36. *The Crystal and Molecular Structure of Certain Dicarboxylic Acids. Part I. Oxalic Acid Dihydrate.*

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The structure of oxalic acid dihydrate is rediscussed in view of results recently obtained by Brill, Hermann, and Peters (*Ann. Physik*, 1942—1943, **42**, 357) which lead to a molecular model with normal or even slightly lengthened carbon–carbon single-bond distance. It is difficult to reconcile the *y* co-ordinates of this structure with the observations. A number of small variations of the structure have been calculated, and some of these show improved agreements. It is concluded that the balance of the evidence is still in favour of a model with a somewhat contracted carbon–carbon bond distance, and with carbon–oxygen distances which are very nearly equal. These findings are consistent with theory, which would appear to demand some double-bond character in the carbon–carbon link, if only to explain the invariance of the coplanar oxalate configuration in many different crystal structures.

The oxalic acid dihydrate structure is redrawn with respect to a different unit cell and space-group description in order to bring out the striking relationship which exists between it and the dihydrates of the acetylenedicarboxylic acid series.

A RECENT determination of the structure of oxalic acid dihydrate by Brill, Hermann, and Peters (*Naturwiss.*, 1939, 677; *loc. cit.*) gives results which differ in some respects from those found by Robertson and Woodward (*J.*, 1936, 1817). In the present paper these results are rediscussed, and the structure is redrawn (Fig. 1) to bring out the striking relationship which exists between it and the acetylenedicarboxylic acids described in Parts II and III.

The oxalic acid dihydrate structure may be represented as in (I), with pairs of water molecules connecting the oxalic acid molecules through hydrogen bridges (dotted lines). The bridge *ab* is of special interest because, with a length of about 2·50 A., it appears to be the shortest known

(I.)
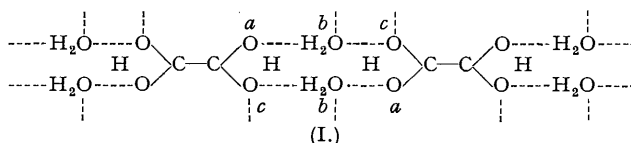
hydrogen bridge between oxygen atoms, and it gives rise to an abnormally large isotope effect (expansion of the crystal spacings) when deuterium is substituted for hydrogen (Robertson and Ubbelohde, *Proc. Roy. Soc.*, 1939, *A*, **170**, 221, 241). The other bridges, *bc*, etc., are of weaker type, measuring between 2·8 and 2·9 A. The actual structure in the crystal is more complicated than shown in (I), which is merely a projection diagram. The eight-membered central portion, consisting of two carboxyl groups and two water molecules, is not a closed circuit, the return bridge *bc* connecting to a molecule arranged vertically above the one shown, the whole forming a spiral arrangement extending throughout the crystal. Cross linkings from the water molecule and from one of the carboxylic oxygen atoms also make further connections to other adjoining molecules.

The position of the carboxylic hydrogen atom is still uncertain, and it may well have passed over to the water molecule with the formation of oxonium oxalate, as in (II). Definite

(II.)
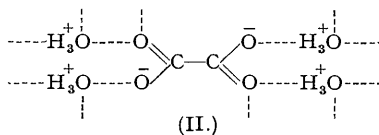
experimental evidence is lacking, owing to the difficulty of locating hydrogen atoms in *X*-ray work, but such an arrangement might account for the abnormally short bridge *ab*. In addition, it is expected that a number of other structures, some of them with a double bond between the carbon atoms, will make contributions to the normal state of the molecule (see Robertson, *Trans. Faraday Soc.*, 1940, **36**, 913).

With regard to the expected molecular dimensions in such a situation, some additional evidence is now available since this structure was last discussed (Robertson, *loc. cit.*). A comprehensive electron-diffraction study of the monomers and dimers of certain carboxylic acids has been made by Karle and Brockway (*J. Amer. Chem. Soc.*, 1944, **66**, 574). Their results show that in free acids (monomers) the C–OH and C=O distances in the carboxyl group are different (1·42 and 1·24 A.). On association there is a tendency towards equalisation of
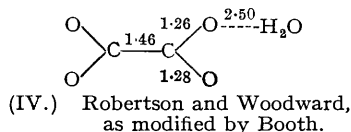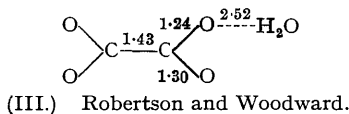
Fig. 1.
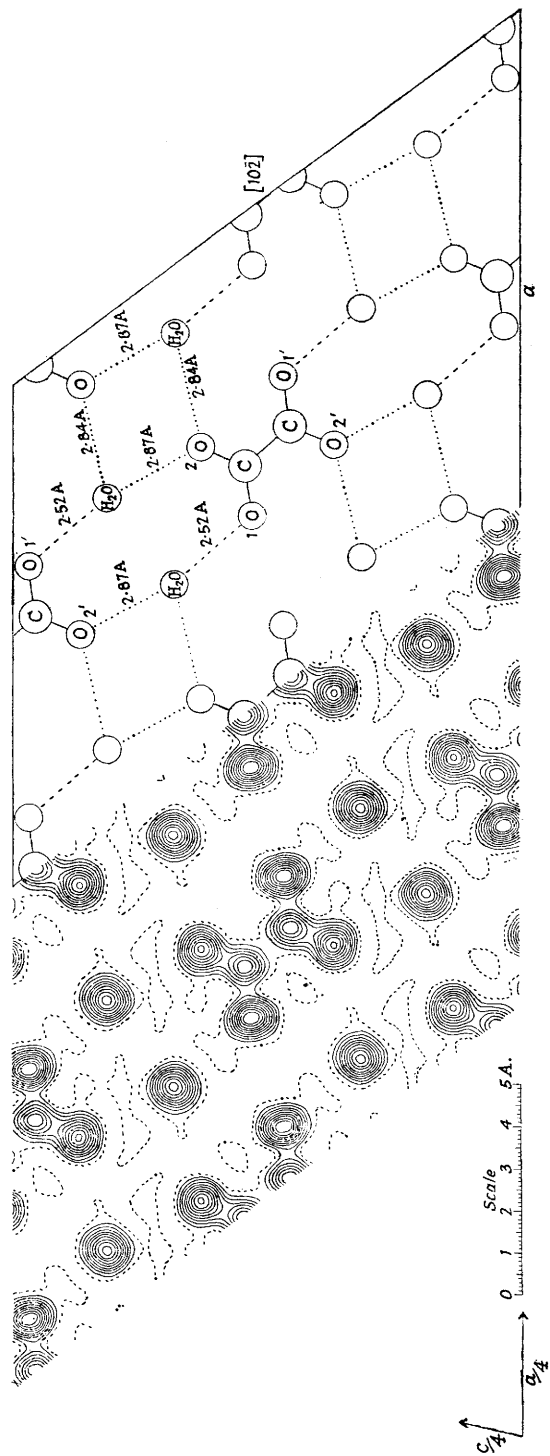
Oxalic acid dihydrate, projected on (010). Each contour line represents a density increment of one electron per A², the one-electron line being dotted.

these distances, the values obtained for dimers being 1·36 and 1·25 A.   Uncertainties of $\pm$ 0·03 or $\pm$ 0·04 A. apply to these figures, but the difference of about 0·10 A. for the dimers is apparently significant.   It is concluded that the hydrogen atom must remain attached more firmly to one of the partners in the dimer than to the other.   In the case of salts, no very precise measurements of these distances are available, but we should expect the ion to display either complete equality of the C–O distances or at least closer equality than is found in the dimers.

If structure (II) is important in oxalic acid dihydrate we would therefore expect the C–O distances to be almost indistinguishable.   This is consistent with our X-ray results (Robertson and Woodward, *loc. cit.*), which gave the C–O distances as 1·30 and 1·24 A., with a probable error of $\pm$ 0·03 or $\pm$ 0·04 A.   The other molecular dimensions obtained are shown in (III).   In the analogous acetylenedicarboxylic acids described in Parts II and III it is also practically impossible to distinguish to two C–O distances.

For the C–C distance in oxalic acid dihydrate we obtained a value of 1·43 A., a contraction form the normal carbon–carbon single-bond value which indicates a considerable amount of conjugation between the carboxyl groups.   As the carbon atoms are situated between the higher electron density peaks of the oxygen atoms (Fig. 1), their positions are more uncertain and this figure may be subject to a somewhat larger error.   Some contraction from the normal value does, however, appear to be definite.

$$
\begin{array}{ccc}
O\diagdown & \overset{1\cdot24}{\diagup}O\text{-----}H_2O & \\
\quad C\overset{1\cdot43}{—}C & & \\
O\diagup & \underset{1\cdot30}{\diagdown}O &
\end{array}
\qquad\qquad
\begin{array}{ccc}
O\diagdown & \overset{1\cdot26}{\diagup}O\text{-----}H_2O & \\
\quad C\overset{1\cdot46}{—}C & & \\
O\diagup & \underset{1\cdot28}{\diagdown}O &
\end{array}
$$

| (III.)   Robertson and Woodward. | (IV.)   Robertson and Woodward, as modified by Booth. |

In the meantime, Booth (*Nature*, 1945, **156**, 51; and private communication) has made a critical examination of the results of Robertson and Woodward (*loc. cit.*) and has derived a set of probable corrections to be applied to their co-ordinates.   The application of these corrections leads to the molecular dimensions given in (IV), thus indicating a more symmetrical model with slightly increased carbon–carbon distance.   This model also leads to slightly improved agreements between the calculated and observed values of the structure factor (see Experimental section).

Brill, Hermann, and Peters (*loc. cit.*, 1942—1943) have carried out an independent and extremely careful examination of this structure, extending the observations to smaller spacing planes and applying elaborate corrections for non-convergence of series, etc.   The molecular dimensions derived from their final results are shown in (V), with normal or even slightly lengthened carbon–carbon single-bond distance, and carbon–oxygen distances which are slightly different from, and in an opposite sense to, those of Robertson and Woodward (*loc. cit.*).   They point out one source of error in the latter results which is probably important, *viz.*, diffraction effects from the oxygen atoms which happen to converge near the carbon atom and may cause an apparent displacement in its position.   We agree that this effect may cause some error, but hardly sufficient to explain the very large difference in the carbon–carbon bond length in the two structures.

Examination of Brill, Hermann, and Peters's x and z co-ordinates shows that they do not differ very much from those of Robertson and Woodward, the displacement of the various atoms being 0·02 A. for H_2O, 0·02 A. for O (1), 0·05 A. for O (2), and 0·06 A. for C.   Booth's corrections, mentioned above, are generally in the same sense but of smaller amount than those required by the latter structure.   On recalculating the structure factors of the ($h0l$) planes from Brill, Hermann, and Peters's co-ordinates, we find slightly improved average agreements (see Experimental section).

It is, however, more difficult to reconcile the Brill, Hermann, and Peters y co-ordinates with those of Robertson and Woodward.   The required displacements of the atoms are 0·03 A. for H_2O, 0·035 A. for O (1), 0·105 A. for O (2), and 0·10 A. for C.   Further, on recalculating the

$$
\begin{array}{ccc}
O\diagdown & \overset{1\cdot28}{\diagup}O\text{-----}H_2O & \\
\quad C\overset{1\cdot55}{—}C & & \\
O\diagup & \underset{1\cdot21}{\diagdown}O &
\end{array}
\qquad\qquad
\begin{array}{ccc}
O\diagdown & \overset{1\cdot25}{\diagup}O\text{-----}H_2O & \\
\quad C\overset{1\cdot51}{—}C & & \\
O\diagup & \underset{1\cdot21}{\diagdown}O &
\end{array}
$$

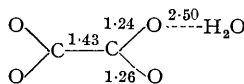| (V.)   Brill, Hermann, and Peters. | (VI.)   Brill, Hermann, and Peters, with Robertson and Woodward's y co-ordinates. |
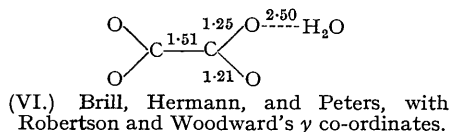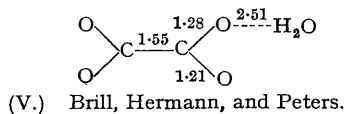
($0kl$) structure factors, the agreements are considerably worse than found by Robertson and Woodward, the average discrepancies being 18·1% as against 12·4%.   If we retain the Brill,

Hermann, and Peters x and z co-ordinates and employ the Robertson and Woodward y co-ordinates, the $(0kl)$ discrepancies are reduced to only $13\cdot0\%$. This composite structure, therefore, gives very good all-round agreements with the observations, and it leads to the molecular dimensions shown in (VI).

The position of the carbon atom is found to have very little effect on the structure-factor calculations, and the two structures shown in (VII) and (VIII), which contain the carbon position as modified by Booth, and the original carbon position of Robertson and Woodward, respectively, are found to give almost equally good general agreements in the structure factor calculations. All the structures (VI)—(VIII) give better agreements than structure (V).
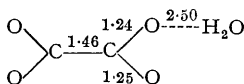
(VII.) Brill, Hermann, and Peters, with Robertson and Woodward's y co-ordinates and Robertson and Woodward–Booth carbon position.	(VIII.) Brill, Hermann, and Peters, with Robertson and Woodward's y co-ordinates and Robertson and Woodward carbon position.

In the Brill, Hermann, and Peters structure (V) the atoms of the acid molecule are strictly coplanar. This fact and also the approximately planar nature of the molecule which is found to hold in the different crystalline modifications of the anhydrous acid, as well as in many oxalates, is a fairly definite indication of double-bond character in the carbon–carbon link. A pure single bond with unrestricted rotation would almost certainly, in some of these structures, lend itself to packing arrangements in which the molecule was not planar. The co-ordinates for structures (III), (IV), and (VI)—(VIII) are found to give certain very slight departures from the strict planar form, the displacements varying from $0\cdot02$ to $0\cdot05$ A. It is unlikely that any real significance can be attached to these displacements. Very minor adjustments to the co-ordinates could easily be made which would result in strictly planar models.

Our conclusions from this discussion cannot be very definite. The balance of the evidence appears to us still to favour a model with a somewhat contracted carbon–carbon bond distance, and with carbon–oxygen distances which are very nearly equal. Structures (IV), (VI), and (VII) satisfy the requirements almost equally well, and they are consistent with theory. The co-ordinates of structure (VII), which we may provisionally accept as most probable, are given in full in the Experimental section. It is quite clear, however, that questions of finer detail, such as the exact equality or otherwise of the carbon–oxygen distances, can only be settled by a very careful and comprehensive three-dimensional Fourier analysis of all the data. In the two-dimensional projections (*e.g.*, Fig. 1) there is always a considerable lack of resolution and fore-shortening of certain distances owing to the inclination of the molecular plane to the projection plane. In Fig. 1 this inclination is about $29°$.

Relation with the Acetylenedicarboxylic Acids.—The similarity between oxalic acid and the acetylenedicarboxylic acids is not at first obvious from the monoclinic cell dimensions, but if the a and c axes of oxalic acid dihydrate are re-named to make the space-group description $P2_1/a$ with acute β angle of $76\cdot6°$, the relationship becomes clearer. We shall therefore make this change in our subsequent references to the oxalic acid dihydrate structure, which was formerly described (Zachariasen, *Z: Krist.*, 1934, **89**, 442; Robertson and Woodward, *loc. cit.*) as $P2_1/n$ with $a = 6\cdot12$, $b = 3\cdot60$, $c = 12\cdot03$ A., $\beta = 106\cdot2°$. The new cell dimensions of oxalic acid dihydrate in comparison with those of the dihydrates of the acetylenedicarboxylic acid series are then as given in Table I.
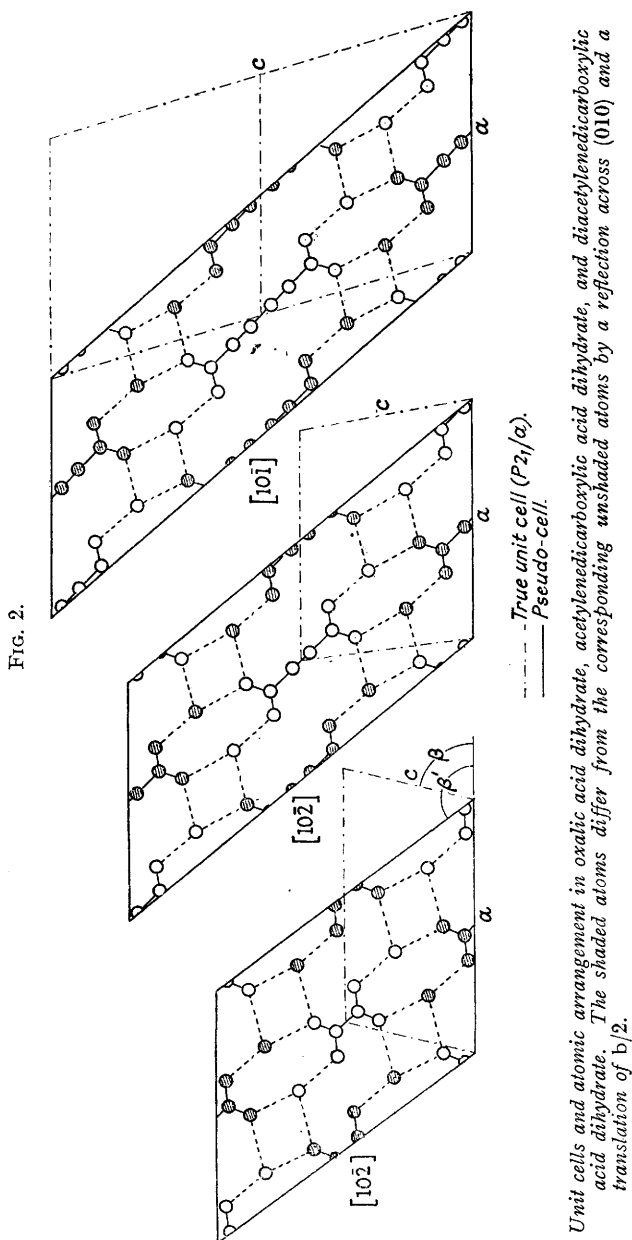
TABLE I.

	Space-group.	a.	b.	c.	β.	c' $[10\bar{2}]$.*	β'.
$C_2H_2O_4,2H_2O$	C_{2h}^5–$P2_1/a$	$11\cdot88$	$3\cdot60$	$6\cdot12$	$76\cdot5°$	$14\cdot94$	$127\cdot2°$
$C_4H_2O_4,2H_2O$	C_{2h}^5–$P2_1/a$	$11\cdot05$	$3\cdot86$	$7\cdot98$	$98\cdot0$	$20\cdot64$	$130\cdot0$
$C_6H_2O_4,2H_2O$	C_{2h}^6–$I2/c$	$11\cdot15$	$3\cdot75$	$20\cdot18$	$107\cdot0$	$25\cdot75$	$131\cdot5$

The a and b axial lengths remain fairly constant, but there is a progressive increase in the c axis and in the angle β as further carbon atoms are added to the chain. The directions of these chains with their pairs of connecting water molecules are roughly along the $[10\bar{2}]$* axis in each case, as will be clear from Fig. 2 which shows the relative dimensions of the unit cells of the

* For oxalic acid dihydrate this direction is $[102]$ if the conventional obtuse β angle is adopted, and for diacetylenedicarboxylic acid dihydrate it is $[10\bar{1}]$ owing to the doubling of the c axis.

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three crystals and the approximate positions of the atoms projected on to the (010) planes. The chain axis is obviously the most important crystal and molecular direction, but it is not convenient to adopt it as a crystallographic axis, because such a description would lead to a cell centred on the (010) face and this would not be a true unit cell in the monoclinic system.   In Fig. 2 the broken line outlines the true unit cells (*a*, *c*, and β) whereas the full line gives the

FIG. 2.

--- - *True unit cell* (P2₁/*a*).
—— *Pseudo-cell.*

Unit cells and atomic arrangement in oxalic acid dihydrate, acetylenedicarboxylic acid dihydrate, and diacetylenedicarboxylic acid dihydrate. The shaded atoms differ from the corresponding unshaded atoms by a reflection across (010) and a translation of b/2.

pseudo-cells of double area (*a*, [10$\bar{2}$], and β′).   These latter cells give the best description of the molecular structure because [10$\bar{2}$] is then the only substantial variable.   The expansion along this axis is approximately that required to accommodate the extra pairs of triply-linked carbon atoms.   These double cells also give the clearest pictures of the atomic arrangement, and they will be used in our subsequent diagrams.

EXPERIMENTAL.

Various positions for the atoms, differing by small amounts from those previously given (Robertson and Woodward, *loc. cit.*) were tested. The calculations were confined mainly to the ($h0l$) and ($0kl$) structure factors. The greatest uncertainties in these calculations probably lie in the values adopted for the atomic (f) scattering curves. For the present purpose of comparing slightly differing structures we have adopted a purely empirical basis, and have derived the best average f-curve for all the atoms considered together, but with the coefficient for carbon taken at 60% of that for oxygen. Details of the data used have already been given (*idem, ibid.*).

The results of these calculations are summarised in Table II for the molecular models (III)—(VIII) as well as for Zachariasen's original structure (*loc. cit.*). The discrepancy is expressed in each case as

$$\frac{\Sigma \left(|\, \mathrm{F_{obs.}} \,| - |\, \mathrm{F_{calc.}} \,| \right)}{\Sigma |\, \mathrm{F_{obs.}} \,|}$$

In spite of the uncertainties and assumptions involved in the atomic scattering factors, these discrepancies are probably the best means available for attaching a figure of merit to the various structure models.

TABLE II.

	Discrepancy, %.	
	($h0l$) including ($00l$).	($0kl$) without ($00l$).
Zachariasen's structure	15·6	20·7
Structure (III), R.W.	12·4	12·4
Structure (IV), R.W.–Booth	11·3	12·5
Structure (V), B.H.P.	10·0	18·1
Structure (VI), B.H.P. with R.W. y co-ords.	10·0	13·0
Structure (VII), do. but with R.W.–Booth carbon	10·0	13·0
Structure (VIII), do. but with R.W. carbon	10·1	13·0

It is our general experience that the residual discrepancy is never better than about 10% when spherically symmetric scattering functions for the atoms are employed. It seems probable that this

FIG. 3.
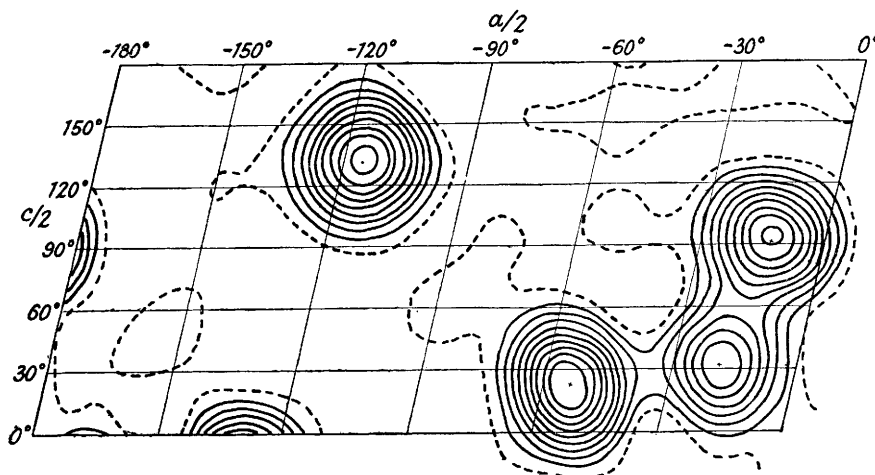
Co-ordinates of structure (VII) *plotted on the asymmetric crystal unit.*

residual is largely due to the distribution of electron density in the direction of the bonds between the atoms, which is not allowed for in the scattering function; as well as, of course, to some inaccuracies in the experimental intensity measurements.

It is clear that a number of these structures (which only differ from each other very slightly) give almost equally good agreements with the observed data. Structure (VII) has been selected as being perhaps the most probable. Its monoclinic crystal co-ordinates are given in Table III (A) for the space-group description $P2_1/n$ and in Table III (B) for the description $P2_1/a$, and these positions are marked with small crosses on the contour map of the asymmetric crystal unit in Fig. 3. The water molecule which is included in the asymmetric unit in these descriptions is the one most closely bound to the carboxyl group. In former descriptions (Zachariasen, *loc. cit.*; Robertson and Woodward, *loc. cit.*) the other water molecule, derived by the operation 2_1, was included instead.

TABLE III.

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

Atom.	x, A.	y, A.	z, A.	$2\pi x/a$.	$2\pi y/b$.	$2\pi z/c$.
(A) Space-group C_{2h}^{5}–$P2_1/n$. Unit cell $a = 6\cdot12$, $b = 3\cdot60$, $c = 12\cdot03$ A., $\beta = 106\cdot2°$.						
C	−0·238	0·120	0·618	− 14·0°	12·0°	18·5°
O (1)	0·507	−0·205	1·778	29·8	−20·5	53·2
O (2)	−1·342	0·770	0·4355	− 78·9	77·0	13·0
H$_2$O	−0·276	0·390	3·874	− 16·2	39·0	115·9
(B) Space-group C_{2h}^{5}–$P2_1/a$. Unit cell $a = 11\cdot88$, $b = 3\cdot60$, $c = 6\cdot12$ A., $\beta = 76\cdot5°$.						
C	−0·611	0·120	0·553	−18·5°	12·0°	32·5°
O (1)	−1·757	−0·205	0·398	− 53·2	−20·5	23·4
O (2)	−0·430	0·770	1·564	− 13·0	77·0	92·0
H$_2$O	−3·824	0·390	2·248	−115·9	39·0	132·2