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The crystal structure of D-threitol at 119 K and 198 K

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ABSTRACT

A sample of DL-threitol, $C_4H_{10}O_4$ (Sigma Chemical Co.), on recrystallization provided crystals of D- and L-threitol. The crystal structure was determined at 119 K and 298 K. The space group of D-threitol is $P3_121$, with three molecules in a unit cell at 119 K [298 K] of a = 10.0995(5) [10.1405(8)], c = 4.8407(4) [4.8767(4)] A. The final agreement R-factor was 0.050 for 302 intensities [0.069 for 244 intensities]. The molecules have the straight carbon-chain conformation with twofold axial symmetry. The hydroxyl groups are hydrogen bonded in infinite chains extending in the direction of the threefold screw axis. One of the hydroxyl hydrogens is twofold disordered, so that alternate chains have reversed donor–acceptor directions.

INTRODUCTION

In the alditols from $C_4H_{10}O_4$ to $C_6H_{14}O_6$, the only molecules for which crystal structure analyses are not available are threitol and altritol (talitol)[1]. This structure analysis was undertaken to complete the structural data on the tetritols. The crystal structure of *meso*-erythritol has been determined by both X-ray and neutron single-crystal analysis[2,3].

When single crystals are obtained from a DL powder sample, they may be separate D and L crystals with a non-centric space group or racemic DL crystals in a centrosymmetric space group, as in DL-arabinose[4]. A crystal structure analysis is one of the ways to distinguish between these two cases. Even with *meso* configurations, D and L conformations are possible; for example, ribitol[5] crystallizes as a DL conformational racemate in space group $P2_1/c$, while xylitol[6] forms separate D and L crystals in the non-centric space group $P2_12_12_1$.

EXPERIMENTAL

Single crystals of D- and L-threitol were obtained by the recrystallization of DL-threitol (Sigma Chemical Company) from 90% ethanol at 4°. The D and L crystals are not visually distinguishable, but the powder patterns of the original DL-threitol, and of authentic L-threitol (Sigma Company), were found to be identical with that of powdered single crystals from the recrystallized sample. These correspond with the powder pattern calculated from the results of the subsequent single crystal structure analysis, as shown in Table I.

The single crystal diffraction data are reported in Table II. From the extinction

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TABLE I

The powder patterns for L-threitol, DL-threitol, and powdered single crystals from DL-threitol

Sample	2θ (*deg*)											
L-Threitol[a]	10.0	17.5	20.1	20.9	25.1	27.1	32.6	35.6		41.2	45.3	
DL-Threitol[a]	10.0	17.4	20.1	21.0	25.1	27.2	32.5	35.5		41.3		
D & L Crystals[b]		17.4	20.1	20.8	25.2	27.2	32.4	35.7		41.3	45.1	
Calculated[c]	10.06	17.48	20.21	20.82	25.32	27.31	32.61	35.75	38.28	41.40	45.26	46.16
hkl	100	110	200	101	111	201	121	301	012	311	401	212

[a] Samples from Sigma Chemical Company. [b] Powdered single crystals from DL-threitol. [c] Based on the room temperature parameters.

TABLE II

Crystal data and structure determination and refinenemt data for D-threitol at 119 K and 298 K

	119 K	*298 K*
Crystal data		
$C_4H_{10}O_4$; mol. wt. 122.1; space group $P3_121$;	$Z = 3$; m.p. 90.2°	
Cell dimensions (Å):		
a	10.0995(6)	10.1405(8)
c	4.8407(4)	4.8767(4)
V (Å^3)	427.6	434.3
D_x (g cm^{-3})	1.422	1.401
Structure determination and refinement data		
CAD-4 diffractometer, Cu$K\alpha$ radiation		
Crystal dimensions (mm^3)	0.22 × 0.42 × 0.48	0.24 × 0.24 × 0.30
2θ limit (deg)	144	128
Intensities measured	655	572
Independent intensities	329	278
Observed intensities [$I > 2\sigma(I)$]	302	244
Absorption correction	$\mu_{CuK\alpha} = 11.20\ \text{cm}^{-1}$ max. 1.335 cm^{-1}, min. 1.224 cm^{-1}	none
Extinction correction	none	none
No. of parameters	55	55
Refinement using UPALS[8], minimizing $w(k\lvert F_o\rvert-\lvert F_c\rvert)^2$, where w =	$1/\sigma^2$	$1/[\sigma^2(F) + (0.003F_o)^2]$
Final agreement factors,		
$R(F)$	0.050	0.069
$R_w(F)$	0.046	0.078

conditions $l = 3n$ for 001 reflections, the possible space groups are $P3_1$, $P3_2$ or higher symmetry $P3_112$, $P3_121$, $P3_212$, and $P3_221$. With three molecules in the unit cell, the higher symmetry space groups require that the molecule has twofold axis symmetry. Although a visual inspection of the symmetry indicated the space groups $P3_121$ or $P3_221$, a complete set of intensity data were collected assuming the lower symmetry. Subsequent comparison of the hkl and khl intensities confirmed the higher symmetry.

The crystal structure was determined by the direct method program MITHRIL[7] from the room temperature data. We have chosen to report the data in terms of the D-threitol structure, for which the space group is found to be $P3_121$. As shown in Fig. 1, the molecules are oriented with the twofold axes perpendicular to the central C–C bond in the direction of the *a* and *b* crystallographic axes. This requires disorder of the hydrogen atoms bonded to O-2 and O-2′. The positions of the hydrogen atoms, including those at the disordered half-occupied sites, were determined directly from the low temperature data.

The final refinement was by full-matrix least-squares using UPALS[8], with anisotropic temperature factors for the carbon and oxygen atoms, and fixed isotropic temperature factors for hydrogen atoms equal to the isotropic temperature factors of the atoms to which the hydrogens were covalently bonded. The structure refinement

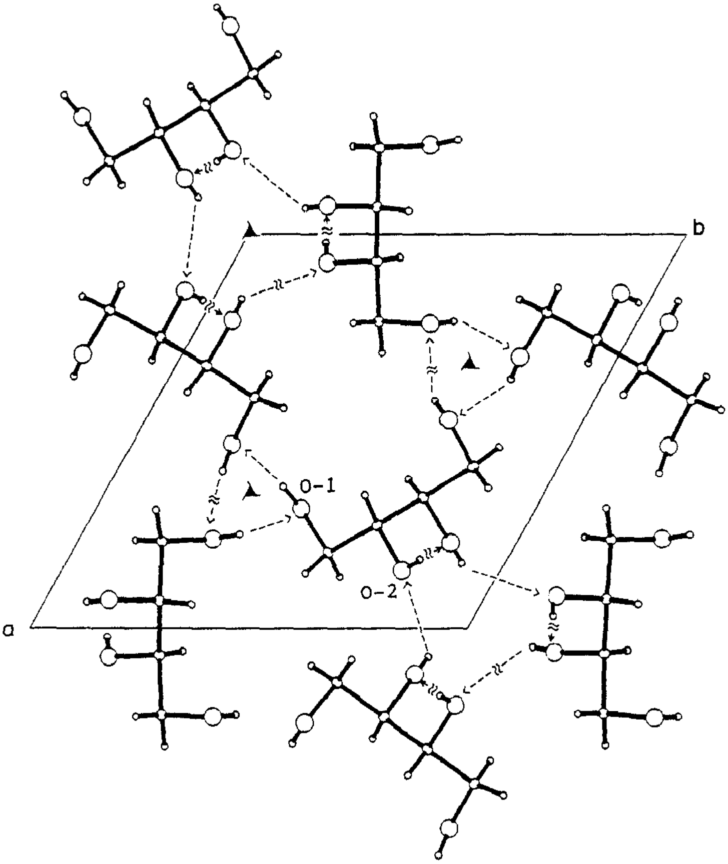

Fig. 1. Crystal structure of D-threitol, viewed down the 3_1 axis. Dashed lines are hydrogen bonds. Only one of the disordered positions is shown for H-O-2.

data are given in Table II. The final atomic parameters for D-threitol are given in Table III. Figure 2 shows the atomic notation and thermal ellipsoids*.

Although in principle the absolute configuration of a carbohydrate can be determined from very accurate Cu*Kα* X-ray data, this was not done, because the absolute configuration of the molecules in a crystal selected from a mixture of D and L crystals, as in this case, is useless information, unless further physical measurements are to be performed on that particular crystal.

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* Lists of anisotropic thermal parameters and observed and calculated structure amplitudes have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/477/*Carbohydr. Res.*, 223 (1992) 11–18.

TABLE III

Atomic positional parameters and equivalent isotropic thermal parameters for D-threitol at 119 K and 298 K[a]

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
119 K				
O-1	6935(3) × 10^{-4}	4680(3) × 10^{-4}	−2445(4) × 10^{-4}	157(8) × 10^{-2}
O-2	8557(3)	7804(4)	2595(7)	290(11)
C-1	8066(4)	5874(5)	−717(8)	158(11)
C-2	7377(4)	6663(4)	904(8)	132(9)
H-1	890(5) × 10^{-3}	668(5) × 10^{-3}	−239(8) × 10^{-3}	
H-1′	856(4)	544(4)	53(7)	
H-2	654(4)	593(3)	221(8)	
H-O-1	647(5)	405(5)	−140(9)	
H-O-2	924(7)	826(7)	216(13)	
H′-O-2	832(8)	801(8)	357(14)	
298 K				
O-1	6948(12) × 10^{-4}	4683(10) × 10^{-4}	−2287(11) × 10^{-4}	26(2) × 10^{-1}
O-2	8558(8)	7832(9)	2592(13)	33(3)
C-1	8076(9)	5875(10)	−678(17)	22(3)
C-2	7373(8)	6674(9)	937(13)	16(2)
H-1	884(9) × 10^{-3}	655(9) × 10^{-3}	−168(13) × 10^{-3}	
H-1′	871(9)	550(8)	84(15)	
H-2	644(9)	583(8)	256(13)	
H-O-1	691(15)	463(16)	−383(22)	
H-O-2	940(16)	867(16)	209(34)	
H′-O-2	822(22)	798(24)	348(32)	

[a] E.s.d. values given in parentheses refer to the least significant digit. $B_{eq} = 4/3(\Sigma_{ij}B_{ij}a_ia_j)$, calculated from the refined anisotropic thermal parameters.

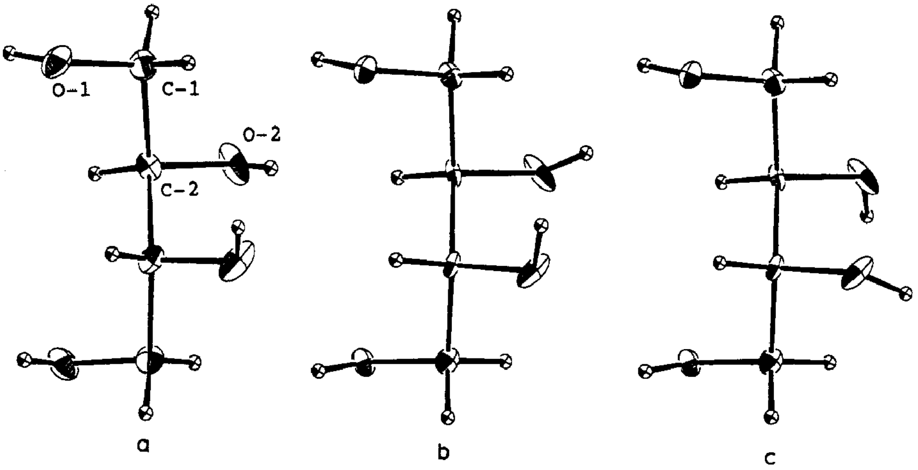

Fig. 2. Atomic notation and thermal ellipsoids at 30% probability for the D-threitol molecule: (a) at 298 K; (b, c) at 119 K, with H-O-2 in different positions.

DISCUSSION

The molecules have the anticipated straight carbon-chain conformation with a twofold axis perpendicular to the C-2–C-2′ bond. The primary C-1–OH bond is *ap* to the secondary C-2–OH bond, and *sc* to the C-2–C-2′ bond.

The bond lengths, bond angles, and torsion angles given in Table IV are normal. The differences in bond lengths at the two temperatures are not significant in terms of the e.s.d.s of the less precise room-temperature data. The corresponding decrease in isotropic equivalent temperature factors is 0.45 Å^2 for the carbon atoms and 0.70 Å^2 for the oxygen atoms.

All the hydroxyl groups are involved as donors and acceptors in a strong cooperative system of hydrogen bonds, which consists of infinite helical chains extend-

TABLE IV

Molecular geometry in the crystal structure of D-threitol at 119 K and 298 K

	119 K	*298 K*
Bond lengths (Å)		
C-1–C-2	1.514(6)	1.537(12)
C-1–O-1	1.443(5)	1.415(13)
C-2–O-2	1.430(5)	1.436(11)
C-2–C-2′	1.524(5)	1.530(11)
C-1–H-1	1.16(5)	0.88(8)
C-1–H-1′	1.01(4)	1.16(8)
C-2–H-2	1.02(4)	1.20(8)
O-1–H-O-1	0.76(5)	0.75(14)
O-2–H-O-2	0.65(8)	0.89(16)
O-2–H′-O-2	0.62(8)	0.62(21)
Bond angles (deg)		
O-1–C-1–C-2	111.1(3)	110.2(8)
O-2–C-2–C-1	107.7(3)	107.5(7)
O-2–C-2–C-2′	110.4(3)	110.4(7)
C-1–C-2–C-2′	113.7(3)	112.5(7)
C-2–C-1–H-1	111(2)	109(6)
C-2–C-1–H-1′	112(2)	109(4)
C-1–C-2–H-2	112(2)	111(4)
C-2′–C-2–H-2	106(2)	110(4)
C-1–O-1–H-O-1	102(4)	127(8)
C-2–O-2–H-O-2	124(6)	129(10)
C-2–O-2–H′-O-2	114(7)	104(10)
H-1–C-1–H-1′	112(6)	101(10)
Torsion angles (deg)		
O-1–C-1–C-2–O-2	178.9(3)	178.0(7)
O-1–C-1–C-2–C-2′	− 58.5(4)	− 60.2(9)
C-1–C-2–C-2′–O-2	− 63.1(4)	− 63.9(9)
O-2–C-2–C-2′–O-2′	58.1(4)	56.1(9)
C-1–C-2–C-2′–C-1′	175.8(3)	176.1(7)
O-1–C-1–C-2–H-2	62(2)	64(4)

TABLE V

The structural parameters of hydrogen bonds in D-threitol at 119 K[a]

i	j	*Distance* (ij)	*Angle* (ij)
O-1–H	O-1$_{2\,655}$	1.73	170
O-2–H	O-2$_{5\,765}$	1.83	144
O-2–H′	O-2$_{4\,556}$	1.73	163

i	j	k	*Distance* (ij)	*Distance* (jk)	*Angle* (ijk)
O-1$_{2\,655}$	O-1$_{1\,555}$	O-1$_{3\,664}$	2.696(5)	2.696(5)	92.1(3)
O-2$_{4\,555}$	O-2$_{1\,555}$	O-2$_{4\,556}$	2.837(5)	2.675(5)	122.8(3)
O-2$_{4\,555}$	O-2$_{1\,555}$	O-2$_{5\,765}$	2.837(5)	2.678(5)	85.5(3)
O-2$_{4\,556}$	O-2$_{1\,555}$	O-2$_{5\,765}$	2.676(5)	2.678(5)	121.6(3)

[a] Bond lengths in Å, angles in deg. O–H bond lengths are normalized to 0.97 Å. The last three digits of the symmetry code give the unit cell translation in the *a, b, c* directions with respect to 555; the first digit specifies one of the following operations: 1, *x, y, z*; 2, −*y, x* − *y*, 1/3 + *z*; 3, *y* − *x*, −*x*, 2/3 + *z*; 4, *y, x*, −*z*; 5, −*x, y* − *x*, 1/3 − *z*; 6, *x* − *y*, −*y*, 2/3 − *z*.

ing in the direction of the threefold axis. There are two tight helices, →O-1–H$_{2655}$→O-1–H$_{1555}$→O-1–H$_{3664}$→ and →O-1–H$_{5665}$→O-1–H$_{4555}$→O-1–H$_{6564}$→, which are related by two-fold axis symmetry and have opposite polarities, as shown in Fig. 1. The other helical chain, →O-1–H$_{4556}$→O-2–H$_{1555}$→O-2–H$_{5765}$→, is more open. In this chain, the cancellation of polarity is achieved by the disorder of the O-2–H hydrogen atom, which reverses the donor–acceptor direction of the chain (see Fig. 1). This donor is similar to that observed in the cyclodextrin hydrates for which a flip-flop mechanism has been proposed[9]. All the hydrogen bonds are two-centered and intermolecular. Their geometry is given in Table V. The hydrogen bond lengths are in the shorter part of the range of values observed for O-H–O bonds in carbohydrate crystal structures[10], due to the strong cooperative component of the hydrogen bond energy.

A differential thermogram spanning the temperatures 323 K to 103 K showed no evidence of a phase transition, which would be an indicator of ordering of the hydroxyl hydrogen atoms over this temperature range.

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