Neutron Diffraction Refinement of the Structure of Pentaerythritol

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The crystal structure of pentaerythritol, $[C(CH_2OH)_4]$, has been refined to $R_w(F) = 0.042$ and $S = 1.40$ for 1118 observed neutron intensities collected at room temperature (294 K) for a unit cell of dimensions $a = b = 6.079(3)$, $c = 8.745(4)$ Å, and space group $I\bar{4}$, $Z=2$, $V = 323.2$ Å^3, $D_c = 1.399$ g cm^{-3}. The bond lengths uncorrected for librational motions are C(C)–C(1) 1.529(2); C(1)–O(1) 1.422 (3); C(1)–H(11) 1.070(6); C(1)–H(12) 1.081(6); O(1)–H(01) 0.933(6) Å. The O···O, H···O hydrogen-bond lengths and O–H···O angle are 2.698(3) Å, 1.790 (4) Å and 163.6(3)°, respectively. The hydrogen bonds form closed quadrilaterals around the $\bar{4}$ axes.

The first determinations of the structure of pentaerythritol, $[C(CH_2OH)_4]$, were reported in 1937 by Llewellyn *et al.*,[1] and by Nitta and Watanabé.[2-3] The structure was subsequently redetermined and refined several times,[4-7] most recently by Eilerman and Rudman,[5] and also by Ladd.[6] The structure was investigated using neutron diffraction by Hvoslef[7] in his now classical work where he located the protons (deuterons) in an $[F_0(D)-F_0(H)]$ differential synthesis based on $hk0$ and $00l$ data. The symmetry of the molecule in the solid state was a point of discussion for a long while until the crystals were established to be tetragonal with space group $I\bar{4}$. Thus, the maximum molecular symmetry is preserved in the solid state, i.e. the asymmetric unit is one quarter of the molecule. Pentaerythritol has attracted interest for other reasons as well. Like many other polyhydroxymethyl compounds, pentaerythritol undergoes a phase transition to a plastic, orientationally disordered cubic phase at elevated temperatures (T_c = 453 K for pentaerythritol).[5,8,9] Pentaerythritol is a model compound for the other members of this series and has therefore been studied widely. Quite recently there has been renewed interest in these materials because the enthalpy change of the transition is sufficiently large to be of potential use in thermal energy storage systems for solar energy applications.[10] Inasmuch as a full three dimensional neutron structure determination was still lacking, the present work was undertaken. This seemed justified not only because of an error in one of the protonic coordinates in the previous neutron study[11] but also because the non-bonded interactions between layers of molecules are entirely dominated by hydrogen-to-hydrogen interactions of the methylenic hydrogen atoms. At a completion of this work, a study at several temperatures between 25 K and room temperature of the homologous $[C(CH_2OD)_4]$ was brought to our attention.[12] Only preliminary results from this study are as yet available.

Experimental

A crystal of volume 51.2 mm^3 with faces {101}, (001) was obtained by slow evaporation from aqueous solution acidified with hydrochloric acid. It was mounted approximately parallel to [001] on an aluminium pin. The neutron diffraction data were collected at room temperature at the JEEP-II reactor at IFE, Kjeller on the CIRCUS four-circle instrument. The cell dimensions and their standard deviations were obtained by least-squares refinements of 2θ values for 31 high angle reflections. The neutron wavelength, 1.256 (1) Å, was determined by measurements on a

Table 1. Crystal data for pentaerythritol [2,2-bis(hydroxymethyl)-1,3-propanediol].

Measurements at 294 K

$a = b = 6.079(3)$ Å
$c = 8.745(4)$ Å
$\lambda = 1.256(1)$ Å

Space group: $I\bar{4}$

Equivalent positions (0,0,0;1/2,1/2,1/2): x,y,z; $-x,-y,z$; $y,-x,-z$; $-y,x,-z$

systematic absences hkl: $h + k + l = 2n + 1$

Crystal mass: 73.5 mg

Absorption coefficient, μ: 2.50 cm^{-1}

Volume of crystal: meas. 51.2 mm^{-3}, calc. 52.6 mm^{-3}

Faces	h	k	l	d/cm[a]	h	k	l	d/cm
	0	0	−1	1.25	0	1	1	1.65
	1	0	1	1.95	0	−1	1	1.65
	−1	0	1	1.95				

[a]Distance from arbitrary origin inside crystal.

standard NaCl crystal. Crystal data are given in Table 1. All accessible reflections with $h+k+l = 2n$ within the sphere for $2\theta < 100°$ were measured using a $\theta/2\theta$ step scan. Scan widths were determined from the relation $\Delta 2\theta = (2.15° + 9.5° \tan\theta)$ for the high-angle data ($40° < 2\theta < 100°$) and were held fixed at 5.1° for the low-angle data ($2\theta < 40°$). Prior to data collection a check of the conditions for systematically absent reflections was carried out. The intensity of one reflection monitored at regular intervals did not vary significantly during the course of the experiment. The 1120 intensity data collected were corrected for absorption using an analytical procedure.[13] The linear absorption coefficient was determined from a transmission experiment employing a crystal of known thickness.

The starting atomic positional and thermal parameters were taken from Eilerman and Rudman.[5] Refinement of the structure parameters was by full-matrix least-squares minimization of the quantity $\Sigma w(|F_0^2|-|F_c^2|)^2$ taking $w^{-1} = \sigma_c^2 + (0.02 \cdot F_0^2)$, where σ_c^2 is the variance derived from counting statistics. The neutron coherent scattering amplitudes (fm), −3.74 for H, 6.65 for C, 5.80 for O, were taken from Koester.[14] The 54 parameters varied in the latter stages of the refinements included one scale factor, the atomic positional and thermal parameters, and the six anisotropic extinction parameters for a type I crystal with a Lorentzian distribution of mosaicity and anisotropy according to Thornley and Nelmes.[15] The indices of fit at convergence were $R_w(F^2) = 0.075$, $R_w(F) = 0.042$ and $S = 1.40$ for the 1118 observed intensities. Two reflections were found to have $E < 0.50$ and were excluded from the refinement. The components of the anisotropic extinction tensor had the least-squares values $g_{11} = 4.3(5)$, $g_{22} = 12.7(4)$, $g_{33} = 1.4(2)$, $g_{12} = -0.1(3)$, $g_{13} = 0.2(1)$, $g_{23} = 0.2(1)$ $rad^{-1} \times 10^{-4}$. For further details of the experimental set-up and program library, see Ref. 16. A list of observed and calculated structure factors is available from the author on request.

Discussion

Final positional parameters are given in Table 2, and anisotropic thermal parameters in Table 3. Fig. 1 shows a drawing of the molecule. The X-ray structure determination by Eilerman and Rudman[5] is confirmed in the present study. Theirs is the most accurate of the previous studies and will serve as comparison below. Also, the atom numbering scheme from their work is adopted in the present work. Each molecule is hydrogen-bonded to four neighbouring molecules in the basal plane by eight hydrogen bonds. The hydrogen-bond system forms quadrilaterals around the $\bar{4}$ axes in the (001) planes. The contacts between the molecule at the origin and those at the cell centres are through the hydrogen atoms and are of purely van der Waals or London type, which explains the easy cleavage along the (001) basal planes. We find H(11)···H(11) to be 2.563(7) Å and H(12)···H(12) to be 2.666(7) Å,

Table 2. Positional parameters. Estimated standard deviations (in parentheses) refer to the last digit given.

Atom	x	y	z
C(C)	0.0	0.0	0.0
C(1)	0.15832(27)	0.12586(29)	−0.10388(20)
O(1)	0.31717(27)	0.24829(34)	−0.02029(27)
H(11)	0.24476(82)	0.01112(71)	−0.17450(52)
H(12)	0.06654(78)	0.23629(73)	−0.17684(49)
H(01)	0.26674(58)	0.39052(55)	−0.00104(47)

Table 3. Anisotropic thermal parameters (Å^2×10^4). The anisotropic thermal parameter is of the form exp[$-2\pi^2$ ($U_{11}a^{*2}h^2$ +···+ $2U_{23}b^*c^*kl$)]. Estimated standard deviations (in parentheses) refer to the last digit.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(C)	224(14)	224[a]	343(14)	0	0	0
C(1)	422(9)	393(9)	449(9)	−62(6)	91(8)	28(8)
O(1)	317(9)	436(13)	824(15)	−63(9)	7(9)	−56(10)
H(11)	764(24)	713(22)	728(21)	−212(22)	379(19)	−166(23)
H(12)	710(28)	726(21)	756(22)	−138(22)	−85(21)	−315(22)
H(01)	551(17)	390(20)	849(21)	−68(14)	65(18)	−18(19)

[a] $U_{11} = U_{22}$.

which is, as expected, slightly shorter than the value of 2.70(3) Å given in Ref. 5.

There are minor discrepancies between the values of the cell parameters in the two studies. Pentaerythritol is reported to form polymerization products during crystallization unless a small quantity of mineral acid is added.[17] Also, the crystals are reported to include traces of water between the layers.[8] We therefore think that the observed differences may be real and that the cell parameters may be sample-dependent.

The coordinates of C(1) in the two studies show good agreement, the largest discrepancy being about 2σ(c) for the z parameter where $\sigma^2(c) = [\sigma^2(n) + \sigma^2(x)]$. Larger discrepancies exist for the oxygen atom, where the position of this atom has been moved roughly 0.013 Å into the region of the lone pairs in the X-ray study.

Expectedly, larger discrepancies are found between the two sets of hydrogen coordinates, and it may well be said that the major improvement of the present work over the previous[5] lies in the more accurate determinations of the parameters of the hydrogen atoms. This is even more evident when the thermal parameters are compared. Eilerman and Rudman[5] also carried out refinement with anisotropic thermal parameters for the hydrogen atoms (Ref. 5 supplementary material); as expected, not much physical information is attached to their values. The thermal motions of the two methylene atoms as probed with neutrons are nearly isotropic and show a large increment over those of the atom to which they are bound. The H(01) atom also has thermal motions somewhat larger than O(1), but shows a similar anisotropy in the motion perpendicular to the hydrogen bond direction. The thermal parameters of the heavy atoms are slightly larger in the present study but also more isotropic. Owing to the possible presence of residual systematic errors due to inadequate extinction corrections in this or both studies, the agreement is considered satisfactory.

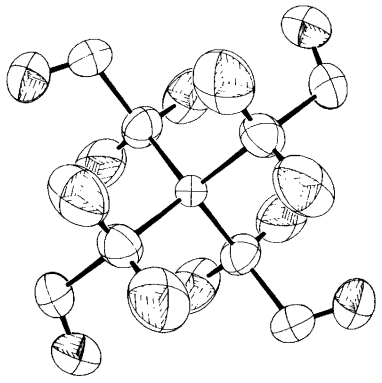

Fig. 1. The pentaerythritol molecule viewed along the unique axis (c). Thermal ellipsoids at 50 % probability as determined by neutron diffraction.

Geometrical details of the molecule are given in Table 4. Bond lengths and angles for the heavy atoms are in perfect agreement in the two studies; the bond lengths involving the hydrogen atoms show the usual foreshortening associated with displacement of valence electrons in the X-ray work.

There is also good agreement between the results presented here and those of the neutron diffraction study of d_4-pentaerythritol at 295 K.[15] Minor differences may probably be attributed to isotope effects.

Bond lengths between carbon and oxygen

Table 4. Some geometrical details of the structure of pentaerythritol, with standard deviations in parentheses.

Bond distances/Å	
C(C)–C(1)	1.529(2)
C(1)–O(1)	1.422(3)
C(1)–H(11)	1.070(6)
C(1)–H(12)	1.081(6)
O(1)–H(01)	0.933(6)
Bond angles/°	
C(1)–C(C)–C(1)^{A}	107.1(3)
C(1)–C(C)–C(1)^{B}	110.7(3)
C(C)–C(1)–O(1)	112.6(2)
C(1)–O(1)–H(01)	110.8(3)
C(C)–C(1)–H(11)	109.0(3)
C(C)–C(1)–H(12)	109.7(3)
O(1)–C(1)–H(11)	107.7(3)
O(1)–C(1)–H(12)	109.2(3)
H(11)–C(1)–H(12)	108.5(4)
Torsion angles/°	
C(1)^{A}–C(C)–C(1)–O(1)	−179.2(3)
C(1)^{A}–C(C)–C(1)–H(11)	−59.7(3)
C(1)^{A}–C(C)–C(1)–H(12)	59.0(3)
C(1)^{B}–C(C)–C(1)–O(1)	−60.1(3)
C(1)^{B}–C(C)–C(1)–H(11)	61.0(3)
C(1)^{B}–C(C)–C(1)–H(12)	179.7(3)
C(1)^{C}–C(C)–C(1)–O(1)	58.5(3)
C(1)^{C}–C(C)–C(1)–H(11)	179.5(3)
C(1)^{C}–C(C)–C(1)–H(12)	−61.7(3)
$^{A}(-x,-y,z)$, $^{B}(y,-x,-z)$, $^{C}(-y,x,-z)$	
Hydrogen bond dimensions/Å	
O···O	2.698(3)
O···H	1.790(4)
O–H	0.933(5)
O–H···O	163.6(3)

atoms also compare well with those given for the C–CH_2–OH group in the low-temperature determination of the structure of erythritol using neutrons,[18] while those involving hydrogen atoms show additional thermal foreshortening in the present work.

Deviations from ideal geometry can be explained in terms of non-bonded repulsions. These occur mainly between neighbouring substituents around the $\bar{4}$ axes. For this reason the C(1)–C(C)–C(1)^{A} angle, between opposite groups, is closed to 107.1°, while C(1)–C(C)–C(1)^{B}, between vicinal groups, is opened to 110.7° (see Table 4). The non-bonded distance H(11)···H(12)^{A} remains reasonably long, 2.418(6) Å. The deviations in the H(11)–C(1)–H(12) and the O(1)–C(1)–H(11) angles are also explicable along these lines. These are almost certainly due to the non-bonded repulsions between H(01) and H(12), and H(01) and H(11)^{B} [2.174(6) Å and 2.449(6) Å, respectively]. Other non-bonded terms affecting the methylene group occur in pairs with counteracting members.

The bond orientation about the C–C bond is close to the ideal staggered arrangement, with the torsion angles differing from 60° by a maximum of 1.7°, or roughly 3σ.

The quadrilateral hydrogen bond arrangement is similar to that found in erythritol,[18] except that it is ordered and that the O···O length is shorter in pentaerythritol [2.698(3) Å vs. 2.734 Å].

Neutron diffraction studies of d_4-pentaerythritol in the temperature range 25 K and up to room temperature are under way.[12] Considering the tetragonal-to-cubic phase transition at 453 K, neutron studies above room temperature, including inelastic scattering, would be very valuable. The crystal and molecular structure of pentaerythritol is particularly simple; their symmetries are high, yet the structure displays atoms in a very varied bonding environment. Good quality single crystals are relatively simple to obtain, and detailed information on static and dynamic properties available from the various neutron scattering technique should be within reach.

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