

Cu-Atom umgebenden, planaren 4-er Gruppe (3 O+1 H₂O).

Das CuSeO₃·2 H₂O ist vom strukturellen Standpunkte aus als $\frac{3}{\infty}[\text{Cu}^{4+1(+1)}\text{Se}^{6+3}\text{O}_3 \cdot \text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ zu formulieren.

Herrn Prof. Dr J. Zemann gilt mein aufrichtigster Dank für viele klärende Diskussionen und wertvolle Hinweise. Frl. M. Binder danke ich für ihre Hilfe bei den numerischen Berechnungen. Die Deutsche Forschungsgemeinschaft stellte in dankenswerter Weise dem Institut apparative Hilfsmittel zur Verfügung.

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A Neutron Diffraction Study of Pentaerythritol

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Neutron diffraction measurements of $hk0$ and $00l$ reflexions of pentaerythritol with H and D in the hydroxy group reveal an ordered distribution of these atoms. The O-H and O-D distances are 0.94 Å and the C-O-H angle is 110°. A Fourier synthesis, based upon the difference between the two sets of amplitudes, shows anisotropy of the thermal vibration for the hydroxy hydrogens. No such anisotropy is found for the other atoms in the projection on (001).

Introduction

While the general features of the crystal structure of pentaerythritol C(CH₂OH)₄ are well known from the work of Llewellyn, Cox & Goodwin (1937) and Nitta & Watanabé (1938), the hydrogen positions remained undetermined. This compound presents an example of hydrogen bonding between the oxygen atoms of an aliphatic alcohol, where each oxygen atom is linked to two other oxygens, the bond lengths being equal. For the position of the hydroxy hydrogen, four possibilities had to be considered:

- I The H atom is closer to the oxygen O₁ at (x, y, z) than to O₂ at (y, \bar{x}, \bar{z}) (see Fig. 4).
- II The H atom is closer to O₂ than to O₁.
- III Two half-hydrogens are placed between O₁ and O₂, constituting a disordered structure similar to that reported for heavy ice (Peterson & Levy, 1957).
- IV The H atom has the same distance from both oxygen atoms.

A neutron diffraction study was started in the hope that in the projection on (001) it would be possible to obtain full resolution of all peaks except the methylene hydrogens. The position of the hydroxy hydrogen would then also be obscured by the neighbouring atoms (see Fig. 4), but this problem could be taken care of by isomorphous replacement of H by D. It may be assumed that this substitution would produce no noticeable change in the parameters. By this procedure it was possible to take advantage of the large difference in scattering amplitude for neutrons between H and D, namely $b_{\text{H}} = -0.378 \times 10^{-12}$ cm. and $b_{\text{D}} = 0.65 \times 10^{-12}$ cm., respectively. The corresponding values for C and O are 0.66×10^{-12} cm. and 0.58×10^{-12} cm.

The procedure of this investigation was first to establish the approximate co-ordinates of the atoms by means of the F^{H} data*. Secondly, the F^{D} data

* Abbreviations: $F^{\text{H}} = F_{hk0}$ of C(CH₂OH)₄ and $F^{\text{D}} = F_{hk0}$ of C(CH₂OD)₄.

were included to make a ($F^D - F^H$) synthesis for a detailed study of the hydroxy hydrogen, and finally separate refinements of each set of data were performed.

Unit cell and space group

The space group is $S_4 - I\bar{4}$. All atoms but the central carbons are in the general eightfold positions, and it should be noted that in the case of a disordered half-hydrogen distribution in the unit cell the hydrogen atoms would not be related by symmetry.

The axial lengths were investigated by X-rays for the normal and for the deuterated compound, but no difference could be detected from oscillation and Weissenberg diagrams, in accordance with the findings of Ubbelohde (1939). Table 1 shows the axial lengths found by the various authors.

Table 1. Axial lengths of pentaerythritol

	a (Å)	c (Å)
Llewellyn, Cox & Goodwin	6.10 ± 0.02	8.73 ± 0.02
Nitta & Watanabé	6.067 ± 0.018	8.779 ± 0.020
Cox, Cruickshank & Shiono	6.083 ± 0.002	8.726 ± 0.002
This investigation	6.07 ± 0.02	8.74 ± 0.02

As pointed out by Nitta & Watanabé, the variation in purity of the specimens is probably responsible for the relatively large discrepancy between the reported values.

Experimental

Crystals of pentaerythritol were grown from aqueous solution by cooling in a Dewar flask. The first crystal chosen was a bipyramid with basic dimensions 6.1×6.7 mm.² and height 7.8 mm., weighing 220 mg. The appearance was milky owing to rapid cooling. Preliminary neutron data were recorded to check whether immersion in liquid nitrogen had any marked effect on the intensity. The effect was appreciable, but extinction could not be completely removed for the strongest reflexions.

In the second crystal the hydroxy hydrogen atom was replaced by deuterium. To achieve this and to keep the methylene group unchanged, pentaerythritol was dissolved in pure D_2O and twice evaporated to dryness. Finally, a large single crystal was obtained by slow cooling in a closed vessel. This crystal was not immersed in liquid nitrogen because of the risk of spalling, but, in order to reduce the extinction somewhat, it was ground to a sphere of diameter 4 mm. The weight was 160 mg. To prevent isotopic exchange of D by H, the crystal was covered with a thin plastic film.

The crystals were mounted on the goniometer described by Andresen (1957) and Barstad & Andresen (to be published). Some improvements were made to facilitate alignment of collimator and crystal. A new table with axis of rotation coaxial with the magnetite monochromator crystal allows easy change of wavelength.

The neutron source was the heavy-water reactor at Kjeller, JEEP, running at levels varying from 250 to 450 kW. The counting rate for weak reflexions at higher angles exceeded the background by only a few per cent, and, in addition, poor collimation caused a large angular spread of the diffracted beam at these angles. It has therefore not been found feasible to integrate intensities out to higher values of $\sin \theta/\lambda$ than 0.60, thus obtaining 22 reflexions in the $hk0$ zone of each crystal. In addition to these, five reflexions of (00 l) were recorded. The wavelengths were 1.129 Å and 1.051 Å for $C(CH_2OH)_4$ and $C(CH_2OD)_4$, respectively.

Preliminary treatment of F^H data

As a starting model it was assumed that the dimensions within the pentaerythritol molecule were those found in most organic compounds, i.e. with tetrahedral angles, C-C distances of 1.54 Å, C-H distances of 1.10 Å and C-O distances of 1.42 Å. The orientation of the molecule was inferred from the values of Llewellyn *et al.* and Nitta & Watanabé. For the hydroxy hydrogen atom all four models had to be considered. With a O-H distance of 1.00 Å, and assuming the H atom to lie on the line connecting the crystallographically equivalent oxygen atoms O_1 and O_2 , the parameter values for the different models could be calculated.

At first only the data for the normal compound were available. These were used to refine the structure as far as possible in order to obtain the correct signs and the proper scaling factor to obtain absolute values of amplitudes.

Fourier analyses were performed with observed intensities for the various models of hydroxy hydrogen

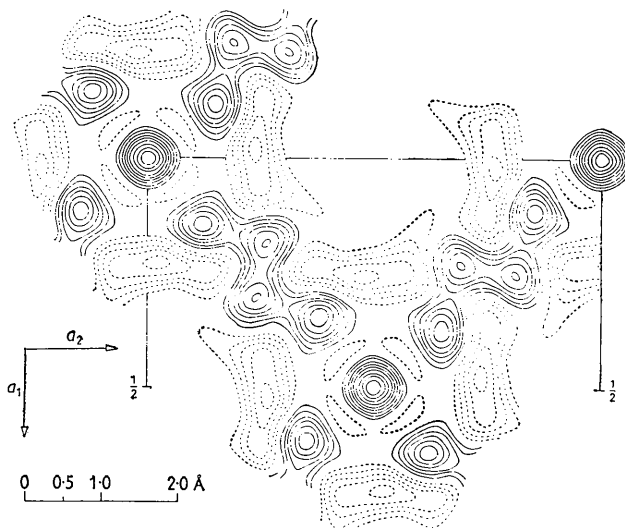


Fig. 1. Fourier projection on (001) of the scattering density of $C(CH_2OH)_4$. Contours are drawn at intervals of 0.27×10^{-2} cm.Å⁻². Full lines are positive, broken lines are negative; the zero contour is omitted.

position. It was, however, immediately apparent that the hydrogen atoms could not be resolved in this projection. They appeared, as expected, in a cluster of negative density between the oxygen atoms. But, because of the false details and distortion of all peaks in the Fourier maps, it was possible to reject the models II and IV. In model III, the influence of the hydroxy hydrogen on the position of C_2 was less serious than in model I, and this made the choice between the two less obvious. The reliability index, which is defined as $R = \Sigma||F_o| - |F_c|| \div \Sigma|F_o|$, was at this stage well above 30% with parameters found from the maps. It should be noted, however, that refinement of parameters based directly upon values read off from the maps was impossible because of overlap of atoms and termination-of-series error. The final Fourier map for model I is shown in Fig. 1. To distinguish between model I and III, Fourier analyses were made in which the amplitudes from all atoms except the hydroxy hydrogen were subtracted from the observed values. The scaling factor was constructed by taking the logarithm of F_o/F_c versus $(2 \sin \theta)^2$. By the same procedure the average B was found equal to 2.85 \AA^2 .

These Fourier analyses immediately showed that the model I was the better one. The parameter values for the hydroxy hydrogen now changed considerably, resulting in an improved reliability index of 20%, not allowing for extinction in (220). The further work involved four successive $(F_o - F_c)$ syntheses and gradual change of scaling factor and B values for the different atoms. The final B values were 2.6 \AA^2 for carbon and oxygen, and 3.2 \AA^2 for hydrogen. At this stage the R index was 8.5%, but it became evident that the experimental data could not distinguish between sets of parameters differing by only a few parts in thousands. More exact temperature parameters would be required for this.

A study of the hydroxy hydrogen atom

The above mentioned results were used to transfer the F_o^D amplitudes to an absolute scale and to give them the correct signs. A Fourier analysis using these data is shown in Fig. 2, and confirms the validity of model I. It was, however, decided not to refine the F^D data further at this stage.

Assuming that the replacement of H by D produces no noticeable change in the positional parameters, a $(F_o^D - F_o^H)$ synthesis will give a Fourier map containing nothing but the differential contribution from both hydrogen atoms. If the coefficients are multiplied by the fraction $b_D/(b_D - b_H)$, a map will result with the proper density of a D atom, permitting a detailed study of that atom. The crucial point is of course the scaling factor. Several trials were made until a scaling factor for F_o^D was obtained which gave the correct signs and a reasonable scaling for both $(F_o^D - F_o^H)b_D/(b_D - b_H)$ and F_o^D . Extinction effects, termination-of-series error and anisotropy of thermal vibrations made this a difficult task. The resulting map, giving the parameters $x = 0.219$ and $y = 0.109$, is shown in Fig. 3. The agreement between the observed and calculated amplitudes, assuming isotropic thermal vibration of the D atom, was, however, poor.

With the parameters found by refinement of the F^H data (0.227, 0.110) the R index improved, but was still unsatisfactory (32%). The Fourier map indicated in fact anisotropic thermal motion of the D atom. Following the procedure described by Hughes (1941) and Cochran (1951), the structure factor may be written

$$F_{hko}(D) = b_D 4 \cos^2 2\pi \cdot \frac{1}{4} (h+k) \\ \times [\cos 2\pi (hx + ky) \exp \{ -(\alpha_D + \beta_D \cos^2 (\Phi - \Psi) s^2) \} \\ + \cos 2\pi (hy - kx) \exp \{ -(\alpha_D + \beta_D \sin^2 (\Phi - \Psi) s^2) \}].$$

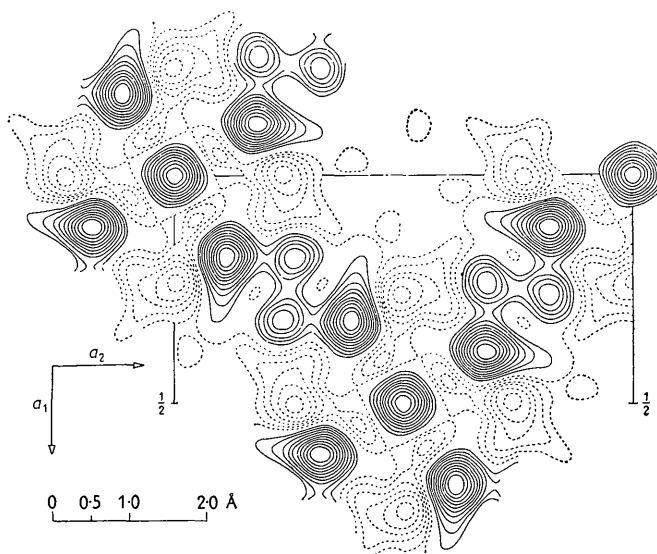


Fig. 2. Fourier projection on (001) of $C(CH_2OD)_4$. Same intervals as in Fig. 1.

Table 2. A survey of parameters found by X-rays and neutrons

X-rays	C ₁			O			H ₁			H ₂			H ₄		
	x	y	z	x	y	z	x	y	z	x	y	z	x	y	z
Llewellyn, Cox & Goodwin	162	123	097	317	247	002	—	—	—	—	—	—	—	—	—
Nitta & Watanabé	160	128	100	312	248	002	—	—	—	—	—	—	—	—	—
Cox, Cruickshank & Shiono	1628	1264	1059	3166	2475	0188	—	—	—	—	—	—	—	—	—
Neutrons															
Input parameters	163*	127*	102*	314*	245*	008*	254*	010*	174*	072*	244*	174*	212	093	—
Results model I	148	122	—	310	239	—	—	—	—	—	—	—	—	—	—
Results model III	154	121	—	316	244	—	—	—	—	—	—	—	—	—	—
$F_o^H - F_c^H((CH_2O)_4C)$	—	—	—	—	—	—	—	—	—	—	—	—	224	110	—
Output after four $(F_o^H - F_c^H)$ syntheses	156	127	—	307	243	—	240	013	—	058	255	—	227	110	—
F^D synthesis	—	—	—	317	237	—	—	—	—	—	—	—	—	—	—
Refined $(F_o^D - F_o^H)$ synthesis	—	—	—	—	—	—	—	—	—	—	—	—	229	108	—
Final result $\frac{F^H}{F^D}$	157	126	099*	310	243	004*	240	013	164*	065 067	254 250	177* 177*	229	108	003

The values with asterisk are calculated on the assumption of tetrahedral carbon valences.

α_D and β_D are constants, Ψ is the angle between the direction of maximum vibration and the x axis, and $(2s, \Phi)$ are the polar co-ordinates in the plane $l = 0$ of the reciprocal lattice.

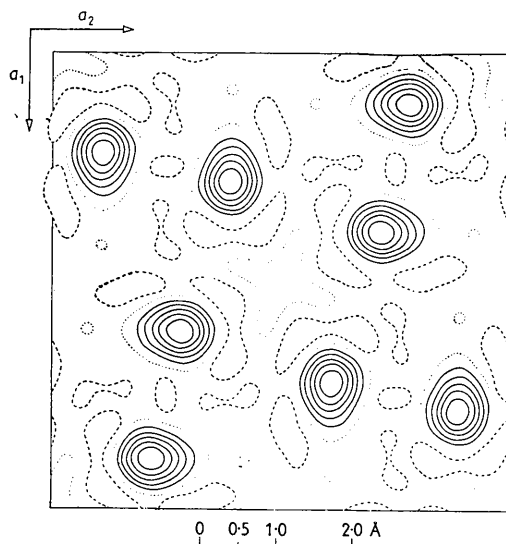


Fig. 3. Fourier projection of the deuterium atoms in pentaerythritol as seen along [001]. The plot is a synthesis of the function $\frac{b_D}{b_D - b_H} (F_o^D - F_o^H)$. Same intervals as in Fig. 1.

In order to study the effect of thermal vibration and termination-of-series error, several synthetic Fourier maps were prepared for various values of the parameters. The best fit was found for $x = 0.229$ and $y = 0.108$, Ψ being zero and the constants α_D and β_D being equal to 1.8 \AA^2 and 2.4 \AA^2 respectively. The displacement of the Fourier peak by 0.010 in the x direction should thus be interpreted as an effect of non-convergence of the coefficients.

The R index was still relatively high, evidently

owing to the large relative error ensuing in small $(F_o^D - F_o^H)b_D/(b_D - b_H)$ values when the errors in F_o^D and F_o^H happen to add up, and to extinction effects in both materials. If the intensities which are affected by extinction are left out, the R index drops to 17.8% for this atom.

A serious objection may be made to the procedure described, namely that the same thermal parameters are assumed for both H and D. The mean value of B is 3.0 \AA^2 , compared with 3.2 \AA^2 for the other hydrogen atoms. The true mean value for B_H is thus probably closer to 3.2 \AA^2 and somewhat lower than 3.0 \AA^2 for B_D . It is possible that this is responsible for some of the discrepancies found. The nature of the temperature function is also certainly too simple.

Final treatment of data

The hydroxy hydrogen parameters being determined, final difference syntheses were made with the F^H 's and F^D 's separately. The inclusion of the anisotropy of the hydroxy hydrogen atom and extinction effects on strong reflexions had some influence on the scaling factors, but no changes resulted in B values of the other atoms. Only minor changes in the parameters for C and O were found, but a discrepancy in the parameters for the methylene hydrogen H_2 between the two sets of data was revealed.

A survey over all parameters found during this work, in addition to X-ray results, is shown in Table 2.

The z parameters were determined by assuming tetrahedral angles for the carbon valences. They are in good agreement with the X-ray results of Llewellyn *et al.* and Nitta & Watanabé, but deviate somewhat from a recent report at the Montreal conference (1957) by Cox, Cruickshank & Shiono. The (00 l) neutron data could not distinguish between small variations, but showed at least that the hydroxy hydrogen atom had a z parameter value close to zero, determined in

fact by assuming it to lie in the plane defined by the oxygens O_1, O_2, O_3 . The B values in this direction were found by trial and error to be $B_C = B_O = 3.1 \text{ \AA}^2$ and $B_{H,D} = 3.5 \text{ \AA}^2$.

A survey of observed and calculated structure factors is shown in Table 3. The strongest intensities

Table 3. Observed and calculated structure factors for $C(CH_2OH)_4$ and $C(CH_2OD)_4$

(hkl)	F_O^D	F_C^D	F_H^H	F_C^H	$\frac{b_D}{b_D - b_H}(F_O^D - F_O^H)$	$F(D)_c$
110	3.33	3.52	2.73	2.78	0.38	0.51
220	6.81	7.11	7.70	8.61	-0.56	-0.91
330	4.05	4.27	3.37	3.24	0.43	0.62
440	<0.30	-0.34	2.64	2.94	-1.86	-2.12
550	1.30	-1.58	<0.30	0.12	-0.90	-1.11
200	4.37	-4.74	1.92	-2.04	-1.55	-1.71
310	2.64	2.57	1.20	-1.20	2.43	2.43
420	4.44	3.85	0.76	-0.92	3.29	2.95
530	1.02	0.57	1.22	0.94	-0.15	-0.23
640	1.65	1.57	1.36	1.42	0.18	0.14
400	3.45	-4.08	2.96	-3.29	-0.31	-0.52
510	1.97	1.28	2.58	2.56	-0.39	-0.72
620	0.58	0.57	1.16	1.15	-0.37	-0.31
600	1.41	1.28	3.65	3.91	-1.42	-1.66
710	2.56	-2.36	<0.30	-0.02	-1.60	-1.52
130	5.05	-6.16	<0.30	-0.07	-3.19	-3.89
240	<0.30	-0.66	1.83	-2.08	0.93	0.99
350	3.07	3.49	2.51	2.47	0.35	0.71
460	0.94	-0.84	0.61	-0.53	-0.21	-0.25
150	<0.30	-0.46	3.07	-2.88	1.75	1.45
260	3.97	4.25	1.72	1.61	1.42	1.65
170	5.72	5.63	4.11	4.11	1.02	0.74
002	12.49	15.41	7.36	7.57	3.25	4.96
004	6.08	7.88	0.65	1.05	3.44	4.34
006	1.82	0.64	5.12	-4.80	4.39	3.43
008	8.94	8.14	4.20	4.20	3.00	2.48
0010	5.98	6.18	3.56	3.60	1.53	1.63

The unobserved reflexions are included by taking half the minimum observable value.

are observed lower than they should be, and this is believed to be due to extinction effects. No attempts were made to correct for this, but the structure factor for (220) was left out in $F^H(hk0)$, and (220) and (130) in $F^D(hk0)$, when calculating the reliability indexes. These were 6.1% for $F^H(hk0)$ and 10.5% for $F^D(hk0)$.

Discussion

Atomic distances

Table 4 shows atomic distances in pentaerythritol, as found by X-rays and neutrons.

A very interesting feature is the short C_1-C_2 distance of 1.50 Å, which is in good agreement with the values found in many organic compounds with similar tetrahedral arrangement around a carbon atom. Cox, Cruickshank & Shiono put $z_{C_2} = 0.1059$, and this causes a considerable deviation from a tetrahedral angle and a larger C_1-C_2 distance.

At first it was assumed that the projection on (001) of $C_1C_2O_1$ and $H_1C_2H_2$ would be two straight lines intersecting at right angles, but if a twist occurs

Table 4. Atomic distances as found by X-rays and neutrons

The results presented for this investigation are based upon tetrahedral angles for the carbon valences

Distance	Llewellyn, Cox & Goodwin	Nitta & Watanabé	Cox, Cruick- shank & Shiono	This investi- gation
C_1-C_2 (Å)	1.50±0.03	1.53	1.548±0.011	1.50±0.02
C_2-O_1 (Å)	1.46±0.03	1.45	1.425±0.014	1.43±0.02
$O_1 \cdots O_2$ (Å)	2.69±0.03	2.70	2.705	2.74±0.02
C_2-H (Å)	—	—	—	1.09, 1.11 ±0.02
O-H } (Å)	—	—	—	0.94±0.03
O-D }	—	—	—	—

around the C_1-C_2 bond this symmetry breaks down. This is actually found to be the case. Assuming the plane defined by $C_1C_2O_1$ still to be a mirror plane for the methylene hydrogens, a shortening of the projection of C_2-H_1 and a lengthening of C_2-H_2 results. As the projected lengths of the C-H bonds are known from the parameters found, the angle of this plane with (001) could be calculated. The parameters obtained from the F^D data for the H_2 atom give an angle for the mirror plane of 86.3° with (001) and a C-H distance of 1.09 Å. The H_2 parameters found from the F^H data results in an angle of 85.3° and a C-H distance of 1.11 Å.

From the positions of $C_1C_2O_1$, however, one finds an angle of 88.6° for the mirror plane. This value is extremely sensitive to parameter variations, and the discrepancy can thus be regarded to be within the limits of error. It might also be due to an effect of non-equal C-H distances or deviation from tetrahedral arrangement.

The hydrogen bond

The length of the hydrogen bridge has been found 0.04 Å longer than reported by X-rays, and the O-H distance 0.06 Å shorter than assumed at the start of this work. The latter distance may be compared with the O-H distance in methyl alcohol of 0.937 Å, found by Ivash & Dennison (1953) by microwave spectra. Their C-O distance is 1.434 Å, which is in good agreement with the value found in this work. In the present investigation the hydroxy hydrogens have been assumed to lie exactly in the planes defined by the oxygen atoms. The O-H direction deviates, however, by 6° from the line connecting the oxygens, thus causing a C-O-H angle of 110°. This is a very important feature in the determination of the position and movement of the hydroxy hydrogen atom. If the hydrogen atom is placed according to model II, a very large deviation from linearity of $O \cdots H-O$ would occur, and this thus gives further support for model I. This is demonstrated in Fig. 4. Model I is also more favourable from packing considerations.

As for the vibration of the hydroxy hydrogen, the direction of maximum amplitude is neither normal to

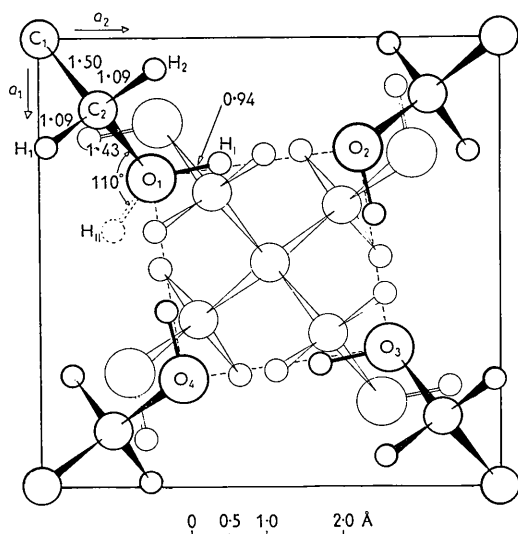


Fig. 4. The atomic arrangement in pentaerythritol, including hydrogen atoms. Heavy lines show molecules in (001), weak lines a molecule in $z = \frac{1}{2}$. The dotted line shows the hypothetical O-H bond for model II if the C-O-H angle is 110° .

the O-H direction, nor to the $O \cdots O$ bond, but has a direction corresponding to vibration in a plane normal to the C-O direction. This plane is defined by the angle C-O-H of 110° and the O-H distance of 0.94 Å. The H atom will thus, during its oscillation, describe a small arc which in projection takes the form of a slightly curved line almost parallel to the a axis. This explains why Ψ is found close to zero.

Anisotropy of the CH_2O group

It has been suggested by Gilbert & Lonsdale (1956) that pentaerythritol is an example of a molecule exhibiting torsional oscillations. Such an effect is not evident from the Fourier maps calculated from X-ray or neutron data. It was hoped that a synthesis of observed neutron amplitudes where the contribution from the hydroxy hydrogen atom was eliminated, i.e. a

$$\left[F_o^D - \frac{b_D}{b_D - b_H} (F_o^D - F_o^H) \right]$$

synthesis would eventually give a hint of such anisotropy, as the C_2 atom no longer is disturbed by the D_1 atom. The map shown in Fig. 5 gives, however, no positive indication in this direction. It is therefore believed that if such effects exist, they are probably small.

The ordering of the hydrogen atoms in pentaerythritol as found by this investigation is in agreement

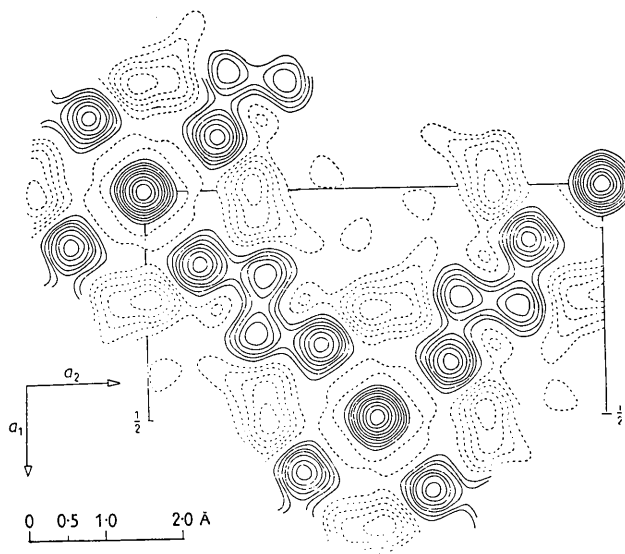


Fig. 5. Fourier projection on (001) of pentaerythritol where the contribution from the hydroxy hydrogen has been eliminated.

with the findings of D. H. Payne and E. F. Westrum jr. in a study of its thermodynamic properties (E. F. Westrum, University of Michigan, private communication).

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