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cis-trans Isomerization of the Azobenzenes Included as Guests in Langmuir-Blodgett Films of Amphiphilic β-Cyclodextrin

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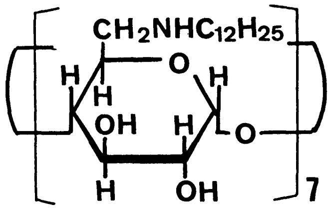
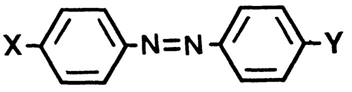
Azobenzenes in the host-guest Langmuir-Blodgett films prepared with amphiphilic β-cyclodextrin and azobenzene derivatives showed a photochromic behavior with complete reversibility owing to the free volume of cyclodextrin cavity, whereas the trans-to-cis isomerization was restricted in the case of the pure LB film prepared with long-chain azobenzene derivative alone. Thermal cis-to-trans isomerizations in the LB films were also studied.

In the previous paper$^{1)}$ we have reported the composite LB films which were comprised of the host-guest complexes of heptakis(6-dodecylamino-6-deoxy) β-cyclodextrin(**CD**) and azobenzene derivatives (**1**,**2**,and **3**). Much attention has been devoted to photoisomerization of azobenzenes in solutions,$^{2)}$ membranes,$^{3)}$ host-guest complexes of cyclodextrins,$^{4)}$ polymers,$^{5)}$ and LB films,$^{6)}$ because they are one of the representative photochromic compounds.$^{2)}$ In this paper we report the cis-trans isomerization of azobenzenes in the host-guest LB films of **CD-1**, **CD-2**, and **CD-3**.

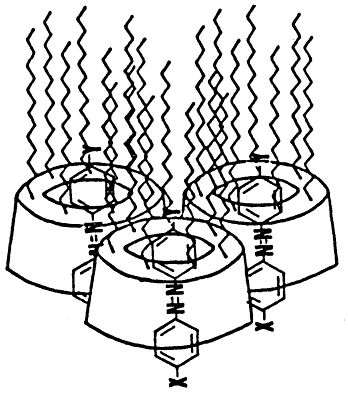


Amphiphilic β-cyclodextrin
CD



Azobenzenes

	X	Y
1 :	X=H	Y=COOH
2 :	X=$(CH_3)_2N$	Y=COOH
3 :	X=$(CH_3)_2N$	Y=SO_3Na



Host-guest LB films
CD-1, **CD-2**, and **CD-3**

The trans-isomers of azobenzenes (**1**, **2**, and **3**) were included in the cavity of **CD** in the chloroform solution, and the host-guest LB films with molar ratio ca. 1:1(50 layers on the both sides)[7)] were deposited as Y-type multilayers on the quartz plates precoated with five monolayers of cadmium eicosanoate, as reported in the previous paper.[1)] The photochemical processes upon irradiations of the films were followed by UV-Vis spectroscopy. The LB films were placed at the angle of 45° both to the irradiation and detection beams for the cross illumination technique. The irradiations were carried out using the monochromatic lights through a monochromator with a 500 W super high-pressure xenon lamp.

Figure 1 shows changes in the electronic absorption spectra with irradiation times for the LB film of **CD-1**. Upon the irradiation with 360 nm light, the absorption bands at 228 and 327 nm decreased while the bands at 255 and 445 nm increased, indicating the trans-to-cis isomerization of **1** similar to the results in the solution.[8)] After the photostationary state upon the 360 nm irradiation was reached, the host-guest LB film was irradiated with 254 nm light. As shown in Fig. 2, the spectral change reversed that in Fig. 1 was observed, indicating the cis-to-trans isomerization. This spectral change occurred similarly upon the irradiation with > 400 nm light exciting n-π* transition of the cis-isomer. In this manner, the alternate irradiation with 360 and 254 (or > 400)nm lights brought the photochromic behavior with the excellent reversibility within 1-2% decrease in the optical density during ten times of alternations. The conversion to the cis-isomer at the photostaionary state was estimated to be about 50-60% from the calculation based on the difference spectra.[9)]

In the cases of **CD-2** and **CD-3**, upon the irradiations with 415 and 400 nm lights respectively, similar spectral changes were observed as shown in Figs.3 and 4. These spectral changes can also be ascribed to trans-to-cis isomerizations on the basis of the spectra measured in the solution at low temperatures.[10)] Although the cis-isomers of **2** and **3** having electron-push-pull substituents were too labile to show photochromism in the solution at room temperature,[2,9)] these isomers were

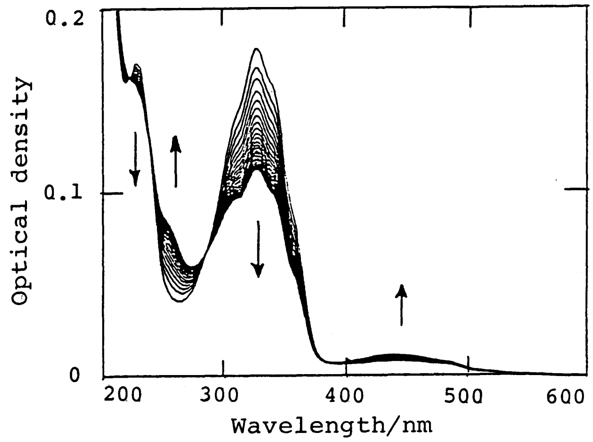


Fig.1. UV-Vis spectral changes of **CD-1** upon 360 nm irradiation (0.40 mW/cm^2). Each irradiation time : 1 min.

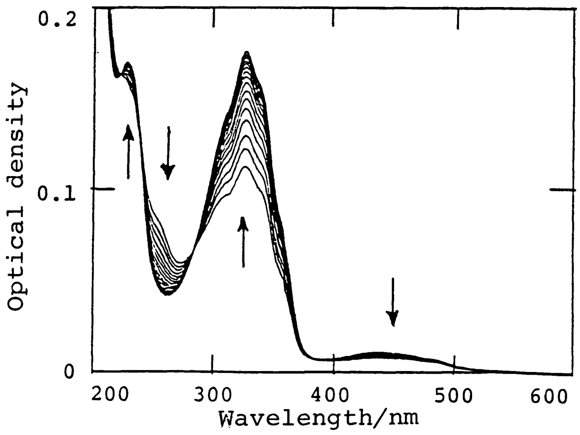


Fig.2. UV-Vis spectral changes of **CD-1** upon 254 nm irradiation(0.67 mW/cm^2) after photostationary state with 360 nm irradiation. Each irradiation time : 5 s.

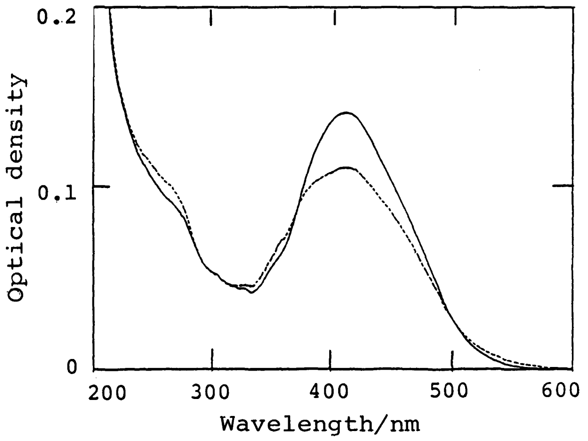


Fig.3. UV-Vis spectra of **CD-2** before (——) and after irradiation (--------) with 415 nm light(1.09 mW/cm^2).

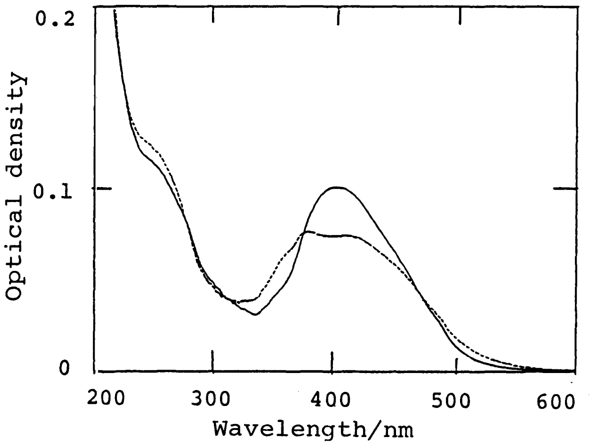


Fig.4. UV-Vis spectra of **CD-3** before (——) and after irradiation (--------) with 400 nm light(1.05 mW/cm^2).

stabilized to be observable even at room temperature in the host-guest LB films. However, the cis-isomers of **2** and **3** converted spontaneously to their trans-isomers with appreciable rates. Both the trans-to-cis photoisomerization and the thermal cis-to-trans isomerization were completely reversible. Needless to say, the 254 and >500 nm irradiations for the cis-isomers in the LB films of **CD-2** and **CD-3** accelerated the cis-to-trans isomerization.

It is noteworthy that the reversible photoisomerizations of azobenzenes were observed in the LB films of **CD-1**, **CD-2**, and **CD-3**, whereas the trans-to-cis isomerization was restricted in the case of the pure LB film prepared with long-chain azobenzene derivative (4-(4-n-octyloxyphenylazo)phenyloxypropanoic acid) alone.11) Also in the cases of LB films containing photochromic compounds such as spiropirans12) and thioindigo dyes,13) the trans-to-cis isomerizations accompanying the increase in molecular area was restricted or severely retarded. Whitten and co-workers have reported that the irreversible cis-to-trans isomerization is attributed to the interfacial effects on potential energy curves of excited-state in the photoisomerizations of monolayer assemblies.14) On the other hand, for the isomerization of azobenzenes, two competing reaction mechanisms have been proposed: a rotational mechanism involving rotation about the N=N bond and an inversion mechanism involving flip-flop inversion of one of the nitrogen atoms.15) Although it is not concluded which mechanism should be prefered in these LB films, both transition

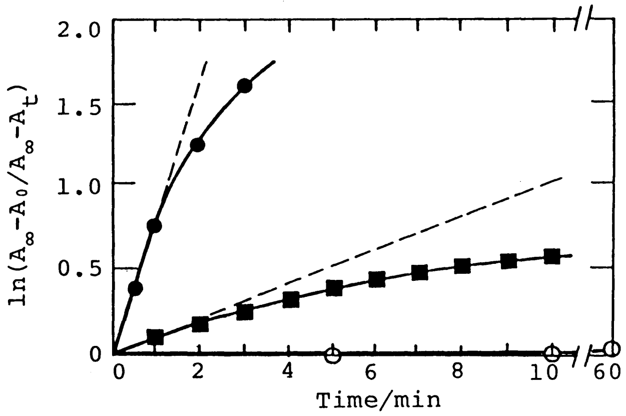


Fig.5. The first order kinetics plots for thermal cis-to-trans isomerization at 20 °C. A_0, A_t, and A_∞ : absorbance at initial state, after t and ∞ min, respectively. ○:**CD-1**, ●:**CD-2**, ■:**CD-3**

states occupy larger molecular area than the trans isomer. Therefore, the reversibility in the LB films of **CD-1**, **CD-2**, and **CD-3** will be explained by the free volume in the cavity of **CD**.

Figure 5 shows the kinetics of thermal cis-to-trans isomerization in the LB films at room temperature. A deviation from the first order kinetics was observed, whereas their corresponding reactions in the solutions proceeded in the first order kinetics. The half-life times of the cis-isomers in the LB films of **CD-1**, **CD-2**, and **CD-3** at 20 °C were 35 h, 55 s, and 13 min, respectively.

In conclusion, a new type of photochromic LB films containing azobenzene chromophores were prepared by the host-guest interaction with the cyclodextrin derivatives. The azobenzenes in the host-guest LB films showed an excellent photochromic behavior probably because of the optimum free volume of **CD** cavity for the cis-trans isomerization. Further investigation on the stability of cis-isomers is in progress.

References

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