Synthesis and Inclusion Properties of Carbonyl-Bridged Analogs of Acyclic *p*-*t*-Butylphenol–Formaldehyde Oligomers

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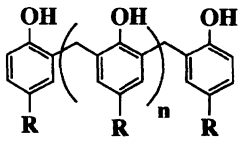
A series of compounds in which a part or all of the methylene bridges of acyclic *p*-*t*-butylphenol–formaldehyde oligomers are replaced by C=O bridge(s) has been synthesized. The carbonyl-bridged tetramers, except for that with no methylene bridge, formed crystalline host–guest complexes with various organic compounds; those with two C=O bridges were superior regarding complexation, regardless of the position of the bridges. Exclusive guest selectivity of the tetramer with one terminal C=O bridge was observed for benzene and its methyl derivatives in a two-component system. The fully carbonyl-bridged dimer, trimer, tetramer, and pentamer had no complexing-capability. The thermal stability of benzene complexes (host : guest=2 : 1) of the tetramers with one C=O bridge, as estimated from their thermal dissociation rates, are remarkably lower than that of the parent tetramer. Oximes derived from the tetramers with one C=O bridge were much more effective than the corresponding carbonyl-bridged ones regarding their complex-forming capability.

Much attention has been paid to the chemistry of calixarenes, cyclic phenol–formaldehyde oligomers,[1] because they have a host–guest complexation ability and are potential candidates for synthetic enzymes and receptors. We have recently reported that acyclic *p*-substituted phenol–formaldehyde oligomers **1** with methylene bridges *ortho* to the phenolic OH group and their sulfur-bridged analogs **2** also have an ability to form crystalline inclusion compounds with various organic compounds.[2] The inclusion behavior was remarkably influenced by the *p*-substituent of the phenol and the number of the phenol units,[2a] as well as by replacing the methylene bridge(s) with sulfur.[2b] Intra- and intermolecular hydrogen bondings between the phenolic OH groups play a crucial role in the construction of the host lattice,[2c] while intermolecular hydrogen bonding between the host and the guest molecule is not essential for complex formation. These results suggest that the introduction of a group capable of forming a hydrogen bond with the phenolic OH groups in the molecule of phenol–formaldehyde oligomers would affect the inclusion behavior.

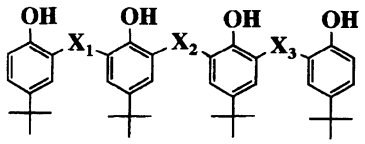
Furthermore, contrary to many other hosts, the oligomers of this type can include guest molecules through conformational changes in the host molecules ("induced-fit" type inclusion).[2c] With this in mind we synthesized carbonyl-bridged analogs (**X-XXXX**, **XXC**, **XCX**, **XCC**, and **CXC**)[3] of acyclic *p*-*t*-butylphenol–formaldehyde oligomers as well as their oxime derivatives (**ZCC**, **CZC**, **ZC**, and **Z**),[3] and investigated their ability to form crystalline inclusion compounds with organic molecules (Fig. 1).

Results and Discussion

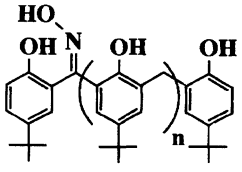
Synthesis of Hosts. Carbonyl-bridged oligomers were prepared via the routes shown in Schemes 1 and 2. Fully carbonyl-bridged oligomers **X-XXXX** were obtained by CrO_3 oxidation of tetraacetoxyl derivatives **4a**—**d** of the parent oligomers (**1a**—**b**, **1d**, and **CCC**) in acetic anhydride, followed by alkaline hydrolysis; the procedure is a modification of the synthesis of oxocalixarenes from calixarenes, which was reported by Ninagawa et al. (Scheme 1).[4] Similarly, monobromo derivative **3b** of the *p*-*t*-butylphenol–formaldehyde trimer **1b** was converted to the corresponding carbonyl-



1
R = alkyl
n = 1~4

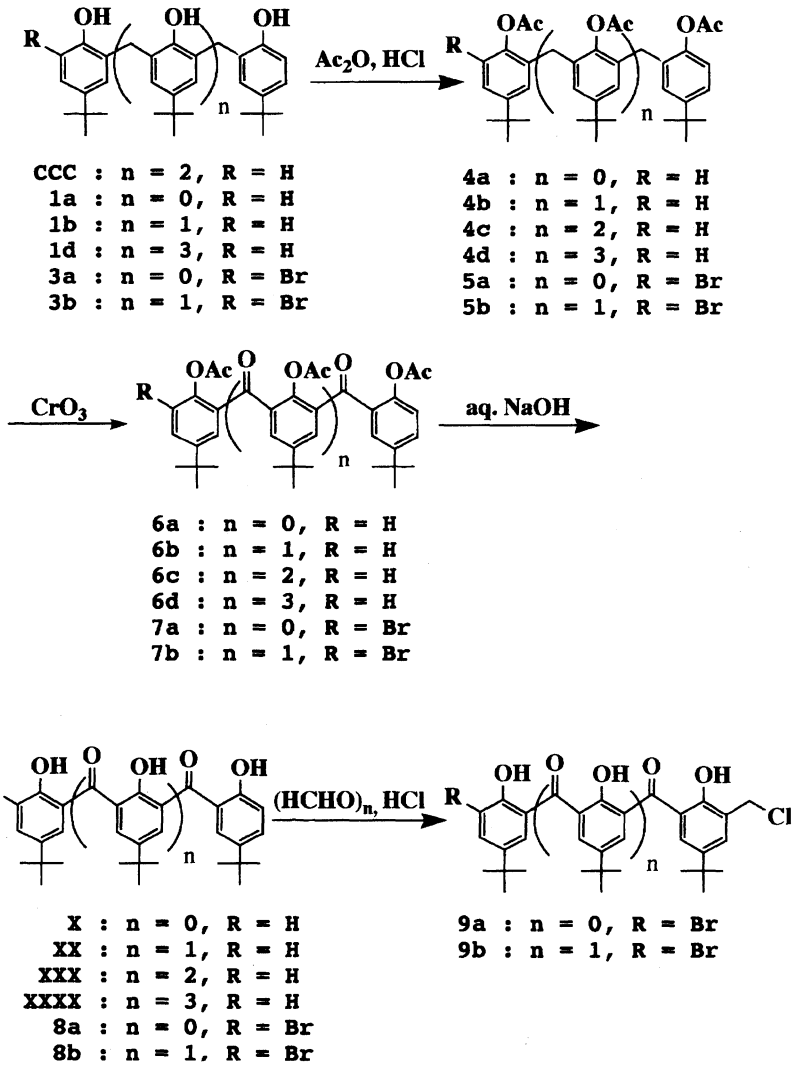


2 : X_n = CH_2 and/or S
XXX : X_1 = X_2 = X_3 = CO
XXC : X_1 = X_2 = CO, X_3 = CH_2
XCX : X_1 = X_3 = CO, X_2 = CH_2
XCC : X_1 = CO, X_2 = X_3 = CH_2
CXC : X_1 = X_3 = CH_2, X_2 = CO
ZCC : X_1 = C=NOH, X_2 = X_3 = CH_2
CZC : X_1 = X_3 = CH_2, X_2 = C=NOH
CCC : X_1 = X_2 = X_3 = CH_2



Z : n=0
ZC : n=1

Fig. 1.



Scheme 1.

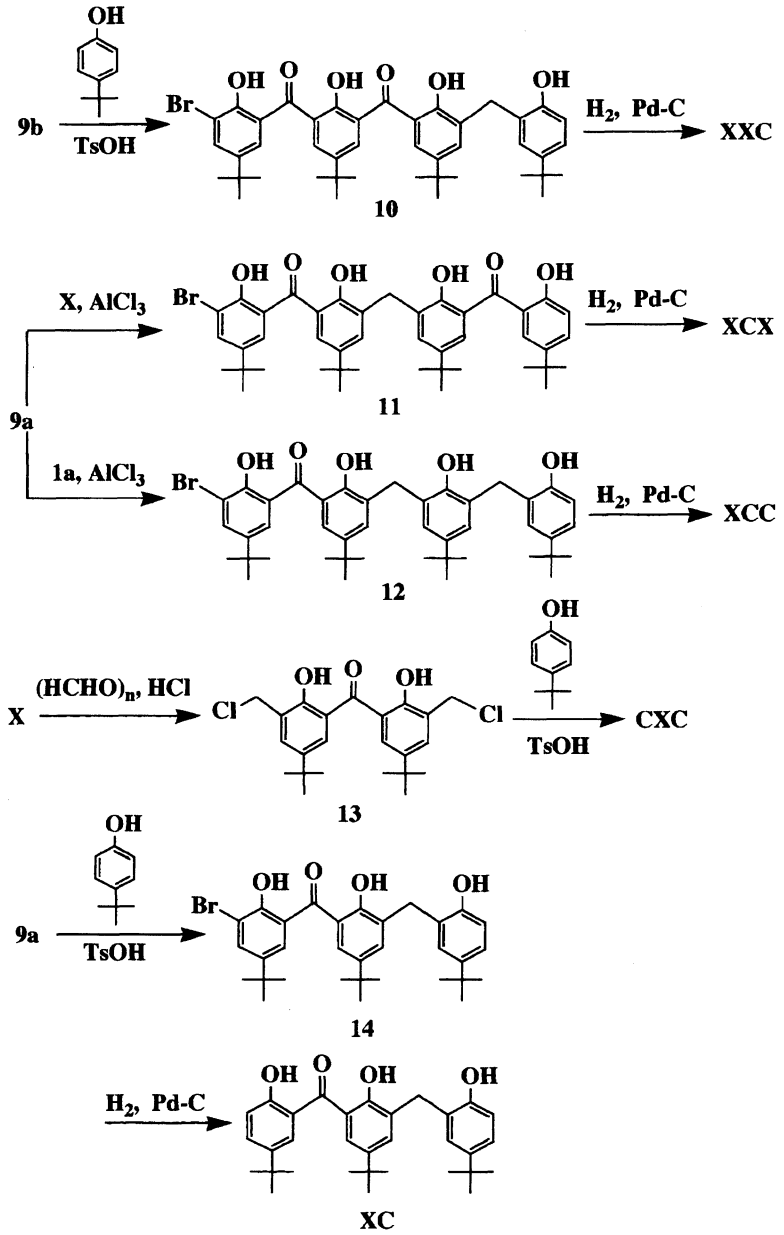
bridged trimer **8b**. The reaction of **8b** with paraformaldehyde, hydrochloric acid, and phosphoric acid in acetic acid gave the chloromethyl derivative **9b**. Subsequent *p*-toluenesulfonic acid (TsOH)-catalyzed condensation of **9b** with *p*-*t*-butylphenol gave the bromo derivative **10**. Catalytic debromination of **10** afforded a tetramer **XXC** bearing two neighboring C=O bridges. A symmetrical tetramer **XCX** with two terminal C=O bridges was synthesized in a similar manner. Namely, an $AlCl_3$-catalyzed condensation of the carbonyl-bridged dimer **X** with 2-bromo-4-*t*-butyl-6-(5-*t*-butyl-3-chloromethylsalicyloyl)phenol (**9a**), followed by debromination of condensation product **11**, yielded **XCX**.

Tetramers with one C=O bridge were synthesized as follows. The $AlCl_3$-catalyzed condensation of chloromethyl derivative **9a** with **1a** and subsequent debromination of product **12** gave an unsymmetrical tetramer **XCC**. On the other hand, bischloromethylation of **X**, followed by a TsOH-catalyzed condensation of a bischloromethyl derivative **13** with *p*-*t*-butylphenol yielded symmetrical tetramer **CXC**.

The IR spectra of the carbonyl-bridged oligomers showed C=O stretching bands at 1610—1630 cm^{-1}, indicating strong (intramolecular) hydrogen bonding between the C=O groups and the phenolic OH groups, as was expected.

Oxime derivatives, **ZCC**, **CZC**, **ZC**, and **Z**, were prepared from **XCC**, **CXC** and carbonyl-bridged *p*-*t*-butylphenol–formaldehyde trimer **XC** and dimer **X**, respectively, by a reaction with hydroxylamine in the usual manner. In the reactions of **XCC** and **XC**, unsymmetric oximes are formed, in which geometric isomers, *E* and *Z*, are considered to exist. In fact, the products comprised two components, although one was predominant in each case. Although recrystallization of the products gave one component (TLC and mp), the configuration of the major component has not yet been clarified.

Inclusion Properties. The inclusion behavior of the tetramers bearing C=O bridge(s) and the oxime derivatives was examined towards various liquid organic compounds by recrystallization method (Tables 1 and



Scheme 2.

2). The tetramers, except for **XXX**, a fully carbonyl-bridged one, were found to have an ability to form crystalline inclusion complexes with many kinds of organic compounds. They preferentially formed complexes with aromatic hydrocarbons and aliphatic polyhalogenated compounds, indicating that, as observed for **1** and **2**, hydrogen bonding was not principally responsible for the host–guest interaction in the complexation. The stoichiometries of the inclusion complexes were 2 : 1 or 1 : 1 (host(H) : guest(G)) in most cases, as those of the parent tetramer **CCC**[2a] and its sulfur-bridged analogs **2**.[2b] The inclusion behavior largely depended on the number of C=O bridges.

Contrary to parent tetramer **CCC**, as well as fully sulfur-bridged tetramer **2** ($\mathbf{X}_1 = \mathbf{X}_2 = \mathbf{X}_3 = \mathbf{S}$), **XXX** did not form an inclusion complex with any of the examined guests. The same was the cases regarding other fully carbonyl-bridged oligomers, **X**, **XX**, and **XXXX**, showing that the crystalline lattices of the parent oligomers changed markedly upon replacing all of the methylene groups with C=O groups. Isomeric tetramers, **XXC** and **XCX**, both of which had two C=O bridges, were superior to **CCC** in their complex-forming capability, and were very similar in selectivity for guest molecules. Tetramers with one C=O bridge, **XCC** and **CXC**, were inferior to **CCC**. A similar tendency was observed for sulfur-bridged analogs **2**; tetramers with one sulfur bridge are poor, while tetramers with two sulfur bridges become effective, independent of the position of the sulfur bridge in the molecules.[2b]

On the other hand, conversion of the C=O bridge into a C=NOH bridge improved the complex-forming

Table 1. Crystalline Inclusion Complexes of the C=O Bridged Analogs of *p*-*t*-Butylphenol–Formaldehyde Tetramer[a)]

Guest (G)	Host (H)											
	XXX		**XXC**		**XCX**		**XCC**		**CXC**		**CCC**[b)]	
	H : G	(°C)	H : G	(°C)	H : G	(°C)	H : G	(°C)	H : G	(°C)	H : G	(°C)
None		(194—196)		(108—110)		(115—117)		(182—184)		(221—223)		(210—211)
Cyclohexane	–		1 : 1	(96—100)	1 : 1	(99—105)	–		3 : 1	(209—217)	1 : 2	(105)
Benzene	–		3 : 1	(95—100)	1 : 1	(70—74)	2 : 1	(176—181)	2 : 1	(205—211)	2 : 1	(123—125)
Toluene	–		2 : 1	(65—72)	2 : 1	(84—89)	2 : 1	(175—178)	–		1 : 1	(133—135)
o-Xylene	–		1 : 1	(58—65)	1 : 1	(73—77)	–		+	(206—217)	2 : 1	(151—153)
m-Xylene	–		2 : 1	(58—65)	2 : 1	(73—77)	2 : 1	(174—178)	+	(205—217)	2 : 1	(128—130)
p-Xylene	–		2 : 1	(67—73)	2 : 1	(65—71)	2 : 1	(176—180)	+	(204—214)	2 : 1	(149—151)
Methanol	–		–		–		–		–		–	
Ethanol	–		–		–		–		–		–	
Dioxane	–		1 : 1	(60—66)	1 : 1	(75—79)	–		+	(217—223)	2 : 1	(163—165)
Acetone	–		+	(75—80)	3 : 1	(70—74)	–		+	(205—212)	–	
Ethyl acetate	–		+	(76—82)	+	(78—81)	–		–		–	
Dichloromethane	–		–		2 : 1	(91—96)	–		–		–	
1,2-Dichloroethane	–		2 : 1	(71—77)	2 : 1	(99—101)	–		–		+	(165—167)
1,2-Dibromoethane	–		1 : 1	(72—81)	2 : 1	(93—98)	3 : 1	(181—183)	+	(226—229)	+	(168—180)
1,1,1-Trichloroethane	–		1 : 1	(69—74)	1 : 1	(95—97)	3 : 1	(169—174)	–		2 : 1	(109—110)

a) –: host–guest complex was not formed. +: host : guest ratio was not clear. b) See Ref. 2a.

Table 2. Crystalline Inclusion Complexes of the Oxime Bridged Analogs of *p*-*t*-Butylphenol–Formaldehyde Tetramer[a)]

Guest (G)	Host (H)							
	ZCC		**CZC**		**ZC**		**Z**	
	H : G	(°C)	H : G	(°C)	H : G	(°C)	H : G	(°C)
None		(176—178)		(118—121)		(166—168)		(137—138)
Cyclohexane	+	(170—172)	2 : 1	(94—102)	–		–	
Benzene	1 : 1	(174—175)	2 : 1	(98—102)	–		–	
Toluene	1 : 1	(175—177)	+	(87—90)	–		–	
o-Xylene	+	(173—174)	2 : 1	(90—94)	+	(158—162)	–	
m-Xylene	+	(172—174)	2 : 1	(104—110)	+	(161—165)	–	
p-Xylene	+	(173—175)	2 : 1	(116—119)	+	(162—165)	–	
Methanol	1 : 1	(172—174)	–		–		+	(130—133)
Ethanol	–		–		–		1 : 1	(95—105)
Dioxane	+	(163—165)	1 : 1	(67—73)	+	(140—143)	2 : 1	(128—130)
Acetone	2 : 1	(165—166)	1 : 1	(86—89)	–		1 : 1	(131—133)
Ethyl acetate	1 : 1	(76—82)	2 : 1	(77—83)	–		–	
Dichloromethane	+	(175—173)	–		2 : 1	(163—166)	–	
1,2-Dichloroethane	2 : 1	(171—173)	2 : 1	(108—112)	+	(155—160)	–	
1,2-Dibromoethane	2 : 1	(170—172)	2 : 1	(81—85)	+	(160—162)	–	
1,1,1-Trichloroethane	2 : 1	(170—173)	1 : 1	(75—80)	2 : 1	(140—141)	1 : 1	(138—140)

a) –: host–guest complex was not formed. +: host : guest ratio was not clear.

capability. Although **XCC** and **CXC** were rather poor hosts, oximes **ZCC** and **CZC** were as effective as **XXC** and **XCX**. Even uneffective dimer **X** and trimer **XC** showed this ability upon being converted into oximes, **Z** and **ZC**.

Moreover, oximes **ZCC** and **Z** formed complexes with alcohols, in contrast to the carbonyl-bridged tetramers and the parent tetramer. This fact suggests the participation of intermolecular hydrogen bonding between the oligomers and guest molecules in the formation of the host–guest complexes. It should be pointed out that **ZCC** is different regarding the H : G ratio from that of **XCC** and **CZC** for complexes with benzene, toluene, or xylenes: 1 : 1 for **ZCC** complex, while 2 : 1 for **XCC** and **CZC** complexes. This indicates a difference in the inclusion mode between them.

The replacement of the methylene bridge(s) in **CCC** by C=O bridge(s) apparently affected the inclusion property, although it is difficult at the present stage to find a general rule which can explain the effects of the C=O bridge(s) concerning this property. An examination of the competitive inclusion in a two-component system of benzene, toluene, and xylene isomers revealed that, although **XCC** forms only a few inclusion complexes, it is excellent regarding inclusion selectivity (Table 3). Tetramer **XCC** almost completely discrimi-

Table 3. Selectivity for the Complexation of **XCC** with Benzene Derivatives

Guest(A)/Guest(B)	Host	
	XCC	**CCC**[a]
	A/B	A/B
Benzene/toluene	0/100	47/53
Benzene/*m*-xylene	0/100	79/21
Benzene/*p*-xylene	0/100	100/0
Toluene/*m*-xylene	100/0	86/14
Toluene/*p*-xylene	0/100	99/1
m-Xylene/*p*-xylene	0/100	34/66

a) See Ref. 2b.

Table 4. Kinetic Data for the Thermal Dissociation of the 2:1 Complexes of **XCC** and **CXC** with Benzene

Complex	Temp °C	$k\times10^4$ s^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}
XCC : benzene	101.4	5.062	
	110.0	6.055	
	130.4	8.545	19.28
CXC : benzene	172.3	3.901	
	180.4	4.560	
	219.9	7.190	24.15
CCC : benzene[a]			123.7
SSS : benzene[a]			110.0

a) See Ref. 2b.

nated between the two components examined: Toluene and *m*- and *p*-xylenes from benzene, *m*- and *p*-xylene from toluene, and *m*-xylene from *p*-xylene. The sequence of affinity of **XCC** for an aromatic hydrocarbon was *p*-xylene>toluene>*m*-xylene>benzene, which was rather different from that of **CCC**; **CCC** preferred benzene over *m*-xylene and toluene over *p*-xylene. Thus, it would be possible to separate one component from another in the two-component mixtures of benzene, toluene, and isomeric xylenes through crystalline inclusion with **XCC**, **CCC**, or their combination.

To evaluate the inclusion ability of a host molecule, it is required to take into account the thermal stability of its complexes as well as its complex-forming capability and selectivity. However, there have been only a limited number of data[2a,2b,5] concerning the thermal stability of crystalline inclusion complexes of synthetic organic hosts with organic guests. In this connection, some kinetic parameters of the 2:1 (H:G) complexes of **XCC** and **CXC** with benzene were determined concerning their thermal dissociation (Table 4). The data indicate that the complexes are considerably less stable than the corresponding **CCC**-complex, and that there is an essential difference in the complexation mode between complexes of the carbonyl-bridged tetramers and the **CCC**-complex. It is assumed that **CCC** forms a cyclic dimer in complexation with benzene, as does the corresponding *p*-cresol–formaldehyde tetramer,[2c] by intra- and intermolecular hydrogen bondings between the phenolic OH groups in the molecule. However, **XCC** and **CXC** are prevented from forming such a cyclic dimer due to the hydrogen bonding of the C=O group to the neighboring phenolic OH groups, resulting in the construction of inclusion lattices characteristic of the carbonyl-bridged tetramers.

Experimental

All of the 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 spectra (70 eV otherwise noted) were recorded on Hitachi EPI-S2 and Hitachi UMU-6MG spectrometers, respectively. TG/DTA curves were recorded on a Seiko TG/DTA30 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 Goley column, U-90 (0.25 mm×90 m).

4-*t*-Butyl-2-[2-acetoxy-5-*t*-butyl-3-[2-acetoxy-5-*t*-butyl-3-(2-acetoxy-5-*t*-butylbenzyl)benzyl]benzyl]-phenyl Acetate (4c). A mixture of **CCC**[2a] (3.7 g, 5.8 mmol), hydrochloric acid (3.0 ml), and acetic anhydride (60 ml) was stirred at 100°C for 4 h. The reaction mixture was poured onto ice and extracted with benzene. The benzene extract was washed with water, dried, and concentrated. The residue was chromatographed on silica gel (Wako C-200, hexane/AcOEt=4/1), giving **4c** (4.6 g, 98%): Colorless powder, mp 210—213°C; IR (KBr) 2980, 2880, 1765, 1600, 1370, 880, and 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.19 (18H, s), 1.26 (18H, s), 2.11 (6H, s), 2.14 (6H, s), 3.76 (6H, s), and 6.82—7.45 (10H, m); MS *m/z* 804 (M^+, 86%). Found: C, 76.09; H, 7.77%. Calcd for $C_{51}H_{64}O_8$: C, 76.09; H, 8.01%.

4-*t*-Butyl-2-[2-acetoxy-5-*t*-butyl-3-[2-acetoxy-5-*t*-butyl-3-(2-acetoxy-5-*t*-butylbenzoyl)benzoyl]benzoyl]phenyl Acetate (6c). A solution of CrO_3 (23 g) in water (25 ml) was added to a solution of **4c** (4.0 g, 5.0 mmol) in acetic anhydride (150 ml) under ice-cooling; the mixture was then stirred at 60°C for 1 h. The reaction mixture was poured onto ice and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with water, dried, and concentrated. The residual crude product was chromatographed on silica gel (Wako C-200; hexane/AcOEt=3/1) and recrystallized from AcOEt to give **6c** (1.3 g, 30%): Colorless powder, mp 233—237°C; IR (KBr) 2960, 1770, 1665, 1600, 1360, 1190, 870, and 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.29 (36H, s), 1.71 (6H, s), 2.03 (6H, s), and 7.04—7.74 (10H, m); MS *m/z* 846 (M^+, 1%). Found: C, 72.10; H, 7.18%. Calcd for $C_{51}H_{58}O_{11}$: C, 72.32; H, 6.90%.

4-*t*-Butyl-2-[5-*t*-butyl-3-[5-*t*-butyl-3-(5-*t*-butylsalicyloyl)salicyloyl]salicyloyl]phenol (XXX). A mixture of **6c** (1.3 g, 1.5 mmol), 10% aqueous NaOH solution (50 ml), and methanol (40 ml) was stirred at 50°C for 8 h. After the reaction mixture was acidified (pH 1) with 10% hydrochloric acid, the resultant crystals were extracted with benzene. The benzene extract was washed with water, dried, and concentrated. The residue was recrystallized from a mixture of hexane and benzene to give **XXX** (0.7 g, 71%): Yellow powder, mp 194—196°C; IR (KBr) 3420, 2965, 1625, 1600, 840, and 825 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.28 (18H, s), 1.30 (18H, s), and 6.97—7.71 (10H, m);

MS m/z 678 (M^+, 50%). Found: C, 76.09; H, 7.59%. Calcd for $C_{43}H_{50}O_7$: C, 76.08; H, 7.42%.

Bis(5-*t*-butyl-2-hydroxyphenyl)ketone (X), 4-*t*-Butyl-2-[5-*t*-butyl-3-(5-*t*-butylsalicyloyl)salicyloyl]phenol (XX), and 4-*t*-Butyl-2-[5-*t*-butyl-3-[5-*t*-butyl-3-(5-*t*-butylsalicyloyl)salicyloyl]salicyloyl]phenol (XXXX). Carbonyl-bridged oligomers, **X**, **XX**, and **XXXX** were prepared from the corresponding parent oligomers (**1a**, **1b**, and **1d**)[2a] via their acetoxyl derivatives (**4a**, **4b**, and **4d**; **6a**, **6b**, and **6d**) analogously to the preparation of **XXX**.

4a: Almost quantitative yield. Colorless oil, bp 173.5 °C/1 mmHg (1 mmHg=133.322 Pa); IR (CCl_4) 2970, 1765, 1605, and 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.27 (18H, s), 2.18 (6H, s), 3.80 (2H, s), and 6.82—7.46 (6H, m); MS m/z 396 (M^+, 63%). Found: C, 75.73; H, 8.29%. Calcd for $C_{25}H_{32}O_4$: C, 75.73; H, 8.13%.

6a: Yield, 65%. Colorless needles, mp 130.5—131°C (hexane/AcOEt); IR (KBr) 2975, 1765, 1660, and 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.32 (18H, s), 1.91 (6H, s), and 7.01—7.65 (6H, m); MS m/z 410 (M^+, 3%). Found: C, 73.11; H, 7.49%. Calcd for $C_{25}H_{30}O_5$: C, 73.15; H, 7.37%.

X: Almost quantitative yield. Yellow needles, mp 102.5—103.5°C (hexane/benzene; lit,[4] 100—102°C); IR (KBr) 3230, 2960, 1625, and 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30 (18H, s) and 7.00—7.71 (6H, m).

4b: Yield, 95%. Colorless powder, mp 120—122°C (hexane); IR (KBr) 2960, 1760, 1600, 870, and 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.18 (9H, s), 1.26 (18H, s), 2.14 (9H, s), 3.76 (4H, s), and 6.86—7.42 (8H, m); MS m/z 600 (M^+, 53%). Found: C, 75.92; H, 8.34%. Calcd for $C_{38}H_{48}O_6$: C, 75.97; H, 8.05%.

6b: Yield, 55%. Colorless oil (chromatography on silica gel; Wako C-200, hexane/AcOEt=3/1); IR (CCl_4) 2970, 1770, 1670, 1600, 880, and 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26 (27H, s), 1.98 (9H, s), and 6.98—7.71 (8H, m); MS m/z 628 (M^+, 9%). Found: C, 72.84; H, 7.31%. Calcd for $C_{38}H_{44}O_8$: C, 72.59; H, 7.05%.

XX: Yield, 59%. Yellow needles, mp 173—175°C (methanol); IR (KBr) 3440, 2975, 1630, 1610, 830, and 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.27 (18H, s), 1.32 (9H, s), and 6.97—7.70 (8H, m); MS m/z 502 (M^+, 100%). Found: C, 76.65; H, 7.73%. Calcd for $C_{32}H_{38}O_5$: C, 76.47; H, 7.62%.

4d: Yield, 82%. Colorless powder, mp 67—69°C (chromatography on silica gel; Wako C-200, hexane/AcOEt=4 : 1); IR (KBr) 2975, 1760, 1600, 870, and 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.18 (27H, s), 1.27 (18H, s), 2.18 (3H, s), 2.20 (6H, s), 2.24 (6H, s), 3.74 (10H, s), and 6.82—7.38 (12H, m); MS m/z 1008 (M^+, 17%). Found: C, 76.00; H, 8.21%. Calcd for $C_{64}H_{80}O_{10}$: C, 76.16; H, 7.99%.

6d: Yield, 16%. Colorless powder, mp 90—93°C (chromatography on silica gel; Wako C-200, hexane/AcOEt=2/1); IR (KBr) 3000, 1780, 1680, 1600, 850, and 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26 (36H, s), 1.35 (9H, s), 1.69 (6H, s), 2.02 (6H, s), 2.32 (3H, s), and 6.69—7.01 (12H, m); MS m/z 1064 (M^+, 3%). Found: C, 71.75; H, 6.99%. Calcd for $C_{64}H_{72}O_{14}$: C, 72.16; H, 6.81%.

XXXX: Yield, 75%. Yellow powder, mp 230—231°C (hexane/benzene); IR (KBr) 3430, 2960, 1645, 1595, 840, 825, 815, and 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25 (9H, s), 1.30 (18H, s), 1.34 (18H, s), and 6.97—7.71 (12H, m); MS m/z 854 (M^+, 5%). Found: C, 75.81; H, 7.44%. Calcd for $C_{54}H_{62}O_9$: C, 75.84; H, 7.31%.

2-(3-Bromo-5-*t*-butylsalicyloyl-4-*t*-butylphenol (8a) and 2-Bromo-4-*t*-butyl-6-[5-*t*-butyl-3-(5-*t*-butylsalicyloyl)salicyloyl]phenol (8b). Brominated carbonyl-bridged oligomers **8a** and **8b** were prepared from the corresponding parent oligomers (**3a** and **3b**)[6] via their acetoxy derivatives (**5a** and **5b**; **7a** and **7b**) analogously to the preparation of **XXX**.

5a: Almost quantitative yield. Colorless oil, bp 203°C/1 mmHg; IR (CCl_4) 2990, 1775, 1380, 1210, 1180, and 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.21 (9H, s), 1.26 (9H, s), 2.18 (3H, s), 2.29 (3H, s), 3.78 (2H, s), and 7.10—7.69 (5H, m); MS (20 eV) m/z 474 (M^+, 39). Found: C, 63.53; H, 6.80%. Calcd for $C_{25}H_{31}BrO_4$: C, 63.16; H, 6.57%.

7a: Yield, 67%. Colorless needles, mp 144—145°C (hexane/AcOEt); IR (KBr) 3530, 2975, 1790, 1780, 1760, 1670, and 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30 (18H, s), 1.96 (3H, s), 2.07 (3H, s), and 7.03—7.84 (5H, m); MS m/z 488 (M^+, 8). Found: C, 61.47; H, 6.06%. Calcd for $C_{25}H_{29}BrO_5$: C, 61.36; H, 5.97%.

8a: Almost quantitative yield. Pale yellow needles, mp 128—129°C (hexane/benzene); IR (KBr) 3390, 2975, 1625, 805, and 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30 (18H, s) and 7.03—7.84 (5H, m); MS m/z 404 (M^+, 45). Found: C, 62.47; H, 6.24%. Calcd for $C_{21}H_{25}BrO_3$: C, 62.23; H, 6.22%.

5b: Almost quantitative yield. Colorless prisms, mp 114—116°C (hexane); IR (KBr) 2970, 2950, 2870, 1770, 1600, 870, and 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.20 (9H, s), 1.24 (18H, s), 2.15 (6H, s), 2.25 (3H, s), 3.75 (4H, s), and 6.60—7.55 (7H, m); MS m/z 706 (M^+, 2%). Found: C, 67.26; H, 7.03%. Calcd for $C_{38}H_{47}BrO_6$: C, 67.15; H, 6.97%.

7b: Yield, 35%. Colorless high viscous oil (chromatography on silica gel; Wako C-200, hexane/AcOEt=9/2); IR (KBr) 3450, 2975, 1770, 1670, 1600, and 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.29 (9H, s), 1.31 (18H, s), 1.63 (3H, s), 2.03 (3H, s), 2.17 (3H, s), and 7.03—7.82 (7H, m); MS m/z 706 (M^+, 2%). Found: C, 64.95; H, 6.19%. Calcd for $C_{38}H_{43}BrO_8$: C, 64.50; H, 6.12%.

8b: Yield 73%. Yellow powder (hexane), mp 106.5—107°C; IR (KBr) 3400, 2970, 1630, 1600, and 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.28 (18H, s), 1.34 (9H, s), and 7.00—7.88 (7H, m); MS m/z 580 (M^+, 100%). Found: C, 66.18; H, 6.54%. Calcd for $C_{32}H_{37}BrO_5$: C, 66.09; H, 6.41%.

2-Bromo-4-*t*-butyl-6-[5-*t*-butyl-3-[5-*t*-butyl-3-(5-*t*-butylsalicyl)salicyloyl]salicyloyl]phenol (10). A mixture of **8b** (2.3 g, 4.0 mmol), paraformaldehyde (0.24 g, 8.0 mmol), H_3PO_4 (7 ml), AcOH (60 ml), and hydrochloric acid (25 ml) was stirred at 80°C for 10 h. The reaction mixture was extracted with benzene. The benzene extract was washed with water, dried, and concentrated, leaving an almost equal mixture (2.3 g) of the unreacted **8b** and the desired 2-bromo-4-*t*-butyl-6-[5-*t*-butyl-3-(5-*t*-butyl-3-chloromethylsalicyloyl)salicyloyl]phenol (**9b**) (TLC, ^1H NMR). Since chloromethylated compound **9b** was not sufficiently stable to isolate, the mixture was used in the next step. A solution of **9b** (2.3 g) contaminated with **8b**, *p*-*t*-butylphenol (6.0 g, 40 mmol), and TsOH (30 mg) in toluene (30 ml) was stirred at 100°C for 10 h. After removing excess *p*-*t*-butylphenol, together with the solvent by steam distillation, the residue was extracted with benzene. The benzene extract was washed with water, dried, and concentrated. The resid-

ual mass was chromatographed on silica gel (Wako C-200, hexane/benzene=1/2) to give **10** (0.5 g, 17% based on **8b**): Yellow powder, mp 99—101°C; IR (KBr) 3430, 2980, 1635, 1600, 860, 830, and 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.24 (9H, s), 1.26 (9H, s), 1.29 (18H, s), 4.02 (2H, s), and 6.75—7.93 (9H, m); MS m/z 742 (M^+, 100%). Found: C, 69.14; H, 6.94%. Calcd for $C_{43}H_{51}BrO_6$: C, 69.44; H, 6.91%.

4-*t*-Butyl-2-[3-[5-*t*-butyl-3-(5-*t*-butylsalicyloyl)salicyloyl]-5-*t*-butylsalicyl]phenol (XXC). Bromo compound **10** was debrominated by catalytic hydrogenation upon stirring a mixture of **10** (0.40 g, 0.35 mmol), NaOH (50 mg), 10% Pd-C (0.1 g), and methanol (10 ml) at room temperature in an atmospheric pressure hydrogenation apparatus. After the calculated amount of H_2 was consumed, the catalyst was filtered off and washed with the solvent. The combined methanol solution was acidified (pH 4) by adding 50% AcOH and extracted with benzene. The benzene extract was washed with water, dried, and concentrated. Recrystallization of the residue from methanol afforded **XXC** (0.3 g, 85%): Yellow plates, mp 108—110°C; IR (KBr) 3430, 2960, 1625, 1600, 860, 830, and 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30 (9H, s), 1.33 (9H, s), 1.37 (18H, s), 4.16 (2H, s), and 6.95—7.71 (10H, m); MS m/z 664 (M^+, 90%). Found: C, 77.70; H, 8.08%. Calcd for $C_{43}H_{52}O_6$: C, 77.68; H, 7.88%.

2-Bromo-4-*t*-butyl-6-(5-*t*-butyl-3-chloromethylsalicyloyl)phenol (9a). A mixture of **8a** (1.0 g, 2.5 mmol), paraformaldehyde (0.11 g, 3.7 mmol), H_3PO_4 (3 ml), hydrochloric acid (15 ml), and AcOH (30 ml) was stirred at 100°C for 10 h. The resultant yellow crystals were filtered and recrystallized from a mixture of hexane and benzene to yield **9a** (1.0 g, 89%): Yellow prisms, mp 158—159°C; IR (CCl_4) 3520, 2970, 1620, 1605, 980, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.31 (18H, s), 4.77 (2H, s), and 7.30—7.89 (4H, m); MS m/z 452 (M^+, 100). Found: C, 58.17; H, 5.86%. Calcd for $C_{22}H_{26}ClBrO_3$: C, 58.23; H, 5.77%.

2-Bromo-4-*t*-butyl-6-[5-*t*-butyl-3-[5-*t*-butyl-3-(5-*t*-butylsalicyloyl)salicyl]salicyloyl]phenol (11). A mixture of **9a** (1.0 g, 2.2 mmol), **X** (720 mg, 2.2 mmol), $AlCl_3$ (0.59 g, 4.4 mmol), and nitrobenzene (8 ml) was stirred at 100°C for 8 h. The solvent was removed by steam distillation, and the residue was extracted with benzene. The benzene extract was washed with water, dried, and concentrated. Chromatographic separation on silica gel (Wako C-200, hexane/benzene=2/1), followed by recrystallization from benzene gave **11** (0.81 g, 50%): Yellow powder, mp 121—124°C; IR (KBr) 3375, 2970, 1620, 1605, 830, 820, and 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.29 (36H, s), 4.13 (2H, s), and 6.95—7.88 (9H, m); MS m/z 742 (M^+, 100%). Found: C, 69.29; H, 7.24%. Calcd for $C_{43}H_{51}BrO_6$: C, 69.44; H, 6.91%.

4-*t*-Butyl-2-[5-*t*-butyl-3-[5-*t*-butyl-3-(5-*t*-butylsalicyloyl)salicyl]salicyloyl]phenol (XCX). Bromo compound **11** was debrominated in a similar manner as described for the synthesis of **XXC** from **10**: Yield, 88%; yellow powder, mp 115—117°C hexane); IR (KBr) 3410, 2970, 1625, 1610, 830, and 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.29 (36H, s), 4.05 (2H, s), and 6.80—7.80 (10H, m); MS (70 eV) m/z 664 (M^+, 100%). Found: C, 77.77; H, 8.07%. Calcd for $C_{43}H_{52}O_6$: C, 77.68; H, 7.88%.

2-Bromo-4-*t*-butyl-6-[5-*t*-butyl-3-[5-*t*-butyl-3-(5-*t*-butylsalicyl)salicyl]salicyloyl]phenol (12). A mixture of **9a** (1.0 g, 2.2 mmol), **1a** (0.81 g, 2.6 mmol), $AlCl_3$ (0.59 g, 4.4 mmol), and nitrobenzene (20 ml) was stirred at 50°C for 8 h. Work-up and column chromatography on silica gel (Wako C-200, hexane/benzene=2/1), followed by recrystallization from benzene gave **12** (0.8 g, 50%): Yellow powder, mp 177—178°C; IR (KBr) 3330, 2970, 1620, 1605, 800, and 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.28 (36H, s), 3.94 (2H, s), 4.01 (2H, s), and 6.72—7.86 (9H, m); MS m/z 728 (M^+, 86%). Found: C, 71.11; H, 7.47%. Calcd for $C_{43}H_{53}BrO_5$: C, 70.77; H, 7.32%.

4-*t*-Butyl-2-[5-*t*-butyl-3-[5-*t*-butyl-3-(5-*t*-butylsalicyl)salicyl]salicyloyl]phenol (XCC). Bromo compound **12** was debrominated in a similar manner as described for the synthesis of **XXC** from **10**: Yield, 100%; yellow powder, mp 182—184°C (benzene); IR (KBr) 3380, 2980, 1630, 1610, and 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.27 (36H, s), 3.92 (2H, s), 3.99 (2H, s), and 6.72—7.70 (10H, m); MS m/z 650 (M^+, 100%). Found: C, 79.01; H, 8.45%. Calcd for $C_{43}H_{54}O_5$: C, 79.35; H, 8.36%.

4-*t*-Butyl-2-(5-*t*-butyl-3-chloromethylsalicyloyl)-6-chloromethylphenol (13). Bischloromethyl compound **13** was prepared from **X** by the chloromethylation as described for the synthesis of **9a** from **8a**: Yield, 89%; yellow powder, mp 190—192°C (hexane/benzene); IR (CCl_4) 3250, 2980, 1625, 1600, 830, and 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.31 (18H, s), 4.76 (4H, s), 7.59 (2H, d, J=1.6 Hz), and 7.68 (2H, d, J=1.6 Hz); MS m/z 422 (M^+, 100%). Found: C, 65.42; H, 6.69%. Calcd for $C_{23}H_{28}Cl_2O_3$: C, 65.25; H, 6.67%.

4-*t*-Butyl-2-[5-*t*-butyl-3-[5-*t*-butyl-3-(5-*t*-butylsalicyl)salicyloyl]salicyl]phenol (CXC). A mixture of **13** (6 g, 3.8 mmol) and *p*-*t*-butylphenol (8.5 g, 57 mmol), TsOH (40 mg), and toluene (25 ml) was stirred at 100°C for 10 h. After removing the excess *p*-*t*-butylphenol by steam distillation, the residue was extracted with benzene. The benzene extract was washed with water, dried, and concentrated. The crude product, thus obtained, was recrystallized from a mixture of hexane and benzene, giving **CXC** (1.7 g, 69%): Yellow powder, mp 221—223°C; IR (KBr) 3500, 2980, 1610, 880, and 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26 (18H, s), 1.30 (18H, s), 4.04 (4H, s), and 6.62—7.80 (10H, m); MS m/z 650 (M^+, 100%). Found: C, 79.38; H, 8.48%. Calcd for $C_{43}H_{54}O_5$: C, 79.35; H, 8.36%.

2-Bromo-4-*t*-butyl-6-[5-*t*-butyl-3-(5-*t*-butylsalicyl)-salicyloyl]phenol (14). Brominated carbonyl-bridged trimer **14** was prepared by the reaction of **9a** with *p*-*t*-butylphenol analogously to the preparation of **CXC**: Yield, 50%; pale yellow powder, mp 86—89°C (hexane/benzene); IR (KBr) 3400, 2970, 1625, and 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.35 (27H, s), 4.10 (2H, s), and 6.72—7.85 (7H, m); MS m/z 566 (M^+, 40%), Found C, 67.28; H, 6.46%. Calcd for $C_{32}H_{39}BrO_4$: C, 67.72; H, 6.93%.

4-*t*-Butyl-2-[5-*t*-butyl-3-(5-*t*-butylsalicyl)salicyloyl]-phenol (XC). Carbonyl-bridged trimer **XC** was obtained by the catalytic debromination of **14**, as described for the preparation of **XXC**: Yield, almost quantitative; pale yellow crystals (benzene), mp 163—165°C; IR (KBr) 3400, 2975, 1630, and 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.28 (18H, s), 1.30 (9H, s), 4.02 (2H, s), and 6.90—7.54 (8H, m); MS (70eV) m/z 488 (M^+, 46%). Found: C, 78.92; H, 8.44%. Calcd for $C_{32}H_{40}O_4$: C, 78.65; H, 8.25%.

Preparation of Oxime (General Procedure). A

mixture of **CXC** (1.5 g, 2.3 mmol), $NH_2OH \cdot HCl$ (0.21 g, 3.0 mmol), $AcONa \cdot 3H_2O$ (0.63 g, 4.6 mmol), water (6 ml), and ethanol (15 ml) was stirred under reflux for 8 h. After removing the solvents, the residue was extracted with benzene. The benzene extract was washed with water, dried, and concentrated. The crude oxime, thus obtained, was chromatographed on silica gel (Wako C-200, hexane–AcOEt=4/1) to yield **CZC** (1.2 g, 78%): Pale yellow powder, mp 190—191°C; IR (KBr) 3350, 2975, 1715, 1615, 890, and 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.08 (9H, s), 1.25 (9H, s), 1.28 (18H, s), 4.01 (4H, s), and 6.71—7.57 (10H, m); MS m/z 665 (M^+, 6%). Found: C, 77.65; H, 8.54; N, 2.07%. Calcd for $C_{43}H_{55}NO_5$: C, 77.56; H, 8.32; N, 2.10%.

Z: Yield, 75%. Pale yellow needles (hexane), mp 137—138°C; IR (KBr) 3575, 3250, 2975, 1620, and 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.01 (9H, s), 1.19 (9H, s), and 6.88—7.50 (6H, m); MS m/z 341 (M^+, 13%). Found: C, 73.89; H, 8.07; N, 3.97%. Calcd for $C_{21}H_{27}NO_3$: C, 73.87; H, 7.97; N, 4.10%.

ZC: Yield, 75%. Pale yellow needles (hexane/benzene), mp 166—168°C; IR (KBr) 3575, 3300, 2975, 1620, 1510, and 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.15 (9H, s), 1.35 (18H, s), 4.10 (2H, s), and 6.75—7.15 (8H, m); MS m/z 503 (M^+, 10%). Found: C, 76.43; H, 8.33; N, 2.77%. Calcd for $C_{32}H_{41}NO_4$: C, 76.30; H, 8.20; N, 2.78%.

ZCC: Yield, 55%. Yellow powder, mp 176—178°C (hexane); IR (KBr) 3575, 3300, 2975, 1610, 1485, and 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.09 (9H, s), 1.26 (18H, s), 1.29 (9H, s), 3.89 (2H, s), 4.00 (2H, s), and 6.86—7.36 (10H, m); MS m/z 665 (M^+, 0.2%). Found: C, 77.79; H, 8.43; N, 2.07%. Calcd for $C_{43}H_{55}NO_5$: C, 77.55; H, 8.33; N, 2.10%.

Preparation of Inclusion Complex. The oligomer was recrystallized by using a minimum amount of an organic solvent (guest). The precipitates were collected by filtration and dried overnight at ambient temperature. The host–guest ratio was determined by means of ^1H NMR spectroscopy. The selectivity in the complexation was examined as follows: The tetramer (100 mg) was recrystallized from an equimolar mixture of liquid guests; the thus precipitated complex was treated using a similar procedure as that described above. Upon heating the complex under reduced pressure, a mixture of the guests was distilled. The composition of the guests was determined by gas chromatography.

Kinetic Study. The weight-decreasing rate of a complex was measured from the TG-DTA curve using Al_2O_3 as a reference. The programmed temperature was increased at a rate of $10°C\,min^{-1}$ up to each temperature. On the basis of the rate constants, thus obtained, the $\Delta H^{\ddagger}$ value was calculated by a least-squares method.

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