

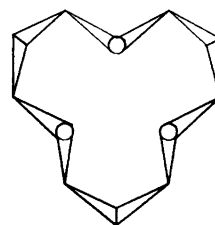
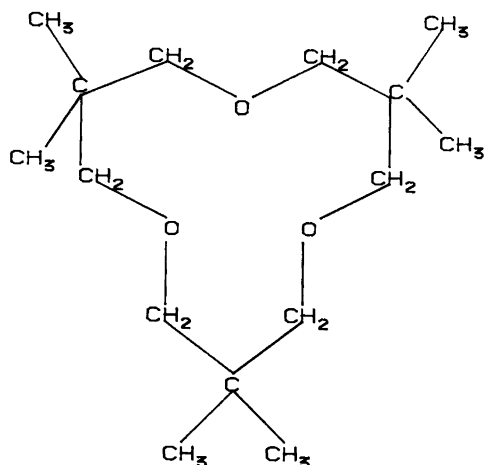
# The Crystal Structure of 3,3,7,7,11,11-Hexamethyl-1,5,9-trioxacyclododecane and its (1:1) Complex with Lithium Perchlorate at $-150^{\circ}\text{C}$

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The crystals of  $\text{C}_{15}\text{H}_{30}\text{O}_3$  (**1**) belong to the monoclinic system with cell dimensions  $a = 5.942(1)$ ,  $b = 15.944(4)$  and  $c = 17.116(4)$  Å;  $\beta = 97.82(2)^{\circ}$ , space group  $P2_1/n$  and  $Z = 4$ . Those of  $\text{C}_{15}\text{H}_{30}\text{O}_3 \cdot \text{LiClO}_4$  (**2**) are triclinic with cell dimensions  $a = 8.686(2)$ ,  $b = 10.980(2)$  and  $c = 10.997(2)$  Å;  $\alpha = 113.03(2)$ ,  $\beta = 90.83(2)$ ,  $\gamma = 91.61(2)^{\circ}$ , space group  $P\bar{1}$  and  $Z = 2$ . The structures were solved by direct methods. The final  $R$ -values were 4.6% (1795 reflections) for **1** and 6.4% (1948 reflections) for **2**. The preferred ring conformations are a biangular [48] for **1** and a non-angular with approximately  $C_{3v}$  symmetry for **2**.



the 12-membered ring conformation is altered by complex formation with lithium perchlorate.

## Experimental

**Crystal and intensity data.** Crystal data for  $\text{C}_{15}\text{H}_{30}\text{O}_3$  (**1**) are:  $a = 5.942(1)$ ,  $b = 15.944(4)$ ,  $c = 17.116(4)$  Å,  $\beta = 97.82(2)^{\circ}$ , space group  $P2_1/n$ ,  $Z = 4$ ,  $D_x = 1.07$  g cm $^{-3}$ ,  $D_m = 1.05$  g cm $^{-3}$  (by flotation),  $V = 1606.6(5)$  Å $^3$ ,  $\mu = 0.78$  cm $^{-1}$  (MoK $\alpha$ ) [ $\lambda(\text{MoK}\alpha) = 0.71069$  Å]. The crystal data for  $\text{C}_{15}\text{H}_{30}\text{O}_3 \cdot \text{LiClO}_4$  (**2**) are:  $a = 8.686(2)$ ,  $b = 10.980(2)$ ,  $c = 10.997(2)$  Å,  $\alpha = 113.03(2)$ ,  $\beta = 90.83(2)$ ,  $\gamma = 91.61(2)^{\circ}$ , space group  $P\bar{1}$ ,  $Z = 2$ ,  $D_x = 1.25$  g cm $^{-3}$ ,  $D_m = 1.23$  g cm $^{-3}$  (by flotation),  $V = 964.5(3)$  Å $^3$ ,  $\mu = 2.33$  cm $^{-1}$  (MoK $\alpha$ ). Data were collected on a Nicolet P3 automatic four-circle diffractometer at ca.  $-150^{\circ}\text{C}$  ( $\pm 5^{\circ}\text{C}$ ).

3,3,7,7,11,11-Hexamethyl-1,5,9-trioxacyclododecane and some of its alkali complexes have been investigated by Dale *et al.*<sup>1</sup> NMR spectroscopic studies suggested that the complexing ring skeleton adopts a non-angular conformation with  $D_3$  symmetry which is different from that of the free ligand.

The X-ray crystal structures of the title compounds were determined in order to verify the NMR-based conclusions and to explore whether

by the  $\omega$ -scan technique ( $2\theta_{\max} = 50^\circ$ ) with MoK $\alpha$  radiation.

The scan rate varied from 3 to 6° min<sup>-1</sup>, 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 were corrected for Lorentz and polarization effects, but no corrections were made for absorption or secondary extinction (crystal sizes 0.3 × 0.4 × 0.4 mm and 0.3 × 0.4 × 0.2 mm for **1** and **2**, respectively). With an observed-unobserved cut-off at 2.5 $\sigma(I)$ , 1795 reflections for **1** and 1948 for **2** were regarded as observed.

*Determination and refinement of the structures.*

The structures were solved by direct methods<sup>2</sup> and refined by the full-matrix least-squares technique.<sup>3</sup> Anisotropic temperature factors were used for non-hydrogen atoms. Hydrogen atom positions were calculated and refined with isotropic thermal parameters. Weights in least-squares were calculated from the standard deviations in intensities,  $\sigma(I)$ , taken as  $\sigma(I) = [C_T + (0.02 C_N)^2]^{1/2}$  where  $C_T$  is the total number of counts and  $C_N$  the net count. The maximum r.m.s. amplitudes of thermal vibration range

from 0.18 to 0.26 Å for **1** and from 0.16 to 0.30 Å for **2**. The final  $R$ -values were  $R = 4.6\%$  ( $R_w = 4.4\%$ ) and  $R = 6.4\%$  ( $R_w = 4.8\%$ ) for 1795 reflections of **1** and 1948 reflections of **2**, respectively. Standard deviations in bond distances, bond angles and torsion angles were calculated from the correlation matrices for the final least-

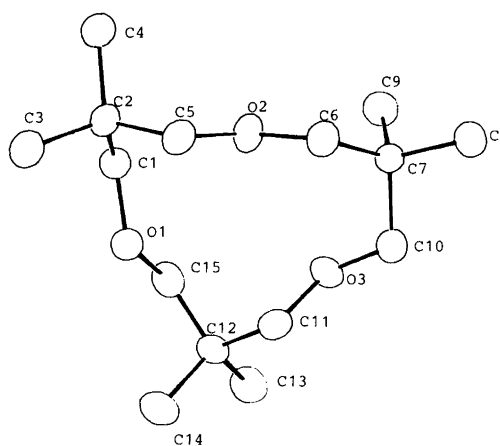


Fig. 1. Perspective drawing of the free ligand showing the numbering of atoms.

Table 1. Final fractional coordinates (e.s.d.'s in parentheses) and equivalent temperature factors for non-hydrogen atoms of the free ligand (**1**).

Atom	x	y	z	$U_{eq}^a$
O1	0.7109(3)	0.1401(1)	0.7390(1)	0.033
O2	0.5996(3)	0.3257(1)	0.7369(1)	0.034
O3	0.6168(3)	0.2562(1)	0.9052(1)	0.035
C1	0.8394(5)	0.1933(2)	0.6954(2)	0.034
C2	0.6826(5)	0.2376(2)	0.6307(1)	0.032
C3	0.5644(6)	0.1744(2)	0.5709(2)	0.043
C4	0.8283(6)	0.2981(2)	0.5897(2)	0.041
C5	0.5003(5)	0.2852(2)	0.6671(2)	0.034
C6	0.4452(5)	0.3794(2)	0.7692(2)	0.034
C7	0.5337(5)	0.4018(2)	0.8545(1)	0.028
C8	0.3976(6)	0.4775(2)	0.8764(2)	0.038
C9	0.7852(5)	0.4234(2)	0.8629(2)	0.039
C10	0.4927(6)	0.3316(2)	0.9124(2)	0.037
C11	0.4827(5)	0.1878(2)	0.8719(2)	0.033
C12	0.6277(5)	0.1095(2)	0.8700(1)	0.032
C13	0.7427(7)	0.0877(2)	0.9531(2)	0.045
C14	0.4740(7)	0.0382(2)	0.8368(2)	0.045
C15	0.8122(5)	0.1247(2)	0.8180(2)	0.036

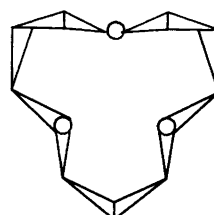
$$^a U_{eq} = (U_{11} + U_{22} + U_{33})/3$$

squares refinement cycles. Final fractional coordinates with estimated standard deviations for non-hydrogen atoms are given in Tables 1 and 3 for **1** and **2**, respectively. Lists of thermal parameters, hydrogen atom parameters, and observed and calculated structure factors are obtainable from the author on request.

## Discussion

*The free cyclic triether (1).* Bond distances, bond angles and torsion angles may be found in Table 2. Fig. 1 is a perspective drawing of the molecule

showing the numbering of atoms. The torsion angles (Table 2) show that the 12-membered ring skeleton adopts a biangular [4 8]<sup>4</sup> conformation:



[4 8]

Table 2. Bond distances (Å), bond angles (°) and torsion angles (°) (e.s.d.'s in parentheses) for the free ligand (**1**).

Distance		Distance	
O1 -C1	1.419(4)	O1 -C15	1.424(4)
O2 -C5	1.414(4)	O2 -C6	1.421(4)
O3 -C10	1.425(4)	O3 -C11	1.423(4)
C1 -C2	1.520(4)	C2 -C3	1.536(5)
C2 -C4	1.530(5)	C2 -C5	1.523(4)
C6 -C7	1.525(4)	C7 -C8	1.527(4)
C7 -C9	1.521(5)	C7 -C10	1.536(4)
C11-C12	1.519(4)	C12-C13	1.532(5)
C12-C14	1.519(5)	C12-C15	1.523(4)
Angle		Angle	
C1 -O1 -C15	114.5(3)	C5 -O2 -C6	112.8(3)
C10-O3 -C11	114.4(3)	O1 -C1 -C2	109.9(3)
C1 -C2 -C3	111.1(3)	C1 -C2 -C4	107.4(3)
C1 -C2 -C5	109.5(3)	C3 -C2 -C4	110.1(3)
C3 -C2 -C5	108.3(3)	C4 -C2 -C5	110.6(3)
O2 -C5 -C2	109.6(3)	O2 -C6 -C7	110.9(3)
C6 -C7 -C8	107.2(3)	C6 -C7 -C9	110.5(3)
C6 -C7 -C10	112.5(3)	C8 -C7 -C9	110.1(3)
C8 -C7 -C10	106.3(3)	C9 -C7 -C10	110.1(3)
O3 -C10 -C7	115.5(3)	O3 -C11 -C12	110.5(3)
C11-C12-C13	110.4(3)	C11-C12-C14	108.0(3)
C11-C12-C15	109.7(3)	C13-C12-C14	110.3(3)
C13-C12-C15	108.3(3)	C14-C12-C15	110.2(3)
O1 -C15-C12	109.7(3)		
Torsion angle			
C15-O1 -C1 -C2	-153.8(3)		
C1 -O1 -C15-C12	150.3(3)		
C6 -O2 -C5 -C2	173.0(3)		
C5 -O2 -C6 -C7	163.8(3)		
C11-O3 -C10 -C7	-107.8(3)		
C10-O3 -C11 -C12	-177.6(3)		
O1 -C1 -C2 -C5	56.1(3)		
C1 -C2 -C5 -O2	42.2(3)		
O2 -C6 -C7 -C10	-79.5(3)		
C6 -C7 -C10 -O3	66.7(3)		
O3 -C11 -C12 -C15	-62.0(3)		
C11 -C12 -C15 -O1	-63.0(3)		

Table 3. Final fractional coordinates (e.s.d.'s in parentheses) and equivalent temperature factors for non-hydrogen atoms of the lithium perchlorate complex (2).

Atom	x	y	z	$U_{eq}^a$
Cl	0.27561(16)	0.29881(14)	0.65801(14)	0.030
O4	0.3013(5)	0.1874(4)	0.6909(4)	0.058
O5	0.1207(4)	0.3426(4)	0.6925(4)	0.045
O6	0.3802(4)	0.4055(4)	0.7321(4)	0.057
O7	0.2936(4)	0.2635(4)	0.5182(4)	0.043
Li <sup>+</sup>	0.8961(9)	0.3313(8)	0.6824(9)	0.028
Cl	0.7766(4)	0.1797(3)	0.5694(3)	0.027
C1	0.6963(7)	0.0935(6)	0.6205(6)	0.034
C2	0.7500(6)	0.1176(5)	0.7609(5)	0.034
C3	0.9208(8)	0.0953(7)	0.7702(7)	0.045
C4	0.6584(9)	0.0150(7)	0.7973(7)	0.049
C5	0.7049(7)	0.2522(6)	0.8586(6)	0.033
O2	0.7846(4)	0.3602(3)	0.8389(3)	0.028
C6	0.7176(7)	0.4853(6)	0.9138(6)	0.033
C7	0.7763(6)	0.5969(5)	0.8740(5)	0.027
C8	0.9499(7)	0.6190(6)	0.8961(6)	0.034
C9	0.6958(8)	0.7216(7)	0.9638(6)	0.039
C10	0.7221(7)	0.5717(6)	0.7327(6)	0.030
O3	0.7893(4)	0.4573(3)	0.6354(3)	0.026
C11	0.7065(6)	0.4166(6)	0.5097(5)	0.031
C12	0.7620(6)	0.2853(5)	0.4089(5)	0.026
C13	0.9346(7)	0.2930(6)	0.3921(6)	0.035
C14	0.6775(8)	0.2631(7)	0.2787(6)	0.038
C15	0.7117(7)	0.1685(6)	0.4441(6)	0.030

$$^a U_{eq} = (U_{11} + U_{22} + U_{33})/3$$

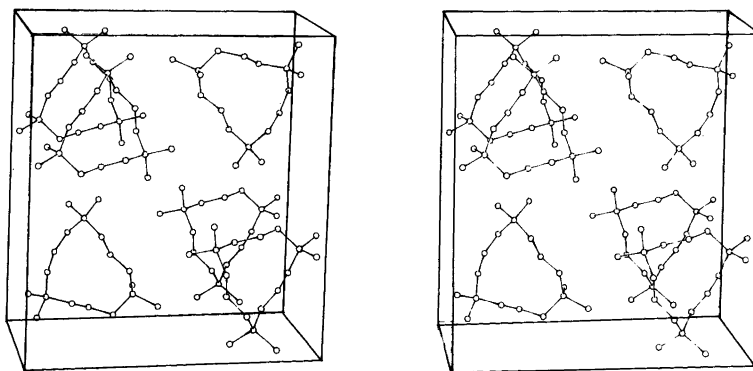
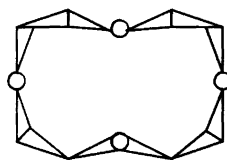


Fig. 2. Stereoscopic view of the unit cell contents for  $C_{15}H_{30}O_3$ .

The crystal conformation of one of the 12-membered rings in 7,16,21,26-tetraoxa-1,4,10,13-tetraazatricyclo[11.5.5.5<sup>4,10</sup>]octacosane complexed with potassium thiocyanate<sup>5</sup> and that of the ligand in the complex between  $CuCl_2$  and

1,4,7,10-tetraoxacyclododecane<sup>6</sup> have also been described as a strained [4 8] conformation. However, this is entirely different from the present conformation:



[ 4 8 ]

Bond distances and angles (Table 2) agree within estimated limits of error with corresponding values found for the (1:1) complex between 1,5,9-trioxacyclododecane and lithium thiocyanate.<sup>7</sup> Fig. 2 is a stereoscopic view of the cell contents.

Table 4. Bond distances (Å), bond angles (°) and torsion angles (°) (e.s.d.'s in parentheses) for the lithium perchlorate complex (2).

Distance		Distance	
Cl -O4	1.427(5)	C1 -O5	1.447(4)
Cl -O6	1.426(5)	C1 -O7	1.443(4)
O5 -Li <sup>+</sup>	1.950(9)	Li <sup>+</sup> -O1	1.908(9)
Li <sup>+</sup> -O2	1.907(10)	Li <sup>+</sup> -O3	1.913(9)
O1 -C1	1.445(7)	O1 -C15	1.439(7)
C1 -C2	1.525(9)	C2 -C3	1.519(9)
C2 -C4	1.540(10)	C2 -C5	1.514(8)
C5 -O2	1.447(7)	O2 -C6	1.441(7)
C6 -C7	1.531(8)	C7 -C8	1.521(8)
C7 -C9	1.535(9)	C7 -C10	1.532(8)
C10-O3	1.439(7)	O3 -C11	1.448(7)
C11-C12	1.531(8)	C12-C13	1.517(8)
C12-C14	1.528(9)	C12-C15	1.532(8)
Angle		Angle	
O4 -C1 -O5	109.3(3)	O4 -C1 -O6	110.0(3)
O4 -C1 -O7	110.3(3)	O5 -C1 -O6	107.9(3)
O5 -C1 -O7	109.0(3)	O6 -C1 -O7	110.3(3)
C1 -O1 -C15	111.9(4)	O1 -C1 -C2	112.3(5)
C1 -C2 -C3	112.4(5)	C1 -C2 -C4	105.4(5)
C1 -C2 -C5	111.5(5)	C3 -C2 -C4	108.6(6)
C3 -C2 -C5	112.4(5)	C4 -C2 -C5	106.1(5)
C2 -C5 -O2	112.8(5)	C5 -O2 -C6	111.5(4)
O2 -C6 -C7	112.8(5)	C6 -C7 -C8	111.0(5)
C6 -C7 -C9	105.9(5)	C6 -C7 -C10	110.7(5)
C8 -C7 -C9	109.5(5)	C8 -C7 -C10	113.6(5)
C9 -C7 -C10	105.8(5)	C7 -C10 -O3	112.7(5)
C10-O3 -C11	110.7(4)	O3 -C11 -C12	112.0(5)
C11-C12-C13	110.8(5)	C11-C12-C14	105.9(5)
C11-C12-C15	111.5(5)	C13-C12-C14	109.8(5)
C13-C12-C15	112.7(5)	C14-C12-C15	105.8(5)
O1 -C15-C12	112.1(5)		
Torsion angle			
C15-O1 -C1 -C2	-172.4(7)		
C1 -O1 -C15-C12	163.2(6)		
O1 -C1 -C2 -C5	67.5(6)		
C1 -C2 -C5 -O2	-67.0(6)		
C2 -C5 -O2 -C6	168.1(6)		
C5 -O2 -C6 -C7	-168.1(6)		
O2 -C6 -C7 -C10	66.6(5)		
C6 -C7 -C10 -O3	-66.3(5)		
C7 -C10 -O3 -C11	164.9(6)		
C10 -O3 -C11 -C12	-172.8(6)		
O3 -C11 -C12 -C15	71.3(5)		
C11 -C12 -C15 -O1	-62.2(5)		

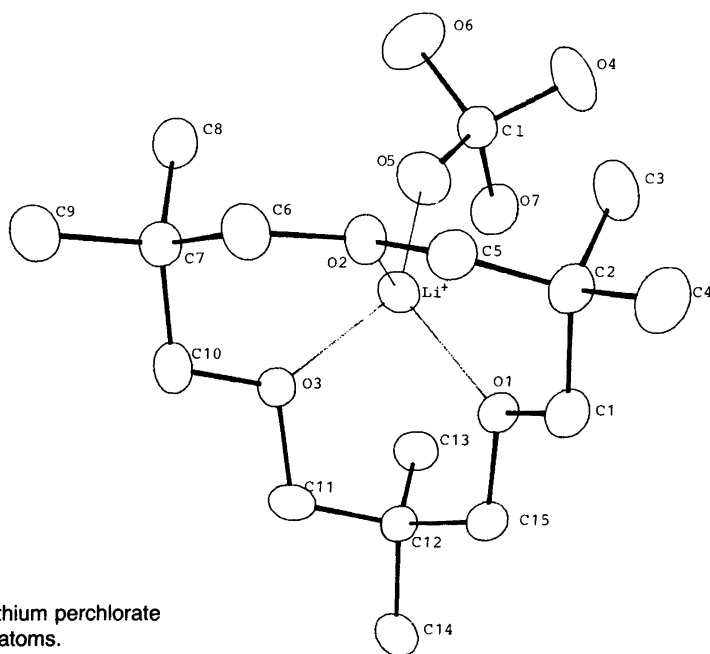


Fig. 3. Perspective drawing of the lithium perchlorate complex showing the numbering of atoms.

*The lithium perchlorate complex (2).* Bond distances, bond angles and torsion angles are listed in Table 4. Fig. 3 is a perspective drawing of the complex showing the numbering of atoms. The torsion angles (Table 4) show that the preferred ring conformation is non-angular with approximately  $C_{3v}$  symmetry, the same conformation as that found in the crystals of the (1:1) complex between 1,5,9-trioxacyclododecane and lithium thiocyanate.<sup>7</sup> In the free ligand only two ether

oxygen atoms are situated on the same side of the "ring-plane". In the complexed ligand all three are on the same side, thus providing good conditions for coordination to the  $Li^+$  cation, which is also coordinated to one of the oxygen atoms of the  $ClO_4^-$  anion. This non-angular diamond-lattice conformation is forbidden for the free ligand due to oxygen lone-pair repulsions. It seems reasonable that relief of conformational strain in the free 12-crown-3 ligand is part of the driving force

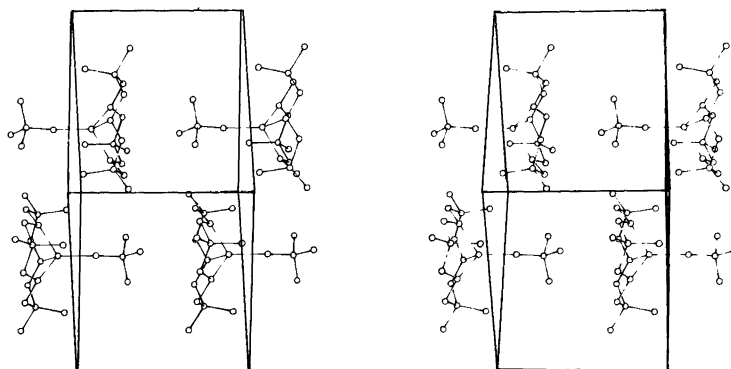


Fig. 4. Stereoscopic view of the unit cell contents for  $C_{15}H_{30}O_3 \cdot LiClO_4$ .

for its strong complex formation. The coordination bond lengths correspond closely to those in the lithium thiocyanate complex,<sup>6</sup> and are typical for tetrahedral coordination of lithium.<sup>8</sup> The lithium cation is displaced somewhat (0.98 Å) out of the plane of the three oxygen atoms towards the perchlorate anion. Bond distances and angles of the cyclic triether do not deviate significantly from those of the free ligand. The Cl–O distances have normal values. Fig. 4 is a stereo view of the unit cell contents. No intermolecular contacts shorter than the sum of the van der Waals radii occur in the structure of the free ligand. The shortest O–H contact in the lithium perchlorate complex (between the complexing oxygen atom, O5, and H82 in position  $x-l, y, z$ ) is 2.44 Å.

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