a normalized value of 98 ± 14. The relative CL from corresponding experiments in air, 42 ± 5, similarly leads to the normalized contribution from cyclohexylperoxyl radicals = (42 − 14)/0.796 = 35 ± 6.[22] The ratio 98/35 = 2.8 ± 0.6 is somewhat higher than our ratios of 1.7 ± 0.1 and 2.1 ± 0.2 (Table V), but the calculation fails to take into account the quenching of excited cyclohexanone by dissolved oxygen (reaction 8), which was probably comparable in magnitude to triplet energy transfer to 9,10-dibromoanthracene in their system. This correction of $k_5[\mathrm{F}]/(k_5[\mathrm{F}] + k_8[\mathrm{O_2}])$ can change the ratio by as much as a factor of two,[21] which would bring it into good agreement with the two values of our study.

All of our results can be described by the conventional "Russell" or concerted termination scheme for peroxyls,[23] with an activation energy about 9 kcal/mol higher for production of a ketone in the triplet than in the ground state. It is tempting, however, to ascribe this ΔE_a to the difference between a stepwise termination of R_2O_4 via $2RO^\bullet$, which gives excited ketones, and a concerted process that does not. The yield of triplet tetralone from THN, measured in an earlier[5] study relative to tetramethyl-1,2-dioxetane with Φ(triplet acetone) = 0.3, was $(2.2 \pm 0.3) \times 10^{-3}$. From the ratio of excited state yields in Table IV, we calculate $\Phi = 8.0 \times 10^{-4}$ for triplet production from $2TOO^\bullet$. Approximating this triplet yield as k_{4T}/k_4 and expanding the terms with the Arrhenius equation, we have $8.0 \times 10^{-4} = k_{4T}/k_4 = (A_{4T}/A_4)\exp(E_4 - E_{4T})/RT$. For a temperature of 41 °C and with our experimental value of $E_4 - E_{4T}$, we calculate $A_{4T}/A_4 = 1500$. This ratio is consistent with our alternate hypothesis, since the concerted transition states proposed for peroxyl termination are cyclic and should have lower A factors because of the loss of rotational modes in the transition state.[24,25]

When the stepwise process of R_2O_4 is considered in detail, one may write an extended sequence

$$[R_2CHO^\bullet\ {}^\bullet OOOCHR_2] \rightarrow [R_2CO\ HOOOCHR_2] \rightarrow [HOO^\bullet\ {}^\bullet OCHR_2] \rightarrow H_2O_2 + R_2CO \quad (11)$$

in competition with cage escape of the species in brackets. The scission-dismutation reactions of R_2O_4 and RO_3H in this sequence can alternatively be described as concerted, four-center elimination processes. The thermolysis of hydrotrioxides is known to produce alcohols, oxygen, and singlet oxygen.[26] We were unable, however, to see an OH signal in the ^{1}H NMR spectrum at low field[26a] from TOOOH in oxidized mixtures of TOOH and ceric ammonium nitrate in acetone-d_6 at −75 °C, although the spectrum was not well resolved. On the basis of economy of assumptions (Occam's razor), the original Russell scheme[23] remains a preferred explanation for generation of both ground- and excited-state species.

It is unfortunate that spin-orbit coupling in the alkoxyl radicals makes it impossible to analyze the system by conventional EPR methods.[27] More definitive evidence on the viability of the alternate schemes involving R_2O_4 may come from molecular orbital calculations and measurement of yields of singlet oxygen now in progress.

Acknowledgment. We thank the 3M Co. for a fellowship to S.-H. Lee and Himont USA for partial support, Dr. G. A. Russell for his continued interest, and a referee for contributing additional references.

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Association, Photodimerization, and Induced-Fit Types of Host–Guest Complexation of Anthracene-Appended γ-Cyclodextrin Derivatives

Akihiko Ueno,*,† Fumio Moriwaki,† Tetsuo Osa,*,† Fumio Hamada,‡ and Koichi Murai‡

Contribution from the Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan, and Department of Fuel Chemistry, Mining College, Akita University, Gakuen-cho, Tegata, Akita 010, Japan. *Received August 31, 1987*

Abstract: γ-Cyclodextrin derivatives bearing one and two anthracene moieties (**1** and **2**, respectively) were prepared, and their host–host and/or host–guest association behaviors were studied by spectroscopy in solution. The host **1** was found to exist as an equilibrium between a monomer and an association dimer with 1.1×10^5 M^{-1} as its association constant. The 1:1 host–guest association constant of **1**, which was obtained by digital simulation analysis of the absorption data, was compared with those of **2** and a β-cyclodextrin derivative bearing an anthracene moiety (**3**). Arguments are presented suggesting that host–guest complexation of these hosts is associated with locational changes of their anthracene moieties. The circular dichroism spectrum of **1** exhibits an exciton coupling band of *R* helicity in the ^{1}B$_b$ transition region of anthracene due to the interaction of the two anthracene moieties in the cavity of the association dimer. The host **2** also exhibits a similar exciton coupling pattern, but this arises from intramolecular interaction of its two anthracene moieties. Fluorescence spectra of **1** and **2** exhibit broad peaks above 470 nm, which are also seen in the spectra of **3** and anthracene-modified methyl α-D-glucoside **4** and are consequently assigned to monomer fluorescence. The photodimerization of anthracene proceeds in the association dimer of **1** as well as in **2** at rates that are suppressed upon addition of *l*-borneol.

Cyclodextrins (CDs) are a series of cyclic oligomers consisting of six or more α-1,4-linked D-glucopyranose units and designated by α, β, and γ for the hexamer, heptamer, and octamer, respectively. The smaller α- and β-CDs usually form 1:1 complexes,[1] but γ-CD has been shown to accommodate two guest molecules in its large cavity (1:2 host–guest complexation).[2-5] This property

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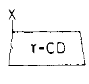
allows γ-CD to be used as a molecular flask in which two species can meet, as shown by the facilitated formation of excimers[2] and charge-transfer complexes[3] as well as by enhanced photodimerization.[4] Another interesting aspect of γ-CD is the unique binding behavior of its derivatives as flexible hosts. For example, the naphthalene moiety of **5** enters the cavity in guest binding and acts as a spacer, which narrows the large γ-CD cavity,[6] while the two naphthalene moieties of **6** change their positions from inside to outside the cavity upon 1:1 host-guest complex formation.[7] Since CDs are usually recognized as rigid hosts with specific cavity sizes, these guest-induced conformational changes of the γ-CD derivatives present new aspects in cyclodextrin chemistry. It is of significant interest to examine how such complexation behaviors of γ-CD derivatives depend on the size of the pendant aromatic moiety. If the size of the aromatic moiety is appropriate, unique systems, in which two host molecules associate with each other using the aromatic moiety as a connector, might be produced. We will now describe further studies of the γ-CD complexation that explore association, photodimerization, and induced-fit types of complexation of anthracene-appended γ-CD derivatives.

Results and Discussion

Synthesis. We prepared γ-CD derivatives **1** and **2** by a simple extension of the work of naphthalene-appended γ-CD derivatives.



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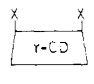

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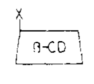

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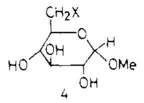

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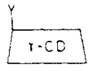

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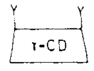

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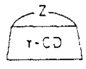

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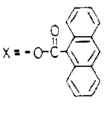

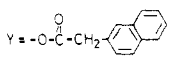

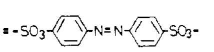

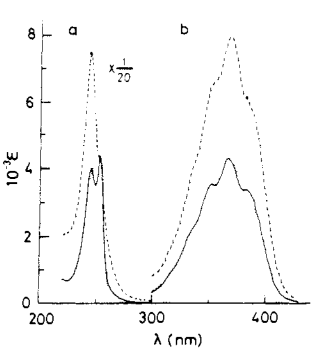

Figure 1. Absorption spectra of **1** (–), **2** (- - -), and **3** (···) in 10% ethylene glycol aqueous solution. The concentrations of the hosts are 1.0 × 10^{-5} (**1**, a), 1.0 × 10^{-4} (**1**, b), 5.0 × 10^{-6} (**2**, a), 5.3 × 10^{-5} (**2**, b), 1.0 × 10^{-5} (**3**, a), and 1.0 × 10^{-4} (**3**, b) M.

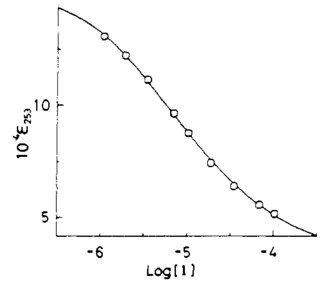

Figure 2. Concentration dependence of the absorption at 253 nm of **1** in 10% ethylene glycol aqueous solution (solid line is the calculated curve for K_D = 1.1 × 10^{-5} M^{-1}).

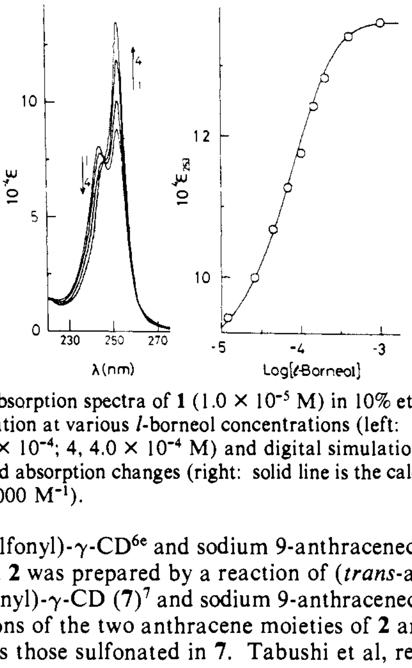

Figure 3. Absorption spectra of **1** (1.0 × 10^{-5} M) in 10% ethylene glycol aqueous solution at various *l*-borneol concentrations (left: 1, 0; 2, 2.6 × 10^{-5}; 3, 1.0 × 10^{-4}; 4, 4.0 × 10^{-4} M) and digital simulation data of the guest-induced absorption changes (right: solid line is the calculated curve for K = 18 000 M^{-1}).

Synthesis of **1** was performed by a reaction of 6-*O*-(2-naphthylsulfonyl)-γ-CD[6e] and sodium 9-anthracenecarboxylate. Compound **2** was prepared by a reaction of (*trans*-azobenzene-4,4′-disulfonyl)-γ-CD (**7**)[7] and sodium 9-anthracenecarboxylate. The positions of the two anthracene moieties of **2** are therefore the same as those sulfonated in **7**. Tabushi et al, reported that β-CD is selectively capped at the primary hydroxyls of the A and D glucose units by *trans*-stilbene-4,4′-disulfonyl dichloride.[8] We also confirmed by high-performance liquid chromatography (HPLC) analysis that the reaction of *trans*-azobenzene-4,4′-disulfonyl dichloride and β-CD gives exclusively a β-CD derivative capped at the A and D positions.[9] Similar selectivity may also be expected for the reaction of γ-CD and *trans*-azobenzene-4,4′-disulfonyl dichloride, by which **7** was prepared. The examination of molecular models indicated that γ-CD may be disulfonated at either the A and D positions or the A and E positions;

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Table I. Host-Guest Association Constants at 25 °C in 10% Eihylene Glycol Aqueous Solution

	K, M^{-1}				
guest	**1**	**2**	**3**	**5**	**6**
l-borneol	18000 ± 150	2900 ± 150	110000 ± 4500	4000 ± 100[b]	1800 ± 140
1-ACA[a]	15000 ± 750	1500 ± 140	410000 ± 25000	4000 ± 500	1000 ± 26
cyclohexanol	37 ± 2	*c*	2800 ± 50	*d*	32 ± 1

[a] 1-Adamantanecarboxylic acid. [b] 5670 M^{-1} in pure water.[6a] [c] The value cannot be determined due to abnormal circular dichroism variaiions. [d] The value cannot be determined accurately. The reported value in pure water is 55 M^{-1}.[6a]

that is, **2** might be a mixture of A-D and A-E isomers. However, no indication of the presence of two isomers was obtained by persistent HPLC analysis [reversed-phase (ODS) column]. This suggested that the properties of both isomers are very similar or either the A-D or A-E isomer is regiospecifically formed.[10] Anthracene-appended β-CD (**3**) was prepared by the reaction of 6-*O*-tosyl-β-CD and sodium 9-anthracenecarboxylate. For comparative studies, anthracene-modified methyl α-D-glucoside **4** was also prepared. The solubility of these compounds in pure water is limited, so we used a 10% ethylene glycol aqueous solution for spectroscopic measurements unless otherwise noted.

Absorption and Circular Dichroism Spectra. Figure 1 shows the absorption spectra of **1-3** in a 10% ethylene glycol aqueous solution. The major electronic transitions of these substances are essentially those of anthracene. The bands in the 240-250- and 340-390-nm regions are attributed to ^1B_b and ^1L_a transitions, respectively. The absorption patterns of **2-4** are not concentration dependent, whereas the pattern of **1** is remarkably concentration dependent, with its extinction coefficient of the ^1B_b band increasing at 244 nm, but decreasing at 253 nm with increasing concentration (an isosbestic point exists at 246 nm). This result suggests that **1** forms an association dimer at high concentrations. An association constant (K_D) of 1.1 × 10^5 M^{-1} was determined by employing the usual procedure[11] for the concentration-dependent absorption data (Figure 2). The analysis also gave values of 1.52 × 10^5 and 2.70 × 10^4 as the extinction coefficients at 253 nm for one anthracene unit in the pure monomer and dimer species, respectively. The absorption pattern of **1**, when measured at 10^{-5} M, was found to be dependent on the guest (G) concentration. The equilibria shown in eq 1 and 2 should be present in this case.

$$2\mathbf{1} \overset{K_D}{\rightleftharpoons} \mathbf{1}_2 \qquad (1)$$

$$\mathbf{1} + \mathrm{G} \overset{K}{\rightleftharpoons} \mathbf{1}{:}\mathrm{G} \qquad (2)$$

A digital simulation method was used to analyze the guest-induced absorption variations of **1**. Figure 3 shows the absorption spectra of **1** in the presence of different amounts of *l*-borneol. The absorption intensity increased above and decreased below 246 nm with increasing *l*-borneol concentration. The digital simulation method gave a calculated curve fitted for the experimental data (Figure 3), and a binding constant of 18 000 M^{-1} was obtained for the 1:1 complexation of **1** and *l*-borneol. By using the same procedure, host-guest association constants of **1** for 1-adamantanecarboxylic acid and cyclohexanol were obtained (Table I). CDs consist of chiral D-glucose units, so the anthracene chromophore of **1-3** may produce induced circular dichroism in its absorption regions. Figure 4 shows circular dichroism spectra of **1-3** in a 10% ethylene glycol aqueous solution. The spectrum of **1** exhibits a simple negative band in the region of ^1L_a transition (350-400 nm) and a peak (266 nm) and a trough (243 nm) in the region of ^1B_b transition. We assigned the latter sinusoidal curve to the exciton coupling band of *R* helicity that originated from the electronic interaction between two anthracene moieties. This assignment was also confirmed by the total similarity of the circular dichroism pattern to that of the rigid compounds, in which the two anthracene residues are oriented clockwise.[12] It was also determined that the molar ellipticities of the exciton coupling band of **1** are concentration dependent and enhanced by a factor of 1.5 with a concentration change from 1.1 × 10^{-5} to 1.1 × 10^{-4} M. This concentration dependency should be due to the association of **1** and is consistent with the absorption data of **1**. Upon addition of *l*-borneol to the solution of **1** (10^{-5} M), the dichroism intensities are markedly reduced over the whole region and a simple negative band appears at 250 nm in place of the exciton coupling band. This *l*-borneol-induced spectral variation suggests that the dimer of **1** dissociates into 1:1 complexes of **1** and *l*-borneol (Figure 5). The absorption spectrum of **2** exhibits a peak at 244 nm, which is distinctly blue shifted from 252 nm of **3** (Figure 1) and suggests that the two anthracene moieties of **2** interact with each other. The rather broad band observed in the ^1L_a transition region is consistent with this argument. The intramolecular nature of the anthracene-anthracene interaction is confirmed by the absence of any concentration dependency of these absorptions. The pattern of the circular dichroism spectrum of **2** is similar to that of **1**, exhibiting a negative band in the 350-400-nm region and an

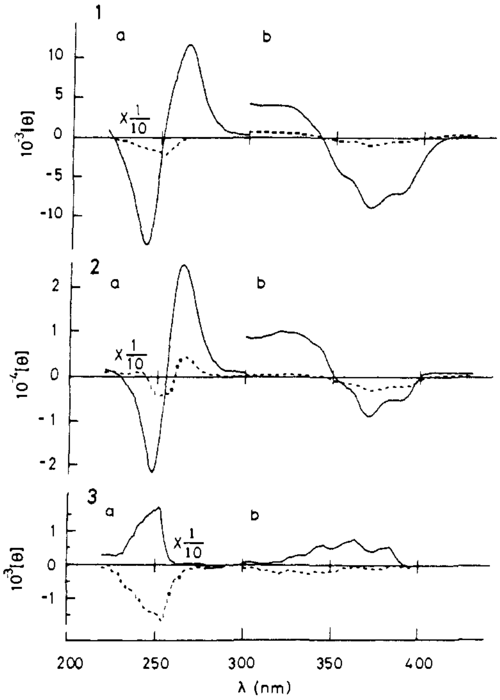

Figure 4. Circular dichroism spectra of **1-3** alone (—) or in the presence of *l*-borneol (---). The concentrations of the hosts are 1.1 × 10^{-5} (**1**, a), 1.1 × 10^{-4} (**1**, b), 3.9 × 10^{-6} (**2**, a), 3.9 × 10^{-5} (**2**, b), 1.0 × 10^{-5} (**3**, a), and 1.0 × 10^{-4} (**3**, b) M. The concentrations of *l*-borneol are 1.0 × 10^{-3} (**1**, a, b), 1.8 × 10^{-3} (**2**, a), 2.0 × 10^{-3} (**2**, b), 6.7 × 10^{-5} (**3**, a), and 1.3 × 10^{-4} (**3**, b) M.

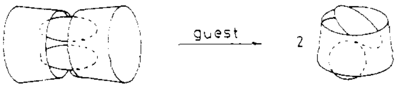

Figure 5. Guest-induced dissociation of the association dimer of **1**.

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(10) Quite recently, we succeeded in the characterization of **2**: The ratio of A-E and A-D isomers is 94:6. This means that regioselective disulfonation occurs in the reaction of *trans*-azobenzene-4,4′-disulfonyl dichloride and γ-CD. Details will be published in a separate paper.

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Figure 6. Induced-fit type of complexation of **2**.

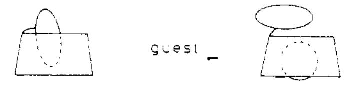

Figure 7. Induced-fit type of complexation of **3**.

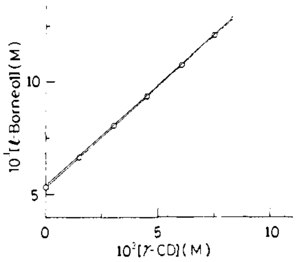

Figure 8. Solubility of *l*-borneol in 10% ethylene glycol aqueous solution as a function of γ-CD concentration.

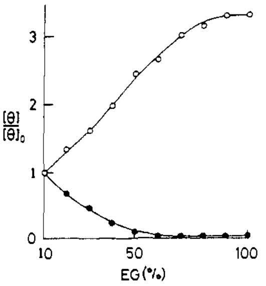

Figure 9. Ethylene glycol (EG) induced circular dichroism variations of **1** (●, 9.6 × 10^{-6} M) and **2** (○, 5.0 × 10^{-6} M). The $[\theta]/[\theta]_0$ value is the intensity ratio of the circular dichroism band around 265 nm of the sample solution and the 10% ethylene glycol aqueous solution.

exciton coupling band of *R* helicity below 300 nm. Different from the case of **1**, this exciton coupling band is supposed to arise from the intramolecular interaction between two anthracene moieties in **2**. It is noted, however, that the molar ellipticities of the circular dichroism band tended to increase above 5 × 10^{-6} M, where no concentration dependency was observed in the absorption spectra, presumably because of the presence of a tiny amount of association dimer of **2** in the concentration range. When a series of circular dichroism measurements were done to obtain the host–guest association constants of **2**, lower concentrations (<5 × 10^{-6} M) of **2** were used to avoid any complications arising from the host–host association. The absolute intensities of all dichroism bands of **2** are markedly reduced in the presence of *l*-borneol (Figure 4), implying that the guest molecule enters the cavity of **2** by extruding the two anthracene moieties from the cavity (Figure 6). Similar circular dichroism variations were observed when 1-adamantanecarboxylic acid was the guest. The guest-induced circular dichroism variations could be analyzed on the basis of the 1:1 host–guest stoichiometry. The circular dichroism spectra of **3** were quite different from those of **1** and **2**, exhibiting positive peaks around 252 and 364 nm, which are reversed in the presence of *l*-borneol. This spectral property of **3** could be related to the fact that **3** can include only one anthracene moiety in its β-CD cavity and such an anthracene–anthracene interaction, as shown in **1** and **2**, is impossible. It is theorized that, when the long axis of the arene guests is parallel to the axis of the CD cavity (axial inclusion), the sign of the induced circular dichroism of the CD–arene complexes is positive in the wavelength regions of the electronic transitions, which are polarized along the long axis of the arenes.[13] Consequently, the positive peak observed in the ^1B_b transition region of **3** suggests that the long axis of the anthracene moiety is parallel to the axis of the β-CD cavity of **3**. Conversely, the negative band observed in the presence of *l*-borneol suggests that the long axis of the anthracene moiety is perpendicular to the axis of the β-CD cavity in the complex (Figure 7). The change in the sign of the circular dichroism, which occurs in guest binding, is consistent with the guest-induced conformational change of **3** from an intramolecular complex to an intermolecular complex form (Figure 7). Similar guest-induced conformational changes were suggested to occur in other β-CD derivatives bearing ferrocene,[14,15] naphthalene,[15,16] and other chromophores.[17]

Host–Guest Association Constants. The host–guest association constants of **1**–**3** are listed in Table I together with those of **5** and **6**. For comparison with these values, we estimated the association constant of γ-CD for *l*-borneol to be 1700 M^{-1} by employing a solubility method (Figure 8).[18] When *l*-borneol was the guest, the host–guest association constant became larger in the order γ-CD ≈ **6** < **2** < **5** < **1** < **3**. Since *l*-borneol is a large guest, the anthracene moiety of **1** is likely to act as a flexible cap rather than a spacer. Examination of molecular models supports this argument. In contrast, on the basis of the observation that the dichroism band of **5** was enhanced by *l*-borneol, it was suggested that the naphthyl moiety of **5** acts as a spacer, being fixed in the chiral CD cavity together with *l*-borneol.[6a] The size of the pendant moiety of γ-CD appears to be a key factor in determining whether the moiety acts as a spacer or a cap for a guest. Cyclohexanol, which is much smaller than *l*-borneol, also forms a 1:1 complex with **1**. Since γ-CD, itself, is likely to form a 1:2 host–guest complex with cyclohexanol, as it does for naphthalene derivatives,[2] the stoichiometry of complex formation changes from 1:2 to 1:1 by modification of γ-CD with an anthracene moiety. The anthracene moiety of **1** in the complex probably acts as a spacer that enables γ-CD to bind one cyclohexanol molecule by narrowing the large cavity. In the case of β-CD, capping of the cavity by a hydrophobic moiety is known to be an effective method of converting β-CD to a better host by enlarging the hydrophobic environment around the cavity.[19,20] The host–guest association constant of **3** for 1-adamantanecarboxylic acid is significantly large, having a value of 410 000 M^{-1}, which is the greatest among the values ever obtained for a guest with modified and native CDs. This remarkable binding ability of **3** may be caused by the action of its anthracene moiety as an effective hydrophobic floor[20,21] in the complex, where the guest is inserted into the cavity from the wider mouth of the secondary hydroxyl site of **3**. The value of **3** for cyclohexanol is also larger than the reported one for β-CD in water (930 M^{-1}).[22] If we compare the magnitude of the host–guest association constant of **3** with that of γ-CD, using *l*-borneol as the guest, the 44-fold larger value of **3** seems feasible because **3** has an effective anthracene cap in addition to the cavity of β-CD, which is more appropriate than that of γ-CD for accommodation of a guest. The hosts **1** and **5**, both having one aromatic moiety, are capable of binding *l*-borneol and 1-adamantanecarboxylic acid more tightly than **2** and **6**, which have two aromatic moieties. This observation indicated that the two

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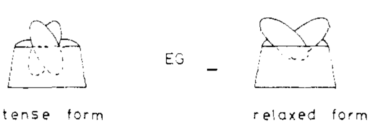

Figure 10. Ethylene glycol (EG) induced conformational change of **2**.

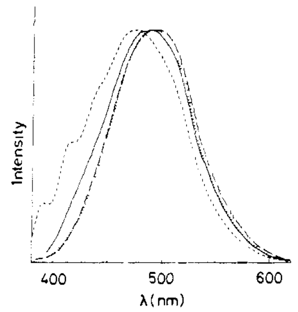

Figure 11. Fluorescence spectra of **1** (–), **2** (- - -), **3** (···), and **4** (– –) in 10% ethylene glycol aqueous solution. The host concentrations are 1.0×10^{-4} (**1–3**) and 4.3×10^{-5} (**2**) M. The peak intensities are normalized and cannot be compared with each other.

aromatic moieties, preincluded in the γ-CD cavity of **2** and **6**, lower the guest-binding ability of the hosts due to the formation of stable intramolecular complexes, whereas the one aromatic moiety of **1** and **5** facilitates guest binding of the hosts as a cap or a spacer.

Solvent Effect of Ethylene Glycol. An unexpected enhancement of the dichroism intensity of the exciton coupling band of **2** was found when the ratio of ethylene glycol in the solution was increased. Figure 9 shows the variations of the dichroism intensities of **1** and **2** vs ethylene glycol content in the sample solutions. With increasing ethylene glycol content, the intensity of the exciton coupling band increased for **2** but decreased for **1**. Since hydrophobic molecules or moieties are bound more weakly to the CD cavity in organic solvents than in aqueous solution because of weakened hydrophobic interaction,[23] the negligible exciton coupling band of **1** in ethylene glycol was readily understood as a result of weakened binding, which caused dissociation of the dimer of **1**. However, the dichroism behavior of **2** is apparently abnormal and requires an explanation. On the basis of the weakened binding of the two anthracene moieties to the cavity of **2**, it is likely that **2** undergoes a conformational change from a "tense" form to a "relaxed" one upon increase of the ethylene glycol content in the solution (Figure 10). The anomalous circular dichroism behavior observed for **2** should be related to this phenomenon. The important feature of this conformational change is that the two anthracene moieties deeply involved in the cavity of **2** in water-rich solution are only shallowly inserted into the cavity in ethylene glycol. The theory of exciton coupling indicates that the magnitude of the exciton coupling band becomes greater with increasing angle between the two chromophores;[12] therefore, the greater magnitude of the relaxed form may be explained by the fact that the angle between the two anthracene moieties is larger in the relaxed form than in the tense one.

Fluorescence Spectra. Fluorescence spectra of **1–4** in a 10% ethylene glycol aqueous solution are shown in Figure 11. The fluorescence spectrum of **1** exhibits a simple excimer-like broad band at 485 nm. However, the band cannot be assigned to excimer emission since no sign of monomer emission appears at shorter wavelengths even at a very low concentration of 10^{-8} M. Other anthracene derivatives such as **2–4** exhibit similar broad bands, which are also not concentration dependent. The fluorescence behavior of these compounds is consistent with that of methyl 9-anthracenecarboxylate reported by Werner et al.[24] They assigned the fluorescence band to monomer emission and explained the anomaly in terms of the excited-state interaction between the anthracene ring and the ester carbonyl. From the data obtained in this study, the broad bands observed in the fluorescence spectra of **1–4** may also be assigned to monomer emission of anthracene.[25] The hosts **1–3**, shift their peaks positioned at 485, 474, and 490 nm, respectively, to the shorter wavelengths near 470 nm upon complexation with *l*-borneol, accompanied by remarkable enhancement in their fluorescence intensity. This fluorescence enhancement may be related to the guest-induced locational changes of the anthracene moiety, shown in Figures 5–7.

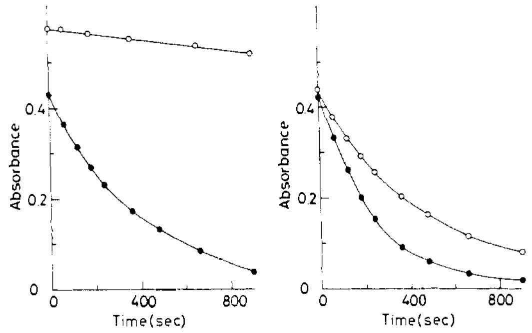

Figure 12. Photoinduced absorption changes of the peak around 365 nm of **1** (left, 1.0×10^{-4} M) and **2** (right, 5.3×10^{-5} M), alone (●) or in the presence of *l*-borneol (○, 2.0×10^{-3} M) in 10% ethylene glycol aqueous solution.

Photodimerization. Anthracene is well-known to undergo photodimerization.[26] In this study, photodimerization of the anthracene derivatives **1–4** was examined by using light with a wavelength greater than 300 nm. Figure 12 shows the absorbance around 365 nm of **1** and **2** as a function of time. The γ-CD derivatives **1** and **2** undergo photodimerization as shown by a decrease in the absorbance.[27] However, no photoreaction was seen in the cases of **3** and **4** under the same experimental conditions. Figure 12 also shows how the rates of photodimerization of **1** and **2** were depressed by *l*-borneol. It was evident that photodimerization was remarkably and slightly depressed for **1** and **2**, respectively. The remarkable inhibition observed in the case of **1** may be due to dissociation of the association dimer induced by *l*-borneol. On the other hand, the lack of a significant inhibitory effect of *l*-borneol on the photodimerization of **2** suggests that its two anthracene moieties are still closely positioned with each other in the complex of **2**. As photoproducts, intermolecular photodimerization of **1** affords a dimer, which contains two CD units, while intramolecular photodimerization of **2** should yield a host, in which the cavity is fully occupied by the anthracene dimer.

Conclusions

The γ-CD derivative **1** exhibits a strong tendency to form an association dimer. Circular dichroism spectra of **1** and **2** are very similar, exhibiting an exciton coupling band of R helicity in the ^1B_b transition region of anthracene. This band was proved to arise from intermolecular and intramolecular anthracene–anthracene interaction for **1** and **2**, respectively. The γ-CD derivatives undergo guest-induced conformational changes to form 1:1 host–guest inclusion complexes, in which the appended anthracene moiety acts as a spacer or cap. In relation to the anthracene–anthracene interaction, photodimerization of anthracene in **1** and **2** was examined and found to proceed in the association dimer of **1** as well as in **2**. The present results may provide a guideline for the use of the cavity of γ-CD or its dimer as a molecular flask in which two species can meet and react. Finally, we note that an important aspect of γ-CD modification is conversion of the rigid native γ-CD, which has a specific cavity diameter, into various flexible hosts, which may have designed voids when assisted by an appropriate spacer or cap.

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(25) This argument does not imply that no anthracene excimer is formed in **2** or in the association dimer of **1**. The excimer in such systems might readily be converted into a photodimer, exhibiting no excimer emission.

(26) For example: (a) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin-Cummings: Menlo Park, CA, 1978; p 457. (b) Birks, J. B. In *Organic Photopysics*; Birks, J. B., Ed.; Wiley: New York, 1975; p 496.

(27) Preliminary results obtained with **2** were previously reported.[4d]

Experimental Section

Materials. γ-CD was a gift from Nihon Shokuhin Kako Ltd. The following commercially guaranteed reagents were used without further purification: 9-anthracenecarboxylic acid, *l*-borneol, 1-adamantanecarboxylic acid, cyclohexanol, ethylene glycol, β-CD.

Procedures. The circular dichroism, UV, and fluorescence spectra were measured at 25 °C with a Jasco J-400X spectrodichrometer, a Shimadzu UV-250 spectrophotometer, and a Shimadzu RF-500 spectrofluorophotometer, respectively. The circular dichroism intensities were expressed as molar ellipticity (deg cm^2 $dmol^{-1}$). Due to the poor solubility of **1**–**3** in pure water, a 10% ethylene glycol aqueous solution was used as the solvent for the usual spectroscopic measurements. HPLC analysis was performed on a Jasco 800 series instrument. Photoirradiation was performed with a 500-W xenon lamp (Ushio Electric. Inc.), using appropriate cutoff filters for isolating UV light greater than 300 nm.

Determination of Host–Guest Association Constants. The association constant of γ-CD and *l*-borneol was obtained by a solubility method.[18] The concentrations of *l*-borneol in the sample solutions after removing insoluble *l*-borneol by filtration (FH type) were analyzed by HPLC with a RI detector, a YMC A-303 column (ODS, 4.6 × 250 mm), and an aqueous 50% acetonitrile solution. The *l*-borneol concentrations were plotted as a function of γ-CD concentration as shown in Figure 8. The association constant (K) was obtained by eq 3, where $[l\text{-borneol}]_0$ is the concentration in the absence of γ-CD.

$$K = \text{slope}/[l\text{-borneol}]_0(1 - \text{slope}) \qquad (3)$$

The host–guest association constants of **1** were obtained by using a digital simulation method. On the basis of the equilibria shown in eq 1 and 2, the absorbance at 253 nm (A) was expressed by eq 4. Here, ϵ_M,

$$A = \epsilon_M[\mathbf{1}] + \epsilon_D[\mathbf{1}_2] + \epsilon_c[\mathbf{1}\cdot\mathrm{G}] \qquad (4)$$

ϵ_D ($=5.40 \times 10^4$), and ϵ_c are absorption coefficients at the wavelength of **1**, $\mathbf{1}_2$, and **1**·G, respectively. The host–guest association constants shown in Table I are the values that gave the best fit between experimental and calculated data.

The host–guest association constants of **2**, **3**, **5**, and 6 were obtained by the analysis of guest-induced circular dichroism variations. It was reported that the association constant of 1:1 host–guest complexation is given by eq 5 when a chiral host changes its circular dichroism intensity

$$K = \frac{\theta_h - \theta_x}{(\theta_x - \theta_c)[C_g - C_h\,(\theta_h - \theta_x)/(\theta_h - \theta_c)]} \qquad (5)$$

upon accommodation of a guest molecule.[28] Here, θ is the molar ellipticity with the subsets θ_x for sample, θ_h for host alone, and θ_c for complex. The values C_h and C_s are the total host concentration and guest concentration, respectively. When the guest is in large excess, eq 6 can be

$$(\theta_h - \theta_x)/C_g = K\theta_x - K\theta_c \qquad (6)$$

derived from eq. 5. The values shown in Table I were obtained by using eq 5 (curve fitting) or eq 6 [plot of $(\theta_h - \theta_x)/C_g$ vs θ_x].

Synthesis. Sodium 9-Anthracenecarboxylate. A mixture of sodium hydroxide (1.11 g, 27.8 mmol) and 9-anthracenecarboxylic acid (5.0 g, 22.5 mmol) in water (20 mL) was stirred at room temperature for 2.5 h. Evaporation of the solvent followed by recrystallization from acetone gave 3.0 g (51%) of the desired product as a powder: IR (KBr) 1530 cm^{-1}. Anal. Calcd for $C_{15}H_9O_2Na\cdot H_2O$: C, 68.70; H, 4.23. Found: C, 68.61; H, 4.10.

(9-Anthracenecarbonyl)-γ-CD (1). A mixture of (2-naphthylsulfonyl)-γ-CD (650 mg, 0.44 mmol) and sodium 9-anthracenecarboxylate (320 mg, 1.2 mmol) in DMSO (4 mL) was heated at 80 °C for 5 h with stirring. The reaction mixture was poured into acetone (250 mL), and the precipitate was collected and washed with water. Purification of the crude product by Sephadex LH-20 column chromatography (eluted with DMF) afforded 250 mg (36%) of **1** as a powder: R_f 0.51 (1-butanol/ethanol/water, 5:4:3); ^1H NMR (DMSO-d_6) δ 8.74 (1 H, s), 8.28–7.88 (4 H, m), 7.72–7.40 (4 H, m), 5.92–5.40 (16 H, m), 5.16–4.64 (8 H, m), 4.52–4.16 (7 H, m), 3.92–2.92 (48 H, m); IR (KBr) 1720 cm^{-1}. Anal. Calcd for $C_{63}H_{88}O_{41}\cdot 4H_2O$: C, 48.09; H, 6.15. Found: C, 48.16, H, 6.11.

Bis(9-anthracenecarbonyl)-γ-CD (2). A mixture of (*trans*-azobenzene-4,4′-disulfonyl)-γ-CD tetrahydrate[7] (600 mg, 0.36 mmol) and sodium 9-anthracenecarboxylate (366 mg, 1.4 mmol) in DMSO (10 mL) was heated at 80 °C for 5 h with stirring. The reaction mixture was poured into acetone (600 mL), and the precipitate was collected. Purification of the crude product by silica gel column chromatography (eluted with 12.5% water in acetonitrile) afforded 40 mg (6.2%) of **2** as a powder: R_f 0.33 (acetonitrile/water, 5:1); ^1H NMR (DMSO-d_6) δ 8.55 (2 H, s), 8.20–7.84 (8 H, m), 7.63–7.44 (8 H, m), 5.90–5.62 (16 H, m), 5.07–4.80 (8 H, m), 4.63–4.33 (6 H, m), 4.04–3.16 (48 H, m); IR (KBr) 1720 cm^{-1}. Anal. Calcd for $C_{78}H_{96}O_{42}\cdot 6H_2O$: C, 51.65; H, 6.00. Found: C, 51.64; H, 6.08.

(9-Anthracenecarbonyl)-β-CD (3). A mixture of tosyl-β-CD (750 mg, 0.58 mmol) and sodium 9-anthracenecarboxylate (430 mg, 1.6 mmol) in DMSO (3 mL) was heated at 80 °C for 6 h with stirring. The reaction mixture was poured into acetone (200 mL), and the precipitate was collected. Purification of the crude product by Sephadex LH-20 column chromatography (eluted with 35% DMF in water) afforded 160 mg of **3** (20%) as a powder: R_f 0.55 (1-butanol/ethanol/water, 5:4:3); ^1H NMR (DMSO-d_6) δ 8.73 (1 H, s), 8.24–7.92 (4 H, m), 7.72–7.40 (4 H, m), 5.80–5.32 (14 H, m), 5.10–4.56 (7 H, m), 4.44–4.06 (6 H, m), 3.92–2.90 (42 H, m); IR (KBr) 1717 cm^{-1}. Anal. Calcd for $C_{57}H_{78}O_{36}\cdot 3H_2O$: C, 49.14; H, 6.08. Found: C, 48.95; H, 6.03.

Methyl (9-Anthracenecarbonyl)-α-D-glucoside (4). A mixture of methyl 6-*O*-tosyl-α-D-glucoside[29] (800 mg, 2.3 mmol) and sodium 9-anthracenecarboxylate (840 mg, 3.2 mmol) in DMSO (7 mL) was heated at 80 °C for 5.5 h with stirring. The reaction mixture was poured into water (250 mL), and the precipitate was collected. Recrystallization from aqueous methanol solution afforded 520 mg (57%) of **4** as a white powder: R_f 0.65 (acetonitrile/water, 7:1); ^1H NMR (DMSO-d_6) δ 8.76 (1 H, s), 8.32–7.88 (4 H, m), 7.76–7.40 (4 H, m), 3.24 (3 H, s), 5.44–2.92 (10 H, m); IR (KBr) 1715 cm^{-1}; MS, m/z 398 (M^+). Anal. Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 65.33; H, 5.62.

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Registry No. **1**, 114583-55-0; **2**, 114583-57-2; **3**, 114583-58-3; **4**, 114594-48-8; (2-naphthylsulfonyl)-γ-CD, 88718-13-2; sodium 9-anthracenecarboxylate, 16336-69-9; (*trans*-azobenzene-4,4′-disulfonyl)-γ-CD, 114583-56-1; tosyl-β-CD, 67217-55-4; methyl 6-*O*-tosyl-α-D-glucoside, 6619-09-6.

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