

The Crystal and Molecular Structure of 1,4:2,5:3,6-Trihydro-D-mannitol at -100°C

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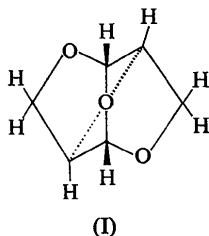
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The compound 1,4:2,5:3,6-trihydro-D-mannitol, $\text{C}_6\text{H}_8\text{O}_3$, crystallizes in the tetragonal space group $P4_12_12$ with $Z=4$ and cell dimensions $a=5.988$ (1), $c=15.840$ (3) Å at -100°C . The molecule has a crystallographic twofold axis and comprises three fused furano rings. An analysis of the thermal motion is given in terms of a rigid body.

Introduction

Recent interest in the crystal structures of anhydro derivatives of carbohydrates (Lechat & Jeffrey, 1972, and references therein; Dreissig & Luger, 1973; Lindberg, Lindberg & Svensson, 1973), prompts this report on the investigation of the crystal structure of 1,4:2,5:3,6-trihydro-D-mannitol (I) (Cope & Shen, 1956) at -100°C . In addition, there is a lack of accurate data on fused anhydro furano ring systems. The symmetry and small size of this tricyclic molecule was expected to make possible an accurate structure determination and therefore to help to provide a better understanding of the conformational properties of fused furano rings.



Experimental

Crystals of the title compound are volatile translucent rectangular parallelepipeds. Precession photographs of the layers $0kl$, $1kl$, $hk0$, hkl , hll , $hl2l$ indicated Laue symmetry $4/mmm$ with systematic absences $0k0$ $k=2n+1$, $00l$ $l=4n+1, 2, 3$, indicating the space group $P4_12_12$.

Crystal data

$\text{C}_6\text{H}_8\text{O}_3$, F.W. 128. 21°C : $a=b=6.023$ (4), $c=15.95$ (1) Å, $V=578.6$ Å³. -100°C : $a=b=5.988$ (1), $c=15.840$ (3) Å, $V=568.0$. ρ_m (21°C by direct measurement of volume and weight) = 1.5 g cm⁻³; ρ_c (-100°) = 1.497 g cm⁻³; $Z=4$; $\mu(\text{Mo } K\alpha)$ = 1.3 cm⁻¹.

A crystal of dimensions $0.27 \times 0.33 \times 0.44$ mm sealed in a Lindemann-glass capillary was used to collect the intensity data on a Picker FACS 1 diffractometer. A general orientation of the crystal was used in order to minimize intrinsic multiple reflexion. The temperature

was maintained at $-100 \pm 5^{\circ}\text{C}$ using an Air Products Joule-Thomson cryotip refrigerator. Despite the lower temperature an intensity decrease of $\sim 10\%$ was observed during data collection which we attributed to sublimation.

Cell dimensions at both room and low temperature were measured using 20 reflexions ($2\theta > 38^{\circ}$). A full octant of the sphere of reflexion was examined $2\theta \leq 60^{\circ}$ at -100° (reflexions used were derived from the combined data). In no case were statistical differences between symmetry-equivalent reflexions encountered. Intensity data were collected with filtered Mo $K\alpha$ radiation using pulse-height analysis and a scan width of 1.1° (increased for dispersion). Ten second background counts were taken at each scan limit. Of the 544 independent reflexions measured, 403 were considered observed ($> 2.3\sigma$).

Structure solution and refinement

The structure solution was obtained from the sharpened Patterson function. Since the molecule was expected to possess twofold symmetry the atoms closest to the symmetry axis were located first and then the remaining atomic coordinates derived. Initial full-matrix least-squares refinement on all the atomic coordinates gave $R=11\%$ after one cycle. The program BUCILS (Chan & Einstein, 1971) was modified to account correctly for the least-squares derivative for the oxygen atom on the twofold axis $x, x, 0$. Refinement proceeded satisfactorily and hydrogen-atom positions were initially located from an electron-density difference map based on data $\sin \theta/\lambda < 0.4$ Å⁻¹. This map also indicated that the non-hydrogen atoms were moving anisotropically. The hydrogen atoms were given isotropic temperature parameters 1.0 Å² greater than the atom to which they were bonded. Hydrogen parameters alone were refined alternately on the low-angle data $\sin \theta/\lambda < 0.4$ Å⁻¹. Initially the data were given unit weights but after refinement of the hydrogen parameters commenced, counter weights were used. An electron-density difference map at this stage ($R=0.050$, $wR=0.051$) showed anisotropic motion of the hydrogen atoms as the major feature. Since we did not ex-

pect that refinement of these variables independently would proceed satisfactorily, a rigid-body analysis of the non-hydrogen atom thermal-motion ellipsoids was carried out. In order to use the *TLS* version (Schomaker & Trueblood, 1968) transformation of atomic parameters such that the twofold axis coincided with a new axial system (c remained constant) was carried out. The molecular motion was constrained to have

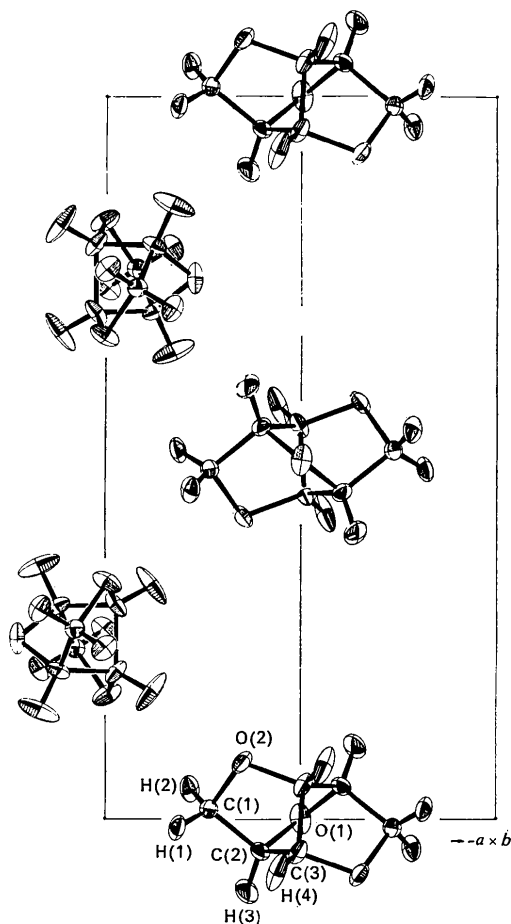


Fig. 1. The 4_1 axis viewed along one of the twofold axes.

twofold symmetry and an excellent fit obtained, r.m.s. $\Delta U_{ij} = 0.0011 \text{ \AA}^2$. Values for the calculated anisotropic motion of the hydrogen atoms were obtained by modification of the program and these values were transformed back to the original axial system. Refinement using the calculated anisotropic parameters (fixed) for the hydrogen atoms led to significant shifts in both the hydrogen and heavy-atom parameters. Hydrogen-atom coordinate parameters were still refined only on alternate cycles using the low-angle data. The final agreement obtained was $R = 0.048$, $wR = 0.049$ and the error of fit $\sqrt{\sum \omega \Delta^2 / NO - \bar{N}V} = 1.66$. The function minimized was $\sum \omega (|F_o| - |F_c|)^2$.*

The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1968) in the case of O and C and from Stewart, Davidson & Simpson (1965) in the case of hydrogen. The final re-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30709 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Rigid-body motion parameters

Axes were transformed by a rotation about z such that x was coincident with the twofold axis.

Rigid-body tensors

T (\AA^2)	257 (7)	0	0
$\times 10^4$		387 (5)	23 (5)
ω (rad^2)	39 (3)	0	0
$\times 10^4$		540 (7)	75 (3)
S (\AA rad)	-59 (14)	0	0
$\times 10^4$		133 (5)	-47 (31)
		-12 (3)	-74 (4)

Axis	Axis shift (\AA)	Screwpitch (\AA rad $^{-1}$)
1	0.051	0.261
2	-0.083	-1.131
3	-0.094	-1.520

Principal r.m.s. amplitudes

T (\AA)	0.198	0.165	0.161
ω (rad)	0.235	0.073	0.062

r.m.s. $\Delta U_{ij} = 0.0011 \text{ \AA}^2$

Table 1. Refined fractional atomic coordinates and thermal-motion parameters (\AA^2)

In this and subsequent tables, the figure in parentheses is the e.s.d. Anisotropic temperature parameters are in the form $\exp[-2\pi^2(U_{11}a^*h^2 + U_{22}b^*k^2 + U_{33}c^*l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	0.2740 (3)	0.2740*	0.0*	0.0396 (8)	0.0396*	0.1167 (20)	-0.0120 (10)	0.0069 (11)	-0.0069*
O(2)	0.6546 (4)	0.3545 (3)	0.0788 (1)	0.0975 (16)	0.0456 (10)	0.0575 (9)	0.0415 (10)	-0.0415 (10)	-0.0082 (8)
C(1)	0.6564 (5)	0.1871 (4)	0.0132 (1)	0.0517 (14)	0.0362 (12)	0.0426 (11)	0.0036 (11)	0.0008 (11)	0.0012 (11)
C(2)	0.4812 (4)	0.2751 (4)	-0.0452 (2)	0.0491 (15)	0.0636 (17)	0.0385 (10)	0.0113 (12)	-0.0072 (11)	-0.0197 (11)
C(3)	0.5334 (4)	0.5210 (5)	-0.0470 (2)	0.0280 (12)	0.0680 (17)	0.0678 (14)	0.0059 (9)	0.0092 (11)	0.0405 (14)
H(1)	0.813 (4)	0.182 (4)	-0.012 (2)	0.0389†	0.0697	0.0737	0.0223	0.0051	0.0234
H(2)	0.613 (4)	0.050 (4)	0.042 (2)	0.0684	0.0305	0.0839	0.0080	0.0144	0.0087
H(3)	0.467 (4)	0.193 (6)	-0.100 (2)	0.1222	0.1377	0.0686	0.0705	-0.0411	-0.0656
H(4)	0.673 (5)	0.559 (6)	-0.075 (2)	0.0336	0.1232	0.1678	0.0273	0.0421	0.1114

* These parameters are not independent as the equivalent position is of the type $(x, x, 0)$.

† These parameters were not varied but calculated (see text).

finer atomic parameters are listed in Table 1. Data describing the rigid-body analysis are provided in Table 2, while interatomic distances and angles are displayed in Table 3. The errors in bond lengths include contributions from correlation and from the cell dimensions. A diagram showing the molecule and the 4_1 axis is given in Fig. 1. Calculations were carried out using the programs described by Chan & Einstein (1971).

Table 3. *Interatomic parameters*

Atoms with the superscript I are related by the twofold operation ($y, x, -z$).

Distances (Å)	Uncorrected	Corrected*
O(1)–C(2)	1.432 (4)	1.453
O(2)–C(1)	1.443 (3)	1.456
O(2)–C(3 ^I)	1.428 (3)	1.433
C(1)–C(2)	1.495 (4)	1.500
C(1)–H(1)	0.972 (27)	0.980
C(1)–H(2)	1.020 (27)	1.029
C(2)–C(3)	1.506 (4)	1.519
C(2)–H(3)	0.999 (29)	0.997
C(3)–C(3 ^I)	1.493 (6)	1.508
C(3)–H(4)	0.969 (30)	1.014

Angles (°)	Uncorrected	Corrected*
C(2)–O(1)–C(2 ^I)	104.0 (2)	103.0
C(1)–O(2)–C(3 ^I)	105.8 (2)	105.6
O(2)–C(1)–C(2)	101.3 (2)	101.9
O(2)–C(1)–H(1)	107.9 (17)	107.5
O(2)–C(1)–H(2)	104.6 (17)	104.4
C(2)–C(1)–H(1)	114.5 (14)	114.2
C(2)–C(1)–H(2)	113.4 (17)	113.3
H(1)–C(1)–H(2)	113.7 (24)	114.4
O(1)–C(2)–C(1)	107.3 (2)	107.0
O(1)–C(2)–C(3)	101.2 (2)	101.8
O(1)–C(2)–H(3)	110.9 (20)	110.6
C(1)–C(2)–C(3)	102.2 (2)	101.9
C(1)–C(2)–H(3)	115.2 (18)	115.3
C(3)–C(2)–H(3)	118.7 (23)	118.8
O(2 ^I)–C(3)–C(2)	113.5 (3)	113.2
O(2 ^I)–C(3)–C(3 ^I)	106.6 (3)	106.6
O(2 ^I)–C(3)–H(4)	110.8 (17)	109.9
C(2)–C(3)–C(3 ^I)	91.1 (2)	91.2
C(2)–C(3)–H(4)	114.8 (23)	114.9
C(3 ^I)–C(3)–H(4)	118.7 (25)	118.6

* Corrected for rigid-body motion.

Discussion

At -100° the trianhydride, which possesses no strong intermolecular contacts, was found to be oscillating significantly within the crystal lattice. Rigid-body analysis (constrained to fit the molecular twofold symmetry) gave an excellent description of this motion and significantly improved interatomic parameters. In many cases the corrected values were well outside the error

limits established by *ORFFE* (see Table 3). In all cases the heavy-atom bonded distances increased on correction.

The most striking feature of the molecular structure is the response of bond angles to the strain of the tricyclic structure and the insensitivity of bonded distances to this strain. Carbon 3 [C(3) or C(3^I)] seems to be most highly perturbed by the involvement in the tricyclic system with bond angles of 91.2 and 118.6° .

In common with other sugars the C–C bond lengths are all somewhat shorter than the value (~ 1.54 Å) generally found for organic compounds. Lechat & Jeffrey (1972) have already suggested that this feature may be related to the number and disposition of the adjacent oxygen atoms. It is also worth noting that a small but corresponding lengthening of the C–O bonds occur in both sets of data. We have examined our data and have been unable to rationalize these results.

The furano ring formed by C(2)–C(3)–C(3^I)–C(2^I)–O(1) is, by necessity of the crystal symmetry, a perfect twist, ${}^3T_{31}$, having carbons 3 and 3^I displaced ± 0.543 Å out of plane. The other furano ring, C(1)–C(2)–C(3)–C(3^I)–O(2), exhibits a 3T_2 conformation with C(3) above the plane by 0.622 Å and C(2) below the plane by 0.264 Å.

The molecular packing shown in Fig. 1 is fully consistent with the presence of only van der Waals forces, as indicated by the ease of sublimation; however, a packing sequence along the twofold axis is consistent with 'head to tail' dipolar packing, the oxygen on the twofold axis is 3.7 Å from the C(3)–C(3^I) bond.

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