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2,5,11,14,19,22,28,31-Octaoxa-8,25-diazatricyclo[30.2.2.2^{15,18}]octatriaconta-15,17,32,34(1),35,37-hexaene

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Abstract. (I) $C_{28}H_{42}N_2O_8.2H_2O$, $M_r = 570{\cdot}7$, monoclinic, $C2/c$, $a = 36{\cdot}453\,(14)$, $b = 10{\cdot}419\,(4)$, $c = 8{\cdot}345\,(4)$ Å, $\beta = 102{\cdot}13\,(3)^\circ$, $V = 3099$ Å^3, $Z = 4$ (the molecule is disposed about a centre of symmetry), $D_x = 1{\cdot}22$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}73$ mm^{-1}, $F(000) = 1232$, $T = 293$ K, $R = 0{\cdot}046$ for 1878 observed reflections with $|F_o| > 3\sigma(|F_o|)$. (II) $C_{28}H_{42}N_2O_8.X$ where X represents unidentified solvent fragments, $M_r = 600{\cdot}7$, triclinic, $P\bar{1}$, $a = 11{\cdot}293\,(2)$, $b = 11{\cdot}343\,(3)$, $c = 14{\cdot}996\,(4)$ Å, $\alpha = 102{\cdot}32\,(2)$, $\beta = 96{\cdot}99\,(2)$, $\gamma = 99{\cdot}56\,(2)^\circ$, $V = 1826$ Å^3, $Z = 2$ (two independent centrosymmetric molecules), $D_x = 1{\cdot}09$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}68$ mm^{-1}, $F(000) = 646$, room temperature, $R = ca\ 0{\cdot}11$ for 3314 observed reflections with $|F_o| > 3\sigma(|F_o|)$. In contrast with the all-oxygen analogue, (I) adopts a conformation in which the macrocycle is self-filling whereas the two independent molecules of (II) adopt conformations with more open geometries though their free pathways are still significantly reduced compared with those in their oxygen counterparts.

Introduction. The observation (Allwood, Spencer, Shahriari-Zavareh, Stoddart & Williams, 1987*a*; Stoddart, 1988) that bis-*p*-phenylene-34-crown-10 (11)† forms a centrosymmetric 1:1 complex with Paraquat† in the solid state with little change in conformation from that observed (Allwood, Spencer, Shahriari-Zavareh, Stoddart & Williams, 1987*b*; Slawin, Spencer, Stoddart & Williams, 1987) for one of the conformations adopted by the free receptor in the solid state has encouraged us to consider the synthesis of a diazamacrobicyclic bipyridinium dication† (Anelli, Stoddart, Slawin & Williams, 1990).

In this paper, we report the X-ray structures of the key intermediate (12)†, a diaza derivative of bis-*p*-phenylene-34-crown-10 (11). The conformational properties of the structures in the solid state are compared.

Experimental. Reaction of 4-benzyloxyphenol with *N*,*N*-bis{2-[2-(*p*-toluenesulfonyl)oxy]ethoxy}ethyl-*p*-toluenesulfonamide (Anelli, Spencer & Stoddart, 1988) in tetrahydrofuran with potassium *tert*-butoxide as base gave a dibenzyl ether which was subjected to catalytic (Pd/C) hydrogenolysis in methanol–dichloromethane to afford *N*,*N*-bis{2-[2-(4-hydroxyphenoxy)ethoxy]ethyl}-*p*-toluenesulfonamide. This diphenol was reacted under similar alkylation conditions with a further equivalent of the above bistosylate to yield the disulfonamide of compound (12). Removal of the *N*-tosyl groups was achieved reductively with lithium aluminium hydride in tetrahydrofuran and the title compound (12) was characterized spectroscopically. Single crystals of (12), suitable for X-ray crystallography, were grown at room temperature by vapour diffusion of *n*-pentane into acetone solution and had two discrete melting points of 345–347 K and 358–359 K.‡ Good quality data were obtained for the lower-melting-point crystals. Crystal size $0{\cdot}33 \times 0{\cdot}40 \times 0{\cdot}27$ mm. Refined unit-cell parameters obtained from setting angles of 18 reflections with $5{\cdot}0 \leq 2\theta \leq 31{\cdot}2^\circ$. Nicolet *R*3*m* diffractometer. 2131 measured, 2098 independent ($R_{\rm int} = 0{\cdot}051$) reflections ($2\theta \leq 116^\circ$), Cu $K\alpha$ radiation (graphite monochromator), ω scan. 1878 [$|F_o| > 3\sigma(|F_o|)$] considered observed, index range h

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† In order to avoid repetition in the presentation of diagrammatic and constitutional formulae, the reader is referred to Fig. 1 and to the structural formulae displayed in Anelli, Stoddart, Slawin & Williams (1990).

† See previous footnote.

‡ The single crystals of the triclinic form (II) of (12) were very heavily solvated and though solvent loss was prevented by coating the crystals with Araldite epoxy resin, refinement of the structure was severely hampered by the total disorder of the appreciable amounts of included solvent molecules. *R* could not be reduced below 0·11 and hence only the important gross structural features of the macrocycles are discussed. Full structural data have been deposited (see deposition footnote).

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$-39/38$, k 0/11, l 0/9; two check reflections measured every 50 reflections, no significant change in net counts; Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods. The non-H atoms were refined anisotropically. A ΔF map revealed the presence of a disordered water molecule. The amine hydrogen on N(7) and three positions for the two water hydrogens were located from a ΔF map and refined isotropically. The positions of the remaining H atoms were idealized, C—H = 0·96 Å, assigned isotropic thermal parameters, $U(\mathrm{H}) = 1{\cdot}2U_{\mathrm{eq}}(\mathrm{C})$, and allowed to ride on their parent C atoms. An empirical extinction correction was applied [g = 0·0037 (7)]. Refinement using F magnitudes by block-cascade full-matrix least squares; R = 0·046; wR = 0·062 [$w^{-1} = \sigma^2(F) + 0{\cdot}00300F^2$]. S = 1·39; 197 refined parameters; $(\Delta/\sigma)_{\max} = 0{\cdot}031$; residual electron density in difference map within 0·23 and $-0{\cdot}19$ e Å^{-3}; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). Computations carried out on an Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1983).

Discussion. The structure of (12) with atomic numbering scheme is shown in Fig. 1. Table 1* lists the fractional atomic coordinates of the non-H atoms and Table 2 the bond lengths and bond angles.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}(Å^2)
O(1)	0·1263 (1)	0·1836 (1)	0·8188 (2)	0·068 (1)
C(2)	0·0971 (1)	0·0943 (2)	0·7801 (3)	0·070 (1)
C(3)	0·0634 (1)	0·1473 (2)	0·8338 (3)	0·074 (1)
O(4)	0·0707 (1)	0·1550 (1)	1·0063 (2)	0·071 (1)
C(5)	0·0397 (1)	0·2001 (2)	1·0694 (3)	0·080 (1)
C(6)	0·0539 (1)	0·2429 (2)	1·2415 (3)	0·075 (1)
N(7)	0·0788 (1)	0·3523 (2)	1·2466 (2)	0·059 (1)
C(8)	0·0979 (1)	0·3881 (2)	1·4128 (3)	0·071 (1)
C(9)	0·1277 (1)	0·4859 (2)	1·4081 (3)	0·072 (1)
O(10)	0·1552 (1)	0·4408 (1)	1·3233 (2)	0·062 (1)
C(11)	0·1799 (1)	0·3525 (3)	1·4141 (3)	0·079 (1)
C(12)	0·2096 (1)	0·3162 (2)	1·3233 (3)	0·070 (1)
O(13)	0·2367 (1)	0·4155 (2)	1·3385 (2)	0·077 (1)
C(14)	0·2701 (1)	0·3878 (2)	1·2942 (2)	0·058 (1)
C(15)	0·2988 (1)	0·4742 (2)	1·3442 (2)	0·063 (1)
C(16)	0·3337 (1)	0·4549 (2)	1·3079 (2)	0·061 (1)
C(17)	0·3398 (1)	0·3467 (2)	1·2211 (2)	0·054 (1)
C(18)	0·3112 (1)	0·2597 (2)	1·1721 (2)	0·056 (1)
C(19)	0·2764 (1)	0·2802 (2)	1·2067 (2)	0·058 (1)
O(20)	0·0235 (1)	0·5476 (2)	1·1404 (2)	0·076 (1)

Table 2. *Bond lengths* (Å) *and angles* (°) *for the monoclinic form* (I) *of* (12)

O(1)—C(2)	1·402 (3)	O(1)—C(17′)	1·379 (2)
C(2)—C(3)	1·498 (3)	C(3)—O(4)	1·410 (3)
O(4)—C(5)	1·423 (3)	C(5)—C(6)	1·489 (4)
C(6)—N(7)	1·451 (3)	N(7)—C(8)	1·463 (2)
C(8)—C(9)	1·498 (3)	C(9)—O(10)	1·420 (3)
O(10)—C(11)	1·396 (3)	C(11)—C(12)	1·493 (3)
C(12)—O(13)	1·418 (3)	O(13)—C(14)	1·375 (3)
C(14)—C(15)	1·378 (3)	C(14)—C(19)	1·383 (3)
C(15)—C(16)	1·384 (3)	C(16)—C(17)	1·382 (3)
C(17)—C(18)	1·378 (3)		
C(18)—C(19)	1·376 (3)		

C(2)—O(1)—C(17′)	117·9 (2)	O(1)—C(2)—C(3)	108·6 (2)
C(2)—C(3)—O(4)	109·6 (2)	C(3)—O(4)—C(5)	113·8 (2)
O(4)—C(5)—C(6)	108·3 (2)	C(5)—C(6)—N(7)	110·6 (2)
C(6)—N(7)—C(8)	113·5 (2)	N(7)—C(8)—C(9)	110·7 (2)
C(8)—C(9)—O(10)	112·3 (2)	C(9)—O(10)—C(11)	113·0 (2)
O(10)—C(11)—C(12)	110·3 (2)	C(11)—C(12)—O(13)	109·5 (2)
C(12)—O(13)—C(14)	117·5 (2)	O(13)—C(14)—C(15)	116·1 (2)
O(13)—C(14)—C(19)	124·7 (2)	C(15)—C(14)—C(19)	119·2 (2)
C(14)—C(15)—C(16)	121·0 (2)	C(15)—C(16)—C(17)	119·3 (2)
C(16)—C(17)—C(18)	119·8 (2)	C(16)—C(17)—O(1′)	124·3 (2)
C(18)—C(17)—O(1′)	115·9 (2)	C(17)—C(18)—C(19)	120·6 (2)
C(14)—C(19)—C(18)	120·1 (2)		

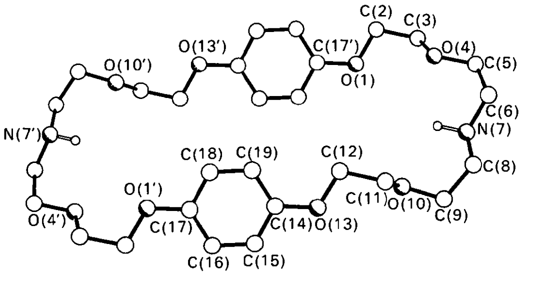

Fig. 1. Ball-and-stick representation of the monoclinic form (I) of (12) in the solid state.

In contrast to bis-p-phenylene-34-crown-10 (11) (Allwood *et al.*, 1987*a*), in the monoclinic crystals, the centrosymmetric macrocycle (12) has a conformation (Fig. 2*a*) where the central hole is filled, the two hydroquinol fragments approaching to within an interplanar separation of 2·7 Å and with a ring centroid–centroid distance of 5·8 Å. In the crystals of the triclinic form of (12) there are – in common with bis-p-phenylene-34-crown-10 (11) – two independent centrosymmetric molecules, both with open structures and noticeably different conformations for their polyheteroatomic chains. Table 3 lists the torsional angle sequences for these chains in the two crystallographically independent conformations of (11), in the triclinic crystals of (12), and in the monoclinic crystals of (12). It is to be noted that the torsional angle sequence within the monoclinic form of (12) matches exactly that of one of the conformations of the triclinic form. Thus, it appears that

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters for (I) and full structural data for (II) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52751 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

small, but not insignificant, differences in the individual values for the torsional angles in the polyheteroatomic chains result in an appreciable change in the cavity shape and size (Fig. 2*b*) within the macrocycle. The separation between the mean planes of the parallel hydroquinol rings for the two independent molecules in the triclinic crystals are 5·5 and 6·0 Å (Fig. 2*b*). Unlike (11), where virtually no change of conformation was necessary for complexation of Paraquat to occur, in the triclinic form of (12), there would have to be enlargements of at least 1 Å in the separations between the mean planes of the two hydroquinol rings in both conformations in order to accommodate a bipyridinium dication. There is also a greater degree of shearing of the parallel hydroquinol units in the triclinic form of (12) with respect to each other, compared with their relative dispositions in bis-*p*-phenylene-34-crown-10 (11). Thus, the centroid–centroid distances (7·1 Å in both conformations) in the triclinic form of (12) are reduced relative to those (both 7·5 Å) in compound (11).

The two independent molecules in the triclinic form of (12) interleave with each other such that the planes of adjacent crystallographically unrelated hydroquinol residues are approximately orthogonal to each other with centroid–centroid separations of *ca* 5·65 Å. Also, both phenoxymethylene groups direct one of their C—H bonds towards the centre of the hydroquinol rings respectively of an adjacent macrocycle. In the absence of any other short intermolecular contacts, we consider that the above contacts probably represent weak electrostatic binding interactions analogous to those involving aromatic π systems we have observed (Alston, Slawin, Stoddart, Williams & Zarzycki, 1987; Moody, Owusu, Slawin, Spencer, Stoddart, Thomas & Williams, 1987; Anelli, Slawin, Stoddart & Williams, 1988) in similar systems. Contacts to the disordered partial-occupancy solvent molecules have not been analyzed.

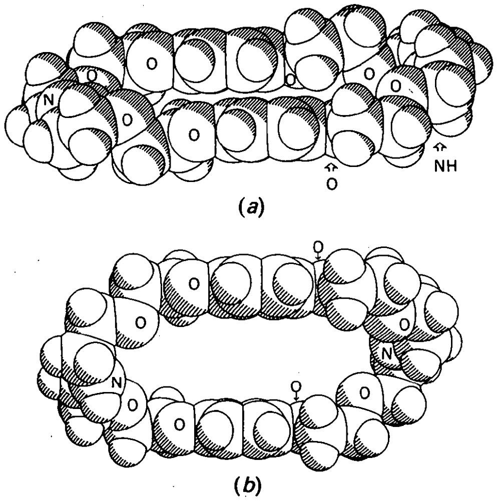

Fig. 2. Space-filling representations of (*a*) the monoclinic (I) and (*b*) the triclinic (II) forms of (12) in the solid state.

Table 3. *A comparison of the torsional angles in the* $OCH_2CH_2OCH_2CH_2XCH_2CH_2OCH_2CH_2O$ ($X = O$ or NH) *units in conformations* 1 *and* 2 *of* (11) *and of the trinclinic form* (II) *of* (12) *and of the monoclinic form* (I) *of* (12)

Compound/Form	Torsion-angle sequence
(11)/Conformation 1	$ag^-g^-aag^-ag^-aag^-a$
(11)/Conformation 2	$ag^-aag^-aag^+aag^+a$
(12)/Trinclinic/Conformation 1	$ag^-aag^-ag^+g^+aag^+a$
(12)/Trinclinic/Conformation 2	$ag^-aag^+aag^+g^-ag^+a$
(12)/Monoclinic	$ag^-aag^+aag^-g^-ag^+a$

Despite short intramolecular contacts of 2·84 and 2·87 Å between N(7) and O(4), and N(7) and O(10), respectively, in the monoclinic form of (12), there is an absence of any intramolecular N—H···O hydrogen bonding involving the inwardly pointing NH H atoms. However, each N atom is hydrogen bonded (N···H—O, 2·87 Å) to the disordered water molecules, which are in turn involved in intermolecular hydrogen bonds (O—H···O, 2·76 and 2·78 Å) with themselves.

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