The Crystal Structures of 2,2,6,6-Tetramethyl-4-oxaheptane-1,7-diol and 2,2,6,6,10,10-Hexamethyl-4,8-dioxaundecane-1,11-diol at −150 °C

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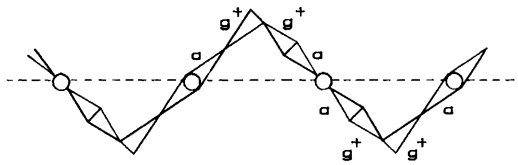
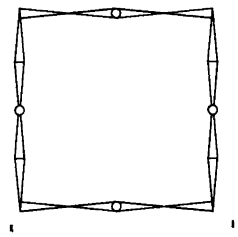
Groth, P., 1987. The Crystal Structures of 2,2,6,6-Tetramethyl-4-oxaheptane-1,7-diol and 2,2,6,6,10,10-Hexamethyl-4,8-dioxaundecane-1,11-diol at −150 °C. – Acta Chem. Scand., Ser. B 41: 487–493.

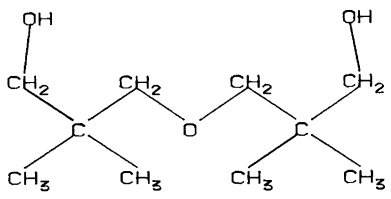
Crystals of $C_{10}H_{22}O_3$ (**1**) belong to the triclinic system with cell dimensions a = 6.430(1), b = 9.970(2) and c = 18.270(3) Å; α = 91.81(1), β = 94.87(1), γ = 90.23(1)°, space group $P\bar{1}$ and Z = 4. Those of $C_{15}H_{32}O_4$ (**2**) are orthorhombic with cell dimensions a = 10.154(3), b = 11.967(5) and c = 28.851(8) Å; space group *Pbca* and Z = 8. The structures were solved by direct methods. The final R-values were 7.1 % (3180 reflections) for **1** and 6.0 % (1678 reflections) for **2**. Data were collected on an automatic four circle diffractometer at ca. −150 °C. The 9- and 13-membered chains adopt conformations in favour of ring formation.

Poly(trimethylene oxide) in its stable (orthorhombic) crystalline form adopts a folded conformation with a repeating $a\ g^+\ g^+\ a$ unit (a = *anti*, g = *gauche*) which is always of the same sign within each chain.[1]



The cyclic analogue 1,5,9,13-tetraoxacyclohexadecane, which is a tetramer of trimethylene oxide and which must have eight *gauche* bonds to be able to form a ring, adopts a square, diamond lattice [4 4 4 4][2] conformation which is in every detail identical with the most stable polymer chain, except that the *gauche* bonds alternate from corner to corner.[3] It is significant that this tetramer is the only cyclic oligomer formed rapidly during polymerization of trimethylene oxide,[4] although lower cyclic oligomers are also formed under





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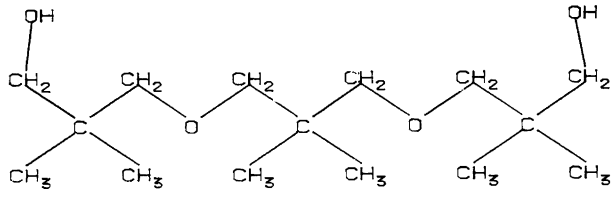

2

Table 1. Final fractional coordinates and equivalent temperature factors with estimated standard deviations for the non-hydrogen atoms of the heptanediol **1**.

Atom	*x*	*y*	*z*	U_{eq} [a]
O1	0.0839(4)	−0.0342(3)	0.0681(1)	0.068
C1	0.2791(5)	0.0281(3)	0.0865(2)	0.038
C2	0.2651(4)	0.1702(3)	0.1195(1)	0.029
C3	0.1492(5)	0.1690(3)	0.1887(2)	0.044
C4	0.4877(6)	0.2217(4)	0.1370(2)	0.051
C5	0.1488(5)	0.2610(3)	0.0648(2)	0.035
O2	0.2513(3)	0.2636(2)	−0.0009(1)	0.029
C6	0.1595(4)	0.3576(3)	−0.0516(1)	0.028
C7	0.2753(4)	0.3544(3)	−0.1208(1)	0.025
C8	0.5055(5)	0.3829(3)	−0.1016(2)	0.034
C9	0.1764(5)	0.4608(3)	−0.1713(1)	0.032
C10	0.2523(5)	0.2163(3)	−0.1594(1)	0.032
O3	0.0431(4)	0.1788(2)	−0.1807(1)	0.048
O4	−0.0492(4)	0.1980(2)	0.6718(1)	0.060
C11	−0.0604(5)	0.3234(3)	0.6370(2)	0.036
C12	−0.2836(4)	0.3659(3)	0.6152(1)	0.027
C13	−0.4074(5)	0.3745(3)	0.6831(2)	0.038
C14	−0.2763(5)	0.5036(3)	0.5810(2)	0.035
C15	−0.3900(4)	0.2642(3)	0.5605(1)	0.027
O5	−0.2847(3)	0.2570(2)	0.4957(1)	0.026
C16	−0.3671(4)	0.1536(3)	0.4452(1)	0.026
C17	−0.2486(4)	0.1535(3)	0.3767(1)	0.025
C18	−0.3372(5)	0.0397(3)	0.3250(1)	0.033
C19	−0.2756(5)	0.2888(3)	0.3388(1)	0.034
C20	−0.0161(4)	0.1340(3)	0.3962(1)	0.028
O6	−0.0358(3)	0.0083(2)	0.4279(1)	0.040

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Table 2. Final fractional coordinates and equivalent temperature factors with estimated standard deviations for the non-hydrogen atoms of the undecanediol **2**.

Atom	*x*	*y*	*z*	U_{eq} [a]
O1	0.9188(3)	−0.0234(3)	0.5623(1)	0.048
C1	0.8314(4)	0.0354(4)	0.5932(1)	0.040
C2	0.8347(4)	−0.0137(4)	0.6419(1)	0.036
C3	0.8009(5)	−0.1366(5)	0.6408(2)	0.049
C4	0.7333(5)	0.0492(5)	0.6714(2)	0.048
C5	0.9711(4)	0.0004(4)	0.6628(2)	0.038
O2	1.0075(2)	0.1136(2)	0.6640(1)	0.042
C6	1.1328(4)	0.1297(5)	0.6858(2)	0.044
C7	1.1708(4)	0.2512(4)	0.6855(1)	0.043
C8	1.0697(6)	0.3225(6)	0.7113(2)	0.059
C9	1.3052(5)	0.2614(6)	0.7096(2)	0.057
C10	1.1815(4)	0.2948(4)	0.6361(1)	0.041
O3	1.2725(2)	0.2286(3)	0.6109(1)	0.043
C11	1.2857(4)	0.2632(4)	0.5637(1)	0.039
C12	1.3489(4)	0.1671(4)	0.5366(1)	0.036
C13	1.4873(4)	0.1452(6)	0.5555(2)	0.049
C14	1.3604(5)	0.2062(5)	0.4855(2)	0.047
C15	1.2687(4)	0.0634(4)	0.5409(2)	0.041
O4	1.1339(3)	0.0786(3)	0.5265(1)	0.052

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Table 3. Bond distances (Å) and angles (°) with estimated standard deviations for **1**. The symmetry operators are: ′: $-x, -y, -z$; ″: $x, y, z-1$; ‴: $-x, -y, 1-z$.

Distance		Distance	
O1 –C1	1.409(5)	C1 –C2	1.529(5)
C2 –C3	1.521(5)	C2 –C4	1.523(5)
C2 –C5	1.521(4)	C5 –O2	1.418(4)
O2 –C6	1.432(4)	C6 –C7	1.522(4)
C7 –C8	1.516(4)	C7 –C9	1.533(4)
C7 –C10	1.528(4)	C10–O3	1.414(4)
O4 –C11	1.419(4)	C11–C12	1.522(5)
C12–C13	1.530(4)	C12–C14	1.530(4)
C12–C15	1.521(4)	C15–O5	1.413(4)
O5 –C16	1.430(4)	C16–C17	1.519(4)
C17–C18	1.531(4)	C17–C19	1.539(4)
C17–C20	1.522(4)	C20–O6	1.426(4)
O1 –O1′	2.735(4)	O1 –O3′	2.727(4)
O3″–O4	2.724(4)	O4 –O6‴	2.710(4)
O6 –O6‴	2.724(4)		
Angle		**Angle**	
O1 –C1 –C2	114.0(3)	C1 –C2 –C3	110.3(3)
C1 –C2 –C4	107.2(3)	C1 –C2 –C5	110.4(3)
C3 –C2 –C4	110.8(3)	C3 –C2 –C5	108.5(3)
C4 –C2 –C5	109.7(3)	C2 –C5 –O2	110.2(3)
C5 –O2 –C6	112.3(3)	O2 –C6 –C7	109.6(3)
C6 –C7 –C8	110.2(3)	C6 –C7 –C9	107.1(3)
C6 –C7 –C10	110.2(3)	C8 –C7 –C9	111.2(3)
C8 –C7 –C10	108.5(3)	C9 –C7 –C10	109.6(3)
C7 –C10 –O3	113.7(3)	O4 –C11 –C12	112.8(3)
C11–C12 –C13	110.0(3)	C11–C12 –C14	108.1(3)
C11–C12 –C15	110.3(3)	C13–C12 –C14	109.8(3)
C13–C12 –C15	108.5(3)	C14–C12 –C15	110.2(3)
C12–C15 –O5	110.3(3)	C15–O5 –C16	112.4(3)
O5 –C16 –C17	109.3(3)	C16–C17 –C18	107.8(3)
C16–C17 –C19	110.2(3)	C16–C17 –C20	110.9(3)
C18–C17 –C19	110.0(3)	C18–C17 –C20	110.5(3)
C19–C17 –C20	107.5(3)	C17–C20 –O6	114.2(3)

equilibrium conditions.[5] The probability that the growing chain folds back to form a square ring must be high; only three corners of alternating sign are needed to bring the reacting ends together for cyclization.[6] The present crystal structure investigatios of the *gem* dimethyl compounds **1** and **2** were undertaken in order to explore whether the 9- and 13-membered open chains follow the poly(trimethylene oxide) scheme or adopt conformations in favour of ring formation.

Experimental

Crystal and intensity data. Crystal data are: **1**: a = 6.430(1), b = 9.970(2), c = 18.270(3) Å, α = 91.81(1), β = 94.87(1), γ = 90.23(1)°, space group $P\bar{1}$, Z = 4, D_x = 1.07 g cm^{-3}, D_m = 1.03 g cm^{-3}, V = 1166.48 Å^3, μ (Mo$K\alpha$) = 0.84 cm^{-1}, λ (Mo$K\alpha$) = 0.71069 Å. **2**: a = 10.154(3), b = 11.967(5), c = 28.851(8) Å, space group *Pbca*, Z = 8, D_x = 1.05 g cm^{-3}, D_m = 1.02 g cm^{-3}, V = 3505.6 Å^3, μ(MoKa) = 0.79 cm^{-1}. Data were collected on a Nicolet *P*3 automatic four-circle diffractometer at ca. −150 °C (±5 °C) by the ω-scan technique ($2\theta_{max}$ = 50°) with Mo$K\alpha$ radiation. The scan rate varied from 3 to 6° min^{-1}, depending on the intensities of the reflections. The intensities of two test reflections remeasured after every 100 reflections showed no significant changes during data collection. The intensities

Table 4. Torsion angles (°) with estimated standard deviations for **1**.

Torsion angle	
O1 –C1 –C2 –C3	58.6(3)
O1 –C1 –C2 –C4	179.3(4)
O1 –C1 –C2 –C5	–61.3(3)
C1 –C2 –C5 –O2	–58.4(3)
C3 –C2 –C5 –O2	–179.4(4)
C4 –C2 –C5 –O2	59.5(3)
C2 –C5 –O2 –C6	–174.4(3)
C5 –O2 –C6 –C7	–179.5(3)
O2 –C6 –C7 –C8	–56.6(3)
O2 –C6 –C7 –C9	–177.6(3)
O2 –C6 –C7 –C10	63.2(3)
C6 –C7 –C10–O3	59.7(3)
C8 –C7 –C10–O3	–179.6(4)
C9 –C7 –C10–O3	–58.0(3)
O4 –C11–C12–C13	58.3(3)
O4 –C11–C12–C14	178.1(4)
O4 –C11–C12–C15	–61.4(3)
C11–C12–C15–O5	–61.7(3)
C13–C12–C15–O5	177.8(3)
C14–C12–C15–O5	57.5(3)
C12–C5 –O5 –C16	174.5(3)
C15–O5 –C16–C17	179.2(3)
O5 –C16–C17–C18	178.6(3)
O5 –C16–C17–C19	–61.3(3)
O5 –C16–C17–C20	57.6(3)
C16–C17–C20–O6	63.2(3)
C18–C17–C20–O6	–56.2(3)
C19–C17–C20–O6	–176.3(3)

were corrected for Lorentz and polarization effects, but no corrections were made for absorption or secondary extinction (crystal sizes 0.2×0.5×0.4 mm and 0.6×0.4×0.3 mm for **1** and **2**, respectively). With an observed-unobserved cutoff at 2.5σ(I), 3180 reflections for **1** and 1678 for **2** were regarded as observed.

Determination and refinement of the structures. The structures were solved by direct methods[7] and refined by the full-matrix least-squares technique. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Hydrogen atoms, the positions of which were partly calculated and partly localized in difference Fourier maps, were refined with isotropic temperature factors. Weights in least-squares were obtained from the standard deviations in intensities, σ(I), taken as $\sigma(I) = [C_T + (0.02C_N)^2]^{1/2}$ were C_T is the total number of counts and C_N the net count. Anisotropic temperature factors were used for non-hydrogen atoms. The final R-values were $R = 7.1\,\%$ ($R_w = 6.5\,\%$) for the 3180 reflections of **1**, and $R = 6.0\,\%$ ($R_w = 5.6\,\%$) for the 1678 reflections of **2**. Standard deviations in bond distances, bond angles and torsion angles were calculated from the correlation matrices of the final least-squares refinement cycles. Final fractional coordinates with estimated standard deviations are given in Tables 1 and 2. The maximum r.m.s. amplitudes of vibration range from 0.19 to 0.37 Å for **1**, and from 0.21 to 0.31 Å for **2**. Lists of hydrogen atom parameters, thermal parameters, and observed and calculated structures factors are obtrainable from the author on request.

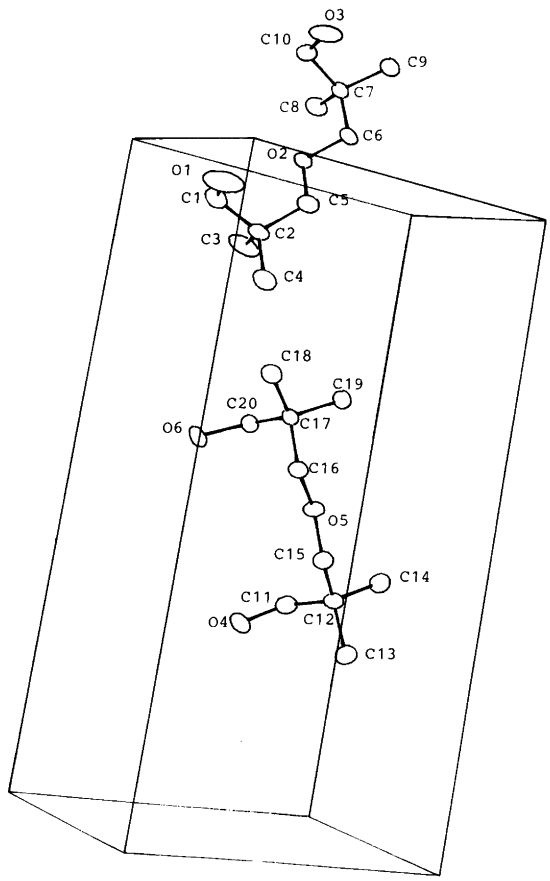

Fig. 1. Schematic drawing showing the two independent heptanediol molecules and the numbering of atoms. Symmetry operations are: ′: $-x, -y, -z$; ″: $x, y, z-1$; ‴: $-x, -y, 1-z$.

Discussion

The heptanediol **1**. Bond distances, bond angles and torsion angles of the two independent molecules in the asymmetric unit are listed in Tables 3 and 4. From Table 4 it may be seen that the torsion angles at the two corners have opposite signs in both molecules, implying that the chains fold back rather than adopt the poly(trimethylene oxide) conformation.

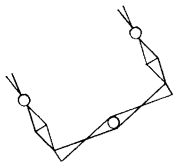

Fig. 1 is a schematic drawing showing the two independent molecules and the numbering of atoms. The bond distances and angles are normal within estimated limits of error. The hydroxy hydrogen atoms were localized in a difference Fourier map which revealed *two* peaks at a distance of about 1 Å from each hydroxy oxygen atom. This evidence of statistically disordered hydroxy hydrogen atoms is in accordance with the observed hydrogen bonding system illustrated in Fig. 2, where the black dots represent the hydrogen atom positions found in the difference Fourier map. This kind of disorder may be compared with that of ice, where each oxygen atom is surrounded by four others with a hydrogen atom as a link between each pair.

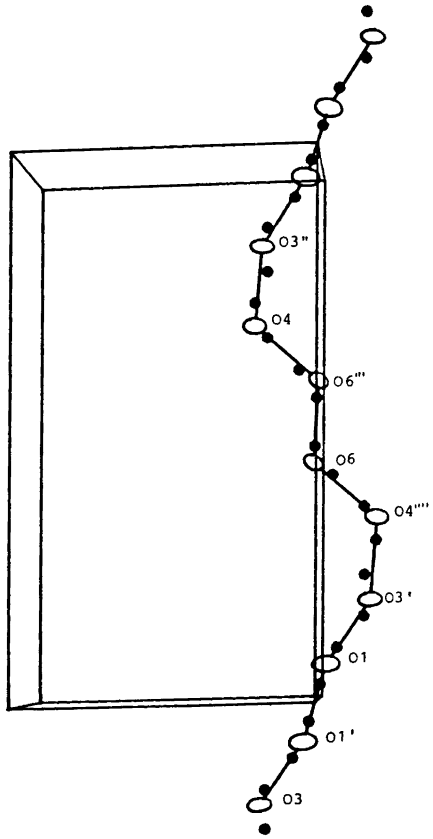

Fig. 2. Schematic drawing showing the hydrogen-bonding system in the heptanediol structure.

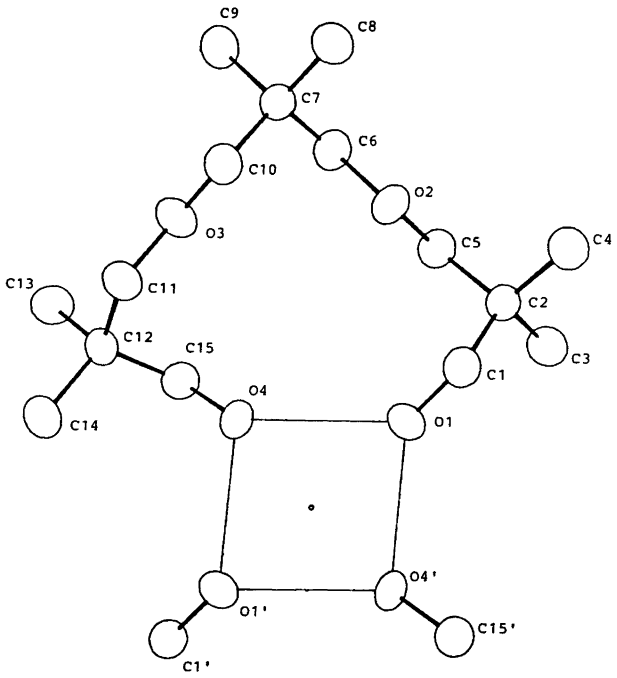

Fig. 3. Schematic drawing of **2** showing the numbering of atoms and the dimer forming hydrogen bonds. Symmetry operation: ': $2-x, -y, 1-z$.

The undecanediol **2**. Bond distances, bond angles and torsion angles are presented in Table 5. It may be seen that the torsion angles at the three corners have alternating signs, which brings the reacting ends in position for cyclization.

Table 5. Bond distances (Å), bond angles (°) and torsion angles (°) with estimated standard deviations for **2**. Symmetry operation: ′: $2-x, -y, 1-z$.

Distance		Distance	
O1 –C1	1.442(6)	C1 –C2	1.524(6)
C2 –C3	1.511(7)	C2 –C4	1.532(7)
C2 –C5	1.518(6)	C5 –O2	1.405(6)
O2 –C6	1.431(5)	C6 –C7	1.504(8)
C7 –C8	1.529(8)	C7 –C9	1.537(7)
C7 –C10	1.522(6)	C10–O3	1.417(6)
O3 –C11	1.429(5)	C11–C12	1.531(7)
C12–C13	1.530(6)	C12–C14	1.552(6)
C12–C15	1.490(7)	C15–O4	1.442(5)
O1 –O4	2.707(4)	O1 –O4′	2.699(4)
Angle		**Angle**	
O1 –C1 –C2	111.6(4)	C1 –C2 –C3	110.5(4)
C1 –C2 –C4	107.9(4)	C1 –C2 –C5	110.0(4)
C3 –C2 –C4	109.7(4)	C3 –C2 –C5	108.9(4)
C4 –C2 –C5	109.8(4)	C2 –C5 –O2	111.0(4)
C5 –O2 –C6	112.1(4)	O2 –C6 –C7	110.9(4)
C6 –C7 –C8	111.4(4)	C6 –C7 –C9	107.6(5)
C6 –C7 –C10	110.8(4)	C8 –C7 –C9	109.4(4)
C8 –C7 –C10	108.2(4)	C9 –C7 –C10	109.5(4)
C7 –C10–O3	109.6(4)	C10–O3 –C11	112.8(4)
O3 –C11–C12	107.9(4)	C11–C12–C13	109.4(4)
C11–C12–C14	106.9(4)	C11–C12–C15	110.7(4)
C13–C12–C14	108.7(4)	C13–C12–C15	109.2(4)
C14–C12–C15	111.8(4)	C12–C15–O4	112.9(4)
Torsion angle			
O1 –C1 –C2 –C3	−56.7(4)		
O1 –C1 –C2 –C4	−176.7(5)		
O1 –C1 –C2 –C5	63.6(4)		
C1 –C2 –C5 –O2	58.1(4)		
C3 –C2 –C5 –O2	179.3(5)		
C4 –C2 –C5 –O2	−60.5(4)		
C2 –C5 –O2 –C6	176.9(5)		
C5 –O2 –C6 –C7	178.4(5)		
O2 –C6 –C7 –C8	59.8(5)		
O2 –C6 –C7 –C9	179.6(5)		
O2 –C6 –C7 –C10	−60.7(4)		
C6 –C7 –C10–O3	−56.3(4)		
C8 –C7 –C10–O3	−178.6(5)		
C9 –C7 –C10–O3	62.3(4)		
C7 –C10–O3 –C11	178.7(5)		
C10–O3 –C11–C12	−162.2(5)		
O3 –C11–C12–C13	−63.2(4)		
O3 –C11–C12–C14	179.3(5)		
O3 –C11–C12–C15	57.3(4)		
C11–C12–C15–O4	55.9(4)		
C13–C12–C15–O4	176.5(5)		
C14–C12–C15–O4	−63.1(4)		

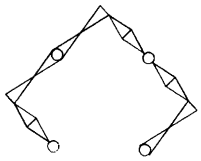

Fig. 3 is a schematic drawing giving the numbering of atoms and showing the centrosymmetric dimers formed by the hydrogen-bonding system. The bond distances, bond angles and torsion angles of Table 4 have normal values within error limits.

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