Tetrahedron Vol. 43, No. 7, pp. 1485 to 1494, 1987
Printed in Great Britain.

0040-4020/87 $3.00+.00
Pergamon Journals Ltd.

REGIO- AND STEREOSELECTIVE PHOTODIMERIZATION OF ANTHRACENE DERIVATIVES INCLUDED BY CYCLODEXTRINS

TAKASHI TAMAKI, TOMOKUNI KOKUBU, and KUNIHIRO ICHIMURA

Research Institute for Polymers and Textiles
Yatabe-Higashi 1-1-4, Tsukuba, Japan

(*Received in UK* 16 *February* 1987)

Abstract - The photodimerization of anthracene derivatives such as 2-anthracenesulfonate or 2-anthracenecarboxylate in aqueous solution was found to proceed regio- and stereoselectively in the presence of β-CyD and γ-CyD, respectively. These reaction selectivities were explained in terms of specific inclusion of these compounds into CyDs.

The host-guest compounds have induced increasing interest in wide fields of science and technology. Cyclodextrin (CyD), which is cyclic oligosaccarides containing six or more D(+)-glucopyranose units, is one of the most important host compounds. A variety of guest compounds comprising ionic species, organic compounds, and pharmaceutical drugs, can be included in the cavity of CyD in aqueous solution.[1]

The CyD inclusion compound is highly stereospecific, greatly stable, and less or non toxic. Hence, CyD is widely investigated as enzymatic models,[2] resolving agents for chiral compounds,[3-7] and molecular capsules of pharmaceutical drugs. CyD is also utilized in photochemical reactions in an attempt to give high product selectivity.[8-11]

Unusual inclusion behavior is current topics in the CyD chemistry. It is of great interest that β- and γ-CyDs which are composed of seven and eight glucopyranose units respectively, are able to form complexes including more than one guest molecules. This has been confirmed by the measurements of induced circular dichroism (i. c. d.),[12-15] excimer emission,[16-23] charge transfer absorption,[24] exciplex emission,[17,25] phosphorescence,[26] fluorescence intensity,[27-29] and precipitation of the complex.[8,30] A ternary inclusion complex may develop a new application of CyDs. If appropriate guest compounds are selected, specific bimolecular reactions between guest compounds would be expected. As yet, however, there are only few papers concerning the CyD-assisted bimolecular reaction.[31]

Recently, we have found that some water-soluble anthracene derivatives, such as anthracenesulfonate or anthracenecarboxylate, are included in aqueous solution by β- and γ-CyDs by up to two molecules resulting in two guest-two host (2 : 2) and two guest-one host (2 : 1) inclusion complexes, respectively and that photodimerization of these guest compounds is greatly accelerated by the complex formation.[15,20]

Results and Discussion

Regio- and Stereoselective Photodimerization

The effects of β- and γ-CyDs on the dianthracene-type photodimerization of water-soluble

Table 1. The inclusion effects on the photodimerization of anthracene derivatives

Guest	Host	Guest:Host Stoichiometry	Quantum Yield of Photodimerization	Relative Yields of Photodimers obtained (1 : 2 : 3 : 4)
2AS	None	-	0.05	1 : 0.8 : 0.4 : 0.05
	β-CyD	1 : 1 & 2 : 2	0.3	1 : 0.01 : - : -
	γ-CyD	2 : 1	0.5	1 : 0.9 : 0.3 : 0.05
1AS	None	-	0.04	1 : 1.2 : 0.01 : 0.4
	β-CyD	1 : 1	0.04	1 : 2.2 : 0.02 : 0.4
	γ-CyD	2 : 1	0.4	1 : 1.2 : 0.02 : 0.2
2AC	None	-	0.05	1 : 1.1 : 0.5 : 0.2
	β-CyD	1 : 1 & 2 : 2	0.2	1 : 0.05 : 0.06 : 0.04
	γ-CyD	2 : 1	0.4	1 : 1.4 : 0.3 : 0.1
1AC & 9AC	CyDs	Little Complexation		
2,6-ADS	None	-	0.05	
	β-CyD	1 : 1	-	
	γ-CyD	2 : 1	0.4	

anthracene derivatives in aqueous solution are summarized in Table 1. The acceleration of the photodimerization by γ-CyD is most prominent for 2-anthracenesulfonate (2AS) and 2-anthracenecarboxylate (2AC), slightly less for 1-anthracenesulfonate (1AS), and scarce for 1- (1AC) and 9-anthracenecarboxylate (9AC). β-CyD is also effective with 2AS and 2AC, but inactive with the other compounds. Although γ-CyD is as powerful with 2,6-anthracenedisulfonate (2,6-ADS) as with mono-substituted anthracene derivatives, β-CyD shows a retarding effect on this compound. α-CyD showed no interaction with all anthracene derivatives examined.

These photochemical consequences can be explained as the result of host-guest interaction between CyDs and these anthracene derivatives. The CPK molecular model indicates that β- and γ-CyDs but not α-CyD can include anthracene axially, which means that the long axis of anthracene is nearly along the molecular axis of the host.[32] If the number of fused aromatic rings is less than in anthracene, an equatorial inclusion in which the long axis of the guest molecule is nearly vertical with respect to the molecular axis of the host is also possible.

It should be noted that this specific inclusion behavior of anthracene is significantly affected by the substituent group attached to the aromatic ring. In the cases of 2AS and 2AC, the hydrophilic substituent group at C-2 position enhances the stability of the inclusion complex greatly, since the aromatic nucleus can be entirely embedded in the hydrophobic host cavity, leaving the hydrophilic group in an outer aqueous phase. In contrary, the meso-substituted group greatly decreases the stability of the inclusion complex, since deep inclusion of the guest compound is prevented by the hydrophilic substituent group. The substituent group at C-1 position shows an intermediate effect on the inclusion behavior.

The good fit of the size of the guest compound in that of the host cavity is most important for the complex stability. It is indicated by the CPK molecular model that the axial inclusion of two anthracene molecules gives the best fit to γ-CyD, the cavity size of which is 8.5 Å in diameter. Indeed, it has been observed that even with a dilute concentration of 2AS or 2AC (1×10^{-5} M), an appreciable number of 2 (guest) : 1 (host) inclusion complexes is formed with γ-CyD. The adjacent guest molecules in the host cavity may take a sandwich configuration which favors the cycloaddition reaction. On the other hand, the cavity size of β-CyD (ca. 7 Å) is too small to include two guest molecules together, but large enough to form a 1 : 1 complex with 1AS, 1AC, 2AS and 2AC. Furthermore, the complexes of the latter two 2-substituted anthracene derivatives are readily self-associated at relatively high guest and host concentrations ($\geq 10^{-4}$ M and $\geq 10^{-3}$ M, respectively) in aqueous solution to give 2 : 2 inclusion complexes which are also favorable for photodimerization. The inclusion complex between 2-substituted anthracene derivatives and CyDs was much more stable than that of 1-substituted anthracene derivatives, for which the multi-

component complex except the 2 : 1 inclusion complex between 1AS and γ-CyD could not be detected. The inclusion behavior of 2,6-ADS is similar to that of 2AS, except that no evidence for the formation of the 2 : 2 complex with β-CyD could be obtained. Hence, this compound is greatly photoreactive in the presence of γ-CyD, but photochemically stable in the presence of β-CyD. These inclusion behaviors have been confirmed by spectroscopic measurements (vide infra).

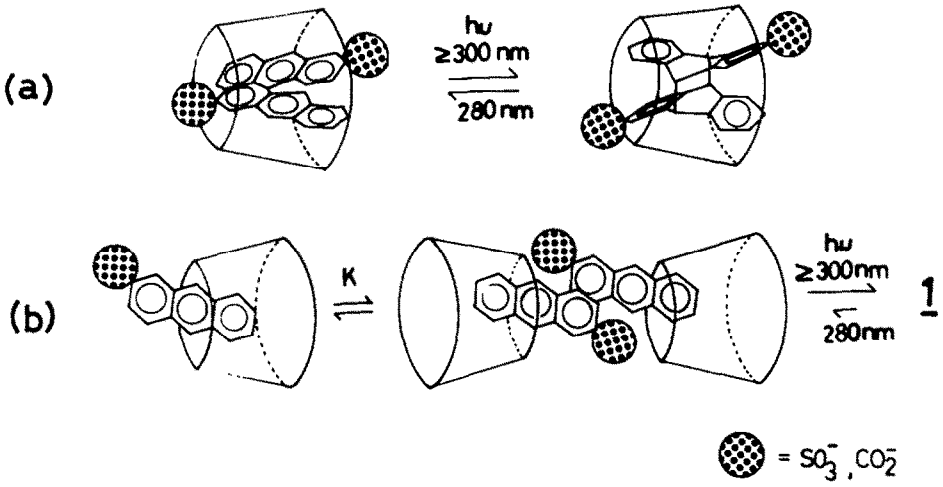

Fig. 1. Schemes for the photoreaction of inclusion complexes with (a) γ-CyD and (b) β-CyD.

As shown in Table 1, in host-free and γ-CyD-containing solutions, 2AS and 2AC yield four isomeric photodimers which are of an anti-head-tail (1), syn-head-tail (2), anti-head-head (3), and syn-head-head (4) conformations. The relative yields of these four isomers are identical in both solutions, suggesting that the guest molecules trapped by γ-CyD take four configurations nonspecifically. Since there was no evidence for static complex formation in the host-free solution of these anthracene derivatives, the photodimerization occurs via an excimer intermediate. In contrary, the CyD-assisted photodimerization is due to the static complex formation in the host cavity. The identical yield ratio of the isomers in these two reaction systems suggests that mutual configuration of reactive monomers is independent of the electronic structure of the component, but due to steric hindrance and electrostatic repulsion of the substituent group. A typical model of inclusion complex between γ-CyD and 2-substituted anthracenes is shown in Fig. 1a.

It is remarkable that the photodimerization of 2AS and 2AC in the presence of β-CyD is strictly regioselective, in contrast to the results of host-free and γ-CyD-containing solutions. The HPLC analysis has indicated that the sole isomer produced in the presence of β-CyD is 1. The severe selectivity of the photoproduct may be due to specific configuration of guest molecules in the host cavity, where two guest molecules take the anti-head-tail configuration. This may be realized by head-to-head association of two 1 : 1 complexes to give rise to the 2 : 2 complex. A plausible model of the inclusion complexes of 2AS or 2AC with β-CyD is shown in Fig. 1b.[33] In the case of the inclusion complex of 2,6-ADS with β-CyD, the guest compound may penetrate into the host cavity, with the sulfonate group being sticking out of both closed and open faces of CyD. Such a tight configuration may prevent association of the inclusion complex mainly due to ionic repulsion of the sulfonate group.

Since CyD is a chiral host compound which is composed by D(+)-glucopyranose units, stereospecific recognition and/or stereoselective reaction would be expected. In fact, although CyD is frequently used for optical resolution of chiral compounds,[3-7] only few papers have been reported concerning the stereoselective reaction.[34-35] In this respect, it has been known that some aromatic compounds in 2 : 1 complex with γ-CyD are in a S-helix configuration.[13,14]

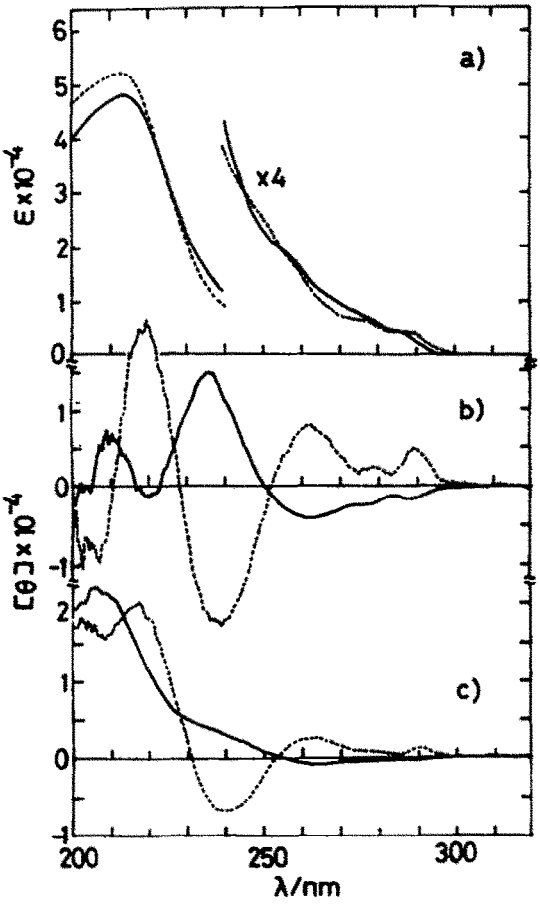

Fig. 2. The UV absorption (a), c. d. (b), and i. c. d. spectra in the presence of γ-CyD (c) of 2 (solid line) and 3 (dotted line) derived from 2AS in aqueous solution.

The 2 : 1 complex studied here is also a similar case. The i. c. d. measurement indicated that two anthracenes in γ-CyD prefer R-helicity.[15] It is of particular interest that this chiral inclusion gives a promise for stereoselective photodimerization of the guest compounds. The c. d. spectra of asymmetric photodimers (2 and 3) of 2AS produced in the presence of γ-CyD are shown in Fig. 2b, together with the UV absorption spectra (2a) and the i. c. d. spectra in the presence of γ-CyD (2c). These photodimers show definite circular dichroism which is different from the i. c. d. spectra, indicating that the photoreaction proceeds stereoselectively, though the same photoproducts in the host-free solution were obtained as racemic mixtures. The enantiomeric excess was roughly estimated from the comparison of molecular ellipticity ($[\theta]$/deg.cm^{2}dmol^{-1}) and molar absorptivity (ε/dm^{3}mol^{-1}cm^{-1}), to be ca. 10%: a value for 3 is slightly larger than that for 2. The photodimerization of 2AC gave identical results, though the optical purity was relatively poor.

An explanation of this stereoselective photodimerization is schematically shown in Fig. 3. There are two possibilities with respect to mutual configuration of the substituent groups of adjacent monomers in R-helix. Each enantiomer of the asymmetric photodimer originates from the respective configuration. Judging from the steric crowding of the substituent group, one is favored over the other. In the case of 2, the formation of the inclusion complex on the right hand side is restricted because of considerable interaction between the substituent groups and the rim of the CyD cavity, the complex on the left hand side being more favorable. In the case of 3, the eclipsed configuration on the right hand side is much less favorable than the staggered configuration on the left hand side. These effects result in a preferential excess of the enantiomer. If the monomers in the host cavity were in S-helix, an analogous steric effect would lead to an excess of opposite enantiomer. Although the absolute conformation of the enantiomer

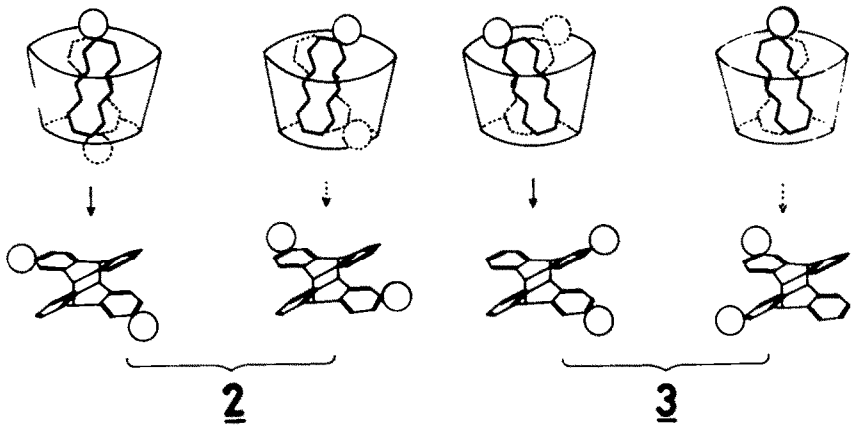

Fig. 3. Schemes of stereoselective photodimerization of 2AS and 2AC included by γ-CyD in aqueous solution.

preferred was not identified, we believe that the chiral inclusion into CyD is primarily responsible for the stereoselective photodimerization.

Spectroscopic Measurements of The Inclusion Complex

The complex formation induces considerable changes in the absorption spectra of the anthracene derivatives in aqueous solution. Typical examples for 2AS/β- and γ-CyD systems are shown in Fig. 4. It is remarkable that the change in the absorption spectra induced by β-CyD is dependent on the concentration of the guest. As the concentration of β-CyD increases, the ^1L_a transition band lying in the wavelength region of 300 nm to 400 nm appears intensified and sharpened at a low concentration of the guest (1×10^{-5} M) in contrast to the decrease in intensity, slight red shift in energy, and significant broadening of the same band at a high concentration of the guest (1×10^{-3} M). These opposite changes in the absorption spectrum confirm that the complex formation involves two equilibrium states. The first and second equilibrium states are corresponding to the 1 : 1 and 2 : 2 complex formation, respectively. The formation of the complex including two guest molecules was supported by the emission measurement. Whereas neither excimer nor dimer emission could be detected for 2AS in the host-free solution, a new emission arose near 500 nm at the expense of monomer fluorescence in the presence of β-CyD.[15] The excitation spectrum of this emission was different from that of the monomer fluorescence, indicating static formation of the dimer.

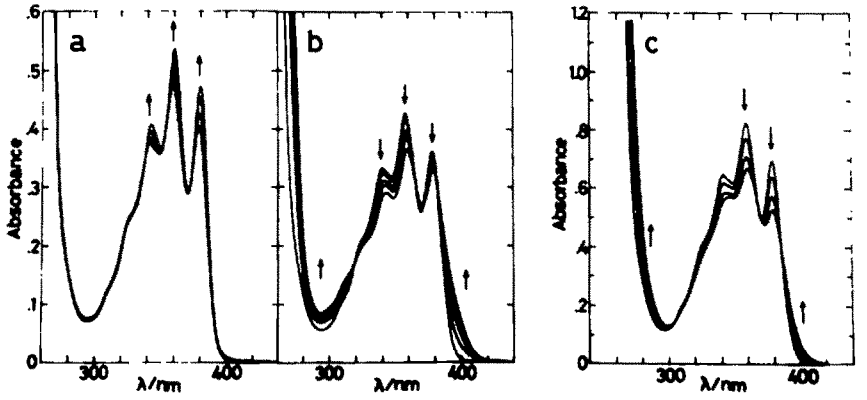

Fig. 4. The absorption spectra of 2AS in the presence of β- (a,b), and γ-CyD (c) in aqueous solution. Concentrations (M) of 2AS and CyD: a, (1.1×10^{-5}), β (0, 0.25, 0.5, 2×10^{-3}); b, (1×10^{-3}), β (0, 0.5, 0.75, 1.0, 1.5×10^{-3}); c, (2×10^{-4}), γ (0, 0.2, 0.6, 1.0×10^{-3}).

This dimer emission was very sensitive to the guest concentration and nearly negligible at $\leq 10^{-5}$ M. On the other hand, γ-CyD induces a monotonous decrease, slight red shifts, and significant diffuse of the absorption spectrum of the guest compound at the guest concentration ranging from 1 x 10^{-5} to 1 x 10^{-3} M. This may suggest that the 1 : 1 complex, if any, is followed by rapid association of another guest molecule to give rise to the two-guest inclusion complex. The monomer fluorescence was decreased by γ-CyD, but no new emission could be observed. It is clear that the efficiency of the photodimerization has a reverse relation with that of excimer emission. It is likely that while two 2AS molecules in γ-CyD have a tight configuration to photodimerize without any need of displacement, the proximate pairs of 2AS associated with β-CyD have a rather loose configuration.

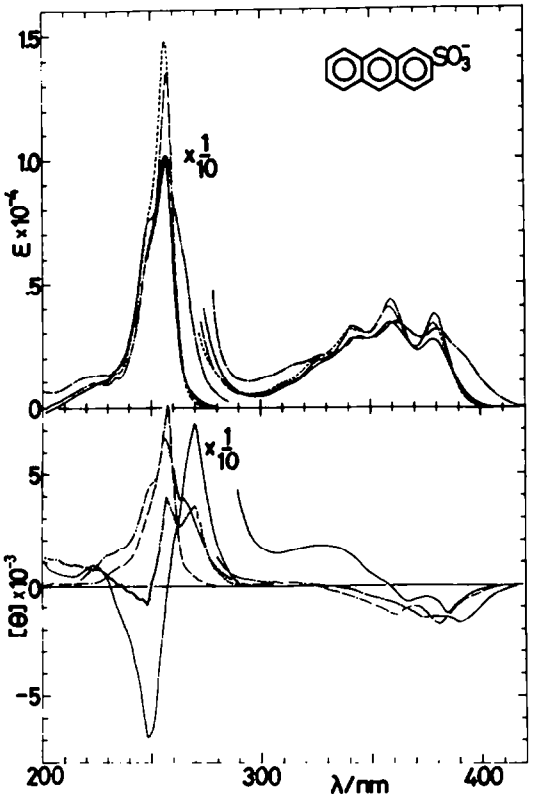

Fig. 5. The UV absorption (upper) and i. c. d. spectra (bottom) of 2AS in the presence and absence of CyDs in aqueous solution. Concentrations (M) of 2AS and β- or γ-CyD; ------ ($1x10^{-4}$), (none); ——— ($1x10^{-4}$), γ ($1x10^{-3}$); ..... ($1x10^{-3}$), γ ($1x10^{-2}$); —·—· ($1x10^{-4}$), β ($1x10^{-3}$); ——·— ($2x10^{-3}$), β ($1x10^{-2}$).

As shown in Fig. 5, the i. c. d. spectrum of 2AS in the presence of β-CyD shows a positive ^1B_b and a negative ^1L_a transition band. This is characteristic of the axial inclusion. The increase of the guest and host concentrations induces a significant diffuse of the spectrum, which is identical with the change in the UV absorption spectrum. The sign of the i. c. d. band is unchanged under these conditions. On the other hand, the i. c. d. spectrum in the presence of γ-CyD shows a Davydov splitting in both ^1B_b and ^1L_a transition bands, indicating a dipole coupling between two 2AS molecules which are in R-helix. The intensity of this split band is sensitive to the guest and host concentrations. While the split band appears sharp and intensive at concentrations of the guest more than 10^{-4} M, a non-interacting band like one in the presence of β-CyD becomes significant at relatively low guest (1 x 10^{-5} M) and high host (1 x 10^{-2} M) concentrations. This substantiates that the 2 : 1 inclusion complex originates from the 1 : 1 complex, though it could not be evidenced by the UV absorption measurement.

The equilibrium stoichiometry of the inclusion complex of 2AS was estimated from the UV and the i. c. d. spectra by using the continuous variation method. Under the experimental condition in which the sum of concentrations of the host and the guest molecules was kept to be 2×10^{-3} M (const.), the 1 : 1 and 2 : 1 stoichiometries were confirmed for β-CyD and γ-CyD, respectively.

The complex formation of the 2-substituted anthracene derivatives with γ-CyD can be written in the following equilibrium in which the 1 : 1 inclusion complex is neglected;

$$2\ A + \gamma\text{-CyD} \overset{K}{\rightleftharpoons} A_2C, \tag{1}$$

$$K = [A_2C]/\{([A] - 2[A_2C])^2([\gamma\text{-CyD}] - [A_2C])\}, \tag{2}$$

where [A] and [γ-CyD] are initial concentrations of the aromatic guest and the host, respectively and $[A_2C]$ is the equilibrium concentration of the 2 : 1 inclusion complex. By neglecting the terms of $[A_2C]^2$ and $[A_2C]^3$ by similar ways to Bender's treatment for absorption changes on complex formation,[36] one can give Eq. 3 on expansion of Eq. 2;

$$[A]^2[\gamma\text{-CyD}]/\Delta d = (1/K)/\Delta\varepsilon + [A]([A] + 4[\gamma\text{-CyD}])/\Delta\varepsilon, \tag{3}$$

where $\Delta\varepsilon = \varepsilon_{A_2C} - 2\varepsilon_A$ and Δd ($= [A_2C] \times \Delta\varepsilon$) is the absorbance change induced by complex formation. The plot for $[A]^2[\gamma\text{-CyD}]/\Delta d$ vs. $[A]([A] + 4[\gamma\text{-CyD}])$ should provide a straight line with a constant slope of $1/\Delta\varepsilon$ and an intercept of $(1/K)/\Delta\varepsilon$ to an ordinate axes. The plots obtained gave straight lines with $\varepsilon_{A_2C}^{359nm} = 3600\ M^{-1}cm^{-1}$ ($\varepsilon_{2AS}^{359nm} = 4150\ M^{-1}cm^{-1}$) and $K = 3.0 \times 10^6\ M^{-2}$.[20]

The fluorescence intensity of the guest was quenched in the presence of γ-CyD. No new emission could be detected. On the assumption that the 2 : 1 inclusion complex is nonfluorescent, one can derive Eq. 4 at sufficiently small [A] ($< 10^{-4}$ M);

$$F/F_o = ([A] - 2[A_2C])/[A], \tag{4}$$

where F and F_o are the fluorescence intensity in the presence and absence of γ-CyD, respectively. If [γ-CyD] > [A], Eqs. 2 and 4 give Eq. 5;

$$F/F_o = -Z + (Z^2 + 2Z)^{1/2}, \tag{5}$$

$$Z = (1/K)/4[A][\gamma\text{-CyD}].$$

The least squares fit to plots observed for 2AS/γ-CyD system gave $K = 3.4 \times 10^6\ M^{-2}$, a value which is in agreement with that obtained from the absorption measurement.[20]

The complex formation with β-CyD is conformed to the following equilibria;

$$A + \beta\text{-CyD} \overset{K_1}{\rightleftharpoons} AC, \tag{6}$$

$$2\ AC \overset{K_2}{\rightleftharpoons} A_2C_2, \tag{7}$$

$$K_1 = [AC]/\{([A] - [AC] - 2[A_2C_2])([\beta\text{-CyD}] - [AC] - 2[A_2C_2])\}, \tag{8}$$

$$K_2 = [A_2C_2]/[AC]^2, \tag{9}$$

where [AC] and $[A_2C_2]$ are equilibrium concentrations of the 1 : 1 and 2 : 2 complexes, respectively. Since $[A_2C_2]$ can be neglected at $[A] \leq 10^{-5}$ M, one can derive Eq. 10 from Eq. 8 by neglecting the term of the second power of [AC];

$$[A][\beta\text{-CyD}]/\Delta d_1 = (1/K_1)/\Delta\varepsilon_1 + ([A]) + [\beta\text{-CyD}])/\Delta\varepsilon_1, \tag{10}$$

where Δd_1 ($= \Delta\varepsilon_1 \times [AC]$) is the absorbance change induced at λ nm by the complex formation and $\Delta\varepsilon_1$ ($= \varepsilon_{AC} - \varepsilon_A$) is the difference between molar absorptivities of AC and A. On the assumption that [AC] is negligible at large values of [A] and [β-CyD], Eq. 11 is derived from Eqs. 8 and 9;

$$K_1^2 \times K_2 = [A_2C_2]/\{([A] - 2[A_2C_2])([\beta\text{-CyD}] - 2[A_2C_2])\}^2 \quad (11)$$

By analogous treatment to that described above, Eq. 12 is given from Eq. 11;

$$[A]^2[\beta\text{-CyD}]^2/\Delta d_2 = (1/K')/\Delta\varepsilon_2 + 4[A][\beta\text{-CyD}]([A] + [\beta\text{-CyD}])/\Delta\varepsilon_2, \quad (12)$$

where $K' = K_1^2 \times K_2$, $\Delta d_2 = \Delta\varepsilon_2 \times [A_2C_2]$, and $\Delta\varepsilon_2 = \varepsilon_{A_2C_2} - 2\varepsilon_A$.

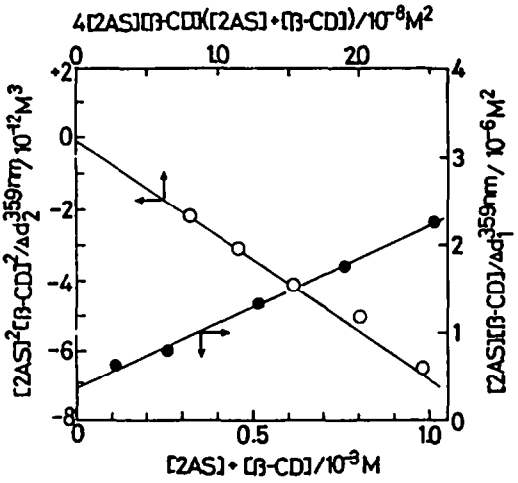

Fig. 6. Determination of the association constants for 2AS/β-CyD system. The data were obtained from Fig. 4a and 4b.

The values of $\Delta\varepsilon$ and the equilibrium constant can be evaluated from Eqs. 10 and 12. The results for 2AS/β-CyD system are shown in Fig. 6. The straight lines obtained give $K_1 = 4800\ M^{-1}$, $K_2 = 76\ M^{-2}$, $\varepsilon_{AC}^{359nm} = 4700\ M^{-1}cm^{-1}$, and $\varepsilon_{A_2C_2}^{359nm} = 4500\ M^{-1}cm^{-1}$. 2-Naphthalenesulfonate (2NS)/β-CyD system also gave satisfactorily linear plots with $K_1 = 340\ M^{-1}$, $K_2 = 150\ M^{-2}$, $\varepsilon_{AC}^{274nm} = 5030\ M^{-1}cm^{-1}$, and $\varepsilon_{A_2C_2}^{274nm} = 8100\ M^{-1}cm^{-1}$ ($\varepsilon_{2NS}^{274nm} = 4780\ M^{-1}cm^{-1}$).

The values of K_1 for the two cases are different by an order of magnitude. Judging from the molecular structure, it is probable that the aromatic nucleus of 2AS is trapped more deeply in the host cavity than that of 2NS. This may be mainly responsible for the difference in equilibrium stability between them. It can be said that the values of K_2 are little dependent on the guest molecule, suggesting that the host-guest interaction is less important in this binding process. This may support the idea that the formation of the 2 : 2 inclusion complex is facilitated by the interaction between the 1 : 1 complexes. Alternatives are, of course, acceptable at this stage of investigation. While the K_1 value of 2NS/β-CyD system is comparable with 685 M^{-1} obtained by analogous method for naphthalene/β-CyD system, the K_2 values of these systems are considerably different. This dissimilarity of the K_2 values is, however, not crucial, because these values were determined by different methods.

The formation of the 2 : 2 complex is guest-specific. No such complex could be formed for the 1-isomer (1AS and 1NS)/β-CyD systems.

Although 1-Pyrenesulfonate showed little interaction with β-CyD, it exhibits a prominent excimer emission in the presence of γ-CyD. The situation is analogous to pyrenylbutyrate/γ-CyD system in which the formation of the 2 : 2 complex has been proposed to elucidate spectrophotometric changes in the binding isotherm.[19]

Reversible Photodimerization in Aqueous Solution and in A PVA Film

The photodimerization of 2AS and 2AC in aqueous solution is greatly dependent on their con-

centration and, in practice, only effective at concentrations higher than 10^{-3} M. The photodimerization of these compounds in the presence of γ-CyD in aqueous solution is quite different from this, because it arises from the inclusion complex in which the guest molecules are trapped in close proximity by the host before photoirradiation. Indeed, the photoreaction occurs in the presence of γ-CyD (1 x 10^{-3} M) even at low concentrations of the guest ($\leq 10^{-4}$ M) with an initial rate practically similar to that at relatively high concentrations of the guest ($\geq 10^{-3}$ M). It is noteworthy that the photodimer as included by γ-CyD undergoes photochemical cycloreversion by the 280 nm-light irradiation into the monomer as efficiently as in the host-free solution. Furthermore, the guest compound is protected from the photooxydation which is significant in the absence of CyD under air atmosphere. Thus, γ-CyD-assisted photodimerization of 2AS and 2AC in aqueous solution is almost quantitatively reversible. However, the inclusion complex of 2AS with β-CyD led to partially reversible photodimerization, inducing irreversible byreactions also.

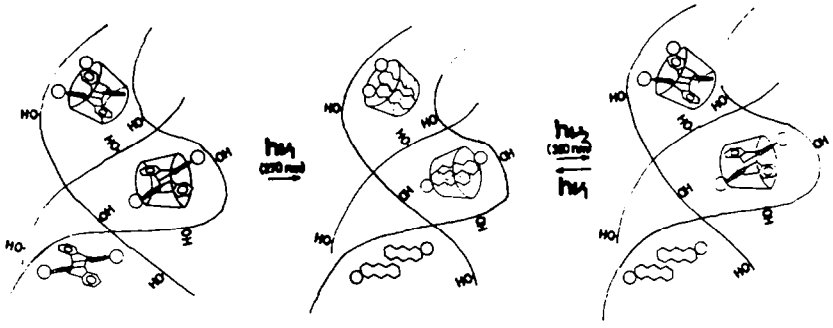

Fig. 7. A scheme of the photoreaction in a PVA film.

The photoreaction in a PVA film containing the inclusion complex with γ-CyD is essentially the same as that in aqueous solution. It has been found that the reversible photodimerization occurs in a PVA film, if the polymer film is prepared to contain both the photodimer and γ-CyD. However, no photodimerization could occur when the monomer was used in place of the photodimer in preparing the polymer film. This is due to the disruption of mutual configuration of monomers in the host cavity during the development of the polymer film. The monomer molecules photogenerated from the photodimer as included by the host in polymer matrices, hold the molecular configuration favorable to photodimerize. These have been confirmed by the i. c. d. measurements. The photodimer could not be regenerated from a host-free polymer film containing the photodimer. In conclusion, both the photodimer and γ-CyD are essential for the preparation of the polymer film which shows reversible photodimerization. This polymer model is shown in Fig. 7. The forward and reverse photodimerization of the inclusion complex can be sequentially repeated by selecting the irradiating wavelength, though the naked aromatic compound shows, no longer, reversible photoreaction. This polymer system may be promising for a memory recording material[37] and the application is under way.

Experimental

The preparation of potassium anthracenesulfonate and anthracenecarboxylate was described in previous papers.[15,20] CyDs were purchased from Tokyo Kasei and used without further purification. The HPLC analysis was done by using a reversed phase column eluted with acidic buffers.[15] PVA films showing reversible photoreaction were prepared from aqueous solutions containing 4% PVA, 2 x 10^{-3} M photodimer of 2AS and 1x10^{-2} M γ-CyD by casting them on quartz plates. The quantum yields of the photodimerization were based on the dimer formation.

References and Notes

1. M. L. Bender and M. Komiyama, 'Cyclodextrin Chemistry,' Springer-Verlag, New York, 1977.
2. I. Tabushi, Acc. Chem. Res., **15**, 66 (1982).
3. F. Cramer and W. Dietsche, Chem. Ber., **92**, 378 (1959).
4. H. P. Benshop and G. R. Van der Berg, J. Chem. Soc., Chem. Commun., **1970**, 1431.
5. a) M. Mikolajczyk, J. Drabowicz, and F. Cramer, J. Chem. Soc., Chem. Commun., **1971**, 317; b) M. Mikolajczyk and J. Drabowicz, Tetrahedron Let., **1972**, 2379.
6. A. Harada, M. Furue, and S. Nozakura, J. Polym. Sci., Polymer. Chem. Ed., **16**, 189 (1978).

7. B. Zsadon, M. Szilasi, and F. Tudos, J. Chromatography, **208**, 109 (1981).
8. H. Takeshita, M. Kumamoto, and I. Kouno, Bull. Chem. Soc. Jpn., **53**, 1006 (1980).
9. I. Nakamura, T. Sugimoto, J. Oda, and Y. Inouye, Agric. Biol. Chem., **45**, 309 (1981).
10. a) R. Chenevert and R. Plante, Can. J. Chem., **61**, 1092 (1983); b) R. Chenevert and N. Voyer, Tetrahedron Let., **25**, 5007 (1984).
11. a) V. Ramamurthy, ACS Sym. Ser., **278**, 267 (1985); b) B. N. Rao, N. J. Turro, and V. Ramamurthy, J. Org. Chem., **51**, 460 (1986); c) S. Singh, G. Usha, C-H Tung, N. J. Turro, and V. Ramamurthy, ibid., **51**, 941 (1986).
12. a) H. Hirai, N. Toshima, and S. Uenoyama, Polymer J., **13**, 607 (1981); b) Bull. Chem. Soc. Jpn., **58**, 1156 (1985).
13. K. Takamura, S. Inoue, and F. Kusu, Chem. Lett., **1983**, 233.
14. N. Kobayashi, Y. Hino, A. Ueno, and T. Osa, Bull. Chem. Soc. Jpn., **56**, 1849 (1983).
15. T. Tamaki and T. Kokubu, J. Inc. Phen., **2**, 815 (1984).
16. A. Ueno, K. Takahashi, and T. Osa, J. Chem. Soc., Chem. Commun., **1980**, 921.
17. S. Hamai, Bull. Chem. Soc. Jpn., **55**, 2721 (1982).
18. K. Kano, I. Takenoshita, and T. Ogawa, Chem. Lett., **1982**, 321.
19. W. G. Herkstroeter, P. A. Martic, and S. Farid, J. Chem. Soc., Perkin Trans., **1984**, 1453.
20. T. Tamaki, Chem. Lett., 53 (1984).
21. J. Emert, D. Kodali, and R. Catena, J. Chem. Soc., Chem. Commun., **1981**, 758.
22. N. J. Turro, T. Okubo, and G. C. Weed, Photochem. Photobiol., **35**. 325 (1982).
23. K. Kano, H. Matsumoto, S. Hashimoto, M. Sisido, and Y. Imanishi, J. Am. Chem. Soc., **107**, 6117 (1985).
24. a) N. Kobayashi, A. Ueno, and T. Osa, J. Chem. Soc., Chem. Commun., **1981**, 340; b) N. Kobayashi, R. Saito, A. Ueno, and T. Osa, Makromol. Chem., **184**, 837 (1983).
25. G. S. Cox and N. J. Turro, J. Am. Chem. Soc., **106**, 422 (1984).
26. A. Kuboyama and S. Matsuzaki, J. Inc. Phen., **2**, 755 (1984).
27. A. Ueno, K. Takahashi, Y. Hino, and T. Osa, J. Chem. Soc., Chem. Commun., **1981**. 194.
28. K. Kano, I. Takenoshita, and T. Ogawa, Chem. Lett., **1980**, 1035.
29. H. Kobayashi, M. Takahashi, Y. Muramatsu, and T. Morita, Bull. Chem. Soc. Jpn., **54**, 2815 (1981).
30. B. U. Nair and G. C. Dismukes, J. Am. Chem. Soc., **105**, 124 (1983).
31. D. C. Rideout and R. Breslow, J. Am. Chem. Soc., **102**, 7817 (1980).
32. a) K. Harata and H. Uedaira, Bull. Chem. Soc. Jpn., **48**, 375 (1975); b) H. Shimizu, A. Kaito, and M. Hatano, Bull. Chem. Soc. Jpn., **52**, 2678 (1979).
33. Since the NMR spectrum of γ-CyD including 2AS showed a much higher upfield shift for interior H_5 than H_3,[15] it is likely that the aromatic guest compound is included toward the closed face of the toroidal host compound. The model of the inclusion toward the more open face shown in a previous paper is incorrect.
34. R. Breslow and M. Hammond, J. Am. Chem. Soc., **102**, 5402 (1980).
35. Y. Tanaka, H. Sakuraba, and H. Nakanishi, J. Chem. Soc., Chem. Commun., **1983**, 947.
36. R. L. VanEtten, J. F. Sebastian, G. A. Clowes, and M. L. Bender, J. Am. Chem. Soc., **89**, 3242 (1967).
37. W. J. Tomlinson, E. A. Chandross, R. L. Fork, C. A. Pryde, and A. A. Lamola, Applied Optics, **11**, 533 (1972).