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An Azobenzene 1,3-Alternate Calix[4]-*bis*-crown and its 1:1 Complex with Cesium.

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Abstract: The preparation of azocalix[4]-bis-crown **1** combining one polyether crown-6 and one azobenzene modified crown-4 O-attached on each side of a calix[4]arene in the 1,3-alternate conformation is reported. The X-ray structures of **1** and of the 1:1 complex **1**.$CsNO_3$ as solvates with nitromethane are also presented. © 1997 Elsevier Science Ltd.

Photoisomerizable azobenzene groups have been introduced in supramolecular structures to produce supramolecular catalysts,[1] chromogenic reagents,[2] photofunctional extractants,[3] ionophores for transport[4] and photo-switchable receptors[5]. With respect to calixarenes, Hamada et al.[6] designed a photoregulated calix[4]arene capped at the lower rim by an azobenzene and bearing N'-benzyl-N-piperazino residues at the upper rim presenting a higher metal binding ability when trans. Saadioui et al.[7] reported the synthesis of two azobenzene modified 1,3-calix[4]-*bis*-crowns as artificial potentially allosteric systems in which the trans-cis isomers ratio depends on the complexed cation. Based on previous reports[8,9] on 1,3-alternate calix[4]-*bis*-crowns-6 as cesium-selective extractants, we report herein the preparation of the 1,3-alternate calix[4]-*bis*-crown **1** (in which one crown ether loop is modified by an azo benzene), its crystal structure and the crystal structure of its 1:1 complex with $CsNO_3$.

The synthesis of **1** is illustrated in Scheme1. Dinitro calix[4]podand **2**[10] was reacted with penta ethylene glycol ditosylate in the presence of K_2CO_3 in refluxing acetonitrile to produce the 1,3-dinitro calix[4]crown-6 **3** which was further reduced into diamino calix[4]crown-6 **4** by reacting with $NH_2NH_2.H_2O$ on graphite.[11] Final cyclization to **1** was performed by oxydative coupling with activated MnO_2 in benzene[12].

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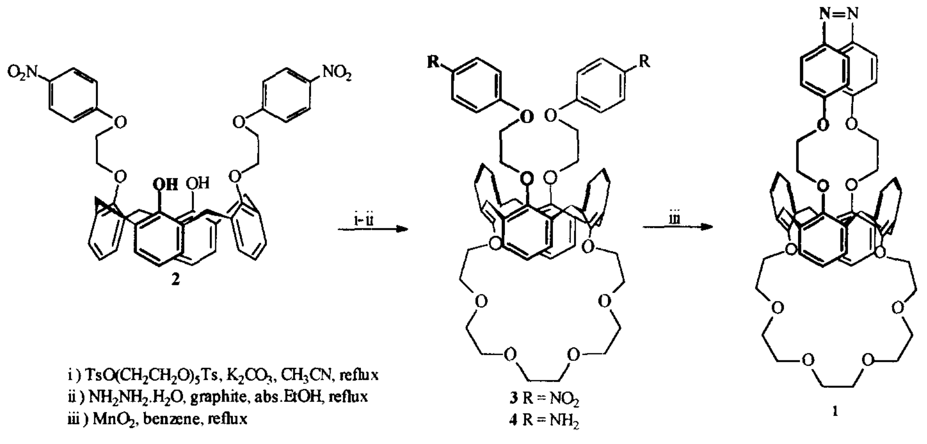

Scheme 1. Synthesis of 1.

The 1,3-alternate conformation of **1** was deduced from the presence of a singlet at 3.77 ppm in its ^{1}H-NMR spectrum (see experimental[13] and Figure 1).

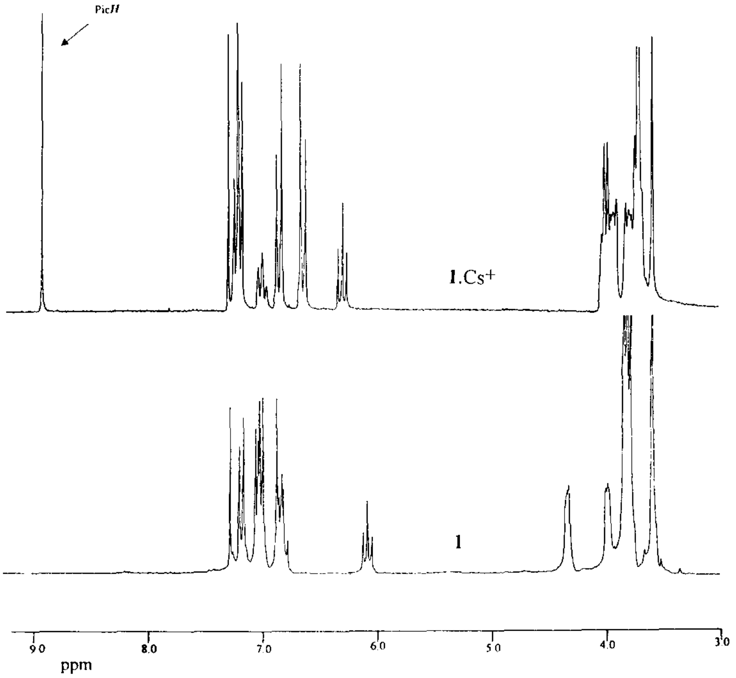

Figure 1. *200 MHz* ^{1}H-NMR spectra of ligand **1** and 1:1 complex 1.Cs$^+$Pic$^-$ in CDCl$_3$.

TLC, UV-Visible and ^{1}H-NMR spectra[13] were in agreement with a cis conformation for the azobenzene unit due to their similarity with already published azobenzene calixcrowns.[10] After 8 days reaction between the solid alkali picrates (Na^+, K^+, Rb^+ and Cs^+) and a chloroform solution of **1** the ratios of metal to ligand in solution, as estimated by integration of the picrate proton (Pic*H*) resonances versus those of the aromatic protons, were 0.2:1 (Na), 0.5:1 (K), 0.4:1 (Rb) and 1.1:1 (Cs). The ^{1}H-NMR spectra of **1** and its 1:1 complex **1**.CsPic did not allowed the location of the cesium in one or the other loop of the potential ditopic ligand **1** (see Figure 1).

According to previous results,[15] we decided to crystallize **1** and prepare its 1:1 complex with $CsNO_3$. Orange single-crystals of **1**.2 CH_3NO_2 were obtained by slow evaporation of a solution of **1** in nitromethane. The complex **1**.$CsNO_3$. CH_3NO_2 was obtained by reaction of **1** dissolved in nitromethane with a large excess of $CsNO_3$ at 70°C during 15 h. The non-reacted $CsNO_3$ was filtered and the solution slowly evaporated yielding orange single crystals suitable for X-ray crystallography.[13] Figure 2 shows both molecular structures of **1** (with one molecule of nitromethane included) and **1**.$CsNO_3$.

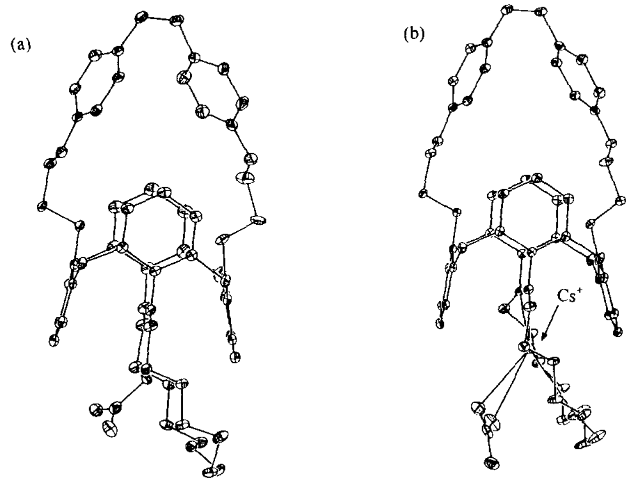

Figure 2. Molecular structures of (a) **1**.2 CH_3NO_2 and (b) **1**.$CsNO_3$. CH_3NO_2. Non-included sovent molecules are omitted.

The cis geometry of the azo benzene was confirmed in both structures. Cesium cation was located in crown-6. Evidence was also given of preorganisation of **1** prior to complexation in agreement with crystal[15] and thermodynamical[16] data on calix[4]-*bis*-crowns-6 and their cesium complexes. In contradistinction to our previous paper[8] the complexation in the crown-6 did not affect the geometry of the azobenzene unit. This probably comes from the fact that the polyether chain containing the azobenzene unit in **1** is shorter and consequently more rigid preventing from thermal isomerism.

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13. **General:** Mps, capillaries under nitrogen, Büchi 500. Chromatography, SiO_2 columns with Kieselgel Merck (Art. 11567). Thin layer chromatography (TLC), SiO_2 Merck plates (Art. 6484). ^1H-NMR in $CDCl_3$, Bruker SY200 (δ in ppm, *J* in Hz). FAB(+), VG-Analytical ZAB HF. Elemental analyses performed at the Service de Microanalyse of the Institut de Chimie de Strasbourg.

Preparation of 3: Dinitro calix[4]podand **2** (2.00 g, 2.64 mmol), K_2CO_3 (3.65 g, 26.40 mmol) and CH_3CN (150 mL) were stirred for 24 h at r.t. under N_2. Pentaethylene glycol ditosylate (1.44 g, 2.64 mmol) was added. After refluxing for 8 days solvents were evaporated to dryness and the residue was dissolved in CH_2Cl_2. The solution was acidified (1N HCl). The organic solution was dried (Na_2SO_4), filtered and evaporated to dryness. Chromatography (SiO_2, 90/10 CH_2Cl_2/acetone) afforded **3** as a white powder (1.25 g, 45%). M.p. 210-211°C. ^1H NMR (200 MHz, $CDCl_3$) 8.13 (d, $J = 9.2$, 4 Ar*H* nitrobenzene), 7.15 (d, $J = 7.5$, 4 Ar*H*), 7.02 (d, $J = 7.5$, 4 Ar*H*), 6.93-6.83 (m, 2 Ar*H* and 4 Ar*H* nitrobenzene), 6.60 (t, $J = 7.5$, 2 Ar*H*), 3.81 (s, 8 CH_2), 3.72 (s, 4 ArCH_2Ar). 3.69-3.63 (m, 2 CH_2), 3.58-3.52 (m, 2 CH_2), 3.44 (t, $J = 5.5$, 2 CH_2). *Anal. Calcd.* For $C_{54}H_{56}N_2O_{14}$: C, 67.77; H, 5.90. *Found.* C, 67.69; H, 5.97.

Preparation of 4. 3 (1.00 g, 1.04 mmol), graphite (8.00 g), $NH_2NH_2.H_2O$ (8.00 g, 159.80 mmol) and absolute EtOH (150 mL) were refluxed under N_2 for 6 days. After cooling to r.t., the solution was filtered over celite and washed with CH_2Cl_2. The solvents were evaporated to dryness. Chromatography (SiO_2, 70/30 CH_2Cl_2/acetone) afforded **4** (0.600 g, 64%) as a viscous oil. ^1H NMR (200 MHz, $CDCl_3$) 7.11 (d, $J = 7.5$, 4 Ar*H*), 7.07 (d, $J = 7.5$, 4 Ar*H*), 6.86 (t, $J = 7.5$, 2 Ar*H*), 6.73-6.58 (m, 2 Ar*H* and 8 Ar*H* aminobenzene), 3.79-3.76 (m, 4 CH_2), 3.72 (s, 4 ArCH_2Ar), 3.69-3.61 (m, 6 CH_2), 3.54-3.43 (m, 4 CH_2), 1.65 (s.large, 2 ArNH_2 exchangeable with D_2O). *Anal. Calcd.* For $C_{54}H_{60}N_2O_{10}$: C, 72.30; H, 6.74. *Found.* C, 72.21; H, 6.50.

Preparation of 1: In a 250 mL round-bottomed flask equipped with a Dean-Stark, **4** (0.600 g, 0.668 mmol), activated MnO_2 (4.00 g, 46.00 mmol) and benzene (150 mL) were stirred vigorously at reflux for 6 days. After filtration through celite, washing with CH_2Cl_2 and drying ($MgSO_4$) the solvents were evaporated to dryness. Crystallization from a mixture of methanol-CH_2Cl_2 afforded pure **1** (0.200 g, 34%). Orange microcrystals. M.p. 198-199°C. TLC (SiO_2, 90/10 CH_2Cl_2/acetone): Rf = 0.34 (more intense) attributed to cis isomer. UV-Visible (acetonitrile, $c = 7.10^{-5}$ M) $\lambda_{trans} = 360$ nm, $\varepsilon_{trans} = 1970$ $mol^{-1}.l.cm^{-1}$; $\lambda_{cis} = 434$ nm, $\varepsilon_{cis} = 266$ $mol^{-1}.l.cm^{-1}$). ^1H-NMR (200 MHz, $CDCl_3$) 7.16 (d, $J = 7.5$, 4 Ar*H*), 7.02 (d, $J = 7.5$, 4 Ar*H*), 7.00 (d, AB system, $J = 8.9$, 4 Ar*H* azobenzene), 6.86-6.76 (m, 2 Ar*H* and 4 Ar*H* azobenzene), 6.06 (t, $J = 7.5$, 2 Ar*H*), 4.32-4.29 (m, 2 N=NArOCH_2), 3.98-3.96 (m, 2 N=NArOCH_2CH_2), 3.82-3.79 (m, 6 CH_2), 3.77 (s, 4 ArCH_2Ar), 3.58 (s large, 4 CH_2). *Anal. Calcd.* For $C_{54}H_{56}N_2O_{10}$: C, 72.63; H, 6.32. *Found.* C, 72.54; H, 6.31.

Crystal data for 1: $O_{14}N_4C_{56}H_{62}$ (including two CH_3NO_2 molecules), $M_r = 1015.14$, triclinic, *P-1*, $a = 10.958(5)$, $b = 11.880(5)$, $c = 21.317(9)$ Å, $\alpha = 104.64(4)$, $\beta = 99.23(3)$, $\gamma = 98.38(4)°$, $V = 2599(9)$ Å^3, $Z = 2$, $D_c = 1.297$ g/cm^3, $\mu = 0.874$ cm^{-1}, $F(000) = 1076$, 8153 unique reflections, 5019 ($I > 2\sigma(I)$) used, $R = 0.056$ ($R_w = 0.067$, $w = 1/\sigma(F)^2$).

Crystal data for 1.$CsNO_3$**:** $Cs_1O_{15}N_4C_{55}H_{59}$ (including one CH_3NO_2 molecule), $M_r = 1149.01$, monoclinic, $P2_1/n$, $a = 12.169(4)$, $b = 29.862(6)$, $c = 15.420(9)$ Å, $\beta = 110.57(4)°$, $V = 5246(7)$ Å^3, $Z = 4$, $D_c = 1.455$ g/cm^3, $\mu = 7.684$ cm^{-1}, $F(000) = 2368$, 9224 unique reflections, 7014 ($I > 2\sigma(I)$) used, absorption correction (ψ-scans), $R = 0.035$ ($R_w = 0.046$, $w = 1/\sigma(F)^2$). In both cases: CAD4 diffractometer, graphite-monochromated Mo$K\alpha$ radiation (0.71073 Å), $\theta_{max.} = 25°$, T = 243 K, structures solved by direct methods with SHELXS-86.[14] Refinement by full-matrix least-squares on *F*. Atomic coordinates and e.s.d.'s have been deposited at the Cambridge Crystallographic Data Centre.

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