(EI): 325 (M^+, 19%), 268 (12), 267 (75), 210 (22), 209 (42), 181 (20), 165 (20), 153 (63), 137 (28) and 121 (47).

Crystal data

$C_{14}H_{15}NO_8$
$M_r = 325.27$
Triclinic
$P\bar{1}$
$a = 5.191\ (4)$ Å
$b = 11.627\ (6)$ Å
$c = 12.998\ (7)$ Å
$\alpha = 75.80\ (4)°$
$\beta = 79.33\ (6)°$
$\gamma = 88.49\ (6)°$
$V = 747.2\ (8)$ Å^3
$Z = 2$
$D_x = 1.446$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 9.5–12.0°$
$\mu = 0.120$ mm^{-1}
$T = 298\ (2)$ K
Lath
$0.31 \times 0.12 \times 0.04$ mm
Pale yellow

Data collection

Stoe Stadi-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: none
2607 measured reflections
1954 independent reflections
734 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.188$
$\theta_{\rm max} = 22.5°$
$h = -5 \rightarrow 5$
$k = -11 \rightarrow 12$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.113$
$S = 0.980$
1946 reflections
209 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0204P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0091 (13)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å)*

O1—C6	1.354 (7)	O1′—C6′	1.361 (8)
O1—C2	1.442 (7)	O1′—C2′	1.438 (8)
C2—O3	1.455 (8)	C2′—O3′	1.433 (8)
O3—C4	1.357 (7)	O3′—C4′	1.359 (8)
C4—O4	1.202 (7)	C4′—O4′	1.209 (8)
C4—C5	1.466 (9)	C4′—C5′	1.463 (9)
C5—C7	1.352 (9)	C5′—C7′	1.347 (9)
C5—C6	1.447 (8)	C5′—C6′	1.454 (9)
C6—O6	1.209 (7)	C6′—O6′	1.211 (8)
C7—N1	1.351 (8)	N1—C7′	1.373 (8)
O6···O6′	3.178 (7)		

The crystal diffracted only weakly at higher angles and accordingly data were collected to only $2\theta_{\rm max} = 45°$, resulting in a low data-to-parameter ratio. The high value of $R_{\rm int}$ reflects the distribution of equivalents over rather weak high-angle data.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1340). Services for accessing these data are described at the back of the journal.

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1,3-Di(ethoxy-ethoxy-methoxy)calix[4]arene†

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Abstract

In the solid state, the title compound, $C_{38}H_{44}O_8$, adopts a cone conformation, which is somewhat distorted. The cone conformation is also observed by NMR spectroscopy in solution. The distortion consists of a

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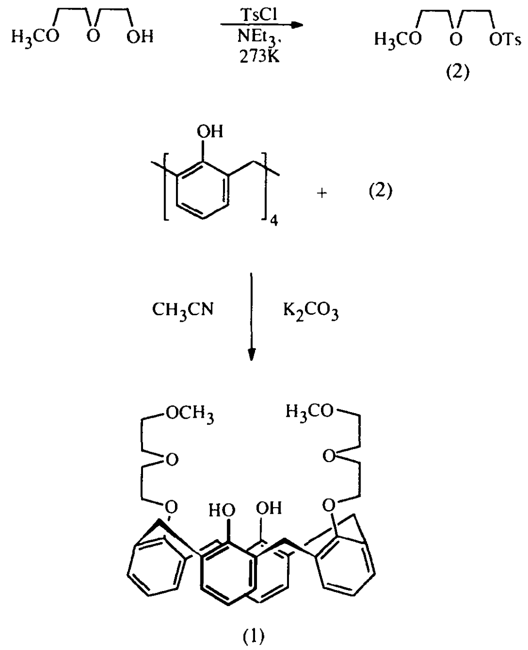
† Alternative name: 26,28-bis(3,6-dioxaheptyloxy)pentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,-19(26),21,23-dodecaene-25,27-diol.

major inward tilt of the two opposite phenolic rings, permitting hydrogen bonding to the ether substituents.

Comment

The calixarenes, first reported by Zinke & Ziegler (1944), have received subsequent synthetic study by Gutsche & Muthukrishnan (1978), Gutsche, Dhawan, No & Muthukrishnan (1981) and Kammerer & Happel (1980). More recently, calixarenes have been shown to be easily prepared and transformed into functionalized derivatives with potential for binding metal cations (Gutsche, 1989; Vicens & Böhmer, 1991). This is of fundamental importance in the quest for a better understanding of natural molecular recognition processes. A further interest in calix[4]arenes is that, upon functionalization, these macrocycles may adopt four extreme conformations, *i.e.* cone, partial cone, 1,2-alternate and 1,3-alternate, thus providing additional shapes for selective molecular recognition. As noted by Izatt *et al.* (1983), these compounds have several features that are valuable to membrane carriers, including low water solubility and formation of neutral complexes with cations through loss of protons.

The synthesis of the title compound, (1), was conducted as shown in the scheme. The cone conformation and the C_2 symmetry of the molecule were shown from its ^{1}H NMR spectrum at 200 MHz in $CdCl_3$. A single *AB* system was observed for the binding methylene groups at 3.36 and 4.44 p.p.m. (J = 13.0 Hz), two triplets at 6.65 and 6.72 p.p.m. (J = 7.3 Hz) for the protons at the *para* position on the aromatic rings, and one singlet at 7.74 p.p.m. for the phenolic OH groups. X-ray diffraction analysis confirmed the crystal structure.



The compound adopts the cone conformation here also, albeit in a very distorted form (Fig. 1). This is revealed clearly by the angles between the mean molecular plane defined by the bridging methylene groups linking the aromatic rings and the planes of the individual benzene rings: 35.0 (1) (*A*), 78.4 (1) (*B*), 39.8 (1) (*C*) and 71.8 (1)° (*D*). Thus, the two benzene rings (*B* and *D*) bearing the polyetheral chains are tilted [interplanar angle 29.8 (1)°], leading to an O1*B*···O1*D* separation of 4.571 (4) Å. The two phenolic rings (*A* and *C*) are tilted so as to place the hydroxy groups inside the cavity, with an O1*A*···O1*C* separation of 3.137 (3) Å. This arrangement allows for easy hydrogen-bond formation between proximal hydroxy and polyetheral functional groups [O1*A*···O1*B* = 2.760 (3), O1*A*···O1*D* = 2.836 (3), O1*C*···O1*B* = 2.914 (4) and O1*C*···O1*D* = 2.716 (3) Å]. This is probably the reason for the relatively large interplanar angle [105.2 (1)°] between the two phenolic rings. In the polyetheral chains, the O—C—C—O torsion angles are −64.9 (4) and −58.5 (5)° for the chain linked to *B*, and −71.7 (4) and −76.8 (6)° for the chain linked to *D*. The C—O—C—C torsion angles range from −163.1 (4) to 168.4 (3)° and from −178.6 (4) to 171.4 (3)° for rings *B* and *D*, respectively.

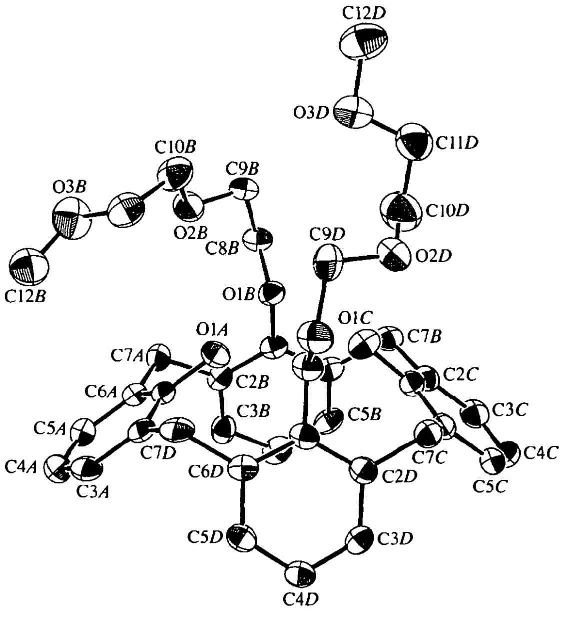


Fig. 1. The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

Experimental

In a preliminary step of the synthesis of the title compound, commercial 2-methoxy-ethoxy-ethanol was treated with one equivalent of sulfonyl chloride in the presence of two equivalents of NEt_3 in CH_2Cl_2 at 273 K to afford the tosylate derivative, (2), which was obtained pure in 75% yield after chromatography on SiO_2 (2:98 acetone–chloroform as eluent). Under conditions developed for related compounds, reaction of calix[4]arene with two equivalents of (2) in the presence of two equivalents of K_2CO_3 in refluxing acetonitrile produced the title compound, (1), in 41% yield after chromatography on SiO_2 (5:95 acetone–chloroform as eluent). Compound (1) was obtained as a white solid melting at 406–407 K after recrystallization from methanol.

Crystal data

$C_{38}H_{44}O_8$
$M_r = 628.76$
Monoclinic
$P2_1/n$
$a = 11.578$ (5) Å
$b = 22.385$ (10) Å
$c = 13.062$ (6) Å
$\beta = 104.21$ (4)°
$V = 3282$ (3) Å^3
$Z = 4$
$D_x = 1.2726$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 5–10$°
$\mu = 0.088$ mm^{-1}
$T = 293$ (2) K
Parallelepiped
0.50 × 0.50 × 0.40 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
4243 measured reflections
4186 independent reflections
2641 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.025$
$\theta_{\rm max} = 26.96$°
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 28$
$l = 0 \rightarrow 10$
5 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.064$
$S = 1.897$
4186 reflections
416 parameters
H atoms riding (see below)
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\rm max} = -0.001$

$\Delta\rho_{\rm max} = 0.326$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.252$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00087 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1*A*—C1*A*	1.361 (4)	O3*B*—C12*B*	1.404 (5)
C2*A*—C7*D*	1.509 (5)	O1*C*—C1*C*	1.371 (4)
C6*A*—C7*A*	1.501 (5)	C6*C*—C7*C*	1.515 (4)
C7*A*—C2*B*	1.512 (5)	C7*C*—C2*D*	1.511 (4)
C1*B*—O1*B*	1.394 (4)	C1*D*—O1*D*	1.397 (4)
C6*B*—C7*B*	1.508 (5)	C6*D*—C7*D*	1.527 (4)
C7*B*—C2*C*	1.502 (5)	O1*D*—C8*D*	1.432 (4)
O1*B*—C8*B*	1.439 (4)	C8*D*—C9*D*	1.495 (5)
C8*B*—C9*B*	1.496 (4)	C9*D*—O2*D*	1.429 (5)
C9*B*—O2*B*	1.418 (4)	O2*D*—C10*D*	1.428 (6)
O2*B*—C10*B*	1.399 (4)	C10*D*—C11*D*	1.448 (6)
C10*B*—C11*B*	1.471 (5)	C11*D*—O3*D*	1.413 (5)
C11*B*—O3*B*	1.356 (5)	O3*D*—C12*D*	1.403 (5)
O1*A*—C1*A*—C2*A*	115.5 (4)	O1*C*—C1*C*—C2*C*	114.9 (4)
C6*A*—C7*A*—C2*B*	113.5 (3)	C2*D*—C7*C*—C6*C*	113.6 (3)
C2*B*—C1*B*—O1*B*	117.8 (3)	C2*A*—C7*D*—C6*D*	114.1 (3)
C2*C*—C7*B*—C6*B*	111.1 (3)	C1*D*—O1*D*—C8*D*	114.7 (3)
C1*B*—O1*B*—C8*B*	114.5 (3)	O1*D*—C8*D*—C9*D*	105.9 (3)
O1*B*—C8*B*—C9*B*	105.6 (3)	O2*D*—C9*D*—C8*D*	108.8 (4)
O2*B*—C9*B*—C8*B*	107.0 (3)	C10*D*—O2*D*—C9*D*	118.2 (4)
C10*B*—O2*B*—C9*B*	116.3 (3)	O2*D*—C10*D*—C11*D*	112.9 (5)
O2*B*—C10*B*—C11*B*	109.6 (4)	O3*D*—C11*D*—C10*D*	108.5 (4)
O3*B*—C11*B*—C10*B*	110.9 (4)	C12*D*—O3*D*—C11*D*	110.4 (4)
C11*B*—O3*B*—C12*B*	115.3 (4)		
C1*B*—O1*B*—C8*B*—C9*B*	168.4 (3)		
O1*B*—C8*B*—C9*B*—O2*B*	−64.9 (4)		
C8*B*—C9*B*—O2*B*—C10*B*	163.1 (3)		
C9*B*—O2*B*—C10*B*—C11*B*	−163.1 (4)		
O2*B*—C10*B*—C11*B*—O3*B*	−58.5 (5)		
C10*B*—C11*B*—O3*B*—C12*B*	163.0 (4)		
C1*D*—O1*D*—C8*D*—C9*D*	171.4 (3)		
O1*D*—C8*D*—C9*D*—O2*D*	−71.7 (4)		
C8*D*—C9*D*—O2*D*—C10*D*	135.9 (4)		
C9*D*—O2*D*—C10*D*—C11*D*	87.7 (6)		
O2*D*—C10*D*—C11*D*—O3*D*	−76.8 (6)		
C10*D*—C11*D*—O3*D*—C12*D*	−178.6 (4)		

H atoms were made to ride on C and O atoms with $U(\rm H) = U_{\rm eq}(\rm C\ or\ O)$, and with torsional freedom for methyl groups.

Data collection: *CAD*-4 *Software* (Enraf–Nonus, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Johnson, 1996). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1134). Services for accessing these data are described at the back of the journal.

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