183. *The Crystalline Structure of the Sugars. Part IV. Pentaerythritol and the Hydroxyl Bond.*

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Although it has been possible to make some progress toward the elucidation of the crystalline structure of the sugars by comparative studies of a large number of compounds (see, *e.g.*, Cox, Goodwin, and Wagstaff, J., 1935, 978, 1495), yet exact quantitative investigation of individual compounds has been hampered by lack of knowledge of various inter-atomic distances for preliminary " trial and error " determinations. No accurate measurements, so far as we are aware, had previously been made (on crystalline substances) either of the length of the link from a carbon atom to an oxygen atom in an aliphatic alcohol, or of the length of the " hydroxyl bond " between two alcoholic groups, and indeed, direct measurements by Fourier analysis of the carbon–carbon bond in purely aliphatic compounds have been restricted to those made on oxalic acid and its derivatives, which are scarcely typical of aliphatic compounds in general. The " hydroxyl bond " in particular undoubtedly plays a very large part in determining the mutual arrangement of the molecules in crystalline sugars and alcohols, while many of the colloidal properties of the polysaccharides can be given satisfactory interpretation by postulating such a link. The present work on pentaerythritol, $C(CH_2{\cdot}OH)_4$, was undertaken in the hope that the relatively small number of parameters in the structure would permit precise determinations of this bond and of the carbon–oxygen distance. Additional interest attaches to pentaerythritol, since it was the centre of acute controversy some years ago owing to the supposed possibility of a pyramidal disposition of the valency bonds around the central carbon atom (see *e.g.*, " Strukturbericht," Vol. 1, p. 643; *Ann. Reports*, 1929, **26**, 74, 304). Our investigation, in addition to providing the data regarding inter-atomic distances for which it was primarily undertaken, has shown that the deviation of the central carbon valencies from the exact tetrahedral distribution is on the average no more than 1½°, an amount very little more than the experimental error and which can easily be accounted for by inter-molecular forces.

Preliminary Crystallographic Data.—Our preliminary results confirmed those previously obtained, *viz.*, that pentaerythritol has a body-centred lattice of at least approximately tetragonal symmetry, with two molecules in the unit cell. The symmetry of pentaerythritol has been discussed at great length by earlier workers (for references, see " Strukturbericht," *loc. cit.*), and the final conclusion was that its space-group is $I\bar{4}$, so that the molecule possesses a four-fold alternating axis, a result which is compatible with the tetrahedral distribution of valencies about the central carbon atom. Since, however, both the measurement of cell dimensions and the intensity data available for the earlier discussions appeared to be limited in scope and accuracy, the possibility was still open that the substance was actually monoclinic–pseudo-tetragonal. Accordingly, experiments were made to determine whether any difference existed between the lengths of the two *a*-axes, and whether the angle between them departed appreciably from 90°. For this purpose a crystal was set up as for rotation about its tetragonal axis, and two successive oscillation photographs were taken on a cylindrical film surrounding it. The two oscillations were exactly 90° apart, and for the second one the film was displaced about 1 mm. parallel to the axis of rotation, so that each (hkl) reflection on the photograph was accompanied by the corresponding $(k\bar{h}l)$ reflection, any difference in the spacing being indicated by a *horizontal* separation of the two spots in addition to the vertical separation of 1 mm. On several such photographs no indication of any horizontal displacement was obtained, and examination of various pairs of planes with high indices showed that they differed in spacing by considerably less than half the separation of the $K\alpha$ doublet of copper, *i.e.*, by less than 0·05%. There is consequently no reason to doubt that the lattice of pentaerythritol is truly tetragonal; this is further confirmed by the observation that within the experimental error the intensities of the four planes (hkl) $(\bar{h}\bar{k}l)$, $(k\bar{h}\bar{l})$, $(\bar{k}h\bar{l})$, are always equal, while the alternating character of the symmetry is shown by the inequality (in general) of the intensities of the planes (hkl) and $(\bar{h}kl)$. These X-ray measurements appear to us to constitute a more searching test of the symmetry than goniometric or other external observations, and, coupled with the absence of reflections from planes for which $h + k + l$ is odd, they show that the space group is indeed $I\bar{4}$. The actual cell dimensions we find to be $a = 6{\cdot}10$, $c = 8{\cdot}73$ A. (each $\pm$ 0·02 A.), whence the calculated density for two molecules in the unit cell is 1·396 g./c.c. (observed, by flotation, 1·390 g./c.c.).

Measurement of Intensities.—In order to make the structure analysis as complete as possible, the intensities of all the reflections obtainable with copper $K\alpha$ radiation were measured, and in addition the $\{hk0\}$ intensities were determined to the limit attainable with molybdenum $K\alpha$ radiation. All the measurements were made photographically, and the intensities were put on the absolute scale by direct photometric comparison of the orders of $\{002\}$, $\{200\}$, and $\{101\}$ with the (400) rock-salt reflection, extended faces and parallel-sided sections of known thickness being used. The remaining intensities were obtained from small crystals completely bathed in the X-ray beam; the $\{h0l\}$ and $\{hk0\}$ reflections were measured by means of a Cambridge micro-photometer, and the $\{hkl\}$ intensities were estimated visually by comparison with the $\{h0l\}$ and $\{hk0\}$ planes. Since the relatively high symmetry of the crystals enables each plane to be observed several times and compared with different standard reflections, visual comparison can be relied upon in this case to give absolute intensities with an accuracy adequate for the purposes of structure analysis ($\pm$ 20% or better for a plane of average intensity).

In Table I the data for the $\{hk0\}$ planes are given; d is the spacing of the plane in A., and Q is the absolute integrated intensity from a crystal of unit volume (for $\lambda = 0{\cdot}710$ A.). The experimental structure factors $F_{\text{obs.}}$ are derived by means of the usual formula

$$Q = \frac{N^2e^4\lambda^3}{2m^2c^4} \cdot \frac{1+\cos^2 2\theta}{\sin 2\theta} \cdot F^2$$

The values of $F_{\text{obs.}}$ for the other planes are given in Table II.

TABLE I.

hk0 *Structure Factors.*

$hk0$.	d.	$Q \times 10^4$.	$F_{\text{obs.}}$.	$F_{\text{calc.}}$.	$hk0$.	d.	$Q \times 10^4$.	$F_{\text{obs.}}$.	$F_{\text{calc.}}$.
200	3·08	11·80	37·2	−33·8	4100	0·57	<0·01	<3·3	5·0
400	1·54	0·20	5·3	1·3	510	1·19	0·90	14·8	12·9
600	1·03	0·11	5·8	5·4	530	1·05	0·03	3·2	4·5
800	0·76	0·04	4·2	4·0	550	0·86	0·02	3·1	− 1·0
1000	0·61	0·02	3·1	− 1·7	570	0·70	<0·01	<2·8	− 0·7
110	4·28	8·23	22·7	22·7	590	0·59	<0·01	<3·2	2·5
130	1·92	<0·06	<2·8	− 2·4	620	0·96	<0·02	<2·8	− 0·9
150	1·19	0·51	11·3	− 9·6	640	0·84	0·09	6·0	6·0
170	0·86	0·67	16·2	20·6	660	0·71	0·04	4·6	− 4·8
190	0·67	0·09	7·1	− 7·3	680	0·61	0·06	6·0	6·5
220	2·14	4·60	24·3	26·7	6100	0·52	0·01	3·2	0·2
240	1·36	0·25	3·7	− 5·9	710	0·86	0·12	6·9	− 8·8
260	0·96	0·07	4·9	5·8	730	0·81	<0·01	<2·8	1·2
280	0·73	0·01	2·6	5·1	750	0·70	<0·01	<2·8	2·7
2100	0·60	<0·01	<3·2	− 2·0	770	0·61	0·01	2·5	2·7
310	1·92	1·06	12·3	− 7·3	820	0·73	<0·01	<2·7	− 2·0
330	1·43	0·76	12·6	13·1	840	0·68	<0·01	<2·9	− 3·8
350	1·05	0·32	9·7	8·7	860	0·61	0·16	10·4	12·8
370	0·80	0·08	6·0	− 7·2	910	0·67	0·10	7·5	8·6
390	0·64	0·02	3·6	6·3	930	0·64	<0·01	<3·1	− 3·7
420	1·36	0·25	7·4	6·5	950	0·59	0·02	3·7	4·1
440	1·07	0·20	7·6	9·7	1020	0·60	0·04	5·2	4·4
460	0·84	<0·01	<2·5	− 1·2	1040	0·57	<0·01	<3·3	5·0
480	0·68	0·02	4·1	− 3·3	1060	0·52	<0·01	<3·5	− 5·0

Apart from the plane (002), the observed structure factors do not appear to suffer from serious errors due to extinction. Thus in the case of the very strong reflection (202), two values of $F_{\text{obs.}}$, obtained severally by reflection from a ground face and by transmission through a plate, were equal within experimental error (32·8 and 34·2), whereas appreciable extinction would have resulted in a higher value in the former case. Measurements which we have made on various planes in the crystals of β-methylxyloside also show that extinction effects are small, so that it is probable that in sugars, sugar alcohols, and similar substances whose molecules are held together mainly by hydroxyl bonds, the crystals approximate to the ideally imperfect type. In the case of the (002) reflection of pentaerythritol, however, extinction is very marked, the intensity from a cleavage face being increased several-fold by grinding and still more by immersion in liquid air. This is probably to be explained by the perfect cleavage parallel to (002) which would result in more perfect alinement of the mosaic blocks parallel to this plane than in other directions, added to which its outstandingly high intensity renders it more susceptible than any other to extinction effects.

The Determination of the Structure.—The unit cell of pentaerythritol contains two carbon atoms in the special positions (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, eight carbon atoms in the general positions $(x_1y_1z_1)$, $(\bar{x}_1\bar{y}_1z_1)$, $(y_1\bar{x}_1\bar{z}_1)$, $(\bar{y}_1x_1\bar{z}_1)$, $(\frac{1}{2}+x_1, \frac{1}{2}+y_1, \frac{1}{2}+z_1)$, etc., and eight oxygen atoms in the general positions $(x_2y_2z_2)$, etc. Six parameters are thus required to determine

TABLE II.

Observed Structure Factors.

hkl.	*F.*	*a.*	*hkl.*	*F.*	*a.*	*hkl.*	*F.*	*a.*	*hkl.*	*F.*	*a.*
000	148·0		501	5·4	217°	323	15·8	259°	325	8·1	180°
110	22·7	0°	521	9·3	325	343	12·1	82	345	<2·6	
130	<2·8		541	6·6	35	413	12·1	148	415	6·1	180
150	11·3	180	611	12·1	340	433	12·1	0	435	<2·4	
200	37·2	180	631	8·5	171	503	5·4	292	505	8·1	180
220	24·3	0	002	60·0	0	523	11·8	281	525	<2·5	
240	3·7	180	112	28·8	304	543	<2·4		006	10·4	0
260	4·9	0	132	11·4	342	613	12·1	323	116	4·7	101
310	12·3	180	152	10·5	159	004	16·2	0	136	13·5	3
330	12·6	0	202	32·4	190	114	20·9	262	206	6·1	165
350	9·7	0	222	32·2	323	134	24·1	357	226	11·4	25
400	5·3	0	242	6·0	106	154	<2·4		246	<2·6	
420	7·4	0	262	8·9	20	204	14·0	193	316	10·5	82
440	7·6	0	312	8·1	246	224	19·8	336	336	<2·6	
510	14·8	0	332	5·4	354	244	<2·4		406	15·1	326
530	3·2	0	352	10·1	47	314	6·6	278	426	<2·6	
600	5·8	0	402	11·1	17	334	2·6	183	516	9·8	66
620	<2·8		422	6·6	67	354	<2·4		107	5·4	164
101	22·1	354	442	<2·6		404	19·1	5	127	11·4	82
121	12·3	237	512	16·7	323	424	6·1	174	147	4·7	349
141	5·4	66	532	<2·4		444	<2·6		217	12·9	40
161	6·7	3	602	7·7	301	514	13·2	335	237	<2·6	
211	33·0	332	622	<2·6		534	<2·4		307	8·1	12
231	23·8	187	103	17·7	204	604	6·6	131	327	<2·6	
251	16·4	23	123	8·1	278	105	11·4	180	417	<2·4	
301	10·1	340	143	13·8	13	125	11·8	0	008	11·1	0
321	11·0	318	163	<2·6		145	16·2	0	118	<2·6	
341	10·4	34	213	36·2	321	215	16·4	0	138	4·7	32
411	18·7	167	233	12·3	191	235	5·4	180	208	5·4	166
431	29·8	0	253	16·6	30	255	7·2	0	228	7·6	36
451	8·5	171	303	26·3	347	305	21·4	0	318	5·4	50

the structure. The only symmetry is that of the four-fold alternating axis (which is also a two-fold rotation axis) and the derived two-fold screw axes, all of which are parallel to [001].

The four parameters x_1, y_1, x_2, and y_2 were determined by two separate methods : (*a*) a Patterson–Harker synthesis using the data of Table II, (*b*) a Fourier analysis of the F-values of Table I. As Harker (*J. Chem. Physics*, **1936**, **4**, 381) has shown, the x and y co-ordinates of all the atoms in a structure having a two-fold axis of symmetry parallel to the z-axis may be found from the positions of the maxima of the Patterson function $P(xy0)$ where

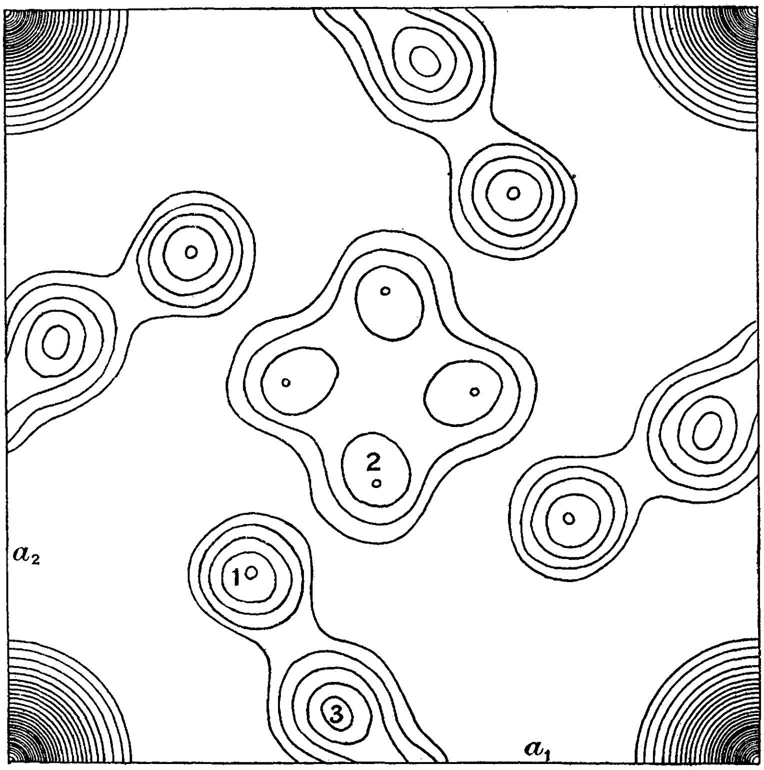
$$P(xy0) = \sum_h\sum_k \cos 2\pi(hx + ky) \,.\, (\sum_l |F(hkl)|^2)$$

Hence, corresponding to the separation of the two symmetrically related atoms at $(x\;y\;z)$ and $(\bar{x}\;\bar{y}\;z)$ in the crystal lattice, there will be a maximum in the value of $P(xy0)$ at $(2x,\ 2y)$. In addition there will be maxima in $P(xy0)$ corresponding to the separation of any two atoms which, although not related by the symmetry of the two-fold axis, have by chance the same, or nearly the same, z-co-ordinates.

The evaluation of $P(xy0)$ was carried out by the method of Beevers and Lipson (*Proc. Physical Soc.*, **1936**, **48**, 772), the squares of all the F values listed in Table II being used. A diagram of the result is shown in Fig. 1, where the contours are plotted over a complete unit cell at intervals of 20 in the value of P, negative contours being omitted. On account of the tetragonal symmetry, every feature is repeated four times in the diagram, so there are actually three fundamental maxima, labelled 1, 2, and 3. (The large peak at the origin is merely an expression of the fact that every atom is at zero distance from itself.) Now in the case of pentaerythritol only two peaks can arise from the separation of atoms which are symmetrically related (" space-group maxima "), *viz.*, one with co-ordinates $(2x_1,\ 2y_1)$ corresponding to the separation of the carbon atoms in the general positions $(x_1y_1z_1)$ and $(\bar{x}_1\bar{y}_1z_1)$, and another with co-ordinates $(2x_2,\ 2y_2)$ similarly derived from symmetrically related oxygen atoms. The existence of a third peak shows that by chance two atoms other than those symmetrically related have nearly the same z-co-ordinates. Thus, either each CH_2 group and its attached hydroxyl group have the same z-co-ordinates (*i.e.*, $z_1 \approx z_2$)

or the four CH_2 groups of each molecule are in the same plane with the central carbon atom (*i.e.*, $z_1 \approx 0$) or the four hydroxyl groups are coplanar with the central carbon atom (*i.e.*, $z_2 \approx 0$). Of these three possibilities it is easy to show on various grounds (by means of the intensities of the orders of {002}, etc.) that the last is actually correct. A further point which now arises is that if $z_2 \approx 0$, there should be, in addition to the two space-group maxima in Fig. 1, two other maxima, *viz.*, one with co-ordinates $(x_2 y_2)$ corresponding to the distance of the hydroxyl groups from the carbon at the origin, and another with co-ordinates $(x_2 + y_2,\ y_2 - x_2)$ corresponding to the distance apart of two hydroxyl groups at $(x_2 y_2 0)$ and $(\bar{y}_2 x_2 0)$. This apparent discrepancy in the number of maxima is completely explained, and the peaks unequivocally assigned to their appropriate atomic distances, when it is observed that the co-ordinates of peak 2 are nearly double those of peak 1. Thus the peak 2 is a space-group maximum representing the O–O separation and has co-ordinates $(2x_2,\ 2y_2)$, the peak 3 is one of the chance maxima with co-ordinates $(x_2 + y_2, y_2 - x_2)$ giving another O–O distance, and the peak 1 is formed by the superposition of two maxima, one the carbon–carbon space-group maximum $(2x_1,\ 2y_1)$ and the other a chance carbon–oxygen maximum $(x_2 y_2)$. Thus from the Patterson–Harker synthesis we find the following atomic co-ordinates (expressed as fractions of the length of the *a*-axis) :

FIG. 1.



Carbon, $x = 0{\cdot}161,\ y = 0{\cdot}123$
Oxygen, $x = 0{\cdot}314,\ y = 0{\cdot}247,\ z \approx 0$

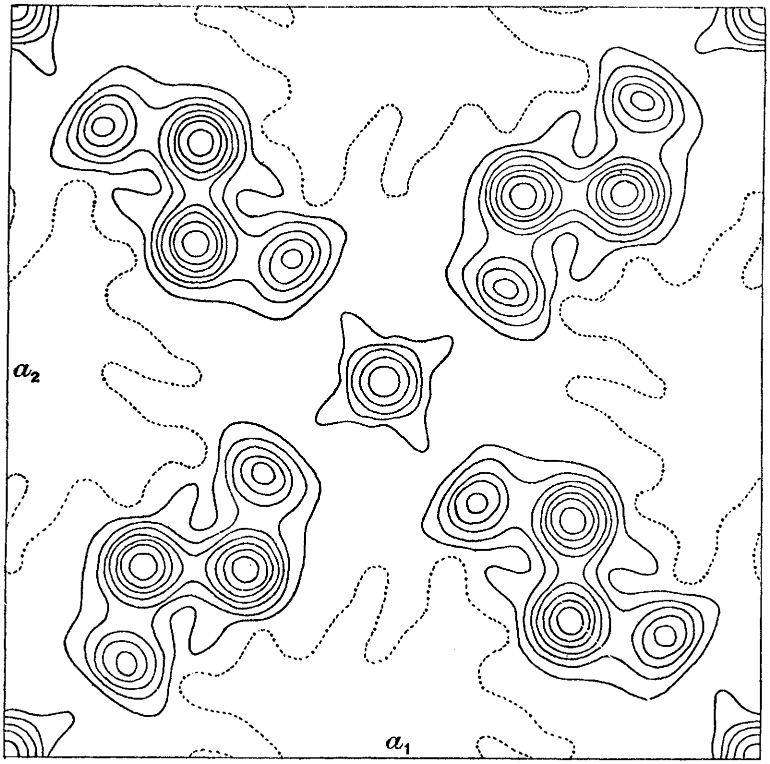
Owing to the overlapping of the two maxima in peak 1, the values of the carbon co-ordinates are not quite so accurate as those of the oxygen.

The x and y co-ordinates were next determined more accurately by means of a two-dimensional Fourier projection of the content of the unit cell on (001), using the F-values for all the $[hk0]$ planes recorded in Table I. [A projection was originally made with the data obtained with copper radiation only, but it was found that the inclusion of the results obtained with molybdenum radiation (all F-values from planes with d less than 0·90 A.) greatly improved the resolution.] The projection on (001) is centro-symmetrical, and the expression for the electron density takes the form

$$\rho(xy) \equiv \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} F_{hk0} \cos 2\pi(hx + ky)$$

so it was only necessary to determine whether the F's are positive or negative; this was done by calculating the structure factors of all the $\{hk0\}$ planes from the atomic co-ordinates obtained in the Patterson synthesis. Since for this purpose great accuracy is unnecessary, much of the calculation was eliminated by using structure contour graphs of the type proposed by Bragg (*Nature*, 1936, **138**, 362; see also Bragg and Lipson, *Z. Krist.*, 1936, **95**, 323). At later stages where calculation was considered necessary, and also in dealing with zones of lower symmetry where the advantage of structure factor graphs is not so marked, it was found helpful to construct a table of the function $y = A\cos 2\pi x$, computed for values of x from 0 to 1·00 at intervals of 0·01 and for values of A from 1·0 to 10·0 at intervals of 0·2. Such a table can be prepared in a few hours with the aid of a multiplying machine, and results in great saving of time when many structure factors have to be calculated.

FIG. 2.

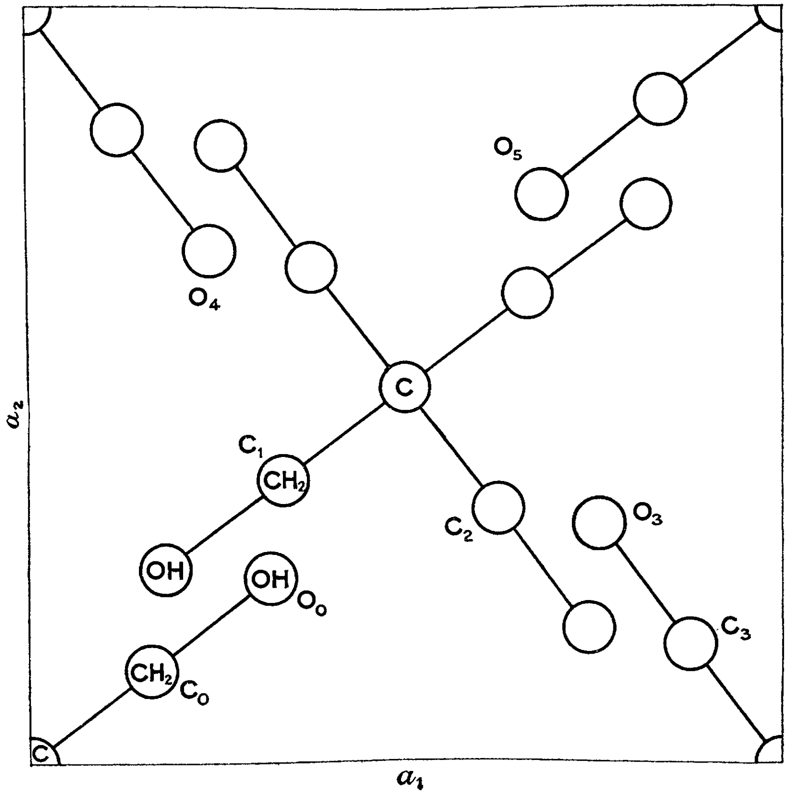


The Fourier synthesis was carried out by the procedure of Beevers and Lipson (*loc. cit.*) with the result shown in Fig. 2, which gives a projection of one complete unit cell on (001), the contours being drawn at intervals of one electron per sq. A., with the one-electron contour dotted. All the atoms in the cell are clearly resolved, and their x and y co-ordinates can be determined with considerable accuracy. Fig. 3 shows how the various peaks in the contour diagram are to be assigned to their respective atoms, while the co-ordinates of the atoms in the general positions are as follows :

Carbon, $x = 0{\cdot}162$, $y = 0{\cdot}123$
Oxygen, $x = 0{\cdot}317$, $y = 0{\cdot}247$

These values appear to be somewhat more reliable than those from the Patterson synthesis, and they have been adopted as final, but it should be observed that the very close agreement between the two sets of figures affords strong evidence as to the accuracy of both, since they have been determined from substantially different data (in the one case from all the $\{hk0\}$ planes with d greater than 0·50 A., and in the other from all $\{hkl\}$ planes with d greater than 0·90 A.). The structure factors calculated from the final co-ordinates are recorded in Table I under $F_{\text{calc.}}$; the figures depend to some extent on the particular atomic scattering factors used in the calculations, but the general agreement with the experimental data is quite satisfactory.

Fig. 3.



The z-co-ordinates were also determined both by the Patterson synthesis and by the usual Fourier method. It has already been shown that the oxygen co-ordinate (z_2) is approximately zero, while from a one-dimensional Fourier synthesis of the orders of $\{002\}$ it was found that the carbon co-ordinate (z_1) is about 0·10. Consideration of these results showed that the atomic positions were such that in a Fourier projection on either (100) or (110) the resolution would be to poor to fix the z-co-ordinates with sufficient accuracy. In order to make the best use of the experimental data it was therefore decided to determine the z-co-ordinates by calculating three-dimensional syntheses along lines which were known from two-dimensional results to pass through the atomic centres. Thus the distance apart of the carbon atom at (000) and the carbon atom at $(x_1y_1z_1)$ will be represented by a maximum in the value of the Patterson function $P(xyz)$ at the point $(x_1y_1z_1)$, so that z_1 can be found by evaluating the function

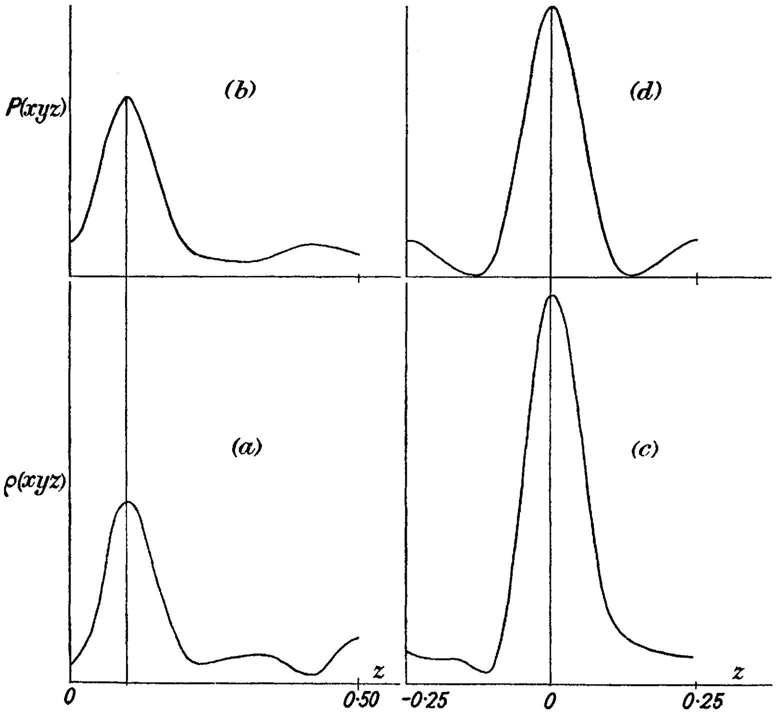
$$P(xyz) \equiv \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} |F_{hkl}|^2 \cos 2\pi(hx + ky + lz)$$

along the line (x_1y_1z) where x_1 and y_1 are the values already determined from the c-axis projections, and finding the value of z_1 for which P is a maximum. In addition z_1 can be determined by finding the maximum electron density when the function

$$\rho(xyz) = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} F_{hkl} e^{2\pi i(hx + ky + lz)}$$

is plotted along the line (x_1y_1z), and both processes can be repeated to find z_2. It should be noted that the z-co-ordinates obtained by these methods are unaffected by small errors in the values of x and y co-ordinates used, since around the maxima in the three-dimensional Patterson and simple F syntheses the contour surfaces are nearly spherical and therefore the appropriate function plotted along a line which does not quite pass through the true centre will still show a maximum at the correct value of z.

FIG. 4.



(*a*) Electron density $\rho(xyz)$ along the line (0·162, 0·123, z).
(*b*) The function $P(xyz)$ along the line (0·162, 0·123, z).
(*c*) Electron density $\rho(xyz)$ along the line (0·317, 0·247, z).
(*d*) The function $P(xyz)$ along the line (0·317, 0·247, z).

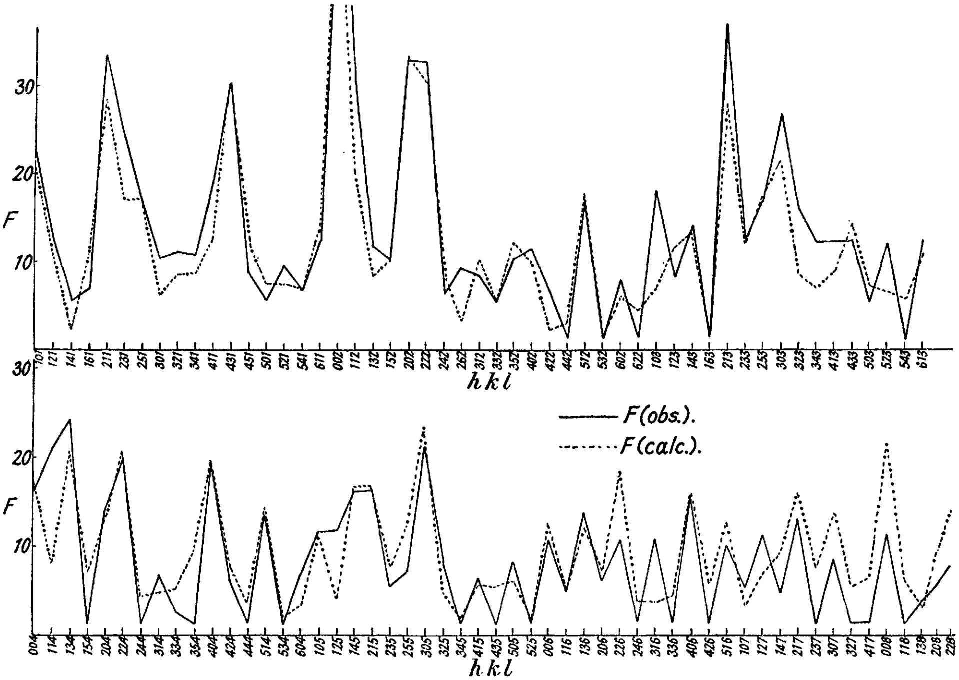
The graphs of the functions $P(x_1y_1z)$ and $P(x_2y_2z)$ (based on all the F-values of Table II) are shown in Fig. 4 (*b*) and 4 (*d*) respectively, the maxima occurring at $z_1 = 0{\cdot}096$ and $z_2 = 0{\cdot}000$. While these results would normally be of high accuracy, they require slight adjustment in this particular case on account of the combined effects of a nearly zero value of z_2 and of symmetry parallel to (001) which is introduced as a consequence of the use of F^2 terms in the Patterson method. Thus, the peak in Fig. 4 (*d*) is actually due to superposition of two maxima at $\pm z_2$, while in Fig. 4 (*b*) the maxima at $(x_1y_1z_1)$ and $(x_2 - x_1, y_2 - y_1, z_1 - z_2)$ combine to give the observed result. On this account, although the values of z_1 and z_2 are probably very close to 0·096 and 0·000 respectively, yet the Fourier syntheses, in which use is made of the phase relations between the F's with the consequent elimination of spurious symmetry, will be more reliable. Since the crystals have no symmetry except in the c-zone, the evaluation of the Fourier syntheses involved a knowledge of the phase angles (α) of all the structure factors in Table II; these were calculated from the previously determined x and y co-ordinates and from the z-co-ordinates obtained from Figs. 4 (*b*) and 4 (*d*) and are given in Table II. The resultant graphs of electron density, which are not symmetrical about the origin, are shown in Figs. 4 (*a*) and 4 (*c*). The final values obtained from these graphs are $z_1 = 0{\cdot}097$ and $z_2 = 0{\cdot}002$.

The co-ordinates which, together with the operations of the space-group $I\bar{4}$, completely determine the structure are thus :

(000) for the carbon atom in the four-fold position, (0·162, 0·123, 0·097) for the carbon atom in the general position, and (0·317, 0·247, 0·002) for the oxygen atom in the general position.

Fig. 5 shows graphically the agreement between the experimental structure factors (continuous line) and those calculated from the above co-ordinates (broken line) for all planes not included in Table I.

Fig. 5.

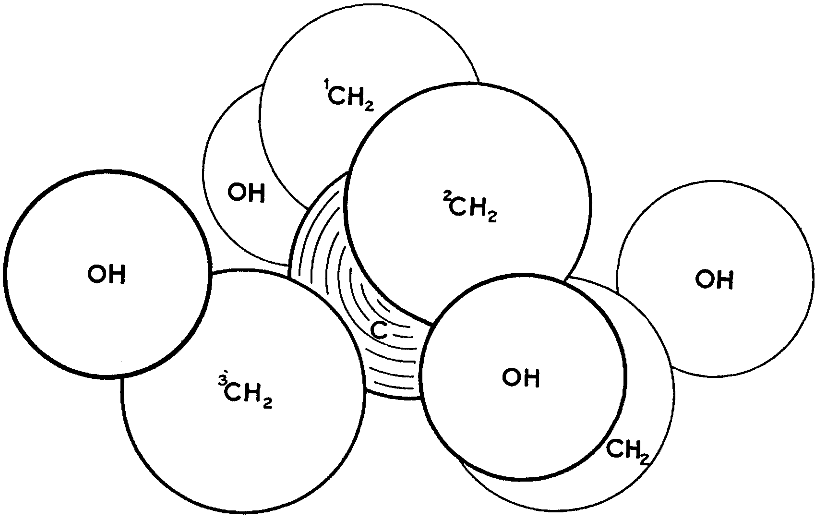


Discussion of the Structure.—A diagrammatic representation of the molecule of pentaerythritol as determined by the preceding analysis is shown in Fig. 6 (in which the vertical direction is parallel to the c-axis). The central carbon atom (shaded) is surrounded by four CH_2 groups at the corners of an almost exact tetrahedron, and each hydroxyl group is attached to its CH_2 by a bond which makes a nearly tetrahedral angle with the C–CH_2 link and is so directed that the four hydroxyl groups lie at the corners of a square. It is of interest to note that this conformation is the same as that possessed by pentaerythritol halogenohydrins in the vapour state (de Laszlo, *Compt. rend.*, 1934, **198**, 2235) and probably also in the solid state if it is assumed that their space-group is $P2$ and not $P2/m$ as suggested by Wagner and Dengel (*Z. physikal. Chem.*, 1932, *B*, **16**, 382; cf. *Ann. Reports*, 1933, **30**, 416). The bond lengths and angles calculated from the measured atomic co-ordinates and cell dimensions are as follows :

Distances.	*Angles.*
C–C = 1·50 A.	^{1}C–C–^{2}C = 111½°
C–O = 1·46 A.	^{1}C–C–^{3}C = 108½°
	C–C–O = 111½°

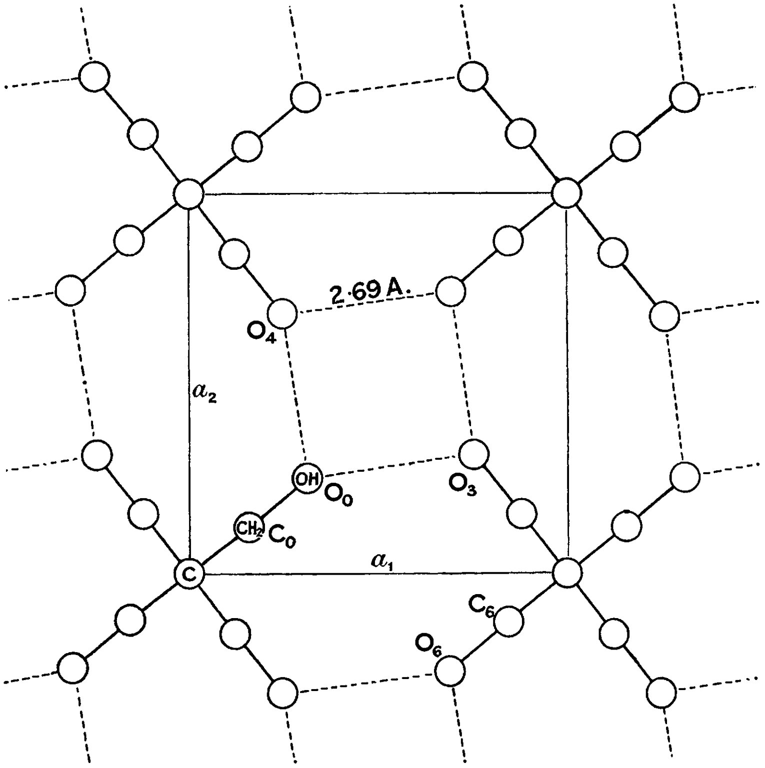
We estimate the probable error in the bond lengths to be not more than ± 0·03 A., while the angles are probably accurate to ± 1°. Thus the divergences of the angles from the true tetrahedral value of 109½° are scarcely more than the experimental error, but the length of the carbon–carbon bond appears to be definitely slightly less than that found in diamond and usually assumed for aliphatic compounds (*viz.*, 1·54 A.), and it is considerably less than the value 1·58 A. found in dibenzyl (Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 348) and in ammonium oxalate monohydrate (Hendricks and Jefferson, *J. Chem. Physics*, 1936, **4**, 102). These last two compounds, however, can hardly be regarded as closely similar to pentaerythritol. No quantitative results are available with which the figure for the C–O link can be strictly compared, since this distance is known to depend to an appreciable extent upon the chemical nature of the groups involved, but the value 1·46 A. is almost exactly equal to the calculated sum of the half bond lengths of carbon and oxygen (see, *e.g.*, Sidgwick, "The Covalent Link in Chemistry," p. 85). If the present measurement is typical of primary alcohols, it appears that the C–O distance in such compounds is the same as or slightly greater than in ethers or cyclic acetals, while it is definitely greater than in phenols, acids, etc. (for comparative figures, see *Ann. Reports*, 1936, **33**, 220).

Fig. 6.



The structure of the lattice as a whole is of a very pronounced layer type; the molecules are linked together by hydroxyl bonds in sheets in the (002) planes, the separation of the sheets being more than 3½ A., thus accounting for the perfect cleavage parallel to {001}. The structure of one of the sheets is shown in Fig. 7, in which the distance of closest approach of hydroxyl groups is shown by broken lines. The minimum separation of oxygen atoms is 2·69 A., and although it is impossible to determine the position of the hydrogen atoms by *X*-rays methods, there is a very strong accumulation of evidence to support the view that this relatively short distance between hydroxyl groups represents a " hydroxyl bond " in which a hydrogen atom binds two oxygen atoms closely together while remaining attached essentially to one of them. Each hydroxyl group in pentaerythritol has two such bonds both nearly in the (002) plane, making an angle of nearly 90° with each other and inclined at 137° and 115° respectively to the carbon–oxygen bond, which is not coplanar with them. This arrangement is similar to that observed in various other instances where hydroxyl bonds have been suggested; in particular there is marked resemblance to the case of resorcinol (Robertson, *Proc. Roy. Soc.*, 1936, *A*, **157**, 79) both in the oxygen–oxygen distance (mean value 2·70 A.) and in the environment of the oxygen atoms (apart from the shorter carbon–oxygen distance). In so far as resorcinol and pentaerythritol are typical of phenols and alcohols respectively, this resemblance is noteworthy in suggesting that the differences between the two classes of compound in the solid state do not extend to the extra-molecular relations of the oxygen atoms, in contrast with the appreciable divergence inside the molecule as expressed by the respective carbon–oxygen separations (1·36 and 1·46 A.). It is reasonably safe to infer that the differences between primary and secondary alcohols in this respect are at least no greater than those between the former and the phenols, and the linking together of secondary alcohols (*e.g.*, sugars) in the solid state is effected by means of hydroxyl bonds whose lengths do not differ greatly from 2·70 A., two such bonds to each oxygen atom being probable.

Fig. 7.



All other inter-molecular distances are very much greater than 2·7 A., and correspond to relatively weak van der Waals forces only; a complete list (up to 4·1 A.) is given below, the various atoms referred to being indicated in Figs. 3 and 7.

$O_0 - O_3 = 2{\cdot}69$ A.
$O_0 - O_4 = 2{\cdot}69$ A.
$O_0 - C_3 = 3{\cdot}56$ A.
$O_0 - C_1 = 3{\cdot}63$ A.
$O_0 - O_6 = 3{\cdot}76$ A.
$O_0 - O_5 = 3{\cdot}80$ A.
$O_0 - C_6 = 3{\cdot}99$ A.
$O_0 - C_2 = 4{\cdot}01$ A.
$C_0 - C_2 = 4{\cdot}10$ A.

EXPERIMENTAL.

The pentaerythritol used in the present investigation was obtained from the Eastman Kodak Company and melted at 250° (uncorr.). Crystals up to 5 mm. or more linear dimensions were readily obtained by slow recrystallisation from aqueous alcohol, but caution was necessary in selecting individuals for *X*-ray measurements on account of the tendency to twinning on {100}. All crystals used for intensity measurements were therefore subjected to a preliminary examination by means of Laue or oscillation photographs to ensure that they were free from twinning, as indicated by the difference in intensities of the planes (*hkl*) and (*khl*).

The absolute intensities of the orders of {002}, {200}, and {101} were measured by reflection from natural and ground faces of large crystals or by transmission through appropriately cut parallel-sided sections, the experiments being carried out with the (400) rock-salt reflection as the standard of reference as previously described (Cox, Wardlaw, and Webster, J., 1936, 780). As an example of the consistency of these measurements, the following values of the structure factor *F* of (004) derived from a series of experiments may be quoted: 16·3, 16·5, 16·9, 15·5, 15·8, 16·2, 16·6, 15·9 (mean 16·2). The intensities of these planes were used to put all the others on the absolute scale by means of measurements on oscillation photographs of small crystals completely bathed in the *X*-ray beam. For this purpose crystals were selected which, by reason of the equal development of {101} and {001}, were roughly spherical in form, so that there were no appreciable errors due to variable absorption of the *X*-ray beam. The {*h*0*l*} and {*hk*0} intensities were measured on a Cambridge microphotometer, care being taken to make measurements only within the photographic density range (up to 1·2 approximately) over which the density is proportional to the *X*-ray intensity. In the visual estimation of each {*hkl*} intensity, comparisons were made only with previously measured planes of nearly the same intensity. Where planes not on the equatorial line of the photographs were measured, the appropriate corrections (Cox and Shaw, *Proc. Roy. Soc.*, **1929**, *A*, **127**, **71**) were made.

SUMMARY.

By means of quantitative *X*-ray measurements the structure of the tetragonal crystals of pentaerythritol has been completely determined. The interatomic distances within the molecule are C–C = 1·50 A. and C–O = 1·46 A., and the deviations of the bond angles from the tetrahedral value of 109½° are negligible. Each hydroxyl group is linked to two others in neighbouring molecules by " hydroxyl bonds " of length 2·69 A., in such a way that a layer structure with pronounced basal cleavage results.

We are indebted to H.M. Department of Scientific and Industrial Research for a Senior Award to one of us (T. H. G.), and to Prof. W. N. Haworth, F.R.S., for his encouragement.

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