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25,27:26,28-Bis(3,9-dioxa-6-aza-undecane-1,11-dioxy)calix[4]arene tetrahydrate

Jong Seung Kim,[a] William P. Jensen,[b] Chang-Hee Lee,[c] Jin-Ho Lee,[c] Moon-Jib Kim,[d] Jin-Gyu Kim[e] and Il-Hwan Suh[e]*

[a]Department of Chemistry, Konyang University, Nonsan, Chungnam 320-711, Korea, [b]The Chemistry Department, South Dakota State University, Brookings, SD 57007, USA, [c]Neutron Physics Department, Korea Atomic Energy Research Institute, PO Box 105, Yusong, Taejon 305-600, Korea, [d]Department of Physics, Soonchunhyang University, Onyang 336-600, Korea, and [e]Department of Physics, Chungnam National University, Taejon 305-764, Korea
Correspondence e-mail: ihsuh@hanbat.chungnam.ac.kr

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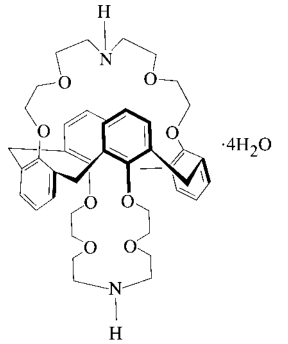
The title compound, $C_{44}H_{54}N_2O_8{\cdot}4H_2O$, has twofold crystallographic symmetry and consists of a calix[4]arene moiety with four phenyl rings arranged alternately in *anti*-orientation fashion and two azacrown units attached on the lower rims of calix[4]arene. This seems to offer a big cavity inside the molecule which might possess a potential for forming host–guest complexes.

Comment

Calix[4]arenes have been of particular interest as organic hosts and selective ionophores in inclusion complexation (Gutsche, 1989) and it is known that the calix[4]arenes are able to exist in the following four different conformations: cone (Guelzim *et al.*, 1997; Harkema *et al.*, 1998), partial cone (Kim *et al.*, 1993), 1,2-alternate and 1,3-alternate (Ungaro & Pochini, 1991). In order to investigate the characteristics of the calix[4]arene compounds, a series of calix[4]arene derivatives has been synthesized and their structures elucidated (Kim *et al.*, 1997; Kim, Pang *et al.*, 1998; Kim, Yu *et al.*, 1998; Kim, Suh *et al.*, 1998; Kim, Kim, Lee *et al.*, 1999; Kim, Kim, Choo *et al.*, 1999).



(I)

In the title compound, (I), a half molecule belongs to an asymmetric unit and a molecule is completed by another half primed molecule translated by twofold symmetry along the *b* axis [symmetry code: (′) $1 - x, y, \frac{1}{2} - z$] (Fig. 1).

Compound (I) consists of the calix[4]arene molecule adopting the 1,3-alternate conformation (two phenyl groups *A* and *B*′ lie above and the other two phenyl groups *A*′ and *B* below the least-squares plane defined by the four bridging methylene groups as clearly illustrated in Fig. 1), two azacrown units (one bonded to phenyl rings *A* and *B*′ and another one to phenyl rings *A*′ and *B*, respectively), and four water molecules not represented in the figure.

The aromatic $Csp^2{-}Csp^2$ distances in the molecule vary from 1.367 (5) to 1.397 (5) Å with an average value of 1.385 (1) Å, $Csp^2{-}Csp^3$ distances vary from 1.511 (4) to 1.522 (4) Å with a mean value of 1.516 (2) Å, $Csp^3{-}Csp^3$ distances vary from 1.480 (5) to 1.490 (5) Å with a mean value of 1.485 (3) Å, $O{-}Csp^3$ distances vary from 1.377 (4) to 1.438 (4) Å with a mean value of 1.414 (2) Å, and the mean value of two $O{-}Csp^2$ bonds is 1.383 (3) Å. All of these are very close to those in 25,27-bis(1-propyloxy)calix[4]arene-26,28-[(5′,6′)(14′,15′)-dibenzo]crown-7 (Kim, Pang *et al.*, 1999) and in 1,3-alternate calix[4]arene-bis(crown-7) (Khrifi *et al.*, 1997).

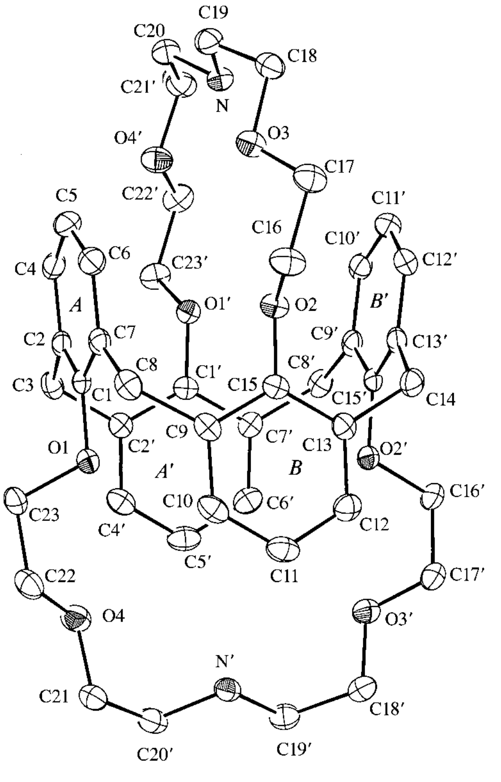


Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I) showing the atom-numbering scheme with water molecules; H atoms omitted for clarity. Displacement ellipsoids are drawn at the 40% probability level. The unprimed atoms belong to an asymmetric unit and a molecule is completed by another primed asymmetric unit translated by $1{-}x, y, \frac{1}{2} - z$.

Bond angles involving the bridging methylenes C2—C3—C2′ 113.7 (4), C7—C8—C9 114.4 (3) and C13—C14—C13′ 114.6 (4)° are larger than the tetrahedral angle due to repulsions among the four phenyl groups.

Two adjacent phenyl rings in the calix[4]arene are perpendicular to each other with a dihedral angle of $A\hat{\ }B$ = 89.76 (8)° so that the calix[4]arene has a fairly perfect square cavity. However, two facing rings *A* and *B*′ are slightly splayed out upwards from the central axis with a dihedral angle of 11.6 (2)° leading to C1···C15′ 5.337 (4) and C5···C11′ 5.870 (5) Å, and the same for the pair of facing rings *A*′ and *B* because of symmetry.

In the azacrown unit, O···O and N···O distances are O1···O2′ 5.135 (3), O3···O4′ 5.311 (4), N···O1′ 4.742 (4) and N···O2 4.800 (4) Å, so that the somewhat flexible cavity lined with four O atoms and an N atom might enable the molecule to introduce a guest atom. Additionally the torsion angles of O2—C16—C17—O3 and O4—C22—C23—O1 in the azacrown unit are both *gauche* being −58.5 (5) and 59.9 (4)°, respectively.

There are four hydrogen bonds involving the N atom in the amine group and the two water molecules in an asymmetric unit and it is especially worth mentioning that two water O atoms donate and accept their H atoms to and from each other as shown in Table 1, where the distances between H2*W*1···H1*W*2 and H2*W*2···H2*W*2 $(2-x, -y, 1-z)$ are 1.76 and 1.74 Å, respectively. This hydrogen-bond scheme makes an infinite molecular chain running in the [201] direction and the closest contact between the molecular chains is O*W*1···HC3 $(\frac{1}{2}+x, -\frac{1}{2}+y, \frac{1}{2}-z)$ = 2.51 Å.

Experimental

Into a three-neck round-bottomed flask under nitrogen, K_2CO_3 (0.96 g, 6.95 mmol), pre-dried *N*,*N*-dimethylformamide (DMF) (60 ml), 25,26,27,28-tetra(5-chloro-3-oxapentyloxy)calix[4]arene (5.00 g, 5.88 mmol) and *p*-toluenesulfonamide (2.11 g, 12.3 mmol) were placed and refluxed for 24 h. DMF was completely removed *in vacuo* and 10% aqueous $NaHCO_3$ (100 ml) and CH_2Cl_2 (100 ml) were added and the organic layer separated. The organic layer was washed with water (2 × 50 ml) and dried over anhydrous $MgSO_4$ and filtered. Evaporation of the CH_2Cl_2 *in vacuo* gave a yellow oil which was purified by column chromatography (R_f = 0.3) using ethyl acetate:hexane (1:8) to provide 4.00 g (65%) of *N*-tosylcalix[4]arene-bis(azacrown-5) as a white solid (m.p. 421–424 K). To a solution of 1,4-dioxane (100 ml) and methanol (20 ml) were carefully added *N*-tosylcalix[4]arene-bis(azacrown-5) (3.00 g, 2.86 mmol) and 6% Na(Hg) amalgam (0.853 g). The reaction mixture was refluxed for 2 d at 353 K. After cooling to room temperature, the solvent was evaporated *in vacuo*. CH_2Cl_2 (50 ml) and water (50 ml) were added and the organic layer was separated. The CH_2Cl_2 layer was washed twice with 10% aqueous Na_2HPO_4 followed by drying over anhydrous $MgSO_4$. After filtration of magnesium sulfate, removal of the solvent *in vacuo* gave calix[4]arene-bis(azacrown-5) as a white solid which was recrystallized with diethyl ether (30 ml) (m.p. 458–461 K, 52% yield). IR (KBr pellet, cm^{-1}): 2926, 1456, 1359, 1176, 1094, 928, 767, 664; ^1H NMR ($CDCl_3$, p.p.m.): δ 7.18–6.64 (*m*, 12H, Ar–H), 3.88 (*s*, 8H, $ArCH_2Ar$), 3.67–3.46 (*m*, 24H, $-CH_2-$), 2.81 (*s*, 8H, $-OCH_2CH_2NCH_2-$); ^{13}C NMR ($CDCl_3$, p.p.m.) 157.3, 134.6, 131.8, 122.7, 71.7, 71.4, 70.9, 49.6, 38.5; FAB MS *m*/*z* (M^+): calculated 738.9, found 739.1.

Crystal data

$C_{44}H_{54}N_2O_8 \cdot 4H_2O$
M_r = 810.96
Orthorhombic, *Pbcn*
a = 15.922 (2) Å
b = 16.7908 (16) Å
c = 16.453 (4) Å
V = 4398.6 (13) $Å^3$
Z = 4
D_x = 1.225 Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 25 reflections
θ = 11.01–12.54°
μ = 0.089 mm^{-1}
T = 288 (2) K
Block, colorless
0.73 × 0.59 × 0.59 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω/2θ scans
4330 measured reflections
3861 independent reflections
2185 reflections with $I > 2\sigma(I)$
θ_{max} = 24.97°

$h = 0 \rightarrow 18$
$k = 0 \rightarrow 19$
$l = -19 \rightarrow 0$
3 standard reflections
frequency: 300 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.205$
S = 0.994
3861 reflections
263 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0944P)^2 + 2.5719P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.55 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.26 e $Å^{-3}$

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*1—H1*W*1···N	0.86	1.99	2.842 (4)	168
O*W*1—H2*W*1···O*W*2	0.87	2.49	2.771 (4)	100
O*W*2—H1*W*2···O*W*1	0.86	1.92	2.771 (4)	167
O*W*2—H2*W*2···O*W*2^i	0.87	2.16	2.788 (7)	129

Symmetry code: (i) $2-x, -y, 1-z$.

An H atom of the amine group and those of C3 and C14 sit on a twofold axis and could be located from a difference Fourier map, and the positions of the four H atoms of two water molecules were calculated using *HYDROGEN* (Nardelli, 1999). Their positions were fixed with $U_{iso}(H) = 1.2U_{eq}$(N, C, O), while all other H atoms were placed in calculated positions and allowed to ride upon the C atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *WinGX* (Farrugia, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1433). Services for accessing these data are described at the back of the journal.

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