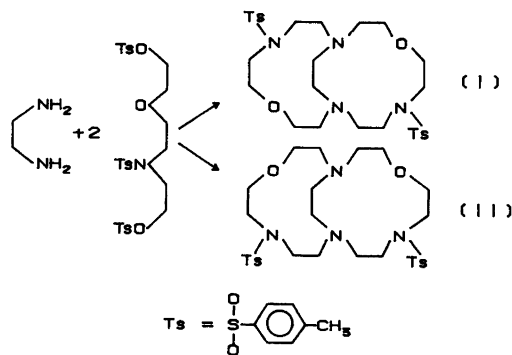


The Crystal Structure of 7,16-Ditosyl-4,13-dioxa-1,7,10,16-tetraaza-dicyclo[8.8.2]-eicosane at Room Temperature

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Outlines for syntheses of multiacrocyclic aminoethers designed for complexation of sodium and similar cations have been described.¹ The structure of the product obtained from the reaction between 1,2-diaminoethane and 1,8-ditosyl-oxy-3-oxa-6-tosylaza-octane, where two isomers are possible, could not be assigned spectroscopically.



Since both products are intermediates needed for such syntheses, a crystallographic structure determination has been carried out.

The crystals of $C_{28}H_{42}N_4O_6S_2$ are monoclinic with space group $P2_1/c$, cell dimensions $a=19.232(4)$, $b=5.327(3)$, $c=15.131(6)$ Å, $\beta=106.56(3)^\circ$, and $Z=2$ ($D_x=1.33$ g cm⁻³, $D_m=1.29$ g cm⁻³). The fact that space group $P1/c$ with $Z=2$ demands C_i symmetry of the molecule, excludes the isomer (II) if the crystal structure is ordered. Numerous examples of disorder phenomena in the crystals of similar ring compounds made it desirable to complete the investigation. With $2\theta_{max}=50^\circ$ and MoK_α -radiation 1037 observed reflections were collected on an automatic four-circle diffractometer at room temperature.

The structure was solved by direct methods² and refined by full-matrix least squares technique.³ [All programs used (except those for

Table 1. Final fractional coordinates with estimated standard deviations. H_m is bonded to C_m . H_{12P} is bonded to C_{12} . H_{mn} is bonded to C_m .

ATOM	X	Y	Z
S	.7112(1)	.2235(5)	.4947(1)
O2	.7509(2)	.0459(10)	.5621(4)
O5	.6614(2)	.1371(10)	.4101(3)
O8	.6610(4)	.4178(16)	.5493(6)
C9	.6115(5)	.5818(20)	.5012(5)
C10	.5730(4)	.7295(21)	.5411(6)
C11	.5821(4)	.7128(19)	.6376(6)
C12	.6316(5)	.5479(20)	.6816(5)
C13	.6706(4)	.3996(19)	.6420(6)
C14	.5405(4)	.8756(19)	.6872(6)
O1	1.1375(2)	.3526(11)	.6416(3)
N1	.7708(3)	.3967(13)	.4673(4)
N2	.9664(3)	.4219(13)	.6054(4)
C1	.8335(4)	.4830(16)	.5428(5)
C2	.8969(4)	.2958(17)	.5628(5)
C3	1.0199(4)	.2354(19)	.6567(5)
C4	1.0932(4)	.3539(17)	.7026(5)
C5	.7959(4)	.5189(17)	.3201(5)
C6	.7479(4)	.5515(17)	.3846(6)
C7	.9908(4)	.5722(16)	.5402(5)
H9	.598(3)	.583(12)	.437(4)
H10	.535(3)	.833(11)	.508(4)
H12P	.851(2)	.656(9)	.524(3)
H13	.706(3)	.305(11)	.675(4)
H11	.817(2)	.518(9)	.600(3)
H12	.638(3)	.530(13)	.751(4)
H21	.893(2)	.200(9)	.500(3)
H22	.885(2)	.170(9)	.604(3)
H31	1.027(2)	.106(11)	.612(4)
H32	1.000(2)	.160(10)	.705(3)
H41	1.116(2)	.254(10)	.756(3)
H42	1.092(2)	.537(11)	.729(3)
H51	.779(2)	.634(12)	.267(3)
H52	.792(3)	.353(16)	.302(5)
H61	.752(2)	.731(9)	.405(2)
H62	.697(2)	.496(10)	.350(3)
H71	1.031(3)	.661(10)	.567(3)
H72	.960(4)	.672(17)	.508(6)
H141	.536(3)	.761(16)	.740(5)
H142	.558(3)	1.044(12)	.682(4)
H143	.491(3)	.896(12)	.649(4)

phase determination) are contained in Ref. 3]. Hydrogen atom positions were calculated except for those of the methyl group which were localized in a difference Fourier map. Anisotropic temperature factors were used for non-hydrogen atoms, and weights in least squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I)=[C_T+(0.02 C_N)^2]^{1/2}$, where C_T is the total number of counts and C_N the net count. The R -value was as high as $R=8.2\%$ ($R_w=5.2\%$), probably due to poor crystal quality. Final fractional coordinates with estimated standard deviations are given in Table

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

DISTANCE		(Å)	DISTANCE		(Å)
S - O2	1.44	(1)	S - O3	1.44	(1)
S - C8	1.77	(1)	S - N1	1.61	(1)
C8 - C9	1.34	(1)	C8 - C13	1.36	(1)
C9 - C10	1.37	(1)	C10 - C11	1.38	(1)
C11 - C12	1.34	(1)	C11 - C14	1.52	(1)
C12 - C13	1.37	(1)	O1 - C4	1.42	(1)
O1 - C5'	1.42	(1)	N1 - C1	1.48	(1)
N1 - C6	1.46	(1)	N2 - C2	1.47	(1)
N2 - C3	1.48	(1)	N2 - C7	1.45	(1)
C1 - C2	1.54	(1)	C3 - C4	1.52	(1)
C5 - C6	1.53	(1)	C7 - C7'	1.56	(1)
ANGLE		(°)	ANGLE		(°)
O2 - S - O5	120.	(1)	O2 - S - C8	108.	(1)
O2 - S - N1	107.	(1)	O3 - S - C8	107.	(1)
O3 - S - N1	107.	(1)	C8 - S - N1	108.	(1)
S - C8 - C9	122.	(1)	S - C8 - C13	120.	(1)
C9 - C8 - C13	118.	(1)	C8 - C9 - C10	121.	(1)
C9 - C10 - C11	122.	(1)	C10 - C11 - C12	117.	(1)
C10 - C11 - C14	123.	(1)	C12 - C11 - C14	120.	(1)
C11 - C12 - C13	122.	(1)	C8 - C13 - C12	121.	(1)
C4 - O1 - C5'	112.	(1)	S - N1 - C1	118.	(1)
S - N1 - C6	119.	(1)	C1 - N1 - C6	118.	(1)
C2 - N2 - C3	109.	(1)	C2 - N2 - C7	113.	(1)
C3 - N2 - C7	115.	(1)	N1 - C1 - C2	112.	(1)
N2 - C2 - C1	111.	(1)	N2 - C3 - C4	112.	(1)
O1 - C4 - C3	111.	(1)	C6 - C5 - O1'	109.	(1)
N1 - C6 - C5	113.	(1)	N2 - C7 - C7'	117.	(1)
DIHEDRAL ANGLE		(°)	DIHEDRAL ANGLE		(°)
C4 - O1 - C5' - C6'	174.	(1)	C4 - O1 - C5' - C6'	174.	(1)
C5 - O1 - C4 - C3	175.	(1)	C5 - O1 - C4 - C3	175.	(1)
S - N1 - C1 - C2	89.	(1)	S - N1 - C1 - C2	89.	(1)
S - N1 - C6 - C5	-129.	(1)	S - N1 - C6 - C5	-129.	(1)
C1 - N1 - C6 - C5	78.	(1)	C1 - N1 - C6 - C5	78.	(1)
C6 - N1 - C1 - C2	-118.	(1)	C6 - N1 - C1 - C2	-118.	(1)
C2 - N2 - C3 - C4	180.	(1)	C2 - N2 - C3 - C4	180.	(1)
C3 - N2 - C2 - C1	157.	(1)	C3 - N2 - C2 - C1	157.	(1)
C2 - N2 - C7 - C7'	-64.	(1)	C2 - N2 - C7 - C7'	-64.	(1)
C7 - N2 - C2 - C1	-74.	(1)	C7 - N2 - C2 - C1	-74.	(1)
C3 - N2 - C7 - C7'	62.	(1)	C3 - N2 - C7 - C7'	62.	(1)
C7 - N2 - C3 - C4	52.	(1)	C7 - N2 - C3 - C4	52.	(1)
N1 - C1 - C2 - N2	155.	(1)	N1 - C1 - C2 - N2	155.	(1)
N2 - C3 - C4 - O1	-89.	(1)	N2 - C3 - C4 - O1	-89.	(1)
O1' - C5 - C6 - N1	-75.	(1)	O1' - C5 - C6 - N1	-75.	(1)
N2 - C7 - C7' - N2'	-180.	(1)	N2 - C7 - C7' - N2'	-180.	(1)

1. Bond distances and angles and dihedral angles may be found in Table 2. Except for C8-C9 which is somewhat short, the bond distances and angles have normal values within estimated limits of error. Fig. 1 is a schematic drawing, showing the numbering of atoms.

From the torsion angles of Table 2 it is clear that the 12-membered ring adopts the [3 9] conformation,⁴ which has been observed earlier.^{5,6}

It should be noted that the two bridge head nitrogens (N2 and N2') play the role as "corner"

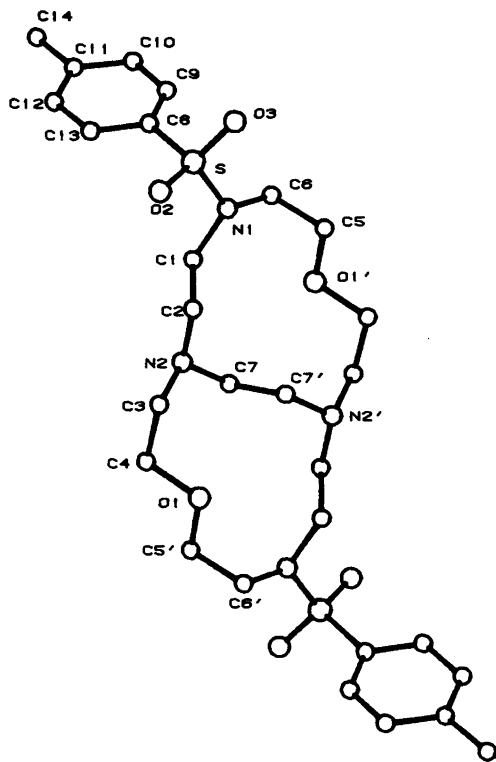
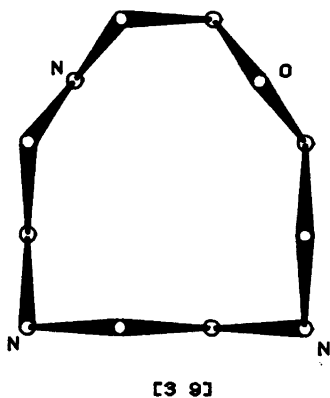


Fig. 1. Schematic drawing showing the numbering of atoms.

atoms. Transannular distances to O1 range from 3.04 to 3.20 Å.

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



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