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25,27-Dihydroxyethoxy-26,28-dipropoxy-*tert*-butylcalix[4]arene

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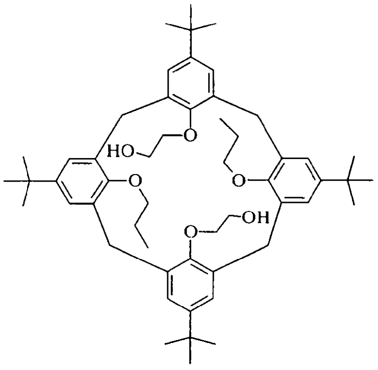
Abstract

In the solid state, the title compound, $C_{54}H_{76}O_6$, adopts a pinched cone conformation, which is somewhat distorted.

Comment

Calixarenes are readily synthesized by the condensation of *tert*-butylphenol and formaldehyde, and are easily modified on both the narrow (lower) rim and the wide (upper) rim by further chemical reactions (Böhmer, 1995). *o*-Alkylation or *o*-acylation of calix[4]arenes by residues larger than ethyl results in one of four basic conformations. Various X-ray structural analyses of tetraethers, with identical or different ether residues, have been reported (Guelzim *et al.*, 1993; Arnaud-Neu *et al.*, 1992), showing the molecule to be usually in a so-called 'pinched' cone conformation, where two opposite aromatic rings are nearly parallel, while the other two rings are bent away from the cavity. No inclusion of guests is usually observed in this conformation.

The title calixarene, (I), adopts this pinched-cone conformation, leading to an O1···O3 separation of 5.538 (2) Å and an O2···O4 separation of 3.668 (2) Å. The shape of the calix cavity can be described by the dihedral angles between the aromatic rings and the mean molecular plane of the four methylene-C atoms (C25–C28) linking them. These angles, facing the cavity (Perrin & Oehler, 1991), are 86.80 (5), 136.61 (6), 93.72 (5) and 133.39 (6)° for rings C1–C6, C7–C12, C13–C18 and C19–C24, respectively. The dihedral angles between opposite rings demonstrate that rings C7–C12 and C19–C24 are perpendicular to each other, with a dihedral angle of 89.99 (6)°, while rings C1–C6 and C13–C18 are nearly parallel, with a dihedral angle of 1.0 (1)°. The dihedral angles between two adjacent aromatic rings are 88.12 (6), 87.16 (6), 86.19 (6) and 85.93 (6)°. Similar behaviour concerning the shape of the cavity is observed in several tetraethers reported previously (Guelzim *et al.*, 1993; Arnaud-Neu *et al.*, 1992).



(I)

The hydroxyethyl ether groups are oriented inwards, and the two hydroxy groups (O5 and O6/O6*B*) form intramolecular hydrogen bonds to the O atoms (O1 and O3/O5) of the adjacent propoxyphenyl units. The O5···O3 distance is in the usual hydrogen-bonding range [2.719 (2) Å], while the O6···O1 and O6*B*···O5 distances of 2.939 (2) Å and 2.951 (1) Å, respectively, are slightly longer. The hydrophobic propyl ether residues, on the other hand, are directed outwards from the cavity, and all the ether residues are oriented in roughly the same direction. The conformation of the

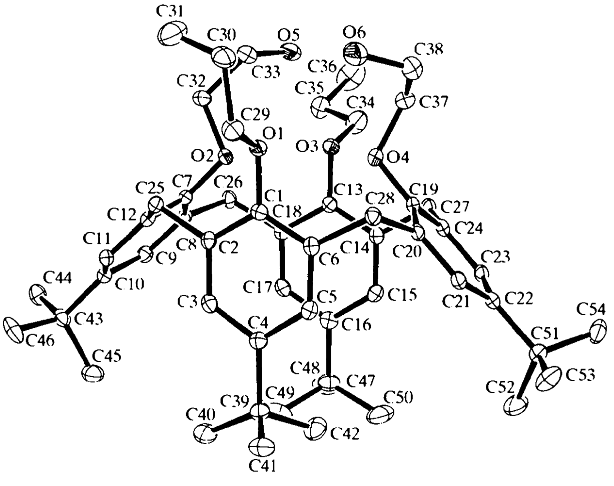


Fig. 1. An *ORTEP*III (Burnett & Johnson, 1996) plot of the title compound, showing the atom-numbering scheme. Anisotropic displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

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substituents at the narrow rim may be further characterized by the following torsion angles: C1—O1—C29—C30 −171.9 (2), C7—O2—C32—C33 178.2 (2), C13—O3—C34—C35 94.6 (2) and C19—O4—C37—C38 −88.9 (2)°.

The absence of solvent molecules in the crystal lattice is related to the close packing of the calixarene molecules. The shape of the cavity and the presence of the strongly shielding side chains on the upper and lower rims also prevent the inclusion of any solvent molecules into the cavity.

Experimental

The title compound, bearing two hydroxyethyl ether residues, was prepared by a method analogous to the literature procedure of Cobben *et al.* (1992), by reduction of the corresponding bis-methoxycarbonylmethyl ether with $LiAlH_4$. Single crystals suitable for X-ray analysis were obtained from the unreacted post-reaction residue of tetra-*ipso*-nitration of (I), by slow evaporation of a solution in dichloromethane/methanol.

Crystal data

$C_{54}H_{76}O_6$
$M_r = 821.15$
Monoclinic
$P2_1/c$
$a = 15.593\ (3)$ Å
$b = 15.596\ (9)$ Å
$c = 20.041\ (6)$ Å
$\beta = 95.12\ (2)°$
$V = 4854\ (3)$ Å^3
$Z = 4$
$D_x = 1.124$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.36–19.54°$
$\mu = 0.071$ mm^{-1}
$T = 173\ (2)$ K
Cubic
0.6 × 0.6 × 0.6 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.918$, $T_{max} = 0.960$
8852 measured reflections
8519 independent reflections
6060 reflections with $I > 2\sigma(I)$

$R_{int} = 0.015$
$\theta_{max} = 25°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 18$
$l = -23 \rightarrow 23$
2 standard reflections frequency: 60 min intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.140$
$S = 1.093$
8519 reflections
580 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0791P)^2 + 1.2862P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.741$ e Å^{-3}
$\Delta\rho_{min} = -0.672$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C1	1.397 (2)	O3—C13	1.391 (2)
O2—C7	1.384 (2)	O4—C19	1.391 (2)
C2—C1—O1	119.20 (15)	O4—C19—C20	119.41 (16)
C6—C1—O1	120.28 (15)	O4—C19—C24	119.52 (15)
O2—C7—C12	119.32 (16)	C12—C25—C2	109.80 (14)
O2—C7—C8	118.92 (15)	C8—C26—C18	110.05 (15)
O3—C13—C18	119.40 (16)	C24—C27—C14	110.90 (14)
O3—C13—C14	119.55 (16)	C20—C28—C6	108.84 (14)
C6—C1—C2—C25	−173.35 (16)		
C2—C1—C6—C28	171.09 (16)		
C12—C7—C8—C26	−171.54 (16)		
C8—C7—C12—C25	168.98 (16)		
C18—C13—C14—C27	−173.01 (16)		
C14—C13—C18—C26	171.54 (16)		
C24—C19—C20—C28	−166.16 (16)		
C20—C19—C24—C27	167.66 (16)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—HO5···O3	0.82	1.93	2.719 (3)	161
O6—H6···O1	0.82	2.16	2.939 (2)	159
O6*B*—H6*B*···O5	0.82	2.22	2.952 (14)	149

The title calix[4]arene tetraether crystallizes in the monoclinic system with one molecule of calixarene. No solvent molecules were found in the cone cavity or anywhere around the calixarene. Two of the lower rim substituents are disordered. Atom C35 in one of the substituents is disordered between two sites, with occupancy factors of 0.792 (6) and 0.208 (6). The other disordered group is the tail of C38—O6, which is also disordered between two sites and which has occupancy factors of 0.899 (3) and 0.101 (3). The temperature factor of C38*B* was constrained (*EADP*) to a reasonable value by equalizing it with the temperature factor of C38. Five geometrical restraints were used to keep some parts of the disordered groups chemically reasonable.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *XCAD*4 (*WinGX*-97; Farrugia, 1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *WinGX*-97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1502). Services for accessing these data are described at the back of the journal.

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Interaction between an oxygen and an alkynyl-carbon atom in 1-(2-nitrophenyl)-4-phenylbutadiyne

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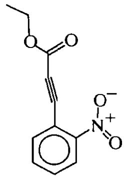
Abstract

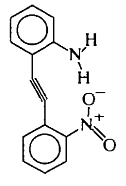
The title compound, $C_{16}H_9NO_2$, studied at 122 K shows a short 1,5 interaction between a nitro-O atom and an alkynyl-C atom. The atomic separation is 2.636 (2) Å, and the dialkyne group is bent from linearity at this C atom only.

Comment

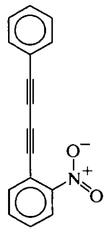
The study of the molecular distortions induced by placing a nucleophilic functional group close to an electrophilic functional group in the same molecule has given insight into the early stages of reaction coordinates (Bürgi & Dunitz, 1994). For example, in *peri*-substituted naphthalenes bearing a dimethylamino group and a carbonyl-containing functional group, the 1,5 interaction between the amino-N atom and carbonyl-C atom models an early stage in the addition of a nucleophile to the carbonyl bond and small pyramidalizations of the carbonyl-C atom's bonding geometry are observed (Schweizer *et al.*, 1978). We have been investigating interactions involving alkyne groups (Pilkington *et al.*, 1995). 1,5 interactions between nitro-O atoms and alkynyl-C atoms have been observed in (I) and (II), both of which show *trans* distortions of the triple bonds, as shown in the structural formulae (Rice & Wallis, 1993; Pilkington *et al.*, 1996). Analysis of the results of *ab initio* calculations on (II) using Bader's theory of atoms in molecules (Bader, 1990) gives evidence of a weak bonding interaction between the nitro-O and alkynyl-C atoms (Pilkington *et al.*, 1996). These interactions may be interpreted as representing the structural consequences of an incipient Michael addition reaction. The structure of the title compound (III), which contains a dialkyne rather than an alkyne group, was determined to extend this investigation.



(I)



(II)



(III)

The overall structure is almost planar, and the interplanar angle between the nitro group and the attached aromatic ring is only 9.93 (16)°. As in (I) and (II) there is a short 1,5 contact between a nitro-O atom and the closest C atom of the dialkyne group. The distance between these atoms is 2.636 (2) Å, and is very similar to those in (I) [2.642 (2) Å] and (II) [2.662 (4) and 2.772 (4) Å]. The dialkyne group deviates from linearity by 7.28 (13)° at the C atom involved in the interaction such that this C atom is displaced from the vector connecting its two neighbours towards the O atom. However, unlike the structures of (I) and (II), there is no significant deviation from linearity at any of the other three C*sp* atoms, where the bond angles lie in the range 178.60 (13) to 179.43 (13)°. There is no difference in the bond lengths of the two alkyne groups [1.203 (2) Å]. Furthermore, the structure contains no unusually short intermolecular contacts.

In structures (I) and (II), the bending induced at the alkyne-C atom not directly involved in the interaction is interpreted as being due to the start of the development of in-plane sp^2 lone-pair electron density as a result of the incipient nucleophilic addition to the other end of the triple bond. In (III), this feature need not be so localized since the developing lone-pair electron density would be able to conjugate with the π system of the second triple bond. This would account for the absence of a second bend in the dialkyne group. Alternatively, it could be argued that only a single bend is required to minimize repulsion between the two groups and, in particular, to increase the distance between O1 and the second alkyne-C atom, C2, to 3.201 (2) Å. However, if repulsive interactions were operating at *ca* 3.0 Å, it would have been expected that the nitro group would have rotated

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