Inclusion Complexes and *Z–E* Photoisomerization of β-Cyclodextrin Bearing an Azobenzene Pendant

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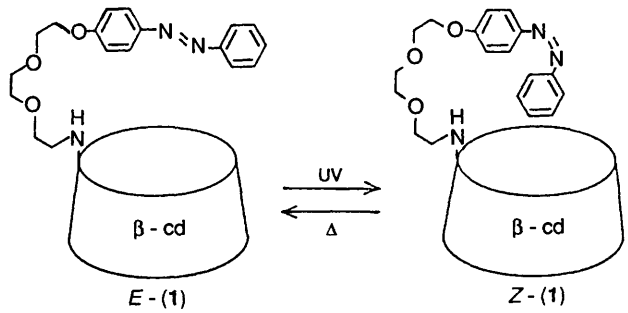
A new photoresponsive host (**1**), β-cyclodextrin (β-cd) bearing an azobenzene moiety, has been prepared for the purpose of regulating guest binding by light. The CD spectrum of the dark-adapted sample of (**1**) exhibits a positive band around 345 nm associated with the azobenzene π–π* transition, suggesting that (**1**) exists as an intramolecular complex, in which the *E*-azobenzene moiety is inserted into the β-cd cavity with its long axis parallel to the cd axis. After the azobenzene moiety of (**1**) has been isomerized from the *E*- to the *Z*-form by UV light irradiation, it exhibits a CD pattern which has strong positive and negative bands at 312 and 425 nm, respectively. The CD intensities of both *E*- and *Z*-forms of (**1**) decrease upon guest addition, and the analysis of the CD variations indicate that the intramolecular complexes of (**1**) are converted into 1:1 host–guest complexes. The *E*-isomer forms binding complexes with adamantane-1-carboxylic acid and adamantan-1-ol *ca.* five times more strongly than the *Z*-form. Less photocontrolled guest binding was observed with other guests. The effects of pH on molecular association behaviour as well as on photocontrol of guest binding of (**1**) are described in connection with the electronic charges that (**1**) possesses.

Cyclodextrins (cds) are torus-shaped cyclic oligosaccharides composed of six or more α-1,4-linked (+)-D-glucopyranose units. Cds with six, seven, and eight glucose units (α-, β-, and γ-cd, respectively) have cavities the internal diameters of which are 4.5, 6.0, and 8.5 Å, respectively, and form inclusion complexes by accommodating a variety of guest molecules into the cavities.[1] This inclusion phenomenon often induces remarkable variations in photophysical and photochemical properties of the guest substances due to the spatial restrictions of the cavities that limit conformation of the included guests as well as due to the change of the medium from aqueous bulk solution to the hydrophobic cavities.[2] Excimer,[3–13] exciplex,[14] and charge-transfer complex formation[15] and photodimerization of anthracene derivatives[16,17] are greatly promoted on this basis. Although native cds are optically inert, they may be converted into photoactive hosts, and recently some fluorescent[18–21] and photoresponsive[22,23] cds have been prepared. Photocontrol of guest binding was accomplished with azobenzene-modified cds[22,23] in which the azobenzene moieties act as either a cap or spacer. It was also shown that catalytic reaction of β-cd can be regulated by light in a simple system of β-cd and 4-carboxyazobenzene.[26] *E–Z* photoisomerization of azobenzene is the basis for such photocontrolled binding and reactions, and recently photoisomerization of azobenzene-β-cd complexes has been studied in detail.[27]

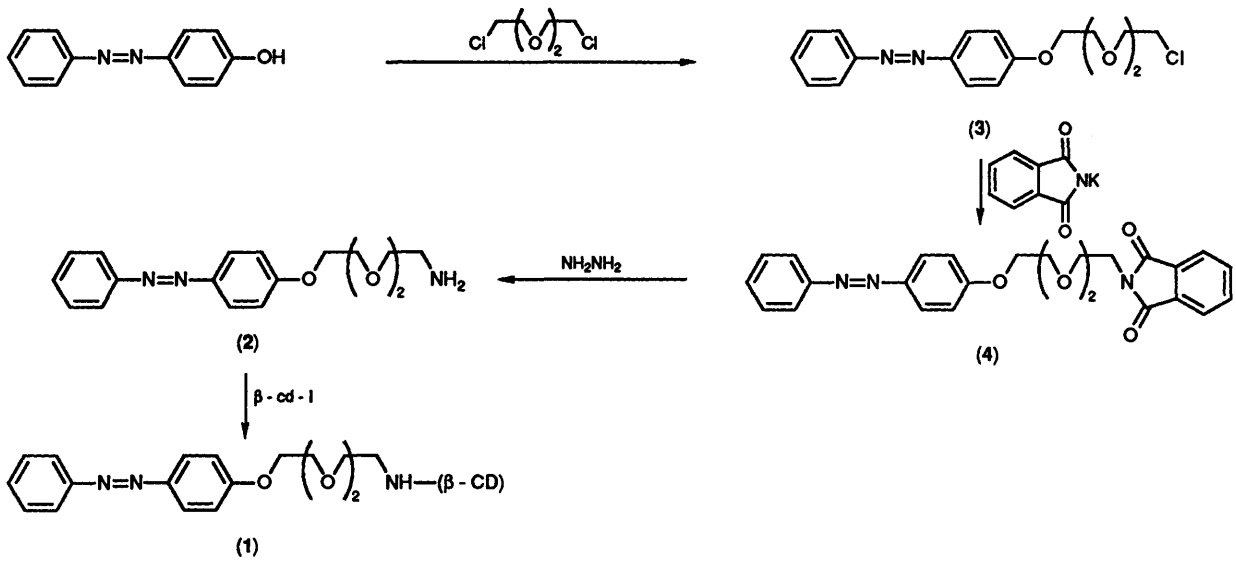
We wish to report here the photochemical properties of a new photoresponsive β-cd derivative that has an azobenzene pendant connected with the primary hydroxy side (narrower face) of β-cd unit through an amino group (**1**). Since the *E*- and *Z*-forms of the pendant have different shapes and polarity and are likely to influence differently the guest binding of (**1**) by acting as intramolecular inhibitors or hydrophobic caps, the guest-binding ability of (**1**) may be photocontrolled in an on–off fashion.



Experimental

1-Chloro-8-(4-phenylazophenoxy)-3,6-dioxaoctane (**3**).—To a solution of glycol-1,2-bis(2-chloroethoxy)ethane (106.2 g, 0.568 mol) and *p*-phenylazophenol (75 g, 0.378 mol) in n-butanol stirred at 130 °C was sequentially added an aqueous solution of sodium hydroxide (21.9 g in 84 cm^3 water) for 2.5 h. The reaction mixture was further stirred for 22 h, and then the solvent was removed under reduced pressure. After water (*ca.* 300 cm^3) was added, the reaction mixture was extracted with chloroform 1 l). Silica-gel column chromatography (n-hexane–ethyl acetate, 2:1) afforded the crude product, which was purified by recrystallization from ethanol, to yield (**3**) as orange crystals, yield 48%, m.p. 48–49 °C (Found: C, 61.85; H, 6.25; N, 8.1; Cl, 10.15. Calc. for $C_{18}H_{21}ClN_2O_3$: C, 61.98; H, 6.07; N, 8.03; Cl, 10.16); δ($CDCl_3$) 3.7–4.2 (12 H, br, CH_2), and 6.9–8.0 (9 H, m, ArH).

N-[8-(4-Phenylazophenoxy)-3,6-dioxaoctyl]phthalimide (**4**).—To a DMF (215 cm^3) solution of (**3**) (31.31 g, 0.0898 mol) stirred at 90 °C was added potassium phthalimide (18.86 g, 0.102 mol). After being stirred at 90 °C for 2 h, the reaction mixture was poured into ice–water (200 g) and extracted with chloroform (500 cm^3). The organic layer was washed with NaOH solution (1 mol dm^{-3}; 120 cm^3) and dried over sodium sulphate. Recrystallization from a mixture of ethyl acetate and n-hexane yielded (**4**) as orange needles, yield 85%, m.p. 97–99 °C (Found: C, 67.85; H, 5.4; N, 9.2. Calc. for $C_{26}H_{25}N_3O_5$: C, 67.96; H, 5.48; N, 9.15); δ($CDCl_3$) 3.3–4.2 (12 H, br, CH_2), and 6.7–8.2 (13 H, m, ArH).



Scheme 1.

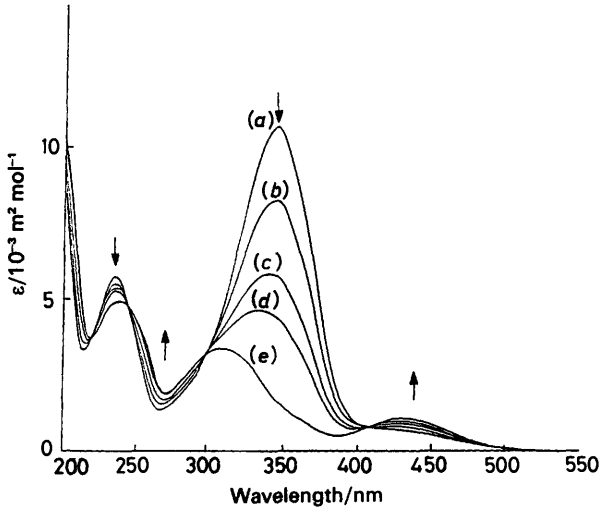


Figure 1. Absorption spectra of (**1**) in aqueous solution (pH 6.7, 4.97×10^{-5} mol dm^{-3}) at different times: (*a*) 0 s; (*b*) 30 s; (*c*) 60 s; (*d*) 100 s; (*e*) 240 s of UV light irradiation.

1-*Amino*-8-(4-*phenylazophenoxy*)-3,6-*dioxaoctane* (**2**).—To a solution of (**4**) (35.1 g, 0.0764 mol) in methanol (430 cm^3) was added hydrazine monohydrate (11 cm^3), and the mixture was refluxed for 1 h. After water (300 cm^3) was added, methanol was removed from the mixture under reduced pressure, and conc. HCl (215 cm^3) was added. After being stirred at 60 °C for 1 h, the solution was neutralized by NaOH solution (5 mol dm^{-3}) and extracted with chloroform (*ca.* 500 cm^3). Silica-gel column chromatography (CH_2Cl_2–EtOH–28% NH_4OH 15:1:1) yielded (**2**) as orange crystals (78%), m.p. 42–45 °C (Found: C, 65.85; H, 7.2; N, 12.85. Calc. for $C_{18}H_{23}N_3O_3$: C, 65.65; H, 7.05; N, 12.75); δ($CDCl_3$) 1.4 (2 H, s, NH_2), 2.9 (2 H, t, NCH_2), 3.4–4.2 (10 H, br, OCH_2), and 6.9–7.9 (9 H, m, ArH).

6-*Deoxy*-6-[8-(4-*phenylazophenoxy*)-3,6-*dioxaoctylamino*]-β-*cd* (**1**).—A solution of 6-deoxy-6-iodo-β-cd[13] (3.0 g, 2.37 mmol) and (**2**) (7.02 g, 0.0213 mol) in DMF (100 cm^3) was stirred at 80 °C for 24 h under nitrogen. After being cooled, the reaction mixture was poured into acetone (2 l), and the precipitates were collected and dried *in vacuo*, to yield the crude product (2.831 g). Repeated recrystallizations from water and the mixture of n-butanol, EtOH, and water (5:4:3 by volume) afforded (**1**) as orange crystals, yield 27%, R_f 0.74 (28% NH_4OH–water–ethyl acetate–Pr^iOH, 1:4:3:5) (Found: C, 48.25; H, 7.2; N, 2.85. Calc. for $C_{60}H_{97}N_3O_{40}\cdot 3\,H_2O$: C, 48.03; H, 6.52; N, 2.80); δ[$(CD_3)_2SO$] 1.7 (1 H, br, NH), 4.1 (2 H, br, CH_2), 4.4 (6 H, br, O^6H of cd), 4.8 (7 H, br, C^1H of cd), 5.7 (14 H, O^2H and O^3H of cd), 6.8–7.9 (9 H, m, ArH), and 3.0–3.8 (58 H, br, other protons).

Measurements. Absorption and CD spectra were measured on a Shimadzu UV-250 photochrometer and a JASCO J-400X circular dichrometer, respectively. Measurements were made for the solutions of (**1**) at pH 6.7, 10.1, and 12.9. The solvent of pH 6.7 was distilled and deionized pure water, while the solution of pH 12.9 was sodium hydroxide solution. The solution of pH 10.1 was buffered with sodium hydrogen carbonate and sodium carbonate (0.0672 mol dm^{-3}).

Photoirradiation. Photoirradiation was performed with a 500 W xenon lamp (Ushio UI-5010) by using a Corning 7-37 filter to isolate the light of $310 < \lambda < 390$ nm. The content of the *Z*-form was 83–89% for (**1**) and (**2**), when estimated from the absorbances at 345 nm, providing that pure *Z*-form has no absorption at this wavelength.

Binding constants. Binding constants were obtained by curve-fitting analysis[19] of the CD intensities at 345 and 312 nm for the *E*- and *Z*-forms, respectively. For the *Z*-form, the analysis was also undertaken by using CD intensities at 450 nm. Both procedures for the *Z*-form gave the same binding constants within experimental error.

Results and Discussion

A new photoresponsive β-cd derivative (**1**) was prepared according to the synthetic route shown in Scheme 1. Since the azobenzene moiety of (**1**) is linked to the amino group of β-cd through a flexible chain composed of six carbons and three oxygens, it is expected to move rather freely as an intramolecular guest.

Figure 1 shows absorption spectra of (**1**) in aqueous solution. The dark-adapted solution exhibits a spectral pattern, which is essentially that of azobenzene itself, with a peak around 345 nm and a broad band above 400 nm associated with the azobenzene π–π* and *n*–π* transitions, respectively. Irradiation with UV light changes the spectral shape associated with the

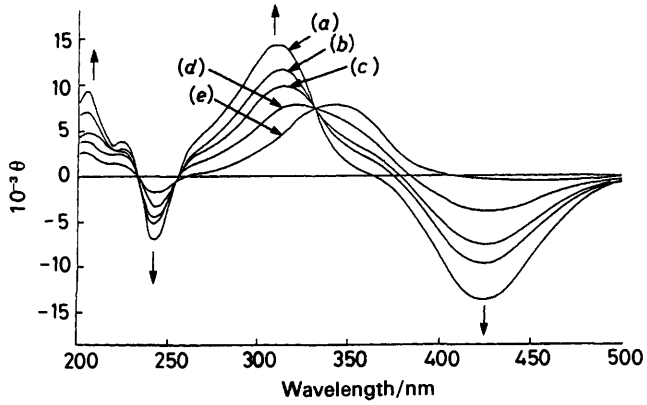


Figure 2. The CD spectra of (**1**) in aqueous solution (pH 6.7, 4.97 × 10^{-5} mol dm^{-3}) at different times: (*a*) 0 s; (*b*) 30 s; (*c*) 60 s; (*d*) 100 s; (*e*) 240 s of UV light irradiation.

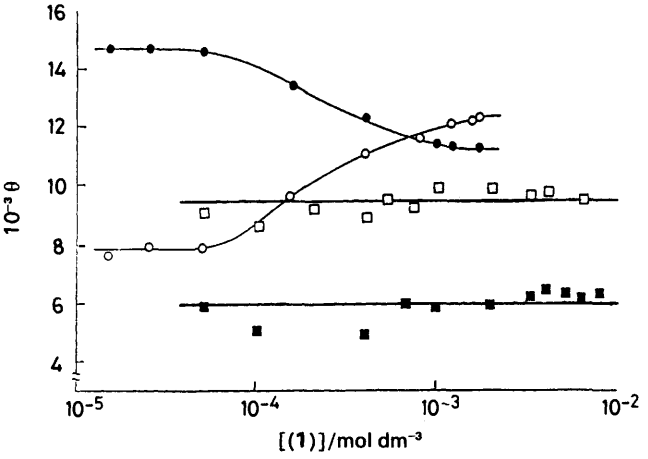


Figure 3. The CD intensities of (**1**) as a function of concentration: ○, *E*-(**1**), pH = 6.7, 345 nm; □, *E*-(**1**), pH = 12.9, 345 nm; ●, *Z*-(**1**), pH = 6.7, 312 nm; ■, *Z*-(**1**), pH = 12.9, 312 nm.

photoisomerization of the azobenene moiety from the *E*- to the *Z*-form, decreasing the π–π^* band and increasing the n–π^* band with isosbestic points at 220, 244, 298, and 408 nm. Under the experimental conditions, the photostationary state was reached within 5 min.

Figure 2 shows CD spectra of (**1**) in aqueous solution. The dark-adapted solution of (**1**) exhibits a peak at 345 nm and a broad trough around 450 nm associated with the azobenzene π–π^* and n–π^* transitions, respectively. Upon irradiation, the spectral shape was converted into that of the *Z*-form, which has a strong peak at 312 nm and a deep trough at 425 nm together with a weaker peak and trough appearing at 228 and 242 nm, respectively. All spectra of (**1**) with different ratios of *E*- and *Z*-forms pass the same points at 233, 253, and 331 nm, confirming that the solution contains only two species of (**1**), the *E*- and *Z*-forms. It is theorized that, when the long axis of an arene guest is parallel to the axis of the cd cavity (axial inclusion), the sign of the induced CD of the cd–arene complex is positive in the wavelength region of the electronic transition, which is polarized along the long axis of the arene.[28,29] Since the π–π^* transition of *E*-azobenzene is polarized in the plane along the long axis of the molecule,[30,31] the positive CD observed in the π–π^* transition region of the *E*-form suggests that the long axis of the azobenzene is parallel to the axis of β-cd. On the other hand, the non-planar structure of the *E*-form makes it difficult to identify its geometry in the intramolecular complex.

Recently, we have shown that γ-cd derivatives having a pendant such as anthracene[19] and pyrene[20] tend to form

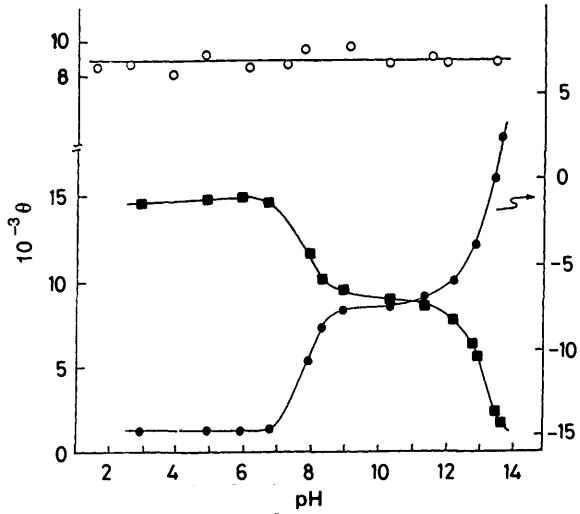
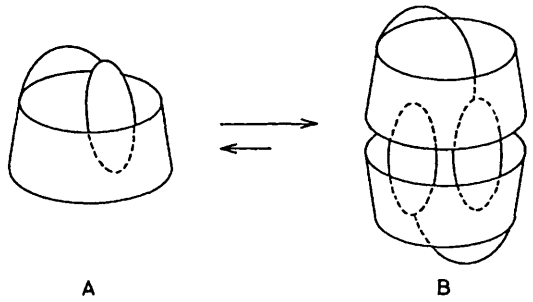


Figure 4. The CD intensities of (**1**) in aqueous solution at 4.97 × 10^{-5} mol dm^{-3} as a function of pH: ○, *E*-(**1**), 345 nm; ■, *Z*-(**1**), 312 nm; ●, *Z*-(**1**), 425 nm.

association dimers, in which two arene moieties meet in the long cylindrical cavity made by two cd units. This type of association is not confined to the γ-cd derivatives since a β-cd derivative that has a naphthyl moiety as a pendant shows remarkable excimer emission in its concentrated solutions.[13] We therefore checked the concentration dependency of the CD intensities for both *E*- and *Z*-forms. Figure 3 shows variations of the CD intensities measured at 345 and 312 nm for the *E*- and the *Z*-forms, respectively. The CD intensity decreased and increased for the *E*- and the *Z*-forms, respectively, with increasing concentration above 10^{-4} mol dm^{-3} in solutions of pH 6.7. This result suggests that both forms associate in their concentrated solutions. If these species are association dimers, in which secondary hydroxy group sides are facing each other, they are expected to dissociate in alkaline solutions due to the ionic repulsion between alkoxide anions of the secondary hydroxy groups.[13,20] Figure 3 shows that the CD intensities of both forms are hardly influenced by the concentration in an alkaline solution. This result suggests that both *E*- and *Z*-isomers of (**1**) form association dimers (**B**), which are in equilibrium with the intramolecular complexes (**A**).



In addition to the secondary hydroxyl groups of the β-cd unit, (**1**) has, as an ionizable group, an amino group which can exist as both protonated and neutral forms. Figure 4 shows the pH dependency of the CD intensities of the *E*- and the *Z*-forms of (**1**). The CD intensity at 345 nm of the *E*-form was hardly affected by pH, whereas the intensities at 312 and 425 nm of the *Z*-form exhibit abrupt changes at pH 7.9 and 13.0, which correspond to pK_a values of the amino moiety and the secondary hydroxy groups of (**1**), respectively. The variations in the CD intensity suggest that (**1**) changes the location or

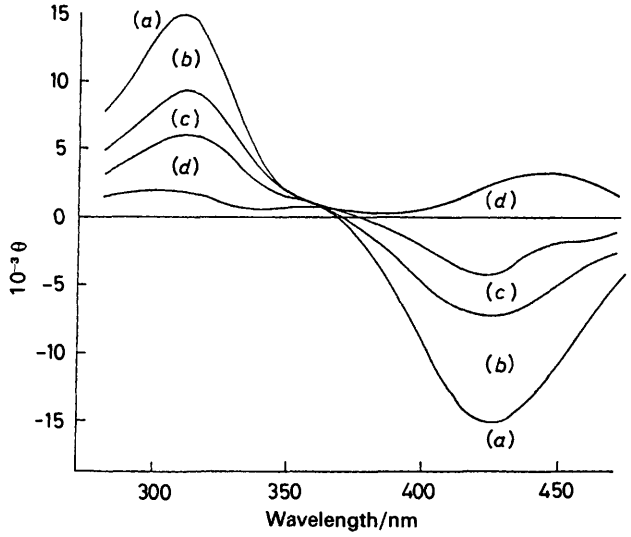


Figure 5. The CD spectra of the *Z*-form of (**1**) in aqueous solution (4.72×10^{-5} mol dm^{-3}): (*a*) pH = 6.7; (*b*) pH = 10.3; (*c*) pH = 12.9; (*d*) pH = 13.6.

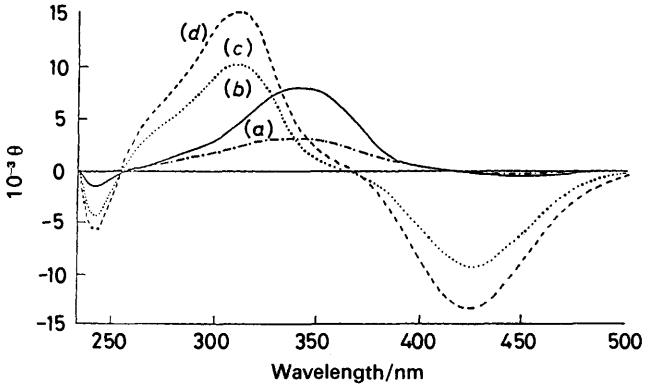


Figure 6. The CD spectra of (**1**) in aqueous solution at pH 6.7: (*a*) before irradiation, in the presence of 1-ACA (7.96×10^{-4} mol dm^{-3}); (*b*) before irradiation; (*c*) after irradiation, in the presence of 1-ACA (7.96×10^{-4} and dm^{-3}); (*d*) after irradiation.

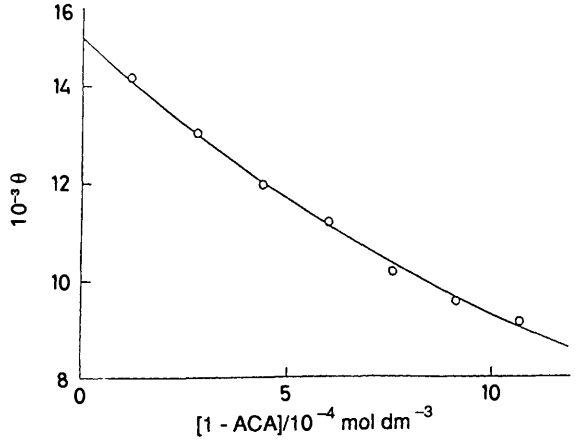


Figure 7. An example of curve-fitting analysis for the intensities at 312 nm of the *Z*-form of (**1**) in aqueous solution (pH 6.7, 4.97×10^{-5} mol dm^{-3}) obtained at different concentrations of adamantane-1-carboxylic acid (1-ACA). The solid line represents the calculated curve (K = 415 mol^{-1} dm^3).

orientation of the *Z*-pendant in the cavity. Figure 5 shows the CD spectra of the *Z*-form. The CD sign of the *Z*-form in the n–π^* transition region changes from negative to positive with increasing pH, confirming that the orientation of the *Z*-form in high pH solutions is different from that in neutral solutions. This different behaviour of the *Z*-form, in comparison with the *E*-form, might be rationalized in terms of the polar nature of the structure, which makes the pendant sensitive to the electronic charges of the amino and secondary hydroxy groups.

Table 1. Binding constants of *trans* and *cis* forms of (**1**) at 25 °C.

Guest	pH	Binding constant/dm^3 mol^{-1}	
		E	*Z*
Cyclohexanol	6.7	9.0	0.84
	12.9	9.8	12.8
[(1*S*)-*endo*]-(−)-Borneol	6.7	406	318
	10.1	75	36
	12.9	144	42
1-ACA[a]	6.7	2 160	415
	12.9	*b*	*b*
1-ACOH[c]	6.7	214	46
	12.9	353	215
Cyclododecanol	6.7	150	349
	12.9	*b*	*b*

[a] 1-ACA, adamantane-1-carboxylic acid. [b] No complex formed. [c] 1-ACOH, adamantan-1-ol.

Figure 6 shows the CD variations of (**1**) caused by 1-adamantanecarboxylic acid in aqueous solution (pH 6.7). Both *E*- and *Z*-forms of (**1**) showed decreased CD intensities in the whole wavelength regions with increasing guest concentration, suggesting that the azobenzene moiety is excluded from the cavity associated with formation of inclusion complexes. The curve-fitting analysis[19] of these guest-induced CD variations has shown that both *E*- and *Z*-isomers of (**1**) form 1:1 host–guest complexes (Figure 7). Table 1 shows binding constants of (**1**) with several guests at 25 °C. It is noted that (**1**) takes protonated, neutral, and anionic forms at pH 6.7, 10.1, and 12.9, respectively. The binding constants of cyclohexanol at pH 6.7 are 9.0 and 0.84 dm^3 mol^{-1} for the *E*- and the *Z*-forms, respectively. The values at pH 12.9 are larger than these values, but still much smaller than the value (930 dm^3 mol^{-1}) reported for the cyclohexanol–β-cd complex.[32] This result suggests that the intramolecular complexes of (**1**), in which the azobenzene moiety is included in the β-cd cavity, are too stable to be converted into intermolecular complexes. This implies that the azobenzene moiety acts as an intramolecular inhibitor for host–guest complexation of (**1**). β-Cd derivatives with hydrophobic caps were reported to have stronger binding ability than β-cd itself due to the enlarged hydrophobic nature of the environment around the included guests.[24,25] The *E*- and *Z*-azobenzene moieties may also be expected to stabilize the intermolecular complexes by acting as the cap although the planar *E*-form seems a better cap than the nonplanar *Z*-form. Consequently, the binding constants should reflect the balance between the inhibitory and the stabilization effects of the azobenzene moiety. Under the circumstances, it is not easy to predict whether the *E*-form of (**1**), which is likely to act not only as an effective inhibitor but also as an effective cap, is better host than the *Z*-form. Adamantane-1-carboxylic acid, which is much larger in its size than cyclohexanol, is bound strongly to both *E*- and *Z*-forms of (**1**) at pH 6.7, the binding constant of the *E*-form being 5.2 times larger than that of the *Z*-form. This result suggests that the effect of capping by the *E*-azobenzene moiety is more remarkable than the *Z*-isomer at least for this complex. The stronger binding ability of the *E*-form was also observed for other guests such as [(1*S*)-*endo*](−)-borneol (pH 6.7, 10.1, 12.9) and adamantan-1-ol (pH 6.7, 12.9). The case of cyclododecanol at pH 6.7 is exceptional since the binding constant of the *E*-form

Table 2. First-order rate constants of the thermal *Z*–*E* isomerization of (**1**) at 45 °C.

(1)[a]	Rate/min^{-1}
pH 6.7	1.56×10^{-3}
pH 6.7, adamantan-1-ol (4.9×10^{-3} mol dm^{-3})	1.59×10^{-3}
pH 12.9	1.69×10^{-3}
Me_2SO	2.50×10^{-3}

[a] The concentration of (**1**) was *ca.* 5×10^{-5} mol dm^{-3}.

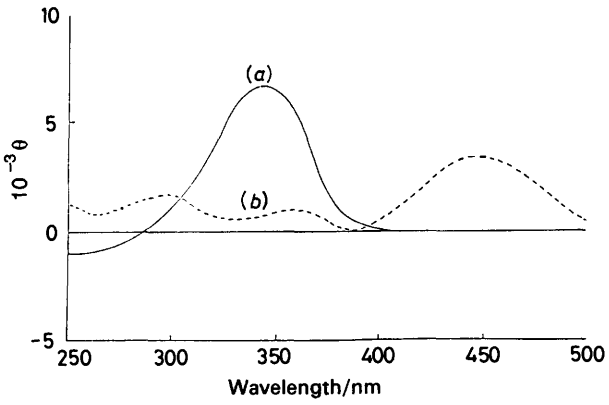


Figure 8. The CD spectra of the solutions containing 5.05×10^{-5} mol dm^{-3} (**2**): (*a*) with β-cd (2.53×10^{-3} mol dm^{-3}), before UV irradiation; (*b*) with β-cd (2.31×10^{-3} mol dm^{-3}), after UV irradiation.

is only 43% of that of the *Z*-form. It is noted that the negative charges of the secondary hydroxy groups of (**1**) at pH 12.9 prohibit (**1**) from accommodating the negatively charged species of adamantane-1-carboxylic acid due to ionic repulsion. The absence of complexation of (**1**) for cyclododecanol at pH 12.9 may also be explained in terms of the polar nature of the charged rim of (**1**), although the guest is neutral. This complexation behaviour suggests that both adamantane-1-carboxylic acid and cyclododecanol prefer the wider face to the narrower one as an entrance to the cavity of (**1**). The situation seems different for cyclohexanol, [(1*S*)-*endo*]-(−)-borneol, and adamantan-1-ol since they can be bound to (**1**) even at pH 12.9. These guests might be inserted into the cavity of (**1**) partly or fully from the narrower face, and complexation occurs even if the inclusion from the opposite wider face is prohibited. The binding constants of [(1*S*)-*endo*]-(−)-borneol for both *Z*- and *E*-forms of (**1**) at pH 10.1 are smaller than those at pH 6.7 and 12.9. Since (**1**) has no electronic charge at pH 10.1, the result suggests that the azobenzene moiety is so tightly included in the cavity that it is hardly replaced by [(1*S*)-*endo*]-(−)-borneol.

The *Z*-form of (**1**) returned to the original *E*-form thermally. Table 2 shows the first-order rate constants of the decay process measured at 45 °C. The rate was hardly influenced by the presence of adamantan-1-ol as the guest. Under alkaline conditions at pH 12.9, (**1**) has negative charges at the wider face of β-cd due to the alkoxide anions of the secondary hydroxy groups. However, this change of the state caused no significant change in the rate. The rate in dimethyl sulphoxide was larger than in aqueous solutions. Since the azobenzene moiety is unlikely to be tightly bound to the β-cd cavity in this organic solvent, the allowed mobility of the *Z*-azobenzene moiety might be reflected in the increased rate.

In connection with the studies on complexation of (**1**), we have examined the complexation between (**2**) and β-cd. Figure 8 shows CD spectra of (**2**) in aqueous solution at pH 6.7. The *E*-form of (**2**) exhibits a positive band around 342 nm similar to that of (**1**). This CD spectrum suggests that the *E*-azobenzene moiety of (**2**) is included into the β-cd cavity with its long axis parallel to the axis of β-cd. The *Z*-form also exhibits a positive band at 447 nm, the sign being the opposite of that found for the *Z*-form of (**1**). Although the CD sign of the *Z*-form cannot be directly related to the orientation of the azobenzene moiety due to its non-planar structure, it seems likely that the orientation of the *Z*-azobenzene moiety of (**2**) is different from that of (**1**). The *Z*-pendant of (**1**) must enter the cavity from the narrower face, but that of (**2**) can enter from both sides of the cavity. This situation might result in the locational or orientational difference of the *Z*-azobenzene moiety between (**1**) and the β-cd complex of (**2**). The moiety of (**2**) may be located near the wider face of β-cd while that of (**1**) is located near the narrower face. The binding constants of the *E*- and *Z*-forms of (**2**) for β-cd are 1 310 and 100 dm^3 mol^{-1}, respectively. This finding confirms that the *E*-form is more tightly involved into the cavity of β-cd than the *Z*-isomer and is consistent with the result previously reported for the complexes between 4-carboxyazobenzene and β-cd.[26]

Conclusions

It was confirmed that (**1**) forms intramolecular complexes, in which either the *E*- or *Z*-form of the azobenzene moiety is included. The intramolecular complexes were converted into 1:1 host–guest complexes upon guest addition. The binding constants of the complexes were different between the *E*- and *Z*-forms of (**1**), and remarkable photocontrol of the binding ability of (**1**) was found for guests such as adamantane-1-carboxylic acid and admantan-1-ol. This type of photocontrol of complexation may be used as the basis for constructing the molecular devices with which reactions and catalytic actions can be regulated by light in an on–off fashion.

Acknowledgements

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