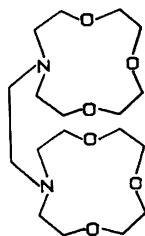


## Crystal Conformation of 10,10'-Ethylene Bis(1,4,7-trioxa-10-azacyclododecane) at $-130^{\circ}\text{C}$

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Enhanced complexation of alkali cations with ligands consisting of two mono-aza-12-crown-4 rings linked together by a single alkylene bridge ( $-\text{CH}_2-\text{CH}_2-$ ) between nitrogen atoms has been observed.<sup>1</sup>



X-Ray crystallographic investigations have been undertaken in order to settle the ring conformational problems (to which  $^{13}\text{C}$  NMR studies<sup>1</sup> gave no definite answers). A crystal structure determination of the (1:1) complex with lithium thiocyanate has recently been reported.<sup>2</sup> The results for the free ligand are now presented.

The crystals of  $\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6$  belong to the monoclinic system with space group  $P2_1/n$ , cell dimensions  $a=10.662(3)$ ,  $b=7.264(3)$ ,  $c=12.926(2)$  Å,  $\beta=92.68(2)^\circ$ , and  $Z=2$  ( $D_x=1.25$  g cm $^{-3}$ ,  $D_m=1.22$  g cm $^{-3}$ ). With  $2\theta_{\text{max}}=50^\circ$ , MoK $\alpha$ -radiation, and an observed-unobserved cutoff at  $2.5\sigma(I)$ , 1552 independent reflections were recorded as observed on an automatic four-circle diffractometer at *ca.*  $-130^\circ\text{C}$ . No corrections for absorption or secondary extinction were applied (crystal size  $0.6\times 0.3\times 0.7$  mm). The structure was solved by direct methods<sup>3</sup> and refined by the full-matrix least squares technique.<sup>4</sup> All programs used (except those for phase determination) are included in Ref. 4. Anisotropic temperature factors were used for O, N and C atoms and the 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. Hydrogen atom positions were calculated. The final  $R$ -value was 2.7% ( $R_w=3.5\%$ ) for 1552 observed reflections.

Final fractional coordinates with estimated standard deviations are listed in Table 1. Bond distances and angles and torsion angles may be found in Table 2. Fig. 1 is a schematic drawing of the centrosymmetric molecule indicating the numbering of atoms.

The dihedral angles of Table 2 correspond to a biangular [6 6] conformation<sup>5</sup> of the 12-membered ring; not surprisingly, the same conformation as that of the free 12-crown-4.<sup>6</sup>

In the crystals of the (1:1) lithium thiocyanate complex,<sup>2</sup> with two independent complexes in the asymmetric unit, the 12-membered rings adopt three different conformations, one of which may be described as [6 6]. It should, however, be pointed out that although both conformations are biangular, they are widely

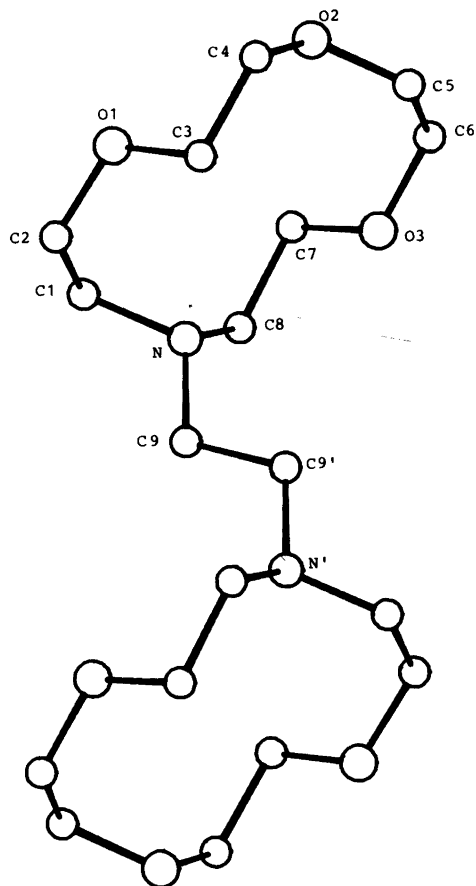


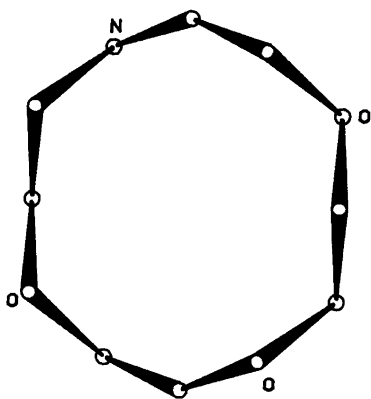
Fig. 1. Schematic drawing of the molecule showing the numbering of atoms. The symmetry code for the primed atoms is  $1-x, -y, 2-z$ .

Table 1. Final fractional coordinates with estimated standard deviations.

ATOM	X	Y	Z
O1	.84645( 6)	.52954(10)	.97788( 5)
O2	.98042( 6)	.16089(10)	1.16494( 5)
O3	.80370( 6)	-.16355(11)	1.13029( 5)
N	.66345( 7)	.01496(12)	.95459( 6)
C1	.74812(10)	.12403(15)	.86947( 8)
C2	.74504(10)	.31792(16)	.90239( 8)
C3	.80741(10)	.35622(16)	1.08223( 8)
C4	.92232(10)	.33797(15)	1.15453( 8)
C5	.92709(11)	.04596(17)	1.24039( 8)
C6	.90924(10)	-.14783(16)	1.20143( 8)
C7	.83679(10)	-.17808(16)	1.02424( 8)
C8	.71626(10)	-.17416(15)	.95811( 9)
C9	.52622( 9)	.01597(16)	.94698( 8)
H11	.6620(10)	.1227(17)	.8036( 8)
H12	.7990(10)	.0640(17)	.8529( 8)
H21	.6695(11)	.3757(17)	.9306( 9)
H22	.7703(11)	.3893(16)	.8424( 8)
H31	.7525(10)	.2300(17)	1.0963( 8)
H32	.7571(10)	.4494(16)	1.0911( 9)
H41	.8973(10)	.3817(17)	1.2239( 8)
H42	.9854(11)	.4222(17)	1.1274( 8)
H51	.8454(10)	.0937(16)	1.2617( 9)
H52	.9848(11)	.0433(17)	1.3052( 8)
H61	.8934(12)	-.2266(16)	1.2605( 9)
H62	.9841(11)	-.1904(17)	1.1690(10)
H71	.8828(10)	-.2943(16)	1.0434( 9)
H72	.8918(11)	-.0754(16)	1.0050( 9)
H81	.6562(11)	-.2563(17)	.9890( 8)
H82	.7327(10)	-.2245(16)	.8876( 8)
H91	.4884(11)	-.0764(17)	.8943( 9)
H92	.4989(10)	.1384(16)	.9208( 9)

Table 2. Bond distances and angles and dihedral angles with estimated standard deviations.

DISTANCE (Å)		DISTANCE (Å)	
O1 - C2	1.425( 1)	O1 - C5	1.431( 1)
O2 - C4	1.431( 2)	O2 - C5	1.428( 1)
O3 - C6	1.424( 1)	O3 - C7	1.435( 1)
N - C9	1.462( 1)	N - C1	1.467( 1)
N - C8	1.465( 1)	N - C9	1.522( 2)
C1 - C2	1.516( 2)	C3 - C4	1.506( 2)
C5 - C6	1.507( 2)	C7 - C8	1.510( 2)
ANGLE (°)		ANGLE (°)	
C2 - O1 - C3	113.8( 1)	C4 - O2 - C5	113.9( 1)
C6 - O3 - C7	113.6( 1)	C9 - N - C1	115.0( 1)
C9 - N - C8	113.7( 1)	C1 - N - C8	112.0( 1)
N - C9 - C8	111.7( 1)	N - C1 - C2	112.5( 1)
O1 - C2 - C1	112.1( 1)	O1 - C3 - C4	108.7( 1)
O2 - C4 - C3	112.8( 1)	O2 - C5 - C6	111.1( 1)
O3 - C6 - C5	112.2( 1)	O3 - C7 - C8	107.4( 1)
N - C8 - C7	111.4( 1)		
DIPEDRAL ANGLE (°)			
C2 - O1 - C3 - C4	177.0( 1)		
C3 - O1 - C2 - C1	-95.8( 1)		
C4 - O2 - C5 - C6	136.1( 1)		
C5 - O2 - C4 - C3	-85.0( 1)		
C6 - O3 - C7 - C8	-174.4( 1)		
C7 - O3 - C6 - C5	104.2( 1)		
C9 - N - C1 - C2	91.3( 1)		
C1 - N - C9 - C8	-153.4( 1)		
C9 - N - C8 - C7	-145.2( 1)		
C8 - N - C9 - C7	77.5( 1)		
C1 - N - C8 - C7	85.1( 1)		
C8 - N - C1 - C2	-159.7( 1)		
N - C1 - C2 - O1	70.0( 1)		
O1 - C5 - C4 - O2	-76.1( 1)		
O2 - C5 - C6 - O3	-76.2( 1)		
O3 - C7 - C8 - N	74.8( 1)		



[6 6]

different. The present ring, with one "corner" next to the nitrogen, corresponds closely to the centrosymmetric 12-crown-4 ring.<sup>6</sup> The [6 6]-ring of the complex, adopted in order to offer satisfactory coordination conditions, is not pseudo centrosymmetric at all, and both corner-atoms are situated next to oxygens. It may also be mentioned that the N--C--C--N torsion angle is *trans* in the present molecule and *gauche* in the complex.

The bond distances and angles of Table 2 are normal within error limits.

Lists of thermal parameters and observed and calculated structure factors are available from the author.

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1. Calverley, M. J. and Dale, J. J. *Chem. Commun.* (1981) 684.
2. Groth, P. *Acta Chem. Scand. A* 38 (1984) 337.
3. Germain, G., Main, P. and Woolfson, M.M. *Acta Crystallogr. A* 27 (1971) 368.
4. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
5. Dale, J. *Acta Chem. Scand.* 27 (1973) 1115.
6. Groth, P. *Acta Chem. Scand. A* 32 (1978) 279.

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