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Tetrasulfinylcalix[4]arenes : Synthesis and Solid State Structural Analysis

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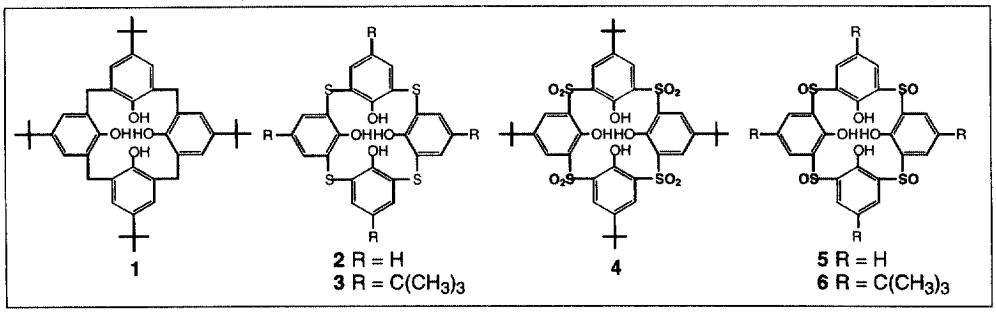
Abstract: The synthesis of two tetrasulfinylcalix[4]arene was achieved by partial oxidation of tetrathiacalix[4]arene precursors. In both cases, the 1,3-alternate conformation of the calix units and the alternate orientation of the sulfoxide groups were demonstrated by X-ray diffraction studies in the solid state. In the case of tetrasulfinylcalix[4]arene, a 3-D network based on stacking interactions between the aromatic groups was observed.

The large number of studies dealing with calixarenes published over the last two decades demonstrates a substantial interest in this class of molecules. Due to considerable synthetic efforts, many calixarenes, in particular calix[4]arene, derivatives bearing a variety of functional groups at the lower and/or upper rims have been synthesised.[1] However, only recently was reported a new class of calix[4]arene derivatives in which the methylene junctions between the phenolic moieties of **1** were replaced by sulfur atoms leading thus to thiacalixarenes **2**[2] and **3**.[3] Furthermore, complete oxidation of the thio ether junctions leading to sulfones such as compound **4** was achieved.[4,5] On the other hand, dealing with sulfur containing calixarenes, the synthesis[6-8] of di- and tetra-mercaptocalix[4]arenes and their complexation ability towards mercury have been also reported.[7,8]

In the present communication, we report the synthesis and the solid state structural analysis of calix[4]arenes **5** and **6** bearing four sulfoxide groups (scheme).



Dealing with the coordination ability of calix[4]arene derivatives, for compound **1**, although, in some cases the contribution of the aromatic π cloud was demonstrated[9], for the majority of reported examples mainly the OH groups take part in the binding of metal cations. The replacement of CH_2 junctions by S atoms in **2** and **3**, SO_2 in **4** and SO in **5** and **6** introduces additional coordination sites into the calix framework.

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Both compounds **5** (20%) and **6** (28%) were obtained by partial oxidation using H_2O_2 in glacial AcOH and *m*-chloroperbenzoic acid in CH_2Cl_2 of the precursors **2** and **3** respectively. Whereas the parent compound **3** was obtained by reacting *p-tert*-butylphenol and elemental sulfur[3], the compound **2**, bearing hydrogen atoms in the *para* positions of phenol moieties, was obtained by $AlCl_3$ assisted dealkylation of **3**.[2]

Although at the earlier stage of development of calixarenes, their conformational mobility was considered as a limitation, due to considerable synthetic as well as structural achievements, today the conformational issue is positively explored in the design of receptors, catalysts and building blocks.[9] For compounds **5** and **6**, in addition to the above mentioned classical conformational mobility, due to the relative orientation of the oxygen atoms and consequently the lone pairs of the sulfur atoms an impressive set of isomers may be obtained (Fig. 1).

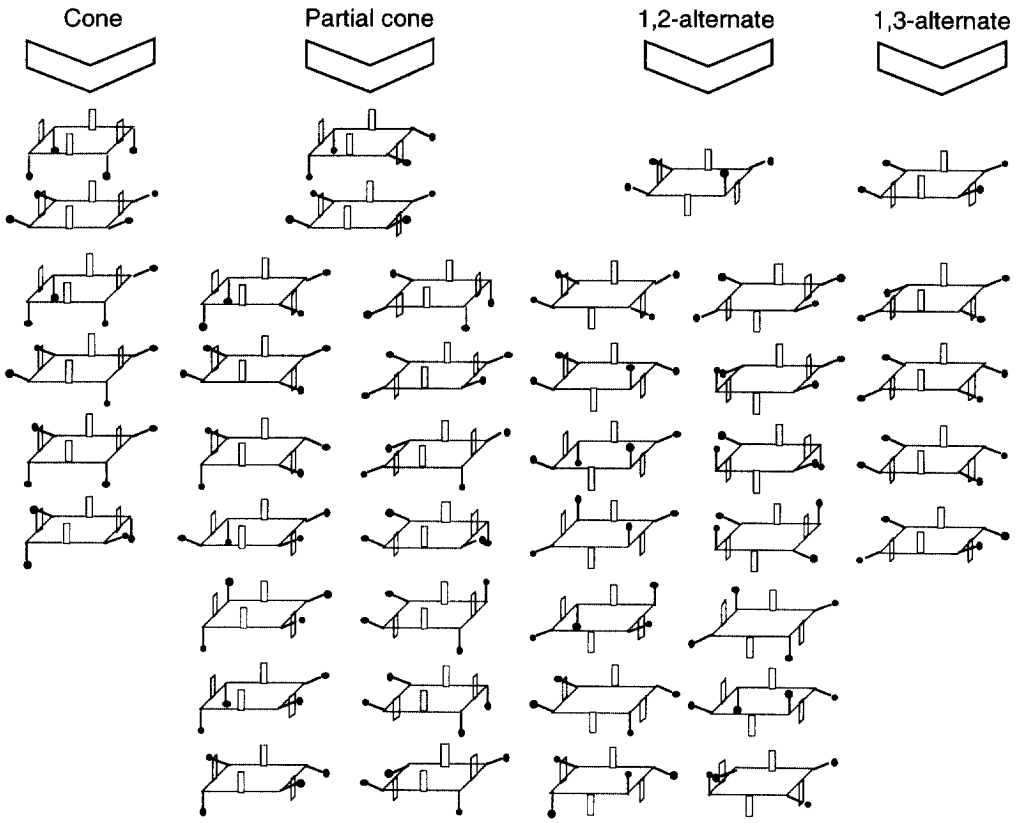

***Figure 1**: schematic representation of conformers and isomers of tetrasulfinylcalix[4]arene derivatives. For SO groups localised between two syn oriented adjacent phenyl groups (cone, partial cone, 1,2-alternate conformers), the O atoms and lone pairs may either occupy equatorial or axial positions. For other situations (1,3-alternate conformer : anti localisation of aromatic fragments), the O atoms and lone pairs occupy pseudo equatorial positions.*

Indeed, on one hand, based on the relative orientation of the aromatic moieties one may, as in the case of the parent compound **1**, envisage four limit conformers (Cone (C), Partial cone (PC), 1,2- and 1,3- alternate). On the other hand, for each sulfoxide group the oxygen atom may occupy either axial (a) or equatorial (e) position with axial-equatorial exchange possibility by a flip-flop process. Thus, for each conformation of the calix, due to the relative orientation of the oxygen atoms, one may define a variety of isomers (Fig. 1). It is

worth noting that, whereas the four conformers may inter convert, as it was demonstrated in the case of **1**, the isomers defined by the relative orientation of the SO groups can not be inter converted without breaking covalent S-C bonds.

The solid state structure of **5** was investigated by X-ray analysis.[10] Suitable monocrystals were obtained upon slow liquid-liquid diffusion of MeOH into a DMSO solution of **5**. The study revealed the following features (Fig. 2): i) **5** crystallised in the tetragonal crystal system with *P* $4_2/n$ as the space group; ii) **5** adopts a 1,3-alternate conformation; iii) four oxygen atoms of the SO groups (d_{SO} = 1.51 Å) were oriented above and bellow the main plane defined by four S atoms leading to the aeae isomer; IV) the aeae isomer with the 1,3-alternate conformer was stabilised by four strong hydrogen bonds with an average OH···OS bond distance of *ca* 2.65 Å between the OH and SO groups; V) interestingly, the packing pattern (Fig. 3) showed a 3-D network obtained by strong stacking interactions between all four aromatic groups of the molecular units (the distance between centroids of the aromatic rings was 3.49 Å). It is interesting to note that **2** was shown to adopt a cone conformation in the solid state stabilised by four intramolecular OH···O hydrogen bonds with an average distance between two adjacent oxygen atoms of 2.78 Å.[2]

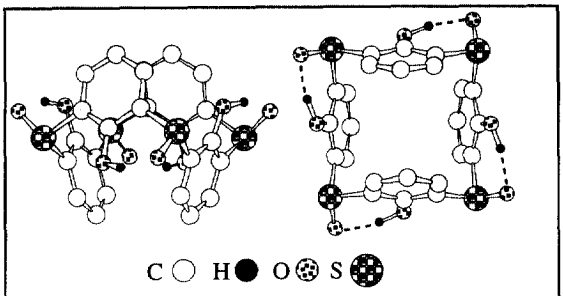

***Figure 2**: Lateral (left) and top (right) views of the solid state structure of **5** showing the 1,3-alternate conformer of the calix unit and alternate orientation of the SO groups (1,3aeae). This conformation is stabilised by four intramolecular H-bonds (2.64 Å) between OH and SO groups. For sake of clarity,H atoms except of the OH type are not presented.*

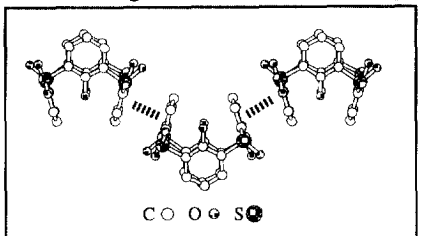

***Figure3** : A portion of the structure of 5 showing the formation of a 3-D network through stacking of the aromatic groups (3.49 Å). For clarity H atoms are not presented.*

The solid state structure of **6** was also investigated by X-ray analysis.[11] Monocrystals were obtained upon slow liquid-liquid diffusion of MeOH into a THF solution of **6**. The study revealed the following features (Fig. 4): i) **6** crystallised in the monoclinic crystal system with *P* $2_1/n$ as the space group; ii) **6** adopts a 1,3-alternate conformation; iii) all four oxygen atoms of the SO groups (average d_{SO} = 1.51 Å) were also oriented above and bellow the main plane defined by four S atoms leading again to the aeae isomer; IV) the aeae isomer with the 1,3-alternate conformer was also stabilised, as in the above mentioned case of **5**, by four strong intramolecular hydrogen bonds with an average OH···OS bond distance of 2.67 Å between the OH and SO groups. Again, it is worth noting that **3** was shown to adopt a cone conformation in the solid state stabilised by four intramolecular OH···O hydrogen bonds with an average distance between two adjacent oxygen atoms of *ca* 2.86 Å.[2] In marked contrast with compound **5** which formed a 3-D network based on stacking interactions between the aromatic groups, in the case of **6**, due to the presence of bulky tert-butyl groups no such a network was observed.

In conclusion, the synthesis of tetrasulfinylcalix[4]arenes **5** and **6** based on partial oxidation of tetrathiacalix[4]arenes **2** and **3** was achieved. The solid state structural study revealed that both compounds adopt the 1,3-alternate conformation stabilised by four strong intramolecular H-bonds. In both cases, the alternate

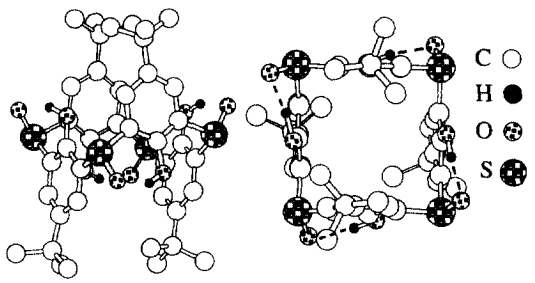

Figure 4 : Lateral (left) and top (right) views of the solid state structure of 6 showing the 1,3-alternate conformer of the calix unit and the alternate orientation of the SO groups (1,3aeae). This conformation is stabilised by four intramolecular H-bonds (average 2.67 Å) between OH and SO groups. For sake of clarity,H atoms except of the OH type are not presented.

axial-equatorial isomers were observed. Whereas for tetrasulfinylcalix[4]arenes **5** a 3-D network based on stacking of the aromatic groups was observed, for *p-tert*-butyltetrasulfinylcalix[4]arenes **6** no such a network was obtained. The use of both compounds **5** and **6** for the design of hollow molecular modules previously obtained with the parent compound **1**[12] as well as their coordination ability towards transition metals are under current investigation.

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9. V. Böhmer, *Angew. Chem. Int. Ed. Engl.* , **1995**, *34*, 713-745.
10. *X-ray data for* **5**-CH_2Cl_2 : $C_{24}H_{16}O_8S_4$, M = 560.65, tetragonal, a = 11.3290 (3), b = 11.3289 (3), c = 8.5401 (1) Å, U = 1096.08 (7) Å^3, space group P 4_2/n, Z = 2, Dc = 1.70 gcm^{-3}, μ(Mo-$K\alpha$) = 0.467 cm^{-1}. Crystal dimensions 0.19x0.15x0.12 mm. Data were measured at 173K on a kapa CCD diffractometer with graphite monochromated Mo-Kα radiation. The structure was solved by direct methods using OpenMoleN 2.2 and refined anisotropically using absorption corrected data to give R = 0.037, Rw = 0.059 for 1133 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
11. *X-ray data for* **6** : $C_{40}H_{48}O_8S_4$, M = 785.08, monoclinic, a = 11.0920 (2), b = 14.5430 (3), c = 24.6830 (4) Å, U = 3966.8 (3) Å^3, space group P 2_1/n, Z = 4, Dc = 1.33 gcm^{-3}, μ(Mo-$K\alpha$) = 0.291 cm^{-1}. Crystal dimensions 0.20x0.20x0.15 mm. Data were measured at 173K on a kapa CCD diffractometer with graphite monochromated Mo-Kα radiation. The structure was solved by direct methods using OpenMoleN 2.2 and refined anisotropically using absorption corrected data to give R = 0.052, Rw = 0.068 for 7008 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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