

Tribenzo-18-crown-6 acetonitrile
disolvate¹Jeffrey C. Bryan,^{a*} Nancy L. Engle,^a Richard A. Sachleben^a
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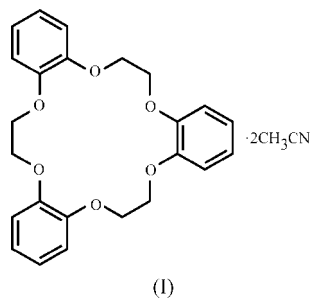
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Tribenzo-18-crown-6 binds two acetonitrile ligands, *i.e.* C₂₄H₂₄O₆·2C₂H₃N, one to each face of the crown ring. The crown conformation is relatively low in energy, but does not appear optimized for cation binding. Few significant intermolecular interactions are observed.

Comment

Chemical substitution of the backbone of a crown-ether molecule can dramatically affect its ability to bind specific metal ions (Hay *et al.*, 1996; Sachleben *et al.*, 1996; Tobe *et al.*, 1998; Vögtle & Weber, 1992). As part of our investigations of the steric effects of benzo-substitution on crown-ether molecules, we structurally characterized tribenzo-18-crown-6 (Pedersen, 1967; Talanova *et al.*, 1999).

As illustrated in Fig. 1, the crown ether crystallizes with two molecules of acetonitrile, (I), forming weak hydrogen bonds between the acetonitrile methyl groups and the crown O atoms. The C_{methyl}···O separations range from 3.080 (2) (C25···O6) to 3.836 (2) Å (C25···O4) and average about 3.4 Å, which is similar to previously reported results (Sachleben *et al.*, 1997).



(I)

The presence of the weakly binding acetonitrile guest molecules suggests that the observed crown-ether conformation could be a relatively low-energy binding mode. A

conformer search using computational methods previously described (Bryan *et al.*, 1998) agreed, finding no lower energy conformers. The oxygen dipoles are not oriented towards the center of the crown cavity, inhibiting efficient coordination of a guest species in the center of the cavity. Moreover, only four (O3–O6) of the six dipoles point out from one face of the crown cavity, weakening binding to a particular face. Such divergence of the donor groups suggests that this conformation will not efficiently bind a cation (Hay & Hancock, 2001). The conformation of the crown ring can be described in terms of the torsion angles (Table 1) around the ring (Dale, 1980), where *g* and *a* represent *gauche* and *anti*, respectively, 0 represents an aromatic O–C–C–O torsion angle, and a superscript following the *g* indicates the sign of the angle. Starting with the O1–C1–C2–O2 angle, the conformation is represented by 0aa g⁺aa 0 ag⁺ g⁺aa 0aa g⁻aa, where the spaces indicate O-atom locations.

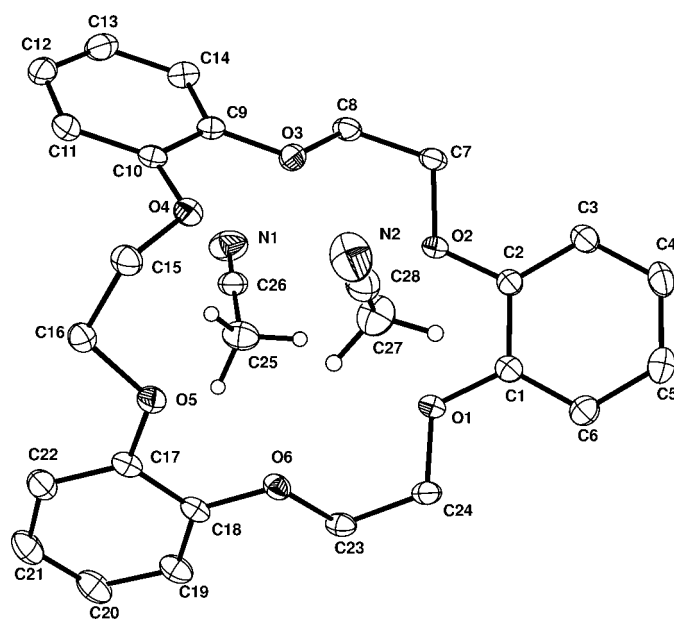


Figure 1

The molecular structure of the title compound showing 50% displacement ellipsoids. For clarity, the C atoms are represented by boundary ellipses, and H atoms, except those on acetonitrile, have been omitted.

There are few significant intermolecular interactions in this structure. No π -stacking of arene rings is observed, but one edge-face arene interaction is apparent [C17–C20···C1ⁱ–C6ⁱ; symmetry code (i) $-x, -y, 1-z$]. Two C–H··· π interactions are also observed, H7B···C9ⁱⁱ–14ⁱⁱ and H24A···C17ⁱⁱⁱ–22ⁱⁱⁱ [symmetry codes: (ii) $-x, -y, -z$; (iii) $1-x, -y, 1-z$].

Experimental

Tribenzo-18-crown-6 was prepared as described elsewhere (Pedersen, 1967). Crystals were prepared by slow evaporation of an acetonitrile solution. The crystals slowly desolvate when removed from the mother liquor. Crystals were removed from the mother liquor to paraffin oil, then quickly mounted and placed under the cold stream of the diffractometer. A 1.1 mm collimator was used.

¹ Systematic name: 2,3,12,15,22,25-hexaoxatetracyclo[24.4.0.0^{6,11}.0^{16,21}]triantaconta-6(11),7,9,16(21),17,19,26(1),27,29-nonaene acetonitrile disolvate

Crystal data

C₂₄H₂₄O₆·2C₂H₃N
M_r = 490.5
 Triclinic, *P* $\bar{1}$
a = 9.109 (2) Å
b = 10.883 (3) Å
c = 13.964 (4) Å
 α = 110.16 (2)°
 β = 96.60 (2)°
 γ = 98.27 (2)°
V = 1265.7 (6) Å³

Z = 2
D_x = 1.29 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 10.1–15.1°
 μ = 0.09 mm⁻¹
T = 100 K
 Block, colorless
 0.56 × 0.49 × 0.43 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 7849 measured reflections
 6714 independent reflections
 5308 reflections with *I* > 2σ(*I*)
R_{int} = 0.016

θ_{\max} = 29.0°
h = -12 → 6
k = -14 → 14
l = -18 → 19
 3 standard reflections
 frequency: 120 min
 intensity decay: 12%

Refinement

Refinement on *F*²
R(*F*) = 0.042
wR(*F*²) = 0.115
S = 1.06
 6714 reflections
 343 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.2556P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.34 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

O1–C1	1.3757 (15)	O4–C15	1.4346 (15)
O1–C24	1.4335 (15)	O5–C16	1.4340 (16)
O2–C2	1.3755 (16)	O5–C17	1.3754 (15)
O2–C7	1.4321 (15)	O6–C18	1.3722 (15)
O3–C8	1.4296 (15)	O6–C23	1.4363 (15)
O3–C9	1.3711 (16)	N1–C26	1.137 (2)
O4–C10	1.3746 (16)	N2–C28	1.1434 (19)
N1–C26–C25	178.51 (16)	N2–C28–C27	179.57 (15)
C24–O1–C1–C2	-169.94 (10)	C16–O5–C17–C18	167.73 (10)
C1–O1–C24–C23	-176.70 (9)	C23–O6–C18–C17	-172.59 (10)
C7–O2–C2–C1	159.27 (10)	C18–O6–C23–C24	178.30 (10)
C2–O2–C7–C8	-171.50 (10)	O1–C1–C2–O2	0.45 (14)
C9–O3–C8–C7	173.57 (9)	O2–C7–C8–O3	66.12 (12)
C8–O3–C9–C10	-179.33 (10)	O3–C9–C10–O4	0.90 (14)
C15–O4–C10–C9	-169.91 (9)	O4–C15–C16–O5	65.78 (13)
C10–O4–C15–C16	76.59 (13)	O5–C17–C18–O6	0.79 (16)
C17–O5–C16–C15	-172.70 (10)	O6–C23–C24–O1	-69.35 (12)

Almost all the H atoms were placed in calculated positions, treated as riding on their attached C atoms, and given an isotropic displacement parameter equal to 1.2 (CH and CH₂) or 1.5 (CH₃) times the equivalent isotropic displacement parameter of the atom to which they were attached. The C–H distances used depended on the type of C atom, *i.e.* methylene C–H = 0.99 Å and arene C–H = 0.95 Å. The positional parameters of the methyl H atoms were allowed to refine [C–H = 0.92 (2)–1.00 (2) Å].

Data collection: CAD-4-PC (Enraf–Nonius, 1993); cell refinement: CAD-4-PC; data reduction: XCAD4 (Harms, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1618). Services for accessing these data are described at the back of the journal.

References

Bruker (1997). *SHELXTL/IRIX*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bryan, J. C., Sachleben, R. A., Lavis, J. M., Davis, M. C., Burns, J. H. & Hay, B. P. (1998). *Inorg. Chem.* **37**, 2749–2755.
 Dale, J. (1980). *Isr. J. Chem.* **20**, 3–11.
 Enraf–Nonius (1993). *CAD-4-PC*. Version 1.2. Nonius, Delft, The Netherlands.
 Harms, K. (1995). *XCAD4*. University of Marburg, Germany.
 Hay, B. P. & Hancock, R. D. (2001). *Coord. Chem. Rev.* **212**, 61–78.
 Hay, B. P., Zhang, D. & Rustad, J. R. (1996). *Inorg. Chem.* **35**, 2650–2658.
 Pedersen, C. J. (1967). *J. Am. Chem. Soc.* **89**, 7017–7036.
 Sachleben, R. A., Bryan, J. C., Lavis, J. M., Starks, C. M. & Burns, J. H. (1997). *Tetrahedron*, **53**, 13567–13582.
 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.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Talanova, G. G., Elkarim, N. S. A., Talanov, V. S., Hanes, R. E. Jr, Hwang, H.-S., Bartsch, R. A. & Rogers, R. D. (1999). *J. Am. Chem. Soc.* **121**, 11281–11290.
 Tobe, Y., Tsuchiya, Y., Iketani, H., Naemura, K., Kobiro, K., Kaji, M., Tsuzuki, S. & Suzuki, K. (1998). *J. Chem. Soc. Perkin Trans. 1*, pp. 485–494.
 Vögtle, F. & Weber, E. (1992). *J. Inclusion Phenom. Mol. Recognit. Chem.* **12**, 75–119.