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Syntheses and structures of novel *m*-xylylene-bridged calix[6]arenes: stabilization of a sulfenic acid in the cavity of calix[6]arene

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Abstract

The syntheses and structures of novel bridged calix[6]arenes **1** with inwardly directed functional groups in the cavity, and application of the bicyclic framework to the stabilization of a sulfenic acid are described. It was found that, unlike their precursors **2**, the tetramethoxy compounds **1** have a tendency to adopt the 1,2,3-alternate conformation at least in the crystalline state, except when the central functionality has a large steric demand. Thermolysis of sulfoxide **1g** at 80°C in toluene afforded the stable sulfenic acid **1h** almost quantitatively; the structure was determined by X-ray analysis. The SOH group was found to be directed into the cavity and surrounded by the calix[6]arene macrocycle with the 1,2,3-alternate conformation, being protected from self-condensation leading to the corresponding thiosulfinate. The high stability of **1h** demonstrates that the framework of the bridged calix[6]arene can effectively regulate the reactivity of the functional group fixed in the cavity.

Keywords: Calix[6]arenes; Sulfenic acids; Steric protection; X-ray analysis; Conformational analysis

1. Introduction

One of the features of the active sites of enzymes is a concave environment with an inwardly directed functionality fixed in the cavity, which leads to the high selectivity and characteristic reactivity [1]. It is also well known that such geometry sometimes results in the stabilization of reactive species in the active site that are otherwise very unstable because of rapid oligomerization reactions. Among such species are sulfenic acids (R-SOH), which have been known to play important roles as reactive intermediates in organosulfur chemistry [2,3]. Usually they are very unstable because of facile self-condensation reactions leading to the corresponding thiosulfinates (RS(O)SR). It has been suggested, however, that oxidation of cysteinyl side chains of papain and glyceraldehyde-3-phosphate dehydrogenase yields stable active-site cystein-sulfenic acid (Cys-SOH) derivatives [3a]. More recently, functional Cys-SOH residues have been identified in the native oxidized forms of the FAD-containing NADH peroxidase and NADH oxidase from *Streptococcus faecalis* [3b,c].

If these unique features of the active site can be translated to an artificial molecular system, a novel type of reaction environment can be developed where highly reactive species are stabilized efficiently. Calix[*n*]arenes are cyclic oligomers that belong to the class of [1_n]-metacyclophanes. They have been widely utilized as a versatile building block of molecular systems with controlled functionalities [4] and are expected to be of great use also for modeling such an environment. However, they are at a disadvantage in that the functionalities in their upper and lower rims tend to diverge away from the substrates held within the cavity, unlike those in

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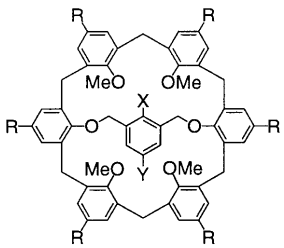
enzymes. As a strategy for introducing an inwardly directed functional group into the cavity of a calix[6]arene, we have designed the *m*-xylylene-bridged calix[6]arenes [5,6] and previously reported the tetramethoxy compounds **1** (Chart 1) bearing an azide [5a], a bromide [5b], a *tert*-butylthio [5c], or a sulfenic acid [5c] functionality at the X position in preliminary communications. For use of these compounds as a reaction environment, it is necessary for their structural features to be fully clarified. We report here the details of the syntheses and structures of the bridged calix[6]arenes **1** with inwardly directed functional groups, and application of this bicyclic framework to the stabilization of a sulfenic acid.



1

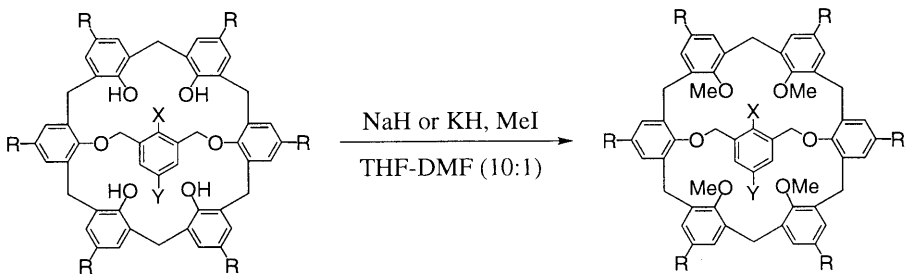
Chart 1.

2. Results and discussion

*2.1. Synthesis and structures of the tetramethoxy compounds **1***

The tetramethoxy compounds **1a**–**f** bearing a bromide, an azide, or a *tert*-butylthio group were prepared by the reaction of the corresponding tetrahydroxy compounds **2a**–**f** [5a–d] with methyl iodide in the presence of NaH or KH in moderate to good yields (Scheme 1). It was found that **1a**–**f** show conformational behavior quite different from that of their precursors **2a**–**f**. Previously we reported that the tetrahydroxy compounds **2a**–**f** have a conformation where the calix[6]arene macrocycle takes a pinched cone conformation and the bridging *m*-xylylene unit lies below it in such a way that it forms the bottom of the cone as exemplified by **2a** (Fig. 1) [5b,d]. In this conformation, the central functionality points out of the cavity. On the other hand, X-ray crystallographic analysis of the tetramethoxy compound **1a** revealed that, in the crystalline state, **1a** adopts a conformation where the bromide functionality is directed into the cavity and surrounded by the calixarene macrocycle (Fig. 2). The conformation of the calix[6]arene moiety of **1a** is classified as the (**u**,u,d,d,d,u) [6a] 1,2,3-alternate conformation, which has been proposed for several bridged calix[6]arenes [6a,7] but has not been established by X-ray crystallography. The central aromatic ring is arranged almost parallel to two of the non-bridged rings at a distance of ca. 3.6 Å, suggesting that there is a favorable π–π interaction among these rings (Fig. 2b).

The ^{1}H-NMR spectrum of **1a** at room temperature shows complex and broadened signals (Fig. 3c), indicating that **1a** undergoes slow conformational interconversion on the NMR timescale. At high temperatures above 120°C, the signals are resolved and at 140°C two *tert*-butyl resonances (ratio 2:1), a singlet for OMe protons, two pairs of doublets for $ArCH_2Ar$ methylenes (ratio 1:2), and a singlet for $ArCH_2O$ methylenes were observed (Fig. 3a). This spectral pattern can be interpreted in terms of a rapid flipping motion of the



2 **1**

	X	Y	R	base	**1**/%
a:	Br	H	*t*-Bu	NaH	50
b:	Br	H	H	NaH	50
c:	Br	*t*-Bu	*t*-Bu	NaH	65
d:	N_3	H	*t*-Bu	NaH	77
e:	S(*t*-Bu)	H	H	KH	82
f:	S(*t*-Bu)	*t*-Bu	H	KH	47

Scheme 1.

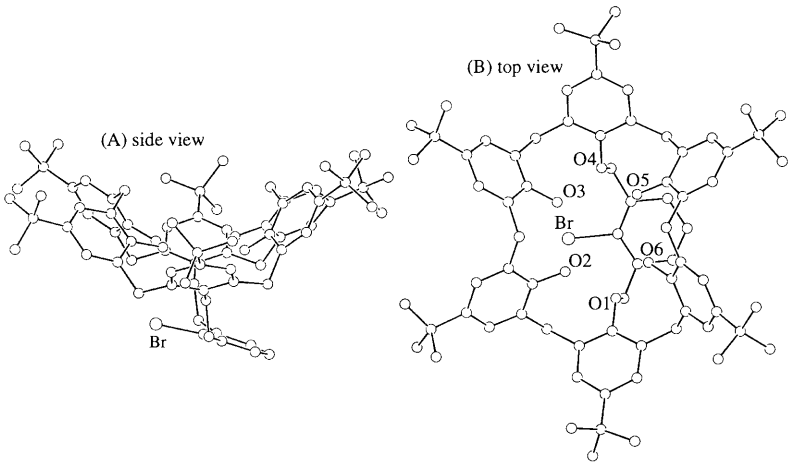


Fig. 1. Structure of the tetrahydroxy compound **2a**.

anisolic rings of **1a** at high temperatures with the OMe groups passing through the annulus (Scheme 2), which results in the equivalence of these rings on the NMR timescale.

The tetramethoxy compound **1b** without *tert*-butyl groups on the calixarene macrocycle showed more broadened signals than **1a** in the ^{1}H-NMR spectrum at room temperature, but at high temperatures above 120°C the spectral pattern of **1b** becomes quite similar to that of **1a**. Compound **1c** bearing a *tert*-butyl group at the *para* position of the bridging aromatic ring showed spectral features essentially the same as those of **1a** and **1b**. These results indicate that the flipping motion of the non-bridged aromatic rings at high temperatures is not affected by the substituents on the upper rim of the calixarene macrocycle and the *para* position of the bridging aromatic ring in these tetramethoxy compounds.

It has been found independently by Lüning [6g] and our group [5d] that the conformational mobility of the tetrahydroxy compounds such as **2a**–**f** is significantly affected by the steric properties of the central functionality. The influence of the central functionality on the conformational behavior of the molecule was also observed in the tetramethoxy compounds **1**. While the bromide **1a** showed slightly broadened signals even at 140°C (Fig. 3a), the azide **1d** afforded a well resolved spectrum with a similar pattern at 80°C (in $CDCl_3$ in a sealed tube), indicating that the flipping motion of the non-bridged aromatic ring is less retarded by the azide group than by the bromide functionality.

On the other hand, the tetramethoxy compounds **1e** and **1f** with a *tert*-butylthio group were found to show spectral features very different from those described above for compounds **1a**–**d**. The ^{1}H-NMR spectra of **1e** ($CDCl_2CDCl_2$) at various temperatures are shown in Fig. 4. At room temperature, **1e** showed slightly broadened signals (Fig. 4c), and at 80°C two singlets (1:1 ratio) for OMe protons, four pairs of doublets (2:1:1:2 ratio) for $ArCH_2Ar$ methylenes, and a singlet for $ArCH_2O$ methylenes were observed (Fig. 4b). This spectral pattern resembles that of the tetrahydroxy compounds **2a**–**f**, and is consistent with a conformation

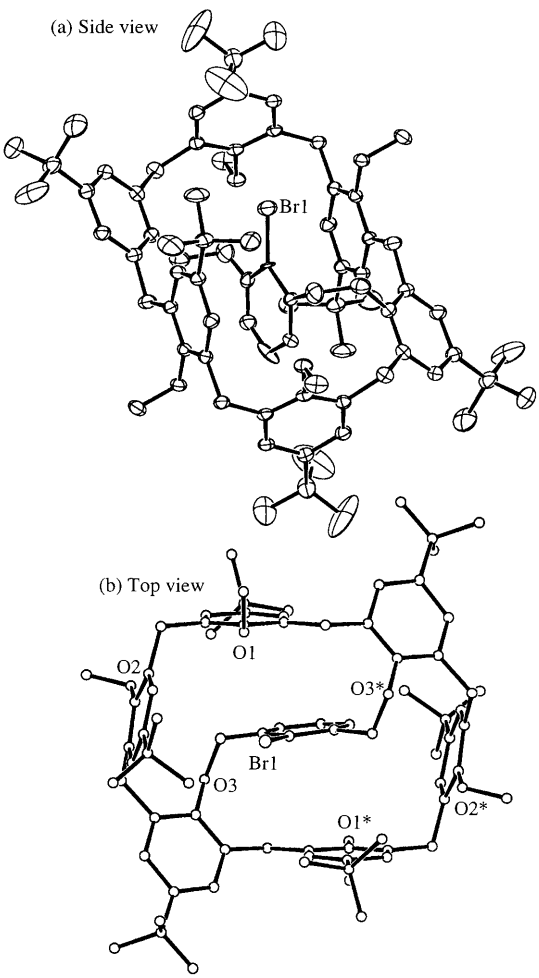


Fig. 2. X-ray structure of **1a**.

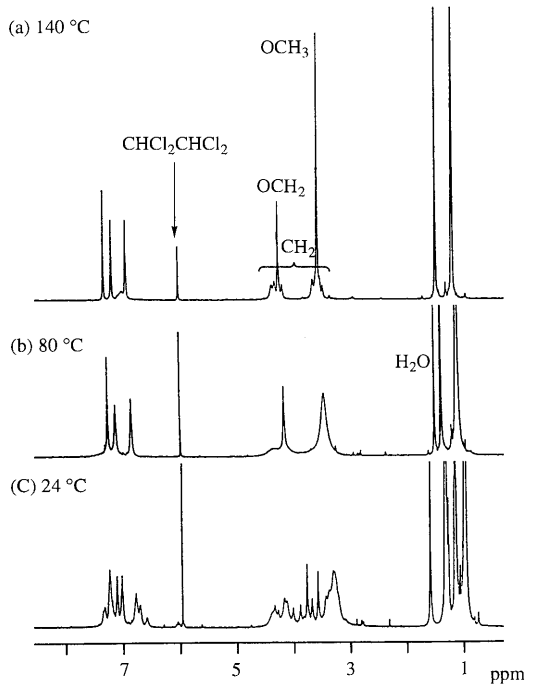
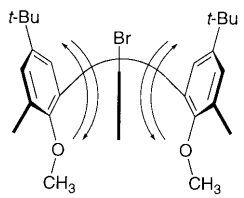


Fig. 3. ^{1}H-NMR spectra of **1a** in $CDCl_2CDCl_2$.



Scheme 2.

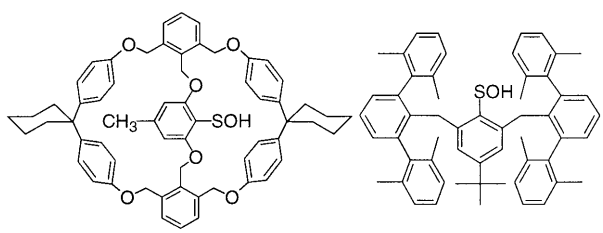
of C_s symmetry which has only one symmetry plane perpendicular to the *m*-xylylene bridge. These results indicate that the bridging unit of **1e** lies below the calix[6]arene macrocycle, similar to the conformation shown in Fig. 1, in a wide range of temperature. Probably, the *tert*-butylthio group is too bulky to enter into the cavity of the calix[6]arene macrocycle during the methylation reaction.

At 140°C, the signals of **1e** are slightly broadened again (Fig. 4a), suggesting that the swinging motion of the bridging unit becomes possible in part at such a high temperature. In this compound, the swinging motion of the bridging unit with a *tert*-butylthio group passing through the annulus is considered to be difficult because of the bulkiness of the substituent. Instead, a swinging motion might occur with the *para* position of the bridging aromatic ring passing through the annulus (Scheme 3).

In order to confirm the swinging motion of the bridging unit of **1e** with the *para* position passing through the annulus, the conformational behavior of compound **1f**, which has a *tert*-butyl group on that position, was studied. The ^{1}H-NMR spectra of **1f** ($CDCl_2CDCl_2$) below 80°C were essentially the same as those of **1e** at the corresponding temperatures. On the other hand, no broadening of the signals at high temperatures up to 140°C was observed for **1f**, unlike **1e**. These results suggest that in compound **1f** the swinging motion of the bridging unit with the *para* position passing through the annulus is suppressed by the *tert*-butyl group, while **1e** can undergo that motion at high temperatures.

2.2. Application to the stabilization of a sulfenic acid

As indicated by the crystal structure of the bromide **1a**, the intracavity functional group of the bridged calix[6]arene of type **1** is surrounded by the calix[6]arene macrocycle from all sides. When reactive species are fixed in this position, bimolecular degradation such as dimerization and self-condensation is expected to be suppressed. Here the stabilization of a sulfenic acid (R-SOH) was investigated. While there have been more than a dozen examples of isolable sulfenic acids to date [8], most of them have been stabilized by the electronic effect of the neighboring substituents or intramolecular hydrogen bonding, which inevitably perturbs the properties of the SOH group. We have recently succeeded in the synthesis of the stable sulfenic acids **3** [9a] and **4** [9b] bearing a bimacrocyclic cyclophane framework and an all-carbon bowl-type framework, respectively (Chart 2). If a sulfenic acid functionality were incorporated into the cavity of **1**, it would provide a good probe to investigate how the bridged calixarene framework can regulate the reactivity of an intracavity functional group. Examination of the CPK molecular models predicts that the concave shielding of the central functionality is more effective in **1** than in the bicyclic cyclophane framework of **3** and the *m*-terphenyl-based framework of **4**.



3 **4**

Chart 2.

As the method of generating a sulfenic acid, thermolysis of a *tert*-butyl sulfoxide was employed because it can be carried out under mild conditions [10]. The CPK models indicate that the cavity of *p*-*tert*-butylcalix[6]arene is too congested when bridged by a *m*-xylylene unit bearing a *tert*-butylthio group. So compound **1e** based on *p*-H-calix[6]arene was prepared

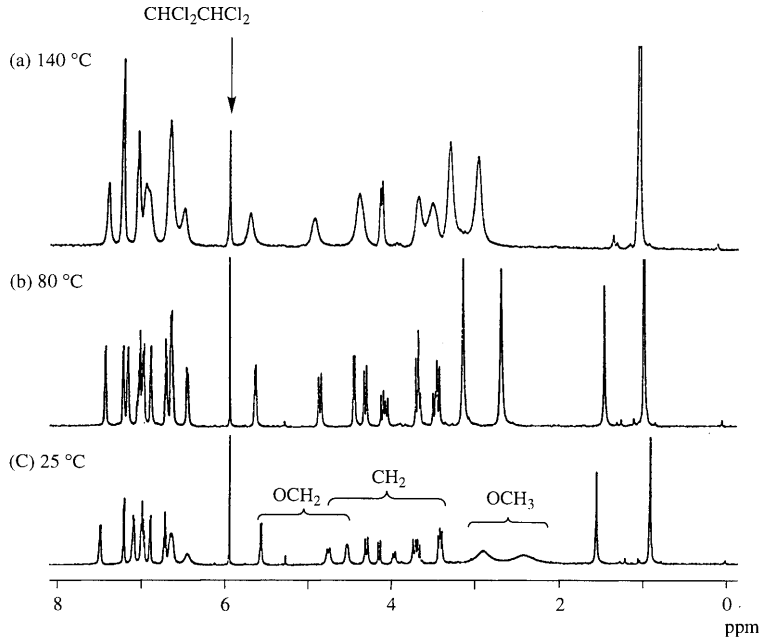


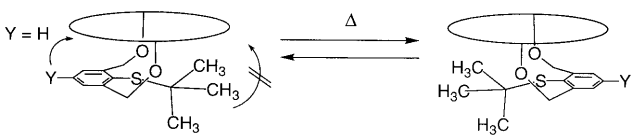
Fig. 4. ^{1}H-NMR spectra of **1e** in $CDCl_2CDCl_2$.

as a starting material as described in the previous section. Sulfoxide **1g** was readily obtained by oxidation of **1e** with mCPBA (Scheme 4) as a mixture of two inseparable conformational isomers (ca. 10:3 ratio by ^{1}H-NMR); the spectrum was complicated by the existence of a chiral center on sulfur.

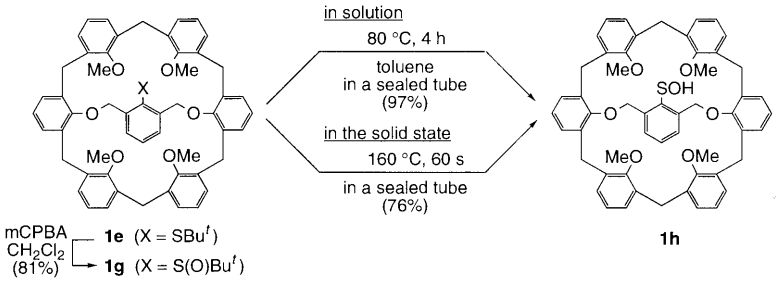
In order to synthesize sulfenic acid **1h**, thermolysis of sulfoxide **1g** in solution was carried out. Monitoring of the thermolysis of **1g** in toluene-d_8 at 80°C in a sealed tube by ^{1}H-NMR indicated that both conformers of **1g** disappeared at a similar rate with concomitant appearance of 2-methylpropene and another compound which shows a very broad ^{1}H-NMR spectrum. After heating at 80°C for 4 h, the starting material completely disappeared and purification of the products by silica gel chromatography afforded sulfenic acid **1h** as colorless crystals in an almost quantitative yield (97%) (Scheme 4). Thermolysis of **1g** in the solid state at 160°C for 60 s also afforded **1h** in 76% yield along with recovered **1g** (15% recovery). These results clearly indicate that **1h** is stable enough to withstand the conditions of the thermolysis and the chromatographic purification in open atmosphere.

The structure of **1h** was determined by X-ray crystallographic analysis (Fig. 5). It has been found that **1h** is solvated by one molecule of toluene and its conformation is the (**u**,u,d,d,d,u) 1,2,3-alternate type, which is the same conformation as that of the bromide **1a** in the solid state. The SOH functionality is directed into the cavity and surrounded by the calix[6]arene macrocycle from all sides, being effectively protected from self-condensation leading to the corresponding thiosulfinate. The central aromatic ring is arranged almost parallel to two of the non-bridged rings at a distance of ca. 3.5 Å, similar to **1a**. The figure might be viewed as an image of a benzenesulfenic acid included in the cavity of calix[6]arene and covalently anchored with the CH_2O linkages. Unfortunately, the disordering at the bridging *m*-xylylene unit makes it difficult to discuss the detailed structural parameters of the benzenesulfenic acid moiety at present. The conformation found here for **1h** is considerably different from that of its precursor **1g**, which is considered to be similar to that shown in Fig. 1 as described above. It is likely that the decrease in the steric demand of the central functionality during the conversion of S(O)Bu^t to SOH resulted in such a conformational change.

The ^{1}H-NMR spectrum of **1h** ($CDCl_2CDCl_2$) showed quite broadened signals at room temperature, which were sharpened at high temperatures (Fig. 6). At 120°C a singlet for OMe protons, two pairs of doublets for $ArCH_2Ar$ methylenes (ratio 1:2), a singlet for $ArCH_2O$ methylenes, and a singlet at δ 2.39 which is most likely assigned to the hydroxy proton of SOH were observed (Fig. 6a). Confirmation of the assignment of the hydroxy proton by a D_2O exchange experiment was unsuccessful because the signal at δ 2.39 only appears at



Scheme 3.



Scheme 4.

high temperatures above ca. 100°C, where partial decomposition of **1h** was observed in the presence of water. The signal broadening at room temperature (Fig. 6c) indicates that conformational interconversion of the calix[6]arene macrocycle is considerably restrained by the *m*-xylylene bridge. At 120°C, the four non-bridged aromatic rings appear equivalent, which can be explained in terms of their rapid flipping motion.

In the IR spectrum in CH_2Cl_2, the OH stretching bands were observed at 3479 and 3282 cm^{-1}. No concentration-dependent shift of these bands was observed, indicating that intermolecular interactions are not involved in these bands. The former band is very close to the OH absorption of sulfenic acids **3** (3494 cm^{-1}) [9a] and **4** (3460 cm^{-1}) [9b] and is probably due to a free hydroxy group, although the possible existence of a weak hydrogen bond cannot be ruled out. The latter band strongly suggests intramolecular hydrogen bonding between the OH group and the ether oxygen atoms in the framework.

The reaction of **1h** with methyl propiolate in $CDCl_3$ at 50°C for 16 h afforded sulfoxide **1i** (86%) (Scheme 5). At room temperature, it took 10 days for the reaction to be completed. This is in sharp contrast to the reaction of sulfenic acid **3** with methyl propiolate, which goes to completion within 12 h at room temperature, indicating that the SOH group of **1h** is more strongly shielded by the calixarene macrocycle.

Sulfenic acid **1h** was found to be stable toward air and moisture, and showed remarkable thermal stability both in the solid state and in solution. In the solid state, it decomposed at 182°C as measured by DSC. Heating of **1h** at 80°C for 4 h in $CDCl_3$ or toluene-d_8 resulted in only slight decomposition. In order to clarify the stabilizing effect of the calixarene framework, a control experiment was carried out using sulfoxide **5** which does not have a macrocyclic structure (Scheme 6). In monitoring of the thermolysis of **5** at 80°C for 1 h in toluene-d_8 by ^{1}H-NMR, two singlets at δ 5.14 ($ArCH_2O$) and 3.5 (SOH) were observed, indicating the formation of sulfenic acid **6**. The generation of **6** was further confirmed by a trapping experiment with methyl propiolate to afford **7**. When the thermolysis was continued, however, **6** decreased with the increase in its self-condensation product **8**. Moreover, chromatographic purification of the reaction mixture including the maximum amount of **6** afforded only thiosulfinate **8** in the yield of 98%. These results clearly demonstrate

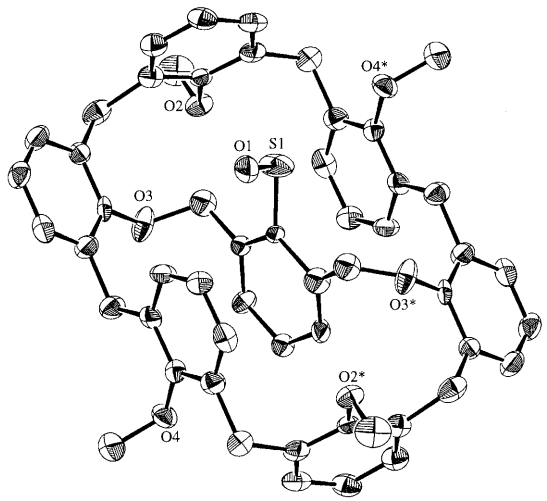


Fig. 5. X-ray structure of **1h**.

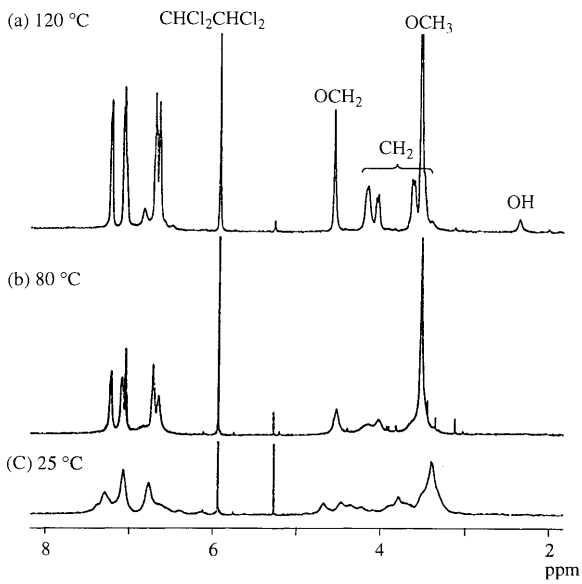
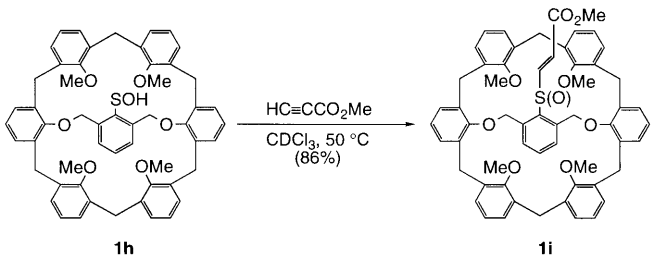
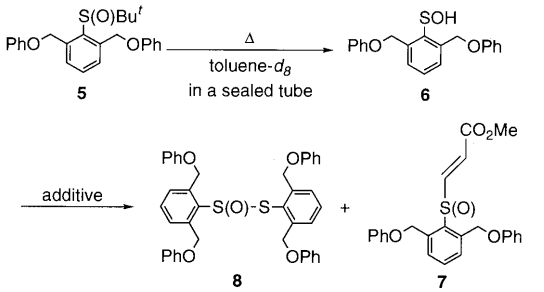


Fig. 6. ^{1}H-NMR spectra of **1h** in $CDCl_2CDCl_2$.



Scheme 5.



conditions	additive	yield /%		
		8	7	5 (recovered)
80 °C, 4 h	none	92	——	——
80 °C, 1 h	HC≡CCO2Me (excess)	44	35	14

Scheme 6.

that in the case of **1h**, encapsulation of the sulfenic acid functionality within the cavity of calix[6]arene effectively prevents its self-condensation, thus rendering it stable enough to be isolated.

3. Conclusion

A series of bridged calix[6]arenes of type **1** has been synthesized and the structural features have been investigated. It was found that they have a tendency to adopt the 1,2,3-alternate conformation, at least in the crystalline state, and the functional group on the bridge stays in the cavity of the calixarene macrocycle when the central functionality has a moderate size. The bridged calix[6]arene **1**, which can fix a functionality in such a way that it points inwards, presents a new mode of functionalization of calixarenes to furnish them with unprecedented properties. The application of **1** to stabilization of a sulfenic acid demonstrates that the cavity of calix[6]arenes can serve as a reaction environment for the intracavity functional group which regulates its reactivities in a unique fashion. A variety of highly functionalized macrocycles would be developed by modifying its upper and lower rims and by making the most of its potential complexing ability.

4. Experimental

^{1}H-NMR spectra were recorded on a Bruker AM-500 spectrometer or a JEOL JNM-A500 spectrometer at 500 MHz, or a JEOL EX-270 spectrometer at 270 MHz. When the solvent was $CDCl_3$, tetramethylsilane was used as an internal standard, and when the solvent was $CDCl_2CDCl_2$, $CHCl_2CHCl_2$ was used as an internal standard. ^{13}C-NMR spectra were recorded on a Bruker AM-500 spectrometer or a JEOL JNM-A500 spectrometer at 125 MHz, or a JEOL EX-270 spectrometer at 68 MHz. ^{13}C chemical shifts were referenced to the resonances in the deuterated solvent. High resolution mass spectra were obtained with a JEOL JMS-SX102XL spectrometer. Infrared spectra were obtained with a Horiba FT-200 spectrometer. Melting points were determined on a Yanaco micro melting point apparatus. All melting points were uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Graduate School of Science, The University of Tokyo. Preparative gel permeation liquid chromatography (GPLC) was performed by LC-908 with JAI gel 1H and 2H columns (Japan Analytical Industry) with chloroform as solvent. For wet column chromatography (WCC) Wakogel C-200 was used. Dry column chromatography (DCC) was performed with ICN silica DCC 60A. Preparative thin-layer chromatography (PTLC) was carried out with Merck Kieselgel 60 PF254 Art 7747. Compound **2f** was prepared by the method similar to that for **2e** [5d]. All solvents used in the reactions were purified by the reported methods. THF was purified by distillation from benzophenone ketyl under argon atmosphere before use. All reactions were carried out under argon atmosphere unless otherwise noted.

*4.1. Synthesis of 5,11,17,23,29,35-hexa-tert-butyl-37,38,40,41-tetramethoxy-39,42-[2-bromo-1,3-phenylenebis(methyleneoxy)]calix[6]arene (**1a**)*

To a suspension of NaH (60%, 241 mg, 6 mmol) in THF (1 ml) was added a solution of **2a** [5d] (349 mg, 0.30 mmol) in THF (9 ml) and DMF (1 ml). After this mixture was stirred at room temperature for 2 h, methyl iodide (0.75 ml, 12 mmol) was added and the reaction mixture was refluxed for 2 days. After addition of water, the mixture was poured into 1 M aq. HCl, extracted with $CHCl_3$, and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was separated by DCC (SiO_2–$CHCl_3$) to give **1a** (181 mg, 50%). **1a**: colorless crystals (from $CHCl_3$–EtOH), m.p. > 300°C. ^{1}H-NMR (270 MHz, $CDCl_2CDCl_2$, 140°C) δ 1.11 (s, 36H, t-Bu), 1.40 (s, 18H, t-Bu), 3.41 (d, $^2J = 15.2$ Hz, 2H, $ArCH_2Ar$), 3.44

(s, 12H, OCH_3), 3.54 (d, $^2J = 15.8$ Hz, 4H, $ArCH_2Ar$), 4.14 (d, $^2J = 15.2$ Hz, 2H, $ArCH_2Ar$), 4.18 (s, 4H, $ArCH_2O$), 4.27 (d, $^2J = 15.8$ Hz, 4H, $ArCH_2Ar$), 6.86–7.25 (br m, 15H). LRMS (FAB) observed m/z 1210 ($[M+H]^+$). Anal. Calc. for $C_{78}H_{97}O_6Br$: C, 77.39; H, 8.08; Br, 6.60. Found: C, 77.14; H, 8.01; Br, 6.26%.

4.2. Synthesis of 37,38,40,41-tetramethoxy-39,42-[2-bromo-1,3-phenylenebis(methyleneoxy)]calix[6]arene (1b)

To a suspension of NaH (60%, 640 mg, 6 mmol) in THF (4 ml) was added a solution of **2b** [5d] (736 mg, 0.9 mmol) in THF (76 ml) and DMF (8 ml). After this mixture was stirred at room temperature for 1.5 h, methyl iodide (2.0 ml, 32 mmol) was added, and the reaction mixture was refluxed for 1 h. After addition of water, the mixture was poured into 1 M aq. HCl, extracted with $CHCl_3$, and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was separated by DCC (SiO_2–$CHCl_3$) to give **1b** (641 mg, 50%). **1b**: colorless crystals (from CH_2Cl_2–MeOH), m.p. > 300°C. ^{1}H-NMR (270 MHz, $CDCl_2CDCl_2$, 130°C in a sealed tube) δ 3.57 (d, $^2J =$ 13.9 Hz, 2H, $ArCH_2Ar$), 3.61 (s, 12H, OCH_3), 3.68 (d, $^2J = 15.5$ Hz, 4H, $ArCH_2Ar$), 4.05 (d, $^2J = 13.9$ Hz, 2H, $ArCH_2Ar$), 4.16 (d, $^2J = 15.5$ Hz, 4H, $ArCH_2Ar$), 4.33 (s, 4H, $ArCH_2O$), 6.43 (br m, 2H), 6.60–6.70 (m, 9H), 7.00–7.22 (m, 10H). HRMS (FAB) observed m/z 873.2815 ($[M+H]^+$), calc. for $C_{54}H_{50}O_6^{79}Br$ 873.2792. Anal. Calc. for $C_{54}H_{49}O_6Br$: C, 74.22; H, 5.65; Br, 9.14. Found: C, 73.98; H, 5.61; Br, 9.14%.

4.3. Synthesis of 5,11,17,23,29,35-hexa-tert-butyl-37,38,40,41-tetramethoxy-39,42-[2-bromo-5-tert-butyl-1,3-phenylenebis(methyleneoxy)]calix[6]arene (1c)

To a suspension of NaH (60%, 80 mg, 2 mmol) in THF (0.5 ml) was added a solution of **2c** [5d] (121 mg, 0.10 mmol) in THF (4.5 ml) and DMF (0.5 ml). After this mixture was stirred at room temperature for 1.5 h, methyl iodide (0.25 ml, 4 mmol) was added, and the reaction mixture was refluxed for 1 day. After addition of water, the mixture was poured into 1 M aq. HCl, extracted with $CHCl_3$, and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was separated by DCC (SiO_2–$CHCl_3$), GPLC, and PTLC (SiO_2–hexane:$CHCl_3$ = 1:1) to give **1c** (83 mg, 65%). **1c**: colorless crystals (from CH_2Cl_2–MeOH), m.p. > 300°C. ^{1}H-NMR (270 MHz, $CDCl_2CDCl_2$, 130°C) δ 1.06 (s, 36H, t-Bu), 1.38 (s, 9H, t-Bu), 1.42 (s, 18H, t-Bu), 3.28 (d, $^2J = 14.5$ Hz, 2H, $ArCH_2Ar$), 3.36 (s, 12H, OCH_3), 3.44 (d, $^2J = 15.2$ Hz, 4H, $ArCH_2Ar$), 4.13 (s, 4H, $ArCH_2O$), 4.23 (d, $^2J =$ 14.5 Hz, 2H, $ArCH_2Ar$), 4.47 (d, $^2J = 15.2$ Hz, 4H, $ArCH_2Ar$), 6.89–7.08 (m, 8H), 7.29 (s, 4H), 7.39 (s, 2H). Anal. Calc. for $C_{82}H_{105}O_6Br$: C, 77.76; H, 8.36; Br, 6.31. Found: C, 77.77; H, 8.46; Br, 5.99%.

4.4. Synthesis of 5,11,17,23,29,35-hexa-tert-butyl-37,38,40,41-tetramethoxy-39,42-[2-azido-1,3-phenylenebis(methyleneoxy)]calix[6]arene (1d)

To a suspension of NaH (60%, 970 mg, 24 mmol) in THF (6 ml) was added a solution of **2d** [5d] (1.34 g, 1.2 mmol) in THF (54 ml) and DMF (6 ml). After this mixture was stirred at room temperature for 1.5 h, methyl iodide (3.0 ml, 48 mmol) was added, and the reaction mixture was refluxed for 2 h. After addition of water, the mixture was poured into 1 M aq. HCl, extracted with $CHCl_3$, and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was separated by WCC (SiO_2–$CHCl_3$) and further purified by GPLC to give **1d** (1.08 g, 77%). **1d**: colorless crystals (from CH_2Cl_2–hexane), m.p. 192–198°C (dec). ^{1}H-NMR (270 MHz, $CDCl_3$, 77°C in a sealed tube) δ 1.06 (s, 36H, t-Bu), 1.31 (s, 18H, t-Bu), 3.33 (d, $^2J = 14.5$ Hz, 2H, $ArCH_2Ar$), 3.38 (s, 12H, OCH_3), 3.47 (d, $^2J = 15.5$ Hz, 4H, $ArCH_2Ar$), 4.21 (s, 4H, $ArCH_2O$), 4.28 (d, $^2J = 14.5$ Hz, 2H, $ArCH_2Ar$), 4.36 (d, $^2J = 15.5$ Hz, 4H, $ArCH_2Ar$), 6.84 (d, $^4J = 2.3$ Hz, 4H), 7.04 (d, $^4J = 2.3$ Hz, 4H), 7.07 (t, $^3J = 7.4$ Hz, 1H), 7.22 (s, 4H), 7.31 (d, $^3J = 7.4$ Hz, 2H). ^{13}C-NMR (68 MHz, $CDCl_3$, 77°C in a sealed tube) δ 30.4 (t), 30.7 (t), 31.5 (q), 31.6 (q), 34.2 (s), 34.3 (s), 60.3 (q), 71.3 (t), 124.8 (d), 125.2 (d), 126.4 (d), 127.0 (d), 127.5 (d), 132.7 (s), 132.9 (s), 133.1 (s), 133.9 (s), 137.6 (s), 145.1 (s), 145.3 (s), 153.9 (s), 154.3 (s). IR (KBr) ν_{N3} 2114 (s), 2141 (s) cm^{-1}. HRMS (FAB) observed m/z 1172.7466 ($[M+H]^+$), calc. for $C_{78}H_{98}O_6N_3$ 1172.7460. Anal. Calc. for $C_{78}H_{97}O_6N_3$: C, 79.89; H, 8.34; N, 3.58. Found: C, 79.90; H, 8.59; N, 3.33%.

4.5. Synthesis of 37,38,40,41-tetramethoxy-39,42-[2-tert-butylthio-1,3-phenylenebis(methyleneoxy)]-calix[6]arene (1e)

To a suspension of KH (1.70 g, 42.4 mmol) in THF (7.5 ml) was added a solution of **2e** [5d] (1.24 g, 1.50 mmol) in THF (67.5 ml) and DMF (7.5 ml). After stirring at room temperature for 1.5 h, methyl iodide (7.6 ml, 122 mmol) was added at room temperature and the reaction mixture was stirred for 3 h. After addition of water, the reaction mixture was poured into 1 M aq. HCl, extracted with $CHCl_3$, and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was separated by DCC (SiO_2–$CHCl_3$) to give **22** (1.08 g, 82%). **22**: colorless crystals (from CH_2Cl_2–EtOH), m.p. 151–153°C. ^{1}H-NMR (500 MHz, $CDCl_3$, 57°C) δ 1.00 (s, 9H, t-Bu), 2.62 (br s, 6H,

OCH_3), 3.08 (br s, 6H, OCH_3), 3.46 (d, $^2J = 15.9$ Hz, 2H, $ArCH_2Ar$), 3.50 (d, $^2J = 13.6$ Hz, 1H, $ArCH_2Ar$), 3.71 (d, $^2J = 14.5$ Hz, 1H, $ArCH_2Ar$), 3.74 (d, $^2J = 15.7$ Hz, 2H, $ArCH_2Ar$), 4.08 (d, $^2J = 13.6$ Hz, 1H, $ArCH_2Ar$), 4.19 (d, $^2J = 14.5$ Hz, 1H, $ArCH_2Ar$), 4.35 (d, $^2J = 15.9$ Hz, 2H, $ArCH_2Ar$), 4.49 (d, $^2J = 9.6$ Hz, 2H, $ArCH_2O$), 4.88 (d, $^2J = 15.7$ Hz, 2H, $ArCH_2Ar$), 5.68 (d, $^2J = 9.6$ Hz, 2H, $ArCH_2O$), 6.46–7.50 (m, 21H). ^{13}C-NMR (125 MHz, $CDCl_3$, 57°C) δ 30.6 (q), 32.8 (t), 33.5 (t × 2), 33.9 (t), 47.2 (s), 59.6 (q), 59.8 (q), 76.1 (t), 122.6 (d), 123.0 (d), 123.2 (d), 127.8 (d), 127.9 (d), 128.6 (d), 128.8 (d), 129.4 (d), 129.8 (d), 131.2 (d), 131.4 (d), 133.59 (s), 133.69 (s), 133.75 (s), 133.88 (s), 133.91 (s), 134.1 (s), 134.2 (s), 143.5 (s), 157.4 (s), 157.5 (s), 157.7 (s). HRMS (FAB) observed m/z 882.3926 (M^+), calc. for $C_{58}H_{58}O_6S$ 882.3954. Anal. Calc. for $C_{58}H_{58}O_6S$: C, 78.88; H, 6.62; S, 3.63. Found: C, 78.61; H, 6.62; S, 3.71%.

4.6. Synthesis of 37,38,40,41-tetramethoxy-39,42-[5-tert-butyl-2-tert-butylthio-1,3-phenylenebis-(methyleneoxy)]calix[6]arene (**1f**)

To a suspension of KH (115 mg, 2.85 mmol) in THF (0.5 ml) was added a solution of **2f** (89 mg, 0.10 mmol) in THF (4.5 ml) and DMF (0.5 ml). After stirring at room temperature for 1.5 h, methyl iodide (0.5 ml, 8 mmol) was added at room temperature and the reaction mixture was stirred for 3 h. After addition of water, the reaction mixture was poured into 1 M aq. HCl, extracted with $CHCl_3$, and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was separated by PTLC (SiO_2–$CHCl_3$) to give **1f** (44 mg, 47%). **1f**: colorless crystals (from CH_2Cl_2–MeOH), m.p. 177–179°C. ^{1}H-NMR (500 MHz, $CDCl_3$, 57°C) δ 0.95 (s, 9H, t-Bu), 1.34 (s, 9H, t-Bu), 2.29 (br s, 6H, OCH_3), 2.77 (br s, 6H, OCH_3), 3.33 (d, $^2J = 14.4$ Hz, 1H, $ArCH_2Ar$), 3.44 (d, $^2J = 15.9$ Hz, 2H, $ArCH_2Ar$), 3.79 (d, $^2J = 13.9$ Hz, 1H, $ArCH_2Ar$), 3.80 (d, $^2J = 16.5$ Hz, 2H, $ArCH_2Ar$), 3.93 (d, $^2J = 13.9$ Hz, 1H, $ArCH_2Ar$), 4.28 (d, $^2J = 14.4$ Hz, 1H, $ArCH_2Ar$), 4.52 (d, $^2J = 15.9$ Hz, 2H, $ArCH_2Ar$), 4.71 (d, $^2J = 10.5$ Hz, 2H, $ArCH_2O$), 4.88 (d, $^2J = 16.5$ Hz, 2H, $ArCH_2Ar$), 5.88 (d, $^2J = 10.5$ Hz, 2H, $ArCH_2O$), 6.54–6.74 (m, 8H), 6.91–7.25 (m, 10H), 7.72 (s, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$, 57°C) δ 30.5 (t), 30.7 (q), 31.1 (q), 32.0 (t), 33.9 (t), 34.8 (s), 35.8 (t), 47.8 (s), 59.5 (q × 2), 76.6 (t), 122.4 (d), 123.1 (d), 123.2 (d), 128.0 (d), 128.1 (d), 128.2 (d), 128.3 (d), 129.2 (d), 129.9 (d), 130.2 (s), 132.1 (d), 133.2 (s), 133.6 (s), 133.8 (s), 134.2 (s), 134.8 (s × 2), 143.5 (s), 152.3 (s), 157.2 (s), 157.7 (s), 158.1 (s). HRMS (FAB) observed m/z 938.4547 (M^+), calc. for $C_{62}H_{66}O_6S$ 938.4580. Anal. Calc. for $C_{62}H_{66}O_6S$: C, 79.28; H, 7.08; S, 3.41. Found: C, 79.07; H, 7.22; S, 3.46%.

4.7. Synthesis of 37,38,40,41-tetramethoxy-39,42-[2-tert-butylsulfinyl-1,3-phenylenebis(methyleneoxy)]-calix[6]arene (**1g**)

To a solution of **1e** (442 mg, 0.50 mmol) in CH_2Cl_2 (5 ml) was added a solution of mCPBA (80%, 130 mg, 0.60 mmol) in CH_2Cl_2 (5 ml) at 0°C. After stirring at the same temperature for 3 h, the mixture was washed with aqueous $NaHCO_3$ and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was separated by DCC (SiO_2–CH_2Cl_2) to give **1g** (360 mg, 81%). **1g**: colorless crystals (from CH_2Cl_2–MeOH), m.p. 112°C (dec, determined by DSC). Anal. Calc. for $C_{55}H_{56}O_7S{\cdot}H_2O$: C, 75.95; H, 6.59; S, 3.50. Found: C, 76.07; H, 6.38; S, 3.97%.

4.8. Thermolysis of **1g** in toluene: preparation of sulfenic acid **1h**

A toluene solution (3 ml) of **1g** (45 mg, 0.050 mmol) in a glass tube of 8 mm diameter and 180 mm length was sealed in vacuo. The tube was heated at 80°C for 4 h and opened. After removal of the solvent, the residue was separated by WCC (SiO_2–hexane:CH_2Cl_2 = 1:1 then CH_2Cl_2) to give **1h** (41 mg, 97%). **1h**: colorless crystals, m.p. 182 °C (dec). ^{1}H-NMR (500 MHz, $CDCl_2CDCl_2$, 120°C) δ 2.39 (br s, 1H, SOH), 3.54 (br d, $^2J = 13.9$ Hz, 2H, $ArCH_2Ar$), 3.56 (s, 12H, OCH_3), 3.65 (d, $^2J = 15.7$ Hz, 4H, $ArCH_2Ar$), 4.08 (d, $^2J = 13.9$ Hz, 2H, $ArCH_2Ar$), 4.20 (br d, $^2J = 15.7$ Hz, 4H, $ArCH_2Ar$), 4.59 (s, 4H, $ArCH_2OAr$), 6.65–6.84 (m, 11H), 7.04–7.09 (m, 6H), 7.22–7.23 (m, 4H). IR (CH_2Cl_2) ν_{OH} 3479 (m), 3282 (m) cm^{-1}. HRMS (FAB) observed m/z 842.3245 (M^+), calc. for $C_{54}H_{50}O_7S$ 842.3277.

4.9. Pyrolysis of **1g** in the solid state

Into four glass tubes of 1 mm diameter and 80 mm length was loaded **1g** (43 mg, 0.048 mmol). The tubes were sealed in vacuo, and soaked for 60 s in an oil bath heated at 160°C. The contents were taken up with CH_2Cl_2. After removal of the solvent, the residue was subjected to PTLC (SiO_2–CH_2Cl_2) to give **1h** (31 mg, 76%) along with recovered **1g** (6 mg, 15% recovery).

4.10. Reaction of **1h** with methyl propiolate

A solution of **1h** (30 mg, 0.035 mmol) and methyl propiolate (0.16 ml, 1.8 mmol) in $CDCl_3$ (0.5 ml) in a glass tube of 8 mm diameter and 180 mm length was sealed in vacuo. The tube was heated at 50°C for 16 h and opened. After removal of the solvent, the residue was separated by WCC (SiO_2–CH_2Cl_2 then CH_2Cl_2:MeOH = 100:3) to give **1i** (28 mg, 86%). **1i**: colorless crystals (from CH_2Cl_2–MeOH), m.p. 190–

195°C (dec). IR (CH_2Cl_2) $\nu_{C=O}$ 1724 (s), 1716 (s) cm^{-1}. HRMS (FAB) observed m/z 927.3481 ($[M+H]^+$), calc. for $C_{58}H_{55}O_9S$ 927.3567. Anal. Calc. for $C_{58}H_{54}O_9S \cdot 3H_2O$: C, 71.00; H, 6.16; S, 3.27. Found: C, 71.24; H, 5.88; S, 3.19%.

4.11. Synthesis of 1,3-bis(phenoxymethyl)-2-tert-butylthiobenzene

A mixture of 1,3-bis(bromomethyl)-2-*tert*-butylthiobenzene [5d] (89 mg, 0.25 mmol), phenol (52 mg, 0.55 mmol), and powdered K_2CO_3 (277 mg, 2.00 mmol) in DMF (2.5 ml) was stirred at room temperature for 2 days. After filtration, the solvent was removed and the residue was partitioned between $CHCl_3$ and saturated aqueous NH_4Cl. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was separated by DCC (SiO_2–hexane:CH_2Cl_2 = 3:1) to give 1,3-bis(phenoxymethyl)-2-*tert*-butylthiobenzene (95 mg, quant.). Colorless crystals, m.p. 95–96°C. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.31 (s, 9H, t-Bu), 5.46 (br s, 4H, $ArCH_2O$), 6.94–6.99 (m, 6H), 7.27–7.31 (m, 4H), 7.45 (t, ^3J = 7.7 Hz, 1H), 7.65 (d, ^3J = 7.7 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 31.6 (q), 49.3 (s), 68.5 (t), 114.8 (d), 120.9 (d), 128.0 (d), 129.4 (s), 129.5 (d), 129.6 (d), 143.5 (s), 158.7 (s). HRMS (EI, 70 eV) observed m/z 378.1676, Calc. for $C_{24}H_{26}O_2S$ 378.1654.

4.12. Synthesis of 1,3-bis(phenoxymethyl)-2-tert-butylsulfinylbenzene (5)

To a solution of 1,3-bis(phenoxymethyl)-2-*tert*-butylthiobenzene (83 mg, 0.22 mmol) in CH_2Cl_2 (4 ml) was added a solution of mCPBA (80%, 57 mg, 0.26 mmol) in CH_2Cl_2 (4 ml) at 0°C. The mixture was stirred for 1 day, during which the temperature was raised to room temperature. The mixture was washed with 5% aqueous $NaHCO_3$ and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was separated by DCC (SiO_2–CH_2Cl_2) to give **5** (74 mg, 85%). **5**: colorless crystals, m.p. 109–113°C (dec). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.32 (s, 9H, t-Bu), 5.10 (d, ^2J = 12.2 Hz, 1H, $ArCH_2O$), 5.37 (d, ^2J = 12.2 Hz, 1H, $ArCH_2O$), 5.75 (d, ^2J = 13.3 Hz, 1H, $ArCH_2O$), 5.77 (d, ^2J = 13.3 Hz, 1H, $ArCH_2O$), 6.94–7.86 (m, 13H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 24.4 (q), 59.8 (s), 64.9 (t), 66.3 (t), 114.8 (d), 114.9 (d), 120.9 (d), 121.4 (d), 128.4 (d), 129.5 (d), 129.6 (d), 130.2 (d), 131.4 (d), 133.7 (s), 138.1 (s), 141.2 (s), 158.1 (s), 158.6 (s).

4.13. Thermolysis of 5 in toluene-d_8

A solution of **5** (6.6 mg, 0.017 mmol) in toluene-d_8 (1 ml) in an NMR tube was sealed in vacuo. After heating at 80°C for 4 h, **5** disappeared. At this time the signals of 2,6-bis(phenoxymethyl)benzene sulfenic acid (**6**) were observed by ^{1}H-NMR (270 MHz) at δ 5.14 (s, 4H, $ArCH_2OPh$) and 3.5 (br s, 1H, SOH) along with those of 2,6-bis(phenoxymethyl)phenyl 2,6-bis(phenoxymethyl)benzenethiosulfinate (**8**). The molar ratio of **6** to **8** was determined as 1:0.61 by the intensity ratio of the $ArCH_2OPh$ methylene protons. After removal of the solvent, the molar ratio of **6** to **8** had changed to 1:1.44. The residue was separated by WCC (SiO_2–hexane:CH_2Cl_2 = 1:1 then CH_2Cl_2) to afford only **8** (5.4 mg, 98%), no **6** being detected. **8**: colorless crystals, m.p. 152–153°C (dec). ^{1}H-NMR (500 MHz, $CDCl_3$, 57°C) δ 5.38 (d, ^2J = 13.1 Hz, 2H, $ArCH_2O$), 5.14 (d, ^2J = 13.1 Hz, 2H, $ArCH_2O$), 5.54 (br s, 4H, $ArCH_2O$), 6.89–6.94 (m, 12H), 7.16–7.21 (m, 8H), 7.49 (t, ^3J = 7.8 Hz, 2H), 7.52 (t, ^3J = 7.6 Hz, 2H), 7.63 (d, ^3J = 7.6 Hz, 1H), 7.69 (br d, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 66.1 (t), 68.6 (t), 115.1 (d), 115.2 (d), 121.2 (d), 121.5 (d), 125.6 (s), 128.5 (d), 128.8 (d), 129.5 (d), 129.6 (d), 131.8 (d), 132.5 (d), 138.8 (s), 143.9 (s × 2), 158.4 (s), 158.6 (s). HRMS (FAB) observed m/z 659.1892 ($[M+H]^+$), calc. for $C_{40}H_{35}O_5S_2$ 659.1926.

4.14. Thermolysis of 5 in toluene-d_8 followed by treatment with methyl propiolate

A solution of **5** (11.3 mg, 0.029 mmol) in toluene-d_8 (1 ml) in an NMR tube was sealed in vacuo. The tube was heated at 80°C for 0.5 h. At this time the molar ratio of **5**, **6**, and **8** was found to be 0.77:1.2:1 (by ^{1}H-NMR). After the tube was opened, methyl propiolate (0.26 ml, 2.9 mmol) was added to the solution and the mixture was left for 1.5 h at room temperature. After removal of the solvent and excess methyl propiolate, the residue was separated by PTLC (SiO_2–CH_2Cl_2) to give thiosulfinate **8** (4.8 mg, 51%) and methyl *trans*-[2,6-bis(phenoxymethyl)phenylsulfinyl]-acrylate (**7**) (2.3 mg, 19%) along with recovered **5** (2.8 mg, 25% recovery). **7**: colorless crystals, m.p. 111–113°C (dec). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.20 (d, ^2J = 12.2 Hz, 2H, $ArCH_2O$), 5.51 (d, ^2J = 12.2 Hz, 2H, $ArCH_2O$), 6.73 (d, ^3J = 15.3 Hz, 1H, CH = C*H*CO_2Me), 6.94–7.01 (m, 6H), 7.28–7.32 (m, 4H), 7.53–7.65 (m, 3H), 7.90 (d, ^3J = 15.3 Hz, 1H, S(O)C*H* = CH). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 52.3 (q), 66.3 (t), 114.6 (d), 121.5 (d), 124.8 (d), 129.7 (d), 129.9 (d), 132.0 (d, CH=*C*HCO_2Me), 136.6 (s), 138.4 (s), 149.3 (d, S(O)*C*H=CH), 157.7 (s), 164.0 (s). HRMS (FAB) observed m/z 423.1318 ($[M+H]^+$), calc. for $C_{24}H_{22}O_5S$ 423.1266.

4.15. X-ray crystallographic analysis of 1a

The single crystals of **1a** were grown by slow evaporation of a saturated solution in toluene at room temperature. The intensity data were collected on an

Enraf–Nonius CAD-4 diffractometer with Cu–K_α radiation ($\lambda = 1.5418$ Å) and the structure was solved by direct methods (MULTAN 78) [11] using a program system UNICS III. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 4692 observed reflections [$I > 3.00\sigma(I)$] and 478 variable parameters with R (R_w) = 0.079 (0.091). Compound **1a** was solvated by two molecules of toluene. The bridging *m*-xylylene moiety including the Br atom exhibited inversional disorder with regard to the center of symmetry, while the structure of calix[6]arene moiety was found common to both of the disordered molecules. . The crystal data for this molecule are summarized in Table 1.

4.16. X-ray crystallographic analysis of **1h**

The single crystals of **1h** were grown by slow evaporation of a saturated solution in toluene and ethanol at room temperature. The intensity data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo–K_α radiation ($\lambda = 0.71069$ Å), and the structure was solved by direct methods (SIR88) [12] and expanded using Fourier techniques (DIRDIF92) [13]. The bridging *m*-xylylene moiety including the SOH group exhibited inversional disorder with regard to the center of symmetry, while the structure of the calix[6]arene moiety was found common to both of the disordered molecules. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms except for those of the SOH group and the solvent were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1948 observed reflections [$I > 3.00\sigma(I)$] and 336 variable parameters with $R(R_w) = 0.117(0.135)$. The crystal data for this molecule are summarized in Table 1.

Table 1
Summary of crystallographic data and intensity collection for **1a** and **1h**

	1a·$2C_6H_5CH_3$	**1h**·$C_6H_5CH_3$
Formula	$C_{78}H_{97}BrO_6$ ·$2C_6H_5CH_3$	$C_{54}H_{50}O_7S$ ·$C_6H_5CH_3$
Temperature (K)	296	296
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	12.495(3)	11.487(3)
b (Å)	15.238(3)	13.776(4)
c (Å)	11.535(3)	7.915(1)
α (°)	111.68(1)	90.19(2)
β (°)	100.73(1)	89.89(2)
γ (°)	90.14(1)	105.29(2)
V (Å^3)	1992.2(9)	1208.2(5)
Z	1	1
Calculated density (g cm^{-3})	1.160	1.285
Reflections measured	5902	5853
Reflections (unique)	4692	5573
R [a]	0.079	0.117
R_w [b]	0.091	0.135
Goodness of fit	1.60	4.13

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $R_w = [(\Sigma w|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$.

5. Supplementary material

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, reference code TOTCAG for **1a** and reference code TEYFOS for **1h**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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