

The Crystal Structure of 2,7-Dimethyl-2,7-octanediol Tetrahydrate

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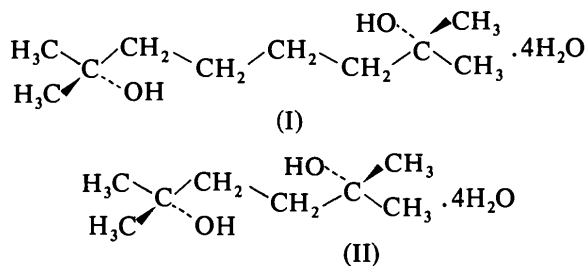
The crystal structure of 2,7-dimethyl-2,7-octanediol tetrahydrate, $\text{HO}(\text{CH}_3)_2\text{C}(\text{CH}_2)_4\text{C}(\text{CH}_3)_2\text{OH} \cdot 4\text{H}_2\text{O}$, is monoclinic $P2_1/n$ with $a = 6.126$ (5), $b = 6.128$ (5), $c = 21.12$ (1) Å, $\beta = 91.66$ (6)°, $Z = 2$. It is a water-layer structure, related to that of 2,5-dimethyl-2,5-hexanediol tetrahydrate [Jeffrey & Shen, *J. Chem. Phys.* (1972), 57, 56–61]. The hydroxyl and water O atoms form the vertices of a hydrogen-bonded layer of face-sharing pentagons. The O...O distances in these layers are between 2.774 and 2.831 Å. The two symmetry-independent pentagons of hydrogen-bonded O atoms are non-planar, with envelope and twist conformations. The layers are separated by the hydrocarbon chains in parallel alignment. There is approximate twofold disorder in the orientation of the octanediol molecules between the layers.

Introduction

Hexahydrates have been reported for several methyl-substituted glycols, *i.e.* for *meso*-2,3-butanediol, 2-methyl-2,3-butanediol, 2,3-dimethyl-2,3-butanediol (pinacol) and 2,5-dimethyl-2,5-hexanediol, but not for higher members of the series (Hatt, 1956).

Jeffrey & Shen (1972) were unable to obtain 2,5-dimethyl-2,5-hexanediol hexahydrate, but crystallized and determined the structure of the tetrahydrate. This tetrahydrate is structurally related to pinacol hexahydrate (Kim & Jeffrey, 1970) and piperazine hexahydrate (Schwarzenbach, 1968). All three structures contain layers of hydrogen-bonded O atoms forming the vertices of sheets of buckled face-sharing pentagons. In the hexahydrates, these layers consist entirely of water molecules, whereas in the tetrahydrate, one-third of the O atoms are the hydroxyls of the dimethylhexanediol molecules. In the hexahydrates, the hydrogen bonds between the water molecules and the functional groups of the glycol or diamine molecules form well defined cages which enclose the methyl or methylene groups. For this reason they could be described as semi-clathrates by analogy with the higher hydrates of the aliphatic amines (Jeffrey, 1969; Jeffrey, Jordan & McMullan, 1967). In the tetrahydrate, the additional chain length of the hexanediol molecule was such that the pentagonal water layers could not be bridged by hydrogen bonds to form cages. The glycol hydroxyls are included in the pentagonal layers and the hydration number reduces from six to four. The hydrogen-bonded lattice of the hexahydrates, which is a framework with voids, becomes an extended layer structure for the tetrahydrates.

The structure of 2,7-dimethyl-2,7-octanediol tetrahydrate (I), herein reported, is a second example of this hydrocarbon–water layer type of structure, the first being that of 2,5-dimethyl-2,5-hexanediol tetrahydrate (II), reported by Jeffrey & Shen (1972).



Experimental

Deliquescent colorless prisms, melting 45°C below the m.p. of a specimen of the anhydrous 2,7-dimethyl-2,7-octanediol, were obtained by cooling a saturated solution to 2°C. The specimen of the anhydrous compound was obtained from the Chemical Samples Company. Most crystals of the hydrate were twinned or multiple and unsuitable for single-crystal X-ray study when observed under the polarizing microscope and by measures of Weissenberg photographs. A crystal which appeared to be single and untwinned was obtained and mounted about the a axis within its mother liquor in a 0.3 mm capillary. Oscillation, zero and first-layer Weissenberg photographs showed no evidence of twinning. The crystal data and those pertaining to the intensity measurements are given in Table 1. The non-standard space-group setting $P2_1/n$ was selected in order to permit comparison with the other pentagonal layer hydrate which shows a progressive increase in the c dimension with increase of hydrocarbon chain length (see Table 2).

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Of the 283 unobserved intensities with $I < 2\sigma(I)$, 87 corresponded to the systematic extinctions for space group $P2_1/n$. The reflection 010 and six reflections of the type $l0l$ with l even were observed together with 27 other $h0l$ reflections with $h + l = 2n + 1$ for which $5\sigma > I > 2\sigma$.

The sharpened Patterson synthesis was examined for features inconsistent with space group $P2_1/n$, but none were found. The structure was then solved using *MULTAN* (Germain, Main & Woolfson, 1971) on 181 reflections with $|E| \geq 1.5$. The E map showed the three symmetry-unique O atoms and five C atoms, in a structure which corresponded to a tetrahydrate with centrosymmetric octanediol molecules centered at $(0,0,0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The R factor was then 0.30. A difference map revealed the presence of a second set of octanediol molecules in a different orientation centered at the alternate symmetry centers at $(0,0,\frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$. Giving both hydrocarbon chains equal weight, isotropic, followed by anisotropic, refinement reduced the

R value to 0.12. The near equality of the temperature factors for the atoms which were not common to both chain orientations, *i.e.* C(1) and C(1*), indicated that a 50/50 disorder was correct. A difference map then showed no additional electron density other than that of the H atoms, which were in reasonable positions with respect to the atoms to which they were attached. The H atoms attached to the O atoms were given the positions observed on the difference maps. Those attached to the C atoms were adjusted to be consistent with tetrahedral valence C—C—H angles. At $R = 0.105$ and 0.077, with and without the unobserved reflections (including the 'observed' systematic extinctions), the difference map showed no features greater than $0.3 \text{ e } \text{Å}^{-3}$. The atomic scattering factors used were those of Cromer & Waber (1965) for C and O, and those of Stewart, Davidson & Simpson (1965) for H.

An attempt was then made to account for the 34 non-space-group reflections of which eight had $|F|$ values greater than 5σ . Since space groups $P2$ and Pm were incompatible with the water-hydroxyl layer structure, a refinement was carried out in $P\bar{1}$. This converged at an R_F of 0.18, 0.14 and an R_{wF} of 0.21. The higher-symmetry space group $P4_2/m$, which is the pseudosymmetry of the structure, is eliminated by the β angle, measured both by film and diffractometer methods. In the absence of a model for the disorder which would remove the centrosymmetric symmetry, refinement in $P1$ was not attempted.

Of the three alternative explanations (a twinned crystal, multiple reflections, or a more complex disorder of the alkyl chains) the former was eliminated by the absence of other additional reflections and the success of the refinement in giving a reasonable structure without any anomalies in the molecular dimensions or thermal parameters. Of the two other explanations, the latter seems the more likely, but we were unable to definitely solve this question either by refinement in lower-symmetry space groups, or by examination of films or difference Fourier syntheses. A low-temperature study of the structure using Mo $K\alpha$ radiation might resolve this problem, if it provided the necessary additional observational data to refine the atomic parameters in the low-symmetry structure.

Table 1. *Crystal data and experimental and refinement parameters*

Crystal data	
$C_{10}H_{22}O_2 \cdot 4H_2O$, $M_r = 246.3$, m.p. $54 \pm 1^\circ\text{C}$	
Space group $P2_1/n$, $Z = 2$	
$a = 6.126$ (5), $b = 6.128$ (5), $c = 21.12$ (1) Å, $\beta = 91.66$ (6)°	
$V = 792.51 \text{ Å}^3$	
$D_m = 1.07 \text{ g cm}^{-3}$ at 23°C by flotation in <i>n</i> -hexane/bromobenzene	
$D_x = 1.032 \text{ g cm}^{-3}$	
$\mu(\text{Cu } K\alpha) = 7.4 \text{ cm}^{-1}$	
$\lambda(\text{Cu } K\alpha) = 1.5418 \text{ Å}$	
Intensity collection data	
Crystal dimensions	0.28 × 0.24 × 0.12 mm
Diffractometer	CAD-4, θ - 2θ mode to limit $2\theta = 140^\circ$
	Scan width (0.75 + 0.25 tan θ)°
Radiation	Graphite-monochromated Cu $K\alpha$
Number of data	1296, of which 283 had $I < 2\sigma(I)$
Refinement data	
Refinement of $R = \Sigma w(F_o - k F_c)^2$, with $w = (A + B F_o + C F_o^2)^{-1}$, where $A = 0.43$, $B = -0.01$, $C = 0.003$	
Final $R_F = 0.105$ (0.077 without unobserved and forbidden reflections)	
Final $R_{wF} = 0.101$	

Table 2. *Melting points, unit-cell dimensions and space groups of the hydrates with pentagonal hydrogen-bonded layer structures*

Formula	m.p.	a	b	c	β	Space group	Reference
$\text{HN}(\text{CH}_2)_4\text{NH} \cdot 6\text{H}_2\text{O}$	44°C	6.309 Å	6.323 Å	14.912 Å	95°	$P2_1/n$	Schwarzenbach (1968)
$\text{HO}(\text{CH}_2)_2\text{C} \cdot \text{C}(\text{CH}_2)_2\text{OH} \cdot 6\text{H}_2\text{O}$	45	5.398	6.398	15.926	90	$P4_2/mnm$	Kim & Jeffrey (1970)
$\text{HO}(\text{CH}_2)_2 \cdot \text{C} \cdot (\text{CH}_2)_2 \cdot \text{C} \cdot (\text{CH}_2)_2\text{OH} \cdot 4\text{H}_2\text{O}$	39	6.158	6.169	17.854	101.8	$P2_1/c$	Jeffrey & Shen (1972)
$\text{HO}(\text{CH}_2)_2 \cdot \text{C} \cdot (\text{CH}_2)_4 \cdot \text{C} \cdot (\text{CH}_2)_2\text{OH} \cdot 4\text{H}_2\text{O}$	54	6.126	6.128	21.120	91.7	$P2_1/n$	This work

Table 3. Fractional atomic coordinates (non-hydrogen $\times 10^4$, hydrogen $\times 10^3$) and isotropic temperature factors ($\times 10^3$), with estimated standard deviations in parentheses

O(1), C(3) and C(5) are common to both dimethyloctanediol molecules and have occupancy factors of 1.0. C(1), C(2), C(4), C(1*), C(2*) and C(4*) are resolved in the two molecules and have occupancy factors of 0.5. Hydrogen atoms attached to O(1), O(2), O(3), and C(5) have occupancy factors of 1.0; those attached to C(1), C(2), C(4), C(1*), C(2*), C(4*) have occupancy factors of 0.5.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
O(1)	1764 (4)	6582 (4)	1734 (1)	495
O(2)	-1520 (5)	3343 (6)	1787 (2)	515
O(3)	-4975 (4)	4776 (5)	2507 (1)	515
C(1)	1014 (13)	9445 (14)	143 (3)	403
C(2)	625 (14)	8424 (15)	799 (3)	303
C(3)	2542 (5)	7431 (1)	1141 (1)	303
C(4)	3552 (16)	5539 (15)	800 (4)	228
C(5)	4290 (8)	9140 (9)	1317 (2)	228
C(1*)	4458 (16)	6045 (15)	144 (3)	324
C(2*)	3469 (17)	5476 (15)	782 (4)	324
C(4*)	574 (13)	8409 (18)	776 (4)	509
H1(O1)	77 (6)	537 (7)	179 (2)	509
H1(O2)	-86 (7)	224 (8)	196 (2)	463
H2(O2)	-255 (7)	414 (7)	194 (2)	463
H1(O3)	-546 (5)	365 (6)	278 (2)	338
H2(O3)	-594 (6)	534 (6)	226 (2)	338
H1(C1)	223 (10)	1036 (11)	19 (3)	473
H2(C1)	155 (11)	814 (11)	-18 (3)	473
H1(C2)	-50 (9)	725 (10)	72 (2)	338
H2(C2)	-12 (9)	962 (10)	111 (3)	338
H1(C4)	439 (10)	453 (11)	107 (3)	473
H2(C4)	252 (11)	479 (11)	57 (3)	473
H3(C4)	435 (10)	571 (10)	41 (3)	338
H1(C5)	560 (6)	817 (6)	154 (2)	473
H2(C5)	490 (6)	952 (6)	92 (2)	473
H3(C5)	347 (6)	1054 (7)	155 (2)	338
H1(C1*)	313 (11)	660 (11)	-18 (3)	463
H2(C1*)	566 (12)	732 (12)	21 (3)	463
H1(C2*)	478 (10)	477 (10)	108 (3)	338
H2(C2*)	217 (10)	432 (11)	69 (3)	338
H1(C4*)	-73 (12)	720 (11)	80 (3)	473
H2(C4*)	-1 (12)	984 (13)	96 (3)	473
H3(C4*)	86 (11)	862 (12)	36 (4)	473

The final parameters, given in Table 3, especially those of the alkyl chains, may therefore be subject to larger systematic errors than indicated by the calculated standard deviations, despite the good internal consistency of the bond lengths and angles.*

Description of the structure

The crystal structure of 2,7-dimethyl-2,7-octanediol tetrahydrate is closely related to that of 2,5-dimethyl-

* Lists of structure factors and the observed values of the forbidden reflections, and tables of anisotropic thermal parameters, bond lengths and valency angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33015 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

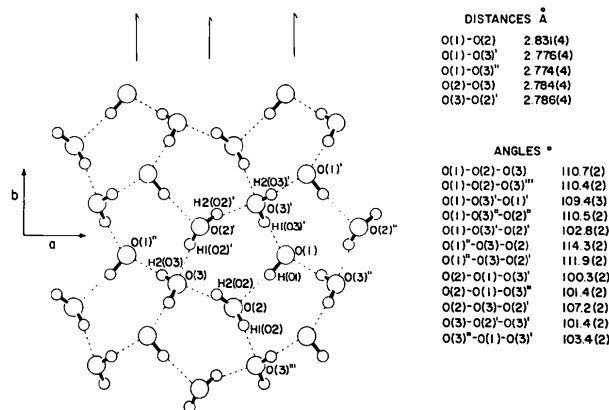


Fig. 1. Hydrogen-bonded water-hydroxyl layer in 2,7-dimethyl-2,7-octanediol tetrahydrate.

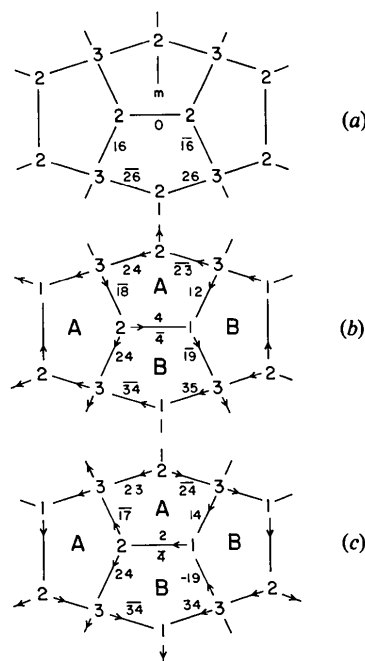


Fig. 2. The geometry of the pentagons in (a) the tetragonal pinacol hexahydrate structure, (b) the monoclinic 2,5-dimethylhexanediol tetrahydrate structure, and (c) the monoclinic 2,7-dimethyloctanediol tetrahydrate structure. Vertices 1 are hydroxyl O atoms, 2 and 3 are water O atoms. The numbers are the values of the internal ring torsion angles in degrees. The arrows indicate the donor direction of the hydrogen bonds.

2,5-hexanediol tetrahydrate (Jeffrey & Shen, 1972). The relationship between these two structures and those of pinacol hexahydrate (Kim & Jeffrey, 1970) and piperazine hexahydrate (Schwarzenbach, 1968) is shown in the unit-cell dimensions given in Table 2. As compared with dimethylhexanediol hydrate, the nearly equal *a* and *b* axes are 0.5% shorter, the *c* axis is 3.3 \AA longer to accommodate the two additional methylene groups.

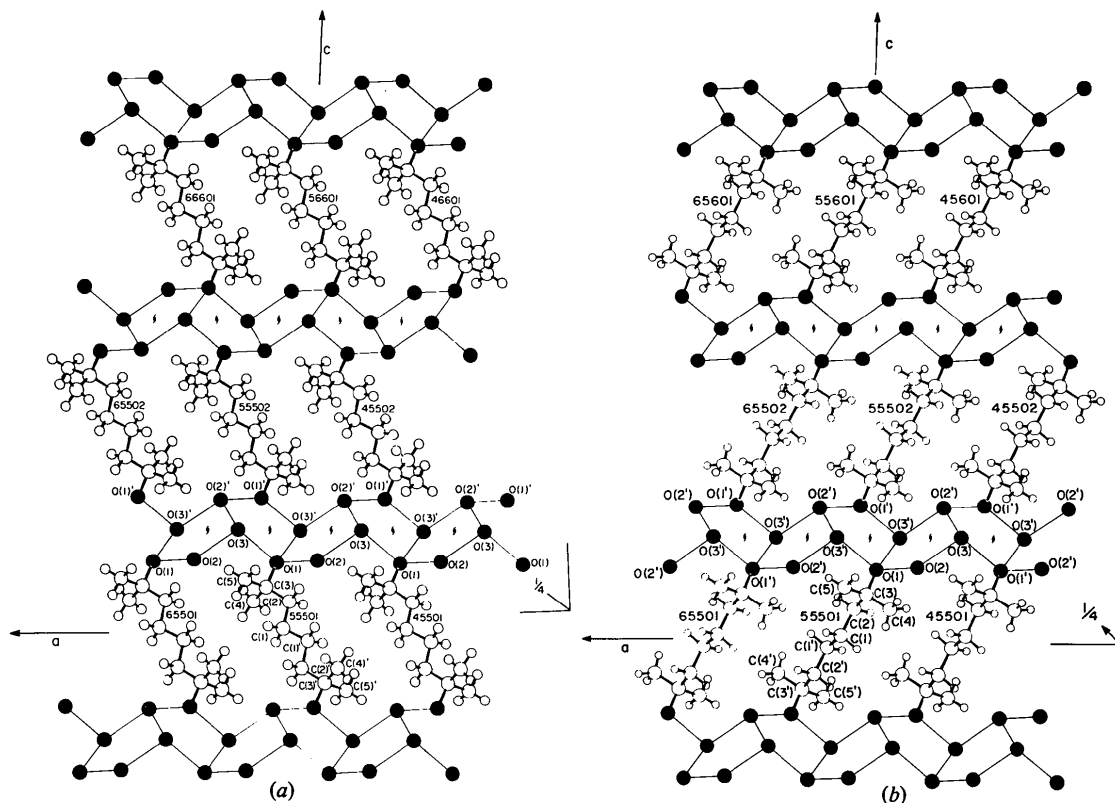


Fig. 3. The structure of dimethyloctanediol tetrahydrate, showing separately the two orientations of the octanediol hydrocarbon chains. (The five-digit numbers refer to the symmetry operations.) The centers of symmetry of the octanediol chains are at $(0,0,0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, etc. in (a), and at $(0,0,\frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$, etc. in (b).

The water-hydroxyl layer consists of a layer of water molecules and hydroxyl groups linked by hydrogen bonds which form a buckled sheet of edge-sharing pentagons, as shown in Fig. 1. As in dimethylhexanediol hydrate, this layer structure is pseudotetragonal; the ideal $P4_2/mnm$ arrangement is found in pinacol hexahydrate where all the O atoms are those of water molecules. In this structure the central four-coordinated water oxygen O(3) is displaced 0.13 Å from the pseudo 4_2 axis and 0.004 Å from the pseudo mirror plane. The layers do not exactly superimpose, as in the tetragonal structure, owing to the β angle of 91.7° . This departure from tetragonal symmetry and orthogonality is a consequence of having hydroxyl groups instead of all water molecules in the pentagonal layers. In this structure, adjacent pentagonal layers nearly superimpose, whereas in the hexanediol hydrate, the adjacent water layers are displaced and only the alternate layers nearly superimpose, because the symmetry is $P2_1/c$ rather than $P2_1/n$.

There are small variations in the hydrogen-bond lengths, as shown in Fig. 1, with the hydroxyl-donor bond O(1)—H...O(2) the longest. However, in the dimethylhexanediol hydrate structure, this bond was one of the shorter. The variation in hydrogen-bond

lengths appears, therefore, to be a function of the geometry of the whole layer structure, rather than of a simple distinction between hydroxyl and water O atoms. As in the hexanediol hydrate, the X-ray evidence indicates that H atoms are ordered in the hydrogen bonds, but the distribution is different, as shown by comparing Fig. 1 with Fig. 1 of the paper by Jeffrey & Shen (1972). These two arrangements represent two of the eleven possible ways of arranging the H atoms in these layers, while preserving the identity of the water molecules and hydroxyl groups. It is not obvious why the bonding should be ordered and different in the two structures.

In the water layer of the tetragonal pinacol hexahydrate, the H atoms are disordered and all the pentagons are identical. They are exact envelopes owing to the crystallographic m symmetry, resulting in zero torsion angles across O(2)—O(2), as shown in Fig. 2(a). The O...O distances are almost equal, 2.815 and 2.822 Å. In the dimethylhexanediol and dimethyloctanediol hydrates, there are two different pentagons. That labelled *A* in Fig. 2(b) and 2(c) consists of four water molecules and one hydroxyl; the other, *B*, consists of three water molecules and two hydroxyls. Both are slightly distorted from the ideal envelope conformation

toward the twist, as shown by the small values of the torsion angles about O(1)—O(2). In both structures, O(1)—O(2) is the largest O...O distance, 2.844 and 2.831 Å.

The water-hydroxyl layers are separated by the hydrocarbon chains as shown in Fig. 3. The two arrangements, which have been given equal weight, are shown separately. They almost completely superimpose except for C(1), C(1') and C(1*), C(1'*). The atoms C(2) and C(2'*) of one chain become C(4*) and C(4') of the second chain. The atoms C(3), C(5) and C(3*), C(5*) are the same in both chains, since in the final refinement, these atoms remained unresolved. The same atomic positions were therefore used for both chains. C(2) and C(4*) were resolved since they were separated by about 0.5 Å. The disorder is assumed to be 50% in each orientation, but this is unlikely to be *exactly* true because the distance between the two terminal hydroxyl O atoms is 0.16 Å shorter for chain 1 than for chain 2. The conformation of the two chains must, therefore, be slightly different. This is the most likely cause of the departure from ideal $P2_1/n$ symmetry as indicated by the forbidden reflections. As described above, we were unable to resolve this detail of the structure with the room-temperature diffraction data available.

Within the accuracy of the analysis, both octanediol molecules have a fully extended main-chain conformation with the O atoms and chain C atoms lying in one plane within ± 0.02 Å and main-chain torsion angles between 173 and 179°. The mean C—C distance is $\langle 1.532 \text{ Å} \rangle$ with values ranging from 1.491 to 1.573 Å and calculated σ 's of 0.011 Å. The C—O distances are

1.449 Å, and the C—H distances range from 0.95 to 1.1 Å. The C—C—C valence angles are greater than tetrahedral, $\langle 113^\circ \rangle$, and the C—C—O angles are less, $\langle 106^\circ \rangle$. The experimental uncertainty is such that the difference in separation of 0.16 Å between O(1) and O(1*) cannot be associated with any particular conformational feature of the chains. The tables of bond distances and valence angles for the dimethyl-octanediol molecule have been deposited.†

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† See deposition footnote.

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