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Short Communications

Crystal Conformation of 4,7,13,16-Tetraoxa-1,10-diazabicyclo-[8.8.2]-eicosane at −130 °C

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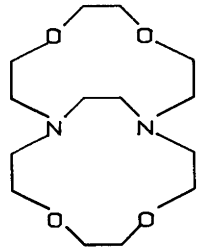
The synthesis and complexing properties of a novel bicyclic type of ligand having one 12-membered ring 1,4-condensed on the other has recently been reported.[1]



The strong Na^+ selectivity, demonstrated by titration with dry alkali thiocyanates in methanol monitored by ^{13}C NMR spectroscopy, was confirmed by pH-metric titration.[2] In order to verify that the Na^+ complex has the expected ligand conformation with both rings in

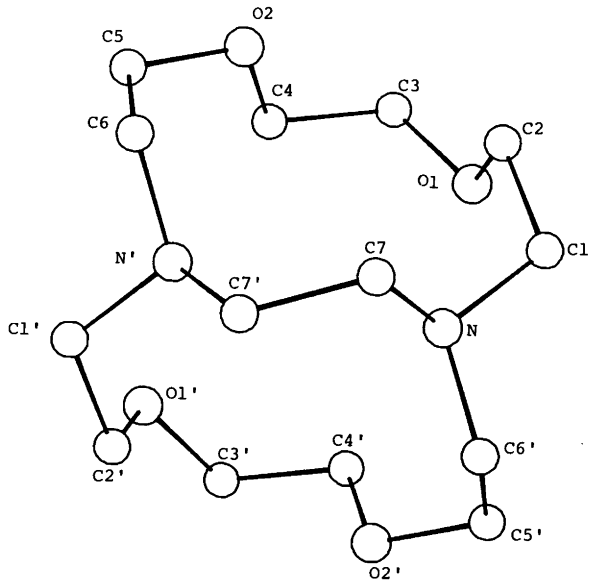


Fig. 1. Schematic drawing of the molecule showing the numbering of atoms. The symmetry code for the primed atoms is $1-x,y,\frac{1}{2}-z$.

0302-4377/85 $2.50

Table 1. Final fractional coordinates with estimated standard deviations.

ATOM	X	Y	Z
O1	.59349(6)	−.02678(13)	.38005(7)
O2	.69332(6)	.08420(13)	.19169(7)
N	.47861(7)	.29441(16)	.35570(8)
C1	.54101(12)	.24742(25)	.43383(12)
C2	.62424(11)	.14535(21)	.39997(12)
C3	.65242(11)	−.11267(22)	.31505(13)
C4	.63816(12)	−.06254(22)	.21338(12)
C5	.67204(12)	.15787(26)	.10150(12)
C6	.61811(11)	.32214(23)	.11226(14)
C7	.51561(12)	.43870(22)	.30143(12)
H11	.5065(11)	.1799(20)	.4820(11)
H12	.5638(12)	.3522(21)	.4670(10)
H21	.6739(11)	.1406(19)	.4516(11)
H22	.6515(10)	.1984(18)	.3429(11)
H31	.6363(11)	−.2345(23)	.3230(11)
H32	.7203(11)	−.0955(19)	.3333(10)
H41	.5711(12)	−.0377(19)	.2018(10)
H42	.6594(12)	−.1585(21)	.1695(12)
H51	.6347(11)	.0750(20)	.0623(11)
H52	.7338(12)	.1818(20)	.0680(11)
H61	.6202(11)	.3843(21)	.0504(12)
H62	.6504(11)	.3946(21)	.1606(12)
H71	.5862(11)	.4352(18)	.3024(10)
H72	.4966(11)	.5520(22)	.3313(10)

the quadrangular [3 3 3 3] conformation[3] of the same chirality, and also to learn how the rings are modified in the other complexes as well as in the free ligand, X-ray crystallographic investigation has been undertaken. The results for the free ligand are now presented.

The crystals of $C_{14}H_{28}N_2O_4$ belong to the orthorhombic system with space group *Pbcn*, cell dimensions a=7.841(3), b=14.072(4), c=14.210(5) Å, and Z=4 (D_x=1.22 g cm^{-3}, D_m=1.20 g cm^{-3}). With $2\theta_{max}$=50°, MoK_α-radiation, and an observed-unobserved cutoff at 2.5$\sigma(I)$, 1063 independent reflections were recorded as observed on an automatic four-circle diffractometer at *ca.* −130 °C. No corrections for absorption or secondary extinction were applied (crystal size 0.5×0.3×0.5 mm). The structure was solved by direct methods[4] and refined by full-matrix least squares technique.[5] All programs used (except those for phase determination) are included in Ref. 5. Anisotropic temperature factors were used for O, N and C atoms and weights in least squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I)=[C_T+(0.02\ C_N)^2]^{\frac{1}{2}}$ 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 3.4 % (R_w=3.5 %) for 1063 observed reflections.

Final fractional coordinates with estimated standard deviations are listed in Table 1. Bond diatances and angles and torsion angles may be found in Table 2. Fig. 1 is a schematic drawing of the molecule (possessing a two-fold axis of rotation) indicating the numbering of atoms.

The dihedral angles of Table 2 correspond to a biangular [3 9] conformation of the 12-membered ring which has been observed earlier.[6,7] Calculations of interatomic contacts show that the cleft between the two rings, arising when both have the conformation

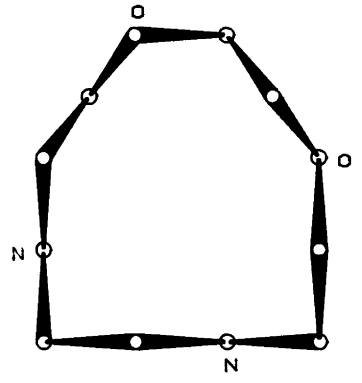
Table 2. Bond distances and angles and dihedral angles with estimated standard deviations.

DISTANCE	(Å)	DISTANCE	(Å)
O1 – C2	1.424(2)	O1 – C3	1.423(2)
O2 – C4	1.425(2)	O2 – C5	1.427(2)
N – C1	1.460(2)	N – C6'	1.463(2)
N – C7	1.463(2)	C1 – C2	1.505(2)
C3 – C4	1.497(2)	C5 – C6	1.506(3)
C7 – C7'	1.514(3)		

ANGLE	(°)	ANGLE	(°)
C2 – O1 – C3	113.7(1)	C4 – O2 – C5	113.6(1)
C1 – N – C6'	112.1(1)	C1 – N – C7	111.7(1)
C6 – N – C7	112.6(1)	N – C1 – C2	111.9(1)
O1 – C2 – C1	108.4(1)	O1 – C3 – C4	114.0(1)
O2 – C4 – C3	110.0(1)	O2 – C5 – C6	111.4(1)
N'– C6 – C5	112.4(1)	N – C7 – C7'	113.2(1)

DIHEDRAL ANGLE				(°)
C2 –	O1 –	C3 –	C4	-77.7(2)
C3 –	O1 –	C2 –	C1	157.0(1)
C4 –	O2 –	C5 –	C6	106.5(2)
C5 –	O2 –	C4 –	C3	-169.9(1)
C1 –	N –	C6'–	C5'	-81.5(2)
C6'–	N –	C1 –	C2	154.3(1)
C1 –	N –	C7 –	C7'	151.8(1)
C7 –	N –	C1 –	C2	-78.3(2)
C6'–	N –	C7 –	C7'	-81.1(2)
C7 –	N –	C6'–	C5'	151.0(2)
N –	C1 –	C2 –	O1	-75.7(2)
O1 –	C3 –	C4 –	O2	85.1(2)
O2 –	C5 –	C6 –	N'	-71.4(2)
N –	C7 –	C7'–	N'	-65.4(2)

[3 3 3 3], is well filled up by hydrogen atoms (at C4 and C4′) by this conformational change.



[3 9]

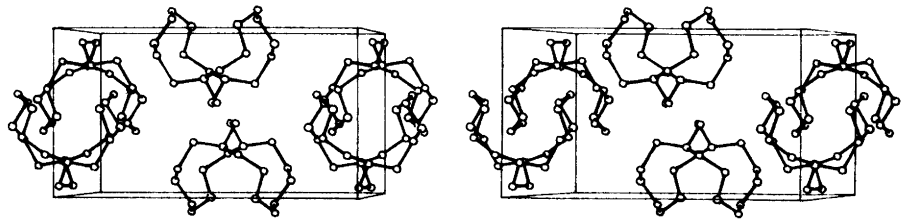


Fig. 2. Stereo view showing the unit cell contents.

Bond distances and angles are normal within error limits.

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

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