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Structure of a Macrobicyclic Diaza Polyether Disulfonamide

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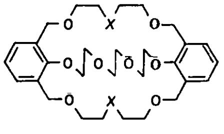
Abstract. *N,N′*-Ditosyl-1,4,7,10,18,24,33,39-octaoxa-21,36-diaza[10.9.9](2,1,3)benzenophane, $C_{44}H_{56}N_2O_{12}S_2$, $M_r = 869{\cdot}0$, orthorhombic, *Pcnb*, $a = 13{\cdot}823$ (3), $b = 16{\cdot}003$ (3), $c = 19{\cdot}268$ (4) Å, $V = 4262$ Å^3, $Z = 4$, $D_x = 1{\cdot}36$ g cm^{-3}, Cu *Kα*, $\lambda = 1{\cdot}54178$ Å, $\mu = 1{\cdot}6$ mm^{-1}, $F(000) = 1848$, room temperature, $R = 0{\cdot}040$ for 2369 unique observed reflections with $|F_o| > 3\sigma(|F_o|)$. The structure of the title compound (2) has C_2 symmetry and the potential molecular cavity is self-filling with the two trisubstituted aromatic rings lying adjacent and parallel to each other. This is in contrast to the asymmetric *V*-shaped molecular conformation adopted by 1,4,7,10,18,21,24,33,36,39-decaoxa[10.9.9](2,1,3)benzenophane (1).

Introduction. Recently, we have investigated (Alston, Slawin, Stoddart & Williams, 1984) the ability of the macrobicyclic polyether (1) to form stable adducts with transition-metal *cis*-diammines, such as $[RhL(NH_3)_2][PF_6]$ where L = 1,5-cyclooctadiene (cod) or norbornadiene (Colquhoun, Doughty, Stoddart & Williams, 1984; Colquhoun, Doughty, Stoddart, Slawin & Williams, 1986). An X-ray crystal structure of (1) has revealed that it adopts a *V*-shaped conformation where the cleft angle between the mean planes of the aromatic rings is 76°. On forming a 1:1 adduct with $[Rh(cod)(NH_3)_2][PF_6]$, the gross conformation of the receptor molecule (1) undergoes very little change: the cleft angle between the mean planes of the aromatic rings is reduced by 8° to 68°.



(1) $X = O$
(2) $X = NSO_2C_6H_4\text{–P–Me}$

In designing a second generation of molecular receptors to encapsulate transition-metal *cis*-diammines, we decided to replace the divalent oxygen atoms at X in (1) by trivalent nitrogen atoms so that a further chain could subsequently be added between these nitrogen atoms at right angles to the existing polyether chains. The intermediate macrobicyclic diazapolyether disulfonamide (2) has been characterized as a crystalline compound and subjected to X-ray structural analysis. Here, we report on the results of this investigation and compare the gross structural features of (2) with those of (1) in the solid state.

Experimental. The crude product from an NaH-promoted reaction in tetrahydrofuran of 1,8-bis[2,6-bis(bromomethyl)phenoxy]-3,6-dioxaoctane with 2 molar equivalents of *N,N′*-bis(2-hydroxyethyl)toluenesulfonamide was subjected to column chromatography on silica gel (Merck Kieselgel 60 H) using ethyl acetate–light petroleum (b.p. 333–353 K) (2:1, *v/v*) as eluant. On standing, the fractions containing the title compound (2) produced crystals (found: C, 61·0; H, 6·5; N, 3·0, S, 7·6%. $C_{44}H_{56}N_2O_{12}S_2$ requires C, 60·8; H, 6·5; N, 3·2; S, 7·4%) with m.p. 402–403 K suitable for X-ray structural investigation. Crystal size 0·4 × 0·2 × 0·2 mm. Refined unit-cell parameters obtained by centring 15 reflections, Nicolet *R*3*m* diffractometer. 2874 independent reflections ($\theta \leq 58°$) measured, Cu *Kα* radiation (graphite monochromator), ω scan. 2369 $[|F_o| > 3\sigma(|F_o|)]$ considered observed, index range *h* 0/15, *k* 0/17, *l* 0/19; two check reflections measured every 50 reflections, net count constant; data brought to uniform scale, Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods; non-hydrogen atoms refined anisotropically; positions of phenyl and methylene H atoms calculated (C—H = 0·96 Å), assigned isotropic thermal parameters, $U(H) = 1{\cdot}2\ U_{eq}(C)$, allowed to ride on parent C atoms; orientation of methyl H atoms determined from ΔF map and group refined as rigid body. Refinement using F magnitudes by block-cascade full-matrix least squares; $R = 0{\cdot}040$; $wR = 0{\cdot}044$ $[w^{-1} = \sigma^2(F) + 0{\cdot}00061F^2]$. $\Delta/\sigma = 0{\cdot}04$; residual electron density in difference map within $-0{\cdot}2$ and $+0{\cdot}2$ e Å^{-3}; atomic scattering factors and dispersion correction from *International Tables for X-ray Crystallography*

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(1974). Computations carried out on Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1983).

Table 1. *Atomic coordinates* (×10⁴) *and temperature factors* (Å² × 10³) *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}*
C(1)	5759 (2)	3361 (2)	−74 (2)	49 (1)
O(2)	6314 (1)	4077 (1)	118 (1)	48 (1)
C(3)	7236 (2)	3839 (2)	392 (1)	46 (1)
C(4)	7157 (2)	3431 (2)	1095 (1)	51 (1)
N(5)	8115 (2)	3214 (1)	1379 (1)	47 (1)
C(6)	8361 (2)	2321 (2)	1438 (2)	67 (1)
C(7)	8769 (2)	1965 (2)	787 (2)	78 (1)
O(8)	8103 (2)	1919 (1)	236 (1)	66 (1)
C(9)	7815 (2)	1094 (2)	62 (2)	53 (1)
C(10)	6909 (2)	1145 (1)	−361 (1)	42 (1)
C(11)	6932 (2)	1110 (2)	−1081 (1)	48 (1)
C(12)	6096 (2)	1210 (2)	−1461 (1)	49 (1)
C(13)	5232 (2)	1348 (1)	−1133 (1)	44 (1)
C(14)	5173 (2)	1385 (1)	−411 (1)	40 (1)
C(15)	6020 (2)	1272 (1)	−34 (1)	40 (1)
O(16)	6028 (1)	1366 (1)	676 (1)	54 (1)
C(17)	5655 (2)	673 (2)	1069 (1)	52 (1)
C(18)	5693 (2)	929 (2)	1816 (1)	58 (1)
O(19)	5070 (1)	1612 (1)	1916 (1)	62 (1)
C(20)	5321 (2)	2130 (2)	2476 (1)	61 (1)
S(21)	8573 (1)	3878 (1)	1931 (1)	47 (1)
O(22)	8570 (1)	4682 (1)	1607 (1)	60 (1)
O(23)	9464 (1)	3534 (1)	2175 (1)	62 (1)
C(24)	7746 (2)	3929 (2)	2630 (1)	46 (1)
C(25)	7690 (2)	3281 (2)	3105 (1)	51 (1)
C(26)	6991 (2)	3301 (2)	3618 (1)	59 (1)
C(27)	6348 (2)	3963 (2)	3670 (1)	62 (1)
C(28)	6414 (2)	4598 (2)	3195 (2)	68 (1)
C(29)	7109 (2)	4592 (2)	2677 (2)	61 (1)
C(30)	5573 (3)	3974 (3)	4220 (2)	92 (2)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

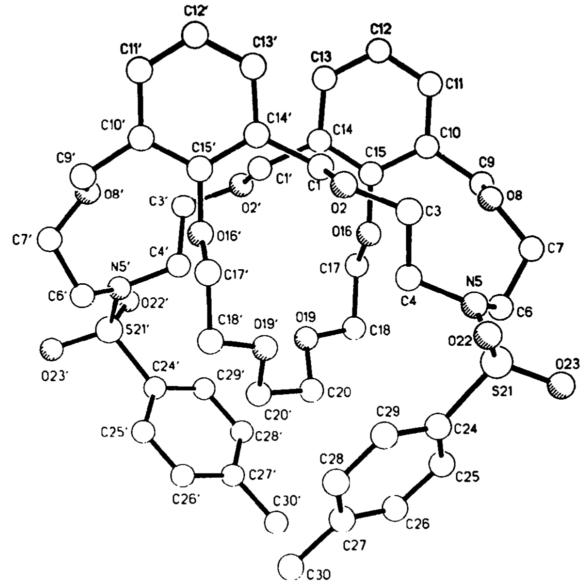

Fig. 1. Ball-and-stick representation of the structure of (2) showing the atomic numbering scheme.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

C(1)—O(2)	1·428 (3)	C(1)—C(14^{i})	1·499 (4)
O(2)—C(3)	1·430 (3)	C(3)—C(4)	1·509 (4)
C(4)—N(5)	1·474 (3)	N(5)—C(6)	1·473 (4)
N(5)—S(21)	1·632 (2)	C(6)—C(7)	1·490 (5)
C(7)—O(8)	1·407 (4)	O(8)—C(9)	1·419 (3)
C(9)—C(10)	1·497 (4)	C(10)—C(11)	1·389 (4)
C(10)—C(15)	1·396 (3)	C(11)—C(12)	1·376 (4)
C(12)—C(13)	1·369 (4)	C(13)—C(14)	1·395 (3)
C(14)—C(15)	1·388 (3)	C(14)—C(1')	1·499 (4)
C(15)—O(16)	1·377 (3)	O(16)—C(17)	1·438 (3)
C(17)—C(18)	1·498 (4)	C(18)—O(19)	1·405 (4)
O(19)—C(20)	1·403 (3)	C(20)—C(20^{i})	1·480 (6)
S(21)—O(22)	1·430 (2)	S(21)—O(23)	1·428 (2)
S(21)—C(24)	1·768 (3)	C(24)—C(25)	1·386 (4)
C(24)—C(29)	1·382 (4)	C(25)—C(26)	1·383 (4)
C(26)—C(27)	1·386 (4)	C(27)—C(28)	1·371 (4)
C(27)—C(30)	1·508 (4)	C(28)—C(29)	1·385 (4)

O(2)—C(1)—C(14^{i})	110·9 (2)	C(1)—O(2)—C(3)	111·2 (2)
O(2)—C(3)—C(4)	112·5 (2)	C(3)—C(4)—N(5)	111·7 (2)
C(4)—N(5)—C(6)	117·7 (2)	C(4)—N(5)—S(21)	115·9 (2)
C(6)—N(5)—S(21)	119·5 (2)	N(5)—C(6)—C(7)	113·1 (2)
C(6)—C(7)—O(8)	114·1 (3)	C(7)—O(8)—C(9)	114·2 (2)
O(8)—C(9)—C(10)	108·2 (2)	C(9)—C(10)—C(11)	121·5 (2)
C(9)—C(10)—C(15)	119·9 (2)	C(11)—C(10)—C(15)	118·4 (2)
C(10)—C(11)—C(12)	120·5 (2)	C(11)—C(12)—C(13)	120·3 (2)
C(12)—C(13)—C(14)	121·2 (2)	C(13)—C(14)—C(15)	117·8 (2)
C(13)—C(14)—C(1^{i})	119·6 (2)	C(15)—C(14)—C(1')	122·2 (2)
C(10)—C(15)—C(14)	121·7 (2)	C(10)—C(15)—O(16)	117·2 (2)
C(14)—C(15)—O(16)	120·8 (2)	C(15)—O(16)—C(17)	115·9 (2)
O(16)—C(17)—C(18)	106·4 (2)	C(17)—C(18)—O(19)	108·9 (2)
C(18)—O(19)—C(20)	114·4 (2)	O(19)—C(20)—C(20^{i})	108·9 (2)
N(5)—S(21)—O(22)	107·5 (1)	N(5)—S(21)—O(23)	107·3 (1)
O(22)—S(21)—O(23)	119·5 (1)	N(5)—S(21)—C(24)	106·1 (1)
O(22)—S(21)—C(24)	106·8 (1)	O(23)—S(21)—C(24)	108·9 (1)
S(21)—C(24)—C(25)	120·3 (2)	S(21)—C(24)—C(29)	119·9 (2)
C(25)—C(24)—C(29)	119·6 (2)	C(24)—C(25)—C(26)	119·6 (2)
C(25)—C(26)—C(27)	121·1 (3)	C(26)—C(27)—C(28)	118·4 (3)
C(26)—C(27)—C(30)	121·0 (3)	C(28)—C(27)—C(30)	120·5 (3)
C(27)—C(28)—C(29)	121·4 (3)	C(24)—C(29)—C(28)	119·7 (3)

C(15^{i})—C(14^{i})—C(1)—O(2)	−91·6 (3)	C(9)—C(10)—C(15)—O(16)	1·7 (3)
C(14^{i})—C(1)—O(2)—C(3)	−175·6 (2)	C(10)—C(15)—O(16)—C(17)	−107·6 (2)
C(1)—O(2)—C(3)—C(4)	−70·2 (3)	C(14)—C(15)—O(16)—C(17)	78·9 (3)
O(2)—C(3)—C(4)—N(5)	−178·3 (2)	C(15)—O(16)—C(17)—C(18)	−177·5 (2)
C(3)—C(4)—N(5)—C(6)	−111·5 (3)	O(16)—C(17)—C(18)—O(19)	63·9 (3)
C(4)—N(5)—C(6)—C(7)	85·5 (3)	C(17)—C(18)—O(19)—C(20)	−154·1 (2)
N(5)—C(6)—C(7)—O(8)	−67·7 (3)	C(18)—O(19)—C(20)—C(20^{i})	173·7 (2)
C(6)—C(7)—O(8)—C(9)	−109·7 (3)	O(19)—C(20)—C(20^{i})—O(19^{i})	−71·3 (2)
C(7)—O(8)—C(9)—C(10)	162·8 (2)	C(4)—N(5)—S(21)—O(23)	176·5 (2)
O(8)—C(9)—C(10)—C(15)	−79·5 (3)	C(6)—N(5)—S(21)—O(22)	156·1 (2)

Symmetry code: (i) 1−*x*, *y*, 0·5−*z*.

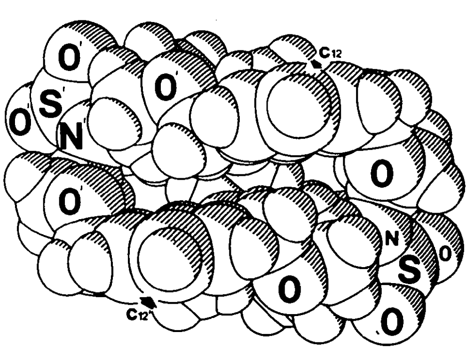

Fig. 2. A space-filling representation of (2) viewed down the crystallographic twofold axis.

Discussion. Table 1* lists the fractional atomic coordinates of the non-hydrogen atoms, Table 2 the bond lengths and angles and selected C—C, C—N, C—O and N—S torsion angles.

The structure of (2) is illustrated in Fig. 1 which gives a side-on view of the molecule and includes the numbering scheme: Fig. 2 gives a plan view down the crystallographic twofold axis of a space-filling representation of (2).

The macrobicyclic diazapolyether disulfonamide (2) is symmetric with a crystallographic twofold axis passing through the C(20)—C(20′) bond of the central polyether chain and between the faces of the trisubstituted aromatic rings. The symmetry of this structure is in marked contrast to the pronounced molecular asymmetry displayed by the all-oxygen analogue (1). Also, the characteristic *V*-shaped conformation adopted by (1), in both its free and second-sphere coordinating forms (Alston, Slawin, Stoddart & Williams, 1984) is no longer present in (2). The molecular cavity in (2) is totally self-filling (Fig. 2) with the two trisubstituted aromatic rings lying almost parallel to each other (4° between their mean planes) and with an inter-ring separation of between 3·45 and 3·54 Å. There are only two significant departures (see Table 2) from conventional *gauche* geometries about the C—C bonds in the polyether chains; these are about the C(3)—C(4) and C(3′)—C(4′) bonds [−178·3 (2)°]. There is also a small pyramidal distortion at N(5) and N(5′), each lying 0·23 (1) Å from the plane of their adjacent carbon and sulfur atoms with a consequent opening out of the bond angles (Table 2) around the nitrogen atom. The bond angles (Table 2) around the sulfur atom reveal a slightly distorted tetrahedral arrangement of bonds. The length [1·632 (2) Å] of the N—S bond indicates that it has partial double-bond character as a result of π bonding between the lone pair of electrons on the nitrogen atom and the empty 3*d* orbitals on the sulfur atom. The conformational orientation of the tosyl groups with respect to the $-CH_2-N-CH_2-$ fragments on the two associated chains is similar to that observed (Smith-Verdier, García-Blanco & Florencio, 1976) in the X-ray structure of the methanesulfonamide of piperidine-4-spiro-2′-(1,3-dioxolane).

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References

ALSTON, D. R., SLAWIN, A. M. Z., STODDART, J. F. & WILLIAMS, D. J. (1984). *Angew. Chem. Int. Ed. Engl.* **23**, 821–823.

COLQUHOUN, H. M., DOUGHTY, S. M., STODDART, J. F., SLAWIN, A. M. Z. & WILLIAMS, D. J. (1986). *J. Chem. Soc. Dalton Trans.* In the press.

COLQUHOUN, H. M., DOUGHTY, S. M., STODDART, J. F. & WILLIAMS, D. J. (1984). *Angew. Chem. Int. Ed. Engl.* **23**, 235–236.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

SHELDRICK, G. M. (1983). *SHELXTL*, revision 4.0, January 1983. *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen.

SMITH-VERDIER, P., GARCÍA-BLANCO, S. & FLORENCIO, F. (1976). *Acta Cryst.* B**32**, 2006–2009.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42759 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a Chiral Bisanisylene Crown Ether, 1,4:1′,4′:3,6:3′,6′-Tetraanhydro-2,2′:5,5′-bis-*O*-[2-methoxy-1,3-phenylenebis(methylene)]di-D-mannitol

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Abstract. $C_{30}H_{36}O_{10}$, $M_r = 556\cdot6$, monoclinic, $C2$, $a = 13\cdot255$ (3), $b = 15\cdot479$ (3), $c = 14\cdot187$ (3) Å, $\beta = 106\cdot36$ (2)°, $V = 2793$ Å^3, $Z = 4$, $D_x = 1\cdot32$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 7\cdot9$ cm^{-1}, $F(000) = 1184$, room temperature, $R = 0\cdot064$ for 1880 unique observed reflections. In this chiral bisanisylene macrocycle DD-(3), the dianhydromannitolo units adopt a 'back-to-back' geometry with respect to each other. This is in

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