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Synthesis and Inclusion Properties of Sulfur-Bridged Analogs of Acyclic Phenol–Formaldehyde Oligomers

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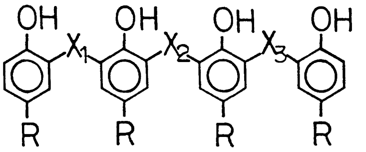
A series of compounds in which a part or all of the methylene bridges of acyclic *p*-methyl- and *p*-*t*-butylphenol–formaldehyde tetramers were replaced by sulfur bridge(s) was synthesized. It was found that though the sulfur-bridged tetramers formed crystalline host-guest complexes with a variety of organic compounds, they were different from the parent tetramers regarding their inclusion behavior. The number and position of the sulfur bridge(s), as well as the *p*-substituent of phenol in the tetramers, had a great influence upon the inclusion property. The thermal stability of complexes of the sulfur-bridged tetramers (**SSS-a,b**) with benzene, as estimated from their thermal dissociation rates, are lower than those of the parent tetramers (**CCC-a,b**).

We recently reported that acyclic *p*-substituted phenol–formaldehyde oligomers with methylene bridges ortho to the phenolic hydroxyl group formed crystalline inclusion compounds with many organic compounds, as did the corresponding cyclic oligomers, calixarenes.1) The inclusion behavior of the acyclic oligomers was remarkably influenced by the *p*-substituent of phenol and the number of phenol units; tetramers and pentamers consisting of four and five phenol units with the *p*-substituent, such as the methyl, *t*-butyl, or cyclohexyl group, were very effective in complex formation. The oligomers included quite a few molecules which had no group to participate in hydrogen-bonding, suggesting that intermolecular hydrogen-bonding between the oligomers and the guest molecules was not essential for complex formation.

An X-ray crystallographic examination of the *p*-cresol tetramer (**CCC-a**)-benzene complex revealed that hydrogen-bonding between the phenolic hydroxyl groups plays a crucial role in the construction of the host lattice.2) Namely, two molecules of the tetramer form a cyclic dimer in the crystalline complex through intramolecular hydrogen-bonding between adjacent phenolic hydroxyl groups in the molecule, as well as an intermolecular one between the phenolic hydroxyl groups of the opposite ends of the two molecules. This is in sharp contrast with the non-complexed tetramer, molecules of which are arranged in the crystalline state to chains of indefinite length by intermolecular hydrogen-bonding.3)

These results suggest that modification in the methylene bridge of the phenol–formaldehyde oligomers affects the inclusion behavior as well. A noteworthy feature of this type of oligomer is that, owing to the bridges between the rigid aromatic skeletons, they can adapt to fit guest molecules through conformational changes in complexation. In the hope of founding a new host family based on phenol–formaldehyde oligomers, we extended our study to their sulfur-bridged analogs. In the present paper we describe the synthesis of sulfur-bridged analogs of acyclic *p*-cresol- and *p*-*t*-butylphenol–formaldehyde tetramers and their ability to form crystalline inclusion compounds with organic guest molecules.



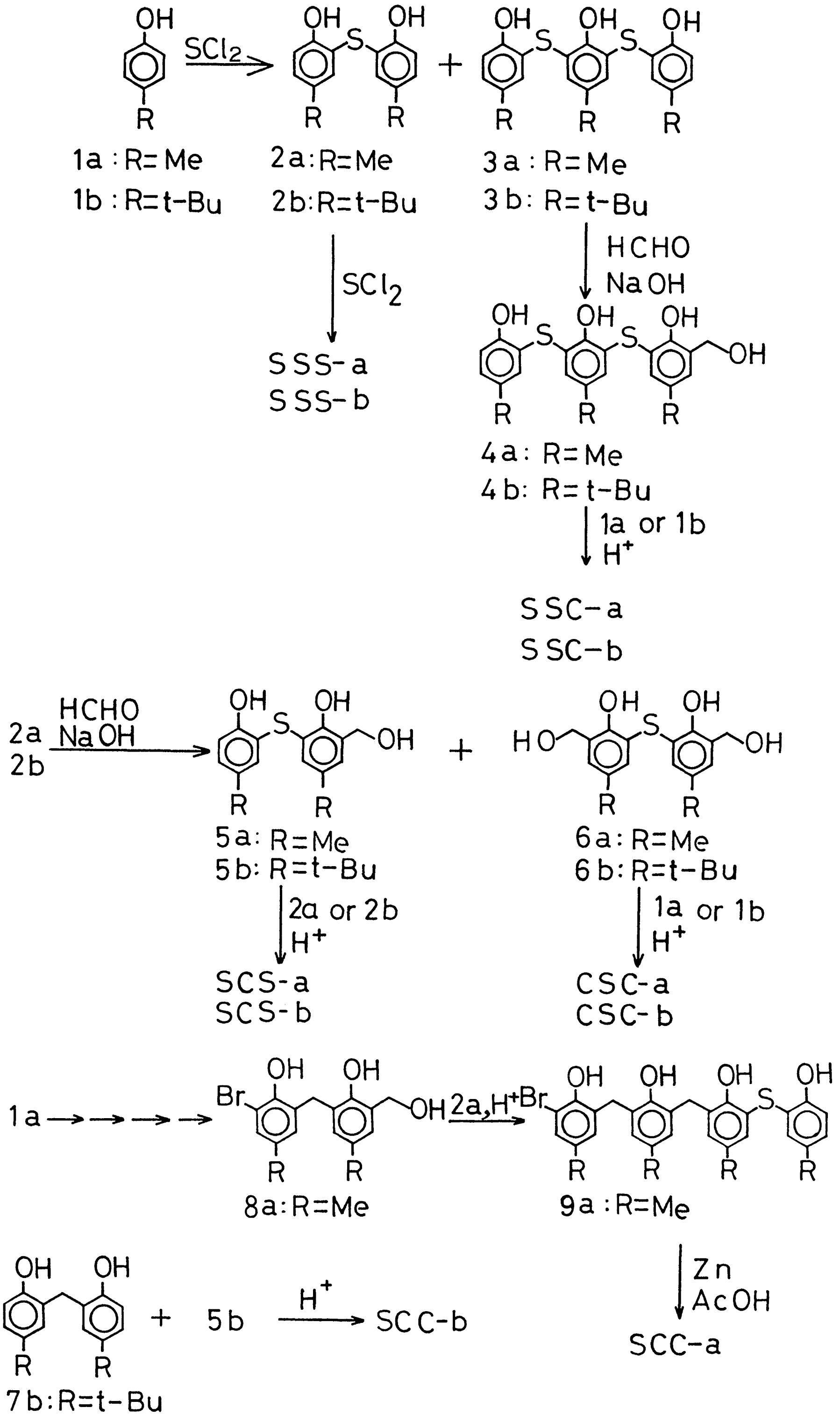
SSS: $X_1=X_2=X_3=S$
SSC: $X_1=X_2=S$, $X_3=CH_2$
SCS: $X_1=X_3=S$, $X_2=CH_2$
CSC: $X_1=X_3=CH_2$, $X=S$
SCC: $X_1=S$, $X_2=X_3=CH_2$
CCC: $X_1=X_2=X_3=CH_2$

a: R=Me
b: R=t-Bu

Results and Discussion

Synthesis of Oligomers. The sulfur-bridged analogs of *p*-cresol- and *p*-*t*-butylphenol–formaldehyde tetramers (**SSS-a,b**; **SSC-a,b**; **SCS-a,b**; **CSC-a,b**; **SCC-a,b**)4) were synthesized as shown in Scheme 1; it involves repeated sulfuration and/or hydroxymethylation of the phenols, followed by condensation of the resulting hydroxymethyl compounds with the phenols.

The reaction of the phenols (**1a,b**) with 0.2 equivalent moles of SCl_2 in CH_2Cl_2 gave phenol–sulfur dimers (**2a,b**) together with a small amount of the corresponding trimers (**3a,b**). Further reaction of **2** (**a,b**) with SCl_2 yielded all sulfur-bridged tetramers, **SSS-a** and **SSS-b**, respectively. The NaOH-catalyzed hydroxymethylation of **3** (**a,b**) with aq formaldehyde, followed by the *p*-toluenesulfonic acid (TsOH)-catalyzed condensation of the resulting hydroxymethyl compounds (**4a,b**) with *p*-cresol (**1a**) or *p*-*t*-



Scheme 1.

butylphenol (**1b**), gave tetramers, **SSC-a** and **SSC-b**, with two neighboring sulfur bridges and one methylene bridge. The symmetrical tetramers, **SCS-a** and **SCS-b**, with one central methylene bridge were synthesized by condensation of the hydroxymethyl derivatives (**5a**,**b**) of **2** (**a**,**b**) with an large excess of **2** (**a**,**b**), while the other symmetrical tetramers, **CSC-a** and **CSC-b**, with one sulfur bridge were obtained analogously from the bis(hydroxymethyl) derivatives (**6a**,**b**) of **2** (**a**,**b**) and the corresponding phenols (**1a**,**b**). On the other hand, treatment of the *p*-*t*-butylphenol–formaldehyde dimer (**7b**) with **5b** in the presence of TsOH afforded the unsymmetrical *p*-*t*-butylphenol tetramer, **SCC-b**. The unsymmetrical *p*-cresol tetra-

Table 1. Molar Ratio and the Melting Points of the Complexes of **SSS-a**, **SSC-a**, **SCS-a**, **CSC-a**, **SCC-a**,[a] and **CCC-a**[b]

Guest (G)	Host (H)											
	SSS-a		**SSC-a**		**SCS-a**		**CSC-a**		**SCC-a**		**CCC-a**	
	H:G	(°C)	H:G	(°C)	H:G	(°C)	H:G	(°C)	H:G	(°C)	H:G	(°C)
None		(138—140)		(163—164)		(133—134)		(152—154)		(180—185)		(174—178)
Cyclohexane	+	(140—148.5)	—		—		—		—		—	
Benzene	2:1	(141—152)	—		—		1:1	(142—149)	—		2:1	(172—175)
Toluene	+	(130—147)	—		—		—		—		—	
o-Xylene	—		—		—		—		—		—	
Thiophene	—		—		—		—		—		—	
Methanol	—		2:1	(108—111)	—		3:1		—		—	
Ethanol	—		2:1	(111—118)	—		—		—		—	
Dioxane	+	(135—145)	2:1	(141—150)	—		1:2	(97—116)	2:1	(167—180)	1:1	(142—143)
Acetone	—		—		—		—		—		—	
Dichloromethane	—		—		—		2:1	(155—158)	—		2:1	(161—162)
1,2-Dichloroethane	+		2:1	(85—93)	—		2:1	(148—152)	—		1:1	(144—146)
1,2-Dibromoethane	—		2:1	(94—97)	—		1:1	(118.5—130)	—		1:1	(152—153)
1,1,1-Trichloroethane	—		—		—		—		—		2:1	(145—147)
Diethylamine	1:2	(59—67)	1:2	(111—120)	1:2	(116—121)	1:2	(104—109)	1:2	(155—165)	1:1	(112—115)
Triethylamine	1:2	(77—88)	1:2	(85—110)	1:1	(84—91)	1:1	(181—185)	1:1	(120—128)	1:1	(94—102)

a) — : host-guest complex does not form. + : host : guest ratio is not clear. b) See Ref. 1.

Table 2. Molar Ratio and the Melting Points of the Complexes of **SSS-b**, **SSC-b**, **SCS-b**, **CSC-b**, **SCC-b**,[a] and **CCC-b**[b]

Guest (G)	Host (H)											
	SSS-b		**SSC-b**		**SCS-b**		**CSC-b**		**SCC-b**		**CCC-b**	
	H:G	(°C)	H:G	(°C)	H:G	(°C)	H:G	(°C)	H:G	(°C)	H:G	(°C)
None		(101.5—103)		(123—124)		(170—174)		(172—173.5)		(174.5 —177.5)		(210—211)
Cyclohexane	2:1	(120—126)	1:1	(118.5—122)	+	(170—173)	—		—		1:2	(105)
Benzene	1:1	(113—118)	2:1	(94—103)	2:1	(170—173)	—		—		2:1	(123—125)
Toluene	2:1	(105—108)	1:1	(100.5—103)	1:1	(173—174.5)	—		1:1	(168—171)	1:1	(133—135)
o-Xylene	1:1	(107—109.5)	—		1:1	(154—165)	—		1:1	(153—163)	2:1	(151—153)
Thiophene	1:1	(125—129)	2:1	(108.5—112)	—		—		—		—	
Methanol	—		—		3:1	(171—175)	—		—		—	
Ethanol	—		—		—		—		—		—	
Dioxane	+		—		+	(169.5—173)	+	(122—167)	—		2:1	(163—165)
Acetone	—		—		—		—		—		—	
Dichloromethane	+	(99.5—101.5)	2:1	(96.5—105)	—		—		—		—	
1,2-Dichloroethane	2:1	(109—113.5)	2:1	(104.5—110)	2:1	(168—172.5)	—		—		+	(165—167)
1,2-Dibromoethane	1:1	(110.5—113)	+		2:1	(153—165)	2:1	(95—158.5)	—		+	(152—153)
1,1,1-Trichloroethane	2:1	(124—130)	1:1	(119—124)	—		—		—		2:1	(109—110)
Diethylamine	1:1	(142—150)	1:1	(120—125)	1:1	(167.5—171)	1:2	(124—132.5)	1:1	(160—162)	1:2	(132—135)
Triethylamine	1:2	(108—123)	1:1	(104—108)	1:1	(120—128)	1:3	(144—148.5)	1:1	(133—143)	1:1	(130—133)

a) — : host-guest complex does not form. + : host : guest ratio is not clear. b) See Ref. 1.

mer, **SCC-a**, was obtained by the condensation of 3-(3-bromo-5-methylsalicyl)-2-hydroxy-5-methylbenzyl alcohol (**8a**)[5] with **2a**, and a subsequent debromination of the product (**9a**) with zinc powder in AcOH.

Inclusion Properties. The inclusion behavior of the tetramers towards organic molecules was examined by recrystallization of the tetramers from various organic solvents. The results are shown in Tables 1 and 2, together with those obtained for **CCC-a** and **CCC-b**.[1] It was found that the tetramers had an ability to form complexes with many organic compounds as the parent tetramers, and that the sulfur-bridged *p*-cresol and *p*-*t*-butylphenol tetramers were different from each other and from the parent tetramers regarding their inclusion behavior. The stoichiometries of the inclusion range from 3 : 1 to 1 : 3 (host : guest); 2 : 1 or 1 : 1 exist in most complexes, except for those with amines whose stoichiometric ratios are 1 : 1 or 1 : 2.[6]

Concerning the sulfur-bridged *p*-cresol tetramers, replacement of the methylene bridge(s) with sulfur(s) in the molecule of **CCC-a** tends to decrease the inclusion ability; **SCC-a**, **SCS-a**, and **SSS-a** are particularly poor. It seems that the position, rather than the number of the sulfur bridge(s), influences the ability. For example, while **CSC-a** is similar to **CCC-a**, **SCC-a** is decidedly inferior, both of the tetramers having one sulfur bridge. Likewise, **SSC-a** exhibits an inclusion property, whereas **SCS-a** and **SSS-a**, which have two terminal sulfur bridges, are almost ineffective. In spite of the low tendency for complex formation, the introduction of a sulfur bridge(s) in place of a methylene bridge(s) gave some of the tetramers (**SSC-a** and **CSC-a**) a new property to include alcohols.

On the other hand, sulfur-bridged *p*-*t*-butylphenol tetramers are, as a whole, superior to the corresponding *p*-cresol tetramers regarding complexation. Moreover, three (**SSS-b**, **SSC-b**, and **SCS-b**) out of the five tetramers form complexes with many more organic molecules than does the parent, **CCC-b**. For example, they form complexes with thiophene and aliphatic halogen compounds; **SSS-b** forms a 1 : 1 complex with 1,1,1-trichloroethylene, a water pollutant. The tetramers, **CSC-b** and **SCC-b**, with one sulfur bridge, however, show a low inclusion ability. Contrary to the observation concerning the *p*-cresol series, the number of sulfur bridge(s) seems to affect the inclusion ability in the *p*-*t*-butylphenol series.

It is interesting to note that, regardless of the *p*-substituent of the phenol, though all of the sulfur-bridged tetramers examined exhibit a high preference for aliphatic amines,[6] they lack the ability to include acetone, and neither of the tetramers of the **SCC** type in both series incorporate the aliphatic halogen compounds.

Guest preferences of the sulfur-bridged phenol tetramers, as observed, are dependent upon the *p*-substituent of the phenols, as well as both the number and position of the sulfur bridges. However, it is difficult to find an obvious rule which can explain all of the sulfur effects on the inclusion behavior. The results obtained here suggest that the tetramers build up characteristic host lattices which depend upon the combination of their building blocks. This assumption needs to be confirmed by X-ray structural studies of individual complexes.

The inclusion selectivities of **SSS-b** were examined for several equimolar mixtures of simple benzene derivatives. The results, together with those obtained for **CCC-b**, are shown in Table 3. In some cases, **SSS-b** shows a strong affinity to one guest in the guest mixtures. For example, **SSS-b** includes preferentially *o*-xylene in mixtures with benzene and *p*-xylene, and *m*-xylene in a mixture with benzene. However, **SSS-b** is generally inferior to **CCC-b** regarding inclusion selectivity. Sequences of the selectivity of **SSS-b** towards isomeric xylenes or benzene homologue are indefinite, suggesting that the conformation of the host molecule changes with the guest molecule to be accommodated.

There are only a few data available concerning the thermodynamic properties of crystalline inclusion

Table 3. Selectivity in the Complexation of **SSS-b** and **CCC-b** for an Equimolar Mixture of Guests

Guest(A)/Guest(B)	Host **SSS-b** (A)/(B)	 **CCC-b** (A)/(B)
Benzene/toluene	36/64	47/53
Benzene/*o*-xylene	8/92	0/100
Benzene/*m*-xylene	6/94	79/21
Benzene/*p*-xylene	54/46	100/0
Toluene/*o*-xylene	61/39	2/98
Toluene/*m*-xylene	37/63	86/14
Toluene/*p*-xylene	45/55	99/1
o-Xylene/*m*-xylene	51/49	77/23
m-Xylene/*p*-xylene	63/37	34/66
p-Xylene/*o*-xylene	5/95	8/92

Table 4. Kinetic Data for the Thermal Dissociation of the Complexes of **SSS-a**, **SSS-b**, **CCC-a**,[a] and **CCC-b**[a] with Benzene

Complex	Temp °C	$k\times10^4$ s^{-1}	$\Delta H^{\neq}$ $kJ\,mol^{-1}$	ln A
SSS-a : benzene	117.1	1.881		
	123.9	3.342		
	128.1	5.835		
	132.3	10.62	145.8	35.6
SSS-b : benzene	85.2	0.2969		
	99.3	0.7506		
	106.4	3.166		
	116.7	4.939	110.0	26.4
CCC-a : benzene[a]			162.6	42.1
CCC-b : benzene[a]			123.7	33.9

a) See Ref. 1.

complexes of artificial organic hosts with organic molecules.[7] In an attempt to estimate the thermal stability of the host-guest complexes, some kinetic parameters for the dissociation of **SSS-a**-benzene (host : guest=2 : 1) and the **SSS-b**-benzene complex (host : guest=1 : 1) were obtained from their dissociation rates (Table 4). The data indicate that the **SSS-a**-benzene complex is less stable than the corresponding **CCC-a**-benzene (2 : 1) complex. Assuming that the complexation mode of **SSS-a** is similar to that of **CCC-a**, the difference between the two complexes regarding thermal stability is principally attributable to difference in the lengths of the C(aromatic)-S(bridge) and C(aromatic)-C(bridge) bonds in the two host molecules.[8] Replacement of the C-C bonds with longer C-S bonds lengthens the distance between the adjacent hydroxyl groups in the molecule of **CCC-a** and, consequently, weakens the strength of the intramolecular hydrogen bonding between the adjacent hydroxyl groups. Thus, **SSS-a** more easily undergoes a conformational change in the molecule upon heating than does **CCC-a**. Alternatively, a lattice which **SSS-a** built up is too large for the guest molecule to fit. On the other hand, difference between **SSS-a**-benzene and **SSS-b**-benzene complexes in the stability arises from difference in the complexation mode.

Experimental

All melting points are uncorrected. NMR spectra were obtained on a Hitachi R-600 spectrometer at 60 MHz, using TMS as an internal reference. IR and mass (70 eV) spectra were recorded on a Hitachi EPI-S2 and on a Hitachi UMU-6MG spectrometers, respectively. TG/DTA curves were recorded on a Seiko TG/DTA 30 instrument with a heating rate of 10 °C min^{-1} under an air stream. Gas chromatographic-analyses were performed on a Hitachi K 53 chromatograph equipped with a standard golei column, U-90 (0.25 mm×90 m).

Synthesis of 2-[3-[3-(2-Hydroxy-5-methylphenylthio)-2-hydroxy-5-methylphenylthio]-2-hydroxy-5-methylphenylthio]-4-methylphenol (SSS-a). The reaction of *p*-cresol (**1a**) with SCl_2 gave 2,2′-thiobis[4-methylphenol] (**2a**; 61%);[11] 2,6-bis(2-hydroxy-5-methylphenylthio)-4-methylphenol (**3a**) was obtained as a minor product (4%).

3a: Colorless powder (hexane), mp 160—161 °C; IR (KBr) 3250, 880, 870, and 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.10 (3H, s), 2.23 (6H, s), and 6.85—7.35 (8H, m) ; MS (70 eV) *m*/*z* (rel intensity) 384 (M^+, 100). Found: C, 65.53; H, 5.28%. Calcd for $C_{21}H_{20}O_3S_2$: C, 65.59; H, 5.24%.

Sulfur dichloride (0.67 g, 6.5 mmol) was added to a solution of **2a** (8.1 g, 33 mmol) in dry CH_2Cl_2 (100 ml) over a period of 35 min at 0 °C; the mixture was stirred at the same temperature for 1 h. The solvent was evaporated and the residue chromatographed on silica gel (Wako C-200; hexane/AcOEt=4/1) to give **SSS-a** (0.83 g, 24%).

SSS-a: Colorless prisms (hexane), mp 138—140 °C; IR (KBr) 3400, 880, and 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.12 (3H, s), 2.22 (9H, s), and 6.50—7.35 (10H, m); MS (70 eV) *m*/*z* 522 (M^+, 100). Found: C, 64.62; H, 5.03%. Calcd for $C_{28}H_{26}O_4S_3$: C, 64.34; H, 5.01%.

Synthesis of 2-[3-[3-(5-*t*-Butyl-2-hydroxyphenylthio)-5-*t*-butyl-2-hydroxyphenylthio]-5-*t*-butyl-2-hydroxyphenylthio]-4-*t*-butylphenol (SSS-b). Sulfur dichloride (5.1 g, 50 mmol) was added to a solution of *p*-*t*-butylphenol (**1b**; 15 g, 0.1 mol) in dry CH_2Cl_2 (100 ml) over a period of 15 min at 0 °C. After stirring for 1 h at the same temperature, the mixture was concentrated and steam-distilled to remove any unreacted **1b**. Crystallization of the residual mass from hexane yielded 2,2′-thiobis[4-*t*-butylphenol] (**2b**; 8.85 g). The mother liquor was concentrated and subjected to medium-pressure liquid column chromatography (Kieselgel 60, 230—300 mesh; hexane/AcOEt=10/1) to afford another crop of **2b** (3.5 g, 75% in total) and 2,6-bis(5-*t*-butyl-2-hydroxyphenylthio)-4-*t*-butylphenol (**3b**; 0.75 g, 6%).

2b: Colorless prism (hexane), mp 101—102 °C; IR (KBr) 3300 and 820 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ=1.24 (18H, s), 6.28 (2H, s, OH), and 6.80—7.45 (6H, m); MS (70 eV) *m*/*z* 330 (M^+, 100). Found: C, 72.94; H, 8.13%. Calcd for $C_{20}H_{26}O_2S$: C, 72.69; H, 7.93%.

3b: Colorless needles (hexane), mp 129—130 °C; IR (KBr) 3350, 880, and 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.12 (9H, s), 1.23 (18H, s), and 6.80—7.30 (8H, m); MS *m*/*z* 510 (M^+, 24). Found: C, 70.29; H, 7.66%. Calcd for $C_{30}H_{38}O_3S$: C, 70.55; H, 7.50%.

Tetramer **SSS-b** was prepared in 51.5% yield by a similar procedure as described regarding the synthesis of **SSS-a** from **2a**.

SSS-b: Colorless needles (hexane), mp 101.5—103 °C; IR (KBr) 3400, 880, and 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.13 (18H, s), 1.25 (18H, s), and 6.70—7.65 (14H, m); MS (70 eV) *m*/*z* 690 (M^+, 100). Found: C, 69.57; H, 7.40%. Calcd for $C_{40}H_{50}O_4S_3$: C, 69.53; H, 7.29%.

Synthesis of 2-[3-[3-(2-Hydroxy-5-methylphenylthio)-2-hydroxy-5-methylphenylthio]-5-methylsalicyl]-4-methylphenol (SSC-a). To a solution of **3a** (2.0 g, 5.2 mmol) in MeOH (1 ml) a 10% NaOH solution (1 ml), and formalin (37%; 0.42 g, 5.2 mmol), were added under ice-cooling; the mixture was then stirred at 50 °C for 80 h in an atmosphere of N_2. The mixture was cooled to room temperature, acidified with 50% AcOH (pH 6), and extracted by $CHCl_3$. After the usual work-up, the product was subjected to medium-pressure column chromatography on silica gel (Kieselgel 60, 230—400 mesh; hexane/AcOEt=4/1) to give 3-[3-(2-hydroxy-5-methylphenylthio)-2-hydroxy-5-methylphenylthio]-2-hydroxy-5-methylbenzyl alcohol (**4a**; 0.65 g, 30%) and unreacted **3a** (0.6 g, 30 %).

4a: Colorless prisms (hexane-AcOEt), mp 163—164 °C; IR (KBr) 3400, 875, and 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.22 (3H, s), 2.29 (6H, s), 4.72 (2H, br s), 6.15 (1H, s, OH), and 6.60—7.35 (7H, m); MS (70 eV) *m*/*z* 384 (M^+, 93). Found: C, 63.99; H, 5.54%. Calcd for $C_{22}H_{22}O_4S_2$: C, 63.74; H, 5.35%.

A mixture of **4a** (0.65 g, 1.6 mmol), **1a** (2.0 g, 18.5 mmol), TsOH (50 mg), and benzene (20 ml) was refluxed for 24 h. The benzene was evaporated and excess **1a** removed by steam distillation. The residual mass was chromatographed on silica gel (Wako C-200; hexane/AcOEt=10/1) to give **SSC-a** (0.65 g, 80%).

SSC-a: Colorless needles (benzene), mp 130—131 °C; IR (KBr) 3400, 880, and 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.05 (3H, s), 2.10 (6H, s), 2.22 (3H, s), 4.40 (2H, s), and 6.60—7.20 (10H, m); MS (70 eV) *m*/*z* 502 (M^+, 100). Found: C, 68.97; H, 5.22%. Calcd for $C_{29}H_{28}O_4S_2$: C, 69.02; H, 5.59%.

Synthesis of 2-[3-[3-(5-*t*-Butyl-2-hydroxyphenylthio)-5-*t*-butyl-2-hydroxyphenylthio]-5-*t*-butylsalicyl]-4-*t*-butylphenol (SSC-b). Hydroxymethylation of **3b** by an analogy of the procedure described for **3a** yielded 3-[3-(5-*t*-butyl-2-hydroxyphenylthio)-5-*t*-butyl-2-hydroxyphenylthio]-5-*t*-butyl-2-hydroxybenzyl alcohol (**4b**; 40%) and unreacted **3b** (52%).

4b: Colorless powder (hexane), mp 84—87 °C; IR (KBr) 3370, 880, and 820 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.10 (9H, s), 1.16 (9H, s), 1.23 (9H, s), 4.80 (2H, br s), and 6.80—7.45 (7H, m); MS (70 eV) *m/z* 540 (M$^+$, 67). Found: C, 69.33; H, 7.34%. Calcd for $C_{31}H_{40}O_4S_2$: C, 68.85; H, 7.46%.

Tetramer **SSC-b** was prepared from **4b** and **1b** in 73% yield, as described regarding the synthesis of **SSC-a**.

SSC-b: Colorless prisms (*o*-xylene), mp 123—124 °C, IR (KBr) 3400, 880, and 820 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.12 (9H, s), 1.21 (9H, s), 1.26 (18H, s), 3.94 (2H, s), and 6.70—7.70 (10H, s); MS (70 eV) *m/z* 672 (M$^+$, 100). Found: C, 73.46; H, 7.98%. Calcd for $C_{41}H_{52}O_4S_2$: C, 73.17; H, 7.79%.

Synthesis of 2-[3-[3-(2-Hydroxy-5-methylphenylthio)-5-methylsalicyl]-2-hydroxy-5-methylphenylthio]-4-methylphenol (SCS-a). Formalin (37%; 11.3 g, 0.14 mol) was added to a mixture of **2a** (10 g, 0.04 mol), a 10% NaOH solution (30 ml) and MeOH (40 ml) over a period of 5 min at 0 °C in an N$_2$ atmosphere. After stirring at 50 °C for 26 h, the reaction mixture was cooled to room temperature, acidified to pH 5 with 10% HCl, and then extracted with CHCl$_3$. The organic layer was washed with H$_2$O and dried over Na$_2$SO$_4$. The solvent was removed, and the residue was chromatographed on silica gel (Wako C-200; hexane/AcOEt=2/1) to give 3-(2-hydroxy-5-methylphenylthio)-2-hydroxy-5-methylbenzyl alcohol (**5a**; 4.15 g, 37%) along with 3,3′-thiobis[2-hydroxy-5-methylbenzenemethanol] (**6a**; 6.7 g, 54%).

5a: Colorless prisms (benzene), mp 100—101 °C; IR (KBr) 3370, 850, and 820 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.12 (3H, s), 2.20 (3H, s), 4.68 (2H, br s), and 6.65—7.40 (5H, m); MS (70 eV) *m/z* 276 (M$^+$, 100). Found: C, 65.46; H, 5.82%. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84%.

6a: Colorless needles (CHCl$_3$), mp 133—134 °C; IR (KBr) 3350 and 880 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.20 (6H, s), 4.00—4.70 (2H, m, OH), 4.73 (4H, s), 6.90 (2H, s), and 7.15 (2H, s); MS (70 eV) *m/z* 306 (M$^+$, 100). Found: C, 62.96; H, 5.94%. Calcd for $C_{16}H_{18}O_4S$: C, 62.72; H, 5.92%.

A solution of **5a** (1.0 g, 3.6 mmol), **2a** (8.0 g, 32.5 mmol), and TsOH (50 mg) in benzene (100 ml) was stirred under reflux for 16 h. The water produced during the reaction was removed by azeotropic distillation using a Dean-Stark condenser. After removing the solvent, the residue was subjected to medium-pressure liquid column chromatography (Kieselgel 60, 230—300 mesh; hexane/AcOEt=4/1) to give **SCS-a** (0.90 g, 50%).

SCS-a: Colorless powder (benzene), mp 160—161.5 °C; IR (KBr) 3350, 860, 820 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.10 (3H, s), 2.14 (9H, s), 3.70 (2H, s), 6.48—7.35 (10H, m); MS (70 eV) *m/z* 504 (M$^+$, 100). Found: C, 68.95; H, 5.64%. Calcd for $C_{29}H_{28}O_4S_2$: C, 69.02; H, 5.59%.

Synthesis of 2-[3-[3-(5-*t*-Butyl-2-hydroxyphenylthio)-5-*t*-butylsalicyl]-5-*t*-butyl-2-hydroxyphenylthio]-4-*t*-butylphenol (SCS-b). 2,2′-Thiobis[4-*t*-butylphenol] (**2b**) was treated with formalin and 10% NaOH in MeOH, as described for **2a**, to give 3-(5-*t*-butyl-2-hydroxyphenylthio)-5-*t*-butyl-2-hydroxybenzyl alcohol (**5b**, 47%), and 3,3′-thiobis[5-*t*-butyl-2-hydroxybenzenemethanol] (**6b**, 33%) and unreacted **2b** (15%).

5b: Colorless prisms (hexane), mp 146—146.5 °C; IR (KBr) 3280, 880, and 820 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.18 (9H, s), 1.20 (9H, s), 4.80 (2H, br s), and 6.70—7.60 (5H, m); MS (70 eV) *m/z* 360 (M$^+$, 48). Found: C, 69.89, H, 7.89%. Calcd for $C_{21}H_{28}O_3S$: C, 69.96; H, 7.83%.

6b: Colorless powder (hexane), mp 93—94 °C IR (KBr) 3350 and 880 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.24 (18H, s), 4.78 (4H, s), 7.15 (2H, br s), 7.35 (2H, br s), and 7.95 (2H, br s); MS (70 eV) *m/z* 390 (M$^+$, 88). Found: C, 67.38; H, 7.80%. Calcd for $C_{22}H_{26}O_4S$: C, 67.66; H, 7.74%.

A solution of **5b** (1.0 g, 2.8 mmol), **2b** (9.2 g, 28 mmol), and TsOH (50 mg) in benzene (70 ml) was stirred under reflux for 21 h. The reaction mixture was worked up as described regarding the synthesis of **SCS-a** to give **SCS-b** (0.8 g, 43%).

SCS-b: Corless plates (hexane), mp 170—174 °C; IR (KBr) 3370, 880, and 820 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.20 (18H, s), 1.26 (18H, s), 3.90 (2H, s), and 6.70—7.65 (10H, m); MS (70 eV) *m/z* 672 (M$^+$, 100). Found: C, 73.24; H, 7.95%. Calcd for $C_{41}H_{52}O_4S_2$: C, 73.17; H, 7.79%.

Synthesis of 2-[3-[3-(5-Methylsalicyl)-2-hydroxy-5-methylphenylthio]-5-methylsalicyl]-4-methylphenol (CSC-a). A solution of **6a** (3.0 g, 9.8 mmol), **1a** (15 g, 0.14 mol), and TsOH (50 mg) in benzene (100 ml) was stirred under reflux for 10 h. After evaporating the solvent excess **1a** was removed by steam-distillation. The crude product was purified by medium-pressure liquid column chromatography (Kieselgel 60, 230—300 mesh; hexane/AcOEt=4/1) to give **CSC-a** (4.1 g, 86%).

CSC-a: Colorless prisms (hexane-AcOEt), mp 157—158 °C; IR (KBr) 3250, 865, and 815 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.20 (6H, s), 2.28 (6H, s), 3.85 (4H, s), and 6.60—7.30 (10H, m); MS *m/z* (70 eV) 486 (M$^+$, 100). Found: C, 74.23; H, 6.23%. Calcd for $C_{30}H_{30}O_4S$: C, 74.05; H, 6.21%.

Synthesis of 2-[3-[3-(5-*t*-Butylsalicyl)-5-*t*-butyl-2-hydroxyphenylthio]-5-*t*-butylsalicyl]-4-*t*-butylphenol (CSC-b): Treatment of **6b** (3 g, 7.7 mmol) with **1b** (23 g, 0.15 mmol) in a similar manner as that described for the synthesis of **CSC-a** from **6a** gave **CSC-b** (4.3 g, 85%).

CSC-b: Colorless prisms (benzene), mp 172—173.5 °C; IR (KBr) 3370, 875, and 815 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.18 (18H, s), 1.24 (18H, s), 3.91 (4H, s), and 6.60—7.55 (10H, m); MS (70 eV) *m/z* 654 (M$^+$, 100). Found: C, 77.01; H, 8.39%. Calcd for $C_{42}H_{54}O_4S$: C, 77.02; H, 8.31%.

Synthesis of 2-[3-[3-(2-Hydroxy-5-methylphenylthio)-5-methylsalicyl]-5-methylsalicyl]-4-methylphenol (SCC-a). 3-(3-Bromo-5-methylsalicyl)-2-hydroxybenzyl alcohol[5] (**8a**; 5.7 g, 17 mmol), **2a** (20.8 g, 84 mmol), and TsOH (100 mg) were dissolved in benzene (50 ml); the solution was then stirred under reflux for 9 h. After the usual work-up, column chromatography (Wako Q-200, hexane/AcOEt=3/1) of the reaction mixture yielded 2-[3-[3-(3-bromo-5-methylsalicyl)-5-methylsalicyl]-2-hydroxy-5-methylphenylthio]-4-methylphenol (**9a**; 4.2 g, 43%).

9a: Colorless prism (benzene-hexane), mp 168—170 °C; IR 3340, 860, 810 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.15 (12H, s), 3.80 (4H, s), 5.30 (4H, br s, OH), and 6.30—7.30 (9H, m); MS (70 eV) *m/z* 564 (M$^+$, 100). Found: C, 63.88; H, 5.16%. Calcd for $C_{30}H_{29}O_4SBr$: C, 63.72; H, 5.17%.

To a refluxing solution of **9a** (1.3 g, 2.3 mmol) in 80% AcOH, zinc powder (15 g, 0.23 mol) was added over a period of 1 h with stirring. After stirring under reflux for 15 h, the mixture was cooled to room temperature and filtered. The filtrate was extracted with $CHCl_3$. The residual zinc was extracted with $CHCl_3$ using a Soxhlet extractor. The combined extracts were concentrated and the residual oil subjected to medium-pressure liquid chromatography (Kiesel gel 60, 230—300 mesh; hexane/AcOEt=4/1) to give **SCC-a** (0.9 g, 80 %).

SCC-a: Colorless needles (benzene), mp 180—185 °C; IR 3300, 860, and 810 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=2.15$ (3H, s), 2.20 (6H, s), 2.25 (3H, s), 3.84 (4H, s), and 6.10—7.40 (14H, m); MS (70 eV) m/z 486 (M^+, 57). Found: C, 73.81; H, 6.25%. Calcd for $C_{30}H_{30}O_4S$: C, 74.05; H, 6.21%.

Synthesis of 2-[3-[3-(5-*t*-Butyl-2-hydroxyphenylthio)-5-*t*-butylsalicyl]-5-*t*-butylsalicyl]-4-*t*-butylphenol (SCC-b). A solution of **5b** (2.0 g, 5.6 mmol), 2-(5-*t*-butylsalicyl)-4-*t*-butylphenol (**7b**; 17.2 g, 51 mmol), and TsOH (50 mg) in benzene (100 ml) was stirred under reflux for 40 h; the water produced during the reaction was removed by azeotropic distillation using a Dean-Stark condenser. The reaction mixture was cooled to room temperature and the precipitate filtered off. The solvent was then evaporated and the residual oil (10.6 g) chromatographed (silica gel Wako Q-200, benzene) to give **SCC-b** (2.55 g, 70%) and unreacted **2b** (7.4 g).

SCC-b: Colorless powder (benzene), mp 174.5—177.5 °C IR (KBr) 3260, 880, and 820 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=1.18$ (9H, s), 1.26 (9H, s), 3.90 (4H, s), and 6.60—7.45 (10H, m) ; MS (70 eV) m/z 654 (M^+, 100); Found: C, 77.09; H, 8.59%. Calcd for $C_{42}H_{54}O_4S$: C, 77.02; H, 8.31%.

Preparation of Inclusion Complexes. The host oligomer was recrystallyzed using a minimum amount of organic solvent (guest). The precipitates were collected by filtration, when necessary, washed with hexane, and dried at ambient temperature overnight. The host-guest ratio was determined by means of ^1H NMR spectroscopy.

Selective guest inclusion was examined as follows: The tetramer **SSS-b** (500 mg) was dissolved in an equimolar mixture of guests by heating. The mixture was treated in a similar manner as the procedure described above. Upon heating the complex under reduced pressure, a liquid mixture was obtained by distillation. The ratio of the components in the distillate was determined by gas chromatography.

Kinetic Study. The weight-decreasing ratio of a complex was measured from the TG-DTA curve using Al_2O_3 as an reference. The programmed temperature was raised at a rate 10 °C min^{-1} up to each temperature. Based on the rate constants, thus obtained, the $\Delta H^{\neq}$, $\ln A$ and E_a values were calculated by a least-squares method.

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