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Synthesis and Properties of Sulfur-Bridged Analogs of *p-tert*-Butylcalix[4]arene[1]

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Abstract : *p-tert*-Butylcalix[4]arene analogs in which up to four methylene bridges were replaced by sulfur bridge(s) were synthesized. NMR studies indicated that the thiacalixarenes were conformationally much more flexible than the parent calixarene in $CDCl_3$ solution; the flexibility was greater with increasing number of the sulfur bridge. The thiacalixarenes serve as inclusion hosts for some organic compounds, forming 2:1 (host:guest) crystalline complexes in many cases.
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Calixarenes, cyclic *p*-substituted phenol-formaldehyde oligomers, are of current interest as versatile hosts and candidates for synthetic receptors and enzymes.[2] Considerable efforts have been made on the modification to develop their potential; many "lower rim" and "upper rim" functionalized calixarenes have appeared in the literatures.[2] Calixarene analogs containing elements other than carbon as bridge are also of interest in this regard.

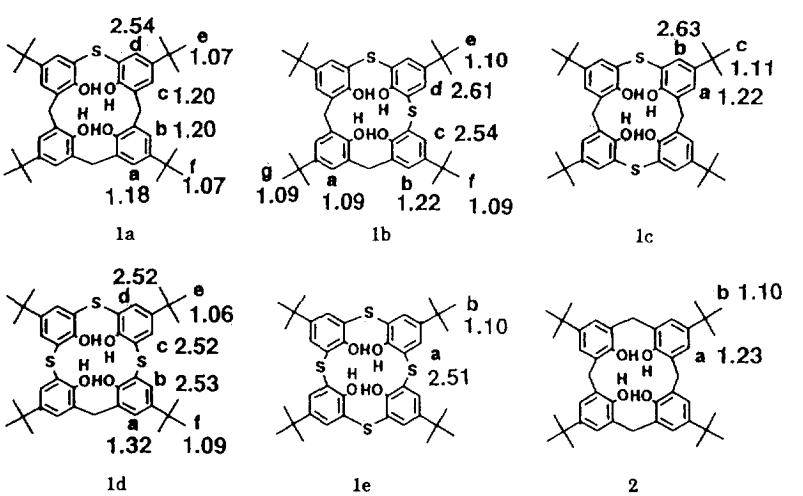
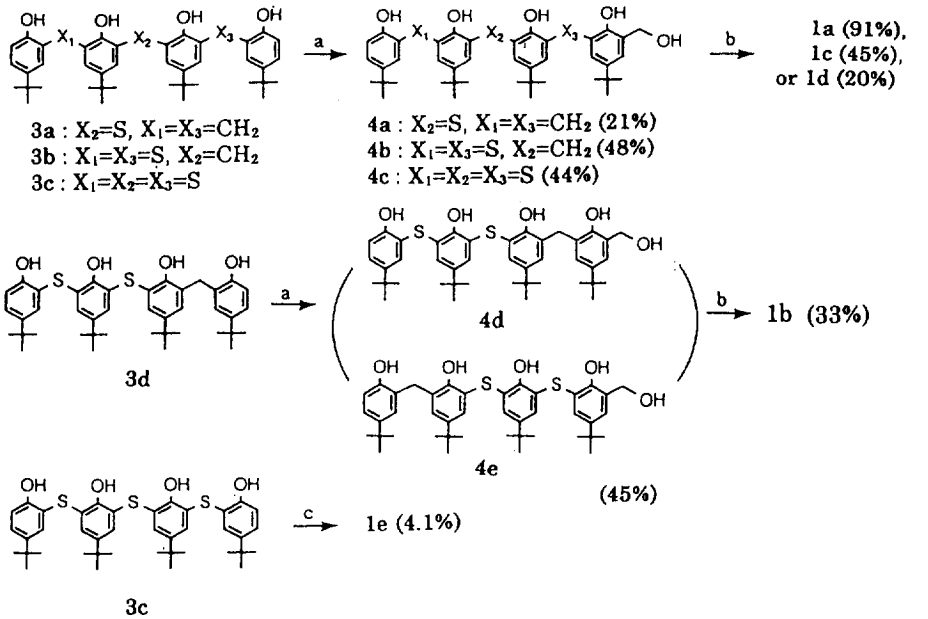


Fig. 1. Thiacalixarenes **1** and their ^1H NMR relaxation times T_1 [s]



Scheme 1. a) HCHO aq., 10% NaOH (or KOH), MeOH, 50~60 ℃. b) HCl, AcOH, high dilution conditions, reflux. c) SCl_2, CH_2Cl_2, room temp..

The replacement of the carbon bridge with other element will have an effect on the conformational and complexation properties of the calixarenes by changing the mode of the circular intramolecular hydrogen bonding characteristic for the calixarenes. Further, some of the hetero atoms can serve as additional coordination sites with the aid of the lone-pair electrons and undergo further modification easily. To our knowledge there is only one precedent, however; silicon-bridged calix[4]arene[3] was presented by König *et al.* recently. As an extension of the study on the inclusion properties of acyclic phenol-formaldehyde oligomer analogs,[4] we investigated the synthesis of sulfur-bridged calix[4]arenes **1** (Fig.1), a new family of the calixarene analogs,[5] their inclusion properties, and dynamic behavior in solution.

The thiacalixarenes **1a-d** were synthesized *via* the corresponding acyclic tetramers **3**[6] by a stepwise procedure; hydroxymethylation of the tetramers **3** with formaldehyde in the presence of 10% NaOH (or KOH), followed by acid-catalyzed cyclization of the resulting alcohols **4** under high dilution conditions (Scheme 1). The hydroxymethylation of **3d** with two neighboring sulfur bridges afforded an isomeric mixture of alcohols, **4d** and **4e** (1:1.3) , which was cyclized to yield **1b**. The yields in the final step drastically decrease from 91% for **4a** to 20% for **4c** with increasing number of the sulfur bridge in the acyclic tetramers **3**. This reflects the greater sensitivity of the C_{Ar}-S bond length and/or C_{Ar}-S-C_{Ar} bond angle[7] in the sulfur bridge to the construction of the cyclic tetramers **1**. The fully sulfur-bridged

Table 1. Crystalline inclusion compounds of **1**[a]

Guest (G)	Thiacalixarene (H)					
	1a	**1b**	**1c**	**1d**	**1e**	**2**
	(H : G)					
benzene	1:1	1:1	2:1	2:1	2:1	1:1
toluene	1:1	2:1	+	+	−	1:1
o-xylene	2:1	+	+	−	−	1:1
acetone	2:1	1:2	2:1	−	−	1:2
methanol	−	−	−	−	−	*
dioxane	1:1	1:1	1:1	1:1	1:1	1:2
dichloromethane	2:1	1:1	2:1	2:1	2:1	1:1
1,2-dichloroethane	2:1	1:1	2:1	2:1	2:1	1:1
1,2-dibromoethane	2:1	1:1	2:1	2:1	−	1:1

[a] + host-guest ratio is not clear. − host-guest complex does not form. * not determined because of low solubility of the host.

calixarene **1e** was prepared in poor yield (4.1%) by the reaction of the acyclic tetramer **3c**[6] with SCl_2. Several attempts to prepare **1e** by other methods were unsuccessful. The structures of thiacalixarenes **1** were characterized by elemental analyses and spectral data.

The thiacalixarenes **1** serve as inclusion hosts for some liquid organic compounds; **1d** and **1e** having more than three sulfur bridges are somewhat inferior in the inclusion ability (Table 1). It is interesting to note that the inclusion behavior of the parent calixarene **2** is apparently influenced by replacing the methylene bridge(s) by sulfur. Thus, in contrast to the parent calixarene **2** which forms 1:1 or 1:2 (host:guest) complexes, the thiacalixarenes **1**, except for **1b**, form 2:1 complexes in many cases.

The IR (KBr disk) and ^{1}H NMR (270 MHz; $CDCl_3$) spectral data suggest that the circular intramolecular hydrogen bonding which contributes to the cone conformation of the parent calix[4]arene **2** exists among the OH groups in the molecules of **1** as well (Table 2). Replacement of the CH_2 group with sulfur, however, weakens the hydrogen bonding, probably as a result of increasing size of the macrocyclic ring in **2**. Thus, the IR spectra of **1** display OH stretching bands in the 3170-3300 cm^{-1} region, while **2** shows the band at 3160 cm^{-1}; the band moves to higher frequency with increasing number of the sulfur bridge. Likewise, each sulfur bridge shifts the OH proton resonance of **2** *ca.* 0.2 ppm to the higher field.

^{13}C NMR spectra of the thiacalixarenes **1**, except for the fully sulfur-bridged **1e**, show the $ArCH_2Ar$ methylene carbon signals at δ 32.7-33.1 indicative of *syn*-oriented adjacent phenol rings in the calix[4]arenes.[10] The CH_2 protons in the ^{1}H NMR spectra of **1a-d**

Table 2. Partial spectral data, coalescence temperatures (T_c), energy barriers (Δ G‡) to conformational inversion, and ^{1}H relaxation times T_1

Compd.	ν_{OH}[a] (cm^{-1})	δ_{OH}[b] (ppm)	δ_{CH_2} (ppm)	δ_{CH_2}[c] (J, Hz; $\Delta\delta$, ppm)	T_c (°C)	Δ G‡ (kcal mol^{-1})	T_1 (s)[d] Ar	t-Bu
2	3160	10.34	32.7	4.26, 3.54(13.9;0.72)	58	15.5	1.23	1.10
1a	3170	10.13	32.9	4.27, 3.57(13.8;0.70)	45	14.8	1.53	1.07
			32.7	4.27, 3.56(13.8;0.71)				
1b	3210	9.95	32.8	4.27, 3.59(14.0;0.68)	38	14.5	1.87	1.09
1c	3210	9.93	33.1	4.27, 3.60(13.9;0.67)	30	14.1	1.93	1.11
1d	3240	9.70	33.1	4.28, 3.62(13.9;0.66)	28	14.0	2.22	1.08
		9.79						
1e	3300	9.53	—	—	(17)[e]	(13.5)[e]	2.51	1.10

[a] in KBr. [b] in $CDCl_3$ at 270MHz. [c] at −30 °C. [d] mean value. [e] estimated using the linear T_1 *vs* T_c or Δ G‡ plot.

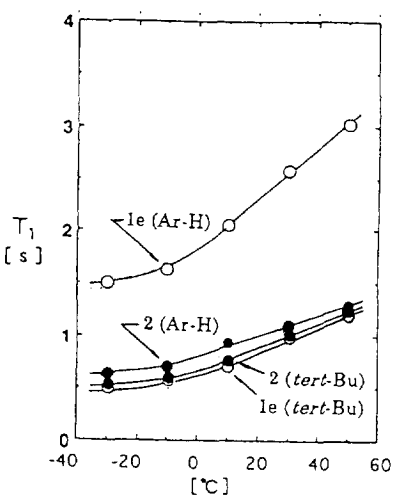


Fig. 2. Temperature dependence of T_1 values of **1e** and **2**

appeared as two broad peaks of equal intensity at room temperature and a singlet at temperature above *ca.* 60 °C. The two broad peaks resolve into a pair (or pairs) of doublets at low temperature; the difference ($\Delta\delta$) in the chemical shifts between the geminal protons is in the range of 0.66-0.71. The behavior indicates that, as predicted by the carbon resonance, the two phenol rings connected with each CH_2 group in the molecules are in a *syn*-orientation with the aryl rings somewhat flattened,[10,11] and that ring inversion of the diarylmethane units through the annulus of the macrocyclic ring occurs. The conformational inversion is slow on the NMR time scale at the low temperature but rapid at the higher temperature in the $CDCl_3$ solution. The coalescence temperatures (T_c) and the

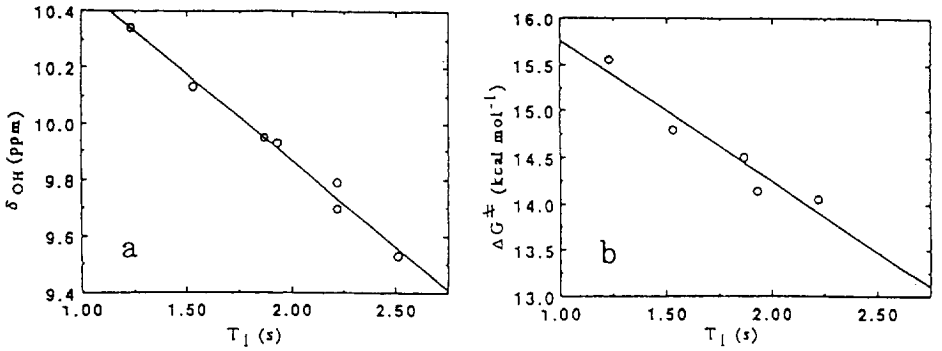


Fig. 3. Correlation between T_1 for the aromatic protons and δ_{OH} or $\Delta G^{\ddagger}$

free energy barriers ($\Delta G^{\ddagger}$) for the conformational inversion which are calculated[12] from the coalescence data are shown in Table 2. Since all the adjacent phenol rings in the molecule are *syn*-oriented, it follows that **1a** exists in a cone conformation as the parent calixarene **2**; the free energy barrier (14.8 kcal mol^{-1}) for the interconversion between the two mirror-image cone conformations is 0.7 kcal mol^{-1} lower than that for **2**. Based on the strong intra-molecular hydrogen bonding observed among the OH groups in the molecules and the CPK molecular models which show that they achieve the most effective intramolecular hydrogen bonding in the cone conformation, the highly sulfur-bridged calixarenes **1b-e** are considered to prefer the cone conformation and behave in a similar manner as **1a** and **2** in the solution. Thus, the T_c and $\Delta G^{\ddagger}$ values for the inversion of the diarylmethane units of **1b-d** practically represent those of the cone-cone interconversion, indicating that the conformational mobility of **1** becomes greater with increasing number of the sulfur bridge.

Measurements of ^{1}H NMR relaxation times (T_1) were made to gain a deeper insight into dynamic behavior of **1** in solution (Fig. 1). The technique has been successfully utilized for elucidating complexation[13] and conformational mobility[14] of some calixarene derivatives. We previously used the T_1 values for a comparison of the conformational behavior of *p-tert*-butyloxocalix[n]arene homologs.[15] More remarkable is that, regardless of the position and the number of the sulfur bridges, the butyl groups have almost the same T_1 values. In addition, the thiacalixarenes **1** are characterized by high T_1 values for the aromatic protons adjacent to the sulfur bridge compared with those next to the CH_2 group. The difference in the T_1 values suggests another type of movement of the aromatic rings coupled with the ring inversion. The T_1 values show a temperature dependence, as illustrated for **1e** (Fig. 2). The values decrease with decreasing temperature, reaching to almost constant below -30 ℃. This is also the case for the parent calixarene **2**, suggesting a similarity in the dynamic behavior between the two. Interestingly, the mean T_1 values for the aromatic protons in the molecules of **1** and **2** give an excellent linear correlation with the strength of the intramolecular hydrogen bonding as judged, *e.g.*, by the OH chemical shifts in the NMR spectra, correlation coefficient R^2 being 0.986 (Fig. 3a).

The finding implies that the strength of the intramolecular hydrogen bonding closely correlates to the total mobility of the aromatic rings in these molecules. The linear relationship is also observed between the T_1 and T_c or $\Delta G^{\ddagger}$ values for the conformational inversion of the diarylmethane units (Fig. 3b; R^2 = 0.936 and 0.925, respectively). These results add support for the assumption that **1** preferentially adopt cone conformation and behave similarly to the parent **2** in the solution. By use of the linear T_1 *vs.* T_c or $\Delta G^{\ddagger}$ plot, T_c and $\Delta G^{\ddagger}$ values for the fully sulfur-bridged **1e**, which lacks the CH_2 group, are estimated from its T_1 value (2.51[s]) to be 17 °C and 13.5 kcal mol^{-1}, respectively.

EXPERIMENTAL

All melting points are uncorrected. IR (KBr disk) and mass spectra (70 eV) were recorded on a Hitachi 228A and on a Hitachi UMU-6MG spectrometer, respectively. ^1H NMR spectra were obtained in $CDCl_3$ on a JEOL JNM-EX270 (270 MHz) spectrometer using TMS as an internal reference, while ^{13}C NMR spectra (22.6 MHz) on a Hitachi R-90H spectrometer. The ^1H NMR assignments of the thiacalixarenes were confirmed by NOE experiments. The ^1H relaxation time T_1 measurements were made by the inversion recovery method at 25 ℃; the deviation of the T_1 values is within 5%.

3-[3-[3-(5-*tert*-Butyl-2-hydroxyphenylthio)-5-*tert*-butyl-2-hydroxyphenylthio]-5-*tert*-butylsalicyl]-5-*tert*-butyl-2-hydroxybenzylalcohol (4d) and 3-[3-[3-(5-*tert*-Butylsalicyl)-5-*tert*-butyl-2-hydroxyphenylthio]-5-*tert*-butyl-2-hydroxyphenylthio]-5-*tert*-butyl-2-hydroxybenzylalcohol (4e); General Procedure for the Hydroxymethylation of the Acyclic Tetramers 3.

To a solution of the acyclic tetramer[6] (**3d**; 200 mg, 0.292 mmol) in methanol (4 ml), 10% aqueous KOH (1 ml) was added under ice-cooling. Then, formaldehyde solution (37%, 0.5 ml) was added dropwise over a period of 5 min and the solution was stirred at 55 ℃ for 20 hr under N_2. After being cooled to room temperature, the reaction mixture was acidified to pH 5 with 10% HCl and extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and then with water, and dried (Na_2SO_4). The solvent was removed and the residue chromatographed on silica gel (Wako C-200; hexane/ethyl acetate=3/1～2/1) to give the isomeric mixture of the benzyl alcohols (90 mg, 45%; **4d**:**4e** or **4e**:**4d**=1:1.3, determined by ^1H NMR) together with the starting **3d** (100 mg, 50%). Medium-pressure chromatography of the mixture on silica gel (Kanto 60N, spherical; hexane/ethyl acetate=3/1) afforded two kinds of alcohol as colorless powder and colorless prisms, the structures of which were not assigned.

The colorless powder, mp 127-128 °C (hexane); 35 mg, 16%. MS m/z 702 (M^+, 6%). IR 3360, 2960, 2870, 1600, 1490, 820 cm^{-1}. ^1H NMR δ 1.16 (9H, s), 1.18 (9H, s), 1.21 (9H, s), 1.24 (9H, s), 3.90 (2H, br s, CH_2), 4.95 (2H, s, $\underline{CH_2}OH$), 6.76 (1H, d, J=8.6 Hz), 6.94 (1H, d, J=2.3 Hz), 7.19 (1H, d, J=2.3 Hz), 7.21 (1H, d, J=2.3 Hz), 7.22-7.28 (3H, m), 7.51 (1H, d, J=2.3 Hz), 7.53

(1H, d, J=2.6 Hz). Calcd for $C_{42}H_{54}O_5S_2$: C, 71.76; H, 7.74. Found: C, 71.85; H, 7.64.
The colorless prisms, mp 123-124°C (hexane-ethyl acetate); 45 mg, 21%. MS m/z 702 (M^+, 12%). IR 3365, 2960, 2870, 1600, 1505, 820 cm^{-1}. ^1H NMR δ 1.21 (18H, s), 1.22 (9H, s), 1.24 (9H, s), 3.82 (2H, br s, CH_2), 4.36 (1H, t, J=5.9 Hz, $CH_2\underline{OH}$), 4.94 (2H, d, J=5.9 Hz, $\underline{CH_2}OH$), 6.57 (1H, d, J=8.6 Hz), 7.00 (1H, dd, J=8.6, 2.3 Hz), 7.15 (1H, d, J=2.3 Hz), 7.22 (1H, d, J=2.3 Hz), 7.27 (1H, d, J=2.6 Hz), 7.42 (1H, d, J=2.6 Hz), 7.46 (1H, d, J=2.6 Hz), 7.47 (1H, d, J=2.6 Hz), 7.58 (1H, d, J=2.6 Hz), 8.42 (1H, br s, OH), 8.81 (1H, br s, OH), 8.83 (2H, br s, OH). Calcd for $C_{42}H_{54}O_5S_2$: C, 71.76; H, 7.74. Found: C 71.74; H, 7.89.
The hydroxymethyl compounds **4a-c** were prepared from the corresponding tetramers **3a-c**[6] by the similar procedure described above for **4e** and **4d** except for using 10% NaOH instead of 10% KOH.

3-[3-[3-(5-*tert*-Butylsalicyl)-5-*tert*-butyl-2-hydroxyphenylthio]-5-*tert*-butylsalicyl]-5-*tert*-butyl-2-hydroxybenzylalcohol (4a).
Yield 21%. Colorless prisms, mp 116-117.5 °C (hexane). MS m/z 684 (M^+, 13%). IR 3325, 2960, 2870, 1600, 1490, 820 cm^{-1}. ^1H NMR δ 1.21 (9H, s), 1.23 (9H, s), 1.24 (18H, s), 3.82 (2H, br s, CH_2), 3.88 (2H, br s, CH_2), 4.83 (1H, t, J=6.2 Hz, $CH_2\underline{OH}$), 4.99 (2H, d, J=6.2 Hz, $\underline{CH_2}OH$), 6.49 (1H, d, J=8.6 Hz), 6.98 (1H, d, J=2.3 Hz), 6.98 (1H, dd, J=8.6, 2.6 Hz), 7.13 (1H, d, J=2.3 Hz), 7.21 (1H, d, J=2.3 Hz), 7.25 (1H, d, J=2.3 Hz), 7.28 (1H, d, J=2.3 Hz), 7.37 (1H, d, J=2.3 Hz), 7.51 (1H, d, J=2.6 Hz), 8.56 (1H, s, OH), 9.15 (1H, s, OH), 9.23 (1H, s, OH), 9.38 (1H, s, OH). Calcd for $C_{43}H_{56}O_5S$: C, 75.40; H, 8.24. Found: C, 75.25; H,8.44.

3-[3-[3-(5-*tert*-Butyl-2-hydroxyphenylthio)-5-*tert*-butylsalicyl]-5-*tert*-butyl-2-hydroxyphenylthio]-5-*tert*-butyl-2-hydroxybenzylalcohol (4b).
Yield 48%. Colorless prisms, mp 112-113.5 °C. MS m/z 702 (M^+, 12%). IR 3365, 2960, 2870, 1600, 1506, 820 cm^{-1}. ^1H NMR δ 1.20 (9H, s), 1.21 (9H, s), 1.22 (9H, s), 1.24 (9H, s), 3.83 (1H, t, J=6.3 Hz, $CH_2\underline{OH}$), 3.89 (2H, s, CH_2), 4.94 (2H, d, J=6.3 Hz, $\underline{CH_2}OH$), 6.71 (1H, d, J=8.6 Hz), 7.09 (1H, d, J=2.3 Hz), 7.18-7.30 (4H, m), 7.39 (1H, d, J=2.3 Hz), 7.47 (1H, d, J=2.6 Hz), 7.52 (1H, d, J=2.6 Hz), 7.99 (1H, br s, OH), 8.60 (1H, br s, OH), 8.69 (1H, br s, OH), 8.90 (1H, br s, OH). Calcd for $C_{42}H_{54}O_5S_2$: C, 71.76; H, 7.74. Found: C, 71.55; H, 7.83.

3-[3-[3-(5-*tert*-Butyl-2-hydroxyphenylthio)-5-*tert*-butyl-2-hydroxyphenylthio]-5-*tert*-butyl-2-hydroxyphenylthio]-5-*tert*-butyl-2-hydroxybenzylalcohol (4c).
Yield 44%. Colorless prisms, mp 86-87 °C (hexane). MS m/z 720 (M^+, 5%). IR 3390, 2960, 2870, 1600, 1480, 820 cm^{-1}. ^1H NMR δ 1.16 (9H, s), 1.18 (9H, s), 1.22 (9H, s), 1.25 (9H, s), 3.13 (1H, t, J=5.6H, OH), 4.89 (2H, d, J=5.6 Hz, $C\underline{H_2}$-OH), 6.84 (1H, d, J=8.6 Hz), 7.10 (1H, d, J=2.3 Hz), 7.20 (1H, d, J=2.3 Hz), 7.28 (1H, dd, J=8.6, 2.6 Hz), 7.32 (1H, br s, OH), 7.33 (1H, d, J=2.3 Hz), 7.38 (1H, d, J=2.3 Hz), 7.45 (1H, d, J=2.3 Hz), 7.48 (1H, d, J=2.3 Hz), 7.51 (1H, d, J=2.6 Hz), 8.00 (1H, br s, OH), 8.23 (1H, br s, OH), 8.41 (1H, br s, OH). Calcd for $C_{41}H_{52}O_5S_3$:C, 68.30; H, 7.27. Found: C, 68.17; H, 7.38.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxy-2,8-dithiapentacyclo[19.3.1.-$1^{3,7}.1^{9,13}.1^{15,19}$]octacosa-1(25),3,5,7(26),9,11,13(27),15,17,19(28),21,23-dodecaene (1b); General Procedure for the Cyclization of the Alcohols 4.

To refluxing acetic acid (500 ml) containing a small amount of HCl (2 ml) was added a solution of the isomeric mixture of alcohols, **4d** and **4e**, (420 mg, 0.6 mmol) in acetic acid (80 ml) over a period 27 hr under N_2 with stirring. During the addition, HCl (6 ml) were added to the solution in three portions at 7 hr intervals. The mixture was refluxed for 52 hr, and then the solvent was removed under reduced pressure. The products were extracted with $CHCl_3$. The extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel (Wako C-200; hexane/ethyl acetate = 3/1) to give **1b** (93 mg, 33%). Colorless crystals, mp >300 °C (hexane). MS m/z 684 (M^+, 100%). IR 3210, 2970, 1480, 880, 820 cm^{-1}. ^1H NMR δ 1.21 (9H, s, H_e), 1.21 (18H, s, H_f) 1.22 (9H, s, H_g), 3.55 (2H, br s, CH_2), 4.25 (2H, br s, CH_2), 7.08 (2H, s, H_a), 7.23 (2H, d, J=2.6 Hz, H_b), 7.47 (2H, d, J=2.6 Hz, H_c), 7.60 (2H, s, H_d), 9.95 (4H, br s, OH). ^{13}C NMR δ 31.3, 32.8, 34.0, 34.1, 120.8, 121.0, 125.8, 127.1, 127.4, 129.6, 132.3, 136.2, 144.2, 144.4, 146.7, 150.8, 155.4. Calcd for $C_{42}H_{52}O_4S_2$:C, 73.64; H, 7.65. Found:C, 73.30; H, 7.87.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxy-2-hiapentacyclo[19.3.1.$1^{3,7}$.-$1^{9,13}.1^{15,19}$]octacosa-1(25),3,5,7(26),9,11,13(27),15,17,19(28),21,23-dodecaene (1a).

Yield 91%. Colorless plates, mp >300 °C. MS m/z 666 (M^+, 100%). IR 3170, 2950, 1475, 860, 805 cm^{-1}. ^1H NMR δ 1.21 (18H ,s, H_e), 1.22 (18H, s, H_f), 3.54 (3H, br s, CH_2), 4.23 (3H, br s, CH_2), 7.06 (2H, d, J=2.3 Hz, H_b), 7.07 (2H, d, J=2.3 Hz, H_a), 7.20 (2H, d, J=2.7 Hz, H_c), 7.46 (2H, d, J=2.7 Hz, H_d), 10.13 (4H,s, OH). ^{13}C NMR δ 31.4, 32.7, 32.9, 34.0, 34.1, 121.3, 125.7, 126.0, 127.2, 127.5, 127.6, 129.5, 132.5, 144.3, 144.4, 146.6, 150.8. Calcd for $C_{43}H_{54}O_4S$: C, 77.44; H, 8.16. Found: C, 77.72; H, 8.28.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxy-2,14- dithiapentacyclo[19.3. 1.$1^{3,7}.1^{9,13}.1^{15,19}$]octacosa-1(25),3,5,7(26),9,11,13(27),15,17,19(28),21,23-dodecaene (1c).

Yield 45%. Color-less plates, mp >300 °C. MS m/z 684 (M^+, 100%). IR 3210, 2950, 1480, 880, 815 cm^{-1}. ^1H NMR δ 1.22 (36H, s, H_c), 3.60 (2H, br s, CH_2), 4.20 (2H, br s, CH_2), 7.21 (4H, d, J=2.7 Hz, H_a), 7.48 (4H, d, J=2.7 Hz ,H_b), 9.93 (4H, s, OH). ^{13}C NMR δ 31.3, 33.1, 34.0, 121.2, 126.9, 129.3, 132.5, 144.3, 150.8. Calcd for $C_{42}H_{52}O_4S_2$:C, 73.64; H, 7.65. Found: C, 73.56; H, 7.82.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxy-2,8,14- trithiapentacyclo[19.3. 1.$1^{3,7}.1^{9,13}.1^{15,19}$]octacosa-1(25),3,5,7(26),9,11,13(27),15,17,19(28),21,23-dodecaene (1d).

Yield 20%. Colorless plates, mp >300 °C. MS m/z 702 (M^+, 100%). IR 3240, 2960, 1480, 885, 815cm^{-1}. ^1H NMR δ 1.21 (18H, s, H_e), 1.22 (18H, s, H_f), 3.62 (1H, br s, CH_2), 4.20 (1H, br s, CH_2), 7.24 (2H, d, J=2.7 Hz, H_a), 7.49 (2H, d, J=2.7 Hz, H_b), 7.61 (2H, d, J=2.7 Hz, H_c), 7.62 (2H, d, J=2.7 Hz, H_d), 9.70 (2H, br s, OH), 9.79 (2H, br s, OH). ^{13}C NMR δ 31.2, 31.3, 33.1,

34.1,34.2, 120.6,120.8, 120.9, 127.0, 129.5, 132.5, 136.1, 136.4, 144.4, 144.6, 150.9, 155.5. Calcd for $C_{41}H_{50}O_4S_3$: C,70.05; H, 7.17. Found: C, 69.82; H, 7.47.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrahydroxy-2,8,14,20-tetrathiapentacyclo-[19.3.-1.$1^{3,7}$.$1^{9,13}$.$1^{15,19}$]octacosa-1(25),3,5,7(26),9,11,13(27),15,17,19(28),21,23-dodecaene (1e).

To a solution of the fully sulfur-bridged acyclic tetramer **3c**[6] (700 mg, 1 mmol) in dry CH_2Cl_2 (20 ml) was added a solution of SCl_2 (400 mg, 4 mmol) in the same solvent (10 ml). The mixture was stirred at room temperature for 2 days and then heated to reflux for 1 hr. After removing the solvent and usual work-up, the residue containing several components (TLC; **1e** R_f=0.28, Merk Silica Gel 60 F_{254}/benzene) was chromatographed on silica gel (Wako C-200/ hexane) twice to give **1e** (30 mg, 4.1%) as the first fraction. Colorless plates, mp >300 °C. MS m/z 720 (M^+, 100%). IR 3300, 2960, 1480, 885, 820cm^{-1}. ^{1}H NMR δ 1.22 (36H, s, H_b), 7.64 (8H, s, H_a), 9.53 (4H, s, OH). ^{13}C NMR δ 31.2, 34.2, 120.5, 136.2, 144.5, 155.5. Calcd for $C_{40}H_{48}O_4S_4$: C, 66.63; H, 6.71. Found: C, 66.91; H, 6.96.

Preparation of Inclusion Complex.

The thiacalixarenes **1** were recrystallized using a minimum amount of the liquid organic compounds (guest). The precipitates were collected by filtration and dried overnight at ambient temperature. The host-guest ratio was determined by means of ^{1}H NMR spectroscopy.

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