C4—C3—N1	122.4 (3)	C3—N1—C2	117.9 (3)
O1—C9—C4	115.6 (3)	C4—C5—C6	121.3 (3)
O1—C9—C8	124.4 (3)	C6—C7—C8	120.8 (3)
C4—C9—C8	120.1 (3)	C5—C6—C7	119.5 (3)
C9—O1—C10	118.4 (3)	N1—C2—C1	111.6 (2)
C3—C4—C9	120.8 (3)	O1—C10—C11	110.8 (3)
C3—C4—C5	120.9 (3)	C10—C11—O2	116.9 (6)
C9—C4—C5	118.3 (3)	C9—C8—C7	120.0 (3)
N1—C3—C4—C9	174.3 (3)	C8—C9—O1—C10	12.7 (5)
N1—C3—C4—C5	−4.9 (5)	C9—O1—C10—C11	159.4 (5)
C4—C3—N1—C2	178.7 (3)	C3—N1—C2—C1	127.3 (3)
C4—C9—O1—C10	−166.5 (3)	O1—C10—C11—O2	−58.1 (7)

The space group could not be determined uniquely from the Laue class and extinctions; it may be C2/c or Cc. The structure was solved in the C2/c space group by direct methods. The positions of atoms H51, H101, H102, H111 and H112 were calculated geometrically, while the remaining H-atom positions were located in a difference synthesis and their displacement parameters refined isotropically. A riding model was used in the refinement of all H-atom positions.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1040). Services for accessing these data are described at the back of the journal.

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Tetrabenzo-24-crown-8†

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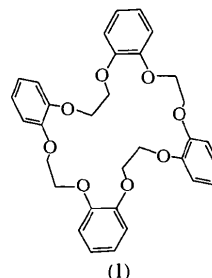
Abstract

The structure of tetrabenzo-24-crown-8, $C_{32}H_{32}O_8$, does not exhibit a binding cavity for alkali metal ions, but is collapsed in on itself. The conformation may be a result of inter- and intramolecular hydrogen bonding. The molecule lies on an inversion center.

Comment

We recently reported that tetrabenzo-24-crown-8, (I), exhibits promise as a selective and efficient extractant for

(1)

Cs⁺ from mixtures of alkali metal ions (Sachleben *et al.*, 1996; Sachleben, Deng & Moyer, 1997). Specifically, it was shown that tetrabenzo-24-crown-8 extracts Cs⁺ more strongly, and is more selective for Cs⁺ over Rb⁺, than a number of other benzo-substituted crown-8 and crown-7 extractants (Sachleben *et al.*, 1996). We undertook to investigate its structure to see if the four arene groups placed on the crown ring facilitate preorganization of this crown for Cs⁺ binding.

The structure of the title compound is depicted in Fig. 1, and clearly demonstrates that the crown cavity is not preorganized for Cs⁺ binding; rather, it is collapsed in on itself, the cavity being filled primarily by methylene groups, as is commonly observed for structures of large uncomplexed crown ether molecules (Sachleben, Bryan *et al.*, 1997). This may be due in part to

† Alternative name: 3,4,13,14,23,24,33,34-octahydro-2,5,12,15,22,25,-32,35-octaoxopentacyclo[34.4.0.0⁶,¹¹.0¹⁶,²¹.0²⁶,³¹]tetraconta-6(11),7,-9,16(21),17,19,26,28,30,36,38,40-dodecaene.

intramolecular hydrogen bonding (Table 2 and Fig. 2) between methylene H and ether O atoms. While many close contacts are made between these two atom types, most have C—H···O angles too low to be considered an effective hydrogen bond (Steiner, 1996). Only those with C—H···O angles greater than 100° are listed in Table 2.
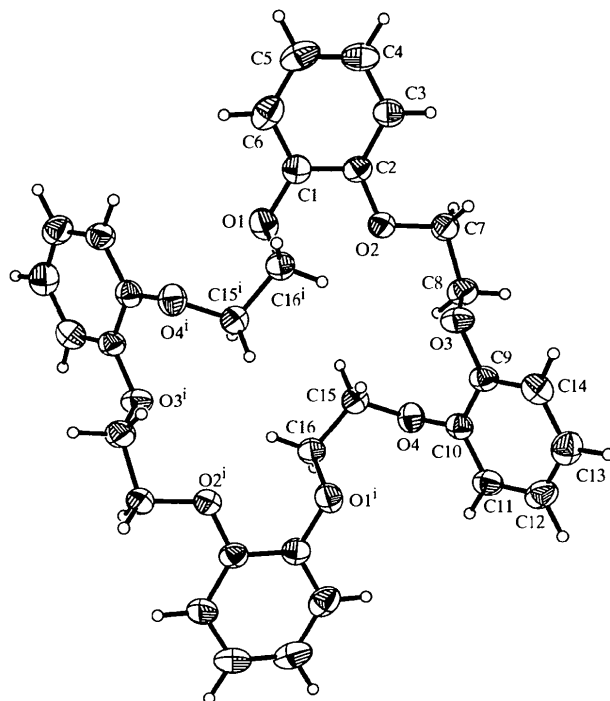

Fig. 1. Molecular structure of (I), showing 50% probability displacement ellipsoids. Symmetry code: (i) $1 - x$, $1 - y$, $-z$.

Despite the large number of arene rings in this compound, no π stacking is observed. However, close C—H···π contacts, some of which may represent hydrogen bonds (Steiner et al., 1996; Gakh et al., 1996), are clearly present (Fig. 2). These weak hydrogen bonds may also play a role in determining the observed crown conformation. The metrical parameters for these potential hydrogen bonds, as calculated by PLATON (Spek, 1998), are presented in Table 2, with ring centroids represented as Cg1 (C1–C6) and Cg2 (C9–C14). Note that two hydrogen bonds are listed for each arene ring, one on each face of a particular ring.

The crown conformation observed here differs qualitatively from the closely related crown ether molecules, dibenzo-24-crown-8 (Hanson et al., 1976) and 4,4′-bis(tert-octylbenzo)-24-crown-8 (Sachleben, Bryan et al., 1997), in that the O atoms more closely outline an approximate circle in the title compound, while the donor atoms in the dibenzo-24-crown-8 roughly define an elongated ellipse. All bond lengths and angles are
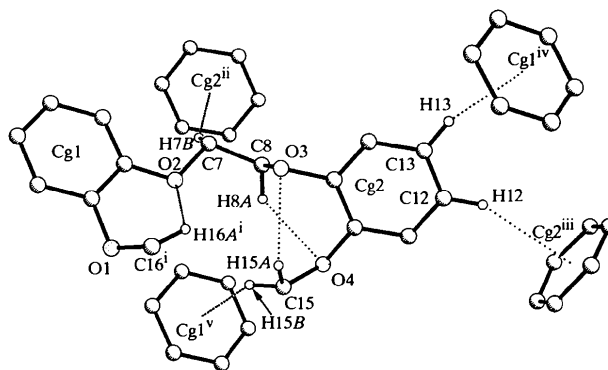

Fig. 2. Hydrogen bond interactions of (I). For clarity, only the asymmetric unit of (I) and fragments of symmetry-equivalent molecules are shown. All atoms are represented as circles, and only H atoms involved in hydrogen bonding are drawn. Symmetry codes are as given in Table 2.

in good agreement with standard values (Allen et al., 1987). For example, the Csp^3—O bond lengths range from 1.425 (2) to 1.443 (2) Å, while those of Csp^2—O range from 1.360 (2) to 1.382 (2) Å (Table 1).

Experimental

Crystal data

$C_{32}H_{32}O_8$	Cu $K\alpha$ radiation
$M_r = 544.60$	$\lambda = 1.54180$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 9.5974$ (13) Å	$\theta = 50.3–55.5°$
$b = 18.9323$ (11) Å	$\mu = 0.81$ mm^{-1}
$c = 7.2881$ (10) Å	$T = 293$ K
$\beta = 94.229$ (12)°	Plate
$V = 1320.6$ (3) Å^3	$0.44 \times 0.29 \times 0.05$ mm
$Z = 2$	Colorless
$D_x = 1.37$ Mg m^{-3}	
D_m not Measured	

Data collection

Rigaku AFC-7R diffractometer	1995 reflections with
	$I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.032$
Absorption correction:	$\theta_{max} = 67.6°$
ψ-scan (TEXSAN;	$h = -11 \rightarrow 11$
Molecular Structure	$k = 0 \rightarrow 22$
Corporation, 1992)	$l = 0 \rightarrow 8$
$T_{min} = 0.75$, $T_{max} = 0.96$	3 standard reflections
2674 measured reflections	every 200 reflections
2387 independent reflections	intensity decay: 0.74%

Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.111$
$S = 1.04$
2387 reflections
229 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.2606P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.377 (2)	O3—C8	1.443 (2)
O1—C16^i	1.437 (2)	O3—C9	1.382 (2)
O2—C2	1.360 (2)	O4—C10	1.377 (2)
O2—C7	1.425 (2)	O4—C15	1.442 (2)
C1—O1—C16^i	114.6 (1)	O2—C7—C8	108.1 (1)
C2—O2—C7	117.1 (1)	O3—C8—C7	108.1 (1)
C8—O3—C9	114.1 (1)	O3—C9—C10	122.1 (2)
C10—O4—C15	116.1 (1)	O3—C9—C14	118.5 (1)
O1—C1—C2	120.9 (1)	O4—C10—C9	121.5 (1)
O1—C1—C6	119.3 (2)	O4—C10—C11	118.5 (1)
O2—C2—C1	115.9 (1)	O4—C15—C16	110.1 (1)
O2—C2—C3	124.9 (1)	O1^i—C16—C15	107.5 (1)
O1—C1—C2—O2	−2.8 (2)	O3—C9—C10—O4	2.0 (2)
O2—C7—C8—O3	−67.2 (2)	O4—C15—C16—O1^i	72.1 (2)

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

Cg1 = centroid of the C1—C6 ring; Cg2 = centroid of the C9—C14 ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C8—H8A⋯O4	1.01 (2)	2.48 (2)	3.062 (2)	116 (2)
C15—H15A⋯O3	1.01 (2)	2.54 (2)	3.008 (2)	107.7 (13)
C16—H16A⋯O2^i	0.96 (2)	2.44 (2)	2.979 (2)	115.4 (11)
C7—H7B⋯Cg2^{ii}	0.98 (2)	2.81	3.70	152
C12—H12⋯Cg2^{iii}	1.00 (2)	2.79	3.72	156
C13—H13⋯Cg1^{iv}	0.99 (2)	2.74	3.65	152
C15—H15B⋯Cg1^v	0.99 (2)	2.80	3.65	144

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

Anisotropic displacement parameters were used for all non-H atoms. All H atoms were located and their positional parameters allowed to refine, and each was given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the C atom to which they were attached. C—H bond lengths are in the range 0.96 (2)–1.01 (2) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Siemens, 1995). Software used to prepare material for publication: *PLATON* (Spek, 1998).

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4-Heptamethyleneimino-7-nitrobenzo-2-oxa-1,3-diazole†

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Abstract

The title compound, $C_{13}H_{16}N_4O_3$, crystallized in the $P\bar{1}$ (No. 2) space group from ethyl acetate. The asymmetric unit contains two molecules with similar geometry. The

† Alternative name: 4-(azocan-1-yl)-7-nitro-2,1,3-benzoxadiazole.