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Two Macrocylic Azacrown Ethers

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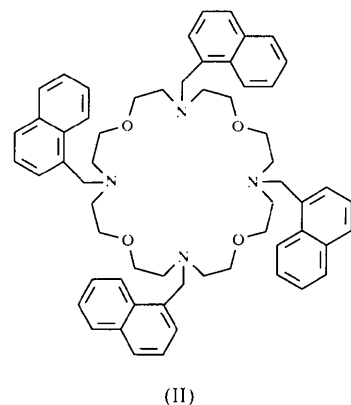
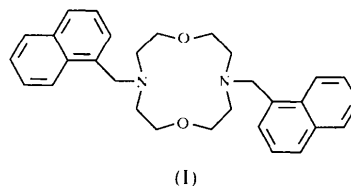
Abstract

The structures of two macrocyclic azacrown ethers, namely, 4,10-bis(1-naphthylmethyl)-1,7-dioxa-4,10-diazacyclododecane, $C_{30}H_{34}N_2O_2$, and 4,10,16,22-tetrakis(1-naphthylmethyl)-1,7,13,19-tetraoxa-4,10,16,22-tetraazacyclotetrasolane as its bis(methylene dichloride) solvate, $C_{60}H_{68}N_4O_4 \cdot 2CH_2Cl_2$, have been determined by single-crystal diffraction. Both molecules are characterized by a cavity suitable for hosting cationic guests.

Comment

Over the past few years, the design of macrocyclic ligands has received increasing attention in view of the photochemical and photophysical properties characterizing the supramolecular adduct obtained by complexing the macrocycle with an appropriate electron acceptor (Lehn, 1995). We report here the structures of two diazacrown ethers, namely, 4,10-bis(1-naphthylmethyl)-1,7-dioxa-4,10-diazacyclododecane, (I), and 4,10,16,22-tetrakis(1-naphthylmethyl)-1,7,13,19-tetraoxa-4,10,16,22-tetraazacyclotetrasolane as its bis(methylene dichloride)

solvate, (II). These compounds were synthesized as part of a study of macrocycles complexing metal and ammonium cations (see, for example, Quici *et al.*, 1996).



Both compounds crystallize in a centrosymmetric space group with half a molecule in the asymmetric unit. In (I), the ether ring forms a cavity with transannular $O1 \cdots O1^i$ and $N4 \cdots N4^i$ distances of 4.231 (2) and 4.504 (2) Å, respectively. The shortest transannular contact is $O1 \cdots C6$ at 3.822 (2) Å. Here and elsewhere, the superscript refers to the symmetry-centre operation which completes the molecule, *i.e.* $-x, -y, 1-z$. The ring adopts a chair-chair conformation with a dihedral angle of 6.0 (2)° between the plane containing atoms N4, C5 and C6, and the plane containing atoms O1, C2 and C3. The torsion angles of this ring are reported in Table 1. The least-squares plane of the naphthalene system forms a dihedral angle of 89.54 (8)° with the plane formed by atoms N4, C5 and C6. The geometric parameters of (I) were compared with those of a similar compound where the naphthalene is substituted by a benzene ring (Mendez *et al.*, 1992). The monoprotonated form of that compound proved suitable for complexing neutral guests such as alcohols. No relevant differences between (I) and that compound were found.

The structure of (II), which contains two CH_2Cl_2 solvent molecules, was determined at $T = 245$ K because at room temperature the crystals lose the solvent and collapse within a few days. The molecule is characterized by a large cavity having the following transannular distances: $N1 \cdots N1^i = 9.619$ (3), $N7 \cdots N7^i = 8.313$ (2), $O4 \cdots O4^i = 8.129$ (2) and $O10 \cdots O10^i = 6.216$ (2) Å. The shortest transannular contact is $C9 \cdots C9^i$ of 5.266 (4) Å. The conformation of the macrocycle is determined by a sequence of essentially *trans* and *gauche* torsion angles; the torsion angles that significantly de-

viate from this motif are reported in Table 2. The two least-squares planes of the symmetry-independent naphthalene rings form a dihedral angle of 68.70 (4)°.

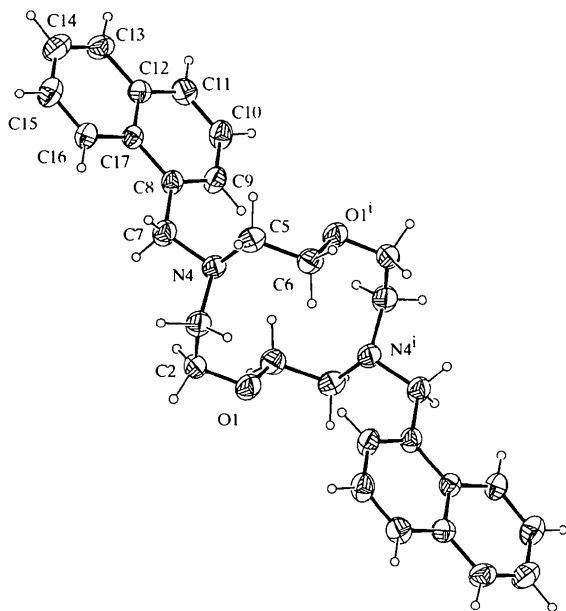


Fig. 1. Plot of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $-x, -y, 1 - z$]

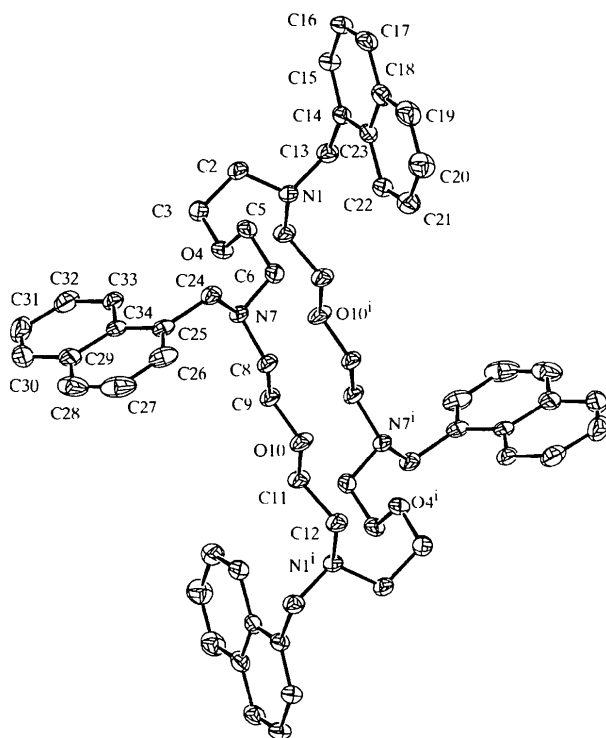


Fig. 2. Plot of (II), without the solvent molecule, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x, -y, 1 - z$]

The solvent molecule is disordered within the cavity of the macrocycle and was modelled as two molecules. In both cases, the two Cl atoms of the solvent point outside the macrocycle.

Experimental

The synthesis of the title compounds will be reported elsewhere (Quici *et al.*, 1998)

Compound (I)

Crystal data

C₃₀H₃₄N₂O₂

$M_r = 454.59$

Monoclinic

$P2_1/c$

$a = 9.7898 (9) \text{ \AA}$

$b = 7.3974 (6) \text{ \AA}$

$c = 17.292 (2) \text{ \AA}$

$\beta = 99.368 (6)^\circ$

$V = 1235.6 (2) \text{ \AA}^3$

$Z = 2$

$D_x = 1.222 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 32 reflections

$\theta = 4.40\text{--}11.87^\circ$

$\mu = 0.076 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Plate

$0.44 \times 0.40 \times 0.20 \text{ mm}$

Almost colourless

Data collection

Siemens $P4$ diffractometer

$\omega/2\theta$ scans

Absorption correction: none

2314 measured reflections

2178 independent reflections

1284 reflections with

$I > 2\sigma(I)$

$R_{int} = 0.015$

$\theta_{max} = 25^\circ$

$h = 0 \rightarrow 11$

$k = 0 \rightarrow 8$

$l = -20 \rightarrow 20$

3 standard reflections

every 197 reflections

intensity decay: 2.99%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.071$

$S = 1.038$

2178 reflections

223 parameters

All H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.001$

$\Delta\rho_{max} = 0.102 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -0.094 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0110 (16)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected torsion angles ($^\circ$)

C6'—O1—C2—C3	−98.3 (2)	C3—N4—C5—C6	76.9 (2)
O1—C2—C3—N4	81.2 (2)	N4—C5—C6—O1'	78.3 (2)
C2—C3—N4—C5	−140.76 (15)		

Symmetry code: (i) $-x, -y, 1 - z$.

Compound (II)

Crystal data

C₆₀H₆₈N₄O₄·2CH₂Cl₂

$M_r = 1079.04$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Triclinic
 $P\bar{1}$
 $a = 11.369 (3) \text{ \AA}$
 $b = 12.175 (3) \text{ \AA}$
 $c = 12.268 (3) \text{ \AA}$
 $\alpha = 64.42 (2)^\circ$
 $\beta = 72.89 (2)^\circ$
 $\gamma = 73.37 (2)^\circ$
 $V = 1438.7 (6) \text{ \AA}^3$
 $Z = 1$
 $D_r = 1.245 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Siemens SMART CCD with
 an LT-2 device for low-
 temperature collection
 Frame scans
 Absorption correction: none
 13 318 measured reflections
 5063 independent reflections

Cell parameters from 65
 reflections
 $\theta = 0-23^\circ$
 $\mu = 0.256 \text{ mm}^{-1}$
 $T = 245 (2) \text{ K}$
 Prism
 $0.33 \times 0.20 \times 0.20 \text{ mm}$
 Pale yellow

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.084$
 $S = 1.073$
 5061 reflections
 502 parameters
 H atoms of CH_2Cl_2 riding;
 coordinates of remaining
 H atoms refined, with U_{iso}
 restrained

3535 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\text{max}} = 25^\circ$
 $h = -14 \rightarrow 14$
 $k = -16 \rightarrow 15$
 $l = -15 \rightarrow 15$
 $w = 1/[\sigma^2(F_o^2) + (0.0533P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = -0.094$
 $\Delta\rho_{\text{max}} = 0.164 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.277 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 2. Selected torsion angles ($^\circ$)

N1—C2—C3—O4	37.7 (2)	C6—N7—C8—C9	-86.0 (2)
C5—C6—N7—C8	160.67 (13)		

Data collection for compound (II) was carried out using a Siemens SMART CCD area detector and standard reflections were, therefore, not measured. The first 50 frames of data were recollected at the end of data collection. No crystal decay was observed.

Data collection: XSCANS (Fait, 1991) for (I); SMART (Siemens, 1994) for (II). Cell refinement: XSCANS for (I); SAINT (Siemens, 1994) for (II). Data reduction: XSCANS for (I); SAINT for (II). For both compounds, program(s) used to solve structures: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structures: SHELXL93 (Sheldrick, 1993); molecular graphics: ZORTEP (Zsolnai & Pritzkow, 1995); software used to prepare material for publication: SHELXL93, PARST (Nardelli, 1983, 1995) and PARST-CIF (Nardelli, 1991).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1370). Services for accessing these data are described at the back of the journal.

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1,2-Bis(2-pyridylformimidoyl)hydrazine†

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Abstract

The title compound, $\text{C}_{12}\text{H}_{12}\text{N}_6$, is the minor *trans* product of the preparation of a dihydrotetrazine. Extensive electron delocalization is shown by the planarity of the molecule, except for one pyridyl group twisted out of plane by $14.1 (1)^\circ$. The $\text{C}=\text{N}-\text{N}=\text{C}$ fragment has a C—N distance of $1.297 (2) \text{ \AA}$ and an N—N distance of $1.404 (2) \text{ \AA}$. All other C—N distances are close to 1.34 \AA , typical of C=N bonds. The NH_2 groups form hydrogen bonds to pyridyl and hydrazine N atoms of adjacent molecules.

Comment

The title compound, (I), can be regarded as a dihydrazidine or an amide azine (Watson & Neilson, 1975). It is formed as the minor product from refluxing picro-

† Alternative name: 1,2-bis[amino(2-pyridyl)methylene]diazane.