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Insights into the reactivity of thiacalix[2]thianthrenes: synthesis and structural studies of sulfoxide and sulfone derivatives

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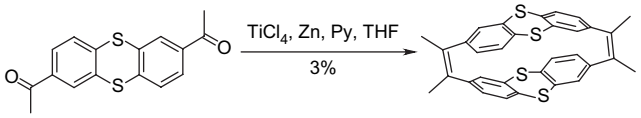
Abstract—We have recently reported a new class of macrocycle, the thiacalixthianthrenes. This paper describes some attempts to modify thiacalixthianthrene and a study of the structure of oxidized derivatives.

1. Introduction

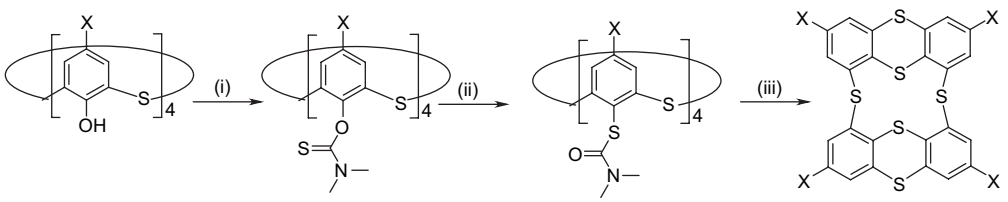
Major developments of the chemistry of calixarenes have concerned applications in the domains of solvent extraction, materials science, and biomedicine.[1] Thiacalixarenes, in which a sulfur bridge replaces the methylene link of calixarenes themselves, have but recently become accessible[2] although there has now been a decade of active research concerning their use for similar applications.[3] We have been interested in thiacalixarenes for specific applications in optical materials technology and coordination chemistry due to the unique properties and strong coordinating ability of these macrocycles.[4–9] Recently, we have reported the synthesis of a new class of macrocycles, the thiacalixthianthrenes.[10,11] The fusion of thianthrene and calixarene chemistry is of considerable promise in areas of supramolecular and solid state chemistry such as the synthesis of non-linear optical materials, of electrochromic and luminescent devices, and of switchable receptors in molecular recognition. The resulting functionalized macrocycles provide new molecular platforms with numerous novel properties. The present work concerns bromination and nitration reactions of thiacalixthianthrenes and we report the first synthesis of a series of oxidized thiacalix[2]thianthrenes.

We recently described the original synthesis of a six-membered thianthrene ring using the Newman–Kwart rearrangement of a thiacalix[4]arene derivative. The so-called thiacalix[2]thianthrenes were thus obtained (Scheme 1).[10,11]

Although thianthrenes in general have attracted strong interest due to the fascinating physical and chemical properties of numerous sophisticated derivatives, the chemistry of thianthrene macrocycles remains very limited. To the best of our knowledge, the only example of thianthrene macrocycle (thianthrenophane) reported in the literature is that obtained by Amthor and co-workers in poor yield (3%) using the McMurry reaction (Scheme 2).[12] It was studied for its interesting complexation, membrane transport, and electrochemical properties.



Scheme 2. Synthesis of a thianthrenophane.



Scheme 1. Synthesis of thiacalix[2]thianthrene: (i) acetone, $(CH_3)_2NCSCl$, Cs_2CO_3, reflux; (ii) 290 °C, 2 h; (iii) 380–410 °C (X=H, *t*-Bu).

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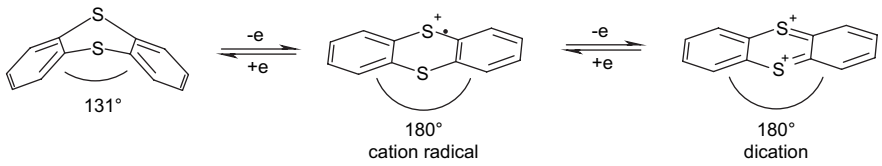


Scheme 3. Formation of radical and dication species by selective oxidation of the sulfur bridges of thianthrene.

It has been shown that thianthrene can undergo a one electron oxidation to give a violet cation radical, or a two electron oxidation yielding blue aromatic dication. We have observed the same behavior with the thiacalixthianthrene (Scheme 3) where it is also possible to oxidize the two thianthrene moieties in the same macrocycle.

It is easy to observe the formation of the colored intermediate radical in, for example, sulfuric acid medium or in the presence of a Lewis acid (Fig. 1). The intense color can be directly related to the change in the structure of the thianthrene when forming the radical.

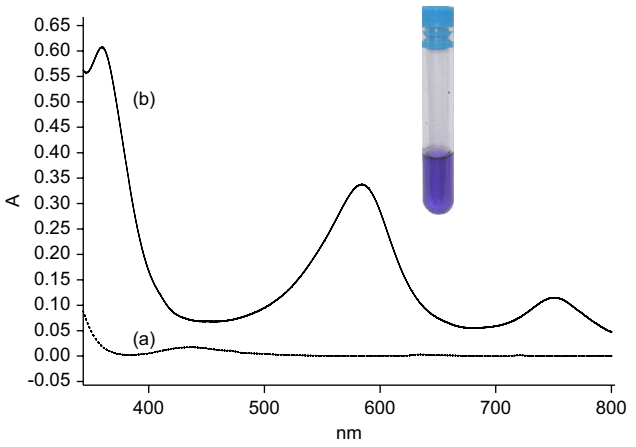


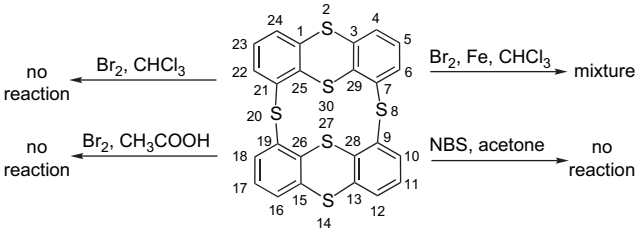
Figure 1. Formation of the colored radical from the thiacalixthianthrene in acidic medium (Brönsted or Lewis acid) and UV–visible spectra of the pure thiacalixthianthrene (a) and the radical (b) in dichloromethane.

Interest in the chemical modifications of the sulfur bridges and aromatic rings of this new macrocycle led us to investigate the possibility of formation of halo- or nitro- derivatives as intermediates to further modification of the macrocycle. We report here the investigation of the reactivity of thiacalixthianthrenes under standard halogenation and nitration conditions.

2. Bromination of thiacalixthianthrenes

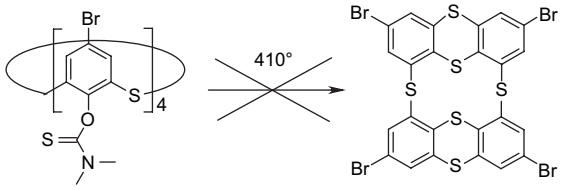
Bromination of the upper rim of thiacalixthianthrenes offers the prospect of functionalization using, for example, Sonogashira coupling.[7,13,14] Thianthrene itself reacts with bromine according to Scheme 4.[15]

Treatment of thiacalixthianthrene with bromine in chloroform solution or in acidic media (glacial acetic acid) led to no reaction and only recovery of starting material. Reaction was promoted by iron but the result was complex mixture, which proved impossible to characterize. An alternative bromination method, NBS/acetone, which is effective, e.g., for bromination of thiacalixarenes,[7] also failed. Thus, we were unable to find a simple procedure for bromination of thiacalixthianthrene (Scheme 5).



Scheme 5. Attempts to prepare the brominated thiacalix[2]thianthrenes.

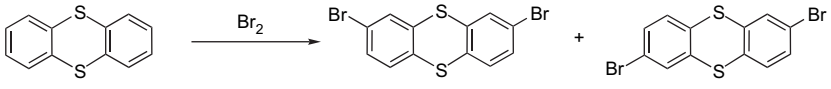
Subsequently, we also investigated the alternative approach of preparing brominated thiacalixthianthrenes from brominated thiacalix[4]arene precursors (Scheme 6). Here, unfortunately, thermal decomposition of the thiocarbamate derivatives did not lead to thianthrene formation.



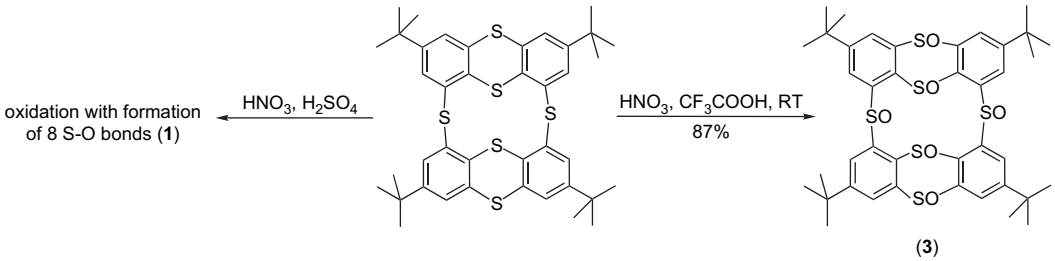
Scheme 6. Reaction from the tetrabromothiacalixarene.

3. Nitration of thiacalixthianthrenes

The common routes to nitration of aromatic compounds were investigated. As with thiacalix[4]arenes,[16] concentrated HNO_3/H_2SO_4 mixtures provided only *S*-oxidized species as identifiable products. Mass spectrometry established the addition of eight oxygen atoms to sulfur in compound **1** (Scheme 7) but the distribution of sulfoxide and sulfone centers could not be determined. Treatment of both *tert*-butyl and de-*tert*-butylated thiacalixthianthrene with nitric acid



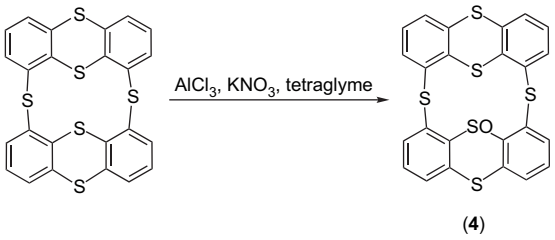
Scheme 4. Bromination of thianthrenes.[15]



Scheme 7. Reactions of tetra-*tert*-butylthiacalixthianthrene with concentrated nitric acid.

in the presence of CF_3COOH or H_2SO_4 under different conditions also failed to cause nitration (Scheme 7). In the case of *tert*-butylthiacalix[2]thianthrene with HNO_3/CF_3COOH, it gave the symmetrical hexasulfoxide (**3**) in good yield (87%) accompanied by thiacalix[2]thianthrene pentasulfoxide (**2**) (13%) after 24 h reaction time and pure 5,11,17,23-tetra-*tert*-butylthiacalix[2]thianthrene-2,8,14,20,27,30-hexasulfoxide (**3**) in the form of two isomers after 48 h reaction time (100%). The structure in the solid state of compound **3** was determined using single crystal X-ray diffraction and is discussed ahead.

Thiacalix[4]arenes have been reported[4] to undergo nitration, without oxidation at sulfur, under mild conditions using nitrosonium nitrate prepared in situ from $KNO_3/AlCl_3$ in tetraglyme. This was not successful with thiacalix[2]thianthrene (Scheme 8), the only isolable product being thiacalix[2]thianthrene-27-sulfoxide (**4**), resulting probably from the reaction of aluminum chloride with the thiacalixthianthrene. The reaction mixture developed an intense blue color indicative of a sulfur-radical intermediate being formed along the pathway to the sulfoxide, and there was no evidence of any nitration of the macrocycle.



Scheme 8. Reaction between thiacalix[2]thianthrene and a nitrosium nitrate complex, giving thiacalix[2]thianthrene-27-sulfoxide (**4**).

The change in molecular symmetry resulting from the mono-oxidation is nicely reflected in the ^1H NMR spectra, the three signals of the reactant becoming six for the product (**4**) as a result of the loss of one plane of symmetry (Fig. 2).

The structure of (**4**) was determined using single crystal X-ray diffraction in order to establish the precise location of the oxygen atom (see ahead). These results show that there must be a marked reactivity difference between thiacalixarene and thiacalixthianthrene species.

Again in analogy to successful reactions with thiacalixarenes,[16] we investigated *ipso*-nitration of *tert*-butylthiacalixthianthrene possessing oxidized sulfur bridges. The oxidized thiacalixthianthrenes proved to be very resistant toward

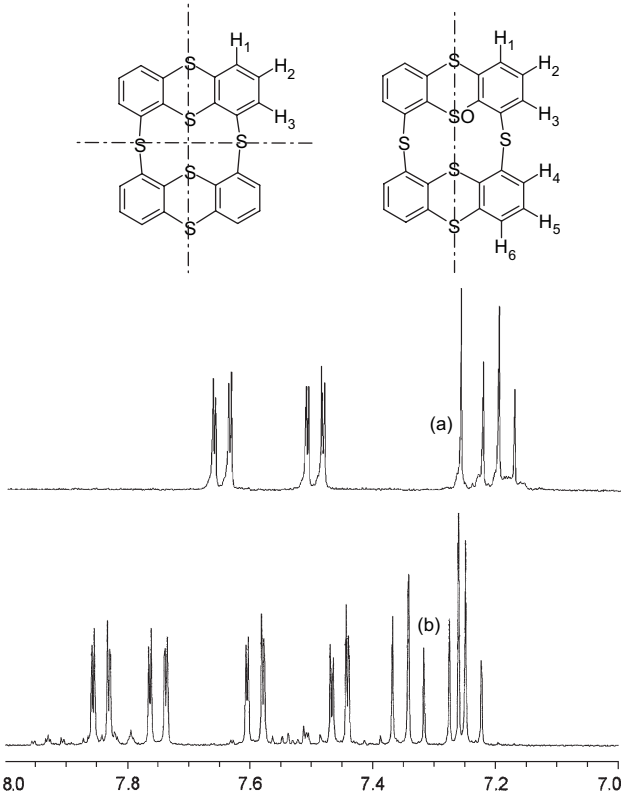


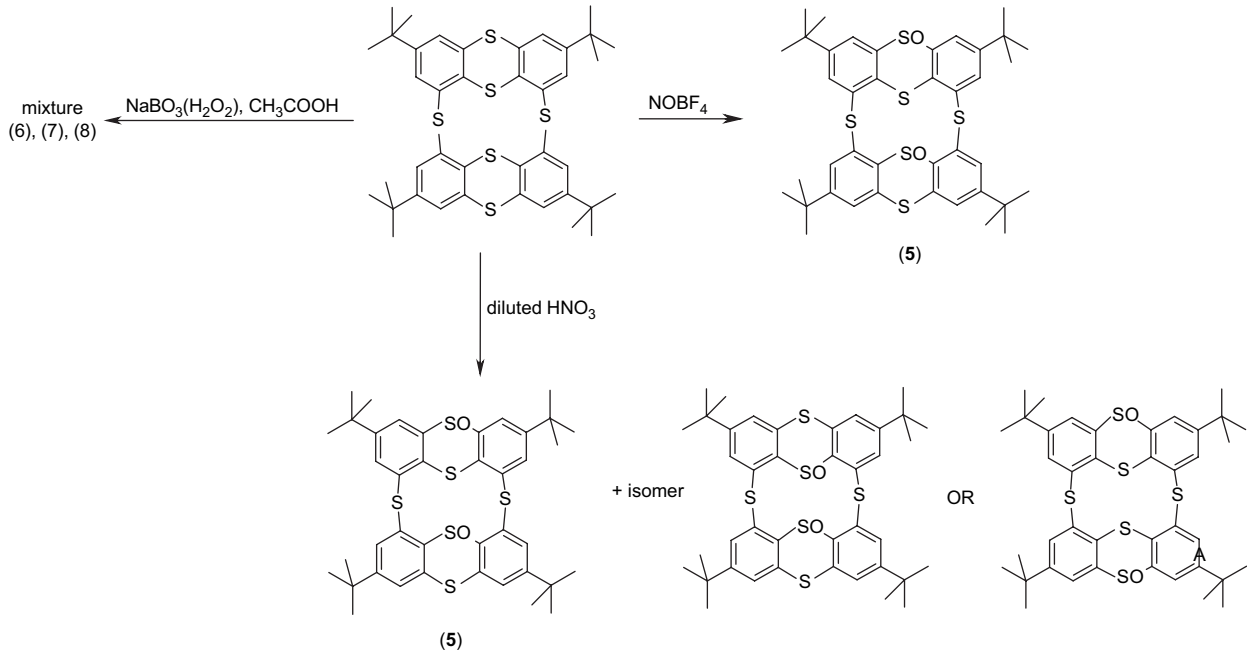
Figure 2. NMR spectra of thiacalix[2]thianthrene (a) and compound (**4**) (b).

ipso-nitration even under extreme conditions. Since all attempts at nitration led at best to sulfur oxidation, we then proceeded to investigate more conventional methods for sulfoxide and sulfone formation.

4. Other methods for the preparation of oxidized thiacalixthianthrenes

Selective oxidation of thianthrene to its monosulfoxide using $NOBF_4$ is a known reaction.[17] Oxidation of 5,11,17,23-tetra-*tert*-butylthiacalix[2]thianthrene with $NOBF_4$ gave selectively 5,11,17,23-tetra-*tert*-butylthiacalix[2]-thianthrene-2,27-disulfoxide (compound **5**) in high yield (95%) (Scheme 9).

A possible explanation of this selectivity is that a cation radical is initially formed on S27, as the most accessible site to an oxidant, and that the conformation change resulting from the preferred planarity of the radical center (Scheme 3) leads



Scheme 9. Oxidation in the presence of $NOBF_4$ or dilute HNO_3 or $NaBO_3(H_2O_2)$: synthesis of 5,11,17,23-tetra-*tert*-butylthiacalix[2]thianthrene-2,27-disulfoxide (**5**).

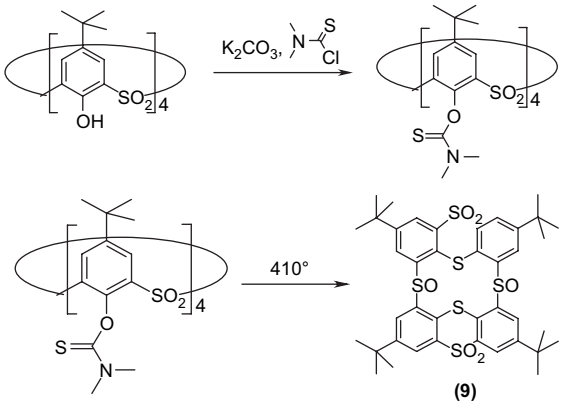
to S2 becoming the preferred site for oxidation in the intermediate monoxide. The reaction mixture develops a deep blue color indicative of the presence of *S*-radicals, which persists for some hours before its loss indicates that reaction is complete. The 1,2-alternate conformation of the product, as described ahead in the solid state structure description, may also be a consequence of the conformational changes induced by radical intermediate formation.

The formation of the disulfoxide derivative (**5**) was also achieved by oxidation with dilute HNO_3 (Scheme 9). In this case, the reaction was less selective and different isomers were evidenced by ^{1}H NMR spectroscopy. Compound (**5**) was obtained in 75% yield, and accompanied by one more symmetrical isomer in 25% yield.

Both isomers were characterized by means of ^{1}H NMR spectroscopy and mass spectrometry, and the structure of (**5**) was obtained by single crystal X-ray diffraction (see ahead).

The action of $NaBO_3$ on thianthrene leads to the formation of the disulfone,[18] and the same reaction on thiacalixarenes gives the tetrasulfone or tetrasulfoxide depending on the reaction conditions.[19–21] In the case of the thiacalixthianthrene, it gave only complex mixtures (Scheme 9). The composition of the mixture was not changed by further addition of perborate nor by heating or prolonging reaction times. The ^{1}H NMR spectrum was very complex. Mass spectrometry showed the presence of 3 species, each possibly a mixture of isomers, with respective formula $C_{40}H_{44}S_6O_5$ (**6**), $C_{40}H_{44}S_6O_6$ (**7**), and $C_{40}H_{44}S_6O_7$ (**8**). The exact structures of **6**–**8** are as yet unknown.

Another approach that was successfully performed on the thiacalixarenes was the *ipso*-nitration of the tetrasulfone derivative.[16] To investigate *ipso*-nitration on a species where the S atoms were already oxidized, the tetra-*tert*-butylthiacalix[4]arene tetrasulfone was converted to its *O*-thiocarbamoyl derivative and heated to induce the Newman–Kwart rearrangement and the cyclization of the macrocycle (Scheme 10). Unfortunately, the process produced only a complex mixture, from which compound (**9**) could be isolated in low yield (4%).



Scheme 10. Synthesis of compound (**9**).

Clearly, a number of side reactions occurred along with cyclization, one of these being partial reduction of the sulfone units, thus explaining the presence of two sulfoxide bridges in (**9**), the structure of which was established by ^{1}H NMR spectroscopy, mass spectrometry, and single crystal X-ray diffraction.

Treatment of compound (**9**) with the *ipso*-nitration mixture (HNO_3/CF_3COOH), did not lead to substitution of any of the *tert*-butyl groups, but only to the formation of three additional S–O bonds, as proved by mass spectrometry. The ^{1}H NMR spectrum of the product showed four different signals in the aromatic region, indicating retention of one plane

of symmetry in the molecule but leaving the distribution of O atoms ambiguous.

5. Solid state structure of the oxidized thiacalixthianthrenes

The structures of compounds (**3**), (**4**), (**5**), and (**9**), determined by single crystal X-ray diffraction,[22] are shown in Figures 3–6. Two conformations, equivalent to those described as 'cone' and '1,2-alternate' for calixarenes were found, the former conformation for (**3**) and (**9**) and the latter for (**4**) and (**5**). It is important to note that the syntheses of compounds (**4**) and (**5**) could possibly proceed through planar cation radical intermediates, which could lead to easy conformational inversion.

The dihedral angles of the thianthrene units in the thiacalixthianthrenes are close to those found in thianthrenes (120–

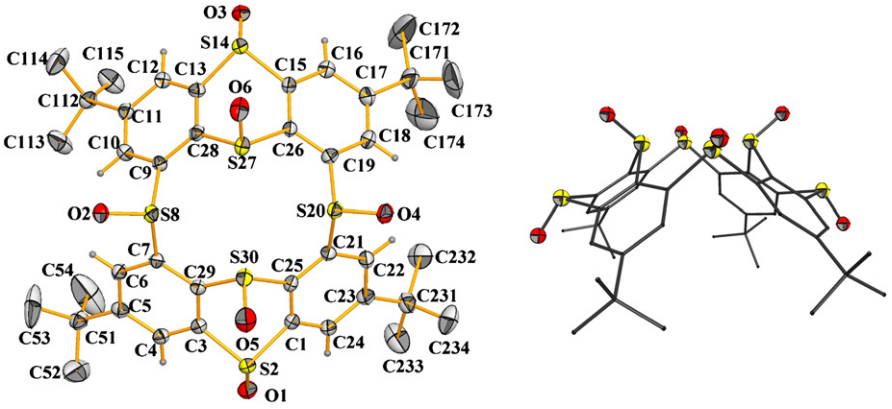


Figure 3. Molecular structure of (**3**).

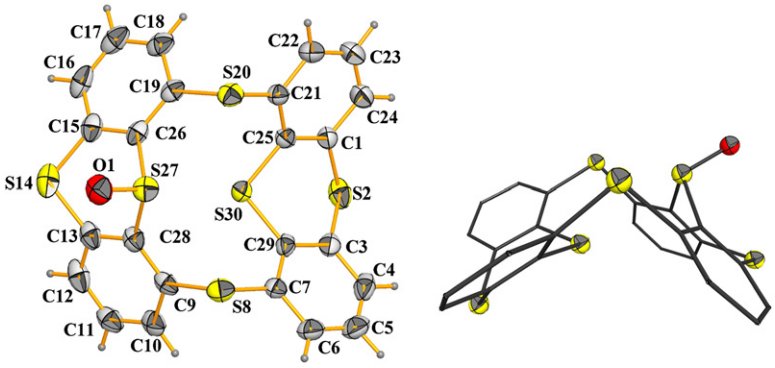


Figure 4. Molecular structure of (**4**).

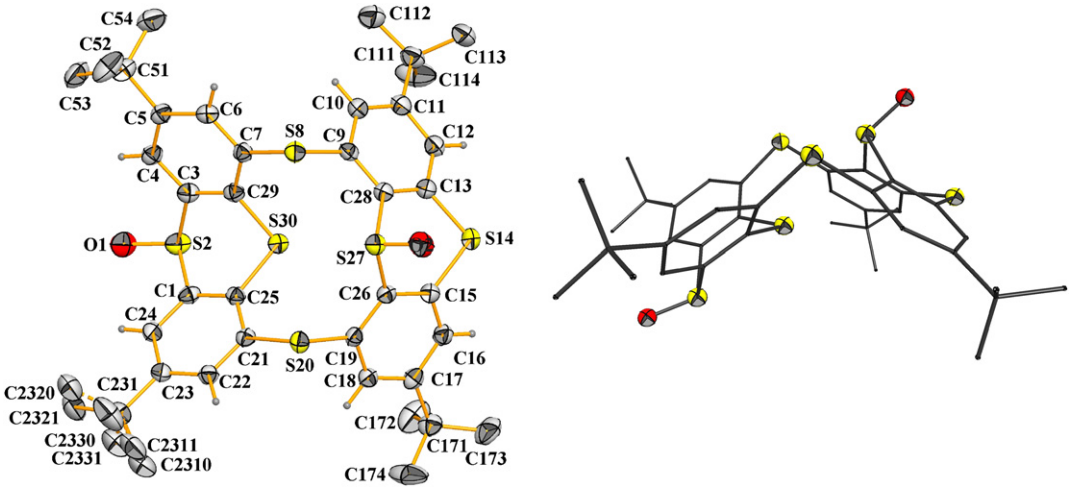


Figure 5. Molecular structure of (**5**).

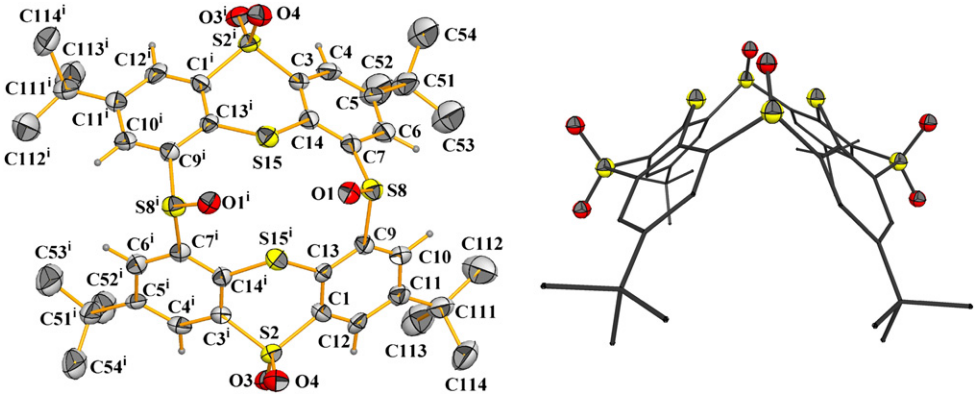


Figure 6. Molecular structure of (**9**).

140°). For the 1,2-alternate species, the torsion angles C25–C21–C19–C26 and C29–C7–C9–C28 are relatively large (30–40°), while for the cone conformations the equivalent angles are much smaller (5–10°).

In summary, we have synthesized a new thianthrene macrocycle by application of the Newman–Kwart rearrangement on a thiacalixarene. Further research will be necessary to find adequate tools for its derivatization, since its reactivity differs from that of both thiacalixarenes and thianthrenes. Nonetheless, this macrocycle possesses the interesting electrochemical properties of thianthrenes, in particular the ability to form colored cation radicals. Selective oxidation of its sulfur atoms is possible and several of the products have been characterized by means of single crystal X-ray diffraction. These structures have shown that at least two conformations, equivalent to those termed 'cone' and '1,2-alternate' for calixarenes, may be adopted by thiacalixthianthrenes. Conformational changes occurring in oxidation reactions are possibly a consequence of the planarity of intermediate sulfur-cation radicals facilitating inversion of one ring of the initial cone species. Further investigations are in progress in order to functionalize the upper rims of these new macrocycles. We believe that derivatives of this macrocycle may have applications including those as synthetic receptors, organic conductors, and switches.

6. Experimental section

6.1. Synthesis of (1): oxidation of tetra-*tert*-butylthiacalix[2]thianthrene with 100% nitric acid

Tetra-*tert*-butylthiacalix[2]thianthrene of 50 mg was dissolved in 0.5 mL of 100% HNO_3 and 0.5 mL of concentrated sulfuric acid was added. The mixture was kept at room temperature for 72 h. Then it was poured into water, neutralized with sodium carbonate, and extracted with chloroform. The chloroform solution was separated, dried over $MgSO_4$, and evaporated, giving 67 mg of product was obtained. ^1H NMR ($CDCl_3$, TMS, 300 MHz) in ppm: 8.57 (d, J=2.1 Hz, 4H, Ar-H), 8.4 (d, J=2.1 Hz, 4H, Ar-H), 1.39 (s, 36H, *t*-Bu). MS (ESI): *m*/*z* calculated for $C_{40}H_{44}S_6O_8$: 844.13; found: 845.3 (MH^+).

6.2. Synthesis of tetra-*tert*-butylthiacalix[2]thianthrene pentasulfoxide (2) and tetra-*tert*-butylthiacalix[2]thianthrene hexasulfoxide (3)

(a) Tetra-*tert*-butylthiacalix[2]thianthrene of 68 mg was dissolved in 5 mL of chloroform and 5 mL of trifluoroacetic acid and 5 mL of 100% HNO_3 were added. The mixture was stirred for 24 h at room temperature and protected from light. Then it was poured in water, neutralized with sodium carbonate, and extracted with chloroform. The chloroform solution was dried over $MgSO_4$ and filtered before evaporation to give a mixture of pentasulfoxide (**2**) and hexasulfoxide (**3**). The pure hexasulfoxide was obtained by crystallization from chloroform–ethanol solution in the form of white crystals, 67 mg (87%). Hexasulfoxide: ^1H NMR ($CDCl_3$, TMS, 300 MHz) in ppm: 8.53 (d, J=1.8 Hz, 4H, Ar-H), 8.36 (d, J=1.8 Hz, 4H, Ar-H), 1.40 (s, 36H, *t*-Bu). MS (ESI): *m*/*z* calculated for $C_{40}H_{44}S_6O_6$: 812.14; found: 813.2 (MH^+). Pentasulfoxide: ^1H NMR ($CDCl_3$, TMS, 300 MHz) in ppm: 8.51 (d, J=2.1 Hz, 2H, Ar-H), 8.31 (d, J=2.1 Hz, 2H, Ar-H), 8.23 (d, J=2.1 Hz, 2H, Ar-H), 8.19 (d, J=2.1 Hz, 2H, Ar-H), 1.40 (s, 18H, *t*-Bu), 1.37 (s, 18H, *t*-Bu). MS (ESI): *m*/*z* calculated for $C_{40}H_{44}S_6O_5$: 796.15; found: 797.2 (MH^+).

(b) Tetra-*tert*-butylthiacalix[2]thianthrene of 102 mg was dissolved in 5 mL of chloroform and 2 mL of trifluoroacetic acid, and 2 mL of 100% HNO_3 was added. The mixture was stirred at room temperature protected from light for 48 h, then poured into water, neutralized with sodium carbonate and extracted with chloroform. The chloroform solution was dried over $MgSO_4$ and filtered. The crude product was a 1:2 mixture of symmetrical and less symmetrical isomers of the hexasulfoxide (**3**). Isomer A: ^1H NMR ($CDCl_3$, TMS, 300 MHz) in ppm: 8.55 (d, J=1.8 Hz, 4H, Ar-H), 8.37 (d, J=1.8 Hz, 4H, Ar-H), 1.42 (s, 36H, *t*-Bu). Isomer B: ^1H NMR ($CDCl_3$, TMS, 300 MHz) in ppm: 8.43 (m, 2H, Ar-H), 8.37 (m, 2H, Ar-H), 8.26 (d, J=2.1 Hz, 1H, Ar-H), 8.14 (d, J=2.1 Hz, 1H, Ar-H), 7.66 (d, J=2.1 Hz, 1H, Ar-H), 7.15 (d, J=2.1 Hz, 1H, Ar-H), 1.49 (s, 9H, *t*-Bu), 1.46 (s, 9H, *t*-Bu), 1,28 (s, 9H, *t*-Bu), 1.26 (s, 9 H, *t*-Bu). MS (ESI): *m*/*z* calculated for $C_{40}H_{44}S_6O_6$: 812.14; found: 813.13 (MH^+).

6.3. Synthesis of thiacalix[2]thianthrene sulfoxide (4)

Thiacalix[2]thianthrene of 72 mg (1.46×10^{-4} mol) was dissolved in 10 mL of chloroform and 0.5 mL of

tetraethyleneglycol dimethylether, 0.1 g (1×10^{-3} mol) of KNO_3 and 0.11 g (8×10^{-4} mol) of $AlCl_3$ were added. The reaction mixture was refluxed overnight. The $CHCl_3$ was evaporated out and the resulting suspension was diluted with methanol and filtered. The solid obtained was chromatographed on silicagel using chloroform as eluant. Major product of 15 mg (20%) was isolated. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) in ppm: 7.87 (dd, *J*=7.5, 0.9 Hz, 2H, Ar-H), 7.75 (d, *J*=7.5, 0.9 Hz, 2H, Ar-H), 7.59 (d, *J*=7.5, 0.9 Hz, 2H, Ar-H), 7.45 (dd, *J*=7.5, 0.9 Hz, 2H, Ar-H), 7.34 (t, *J*=7.5 Hz, 2H, Ar-H), 7.25 (t, *J*=7.5 Hz, 2H, Ar-H). MS (ESI): *m/z* calculated for $C_{24}H_{12}S_6O$: 507.92; found: 509.0 (MH^+).

6.4. Synthesis of tetra-*tert*-butylthiacalix[2]thianthrene disulfoxide (5)

6.4.1. First method. Tetra-*tert*-butylthiacalix[2]thianthrene of 100 mg (1.4×10^{-4} mol) was dissolved in 20 mL of chloroform and 20 mg of $NOBF_4$ (1.71×10^{-4} mol) was added. The mixture was stirred at room temperature in air until the blue color disappeared. The solvent was evaporated and the crude product was purified by column chromatography on SiO_2 using chloroform–acetone 10:1 as eluant. White solid of 100 mg (95%) was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz) in ppm: 7.94 (d, *J*=1.8 Hz, Ar-H, 2H), 7.79 (m, Ar-H, 4H), 7.63 (d, *J*=1.8 Hz, Ar-H, 2H), 1.38 (s, *t*-Bu, 18H), 1.29 (s, *t*-Bu, 18H). MS (ESI): *m/z* calculated for $C_{40}H_{44}S_6O_2$: 748.16; found: 749.2 (MH^+).

6.4.2. Second method. Oxidation of tetra-*tert*-butylthiacalix[2]thianthrene with dilute nitric acid. Tetra-*tert*-butylthiacalix[2]thianthrene of 101 mg (1.39×10^{-4} mol) was dissolved in 5 mL of $CHCl_3$ and 3 mL (4.2×10^{-4} mol) of 0.14 M solution of 100% HNO_3 in chloroform was added. After 30 min of stirring at room temperature, the reaction mixture was poured into water, neutralized with sodium carbonate, and extracted with chloroform. The chloroform layer was separated, dried over $MgSO_4$, and evaporated to dryness. The products were separated using column chromatography on SiO_2 with chloroform–acetone 10:1 mixture as eluant. Disulfoxide (**5**) of 81 mg (75%) and 27 mg (25%) of isomeric disulfoxide were isolated. Isomeric disulfoxide: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) in ppm: 8.07 (d, *J*=2.1 Hz, 4H, Ar-H), 7.63 (d, *J*=2.1 Hz, 4H, Ar-H), 1.39 (s, 36H, *t*-Bu). MS (ESI): *m/z* calculated for $C_{40}H_{44}S_6O_2$: 748.16; found: 749.3 (MH^+).

6.5. Synthesis of (6), (7), and (8): oxidation of tetra-*tert*-butylthiacalix[2]thianthrene with sodium perborate

Tetra-*tert*-butylthiacalix[2]thianthrene of 100 mg was dispersed in acetic acid and 100 mg of $NaBO_3$ was added. The reaction mixture was stirred at room temperature for 2 days. An inseparable mixture was obtained, the composition of which was unchanged by further addition of perborate or heating or prolonging the reaction time. The NMR spectrum was very complex and the mass spectrum revealed the presence of three species, each possibly a mixture of isomers. MS (ESI): *m/z* calculated for $C_{40}H_{44}S_6O_5$: 796.15; found: 797.3 (MH^+), *m/z* calculated for $C_{40}H_{44}S_6O_6$: 812.14; found: 813.2 (MH^+), *m/z* calculated for $C_{40}H_{44}S_6O_7$: 828.14, found: 829.1 (MH^+).

6.6. Synthesis of tetra-*tert*-butylthiacalix[2]thianthrene disulfone disulfoxide (9)

To a dispersion of 10 g (11.8 mmol) of 5,11,17,23-tetra(*tert*-butyl)thiacalix[4]arene tetrasulfone in 200 mL of acetone, 10 g (70.6 mmol) of K_2CO_3, and 9 g (70.6 mmol) of $(CH_3)_2NCSCl$ were added. The reaction mixture was refluxed under argon for 48 h, then it was poured into the water and neutralized with dilute HCl. The resulting suspension was filtered through a glass frit and the solid collected washed abundantly with methanol, to give 11.7 g (82%) of white product. ^{1}H NMR ($CDCl_3$, 300 MHz) in ppm: 8.47 (s, Ar-H, 8H), 3.39 (s, N–CH_3, 12H), 2.29 (s, N–CH_3, 12H), 1.39 (s, *t*-Bu, 36H). MS (ESI): *m/z* calculated for $C_{52}H_{68}N_4S_8O_{12}$: 1196.25; found: 1197.0 (MH^+).

Tetra-thiocarbamoyl derivative of 5.0 g was placed in a Schlenk tube and heated to 410 °C under air, for approximately 3 min to completely transform the reactant. The resulting dark product was let cool to room temperature and dissolved in 50 mL of chloroform. The solution was filtered, concentrated under reduced pressure and a solid precipitated with methanol. This was collected and chromatographed on silica, using chloroform–acetone (10:1) as eluant. The product was recrystallized from mixture of chlorofom and ethanol, to give 140 mg (4%) of **9**. ^{1}H NMR ($CDCl_3$, 300 MHz) in ppm: 8.33 (m, Ar-H, 4H), 8.20 (d, *J*=2.1 Hz, Ar-H, 2H), 8.16 (d, *J*=2.1 Hz, Ar-H, 2H), 1.34 (s, *t*-Bu, 36H). MS (ESI): *m/z* calculated for $C_{40}H_{44}S_6O_6$: 812.14; found: 813.1 (MH^+).

6.7. Attempted nitration of tetra-*tert*-butylthiacalix[2]-thianthrene disulfone disulfoxide: synthesis of compound (10)

Tetra-*tert*-butylthiacalix[2]thianthrene tetrasulfone (**9**) of 50 mg was dissolved in 5 mL of chloroform and 5 mL of CF_3COOH, and 5 mL of 100% HNO_3 was added. The reaction mixture was stirred at 70 °C under argon for 24 h. It was then cautiously poured into water and neutralized using Na_2CO_3. The solution was twice extracted with chloroform, and the combine extracts were dried over $MgSO_4$ and evaporated to dryness, to give 48 mg (95%) of essentially pure product. ^{1}H NMR ($CDCl_3$, 300 MHz) in ppm: 8.60 (d, *J*=2.1 Hz, Ar-H, 2H), 8.56 (d, *J*=2.1 Hz, Ar-H, 2H), 8.45 (d, *J*=2.1 Hz, Ar-H, 2H), 8.37 (d, *J*=2.1 Hz, Ar-H, 2H), 1.39 (s, *t*-Bu, 18H), 1.38 (s, *t*-Bu, 18H). MS (ESI): *m/z* calculated for $C_{40}H_{44}S_6O_9$: 860.13; found: 861.2 (MH^+).

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22. Crystallographic data for compounds (**3**), (**4**), (**5**) and (**9**) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC 645782, 645783, 645781, and 645780 respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk). The crystal data of (**3**): empirical formula: $C_{45}H_{46}Cl_6O_6S_6$; formula weight: 1051.94; crystal color, habit: colorless, needle; crystal dimensions: 0.11×0.24×0.50 mm; crystal system: monoclinic; lattice parameters: a=12.340(5) Å, b=9.696(5) Å, c=41.755(5) Å, β=97.484(5)°, V=4953(5) Å^3; space group: $P12_1/n1$; Z=4; D_{calcd}=1.410 g/cm^3; $F000$=2176; diffractometer: Nonuis KappaCCD; residuals: R, Rw: 0.056, 0.070. The crystal data of (**4**): empirical formula: $C_{24}H_{12}OS_6$; formula weight: 508.75; crystal color, habit: colorless, block; crystal dimensions: 0.13×0.11×0.10 mm; crystal system: orthorhombic; lattice parameters: a=7.916(4) Å, b=13.654(6) Å, c=19.670(1) Å, V=2126(5) Å^3; space group: $P2_12_12_1$; Z=4; D_{calcd}=1.589 g/cm^3; $F000$=1040; diffractometer: Nonuis KappaCCD; residuals: R, Rw: 0.049, 0.055. The crystal data of (**5**): empirical formula: $C_{47}H_{52}O_2S_6$; formula weight: 841.32; crystal color, habit: colorless, block; crystal dimensions: 0.06×0.10×0.11 mm; crystal system: monoclinic; lattice parameters: a=10.133(5) Å, b=17.000(5) Å, c=25.568(5) Å, β=94.500(5)°, V=4391(3) Å^3; space group: $P12_1/n1$; Z=4; D_{calcd}=1.273 g/cm^3; $F000$=1784; diffractometer: Nonuis KappaCCD; residuals: R, Rw: 0.053, 0.061. The crystal data of (**9**): empirical formula: $C_{80}H_{88}O_{12}S_{12}$; formula weight: 1626.36; crystal color, habit: colorless, plate; crystal dimensions: 0.13×0.24×0.49 mm; crystal system: monoclinic; lattice parameters: a=21.727(5) Å, b=12.962(5) Å, c=22.830(5) Å, β=113.449(5)°, V=5899(5) Å^3; space group: $C12/c1$; Z=2; D_{calcd}=0.916 g/cm^3; $F000$=1712; diffractometer: Nonuis KappaCCD; residuals: R, Rw: 0.086, 0.098.