

2,5-*O*-Methylene-*D*-mannitol: two polymorphs and the NaI complex

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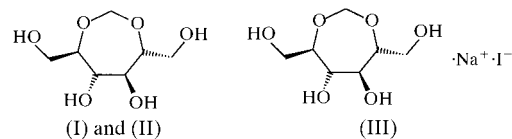
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Two polymorphs of the title compound, (4*R*,5*R*,6*R*,7*R*)-4,7-bis(hydroxymethyl)-1,3-dioxepane-5,6-diol, C₇H₁₄O₆, both have $Z' = 2$ at 100 K, and differ in their hydrogen-bonding patterns. The sodium iodide complex, NaI·C₇H₁₄O₆, is isomorphous with the NaCl complex, and has the mannitol, cation and anion all lying on twofold axes.

Comment

The conformational forms of 1,3-dioxepane and its derivatives have long been of interest, and many methods have been employed to determine their three-dimensional structures. NMR studies suggested that the 1,3-dioxepane seven-membered rings exist predominantly with the twist-chairs (TC) as lowest energy conformations (Yavari, 1980; Grindley *et al.*, 1969; Stoddart & Szarek, 1971). Early NMR study (Stoddart & Szarek, 1971) of the title mannitol compound indicates that the 2,5-*O*-methylene H atoms are magnetically equivalent (5.22 δ , singlet). This means that the two H atoms may be interchanged by a C₂ symmetry operation in solution. A search of the Cambridge Structural Database (Allen & Kennard, 1993) revealed six other structures with the 2,5-*O*-methylene-*D*-mannitol core. While the structure of the complex of the title compound with NaCl has been reported (Wood *et al.*, 1976), that of the uncomplexed compound has not appeared. We present here the low-temperature structures of two polymorphs of 2,5-*O*-methylene-*D*-mannitol, (I) and (II), one of which was crystallized in an attempt to prepare the CsCl complex, and also the structure of the NaI complex, (III). The title compound is composed of a 1,3-dioxepane ring and four free hydroxyl groups, which offer good possibilities of intermolecular/intramolecular hydrogen bonds. The purposes of the elucidation of the crystal structure of the title

compound were to compare the solid-state conformations of several 1,3-dioxepane rings and to study the effects of the four hydroxyl groups on the twofold symmetry and TC conformation of the seven-membered rings.



Both forms (I) and (II) have $Z' = 2$ at 100 K. The cell dimensions of form (II) at 298 K, determined using the same crystal, are $a = 7.2389$ (9), $b = 14.035$ (2), $c = 9.2868$ (12) Å, $\beta = 110.667$ (12) $^\circ$ and $V = 882.8$ (4) Å³; thus two independent molecules are also present at room temperature, and apparently no phase change occurs on cooling. The mannitol moiety of the NaI complex, as well as the cation and anion, all lie on crystallographic twofold axes.

The internal agreement among chemically equivalent bond distances (typically nine) over the three structures is excellent. Mean values and differences (Å) between maximum and minimum values for each bond type are: O1—C1 1.428, 0.006 (4); O2—C2 1.437, 0.008 (4); O2—C7 1.409, 0.014 (4); O3—C3 1.429, 0.011 (4); C1—C2 1.518, 0.016 (3); C2—C3 1.532, 0.011 (4); C3—C4 1.531, 0.010 (4).

In Table 1, the torsion angles of the seven-membered ring in the title compounds are compared with those in other reported 2,5-*O*-methylene-*D*-mannitol-based 1,3-dioxepanes. The structure of the NaI complex is isomorphous with that of the previously described NaCl complex (Wood *et al.*, 1976), and will not be described in detail here. Although the NaCl complex is said to be the *D*-isomer, the coordinates describe the *L*-isomer, and no mention is made of any attempt to determine the absolute configuration from the X-ray data. The published coordinates of 1,3,4,6-tetra-*O*-acetyl-2,5-*O*-methylene-*D*-mannitol (Cameron *et al.*, 1977) also describe the *L*-isomer. In Table 1, we have thus changed the signs of all torsion angles for these two compounds. All 1,3-dioxepane rings described in Table 1 are in the TC conformation (Wood *et al.*, 1976; Cameron *et al.*, 1977; Hanson, 1986) of approx-

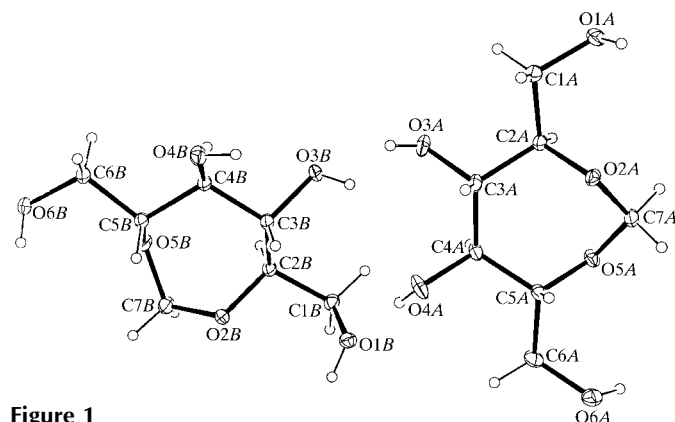


Figure 1

The two independent molecules of (I) with 50% probability ellipsoids. H atoms are shown as small spheres of arbitrary radii.

imate or exact C_2 symmetry. For forms (I) and (II), differences in individual pairs of endocyclic torsion angles across local twofold axes are small, *viz.* 0.3 (4)–4.3 (4)°.

The only substantial conformational differences among the molecules reported herein involve the OH groups. The exocyclic O3–C3–C4–O4 torsion angle varies over a 9.6 (3)° range over the four molecules of forms (I) and (II), with a mean value of -73.0° , while that in the NaI complex is somewhat smaller in magnitude, with a value of $-58.61 (15)^\circ$, in good agreement with that of the NaCl complex (Wood *et al.*, 1976), whose mean value is $-61.0 (3)^\circ$. This can be attributed to the chelation of Na^+ by this *trans*-glycol moiety in the complexes. The OH groups at C1 and C6 form O–C–C–O torsion angles with the ring O atoms having magnitudes in the range 54.50 (18)–72.3 (3)° over the nine individual measurements reported here. In the *A* molecule of form (I), the torsion angles about C1–C2 and C5–C6 have the same sign, approximating C_2 molecular symmetry, while in the *B* molecule, these O–C–C–O torsion angles have opposite signs. This same pattern is seen in the *A* and *B* molecules of form (II). In the NaI complex, the signs and magnitudes are equal as a result of the crystallographic symmetry.

These conformational differences can be correlated to differences in the hydrogen bonding of the OH groups. In all three compounds, all OH groups donate hydrogen bonds. However, the patterns in forms (I) and (II) differ in the use of the terminal (O1 and O6) *versus* internal (O3 and O4) OH groups as acceptors. In form (I), there is a mixture of terminal and internal acceptors for both the *A* and *B* molecules, as well as involvement of a dioxepane O atom, O5B, as acceptor. In form (II), the *A* molecule donates to only terminal OH acceptors, the *B* molecule donates to only interior acceptors, and no dioxepane O atoms are involved. In the NaI complex, all OH groups donate essentially linear hydrogen bonds to iodide.

From the observed extensive hydrogen-bonding patterns and TC conformations of the dioxepane rings, we conclude that hydrogen bonding by the four free hydroxy groups is not enough to promote the twist-boat (TB) geometry, which is

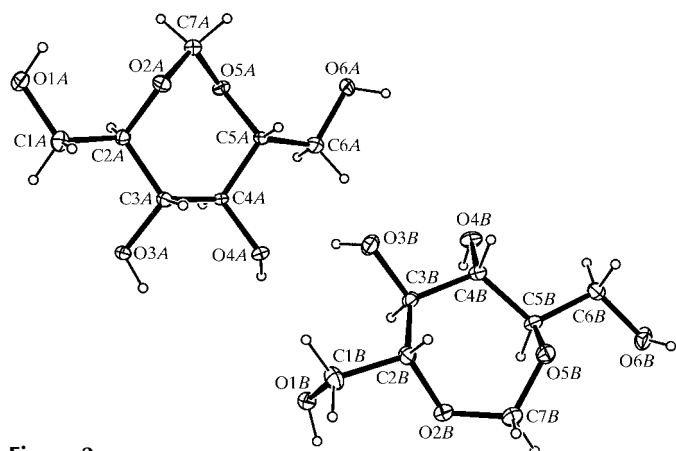


Figure 2

The two independent molecules of (II) with 50% probability ellipsoids. H atoms are shown as small spheres of arbitrary radii.

10 kJ mol⁻¹ higher in energy than the TC (Hendrickson, 1967). Interestingly, the 1,3-dioxepane ring in (\pm)-*cis*-6-acetylamino-5-hydroxy-1,3-dioxepane (Vinkovic & Dumic, 1992) adopts a TB conformation. An intramolecular hydrogen bond in that compound apparently fixes the conformation of the seven-membered ring.

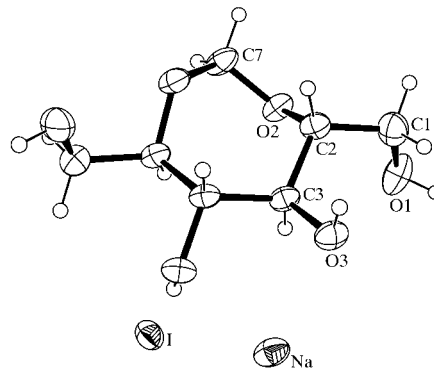


Figure 3

Compound (III) with 50% probability ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Experimental

The title compound was prepared from 1,3:2,5:4,6-tri-*O*-methylene-*D*-mannitol (Ness *et al.*, 1943). Suitable crystals of form (I) were obtained by slow evaporation of an ethanol solution at room temperature. Crystals of the NaI complex were obtained by slow evaporation of an aqueous solution of 2,5-*O*-methylene-*D*-mannitol and NaI. An attempt to form the CsCl complex in the same fashion yielded crystals of form (II).

Compound (I)

Crystal data

$\text{C}_7\text{H}_{14}\text{O}_6$
 $M_r = 194.18$
 Monoclinic, $P2_1$
 $a = 4.5100 (4) \text{ \AA}$
 $b = 14.4620 (10) \text{ \AA}$
 $c = 13.2310 (10) \text{ \AA}$
 $\beta = 98.823 (7)^\circ$
 $V = 852.76 (12) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.512 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 9.7\text{--}18.3^\circ$
 $\mu = 0.133 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
 Needle fragment, colorless
 $0.37 \times 0.35 \times 0.25 \text{ mm}$

Data collection

Enraf-Nonius CAD-4 diffractometer (with Oxford Cryosystems Cryostream cooler)
 ω - 2θ scans
 7174 measured reflections
 7174 independent reflections
 5701 reflections with $I > 2\sigma(I)$

$\theta_{\text{max}} = 45.0^\circ$
 $h = 0 \rightarrow 8$
 $k = 0 \rightarrow 28$
 $l = -26 \rightarrow 25$
 3 standard reflections
 frequency: 60 min
 intensity decay: 5.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.151$
 $S = 1.10$
 7174 reflections
 236 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.5679P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.70 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.52 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.016 (3)

Table 1
Torsion angles ($^{\circ}$) in some 1,3-dioxepanes.

Atoms	(I) <i>A</i> ^a	(I) <i>B</i> ^a	(II) <i>A</i> ^a	(II) <i>B</i> ^a	(III) ^a	<i>b</i>	<i>c</i>	<i>d</i>
C2/C3/C4/C5	43.8 (2)	40.9 (2)	47.9 (3)	40.3 (3)	49.82 (17)	47.5 (3)	48.8 (6)	45.1 (4)
O2/C2/C3/C4	-65.01 (18)	-64.27 (18)	-69.5 (2)	-62.5 (3)	-68.89 (17)	-67.3 (2)	-69.6 (6)	-61.5 (4)
C3/C4/C5/O5	-66.51 (18)	-62.54 (18)	-67.3 (3)	-62.8 (3)	-68.89 (17)	-67.3 (2)	-69.2 (6)	-69.9 (4)
C7/O2/C2/C3	96.57 (16)	98.03 (16)	96.8 (2)	94.1 (2)	96.52 (15)	97.0 (2)	97.1 (6)	94.5 (4)
C7/O5/C5/C4	96.99 (16)	95.05 (16)	97.5 (2)	95.9 (2)	96.52 (15)	97.0 (2)	94.9 (6)	98.5 (4)
C2/O2/C7/O5	-48.8 (2)	-48.8 (2)	-45.2 (3)	-46.4 (3)	-47.30 (10)	-47.7 (2)	-47.6 (7)	-50.2 (4)
C5/O5/C7/O2	-46.1 (2)	-47.3 (2)	-49.5 (3)	-48.5 (3)	-47.30 (10)	-47.7 (2)	-44.3 (7)	-45.6 (4)
O1/C1/C2/O2	60.42 (19)	-57.86 (18)	63.7 (3)	-60.0 (3)	-54.50 (18)	-53.8 (2)	-173.1 (5)	65.3 (4)
O3/C3/C4/O4	-72.18 (7)	-78.21 (16)	-68.6 (2)	-73.1 (2)	-58.61 (15)	-61.0 (3)	-72.0 (5)	-72.4 (4)
O5/C5/C6/O6	65.76 (9)	56.26 (19)	58.5 (3)	72.3 (3)	-54.50 (18)	-53.8 (2)	-172.0 (4)	68.8 (4)

Notes: (a) this work; (b) NaCl complex (Wood *et al.*, 1976); (c) 1,3,2,5,4,6-tri-*O*-methylene-D-mannitol (Hanson, 1986); (d) 1,3,4,6-tetra-*O*-acetyl-2,5-*O*-methylene-D-mannitol (Cameron *et al.*, 1977).

Table 2
Hydrogen-bonding geometry (\AA , $^{\circ}$) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1A—H1OA...O5B ⁱ	0.84	2.02	2.8110 (19)	156
O1A—H1OA...O6B ⁱ	0.84	2.54	3.109 (2)	126
O3A—H3OA...O6A ⁱⁱ	0.84	1.82	2.661 (2)	177
O4A—H4OA...O1B	0.84	1.88	2.7187 (19)	173
O6A—H6OA...O3B ⁱⁱⁱ	0.84	1.92	2.745 (2)	168
O1B—H1OB...O6B ^{iv}	0.84	1.92	2.7447 (19)	166
O3B—H3OB...O3A	0.84	2.12	2.8111 (19)	140
O4B—H4OB...O6A ⁱⁱ	0.84	2.14	2.967 (2)	166
O6B—H6OB...O1A ^v	0.84	1.82	2.646 (2)	170

Symmetry codes: (i) $x-1, y, z-1$; (ii) $-x, y-\frac{1}{2}, 1-z$; (iii) $1-x, \frac{1}{2}+y, 1-z$; (iv) $1-x, \frac{1}{2}+y, 2-z$; (v) $x, y, 1+z$.

Compound (II)

Crystal data

C₇H₁₄O₆
M_r = 194.18
 Monoclinic, *P*2₁
a = 7.218 (3) \AA
b = 14.042 (7) \AA
c = 9.160 (2) \AA
 β = 110.64 (2) $^{\circ}$
V = 868.9 (6) \AA^3
Z = 4

Data collection

Enraf-Nonius CAD-4 diffractometer (with Oxford Cryosystems Cryostream cooler)
 ω -2 θ scans
 3107 measured reflections
 3107 independent reflections
 2660 reflections with $I > 2\sigma(I)$

D_x = 1.484 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 9.0–12.7 $^{\circ}$
 μ = 0.131 mm⁻¹
T = 100 K
 Prism, colorless
 0.23 \times 0.18 \times 0.15 mm
 θ_{max} = 32.0 $^{\circ}$
h = 0 \rightarrow 10
k = 0 \rightarrow 20
l = -13 \rightarrow 12
 3 standard reflections
 frequency: 60 min
 intensity decay: 2.0%

Table 3
Hydrogen-bonding geometry (\AA , $^{\circ}$) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1A—H1OA...O6B ⁱ	0.84	1.95	2.765 (3)	164
O3A—H3OA...O6A ⁱⁱ	0.84	1.84	2.679 (3)	173
O4A—H4OA...O1A ⁱⁱⁱ	0.84	1.85	2.678 (3)	167
O6A—H6OA...O1B ^{iv}	0.84	1.87	2.705 (3)	175
O1B—H1OB...O4B ⁱⁱ	0.84	1.97	2.726 (3)	150
O3B—H3OB...O4A	0.84	1.88	2.716 (3)	172
O4B—H4OB...O3A ⁱⁱⁱ	0.84	2.02	2.854 (3)	173
O6B—H6OB...O3B ^v	0.84	1.99	2.781 (3)	156

Symmetry codes: (i) $x, 1+y, z$; (ii) $x-1, y, z$; (iii) $1-x, y-\frac{1}{2}, 1-z$; (iv) $1+x, y, z$; (v) $2-x, y-\frac{1}{2}, 2-z$.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.113$
S = 1.07
 3107 reflections
 235 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.4465P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.39 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.32 \text{ e } \text{\AA}^{-3}$

Compound (III)

Crystal data

Na⁺·I⁻·C₇H₁₄O₆
M_r = 344.07
 Orthorhombic, *C*222₁
a = 6.948 (3) \AA
b = 11.4543 (6) \AA
c = 15.3050 (7) \AA
V = 1218.1 (5) \AA^3
Z = 4
D_x = 1.876 Mg m⁻³

Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 22.0–31.3 $^{\circ}$
 μ = 2.67 mm⁻¹
T = 297 K
 Prism, colorless
 0.38 \times 0.32 \times 0.20 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\text{min}} = 0.430$, $T_{\text{max}} = 0.598$
 3069 measured reflections
 2871 independent reflections
 2628 reflections with $I > 2\sigma(I)$

R_{int} = 0.019
 θ_{max} = 40.0 $^{\circ}$
h = 0 \rightarrow 12
k = 0 \rightarrow 20
l = -21 \rightarrow 27
 3 standard reflections
 frequency: 166 min
 intensity decay: 1.0%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.059$
S = 1.091
 2871 reflections
 73 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0265P)^2 + 0.4538P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.66 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.86 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0144 (5)
 Absolute structure: Flack (1983), 758 Friedel pairs
 Flack parameter = -0.025 (18)

H atoms were located in difference maps and were placed in calculated positions with C—H bond distances in the range 0.97–1.00 \AA and O—H distances in the range 0.82–0.84 \AA , and thereafter treated as riding. A torsional parameter was refined for each OH group and displacement parameters were assigned as $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the attached C atom (1.5 for OH). For (I), the maximum residual density was 0.66 \AA from O2B and the deepest hole was 0.53 \AA from

Table 4

Selected geometric parameters (Å, °) for (III).

Na—O1 ⁱ	2.3112 (17)	Na—O3 ⁱⁱ	2.4047 (15)
Na—O2 ⁱ	2.4393 (11)		
O1 ⁱ —Na—O1 ⁱⁱⁱ	95.49 (11)	O3 ⁱⁱ —Na—O2 ⁱ	87.05 (4)
O1 ⁱ —Na—O3 ⁱⁱⁱ	153.05 (5)	O1 ⁱ —Na—O2 ⁱⁱⁱ	102.75 (5)
O1 ⁱⁱⁱ —Na—O3 ⁱⁱ	101.69 (6)	O1 ⁱⁱⁱ —Na—O2 ⁱⁱⁱ	68.87 (5)
O1 ⁱ —Na—O2 ⁱ	68.87 (5)	O3 ⁱⁱ —Na—O2 ⁱⁱⁱ	102.74 (5)
O1 ⁱⁱⁱ —Na—O2 ⁱ	102.75 (5)	O2 ⁱ —Na—O2 ⁱⁱⁱ	168.07 (7)

 Symmetry codes: (i) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (ii) $2 - x, y, \frac{3}{2} - z$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.

Table 5

Hydrogen-bonding geometry (Å, °) for (III).

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1O...I ⁱ	0.82	2.63	3.4447 (14)	174
O3—H3O...I ⁱⁱ	0.82	2.69	3.5095 (13)	177

 Symmetry codes: (i) $1 - x, -y, z - \frac{1}{2}$; (ii) $2 - x, -y, z - \frac{1}{2}$.

C3A. The absolute configurations of forms (I) and (II) could not be determined directly from the diffraction data, but were assigned to correspond with that determined for the NaI complex and with the known configuration of D-mannitol.

For all compounds, data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *maXus* (Mackay *et al.*, 1999) for compound (I), *XCAD4* (Harms & Wocadlo, 1995) for other compounds; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993) for compound (I), *SHELXS97* (Sheldrick, 1997) for other compounds; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* for compound (I), *WinGX* (Farrugia, 1999) for other compounds.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1162). Services for accessing these data are described at the back of the journal.

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