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PHOTORESPONSIVE BINDING ABILITY OF AZOBENZENE-APPENDED γ-CYCLODEXTRIN

Akihiko Ueno,* Yoko Tomita, and Tetsuo Osa*

Pharmaceutical Institute, Tohoku University
Aobayama, Sendai 980, Japan

Abstract: Azobenzene-appended γ-cyclodextrin, which can form 1:1 complexes with a variety of guests in its trans form, exhibits promoted binding ability for (-)-borneol and (+)-fenchone by photoirradiation.

The cis-trans isomerizm of azobenzene has recently been utilized as a photosensitive "switch" to regulate chemical and physical phenomena.[1] Much effort has been invested to construct photoregulation systems for substrate[2] and ion[3] binding, catalytic activity,[4] membrane potential[5] and permeability,[6] polymer conformation,[7] ion transport,[8] and others.[9] This communication deals with photocontrol of substrate binding by azobenzene-appended γ-cyclodextrin (1).[10] In contrast to the previously reported azobenzene-capped β-cyclodextrin,[2] 1 has a flexible azobenzene moiety on γ-cyclodextrin (γ-CD), which has poor or no binding ability for usual organic substrates owing to its large cavity size.[11]

Compound 1 was prepared by reaction of γ-CD with one equiv. of p-(chlorocarbonyl)azobenzene in pyridine. Recrystallization of the crude product from water afforded the pure monohydrate of 1 in ca. 10% yield.[12] Found (Calc'd. for $C_{61}H_{88}N_2O_{41}\cdot H_2O$): C, 47.94 (48.09); H, 5.71 (5.97); N, 1.92 (1.84).

Figure 1 shows the circular dichroism spectra of 1 in water (5×10^{-5} M, Tris buffer pH 7.2) before and after photoirradiation, alone or in the presence of excess cyclohexanol and (-)-borneol. Compound 1 before photoirradiation represents induced circular dichroism bands in the azobenzene π-π* (332 nm) and n-π* (410 nm) regions. The π-π* circular dichroism band changes remarkably on addition of guest molecules; it is enhanced with a wavelength shift to 343 nm by cyclohexanol, whereas it nearly vanish in the presence of excess (-)-borneol. According to the circular dichroism behavior of trans-1, the guest molecules examined here can be divided into two groups, smaller ones (group I: cyclohexanol, anisole, and benzyl alcohol) and larger ones (group II : (+)-fenchone and (-)-borneol) which enhance and depress the circular

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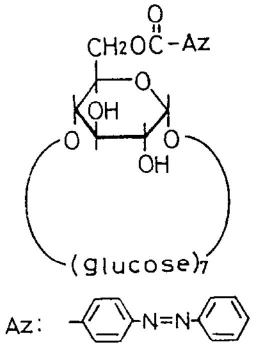

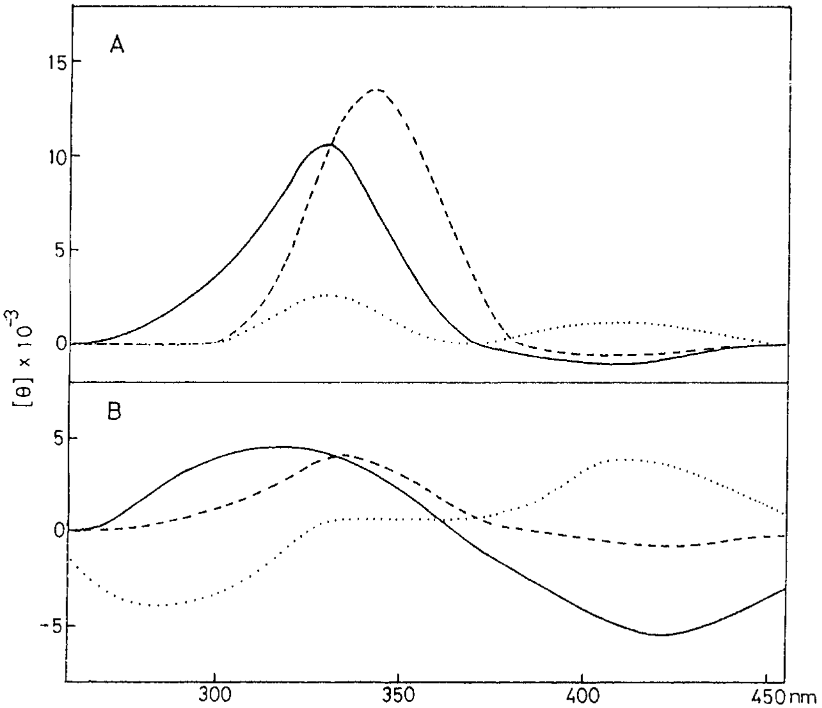

Fig. 1. Circular dichroism spectra of 1 before (A) and after (B) photoirradiation, alone (——) or in the presence of cyclohexanol (- - - ; 8.1 x 10^{-2} M) and (-)-borneol (····· ; 6.2 x 10^{-4} M in A, 3.7 x 10^{-4} M in B). [1] was 5 x 10^{-5} M in Tris buffer (pH 7.2).

dichroism band, respectively. The enhancement in the circular dichroism may be caused by the limited movement of the azobenzene moiety involved in the γ-CD cavity together with a guest molecule of group I (i). Similar phenomenon was observed in the circular dichroism spectrum of naphthalene-appended γ-CD when a guest molecule was included in the cavity.[13] In both cases, the appended moieties act as spacers which narrow the large γ-CD cavity to allow inclusion of small guests. On the other hand, the depressed circular dichroism caused by the guests of group II suggests that complexes are formed by excluding the appended azobenzene moiety from the interior of the cavity (ii).

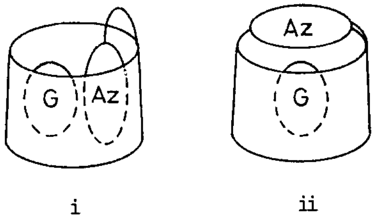

Fig. 2. Schematic representations for complexation of 1 with a guest molecule (G).

Photoirradiation of 1 with the light of 320-390 nm (Corning 7-37 filter) causes

Table 1. Binding Constants for Complexes of trans-1 and cis-1 with Various Guests[a]

Guest	Group	Binding constants (mol^{-1} l)	
		Trans-1	cis-1
cyclohexanol	I	78	b
anisole	I	105	b
benzyl alcohol	I	144	b
(+)-fenchone	II	733	1630
(-)-borneol	II	2870	5790

[a] In 0.05M Tris buffer (pH 7.2) at 25 °C. [b] Values were not determined owing to interactions other than 1:1 complexation.

trans-cis isomerization of the appended azobenzene moiety, the cis per cent being ca. 70 at the photostationary state. The thermal decay from cis to trans form of 1 was negligible during the circular dichroism measurements. The irradiated solution of 1 shows an intense circular dichroism in the azobenzene n-π* region. The ellipticity of this band changes remarkably by addition of the guests (B in Figure 1).

The circular dichroism behavior of trans-1 and cis-1 was analyzed[14] by using the ellipticities of the azobenzene π-π* and n-π* bands for trans-1 and for cis-1, respectively (Table 1). The binding constants of trans-1 for the guests of group II are large ($K>700$) in comparison with those for the guests of group I ($K<150$). Furthermore, cis-1 reveals promoted binding ability for the guests of group II. Unfortunately, the binding constants of cis-1 for the guests of group I could not be obtained probably owing to 1:2 host-guest complexation. Since all guests examined here are too small to form stable 1:1 complexes with native γ-CD, the appended azobenzene plays effective roles to promote binding ability of γ-CD.

The present results suggest that there are at least two different ways of complexation; the azobenzene moiety acts as a spacer (i) or softly capps the guests (ii).[15] Further work is needed to establish the geometrical details of the complexes.

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