215. *The Crystal and Molecular Structure of Certain Dicarboxylic Acids. Part III. Diacetylenedicarboxylic Acid Dihydrate.*

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The crystal and molecular structure of diacetylenedicarboxylic acid dihydrate, $HO_2C{\cdot}C{\equiv}C{-}C{\equiv}C{\cdot}CO_2H,2H_2O$, has been determined from *X*-ray data, and is shown to be similar in general outline to that of oxalic acid dihydrate and acetylenedicarboxylic acid dihydrate (Parts I and II, this vol., pp. 142, 148). A network of hydrogen bridges extends throughout the crystal and links the water molecules (or oxonium ions) to the adjoining acid molecules.

In the present crystal there is, however, a space-group change, from C_{2h}^5 to C_{2h}^6, and the molecules possess a two-fold axis of symmetry instead of a centre. The configuration is no longer coplanar, the carboxyl groups at opposite ends of the molecule lying nearly in two planes inclined to one another at about 57°.

The bond distances within the molecule are shown in Fig. 3, and should be accurate to within about ± 0·05 A., except in the carbon chain [C(2)–C(1) and C(1)–C(1′)] where a considerably higher accuracy of about ± 0·02 A. should apply. The central single bond of 1·33 A. is the shortest formal single bond so far discovered. This result is discussed, and also the question of whether the carbon–carbon triple bond in acetylene itself is really a suitable standard for the "normal" triple bond type.

IN previous papers (*loc. cit.*) we have discussed the structure of oxalic acid dihydrate and acetylenedicarboxylic acid dihydrate and shown that they are of the same type. The two water molecules (or oxonium ions) are situated between the carboxyl groups of adjoining acid molecules, to which they are bound by one very strong and two rather weaker types of hydrogen bridge. These connections form a spiral network which extends throughout the crystal and confers considerable stability on the whole structure. In these crystals the acid molecules possess a centre of symmetry, the carboxyl groups are nearly symmetrical, and the whole molecule is either planar or very nearly so, as would be expected from general chemical evidence.

We have now completed a similar detailed study of diacetylenedicarboxylic acid dihydrate. In this structure there is a space-group change, from $C_{2h}^5(P2_1/a)$ to $C_{2h}^6(I2/c)$ and a consequent doubling of the c axis. At first sight, and indeed in the principal projection of the structure (Fig. 1), the whole arrangement appears to be entirely analogous to that of the other two structures, apart from the lengthened carbon chain and the c axis doubling. The analysis of the principal zone, $(h0l)$, offers no particular difficulty, and proceeds on the same lines as before. In attempting to explain the intensities of other zones of reflections, however, serious difficulties were encountered. These could only be resolved on the assumption that the molecule of diacetylenedicarboxylic acid does not contain a symmetry centre and that the two carboxyl groups are not coplanar but lie in two planes inclined to one another at about 57°. The opposite ends of the molecule are related by a two-fold axis of symmetry which passes through its centre. In Fig. 1 the projection of this two-fold axis gives rise to a centre of symmetry and makes this picture precisely analogous to those already described for the other structures.

This change in configuration is difficult to understand, particularly as the bond-length measurements indicate that resonance effects extend throughout the molecule and these should tend to produce a coplanar form. As discussed more fully below, the configuration adopted in this case appears to be governed by the strongly directed intermolecular hydrogen bridging which exists in the crystal.

Apart from these curious effects, this structure is of special interest in providing fairly reliable measurements on a system of conjugated triple bonds. The linear carbon chain lies in the (010) plane, and two-dimensional Fourier methods provide excellent resolution of the various atoms. Both the triple bonds and their connecting link are found to be somewhat shorter (Fig. 3) than previous measurements on other compounds have indicated. These facts are discussed more fully below after the structure has been described.

Description of the Structure.—Crystal data. Diacetylenedicarboxylic acid dihydrate, $C_6H_2O_4,2H_2O$; *M*, 174·1; m. p. (decomp. with charring) 95—100°; *d*, calc. 1·43, found 1·43—1·45; monoclinic prismatic, $a = 11{\cdot}15 \pm 0{\cdot}03$, $b = 3{\cdot}75 \pm 0{\cdot}01$, $c = 20{\cdot}18 \pm 0{\cdot}08$ A., $\beta = 107{\cdot}0° \pm 0{\cdot}5°$. Absent spectra, (hkl) when $h + k + l$ is odd; $(h0l)$ when either h or l is odd. Space-group, $C_s^4(Ic)$ or $C_{2h}^6(I2/c)$. (C_{2h}^6 assumed in this analysis.) Four molecules per unit cell. Molecular symmetry, centre or two-fold axis. (Two-fold axis assumed in this analysis.) Volume of unit cell, 806·7 A.^{3}. Absorption coefficient for *X*-rays, $\lambda = 1{\cdot}54$, $\mu = 13{\cdot}4$ cm.$^{-1}$. Total number of electrons per unit cell = F(000) = 360.

Diacetylenedicarboxylic acid was first prepared by Baeyer (*Ber.*, 1885, **18**, 676, 2270) and his method of preparation was followed. Our final product, however, was not identical with that obtained by Baeyer, his being described as the monohydrate while ours was without doubt the *dihydrate*.

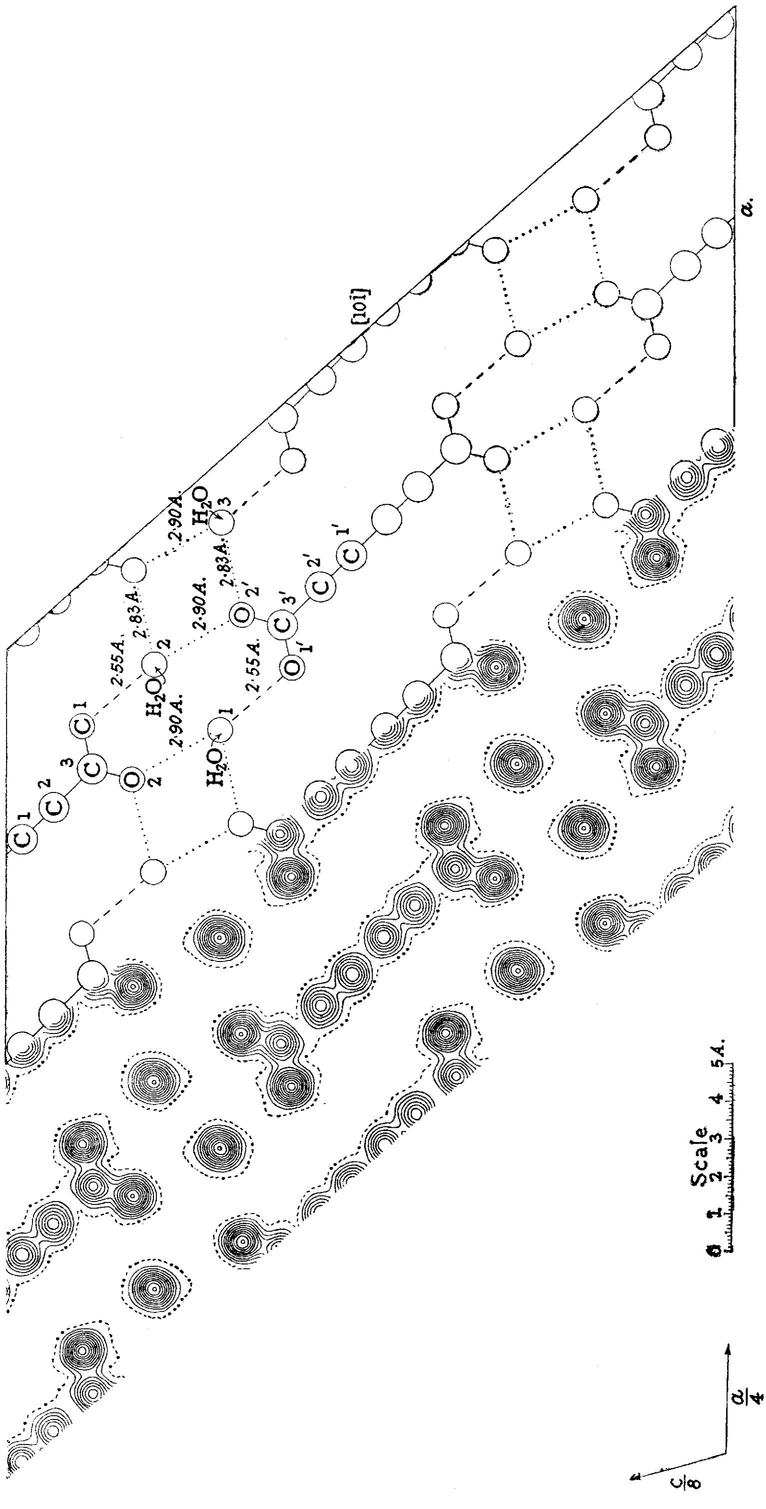
Crystals were obtained from water as small, faintly pink or yellow, sword-like needles, elongated in the b-axis direction. The (001) face was always prominently developed and the (101) also appeared, other faces being generally absent. The crystals deepen in colour when exposed to light, becoming purple and eventually black; exposure to *X*-rays causes them to become quite black almost immediately.

Structure analysis. The dimensions of the unit cell compared with oxalic acid dihydrate and acetylenedicarboxylic acid dihydrate suggested that the main features of the structure were the same as in these two compounds (see Table I, Part I, *loc. cit.*). The inclination of the $[10\bar{1}]$ axis to the a axis is still about 50° and the increase in its half-length (the c axis is doubled) as compared with acetylenedicarboxylic acid dihydrate (2·55 A.) is again just about the amount required to accommodate an extra pair of carbon atoms.

A trial model set up on the assumption that the long axis of the molecule was lying along $[10\bar{1}]$ with the planes of the carboxyl groups inclined at about 30° to the (010) plane gave good agreements for the observed $(h0l)$ intensities. The x and z co-ordinates were then refined by two successive Fourier syntheses, giving projections on the (010) plane. The final projection is shown in Fig. 1, from which accurate values of these co-ordinates can be obtained.

To determine the y co-ordinates in the structure, it is necessary to decide between certain alternative arrangements that are possible in the space-group C_{2h}^6. The centres of the molecules must lie on special positions, but these may be (*a*) the centres of inversion on the glide plane *a*, (*b*) the centres of inversion on the glide plane *c*, (*c*) the two-fold rotation axes. This choice of

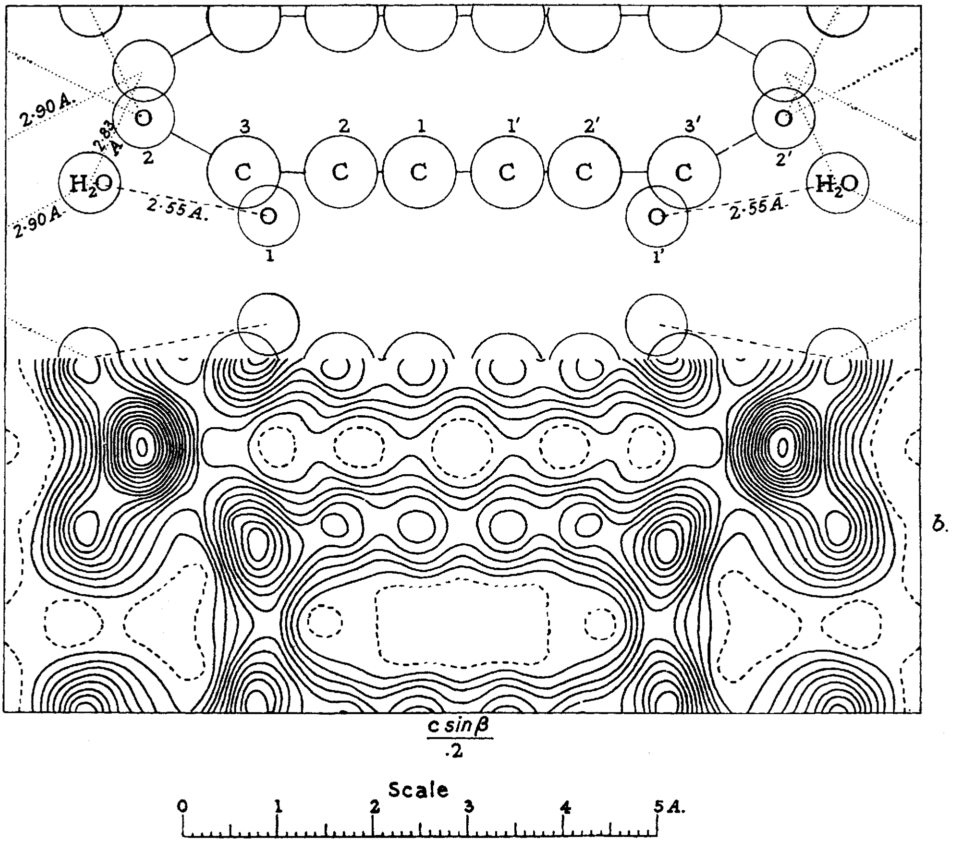
FIG. 1.



Projection along the b *axis, on the* (010) *plane, covering one unit cell. Each contour line represents a density increment of approximately one electron per* A.^{2}, *the one-electron line being dotted.*

origins does not affect the projection on (010) described above, but it does affect the general planes and especially the (0*kl*) structure factors, which were next examined in detail. Alternative (*a*) was eliminated by trial methods, and as (*b*) seemed much more likely than (*c*), by analogy with the previous structures, this possibility was examined in considerable detail. It was not possible to obtain good agreements between the calculated and the observed structure factors, the mean discrepancy always being about 30%. A Fourier projection was made, using terms whose sign seemed reasonably certain, but this projection was unsatisfactory and did not lead to any further refinement of the assumed co-ordinates. The idea of a molecular centre of symmetry was therefore abandoned, and possibility (*c*) was next explored. A two-fold rotation axis permits new molecular configurations and it was soon found that a model, consistent with the projection in Fig. 1, but with the planes of the carboxyl groups oppositely inclined, each at about 30° to (010), led to greatly improved agreements for the (0*kl*) and general structure factors, the mean discrepancy being reduced to less than 20%. The *y* co-ordinates were then refined by Fourier projections along the *a* axis, and the final diagram is shown in Fig. 2. The resolution of the atoms in Fig. 2 is not very complete, and it will be seen from the explanatory diagram that considerable overlapping must be expected. It is nevertheless possible to assign *y* co-ordinates which account fairly well for the shape of the contours. These co-ordinates are rather less certain than the *x* and *z* co-ordinates, especially for the atoms C(3), O(1), O(2), and H_2O.

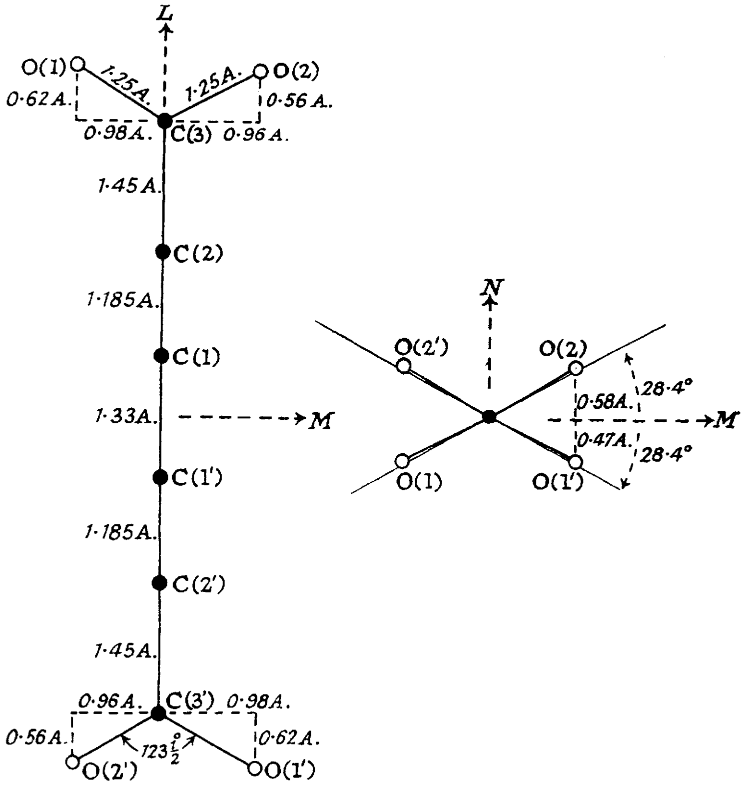
FIG. 2.



Projection along the a *axis, covering half a unit cell. The centres of the molecules are situated on rotation axes, at* 0·11 A. *from the glide plane* c. *Contour scale as in Fig.* 1, *except that the two-electron line is dotted.*

Molecular dimensions and co-ordinates. The *x* and *z* crystal co-ordinates obtained from the final Fourier projection on (010) are shown in Fig. 5, and are listed, together with the *y* co-ordinates, in Table I. These co-ordinates lead to the molecular model given in Fig. 3 and to the intermolecular distances of Fig. 1. The orientation of the molecule in the crystal is given in Table II, the molecular axis *L* being the direction of the carbon chain, *N* the direction of the two-fold rotation axis, and *M* the normal to the *LN* plane. Molecular co-ordinates referred to these axes are given in Table III.

FIG. 3.



Dimensions of the diacetylenedicarboxylic acid molecule *Projections of the molecule are drawn on the* LM *and* MN *planes.*

TABLE I.

Observed co-ordinates. Centre of symmetry on glide plane *c* as origin; *x, y, z* are referred to monoclinic crystal axes *a, b, c*; *x', y, z'* are 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.	$\frac{2\pi x}{a}$.	$\frac{2\pi y}{b}$.	$\frac{2\pi z}{c}$.
C(1)	0·332	0·11	4·555	−0·999	4·355	10·7°	10·5°	81·3°
C(2)	0·920	0·11	3·687	−0·157	3·525	29·7	10·5	65·8
C(3)	1·642	0·11	2·625	0·875	2·51	53·0	10·5	46·8
O(1)	2·856	−0·36	2·899	2·009	2·772	92·2	−34·6	51·7
O(2)	1·046	0·69	1·503	0·607	1·436	33·8	65·4	26·8
H_2O	3·945	0·00	0·920	3·676	0·880	127·4	0	16·4
Centre of molecule ...	0	0·11	5·045	−1·475	4·824	0	10·5	90·0

TABLE II.

Orientation of the molecule in the crystal. The symbols χ_L, ψ_L, ω_L; χ_M, ψ_M, ω_M; χ_N, ψ_N, ω_N have the same meanings as in Part II, Table II.

$\chi_L = -44{\cdot}5°$ $\cos\chi_L = 0{\cdot}7133$	$\chi_M = -134{\cdot}5°$ $\cos\chi_M = -0{\cdot}7009$	$\chi_N = 90°$ $\cos\chi_N = 0$
$\psi_L = 90°$ $\cos\psi_L = 0$	$\psi_M = 90°$ $\cos\psi_M = 0$	$\psi_N = 0°$ $\cos\psi_N = 1$
$\omega_L = -134{\cdot}5°$ $\cos\omega_L = -0{\cdot}7009$	$\omega_M = 135{\cdot}5°$ $\cos\omega_M = -0{\cdot}7133$	$\omega_N = 90°$ $\cos\omega_N = 0$

TABLE III.

Co-ordinates referred to orthogonal molecular axes *L*, *M*, *N*. The origin of these co-ordinates is situated in the crystal at $x = 0$, $y = 0{\cdot}11$ A., $z = 5{\cdot}045$ A. ($c/4$).

	L, A.	*M*, A.	*N*, A.		*L*, A.	*M*, A.	*N*, A.
C(1)	0·665	0	0	O(1)	3·92	−0·98	−0·47
C(2)	1·85	0	0	O(2)	3·86	0·96	0·58
C(3)	3·30	0	0				

Discussion of Results.—Hydrogen bonding and molecular configuration. Comparison of Fig. 1 with the corresponding projections for oxalic acid dihydrate and acetylenedicarboxylic acid dihydrate (Part I, Fig. 1, and Part II, Fig. 1) shows that the same type of structure appears to exist in all three crystals. So far as the intermolecular hydrogen bonding is concerned, the three crystals are almost identical, the relevant distances in diacetylenedicarboxylic acid dihydrate being O(1)–H_2O = 2·55 A., O(2)–H_2O = 2·90 A. and 2·83 A., almost exactly the same as in acetylenedicarboxylic acid dihydrate. The spiral arrangement described in Parts I and II is exactly reproduced in this compound, the apparently closed circuit O(1), H_2O, O(2′), C(3′), O(1′), H_2O, O(2), C(3), O(1) being actually a spiral which returns to an atom one translation along the *b* axis from the original atom; the closed four-membered ring formed by the weaker bonds of 2·83, 2·90, 2·83, 2·90 A. is again exactly analogous to the previous cases.

The molecule of diacetylenedicarboxylic acid is, however, clearly different in its geometric configuration from those of oxalic acid and acetylenedicarboxylic acid, which possess a centrosymmetric coplanar structure; even in those structures postulated for oxalic acid with a central bond of the normal single-bond distance the essential planarity of the molecule is not doubted (Part I), although in some of its salts the oxalate group has been reported non-coplanar (Hendricks and Jefferson, *J. Chem. Physics*, 1936, **4**, 102). The diacetylenedicarboxylic acid molecule is found to possess not a centre of inversion, but a two-fold rotation axis, and the carboxyl groups at opposite ends of the molecule do not lie in the same plane. If two planes are taken, passing through the linear carbon chain and oppositely inclined to the (010) or *LM* plane at an angle of 28·4°, the carboxyl groups lie one on each of these planes. (The observed co-ordinates show that the oxygen atoms of the carboxyl groups are actually at 0·05 A. from these planes, but this deviation is probably not significant.)

The normal configuration for this molecule is almost certainly a coplanar one. A conjugated system of the type shown by diacetylenedicarboxylic acid should confer appreciable double-bond character on the single bonds, and the distances observed in the carbon chain, which are further discussed below, show that this is the case. In the absence of any distorting forces such as steric or similar effects, a coplanar structure therefore seems clearly indicated as being the most stable.

It is seen from Fig. 4(*c*) that a planar centrosymmetric molecule in the space group C_{2h}^{6} would lead to a system of hydrogen bonding in the form of a closed circuit, different from that observed in oxalic acid dihydrate and acetylenedicarboxylic acid dihydrate, where infinite spirals of hydrogen bonds occur. Now the structure shown in Fig. 4(*c*) is a possible structure, and the fact that it does not occur in the crystal shows that it must have a higher total energy than the structure of Fig. 4(*b*). The non-coplanar configuration for the molecule is, on the other hand, almost certainly of a higher energy than a coplanar configuration, and the energy difference between these two configurations must be more than compensated by the energy difference between the two possible systems of hydrogen bonding. It seems clear that intermolecular hydrogen bonding must be the governing factor in this type of crystal structure, and that it is sufficiently stable and invariant to cause appreciable distortion from the natural coplanar shape of the molecule.

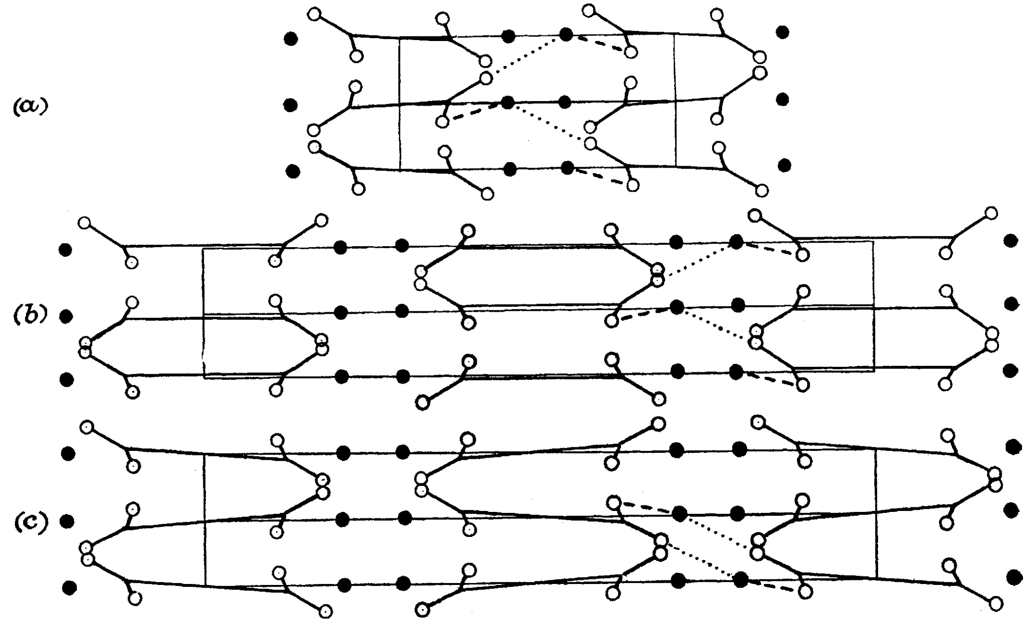
The strong directive power of hydrogen bonds has previously been noted as being able to preserve an open crystal structure which collapses, either partly as in resorcinol (Robertson and Ubbelohde, *Proc. Roy. Soc.*, 1938, *A*, **167**, 122, 136) or completely as in ice, on breaking the bonds by heating. In diacetylenedicarboxylic acid dihydrate the directive power of the hydrogen bonds is sufficient to produce considerable distortion in the molecule itself. Such a directive power seems to indicate a certain amount of covalent character in the hydrogen bond.

The above argument may explain why the expected coplanar configuration for the molecule may not occur in the space-group C_{2h}^{6}, but it gives no reason for the change in space-group from C_{2h}^{5} in which the other compounds in this series occur. We would expect that the centrosymmetric planar molecule with an infinite spiral arrangement of the hydrogen bonds should exist in the space-group C_{2h}^{5} with a lower energy than that of the structure observed.

Bond lengths within the molecule. In the carboxyl group we are again unable to distinguish between the carbon–oxygen bond lengths and find them both 1·25 A. (In acetylenedicarboxylic acid dihydrate these bonds were 1·26 and 1·27 A., and in oxalic acid dihydrate, 1·24 and 1·25 A.; see Parts I and II.) The uncertainty here is of the same order as before, *viz.*, about 0·05 A., but the three results taken together seem to indicate that the carbon–oxygen distances in the carboxyl group are probably equal, and support the view that the structures are likely to be ionic.

In the carbon chain the distance C(2)–C(3), measured as 1·45 A., is also rather uncertain, but the fact that it is found to be slightly greater than the corresponding distance in acetylenedicarboxylic acid (1·43 A.) may be significant. In the diacetylenedicarboxylic acid molecule the atoms no longer lie in one plane. The amount of double-bond character in the bond C(3)–C(2) must therefore be reduced with a consequent increase in the length of the bond.

FIG. 4.



(a) *The acetylenedicarboxylic acid dihydrate structure.*
(b) *The diacetylenedicarboxylic acid dihydrate structure.*
(c) *A hypothetical diacetylenedicarboxylic acid dihydrate structure with a coplanar molecule in the space-group* C_{2h}^{6}.

These diagrams show one unit cell of the structures projected along the a *axis. Oxygen atoms are shown as open circles, water molecules as black circles. For the sake of clarity only one hydrogen bond circuit (dotted lines) is shown in each case.*

A considerably higher accuracy, probably to within about 0·02 A., should apply to the remaining bond length measurements. The results are rather unusual, and for comparison Table IV shows the values which have been reported during the last few years for the various types of bond involved in triple-bonded systems.

We should expect bonds of the type $\equiv\text{C}-\text{C}<$ and $\equiv\text{C}-\text{C}\equiv$ to be considerably shortened from the normal single-bond distance of 1·54 A., and the values found in the present investigation and for acetylenedicarboxylic acid are indeed much lower than 1·54 A. The central bond of 1·33 ± 0·02 A. is the shortest formal single bond yet reported, and it is, in fact, of just the length usually associated with a pure double bond. Accepting the value of 1·36 ± 0·03 A. for this bond in diacetylene (Table IV), we might expect some further shortening in the present compound, due to the extra conjugation effects of the carboxyl groups. Wiebenga's value of 1·39 ± 0·03 A. in diphenyldiacetylene seems rather high.

It should be noted that the general problem of contractions in triple-bonded systems has been given an alternative treatment by Conn, Kistiakowsky, and Smith (*J. Amer. Chem. Soc.*,

TABLE IV.

Bond-length measurements in triple-bonded systems.

[*X*-Ray = *X*-Ray crystal analysis. Sp. = Spectroscopic measurements. E.D. = Electron-diffraction measurements (vapours).]

Bond type.	Compound.	Bond distance, A.	Reference.	Method.
≡C—C≤	Methylacetylene	1·462 ± 0·002	Herzberg, Patat, and Verleger, *J. Physical Chem.*, 1937, **41**, 123.	Sp.
		1·462 ± 0·002	Badger and Bauer, *J. Chem. Physics*, 1937, **5**, 594.	Sp.
		1·46 ± 0·02	Pauling, Springall, and Palmer, *J. Amer. Chem. Soc.*, 1939, **61**, 927.	E.D.
	Dimethylacetylene	1·47 ± 0·02	do.	E.D.
	Dimethyldiacetylene	1·47 ± 0·02	do.	E.D.
≡C—C	Tolan	1·40 ± 0·02	Robertson and Woodward, *Proc. Roy. Soc.*, 1938, *A*, **164**, 436.	*X*-Ray *X*-Ray
	Diphenyldiacetylene	1·44 ± 0·03	Wiebenga, *Z. Krist.*, 1940, **102**, 193.	*X*-Ray
	Acetylenedicarboxylic acid	1·43 ± 0·04	This series, Part II.	*X*-Ray
	Diacetylenedicarboxylic acid	1·45 ± 0·05	This series, Part III.	*X*-Ray
≡C—C≡	Diacetylene	1·36 ± 0·03	Pauling, Springall, and Palmer, *loc. cit.*	E.D.
	Cyanogen	1·37 ± 0·02	do.	E.D.
	Dimethyldiacetylene	1·38 ± 0·03	do.	E.D.
	Diphenyldiacetylene	1·39 ± 0·03	Wiebenga, *loc. cit.*	*X*-Ray
	Diacetylenedicarboxylic acid	1·33 ± 0·02	This series, Part III.	*X*-Ray
—C≡C—	Acetylene	1·204 ± 0·002	Herzberg, Patat, and Spinks, *Z. Physik*, 1934, **92**, 87.	Sp.
	Methylacetylene	1·20 ± 0·03	Pauling, Springall, and Palmer, *loc. cit.*	E.D.
	Dimethyldiacetylene	1·20 ± 0·02	do.	E.D.
	Diacetylene	1·19 ± 0·03	do.	E.D.
	Tolan	1·19 ± 0·02	Robertson and Woodward, *loc. cit.*	*X*-Ray
	Diphenyldiacetylene	1·18 ± 0·03	Wiebenga, *loc. cit.*	*X*-Ray
	Acetylenedicarboxylic acid	1·19 ± 0·02	This series, Part II.	*X*-Ray
	Diacetylenedicarboxylic acid	1·185 ± 0·02	This series, Part III.	*X*-Ray

1939, **61**, 1868), who suggest an explanation on the grounds of reduced steric hindrance in the acetylene compounds. Some of the contraction may also be due to change in effective single-bond radius (Robertson and Woodward, *Proc. Roy. Soc.*, 1938, *A*, **164**, 436; Penney and Kynch, *ibid.*, p. 409). The results of Crawford and Rice (*J. Chem. Physics*, 1939, **7**, 437) and of Osborne, Garner, and Yost (*ibid.*, 1940, **2**, 131), who show that for dimethylacetylene there is little or no potential barrier to free rotation of the methyl groups, are also significant in this connection and show that double-bond character in the usual sense need not always be present when there is contraction. In view of these results it becomes easier to reconcile the non-coplanar form of the diacetylenedicarboxylic acid molecule with our bond-length measurements.

For the triple bond we obtain a value of 1·185 ± 0·02 A. in our present investigation, and for acetylenedicarboxylic acid the value was 1·19 ± 0·02 A. In general, the values recorded for the triple bond in carbon compounds (Table IV) are usually less than, and never greater than, the value in acetylene itself (1·204 ± 0·002 A.). On the other hand, we might expect that in such conjugated systems the value should be slightly greater than the normal carbon–carbon triple-bond value (see also Penney and Kynch, *loc. cit.*). Although the limits of error are in all cases such that a value of 1·20 A. is admissible, yet the fact that these values are so consistently low may be significant.

One reason for the discrepancy may be that the acetylene value of 1·204 A. is obtained spectroscopically and may not be exactly comparable to the *X*-ray values (see Robertson and Woodward, *Proc. Roy. Soc.*, 1938, *A*, **164**, 436). As far as possible, however, we try to make allowances for displaced electron distributions in the *X*-ray work.

Another more fundamental reason for the discrepancy may be that acetylene is not a suitable standard on which to base a " normal " triple-bond length. Acetylene shows well-marked acidic properties and the C–H link must bear considerable ionic character. Structures of the type

$$\overset{+}{\mathrm{H}}\overset{-}{\mathrm{C}}\equiv\mathrm{C{-}H} \qquad \mathrm{H{-}}\overset{-}{\mathrm{C}}\equiv\mathrm{C}\overset{+}{\mathrm{H}} \qquad \overset{+}{\mathrm{H}}\overset{-}{\mathrm{C}}\equiv\overset{-}{\mathrm{C}}\overset{+}{\mathrm{H}}$$

must play some part in this molecule and they should have the effect, by resonance energy and by electrostatic attraction, of increasing the C–H bond strength and decreasing the C–H distance. The observed value for this distance in acetylene is 1·057 A., as against 1·093 A. in methane, although the contraction may be partly due to an increase in the *s* character of the hybridised carbon orbitals.

In a similar way, if these structures are important, the ionic forces involved should lead to some increase in the distance between the carbon atoms. The triple-bond distance observed in acetylene may therefore represent a " stretched " rather than a " normal " triple bond.

The amount of this stretching is extremely difficult to calculate because so many different types of energy are involved. A very approximate treatment may be effected by considering only the coulombic repulsion between the two negatively charged atoms in the structure $\overset{+}{\mathrm{H}}\overset{-}{\mathrm{C}}\equiv\overset{-}{\mathrm{C}}\overset{+}{\mathrm{H}}$. It must, of course, be remembered that this structure is less important than the other two mentioned above, on account of the adjacent charges.

We consider the problem as a two-atom one and make use of the Morse function

$$V(r) = D(-\ 2e^{-a(r-\beta)} + e^{-2a(r-\beta)})$$

For the triple bond the dissociation energy D is taken as 190 k.-cals. mol.$^{-1}$. There is considerable doubt about the value of this constant owing to the uncertain value of the heat of sublimation of diamond. The value adopted is approximately that given by Skinner (*Trans. Faraday Soc.*, 1945, **41**, 645) assuming $L = 170$; a is the Morse constant, $\sqrt{K/2D}$, where K is the force constant, taken as 15×10^5 dynes cm.$^{-1}$ or 2180 k.-cals. mol.$^{-1}$ A.$^{-2}$; a thus has the value 2·4, and β is the correct " ideal " bond length corresponding to maximum stability.

The curve for the triple bond in acetylene has an additional term due to the coulombic repulsion of the two negatively charged carbon atoms, and it may therefore be represented as

$$V = 190(-\ 2e^{-2\cdot4(r-\beta)} + e^{-4\cdot8(r-\beta)}) + \frac{(\delta e)^2}{r}$$

where δ = fraction of ionic character in the bond. This function has $(\partial v/\partial r)_\beta = 0$ at $r = 1\cdot20$ A.

$$\text{or} \qquad \left(\frac{\partial v}{\partial r}\right) = 4\cdot8 \times 190\,\{e^{-2\cdot4(1\cdot20-\beta)} - e^{-4\cdot8(1\cdot20-\beta)}\} - \frac{(\delta e)^2}{r^2} = 0$$

$$\text{or} \qquad 912\{e^{-2\cdot4(1\cdot20-\beta)} - e^{-4\cdot8(1\cdot20-\beta)}\} = \frac{(\delta e)^2}{1\cdot20^2}$$

By graphical solution of this equation for various values of δ the results in Table V were obtained. These figures show that the " ideal " triple-bond distance, β, may be somewhat shorter than the acetylene value.

TABLE V.

δ.	$(\delta e)^2/1\cdot20^2$, k.-cal. mol.$^{-1}$.	β, A.	δ.	$(\delta e)^2/1\cdot20^2$, k.-cal. mol.$^{-1}$.	β, A.
0·10	2·3	1·199	0·30	19·7	1·191
0·20	9·2	1·196	0·40	36·8	1·182

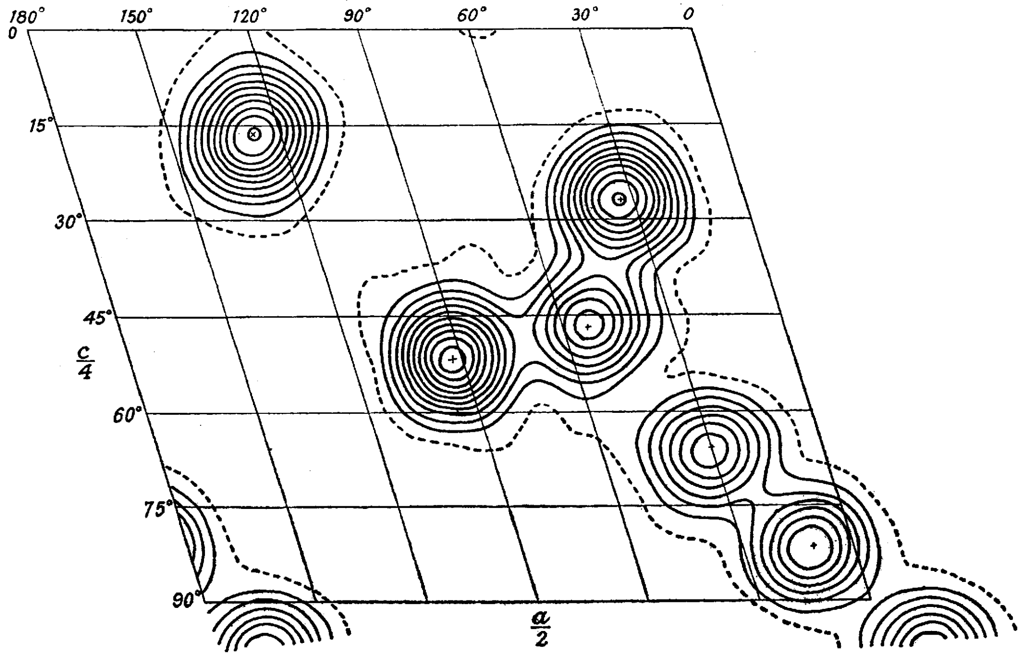
We consider, therefore, that acetylene may not be a suitable standard for the triple-bond length. One compound which might be considered to possess the " normal " triple bond is di-*tert.*-butylacetylene, the synthesis of which has recently been announced by Hennion and Banigan (*J. Amer. Chem. Soc.*, 1946, **68**, 1202). A detailed *X*-ray analysis of this compound would be very interesting.

EXPERIMENTAL.

Preparation and Properties.—Diacetylenedicarboxylic acid was prepared by oxidation of the copper compound of propiolic acid with alkaline ferricyanide after Baeyer (*loc. cit.*, p. 2270). The extraction of the acid was difficult and the yields obtained were very poor, being only of the order of a few mg. from about 2 g. of propiolic acid. The compound obtained by us does not correspond to that of Baeyer, which was a monohydrate in the form of rhombic tablets, which darkened at 100°, exploded at 177°, and changed in light to a purple mass. Our product (crystallised from water or aqueous ether–light petroleum) was in the form of pale yellow monoclinic sword-like needles, elongated along the *b* axis. These crystals darkened at 95—100°, decomposed on further heating without explosion, and behaved similarly to Baeyer's product in light. Microanalysis (Found: C, 41·4; H, 3·8. $C_6H_2O_4,H_2O$ requires C, 46·2; H, 2·6%. $C_6H_2O_4,2H_2O$ requires C, 41·4; H, 3·5%) indicated that our compound is *diacetylenedicarboxylic acid dihydrate.* This was further confirmed by density data; the *X*-ray density for 4 molecules of monohydrate per unit cell is 1·28 g./c.c., or for 4 molecules of dihydrate per unit cell 1·43 g./c.c., while the observed density, determined by flotation in a mixture of ethylene bromide and benzene, is 1·43—1·45 g./c.c.

The crystals became purple on exposure to light and almost black on exposure to *X*-rays. With large crystals exposed to *X*-rays, the blackening was confined to that section of the crystal which was in the actual *X*-ray beam. The nature of the decomposition product was not determined, but its amount must have been very small, since quite black crystals gave *X*-ray photographs which showed no trace of powder rings. Prolonged exposure to *X*-rays did, however, produce photographs complicated by powder rings. The crystals do not lose their water of crystallisation as easily as acetylenedicarboxylic acid dihydrate, but the mosaic character of the crystals is ensured by their decomposition by light and *X*-rays. Copper-*K*α radiation was used throughout.

FIG. 5.



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

Space-group Determination.—The following photographs were used to determined the unit cell and space-group. Rotation photographs about the *a*, *b*, *c* axes, and about [101], [111], [011] gave the dimensions of the unit cell and showed that this was body-centred. Oscillation photographs about the *b* axis and moving-film photographs of the (0*kl*), (*h*0*l*), and (*hll*) zones showed that the following halvings occurred: (*hkl*) appeared only when (*h* + *k* + *l*) was even; (*h*0*l*) appeared only when both *h* and *l* were even.

These halvings are characteristic of both the space-groups C_s^4 and C_{2h}^6, and these cannot be distinguished by *X*-rays since they differ only in the presence or absence of a centre of symmetry. An experiment to distinguish between these space-groups by pyroelectric effect was inconclusive. Finally, the space-group of higher symmetry C_{2h}^6 was assumed, since the calculations are considerably simplified if the structure possesses a centre of symmetry; we consider this assumption to be justified by the subsequent results.

Intensity Measurements.—Intensity estimates were carried out for the (*h*0*l*) and (0*kl*) zones. For the former the specimen employed had cross-section normal to the *b* axis of 0·13 mm. × 0·31 mm., while that used for the (0*kl*) zone had cross-section normal to the *a* axis of 0·29 mm. × 0·21 mm. The intensities were estimated, and the F values derived from them, in the same way as for acetylenedicarboxylic acid dihydrate (*loc. cit.*). The range of observed intensities was about 3000 to 1.

Fourier Analysis.—The usual formulæ for $\rho(x, z)$ and $\rho(y, z)$ were employed. For $\rho(xz)$ the series was summed at 900 points over the asymmetric unit, an eighth of the unit cell, the axial subdivisions being $a/60$ = 0·186 A. and $c/120$ = 0·168 A. Three-figure methods (Robertson, *Phil. Mag.*, 1936, **21**, 176) were used, and the positions of the contour lines were 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. 5, where the final positions assigned to the atoms are indicated by small crosses.

TABLE VI.

Measured and calculated values of the structure factor.

hkl.	sin θ (λ = 1·54).	F, meas.	F, calc.
200	0·144	10	− 7
400	0·289	52	− 46
600	0·433	34	− 32
800	0·578	27	+ 25
10,00	0·722	15	− 15
12,00	0·866	11	+ 9
020	0·411	60	+ 82
040	0·822	8	+ 9
002	0·080	12	+ 5
004	0·160	55	− 58
006	0·239	14	− 11
008	0·319	29	− 29
00,10	0·399	52	− 60
00,12	0·479	23	− 20
00,14	0·559	25	+ 25
00,16	0·638	13	+ 9
00,18	0·718	10	− 7
00,20	0·798	13	− 7
00,22	0·878	14	+ 11
00,24	0·958	< 3	− 2
011	0·210	22	− 17
013	0·238	32	− 35
015	0·287	43	− 51
017	0·347	6	+ 6
019	0·414	34	+ 41
01,11	0·485	12	+ 12
01,13	0·558	< 8	− 3
01,15	0·633	<10	− 2
01,17	0·709	<10	− 8
01,19	0·786	8	− 9
01,21	0·863	8	+ 4
01,23	0·941	6	+ 4
022	0·419	24	− 21
024	0·442	6	+ 3
026	0·476	24	+ 24
028	0·521	8	+ 7
02,10	0·573	20	− 21
02,12	0·631	22	− 29
02,14	0·694	10	− 10
02,16	0·759	< 8	+ 1
02,18	0·828	< 8	+ 3
02,20	0·898	< 8	+ 1
02,22	0·969	8	+ 9
031	0·618	<10	− 1
033	0·629	12	+ 10
035	0·649	<10	− 7
037	0·677	<10	0
039	0·714	<10	+ 6
03,11	0·757	12	− 8
03,13	0·806	<10	− 4
03,15	0·860	10	+ 6
03,17	0·917	< 8	+ 1
03,19	0·978	< 6	− 4
042	0·827	< 8	+ 1
044	0·838	< 8	+ 5
046	0·857	< 8	− 1
048	0·882	< 8	− 4
04,10	0·914	< 8	− 1
04,12	0·952	< 6	− 4
20,22	0·925	5	+ 4
20,20	0·847	8	− 9
20,18	0·769	15	− 14
20,16	0·691	15	− 17
20,14	0·613	10	− 15
20,12	0·536	21	+ 19
20,10	0·460	54	+ 57
208	0·384	11	+ 9
206	0·311	21	− 17
204	0·244	120	+105
202	0·183	108	−107
$20\bar{2}$	0·144	39	+ 41
$20\bar{4}$	0·182	25	+ 33
$20\bar{6}$	0·240	93	− 93
$20\bar{8}$	0·309	98	−102
$20,\bar{1}\bar{0}$	0·380	16	+ 21
$20,\bar{1}\bar{2}$	0·456	20	+ 19
$20,\bar{1}\bar{4}$	0·534	4	− 3
$20,\bar{1}\bar{6}$	0·613	25	+ 28
$20,\bar{1}\bar{8}$	0·690	44	+ 46
$20,\bar{2}\bar{0}$	0·768	18	− 18
$20,\bar{2}\bar{2}$	0·847	7	− 8
$20,\bar{2}\bar{4}$	0·925	< 3	− 2
40,20	0·924	7	+ 5
40,18	0·846	4	− 4
40,16	0·772	11	− 9
40,14	0·698	8	+ 9
40,12	0·624	13	+ 13
40,10	0·554	11	+ 16
408	0·487	48	+ 47
406	0·423	23	− 24
404	0·366	18	− 9
402	0·320	119	−118
$40\bar{2}$	0·277	16	− 13
$40\bar{4}$	0·288	13	+ 11
$40\bar{6}$	0·317	101	+107
$40\bar{8}$	0·362	48	+ 52
$40,\bar{1}\bar{0}$	0·419	26	− 30
$40,\bar{1}\bar{2}$	0·481	< 4	0
$40,\bar{1}\bar{4}$	0·549	28	+ 27
$40,\bar{1}\bar{6}$	0·619	41	− 32
$40,\bar{1}\bar{8}$	0·689	8	+ 5
$40,\bar{2}\bar{0}$	0·765	< 5	+ 2
$40,\bar{2}\bar{2}$	0·842	< 4	− 1
$40,\bar{2}\bar{4}$	0·916	10	− 9
60,18	0·936	8	+ 9
60,16	0·866	5	+ 7
60,14	0·796	13	− 11
60,12	0·730	14	− 18
60,10	0·665	9	− 11
608	0·606	22	+ 16
606	0·549	37	− 42
604	0·501	26	+ 27
602	0·461	27	+ 20
$60\bar{2}$	0·417	< 5	− 1
$60\bar{4}$	0·422	48	+ 40
$60\bar{6}$	0·430	39	+ 34
$60\bar{8}$	0·458	23	+ 22
$60,\bar{1}\bar{0}$	0·498	10	+ 7
$60,\bar{1}\bar{2}$	0·544	40	− 42
$60,\bar{1}\bar{4}$	0·599	17	− 17
$60,\bar{1}\bar{6}$	0·660	30	− 31
$60,\bar{1}\bar{8}$	0·724	9	+ 9
$60,\bar{2}\bar{0}$	0·791	< 5	+ 3
$60,\bar{2}\bar{2}$	0·860	5	+ 6
$60,\bar{2}\bar{4}$	0·930	10	+ 9
80,16	0·972	< 3	− 2
80,14	0·908	< 4	+ 1
80,12	0·845	< 5	0
80,10	0·786	30	− 32

TABLE VI.—*continued.*

Measured and calculated values of the structure factor.

hkl.	sin θ (λ = 1·54).	F, meas.	F, calc.	*hkl.*	sin θ (λ = 1·54).	F, meas.	F, calc.
808	0·734	13	+ 12	$10,0\bar{4}$	0·691	< 5	+ 5
806	0·684	29	+ 24	$10,0\bar{6}$	0·689	13	− 13
804	0·640	10	+ 13	$10,0\bar{8}$	0·696	29	− 29
802	0·605	12	+ 14	$10,0,\overline{10}$	0·715	39	+ 37
$80\bar{2}$	0·559	12	− 5	$10,0,\overline{12}$	0·741	23	+ 18
$80\bar{4}$	0·551	56	− 50	$10,0,\overline{14}$	0·775	5	+ 5
$80\bar{6}$	0·556	28	− 28	$10,0,\overline{16}$	0·815	< 5	+ 1
$80\bar{8}$	0·574	10	+ 8	$10,0,\overline{18}$	0·857	< 5	− 1
$80,\overline{10}$	0·599	22	+ 17	$10,0,\overline{20}$	0·909	3	− 4
$80,\overline{12}$	0·634	28	− 26	$10,0,\overline{22}$	0·961	8	− 8
$80,\overline{14}$	0·678	23	+ 23				
$80,\overline{16}$	0·727	< 5	0	12,06	0·961	< 3	− 3
$80,\overline{18}$	0·781	4	− 5	12,04	0·923	7	− 8
$80,\overline{20}$	0·839	7	+ 7	12,02	0·891	< 4	− 4
$80,\overline{22}$	0·902	< 4	+ 2	$12,0\bar{2}$	0·845	8	+ 7
$80,\overline{24}$	0·966	< 3	+ 2	$12,0\bar{4}$	0·834	< 5	− 1
				$12,0\bar{6}$	0·828	21	+ 15
10,0,12	0·969	< 3	+ 8	$12,0\bar{8}$	0·831	3	− 4
10,0,10	0·914	< 4	+ 3	$12,0,\overline{10}$	0·841	6	− 5
10,08	0·865	5	− 3	$12,0,\overline{12}$	0·860	5	− 4
10,06	0·819	5	− 7	$12,0,\overline{14}$	0·885	6	+ 5
10,04	0·779	6	+ 6	$12,0,\overline{16}$	0·916	3	+ 1
10,02	0·746	6	+ 8	$12,0,\overline{18}$	0·953	9	− 8
$10,0\bar{2}$	0·700	10	− 9				

The y co-ordinates together with a check on the z co-ordinates were obtained from the projection along the a axis shown in Fig. 2. $\rho(yz)$ was summed at 225 points over the asymmetric unit, the axial subdivisions being $b/30 = 0{\cdot}125$ A. and $(c \sin \beta)/60 = 0{\cdot}322$ A. The summations were carried out, and the contour map drawn, as described above for the b projection. Considerable overlapping occurs in the a axis projection and the y co-ordinates are not fixed as rigorously as we should like, but no better resolution can be obtained by two-dimensional methods and any ambiguity can be resolved only by means of three-dimensional Fourier synthesis.

From the final co-ordinates (Table I), all the structure factors were recalculated and the results are given in Table VI. For this calculation the structure factor F has been expressed in the form $fS = F$. For f we have used a composite empirical atomic scattering factor which gives better results than that used in the case of acetylenedicarboxylic acid dihydrate and oxalic acid dihydrate (*q.v.*). 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	0·9	1·0
f	334	282	224	167	113	80	54	34	19	13

The maximum value of f, at $\sin \theta = 0$, may be taken as F (000) = 360, the total number of electrons in the unit cell.

S is the geometric structure factor. It is conveniently put into the form

$$60\,S = \Sigma 8A \cos 2\pi\left(\frac{hx}{a} + \frac{lz}{c}\right) \cos 2\pi \frac{hy}{b}, \text{ when } l \text{ is even}$$

$$60\,S = \Sigma - 8A \sin 2\pi\left(\frac{hx}{a} + \frac{lz}{c}\right) \sin 2\pi \frac{hy}{b}, \text{ when } l \text{ is odd}$$

The carbon and oxygen coefficients are weighted in the ratio of 6 to 9, so that for a carbon atom $A = 1$ and for an oxygen atom $A = 1{\cdot}5$. Since there are six atoms in the asymmetric unit, three of which have $A = 1$ and three $A = 1{\cdot}5$, the maximum value of S is conveniently taken as unity.

The percentage discrepancy finally obtained, expressed as

$$\frac{\Sigma(\,|\text{F meas.}| - |\text{F calc.}|\,)}{\Sigma\,|\text{F meas.}|} \times 100$$

is 11·0 for the ($h0l$) reflections, 14·8 for the ($0kl$) reflections, and 11·9 for all reflections.

In the b axis projection (Fig. 1) the F values for the ($80\bar{2}$) and (10, 0, 8) planes were omitted from the Fourier summation owing to uncertainty of sign.

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