Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

N-Ethylazatribenzo-21-crown-7

Jeffrey C. Bryan,[a]* Jerôme M. Lavis,[a] Benjamin P. Hay[b] and Richard A. Sachleben[a]

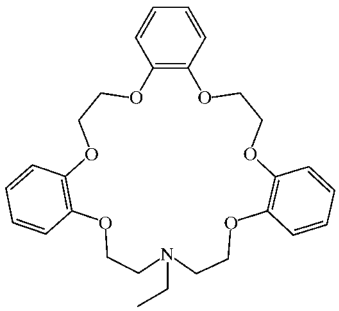
[a] Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6119, USA, and [b] Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352, USA
Correspondence e-mail: bryanjc@ornl.gov

Received 10 November 1999
Accepted 17 December 1999

The structure of the title compound, 25-ethyl-2,5,12,15,22,28-hexaoxa-25-azatetracyclo[27.4.0.0^{6,11}.0^{16,21}]tritriaconta-1(29),6(11),7,9,16(21),17,19,30,32-nonaene, $C_{28}H_{33}NO_6$, does not exhibit a binding cavity for cations, but is collapsed in on itself. The conformation is unique among known tribenzo-21-crown-7 structures, and may be a result of intermolecular (C—H$\cdots\pi$) and intramolecular (C—H$\cdots$O) hydrogen bonding.

Comment

We reported recently that tribenzo-21-crown-7 exhibits modest selectivity for large alkali metal cations over smaller ions (Sachleben *et al.*, 1996). This selectivity was subsequently illuminated by a crystallographic and molecular-mechanics study of six different conformations of the free and complexed crown ether ligand (Bryan *et al.*, 1998). Further examination of the Cs(tribenzo-21-crown-7)NO_3 structure reported as part of that study showed that one of the seven crown ether O-donor atoms is significantly further from Cs^+ and its dipole is roughly orthogonal to the Cs—O bond, suggesting that it binds the cation relatively weakly (Hay & Rustad, 1994). Replacement of this O atom with an N*R* group may result in orientation of the amine dipole more directly towards Cs^+, allowing enhanced binding and selectivity towards Cs^+. In this paper, we describe the structure and synthesis of such an N*R*-containing crown ether, (I).



(I)

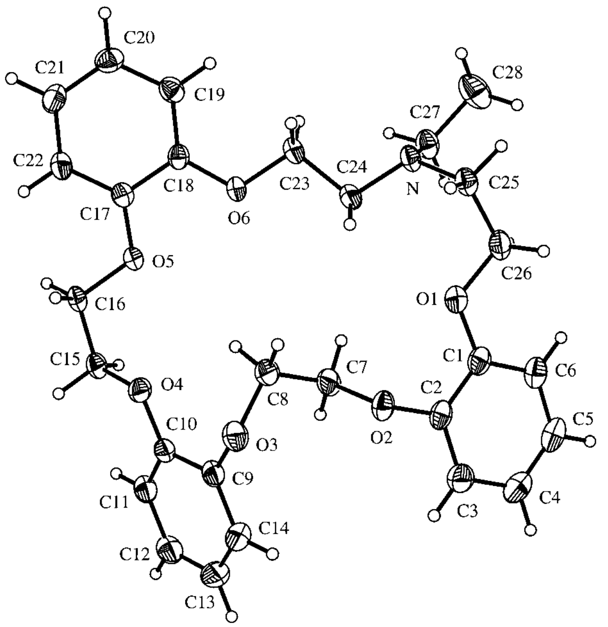


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids.

The structure of (I) is depicted in Fig. 1, which clearly demonstrates that it is not pre-organized for cation binding as the ring has collapsed in on itself, which is commonly observed in large uncomplexed crown ether structures (Bryan *et al.*, 1998, 1999, and references therein). In doing so, the crown fills its cavity with methylene groups, which allows for intramolecular hydrogen bonding between methylene H and ether O atoms (Table 2 and Fig. 2). Only those interactions with C—H$\cdots$O angles greater than 100° and C$\cdots$O separations less than 3.72 Å are listed in Table 2 (Steiner, 1996).

No π stacking of arene rings is observed in the structure. However, close C—H$\cdots\pi$ contacts, some of which may represent hydrogen bonds (Steiner *et al.*, 1996; Bryan *et al.*, 1999) or edge-face arene interactions, are clearly present (Fig. 2). These weak intermolecular bonds may also play a role

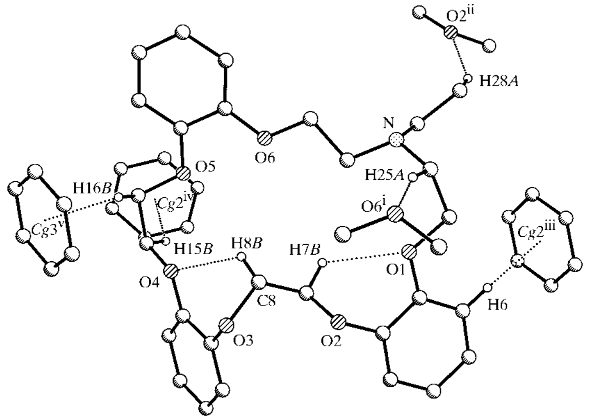


Figure 2
The hydrogen-bond interactions of (I). For clarity, only fragments of symmetry-equivalent molecules are shown, all atoms are represented as circles, and only H atoms functioning as hydrogen-bond donors are drawn. [Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $x, y, z-1$; (iii) $-x, 1-y, -z$; (iv) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (v) $x, \frac{3}{2}-y, \frac{1}{2}+z$.]

in determining the observed crown conformation. The metrical parameters for these potential hydrogen bonds, as calculated by *PLATON* (Spek, 1999), are presented in Table 2, with ring centroids represented as *Cg*2 (C9–C14) and *Cg*3 (C17–C22).

The crown conformation observed here differs slightly from that of the closely related compound 4,4′-bis(*tert*-butylbenzo)-benzo-21-crown-7 (Bryan *et al.*, 1998). For instance, the O—C—C—O torsion angles follow the patterns $0g^-0g^-0ag^-$ and $0g^+0g^+0ag^+$ in the two conformations of the previously reported crown, while the analogous angles in (I) follow the pattern $0g^-0g^+0ag^-$. All bond lengths and angles are in good agreement with standard values (Allen *et al.*, 1987). For example, the Csp^3—Csp^3 bond lengths range from 1.493 (3) to 1.513 (3) Å, while the Csp^2—Csp^2 lengths range from 1.377 (3) to 1.410 (2) Å.

Experimental

The title compound was synthesized in 63% yield by heating 1,2-bis[2-(2-hydroxyphenoxy)ethoxy]benzene (1.3 mmol), *N*,*N*-bis(2-chloroethyl)ethylamine (1.3 mmol) and caesium carbonate (13 mmol) in acetonitrile (10 ml) at reflux under argon for 1 h. Aqueous work-up was followed by chromatographic purification on silica gel (ether/methanol gradient elution). Crystals were grown by slow evaporation of a diethyl ether solution.

Crystal data

$C_{28}H_{33}NO_6$
$M_r = 479.6$
Monoclinic, $P2_1/c$
$a = 11.0160$ (12) Å
$b = 23.084$ (3) Å
$c = 9.9323$ (12) Å
$\beta = 98.977$ (9)°
$V = 2494.8$ (5) Å^3
$Z = 4$

$D_x = 1.28$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.1$–12.7°
$\mu = 0.09$ mm^{-1}
$T = 173$ K
Block, colourless
0.57 × 0.48 × 0.43 mm

Data collection

Nonius CAD-4 diffractometer with cryostat
ω scans
6915 measured reflections
4373 independent reflections
3312 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$

$\theta_{\rm max} = 25°$
$h = -13 \rightarrow 8$
$k = -16 \rightarrow 27$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: 9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.110$
$S = 1.03$
4373 reflections
317 parameters
H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.2606P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}

All H atoms were placed in calculated positions, refined using a riding model, and given isotropic displacement parameters equal to 1.2 (CH_2) or 1.5 (CH_3) times the equivalent isotropic displacement parameter of their parent atoms. The C—H distances used depend on the type of C atom: aromatic C—H = 0.95 Å, primary C—H = 0.98 Å and secondary C—H = 0.99 Å. Methyl H atoms were allowed to rotate about C—C.

Data collection: *CAD*-4-*PC* (Nonius, 1993). Cell refinement: *CAD*-4-*PC*. Data reduction: *XCAD*4 (Harms, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Siemens, 1995). Software used to prepare material for publication: *PLATON* (Spek, 1999).

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.369 (2)	O5—C16	1.436 (2)
O1—C26	1.437 (2)	O5—C17	1.373 (2)
O2—C2	1.382 (2)	O6—C18	1.367 (2)
O2—C7	1.443 (2)	O6—C23	1.438 (2)
O3—C8	1.451 (2)	N—C24	1.464 (2)
O3—C9	1.379 (2)	N—C25	1.465 (2)
O4—C10	1.364 (2)	N—C27	1.460 (2)
O4—C15	1.433 (2)		
C1—O1—C26	117.6 (1)	C18—O6—C23	116.2 (1)
C2—O2—C7	113.3 (1)	C24—N—C25	115.0 (1)
C8—O3—C9	115.4 (1)	C24—N—C27	112.4 (1)
C10—O4—C15	117.1 (1)	C25—N—C27	114.8 (1)
C16—O5—C17	114.9 (1)		
N—C25—C26—O1	−72.4 (2)	O4—C15—C16—O5	62.9 (2)
O1—C1—C2—O2	−3.1 (3)	O5—C17—C18—O6	−2.1 (2)
O2—C7—C8—O3	−72.5 (2)	O6—C23—C24—N	172.4 (1)
O3—C9—C10—O4	0.7 (3)		

Table 2
Hydrogen-bond and short-contact geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7B···O1	0.99	2.52	3.071 (2)	115
C8—H8B···O4	0.99	2.27	2.918 (2)	122
C25—H25A···O6$^{\rm i}$	0.99	2.58	3.527 (2)	160
C28—H28A···O2$^{\rm ii}$	0.98	2.52	3.416 (2)	152
C6—H6···$Cg2^{\rm iii}$	0.95	3.05	3.84	142
C15—H15B···$Cg2^{\rm iv}$	0.99	2.81	3.56	134
C16—H16B···$Cg3^{\rm v}$	0.99	2.46	3.37	154

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $x, y, z-1$; (iii) $-x, 1-y, -z$; (iv) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (v) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy, under contract number DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1254). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* II, pp. S1–19.
Bryan, J. C., Bunick, G. J. & Sachleben, R. A. (1999). *Acta Cryst.* C**55**, 250–252.
Bryan, J. C., Sachleben, R. A., Lavis, J. M., Burns, J. H. & Hay, B. P. (1998). *Inorg. Chem.* **37**, 2749–2755.
Harms, K. (1995). *XCAD*4. University of Marburg, Germany.
Hay, B. P. & Rustad, J. R. (1994). *J. Am. Chem. Soc.* **116**, 6316–6326.
Nonius (1993). *CAD*-4-*PC*. Version 1.2. Nonius, Delft, The Netherlands.
Sachleben, R. A., Deng, Y., Bailey, D. R. & Moyer, B. A. (1996). *Solvent Extr. Ion Exch.* **14**, 995–1015.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Siemens (1995). *SHELXTL*5.03/IRIX. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1999). *PLATON*. University of Utrecht, The Netherlands.
Steiner, T. (1996). *Crystallogr. Rev.* **6**, 1–57.
Steiner, T., Starikov, E. B. & Tamm, M. (1996). *J. Chem. Soc. Perkin Trans.* II, pp. 67–71.