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A 2,2′-azobenzene-substituted calix[4]-arene-crown-6†

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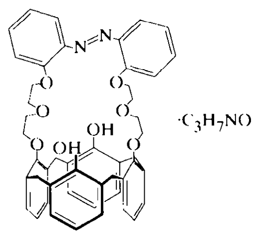
Abstract

The calix[4]arene macrocycle, 25,27-dihydroxy-26,28-(*O*,*O*′-azobenzene)calix[4]arene-crown-6 [which crystallizes as an *N*,*N*-dimethylformamide solvate ($C_{48}H_{46}N_2O_8{\cdot}C_3H_7NO$)], in the cone conformation, has two opposite phenolic rings bridged by an $-(O—CH_2—CH_2)_2O—C_6H_4—N{=}N—C_6H_4—(O—CH_2—CH_2)_2O–$ unit. The two other phenolic O atoms are unsubstituted. The azobenzene geometry is the more stable *trans* one. This structure is compared to other previously reported structures, involving differently bonded azobenzene moieties.

Comment

In the course of our investigation of calixcrown compounds, *i.e.* molecules resulting from the fusion of a calix[4]arene platform and one or two crown ether loops (which may contain some substituents), we have been interested in compounds comprising a photoisomerizable azobenzene unit. Calixcrowns with simple ether bridges containing six O atoms have proven to be efficient selective complexants for caesium ions and we have used X-ray crystallography to gain some insight into this property which may be of interest for caesium recovery during nuclear-fuel reprocessing (Thuéry, Nierlich *et al.*, 1997, and references therein). The long-term goal of this study of azobenzene-containing calixcrowns is to reach a photocontrol of ion complexation.

We have already reported the structures of ligands with an azobenzene-containing chain of variable length (four to eight O atoms) bridging two opposite phenolic groups of the calixarene unit, with or without additional substituents (ether chains or ether bridge) on the other two phenolic O atoms (Saadioui *et al.*, 1997; Thuéry, Lance *et al.*, 1997). This work led us to put in evidence the effect of crown length and calixarene conformation (cone or 1,3-alternate) on the geometry (*cis* or *trans*) of the azobenzene group. Recently, we have also reported the existence of conformational polymorphism and a phase transition in one of those compounds, resulting from the high flexibility of the bridges (Thuéry *et al.*, 1999). In the compounds investigated up to now, the azobenzene moiety was bonded in a 4,4′ fashion, *i.e.* the N atom and the ether O atom were in *para* positions on the aromatic rings. We report herein the first structure of a compound in which the azobenzene is bonded in a 2,2′ fashion (N and O in *ortho* positions), (I).



(I)

The asymmetric unit is composed of two calixcrown and two *N*,*N*-dimethylformamide molecules. One of the molecules is represented in Fig. 1. The two calixcrown molecules are different as to the bridge conformation, with no evidence of disorder. Since there is no substituent on the phenolic O atoms, O7 and O8, the calixarene adopts the cone conformation, as already observed in other members of the series (Thuéry, Lance *et al.*, 1997). As in the previous cases, the two phenolic rings bearing the bridge are more 'vertical' than the two other ones with respect to the plane defined by the four methylene C atoms [defined within ±0.084 (2) and ±0.187 (3) Å for molecules *A* and *B*, respectively]: the corresponding dihedral angles are 71.03 (8), 65.58 (8) (molecule *A*), 73.02 (10) and 77.37 (9)° (molecule *B*) for the rings bonded to the bridge, and 50.49 (9), 44.41 (12) (molecule *A*), 45.36 (11) and 42.53 (14)° (molecule *B*) for the other rings. Those values compare well with those previously found. Some O···O distances are compatible with the existence of hydrogen bonds that could stabilize the cone conformation: O1*A*···O7*A* 2.752 (3), O6*A*···O8*A* 2.643 (4), O1*B*···O7*B* 2.743 (4) and O6*B*···O8*B* 2.796 (4) Å. This is confirmed by the location of the phenolic H atoms on the Fourier-difference map.

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† IUPAC name: 3,6,9,24,27,30-hexaoxa-16,17-diaza-octacyclo-$[30.15.7.1,^{38,42}.1^{49,53}.0^{2,44}.0^{10,15}.0^{18,23}.0^{31,36}]$hexapentaconta-1,10,-12,14,16,18,20,22,31,33,35,38,40,42(55),44,46,49(56),50,52-nonadecene-55,56-diol–*N*,*N*-dimethylformamide (1/1).

The bridge conformations are not directly comparable to those in the compounds already reported since the azobenzene is not identically bonded to the ether chain. The present bonding mode presumably induces less strain in the chain than the *para* bonding. As a result, the azobenzene is in the more stable *trans* conformation in the present case (C—N—N—C torsion angles: 174.0 (4) and 176.6 (4)° in *A* and *B*, respectively), whereas it was in the *cis* conformation in the previous case, with six O atoms in the chain and a calixarene cone conformation. The *cis* geometry has been shown to be stabilized in the case of the more strongly strained chains. However, it must be noted that UV-vis spectrophotometry has shown that both azobenzene geometries exist in solution in the present case (82% *trans*, 18% *cis*) whereas only *trans* is present in the solid. The flexibility of the bridges evident from this result is further exemplified by the differences between molecules *A* and *B*. The bridge conformations can be characterized by the torsion angles (Fyles & Gandour, 1992). The O—C—C—O torsion angles correspond to a $g^+g^+g^-g^+$ sequence in *A* and a $g^+g^+ag^+$ one in *B*. Furthermore, some *anti* C—O—C—C angles become *gauche* ones in both molecules. We have previously shown that the bridge flexibility in calixcrowns could only be reduced by solvent or cation complexation (Thuéry, Nierlich *et al.*, 1997) and also, as stated above, that it could be so important in one case as to lead to conformational polymorphism.

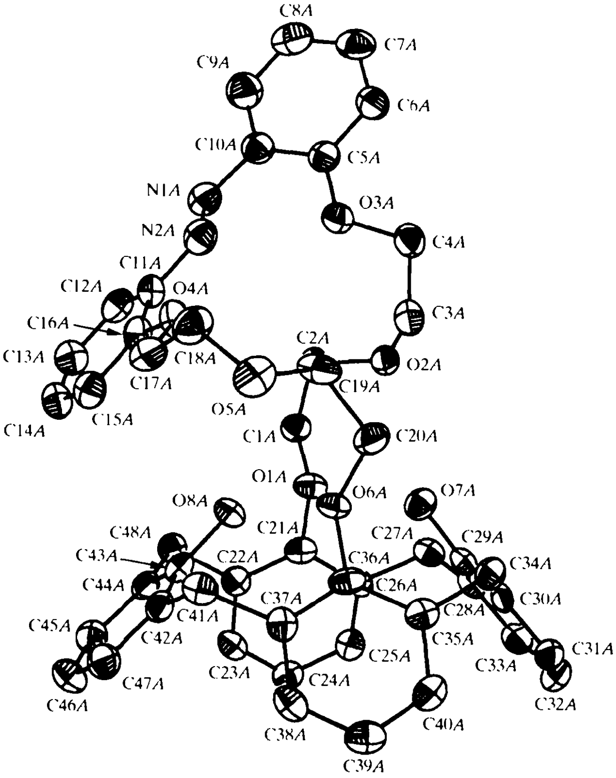

Fig. 1. Molecule *A* of the title complex (molecule *B*, solvent molecules and H atoms omitted for clarity) with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Commercial 2,2′-dihydroxyazobenzene (Aldrich) [HOC_6H_4-$N{=}NC_6H_4OH$] was treated with 2-(2-chloroethoxy)ethanol [$Cl(CH_2)_2O(CH_2)_2OH$] in the presence of potassium carbonate in refluxing acetonitrile to afford the diol $HO(CH_2)_2O(CH_2)_2$-$OC_6H_4N{=}NC_6H_4O(CH_2)_2O(CH_2)_2OH$ in quantitative yield. This diol was transformed into its ditosylate derivative, $TsO(CH_2)_2O(CH_2)_2OC_6H_4N{=}NC_6H_4O(CH_2)_2O(CH_2)_2OTs$, by reacting with tosyl chloride in the presence of NEt_3 in dichloromethane (67% yield). This ditosylate was used to bridge calix[4]arene (Acros Chimica) in a 1,3-selective manner as already reported (Asfari *et al.*, 1995), with a 19% yield. The 1,3-selective capping of calix[4]arene and its cone conformation were deduced from proton NMR data. The azobenzene conformation *trans*/*cis* ratio was found to be 82/18 by UV-vis spectrophotometry. The title compound was further recrystallized in *N*,*N*-dimethylformamide to yield, upon slow evaporation, crystals suitable for X-ray crystallography.

Crystal data

$C_{48}H_{46}N_2O_8{\cdot}C_3H_7NO$
$M_r = 851.96$
Monoclinic
$P2_1/c$
$a = 25.867\ (2)$ Å
$b = 17.085\ (2)$ Å
$c = 20.363\ (3)$ Å
$\beta = 106.328\ (2)°$
$V = 8636.4\ (15)$ Å^3
$Z = 8$
$D_x = 1.310$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 36813 reflections
$\theta = 2.99$–$30.07°$
$\mu = 0.090$ mm^{-1}
$T = 123\ (2)$ K
Irregular
0.24 × 0.24 × 0.18 mm
Translucent intense orange

Data collection

Nonius Kappa-CCD area detector diffractometer
φ rotation scans with 2° steps
Absorption correction: none
36 813 measured reflections
20 670 independent reflections

4835 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\rm max} = 30.07°$
$h = -35 \rightarrow 36$
$k = -22 \rightarrow 0$
$l = -24 \rightarrow 24$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.164$
$S = 0.822$
20 546 reflections
1139 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.218$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.215$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data collection: *Nonius Kappa-CCD Software* (Nonius, 1997). Cell refinement: *HKL Package* (Otwinowski & Minor, 1997).

Data reduction: *HKL Package*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1997). Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1018). Services for accessing these data are described at the back of the journal.

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N,N′-Bis(2-methoxyethyl)pyromellitimide[†]

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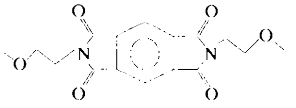
Abstract

The structure of the title compound, $C_{16}H_{16}N_2O_6$, is organized in layers perpendicular to the *b* axis. The central part of the molecule is planar; the lateral chains are also planar and are almost perpendicular (79°) to the ring plane.

Comment

We recently undertook the study of the structure of a family of copolymers in which aromatic moieties and oxyethylene segments alternate in the main chain (Djurado *et al.*, 1997). These systems are used as electrodes in electrochemical or electrochromic devices because of their electroactive properties (Michot *et al.*, 1995).

In this framework, the title compound, PMT, can be considered as the elementary chemical unit constituting these polymers. Its structure was solved in order to obtain details about the stacking mode of the aromatic units. This knowledge could give us a reliable starting point for modelling the structure of semi-crystalline phases of copolymers which can only be studied by X-ray powder diffraction. In the molecule of PMT, the lateral chains can rotate around the N10—C15 and N20—C25 bonds. The planes through these chains make two angles of 79° [79.47 (6) and 79.17 (6)°] with the plane through the benzenoid ring of the aromatic unit. We observed neither disorder nor abnormally high displacement parameters for the ends of the chains. The molecule was found to be almost perfectly centrosymmetrical (*BUNYIP*; Hester & Hall, 1995), but the additional inversion centre is not a crystallographic one and does not lead to another space group.



PMT

The structure of PMT can be described as a regular stacking of layers perpendicular to the *b* axis, in which π overlapping between the aromatic parts is not at a maximum.

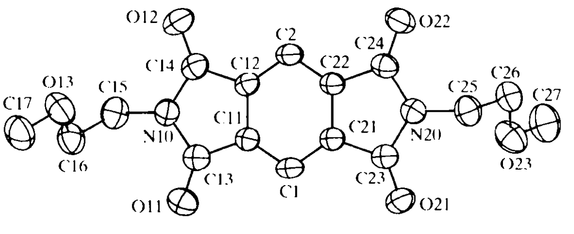


Fig. 1. The molecular structure of PMT showing the atom numbering, with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

Experimental

PMT was synthesized by M. Armand. Crystals were obtained by evaporation of a solution of acetonitrile at 277 K. The same

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[†] Alternative name: 2,6-bis(3-oxabutyl)-2,3,6,7-tetrahydro-1*H*,5*H*-pyrrolo[3,4-*f*]isoindole-1,3,5,7-tetrone.

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