

Monosulfinyl Thiocalix[4]biscrown-5 and Its Crystal Structure

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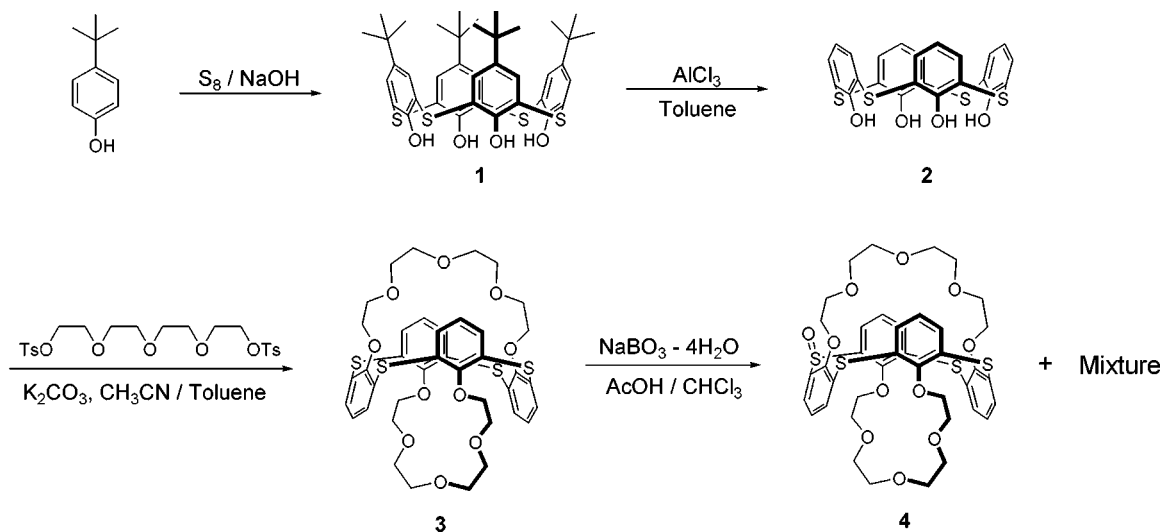
Calixarenes have been used as suitably preorganized building blocks for the construction of more elaborate structures, receptors and molecular assemblies.¹ As one of calixarene family, thiocalixarenes having four sulfur atoms instead of methylene bridges have attracted considerable interest as a ligating agent bearing additional coordination sites, modifying the dimensions of the cavity.² Unlike calix[4]arenes, thiocalix[4]arenes showed affinity for transition metal ions because the sulfur atoms in the calixarene framework take part in the metal ion complexation.³

The synthesis of 1,3-thiocalix[4]bis(crown-5 and crown-6) ethers, which are the first representatives of crown-bridged compounds in the thiocalixarene series has been reported.⁴ Studies of the complexing abilities of these compounds towards alkali cations (Na⁺, K⁺, Rb⁺, and Cs⁺) have shown that they were less efficient extractants than the related 1,3-calix[4]bis(crown-5 and crown-6) ethers.⁴ This discrepancy was explained by a thiocalix[4]arene macro-ring larger by about 0.5 Å, as evidenced by the crystal structures.⁴ It was also reported that 1,3-thiocalix[4]mono(crown-5 and crown-6) ethers in the 1,3-*alternate* conformation could be

prepared by condensation of 1,3-dialkoxythiocalix[4]arenes with polyethylene glycol ditosylates or diiodides.⁵ We recently reported that thiocalix[4]bis(crown-5 and crown-6) compounds behave as K⁺ and Cs⁺ ion receptors, respectively, but showed a low binding ability, which was proven by X-ray crystallography and NMR chemical shift change.⁶

Oxidation of the sulfur atoms of the thiocalix[4]arene into sulfinyl and sulfonyl groups, giving novel building blocks that could find many possible applications in supramolecular chemistry, has previously been described.^{5,7} This led us to investigate the oxidation of thiocalix[4]biscrown-5. We report herein the synthetic method and the physical properties and crystal structure of the resulting molecules.

In a first step, *para-tert*-butylphenol was cyclized with sulfur to give *para-tert*-butylthiocalix[4]arene (**1**) as shown in Scheme 1. Dealkylation using AlCl₃ in phenol and toluene provided thiocalix[4]arene (**2**) in moderate yield.^{3(b,c)} Subsequently, 1,3-*alternate* thiocalix[4]biscrown-5 (**3**) was obtained from the reaction of thiocalix[4]arene (**2**) with tetraethylene glycol ditosylate in the presence of K₂CO₃.⁵ Oxidation of **3** has been carried out using 0.5 equivalent



Scheme 1. Synthetic route for compound **4**.

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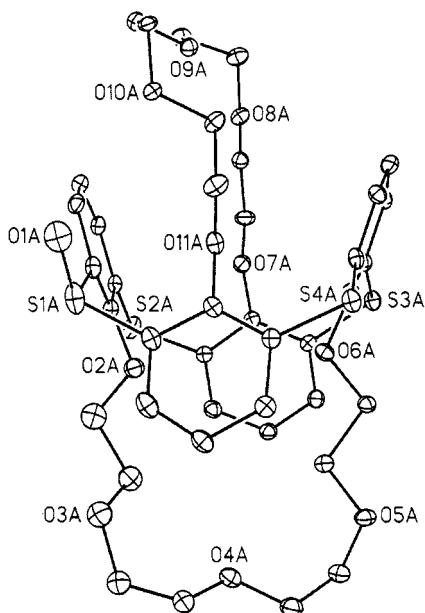


Figure 1. Crystal structure of **4** (molecule A). Hydrogen atoms and solvent molecule are omitted for clarity. Displacement ellipsoids are drawn at the 10% probability level.

$\text{NaBO}_3/\text{AcOH}$ to give monosulfinylcalix[4]biscrown-5 (**4**) in 33% yield. It is noteworthy that the oxidation of the thiacalixarene gave a number of different derivatives such as monosulfinyl, disulfinyl, trisulfinyl etc, as well as monosulfonyl, disulfonyl, trisulfonyl and their combinative derivatives.⁸ So, in order to easily and purely separate the monosulfinylcalix[4]biscrown-5 with the highest possible yield, we decided to use less than one equivalent of NaBO_3 . Use of more than 1.0 equivalent of NaBO_3 and increasing reaction temperature provided more complicated mixtures. Alternatively, the oxidation using H_2O_2 ^{3c} in acetic acid gave a corresponding spot on TLC but we failed in purifying the resulting compound by either column chromatography or thin-layer chromatography. The 1,3-alternate conformation of **4** was confirmed by X-ray crystallography.

Compound **4** crystallizes in the monoclinic space group $P2_1/c$. The repeat unit contains two independent thiacalix-crown molecules (denoted A and B hereafter) and one ethyl acetate molecule. Molecule A is represented in Figure 1. The two macrocycles differ by the disorder affecting some sulfinyl and ether groups. The thiacalix[4]arene platform in both A and B molecules is in the 1,3-alternate conformation. The mean planes defined by the four sulfur bridges [which are located alternately above and below this plane with deviations of 0.168(2) and 0.095(2) Å in A and B, respectively] can be taken as reference planes. The dihedral angles between the four aromatic rings and this S_4 plane are 77.0(2), 66.2(2), 69.4(2) and 71.8(2)° in molecule A and 74.4(2), 80.4(2), 85.1(2) and 68.4(2)° in molecule B. These values span a large range, but compare well with those in thiacalix[4]-bis crown-5,⁴ which are in the 61.3(1)-80.9(1)° range. The varying dihedral angles are probably related to the different ether conformations. One of the crown ether

chains in molecule A is also disordered. The O-C-C-O torsion angles in the ether chains are not all *gauche* ones, whereas the C-O-C-C torsion angles are not all *anti*, which results in much distorted conformations, different for the four ether chains, with in no cases all the oxygen lone pairs directed towards the crown center. This is usual for chains not involved in metal ion complexation or interactions with solvent molecules⁹ and was also observed in thiacalix[4]-bis(crown-5).⁴ The sulfinyl oxygen atom in molecule B is disordered over three positions corresponding to three different sulfur bridges. Further disorder of sulfinyl groups in both molecules is likely present, but could not be satisfyingly modelled. The S-C bond lengths [mean value 1.77(2) Å], C-S-C angles [mean value 105(1)°], S...S (adjacent) [mean value 5.57(2) Å] and S...S (non adjacent) [mean value 7.87(2) Å] distances are in agreement with literature values.⁴

Further purification of multisulfinyl and multisulfonyl thiacalix[4]biscrowns and their complexation ability toward metal cations are under investigation and will be reported soon.

Experimental Section

Synthesis. Compound **1-3** were prepared following procedures reported in literature.²⁻⁴ 2,8,14,20-Tetrathia-mono-sulfinylcalix[4]-bis-crown-5 (**4**). A solution of (0.50 g, 0.61 mmol) of thiacalix[4]biscrown-5 and sodium perborate tetrahydrate (0.09 g, 0.58 mmol) in chloroform (30 mL) and acetic acid (50 mL) was stirred at room temperature for 10 h. After the reaction completion, 200 mL of CHCl_3 and 200 mL of NaHCO_3 solution were added to the reaction solution. The organic layer was separated and dried over anhydrous MgSO_4 . Removal of the organic solvent *in vacuo* gave a white solid. Purification by thin layer chromatography using ethyl acetate/hexane (1 : 2) as eluents gave **4** as a white solid. Yield 33%. Mp 297.4-298.7 °C: IR (KBr pellet, cm^{-1}): 2872, 1567, 1436, 1359, 1306, 1235, 1135, 1050; ¹H NMR (400 MHz, CDCl_3): δ 8.06-6.89 (m, 8H, Ar- H_m ; 4H, Ar- H_p), 4.52-3.14 (m, 32H, $-\text{OCH}_2\text{CH}_2\text{O}-$); FAB MS, m/z (M^+) calcd 829.03, found: 829.03.

Crystallography. The data were collected on a Nonius Kappa-CCD area detector diffractometer¹⁰ using graphite-monochromated Mo- $K\alpha$ radiation (λ 0.71073 Å). The crystal was introduced in a glass capillary with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. A 180° ϕ -range was scanned with 2° steps during data collection, with a crystal-to-detector distance fixed to 28 mm. The data were processed with DENZO-SMN.¹¹ The structure was solved by direct methods with SHELXS-97¹² and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.¹² Absorption effects were corrected empirically with the program DELABS from PLATON.¹³ One oxygen and one carbon atoms in an ether chain of molecule A are disordered over two positions. The oxygen atom of the sulfinyl group in

molecule B is also disordered over three positions. These disordered positions have been refined with occupancy factors constrained to sum to unity. All non-hydrogen atoms were refined with anisotropic displacement parameters, except some of the disordered ones. Some restraints on bond lengths and/or displacement parameters were applied for some badly behaving atoms, particularly in the disordered parts. Hydrogen atoms were introduced at calculated positions, except in the disordered parts, and were treated as riding atoms with a displacement parameter equal to 1.2 (CH, CH₂) or 1.5 (CH₃) times that of the parent atom. The molecular plots were drawn with SHELXTL.¹⁴ All calculations were performed on a Silicon Graphics R5000 workstation. CCDC reference number for this crystal is 203155.

Crystal data: C₈₄H₉₆O₂₄S₈, *M* = 1746.09, monoclinic, space group *P*2₁/*c*, *a* = 11.2279(12), *b* = 17.7360(8), *c* = 41.920(2) Å, β = 96.027(4)°, *V* = 8301.7(11) Å³, *Z* = 4, *D*_c = 1.397 g cm⁻³, μ = 0.292 mm⁻¹, *F*(000) = 3680, *T* = 100(2) K. Refinement of 1079 parameters on 14076 independent reflections out of 40856 measured reflections (*R*_{int} = 0.088) led to *R*₁ = 0.099, *wR*₂ = 0.220 and *S* = 0.977.

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