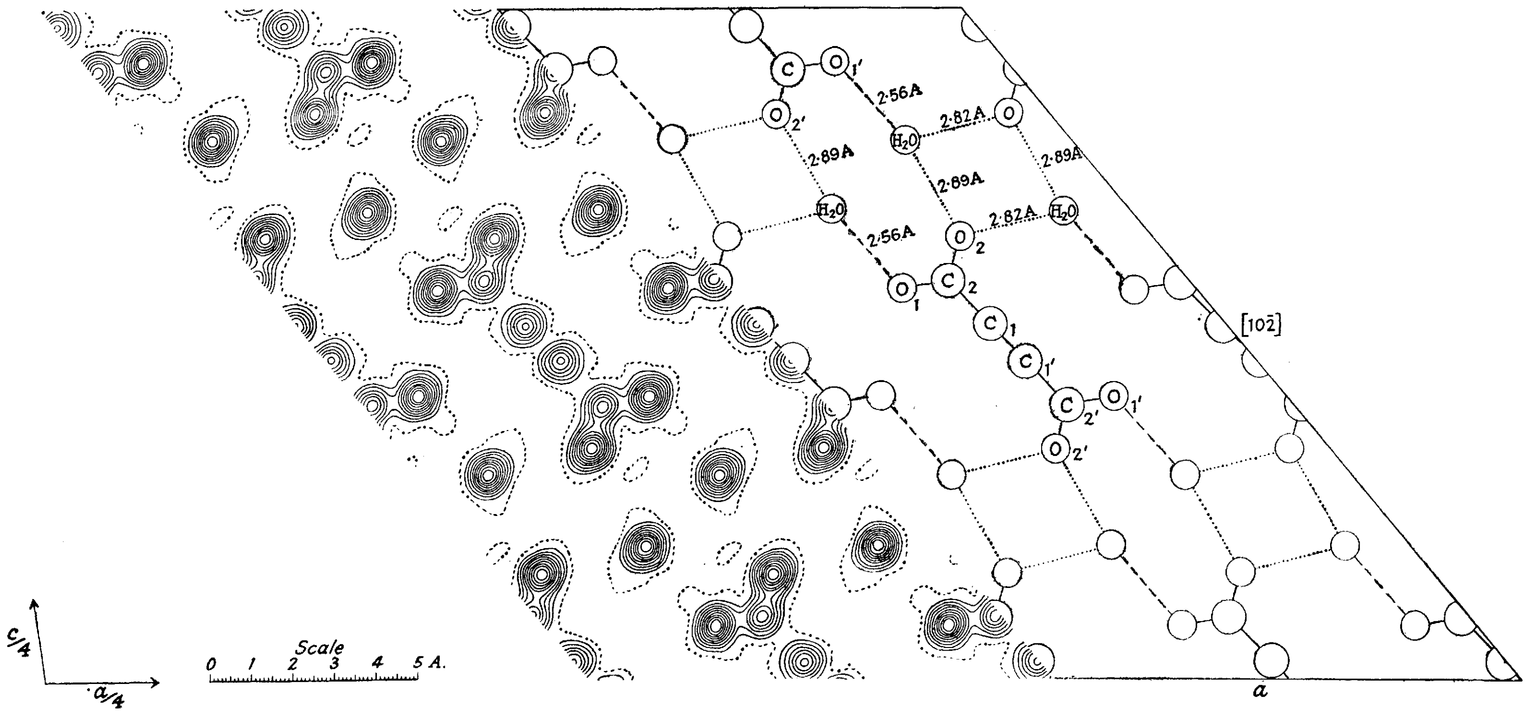
Structure Analysis.—Similarities in the dimensions of the unit cells of oxalic acid dihydrate and acetylenedicarboxylic acid dihydrate (compare Table I, preceding paper) first suggested the main outlines of the structure. In particular, the short *b* axis and the inclination of the $[10\bar{2}]$ axis to the *a* axis (about 50°) give roughly the direction of the molecular chains, while the increase in length of the $[10\bar{2}]$ axis as compared with oxalic acid (2·85 A.) is just about the amount required to accommodate the extra atoms.

A trial model was accordingly set up on these lines and the co-ordinates were refined by three successive Fourier syntheses giving projections of the structure on the (010) plane. The final projection is shown in Fig. 1, from which accurate values of the *x* and *z* co-ordinates of all the atoms can be obtained.

The *y* co-ordinates were obtained by trial and checked by another Fourier projection made along the *c* axis using the ($hk0$) structure factors. This is shown in Fig. 2. As only two of the five atoms in the asymmetric unit are separately resolved, the information afforded by this result is not very complete. Nevertheless, Figs. 1 and 2 considered together are sufficient to yield a reasonably precise picture of the whole structure.

Molecular Dimensions and Co-ordinates.—The co-ordinates assigned to the atoms as a

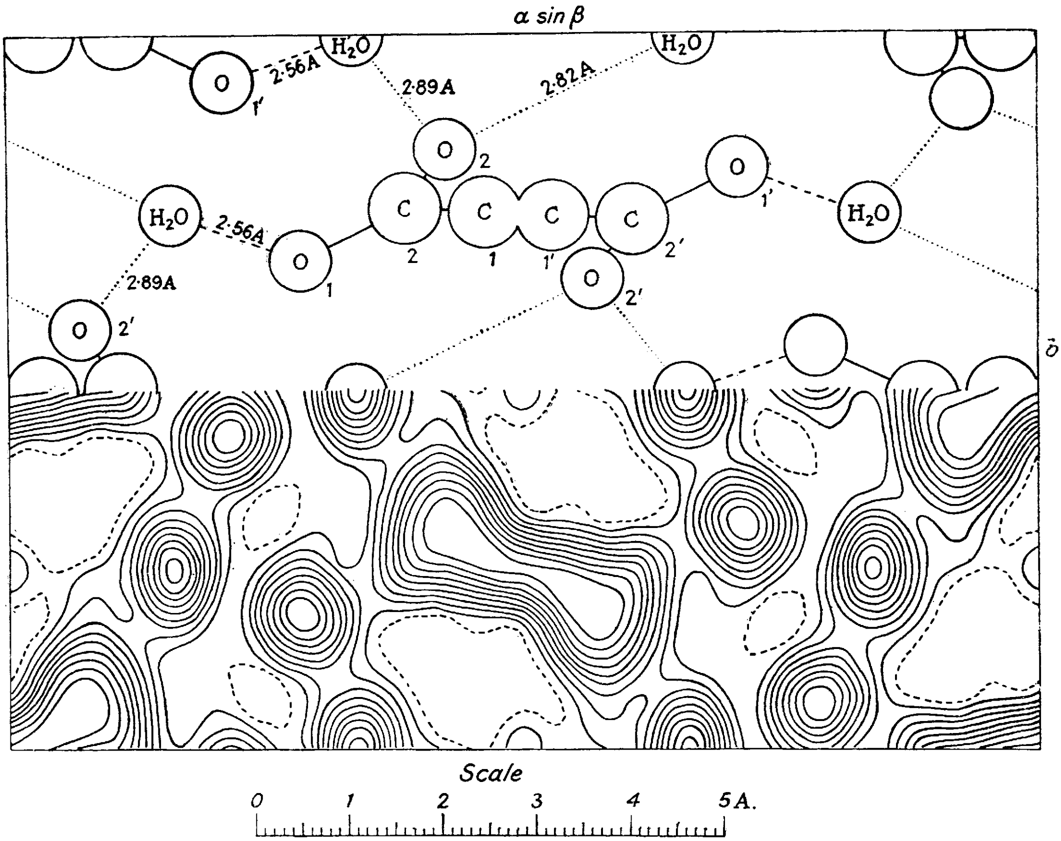
FIG. 1.



Projection along the b *axis, on the* (010) *plane, covering two unit cells. The plane of the acid molecule is inclined to the projection plane at* 33° (ψ_N). *Each contour line represents a density increment of approximately one electron per* A.², *the one-electron line being dotted.*

result of the final Fourier summations are indicated in Fig. 4 and listed in Table I. These co-ordinates lead to the molecular and intermolecular dimensions given in Figs. 1 and 3, where the atoms of the acid molecule are coplanar and the carbon chain is linear. The orientation of this molecule with respect to the crystal axes is given by the angles in Table II. χ_L, ψ_L, ω_L, χ_M, ψ_M, ω_M and χ_N, ψ_N, ω_N are the angles between the molecular axes L, M, and N, and the crystal axes a, b, and c', c' being perpendicular to a and b. The molecular axis L is the direction

FIG. 2.



Projection along the c *axis. Contour scale as in Fig.* 1.

TABLE I.

Co-ordinates. Centre of symmetry as origin, x, y, z, *are referred to the monoclinic crystal axes,* x′, y, z′, *are rectangular co-ordinates referred to the* a *and* b *crystal axes, and their perpendicular,* c′.

Atom (cf. Fig. 1).	*x*, A.	*y*, A.	*z*, A.	*x′*, A.	*z′*, A.	$2\pi x/a$.	$2\pi y/b$.	$2\pi z/c$.
C (1)	−0·36	−0·02	0·43	−0·42	0·42	− 11·6°	− 2·0°	19·3°
C (2)	−1·22	−0·07	1·46	−1·42	1·44	− 39·6	− 6·6	65·6
O (1)	−2·35	0·50	1·27	−2·53	1·26	− 76·7	47·1	57·3
O (2)	−0·78	−0·70	2·52	−1·13	2·49	− 25·5	−65·3	113·6
H_2O	−3·77	0·00	3·16	−4·21	3·13	−122·9	0·0	142·6

TABLE II.

Orientation of the molecule in the crystal.

χ_L = 134·5°, cos χ_L = −0·7004	χ_M = 52·3°, cos χ_M = 0·6114	χ_N = 68·4°, cos χ_N = 0·3680
ψ_L = 92·0°, cos ψ_L = −0·0349	ψ_M = 123·0°, cos ψ_M = −0·5446	ψ_N = 33·0°, cos ϕ_N = 0·8380
ω_L = 44·5°, cos ω_L = 0·7128	ω_M = −55·0°, cos ω_M = 0·5741	ω_N = 66·2°, cos ω_N = 0·4028

of the carbon chain; M lies in the plane of the molecule and is perpendicular to L; N is the normal to the molecular plane. The co-ordinates of the atoms with respect to these molecular axes are given in Table III.

TABLE III.

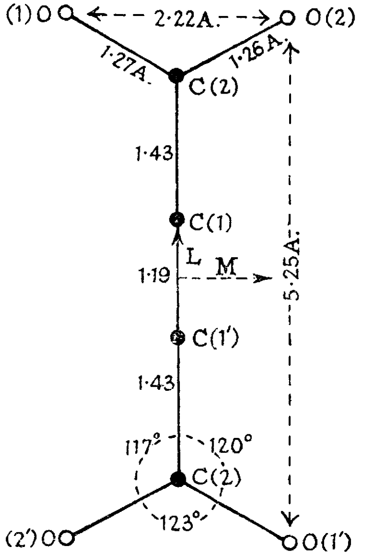
Co-ordinates of atoms with respect to molecular axes.

Atom	C_1	C_2	O_1	O_2
L, A.	0·595	2·025	2·655	2·595
M, A.	0	0	−1·10	1·12

DISCUSSION OF RESULTS.

It is immediately clear that the same kind of structure exists in crystals of oxalic acid dihydrate, acetylenedicarboxylic acid dihydrate, and, with minor space-group deviations noted in Part III, in diacetylenedicarboxylic acid dihydrate. In all these structures the two molecules of water of crystallisation and the carboxyl groups at each end of the carbon chains are the common factors which determine the manner in which the crystals are built. The relative positions of the oxygen atoms display quite a remarkable constancy in all these structures, a fact which is well illustrated in Fig. 2 of the previous paper. Although the carbon chain is different for each acid this has very little influence on the forces holding the molecules together in the crystal. The only effect is a slight tightening in the lateral packing on passing from oxalic acid to the acetylene acids, indicated by a decrease of about 0·8 A. in the length of the a axis, and possibly some weakening of packing in the direction of the b axis, which shows a small increase in length from 3·60 A. in oxalic acid to 3·86 and 3·75 A. in the two acetylene acids.

FIG. 3.



Dimensions of the acetylenedicarboxylic acid molecule.

As in the oxalic acid structure, a very short hydrogen bridge exists between the oxygen atom O(1) and the water molecule (Fig. 1). This bridge measures 2·56 A., as against 2·51 A. in oxalic acid, and it is the only hydrogen bridge formed by the oxygen atom O(1), the next nearest approach of a water molecule being over 4 A. The other carboxylic oxygen atom O(2) forms two hydrogen bridges of a much weaker type (2·89 and 2·82 A.) with two other water molecules. Each water molecule in turn forms three hydrogen bridges (2·56, 2·82, and 2·89 A.) to surrounding carboxylic oxygen atoms. It is clear, therefore, that each water molecule engages three hydrogen atoms; but whether these three hydrogen atoms should all be regarded as permanently attached to the water molecule, with the formation of an oxonium ion, is a question that cannot be answered definitely from the experimental evidence before us. If the mechanism of the hydrogen bridge is entirely electrostatic, this may be the case. On the other hand, there is obviously a great difference in quality between the three bridges, one of them being 0·3 A. shorter than the other two. The possibility of the ready transfer of a hydrogen atom across the short bridge is a factor which must obviously receive serious consideration. From the purely electrostatic point of view, this transfer will have taken place from the hydroxyl oxygen of the carboxyl group, leaving this oxygen with a negative charge and so accounting for the extra short hydrogen bridge. This view receives support from the work of Brill, Hermann, and Peters (*Ann. Physik*, 1942—1943, **42**, 357), who claim to have differentiated the carbon–oxygen bond lengths in oxalic acid dihydrate and identify the oxygen atom O(1) which gives the short hydrogen bridge as the hydroxyl oxygen. In our present results we are not able to distinguish the two oxygen atoms as giving measurably different carbon–oxygen bond lengths in the acetylene acids, and in our former work on oxalic acid (see previous paper) this matter is also in doubt.

With regard to the general arrangement of the molecules in the crystal, it should be observed that the acid molecules are not, as might be inferred from Fig. 1, arranged in series of infinite chains linked by hydrogen bridges, but in infinite spirals. The apparently closed ring formed by the atoms H_2O, O(1), C(2), O(2), H_2O, O(1′), C(2′), O(2′), H_2O is actually a spiral, the return connection leading to a molecule one translation further along the *b* axis, as will be clear from Fig. 2. However, the four-membered ring formed by the weaker bridges, 2·89, 2·82, 2·89, and 2·82 A., is actually a closed circuit as represented in Fig. 1. In these respects the structure is similar to that of oxalic acid dihydrate.

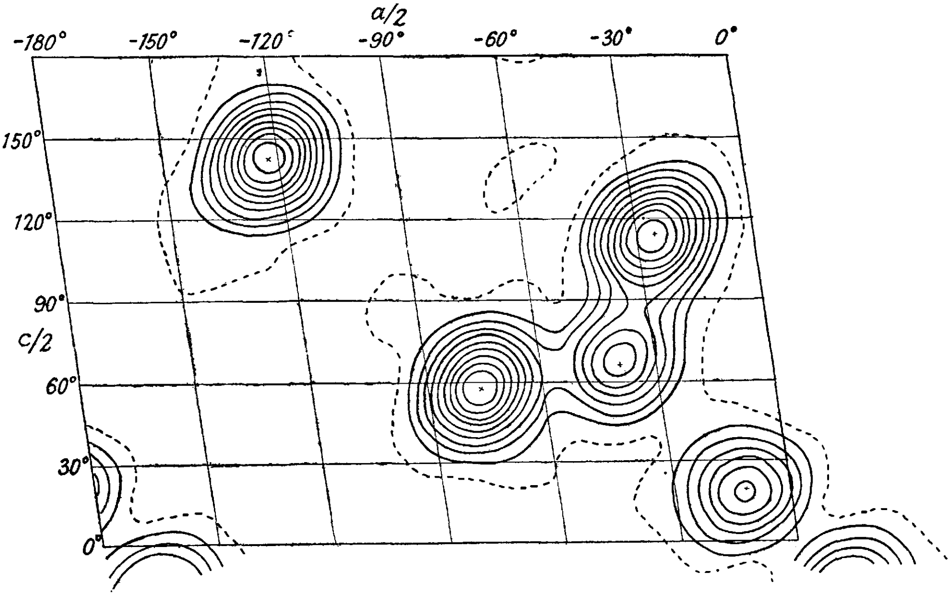
The internal dimensions which we find for the acetylenedicarboxylic acid molecule are indicated in Fig. 3. It is very difficult to make a reliable assessment of limits of accuracy which should be attached to these figures. The considerable divergence between the results of different observers in the case of oxalic acid dihydrate (see previous paper) is a warning that, especially in the case of the carboxyl group of atoms, there are many possible sources of error. In the present analysis we have not attempted any elaborate corrections for diffraction effects due to non-convergence of the series, etc., as the experimental data scarcely seem sufficiently reliable to justify such work. To the data as they stand in Fig. 3 we would attach a possible error of about ± 0·04 A. for the carbon–oxygen distances, and for the single-bond carbon–carbon distance of 1·43 A. The triple-bond carbon–carbon distance of 1·19 A. should be considerably more reliable than this owing to more favourable resolution, and we would assess the possible error in this case at about ± 0·02 A.

Our results are strongly in favour of a symmetrical or very nearly symmetrical co-planar structure for the molecule with considerable resonance effects extending throughout its structure. The formal single bond of 1·43 A. adjacent to the triple bond may be compared with the corresponding bond in tolan, where the value obtained was 1·40 A. (Robertson and Woodward, *Proc. Roy. Soc.*, 1938, **164**, *A*, 436), and in diphenyldiacetylene, where the value of 1·44 A. was reported by Weibenga (*Z. Krist.*, 1940, **102**, 193). This bond length and also the somewhat contracted value of 1·19 A. which we find for the triple bond distance are further discussed in Part III.

EXPERIMENTAL.

Preparation, and Determination of Data.—Acetylenedicarboxylic acid was prepared in good yield from αβ-dibromosuccinic acid (*Org. Synth.*, 1938, **18**, 3). Crystals of the dihydrate obtained from aqueous solution were usually too large for accurate *X*-ray work, but specimens of suitable dimensions could be cut with a razor blade.

FIG. 4.



Co-ordinates assigned to the atoms in the asymmetric crystal unit.

Copper-*K*α radiation, λ = 1·54, was used throughout, and rotation, oscillation, and moving-film photographs of the principal zones were taken. For the (*h*0*l*) zone the specimens employed for most of the intensity work had cross-sections normal to the *b* axis of (*a*) 0·29 by 0·33 mm. and (*b*) 0·56 by 0·50 mm. Crystals of the dihydrate smaller than (*a*) tend to decompose by loss of water before completion of the exposure, but with slightly larger crystals the partial dehydration of the surface layers during experiment does not result in any loss of accuracy. If anything, it is an advantage in so far as it ensures the true mosaic character of the specimen, which is usually assumed. For the (*hk*0) zone a specimen of cross section 0·55 by 0·65 mm. normal to *c* was employed. These various crystals were completely immersed in the *X*-ray beam, and the spectra recorded up to the limit for $\lambda = 1{\cdot}54$ A. on series of moving films. The multiple-film technique (Robertson, *J. Sci. Instr.*, 1943, **20**, 175) was used for correlation of intensities, and the total range covered was about 2000 to 1. Two independent sets of visual estimates were made on the films from one of the *b* rotation crystals, and one set from the

TABLE IV.

Measured and calculated values of the structure factor.

hkl.	$\sin\theta$ (λ = 1·54).	F, meas.	F, calc.
200	0·141	<1·5	+1·5
400	0·282	11	−9
600	0·423	7	−3·5
800	0·564	9·5	−9
10,00	0·705	<3·5	−1·5
12,00	0·845	<3	−1
020	0·399	27	+25
040	0·798	4	+5
001	0·098	5·5	+5·5
002	0·195	21·5	−16
003	0·293	4·5	+1·5
004	0·390	21·5	−25
005	0·488	11·5	+12
006	0·586	12	+12
007	0·683	<3·5	+5
008	0·781	8	−10
009	0·879	6	−6·5
00,10	0·976	<1·5	+0·5
209	0·912	<2·5	+0·5
208	0·816	6	−5·5
207	0·718	7·5	+11
206	0·623	5	−8
205	0·528	17	−22·5
204	0·433	20·5	+21·5
203	0·344	9·5	+9
202	0·256	33	+32·5
201	0·183	32·5	+36·5
$20\bar{1}$	0·162	24	−25
$20\bar{2}$	0·225	27·5	−25
$20\bar{3}$	0·308	45·5	+47
$20\bar{4}$	0·397	9	+8
$20\bar{5}$	0·490	7·5	−5
$20\bar{6}$	0·586	3·5	+5
$20\bar{7}$	0·680	22·5	−27·5
$20\bar{8}$	0·778	6·5	−5·5
$20\bar{9}$	0·876	5	+4
$20,\bar{1}\bar{0}$	0·972	<1·5	+0·5
409	0·961	<2	−2·5
408	0·867	<3	0
407	0·776	<3·5	+1
406	0·686	4·5	+6
405	0·599	<3·5	−3
404	0·514	17	+21
403	0·437	4	+5·5
402	0·367	21	−20·5
401	0·313	40·5	+39·5
$40\bar{1}$	0·287	3·5	+2
$40\bar{2}$	0·322	41·5	+40
$40\bar{3}$	0·380	14·5	−14
$40\bar{4}$	0·450	16	−14·5
$40\bar{5}$	0·531	18	−16
$40\bar{6}$	0·616	6	−4
$40\bar{7}$	0·705	<3·5	−2
$40\bar{8}$	0·794	<3·5	−0·5
$40\bar{9}$	0·890	4·5	+4
$40,\bar{1}\bar{0}$	0·982	6	−4·5
608	0·941	4	+5
607	0·852	<3	+1
606	0·768	8·5	−10·5
605	0·691	4·5	+7·5
604	0·617	<3·5	+2
603	0·545	10·5	+11·5
602	0·493	19	+20
601	0·449	9	+9·5
$60\bar{1}$	0·423	26·5	−22·5
$60\bar{2}$	0·443	17·5	+16·5
$60\bar{3}$	0·437	13	−10
$60\bar{4}$	0·538	16·5	−14
$60\bar{5}$	0·606	18	+15
$60\bar{6}$	0·676	11·5	−13·5
$60\bar{7}$	0·756	6·5	−5·5
$60\bar{8}$	0·839	<3	+0·5
$60\bar{9}$	0·926	7	−3
807	0·946	<2	−1
806	0·873	<3	−0·5
805	0·797	10	+14
804	0·731	10·5	+13·5
803	0·673	6·5	−9
802	0·623	4	+6·5
801	0·588	12·5	−14·5
$80\bar{1}$	0·557	23·5	+25·5
$80\bar{2}$	0·574	<3	−1
$80\bar{3}$	0·601	9	−9
$80\bar{4}$	0·644	13	−12·5
$80\bar{5}$	0·695	7·5	−7·5
$80\bar{6}$	0·758	4·5	−4
$80\bar{7}$	0·829	4·5 *	−1·5
$80\bar{8}$	0·900	6	+5·5
$80\bar{9}$	0·977	3·5	−2
10,06	0·978	3	+5
10,05	0·914	<2·5	+0·5
10,04	0·854	4	−4·5
10,03	0·801	<3·5	−3
10,02	0·758	<3·5	+3
10,01	0·728	7·5	+10·5
$10,0\bar{1}$	0·700	5	+3
$10,0\bar{2}$	0·705	14	−16·5
$10,0\bar{3}$	0·728	18·5	−19·5
$10,0\bar{4}$	0·759	11·5	+9·5
$10,0\bar{5}$	0·803	<3	0
$10,0\bar{6}$	0·856	<3	+0·5
$10,0\bar{7}$	0·916	<2·5	+1
$10,0\bar{8}$	0·982	6	−3·5
12,04	0·979	1·5 *	−2
12,03	0·934	3·5	+5·5
12,02	0·897	<3	+1
12,01	0·869	5	−5·5
$12,0\bar{1}$	0·843	7·5	−6·5
$12,0\bar{2}$	0·845	4	−1·5
$12,0\bar{3}$	0·861	4	+3
$12,0\bar{4}$	0·886	3·5	+2
$12,0\bar{5}$	0·920	3	−2
$12,0\bar{6}$	0·966	7·5	−5
110	0·212	26·5	+26·5
210	0·245	17	−7·5
310	0·291	21	+17
410	0·346	32·5	−26·5
510	0·405	<2	−3
610	0·467	5	+5
710	0·532	19·5	−18·5
810	0·598	<2	−3
910	0·665	10·5	+13
10,10	0·733	4·5	+5
11,10	0·801	3	−2·5
12,10	0·869	<2	+1
13,10	0·937	4	−3
120	0·406	7	+8
220	0·424	5	+0·5
320	0·452	20·5	−23
420	0·489	2	−9
520	0·533	<2	−2
620	0·581	9	+14·5
720	0·635	<2	+1
820	0·691	4·5	+5·5
920	0·745	<2	0
10,20	0·810	<2	−2
11,20	0·872	2·5	+4
12,20	0·935	2	−2
130	0·603	2·5 *	−4·5
230	0·615	<2	+2
330	0·635	7	+12·5
430	0·662	4·5	−3
530	0·695	3	−4·5
630	0·733	6 *	+3
730	0·775	2·5	+5·5
830	0·823	2	−2·5
930	0·872	2·5	+3·5
10,30	0·925	1·5	+0·5
11,30	0·979	<1	0
140	0·801	<2	+0·5
240	0·811	4	+4·5
340	0·826	2	+3
440	0·846	<2	−4·5
540	0·873	2 *	+2
640	0·903	<2	+2·5
740	0·938	<2	+0·5
840	0·977	<1	+1

other crystal. The mean of these three estimates was accepted as correct. For the *c* rotation similar methods were adopted. Absorption corrections were not employed, as the dimensions of the crystal specimens render them unnecessary. F values were finally derived by the usual formulæ for mosaic crystals and are listed in Table IV. Absolute measurements were not carried out, and the scale of the F values was obtained by correlation with the values finally calculated from the atomic positions found.

Structure Determination.—After preliminary determination of atomic positions by trial, the structure was refined by three successive two-dimensional Fourier syntheses giving projections on (010) and one giving a projection normal to the *c* axis. The usual formulæ for $\rho(x, z)$ and $\rho(x, y)$ were employed. For $\rho(x, z)$ the series were summed at 450 points on the asymmetric crystal unit, the axial sub-divisions being $a/60 = 0{\cdot}184$ A. and $c/30 = 0{\cdot}266$ A. Three-figure methods (Robertson, *Phil. Mag.*, 1936, **21**, 176) were employed, and the positions of the contour lines plotted on a scale of 5 cm. to 1 A. by graphical interpolation from the arrays of summation totals. The final plot of the asymmetric unit for the *b* projection is shown in Fig. 4, and in this diagram the final positions assigned to the atoms are indicated by small crosses.

These co-ordinates are found to be consistent with the molecular model given in Fig. 3, and the orientation listed in Table II. An independent check on the *y* co-ordinates is, of course, obtained from the projection along the *c* axis shown in Fig. 2. From the final co-ordinates (Table I) all the structure factors were recalculated and the results are given in Table IV. For this calculation the composite empirical atomic scattering curve used in the case of oxalic acid dihydrate (Robertson and Woodward, *J.*, 1936, 1817) was again employed, but with the carbon and oxygen coefficients weighted in the ratio 6 to 9, instead of 6 to 10. This alteration, suggested empirically by the data, is probably due to a slightly different form of temperature factor. There is, of course, no theoretical justification for the use of a single *f*-curve for all the atoms. It is employed at present merely because it is found to give a sufficiently good approximation for the purpose on hand. The discrepancy finally obtained, expressed as

$$\frac{\Sigma\,(|\,F_{\text{meas.}}\,| - |\,F_{\text{calc.}}\,|)}{\Sigma\,|\,F_{\text{meas.}}\,|}$$

is 14·9% for the (*h*0*l*) reflections, 25·4% for the (*hk*0) reflections, and 17·5% for all reflections.

The rather large discrepancy in the case of the (*hk*0) reflections is difficult to explain. The expansion of the *b* axis to 3·85 A. as compared with 3·60 A. in oxalic acid dihydrate probably indicates a rather looser form of packing in this direction, and the atomic *f* curves which we have employed in these calculations may not be applicable, owing to differences in the temperature factor. It is clear that we must accept a considerable uncertainty in the *y* co-ordinates of the atoms. This will not, however, have much effect on the dimensions of the carbon chain, which are determined principally from the (*h*0*l*) projection.

In the *b* axis projection the F values for the (807) and (12,04) planes, and in the *c* axis projection the F values for the (130), (630), and (540) planes (marked by an asterisk in Table IV), were omitted from the Fourier summations owing to uncertainty of sign. The sign of F (220) is very doubtful, but this term has been included.

We thank the Royal Society for a grant which defrayed the cost of some of the apparatus used in this work, and one of us (J. D. D.) is indebted to the Carnegie Trustees for a Scholarship.

UNIVERSITY OF GLASGOW. [*Received, May* 31*st*, 1946.]