

## On the Structure of Pentaerythritol

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### Abstract

Earlier crystallographic studies of pentaerythritol ( $C_5H_{12}O_4$ ) are reviewed. The structure has been refined, and errors in the published coordinates have been detected and corrected.

### Introduction

Pentaerythritol has been subjected to numerous crystallographic investigations. The early work consists of about eighteen papers, summarized by Wyckoff (1966). The structure, excluding H atoms, was determined by Llewellyn, Cox & Goodwin (1937), hereinafter LCG, and later by Nitta & Watanabé (1937). LCG measured X-ray intensities with both Cu  $K\alpha$  and Mo  $K\alpha$  radiations, and attained a precision of better than  $\pm 10\%$  in  $|F_o|$ . Shiono, Cruickshank & Cox (1958), hereinafter SCC, refined the data of LCG to  $R = 22.0\%$ , and, in addition, collected new intensities with Cu  $K\alpha$  radiation. These data were not published, and their precision is not reported, but the structure based on them was refined to  $R = 18.6\%$ . Hvoslef (1958) determined the positions of the H atoms by neutron diffraction. Only the  $hk0$  and  $00l$  reflexions were measured, and it will become clear that the published coordinates for the hydroxyl H atom are erroneous, possibly through an incorrect reconstruction of the spatial coordinates from the projections.

This situation came to light while the present author was preparing a stereoscopic illustration of  $C(CH_2OH)_4$ . Although the O–H length is acceptable, the C–O–H bond angle calculated with the published coordinates is  $44.5^\circ$ . These coordinates are also those listed by Wyckoff (1966), to which Kennard, Allen & Watson (1977) refer.

This paper is concerned with a further refinement of the structure, a correction of the coordinates of the hydroxyl H atom, and a discussion of the structure in the light of *ab initio* MO calculations.

### Experimental

It was clear that the data of LCG were susceptible to further refinement and, in the light of the number of

variables, compared favourably in quality and quantity with the later data of SCC. Thus, they were used, with the cell dimensions of SCC and space group  $I4$  ( $Z = 2$ ), to carry out a full-matrix least-squares refinement.

In the first instance, the heavy atoms were refined anisotropically, and a difference map was prepared. Two peaks of height about  $5 \text{ e } \text{\AA}^{-3}$  were found near the positions given for the methylene H atoms by Hvoslef (1958). The hydroxyl H atom was less clearly indicated, for reasons which will be discussed later. Peaks of height about  $2 \text{ e } \text{\AA}^{-3}$  were noted about  $1 \text{ \AA}$  from the O atom, along the O...O vectors in the (001) plane and approximately parallel to both **a** and **b**, and a choice could not be made from the difference map alone. Since the work of Hvoslef (1958) showed one similar orientation of the hydroxyl H atom, with no indication of a disordered structure, the position along O...O in the **b** direction was taken to be confirmed. The structure was then refined to  $R = 10.9\%$ . While refinement of the H atoms as well reduced  $R$  to  $10.5\%$ , the bond lengths and angles involving H atoms tended to rather erratic values. Consequently, the results reported here are based on the interpretation of the difference map. The refinement was conducted with the *CRYLSQ* link of XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), with the form factors contained therein, and the bond lengths and angles were calculated through the *BONDLA* link.\*

### Discussion

The fractional coordinates and thermal parameters are listed in Table 1, bond lengths and angles in Table 2. The bond lengths and angles are not significantly different from standard values. The corresponding values obtained from the earlier studies are also listed in Table 2 for comparison. It seems probable that the coordinates given by Hvoslef (1958) for the hydroxyl  $H_A$  should be changed to  $\frac{1}{2} - x, \frac{1}{2} - y, z$ . The e.s.d.'s of the coordinates and bond lengths are comparable with those given by SCC. In view of the present refinement,

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34276 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and thermal parameters* ( $\text{\AA}^2$ )

The temperature factor is of the form  $\exp[-2\pi^2(h^2 a^{*2} U_{11} + \dots + 2hka^* b^* U_{12} + \dots)]$ , anisotropic, and  $\exp(-8\pi^2 U \lambda^{-2} \sin^2 \theta)$ , isotropic.

	C(1)	C(2)(methylene)	O	H(1)	H(2)	H(3)(hydroxyl)
<i>x</i>	0	0.1607 (25)	0.3194 (14)	0.240	0.070	0.270
<i>y</i>	0	0.1231 (21)	0.2462 (14)	0.010	0.250	0.390
<i>z</i>	0	0.1108 (17)	0.0214 (13)	0.160	0.180	0.000
$U_{11}$	0.0116 (55)	0.0214 (61)	0.0146 (39)			
$U_{22}$	0.0116 (55)	0.0163 (59)	0.0144 (39)			
$U_{33}$	0.0282 (204)	0.0207 (75)	0.0374 (65)			
$U_{12}$	0	-0.0082 (45)	0.0067 (37)			
$U_{13}$	0	-0.0045 (97)	0.0044 (62)			
$U_{23}$	0	-0.0121 (82)	-0.0026 (64)			
$U$				0.05	0.05	0.05

Table 2. *Bond lengths* ( $\text{\AA}$ ) *and angles* ( $^\circ$ )

	This work	LCG	SCC	Hvoslef
C(1)–C(2)	1.566 (14)	1.50 (3)	1.548 (11)	1.50 (2)
C(2)–O	1.450 (17)	1.46 (3)	1.425 (14)	1.43 (2)
C(2)–H(1)	0.94			1.09 (2)
C(2)–H(2)	1.12			1.11 (2)
O–H(3)	0.94			0.94 (3) <sup>a</sup>
H(3)⋯O <sup>b</sup>	1.78			
O⋯O <sup>b</sup>	2.706 (12)	2.69 (3)	2.70	2.74 (2)
C(2)–C(1)–C(2) <sup>c</sup>	112.4 (7)	111.5	110.9 (5)	
C(2)–C(1)–C(2) <sup>d</sup>	103.7 (8)	108.5	106.7 (12)	
C(1)–C(2)–O	109.3 (10)	111.5	111.1 (10)	
C(1)–C(2)–H(1)	105			
C(1)–C(2)–H(2)	111			
O–C(2)–H(1)	106			
O–C(2)–H(2)	105			
H(1)–C(2)–H(2)	121			
C(2)–O–H(3)	112			

(a) Not confirmed by the coordinates listed. (b)  $y$ ,  $1-x$ ,  $\bar{z}$  or  $1-y$ ,  $x$ ,  $\bar{z}$ .  
(c)  $\bar{y}$ ,  $x$ ,  $\bar{z}$ . (d)  $\bar{x}$ ,  $\bar{y}$ ,  $z$ .

it would seem likely that the e.s.d.'s quoted by SCC are too low by a factor of at least two.

The structure of pentaerythritol and the molecular packing are illustrated in Fig. 1. The hydrogen bond links molecules in the (001) plane, and the O–H⋯O link is linear, within experimental error. There are no other unusual van der Waals contacts in the crystal.

An *ab initio* MO calculation has been carried out. The total electronic energy  $E$  has been determined as a function of the rotation angle  $\phi$  of O–H(3) with respect to O–C(2), with the result shown in Fig. 2. The deep minimum at  $\phi = 180^\circ$  corresponds to a planar *trans* C(1)–C(2)–O–H(3) chain, and that at  $0^\circ$  corresponds to the chain in a planar *cis* form. In the crystal, hydrogen bonding maintains  $\phi$  at  $90^\circ$  ( $270^\circ$ ), the least stable position in the free molecule, where H(3) is eclipsed by H(1) and H(2). The calculation also indicated the number of electrons associated with each atom:

C(1)	C(2)	O	H(1)	H(2)	H(3)
6.0	6.0	8.6	0.9	0.9	0.6.

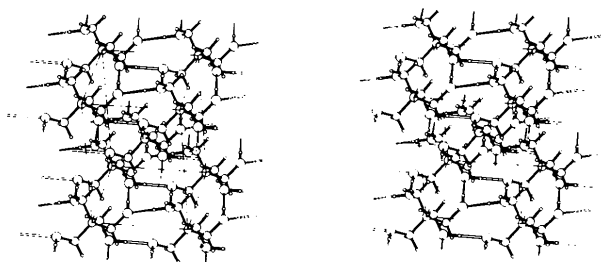


Fig. 1. Stereoscopic illustration of the crystal structure of pentaerythritol; the viewing direction is approximately along  $[-1, \frac{1}{2}, \frac{1}{2}]$ . The illustration was prepared by PLUTO (W. D. S. Motherwell, Cambridge); hydrogen bonds are shown by double lines.

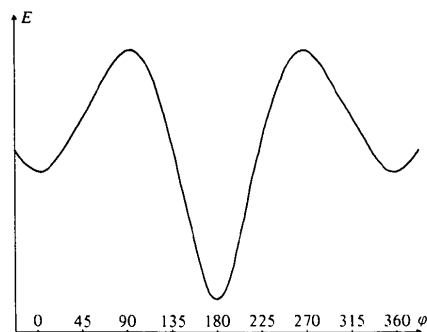


Fig. 2. Variation of total electronic energy  $E$  as a function of  $\phi$ , the angle of rotation of H(3)–O with respect to O–C(2), from an *ab initio* MO calculation. The free molecule corresponds to  $\phi = 180^\circ$ , but in the crystal hydrogen bonding constrains  $\phi$  to  $90^\circ$  ( $270^\circ$ ).

This result is significant. It shows how it is reasonable to obtain the positions of H(1) and H(2) from the difference map while that of H(3) is ambiguous [its height is commensurate with  $\sigma(\rho_o)$ ]. It is clear also that the neutral-atom scattering factor for O does not represent this species precisely in this structure. Again, the difference map provides evidence in support of this: the maximum of  $\rho_o - \rho_c$  at the O atom site was  $3 \text{ e } \text{\AA}^{-3}$  whereas at C(1) and C(2) the values were zero.

The earlier papers commented upon a short C—C bond and on extinction effects. These results are not supported by this work; the inclusion of an extinction parameter in the least-squares calculations had a negligible effect on the refinement.

*Note added in proof:* An independent report by Eilerman & Rudman (1979) on the structure of pentaerythritol appears in this issue. This work uses new data, and represents a higher degree of refinement. However, the differences in molecular geometry are, in the main, not significant at the  $3\sigma$  level. The changes in sign of the atomic  $z$  coordinates relate, of course, to the crystal structure and not that of the molecule. The most marked differences arise in the O—H...O geometry where Eilerman & Rudman, in quoting the results in their Table 2 with little reservation, may have placed too much weight on the least-squares coordinates for hydrogen. This author is indebted to D. Eilerman and R. Rudman for the privilege of reading a copy of their paper before publication.

### References

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