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Inclusion Properties of Acyclic *p*-Substituted Phenol-Formaldehyde Oligomers

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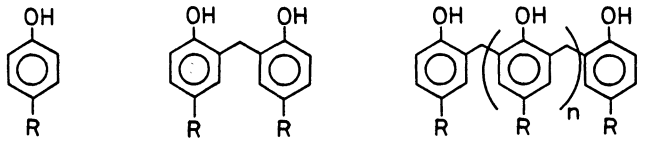
Acyclic para-substituted phenol-formaldehyde oligomers (R=H, Me, *n*-Bu, *t*-Bu, and cyclohexyl; the number of phenol units=3—6) form host-guest complexes with various organic compounds. The inclusion property of the acyclic oligomers is greatly influenced by the *p*-substituents of phenol and the number of phenol units in the oligomers; for example, a) while the *t*-butyl tetramer is effective, the corresponding butyl tetramer has a poor ability for the complex formation, and b) the tetramers and pentamers are good hosts for organic compounds, forming 2 : 1 (host : guest) complexes in many cases.

Cyclic *p*-substituted phenol-formaldehyde oligomers with methylene bridges in positions ortho to the phenolic hydroxyl group, named "calixarene," are well-known to have the property of forming host-guest complexes with organic molecules.[1] The corresponding acyclic oligomers have also been found to form stable complexes, although only a few examples are available. For example, the trimer based on phenol (phenol trimer; **3e**) forms a complex with benzene;[2] the *p*-cresol tetramer (**4a**) forms complexes with $ClCH_2CH_2Cl$[3] or toluene;[4] the *p*-*t*-butylphenol tetramer (**4b**) forms a complex with cyclohexane.[5] It has been shown by X-ray analysis that the cyclic and acyclic oligomers are quite different from each other in conformation in the crystalline state[1,2] which plays an important role in the complex formation. This suggests that the inclusion property of acyclic oligomers differ from that of cyclic ones. There has, however, been no systematic study on the inclusion property of acyclic oligomers. We have investigated the subject and found that *p*-substituents of phenol and the number of phenol units in the oligomers have a striking effect on the inclusion property. The results will be reported.



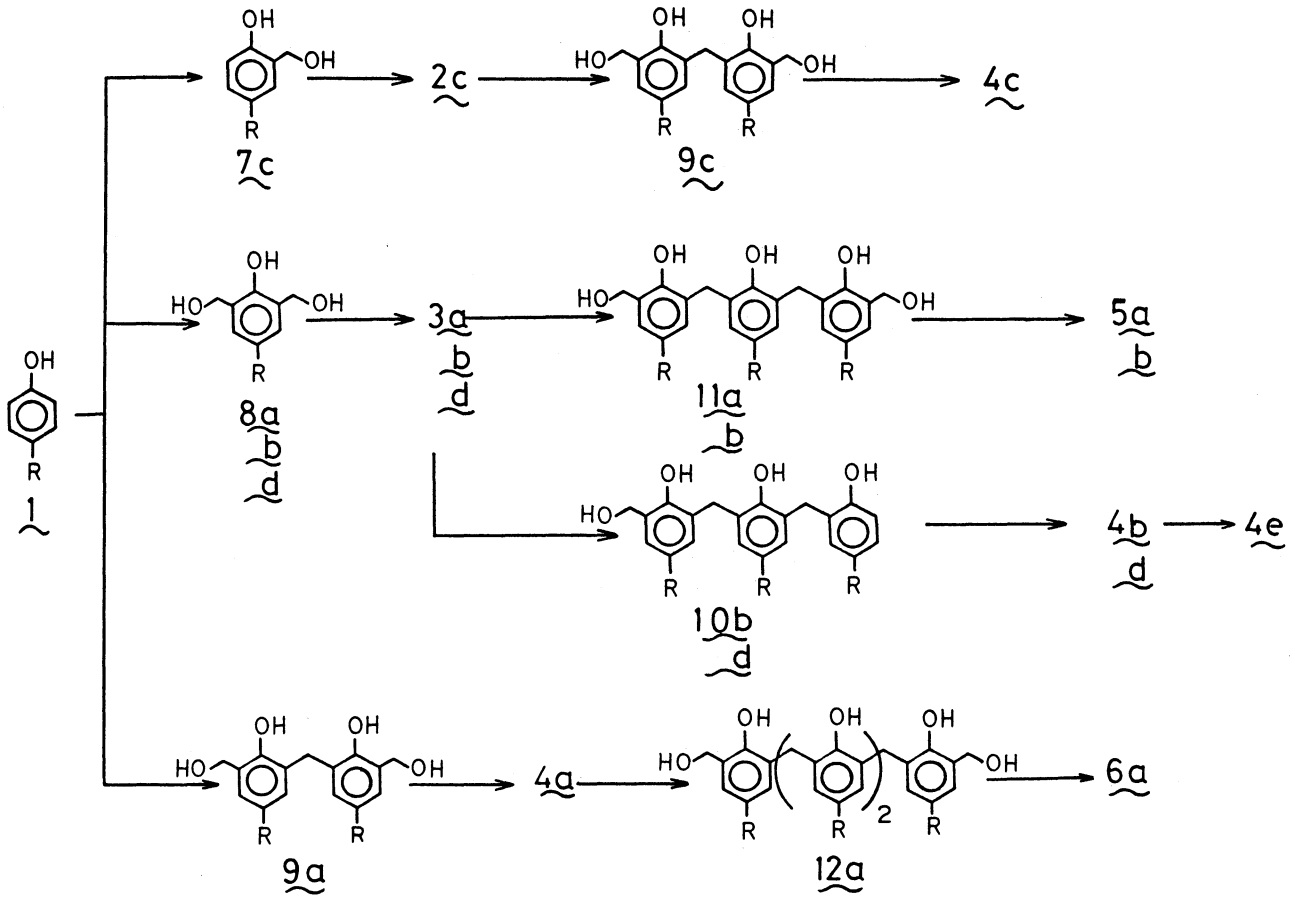
1 2 3: n=1 4: n=2 5: n=3 6: n=4

a: R=Me-
b: R=t-C_4H_9-
c: R=C_4H_9-
d: R=⬡-
e: R=H

Results and Discussion

Synthesis of Oligomers. In general, *p*-substituted phenol-formaldhyde oligomers are synthesized by the stepwise procedure[6,7] based on repeated hydroxymethylation-arylation reaction sequences on phenolic substrates. Except for the *p*-butylphenol tetramer (**4c**) and *p*-cyclohexylphenol tetramer (**4d**), all oligomers used in this study have been known. However, some of the oligomers could not be obtained in satisfactory yields by the reported procedures. Therefore, the synthetic routes were modified in such cases. For example, the tetramers **4a** and **4b** have been synthesized by the condensation of the bis(hydroxymethyl) dimer (**9a** or **9b**) with the corresponding phenol **1a** or **1b**. But **9b** could not be obtained in one step by the base-induced hydroxymethylation of *p*-*t*-butylphenol (**1b**) as described in the literature.[5] Such is also the case with the bis(hydroxymethyl) dimers **9c** and **9d**. The HCl-catalyzed condensation of **8b** with 10 molar equiv of **1b** gave the trimer **3b** in good yield. The NaOH-induced hydroxymethylation of **3b** with aq formaldehyde yielded the mono(hydroxymethyl) trimer **10b**, which was reacted with **1b** to afford **4b**. The tetramer **4d** was obtained by a similar method. On the other hand, the tetramer **4c** was synthesized by starting with 4-butyl-2-(hydroxymethyl)phenol (**7c**); the dimer **2c** which has been prepared by treating **7c** with excess *p*-butylphenol (**1c**) was hydroxymethylaled under basic conditions and the resultant bis(hydroxymethyl) dimer **9c** was again reacted with excess **1c** to afford **4c**. The phenol tetramer (**4e**) was easily produced by the debutylation of **4b** with $AlCl_3$, the procedure being analogous to that employed in the synthesis of unsubstituted calixarenes.[8] The synthetic pathway of the oligomers is illustrated in Scheme 1.

Inclusion Properties. Inclusion ability of oligomers toward organic molecules was examined by recrystallization of oligomers from various organic solvents. It was found that the oligomers had an ability to form complexes with a variety of molecules and that the complexation was dependent upon substituents in the *p*-position of phenol and the number of phenol units in the oligomers. While calixarene has been reported to form 1 : 2 (host : guest) or 1 : 1 complexes,[8-15] the corresponding acyclic oligomers form 2 : 1 complexes in many cases, suggesting that modes of host-guest association are quite different between



Scheme 1.

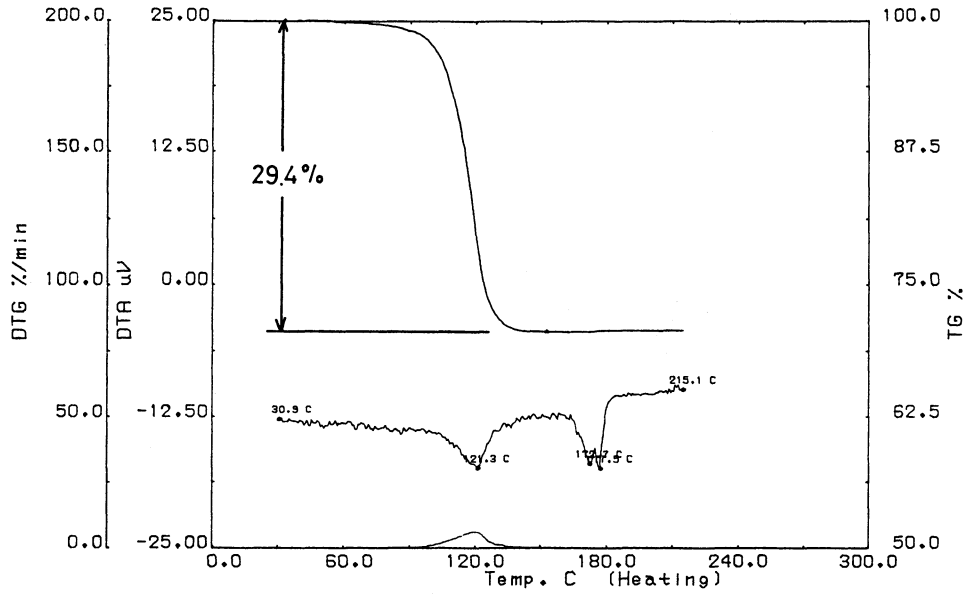


Fig. 1. TG-DTA curves of the complex of **4a** with 1,2-dibromoethane.

the cyclic and acyclic oligomers. The results are summarized in Tables 1 and 2.

The host-guest ratio was determined by ^{1}H NMR spectroscopy and thermogavimetry (TG). The TG-DTA (differential thermal analysis) patterns of a complex obtained from the tetramer **4a** and 1,2-dibromoethane are shown in Fig. 1 as an example. The TG curve indicates that the complex is stable up to 80 °C and the crystal morphology of the complex seems to change on heating. The weight loss corresponds accurately to the 1,2-dibromoethane content of the 1 : 1 complex of **4a** with 1,2-dibromoethane. The

stoichiometric ratio was ascertained by ^{1}H NMR integration as well as elemental analysis.

Table 1 shows that the inclusion properties of tetramers **4a—e** are greatly influenced by the *p*-substituent of phenol. The methyl-substituted tetramer **4a** forms host-guest compounds mainly with halogenated hydrocarbon compounds and not with aromatic compounds except for benzene. The unsubstituted tetramer **4e** is similar to **4a** in forming complexes with haloganated hydrocarbons but fails to form complexes with benzene. On the other hand, the *p*-*t*-butyl-substituted tetramer **4b** preferentially includes benzene and its alkyl derivatives. The host : guest molar ratios (2 : 1 and 1 : 1) suggest that different modes of complexation are expected between the benzene and toluene complexes. On the contrary, the butylphenol tetramer (**4c**) has a poor ability for the complex formation. The only difference between **4b** and **4c** is in the bulkiness of the butyl groups. These facts suggest that the linear and flexible butyl group at the *p*-position prevents the incorporation of the guest molecules into the crystalline lattice. The cyclohexyl-substituted tetramer **4d** differs from the others in forming complexes with ketones. Furthermore, **4d** gives a complex only with *o*-xylene among the isomeric xylenes.

Table 2 shows that the number of the phenol units also affects inclusion properties. The *p*-cresol (**4a**) and *t*-butylphenol tetramers (**4b**) and the corresponding pentamers (**5a** and **5b**) form efficiently complexes with many organic guests; the tetramer and the correspond-

Table 1. Molar Ratio and the Melting Points of the Complexes of **4a—4e**[a]

Guest (G)	Host (H)				
	4a	**4b**	**4c**	**4d**	**4e**
	H : G (°C)	H : G (°C)	H : G (°C)	H : G (°C)	H : G (°C)
None	(174—178)	(210—211)	(117—118)	(186—190)	(161—162)
Cyclohexane	−	1 : 2(105)	−	−	−
Benzene	2 : 1(172—175)	2 : 1(123—125)	−	−	−
Toluene	−	1 : 1(133—135)	−	2 : 1(186—190)	−
o-Xylene	−	2 : 1(151—153)	−	2 : 1(178—182)	−
m-Xylene	−	2 : 1(128—130)	−	−	−
p-Xylene	−	2 : 1(149—151)	−	−	−
Dioxane	1 : 1(142—143)	2 : 1(163—165)	−	−	2 : 1(147—149)
Acetone	−	−	+ (115—117)	2 : 1(167—172)	−
Methyl ethyl ketone	−	−	+ (115—117)	1 : 1(169—172)	−
Methanol	−	−	−	−	−
Ethanol	−	−	−	−	−
Dichloromethane	2 : 1(173—176)	−	−	−	2 : 1(161—162)
1,2-Dichloroethane	1 : 1(144—146)	+ (165—167)	−	2 : 1(172—176)	2 : 1(158—160)
1-Bromo-2-chloroethane	2 : 1(147—148)	−	−	1 : 1(167—170)	−
1,2-Dibromoethane	1 : 1(152—153)	+ (168—170)	−	1 : 1(172—177)	−
1,1,1-Trichloroethane	2 : 1(145—147)	2 : 1(109—110)	−	+ (165—169)	2 : 1(161—162)
Trichloroethylene	2 : 1(170—171)	−	−	−	−

a) −: host-guest complex does not form. +: host : guest ratio is not clear.

Table 2. Molar Ratio and the Melting Points of the Complexes of **3a**, **4a**, **5a**, **6a**, **3b**, **4b**, and **5b**[a]

Guest (G)	Host (H)						
	3a	**3b**	**4a**	**4b**	**5a**	**5b**	**6a**
	H : G (°C)	H : G (°C)	H : G (°C)	H : G (°C)	H : G (°C)	H : G (°C)	H : G (°C)
None	(214—215)	(221—222)	(174—178)	(210—211)	(127—128)	(218—219)	(215—216)
Benzene	+ (214—215)	+ (219—221)	2 : 1 (172—175)	2 : 1 (123—125)	2 : 1 (120—122)	2 : 1 (136—137)	2 : 1 (203—204)
Toluene	−	−	−	1 : 1 (133—135)	−	1 : 1 (139—141)	−
Acetone	−	−	−	−	−	1 : 1 (135—140)	−
Methanol	+ (214—215)	+ (224—227)	−	−	−	−	−
Ethanol	−	−	−	−	−	−	−
Dichloromethane	−	−	2 : 1 (173—176)	−	−	−	−
1,2-Dichloroethane	−	−	1 : 1 (144—146)	−	1 : 1 (119—120)	+ (135—136)	−

a)−: host-guest complex does not form. +: host : gest molar raio is not clear.

Table 3. Kinetic Data for the Thermal Dissociation of the Complexes of **4a**, **4b**, and **5a** with Benzene

Complex	Temp/°C	$k/10^{-4}\,s^{-1}$	E_a/kJ mol^{-1}	ln A
4a-benzene	116.4	1.174		
	121.8	2.178		
	126.6	3.950		
	134.3	11.07	165.9	42.1
4b-benzene	94.2	3.952		
	103.7	16.47		
	112.2	40.26		
	119.9	58.23	127.0	33.9
5a-benzene	94.7	8.953		
	98.1	17.14		
	102.4	25.25		
	111.7	57.00	123.7	33.1

ing pentamer include similar guests in each series. On the other hand, the trimers (**3a** and **3b**) exhibit almost no inclusion properties, and guests of the hexamer **6a** are rather limited. These results suggest that the molecular size of the trimers is not large enough to form lattice voids appropriate for the complex formation, whereas that of the hexamer is too large to form voids.

Besides the guests listed in the tables, the cresol tetramer (**4a**) forms complexes with chloroform (1 : 1), tetrahydrofuran (1 : 1), diethylamine, triethylamine (1 : 1), and chlorobenzene (2 : 1), but not with isopropyl alcohol, acetonitrile, cyclohexene, or aniline. None of the oligomers gave inclusion compounds with hexane or thiophene.

It should be noted that not a few molecules which possess no group to participate in hydrogen bonding are included by the oligomers; hydrogen bonding between hosts and guest molecules is not primarily responsible for complex formation. This makes a sharp contrast with the situation for many other phenolic hosts.[16-18]

Finally, in an attempt to estimate the thermal stability of host-guest complexes, some kinetic parameters for the dissociation of the complexes (host : guest=2 : 1) of **4a**, **4b**, and **5a** with benzene were obtained from their dissociation rates (Table 3). The thermal stability is dependent upon the substituents in the *p*-position or the size of the oligomers. For the tetramers methyl group is more favorable than *t*-butyl group for the formation of stable complex, whereas for the cresol oligomers the tetramer **4a** is more favorable than the pentamer **5a**.

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 a Hitachi UMU-6MG spectrometer, respectively. TG/DTA curves were recorded on a Seiko TG/DTA30 instrument with a heating rate of 10 °C min^{-1} under air stream.

The following oligomers were prepared according to the methods reported in literatures. **3a**: mp 214—215 °C (lit,[19] mp 215 °C). **4a**: mp 174—178 °C (lit,[5] mp 173 °C). **5a**: mp 127—128 °C (lit,[19] mp 130 °C). **6a**: mp 215—216 °C (lit,[19] 217 °C). **3b**: mp 221—222 °C (lit,[20] 220—221 °C). **5b**: mp 218—219 °C (lit,[20] 217—218 °C).

Synthesis of 2-[3-[3-(5-*t*-Butylsalicyl)-5-*t*-butylsalicyl]-5-*t*-butylsalicyl]-4-*t*-butylphenol (4b). Formalin (37%; 1.3 g, 16.1 mmol) was added with stirring over a period of 30 min to a mixture of **3b** (7.7 g, 16.1 mmol), 10% aqueous NaOH solution (30 ml), and methanol (30 ml) at 60 °C under an N_2 atmosphere. After stirring under reflux for 35 h, the reaction mixture was cooled to room temperature, acidified to pH 4 with 50% acetic acid, and extracted with chloroform. The organic layer was washed with water and dried over Na_2SO_4. The solvent was evaporated and the residue was chromatographed on silica gel (hexane/ethyl acetate=3/1) to give **10b** (2.7 g, 34%; mp 187—189 °C (lit,[5] mp 188.5—189 °C)), and **11b** (1.0 g, 12%; mp 143—145 °C (lit,[5] mp 140—145 °C)) together with unchanged **3b** (2.5 g, 33%).

A solution of **10b** (1.25 g, 2.48 mmol), *p*-*t*-butylphenol (**1b**; 20 g, 0.133 mol), and *p*-toluenesulfonic acid (45 mg) in benzene (30 ml) was stirred under reflux for 24 h; the water produced during the reaction was removed by azeotropic distillation using a Dean-Stark condenser. The benzene was evaporated and excess **1b** was removed by steam distillation. The residual mass was crystallized from cyclohexane to give the **4b**-cyclohexane complex (**4b**: cyclohexane=1 : 2) as a white powder (1.3 g, mp 105 °C (lit,[5] mp 105 °C)). This complex was heated at 80 °C under reduced pressure (1 mmHg; 1 mmHg=133.322 Pa) for 8 h to give cyclohexane-free **4b** as white powder (1.0 g, 64%; mp 210—211 °C (lit,[5] mp 212—213 °C)).

Synthesis of 2-[3-[3-(5-Butylsalicyl)-5-butylsalicyl]-5-butylsalicyl]-4-butylphenol (4c). To a mixture of *p*-butylphenol (**1c**; 10.0 g, 67 mmol) and formalin (5.4 g, 67 mmol) 10% aqueous NaOH solution (33 ml) was added with stirring under ice-cooling, and the reaction mixture was stirred at 50 °C for 6 h under an N_2 atmosphere. Then, another 5.4 g of formalin was added to the mixture, and the mixture was stirred for an additional 1 h. After being cooled to room temperature, the mixture was acidified with 50% acetic acid (pH 5) and extracted with benzene. After a usual work-up, the product was chromatographed on silica gel (Wako C-200; hexane/ethyl acetale=2/1) to give 4-butyl-2-(hydroxymethyl)phenol (**7c**; 2.0 g, 17%) and 4-butyl-2,6-bis(hydroxymethyl)phenol (**8c**; 7.5 g, 54%) together with unreacted **1c** (3.0 g, 30%).

7c: white plates; mp 79—80.5 °C; IR (KBr) 3450 (OH stretching) and 815 cm^{-1} (trisubstituted phenyl); ^{1}H NMR ($CDCl_3$) δ=0.92 (3H, t, J=5 Hz), 1.10—1.90 (4H, m), 2.30—2.75 (2H, m), 4.80 (2H, s), and 6.60—7.30 (3H, m); MS m/z 180 (M^+, 42%); Anal. ($C_{11}H_{16}O_2$) C, H.

8c: colorless prisms, mp 65—66 °C; IR (KBr) 3400, 3280 (OH stretching), and 880 cm^{-1} (tetrasubstituted phenyl); ^{1}H NMR ($CDCl_3$) δ=0.90 (3H, t, J=5 Hz), 1.10—1.95 (4H, m), 2.35—2.80 (2H, m), 3.80 (2H, s, OH), 4.40—5.00 (4H, m), 6.80 (2H, s), and 8.2 (1H, s, Ar-OH); MS m/z 210 (M^+, 34%); Anal. ($C_{12}H_{18}O_3$) C, H.

Hydrochloric acid (2 ml) was added to a mixture of **7c** (3.0 g, 17 mmol) and **1c** (7.7 g, 51 mmol), and the mixture was stirred at 110 °C for 6 h. After removing excess **1c** from the

reaction mixture by steam distillation, the residue was extracted with chloroform. A usual work-up gave a crude product, which was purified by medium-pressure column chromatography on silica gel (Kieselgel 60, 230—400 mesh; hexane/ethyl acetate=4/1) to give the *p*-butylphenol dimer (**2c**; 4.2 g, 79%).

2c: colorless powder; mp 66.5—67.0 °C; IR (KBr) 3250 (OH stretching) and 820 cm^{-1} (trisubstituted phenyl); ^1H NMR ($CDCl_3$) δ=0.90 (6H, t, J=5 Hz), 1.10—1.95 (8H, m), 2.30—2.75 (4H, m), 3.85 (2H, s), and 6.55—7.25 (6H, m); MS m/z (rel intensity) 314 (M^+, 100); Anal. ($C_{21}H_{28}O_2$) C, H.

To a mixture of **2c** (4.1 g, 13 mmol), 20% aqueous KOH solution (15 ml), and dioxane (20 ml), formalin (40 ml, 0.53 mol) was added over a period of 1 h under ice-cooling. The mixture was stirred at 60 °C for 20 h under an N_2 atmosphere. After being cooled to room temperature, the mixture was acidified with 50% acetic acid (pH 4) and extracted with benzene. After a usual work-up, the crude product was separated by medium-pressure liquid chromatography on silica gel (Kieselgel 60, 230—400 mesh; ethyl acetate/hexane=1/2) and recrystallized with chloroform-hexane to give the bis(hydroxymethyl) derivative (**9c**; 1.6 g, 33%) of **2c**.

9c: white powder; mp 123—124 °C; IR (KBr) 3375 (OH stretching) and 870 cm^{-1} (tetrasubstituted phenyl); ^1H NMR ($CDCl_3$) δ=0.90 (6H, t, J=5 Hz), 1.10—1.90 (8H, m), 2.00—2.80 (4H, m), 3.80 (2H, s), 4.70 (4H, s), and 6.60—7.30 (4H, m); MS m/z 372 (M^+, 14%); Anal. ($C_{23}H_{32}O_4$) C, H.

A mixture of **9c** (1.4 g, 3.7 mmol), **1c** (5.6 g, 37 mmol), and HCl (1 ml) was stirred at 100 °C for 3.5 h. Excess **1c** was removed by steam distillation and the residue was extracted with chloroform. After a usual work-up, the crude material was recrystallized from hexane to give **4c** (1.8 g, 75%).

4c: white powder; mp 117—118 °C; IR (KBr) 3250 (OH stretching), 875 (tetrasubstituted phenyl), and 820 cm^{-1} (trisubstituted phenyl); ^1H NMR ($CDCl_3$) δ=0.90 (12H, t, J=5 Hz), 1.10—2.00 (16H, m), 2.25—2.80 (8H, m), 3.80 (6H, s), and 6.75—7.30 (10H, m); MS m/z 636 (M^+, 76%); Anal. ($C_{43}H_{56}O_4$) C, H.

Synthesis of 2-[3-[3-(5-Cyclohexylsalicyl)-5-cyclohexylsalicyl]-5-cyclohexylsalicyl]-4-cyclohexylphenol (4d). A mixture of *p*-cyclohexylphenol (**1d**; 5.0 g, 28 mmol), 20% KOH (20 ml), and formalin (50 ml) was heated with stirring at 60 °C for 30 h under an N_2 atmosphere. The reaction mixture was cooled to room temperature, acidified to pH 5 with 10% aqueous HCl (50 ml), and extracted with chloroform (100 ml). After a usual work-up, the product was subjected to silica-gel column chromatography (hexane/ethyl acetate=2/1) to give 4-cyclohexyl-2,6-bis(hydroxymethyl)-phenol **8d** (5.7 g, 82%, mp 112—113 °C (lit,[21] 106—107 °C)).

A mixture of **8d** (2.7 g, 11.4 mmol), **1d** (10.0 g, 56.7 mmol), and HCl (2 ml) was stirred at 130 °C for 8 h. A work-up similar to the one described for the synthesis of **4c** from **9c** afforded the *p*-cyclohexylphenol trimer (**3d**), which was recrystallized from toluene to give pure **3d** (3.6 g, 57%).

3d: colorless needles; mp 186—188 °C; IR (KBr) 3300 (OH stretching), 865 (tetrasubstituted phenyl), and 810 cm^{-1} (trisubstituted phenyl); ^1H NMR ($CDCl_3$) δ=0.80—2.70 (33H, m), 3.90 (4H, s), and 6.60—7.30 (8H, m); MS m/z 552 (M^+, 21%); Anal. ($C_{38}H_{48}O_3$) C, H.

The hydroxymethyl derivative **10d** of **3d** was synthesized from **3d** in 33% yield in a similar manner as described for the synthesis of **10b** from **3b**.

10d: colorless needles; mp 156—157 °C; IR (KBr) 3280 (OH stretching), 865 (tetrasubstituted phenyl), and 815 cm^{-1} (trisubstituted phenyl); ^1H NMR ($CDCl_3$) δ=0.80—2.80 (33H, m), 3.80 (4H, s), 4.70 (2H, s), and 6.50—7.30 (7H, m); MS m/z 582 (M^+, 8%); Anal. ($C_{39}H_{50}O_4$) C, H.

A mixture of **10d** (1.2 g, 2.1 mmol), **1d** (4.0 g, 22.7 mmol), *p*-xylene (2 ml), and HCl (3 ml) was stirred at 130 °C for 12 h. After a usual work-up, the product was subjected to medium-pressure column chromatography on silica gel (Kieselgel 60, 230—400 mesh; hexane/ethyl acetate=5/1) to give **4d** (0.9 g, 58%).

4d: white powder; mp 179—182 °C; IR (KBr) 3250 (OH stretching), 870 (tetrasubstituted phenyl), and 815 cm^{-1} (trisubstituted phenyl); ^1H NMR ($CDCl_3$) δ=1.80—2.60 (44H, m), 3.85 (6H, s), and 6.60—7.30 (10H, m); MS m/z 740 (M^+, 0.1%); Anal. ($C_{51}H_{64}O_4$) C, H.

Synthesis of 2,2′-Methylenebis[6-(2-hydroxybenzyl)phenol] (4e). The procedure is a modification of the method used for the synthesis of calix[4]arene from *p-t*-butylcalix[4]arene.[8] Aluminum chloride (1.1 g, 8.2 mmol) was added to a solution of **4b** (1.0 g, 1.57 mmol) in toluene (50 ml), and the mixture was stirred at 50 °C for 2 h. The reaction mixture was cooled to 5 °C, and then dilute HCl (3%, 25 ml) was added to this mixture. A work-up and medium-pressure column chromatography (Kieselgel 60, 230—400 mesh, hexane/ethyl acetate=2/1) gave **4e** (0.42 g, 65%; mp 158—159 °C (lit,[2] mp 163 °C)).

Preparation of Inclusion Complex (General Procedure). The host oligomer (0.3 g) was dissolved in a minimum amount of organic solvent (guest) by heating and the solution was cooled to room temperature. The precipitates were filtrated, where necessary, washed with hexane, and dried at room temperature for 12 h. The guest-host ratio was determined by ^1H NMR (solvent $CDCl_3$) and/or TG measurements.

Kinetic Study. The weight decreasing rate of a complex was measured at four points using Al_2O_3 as an reference. The programmed temperature was raised at a rate of 10 °C min^{-1} up to each temperature. Based on the rate constants thus obtained, $\ln A$ and E_a values were calculated by the least-squares method. The results are shown in Table 3.

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