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PHOTOCONTROL OF CHIRAL RECOGNITION BY CAPPED CYCLODEXTRIN†

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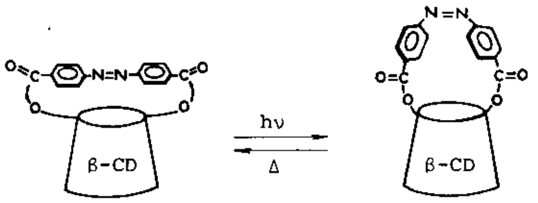
Abstract —— Azobenzene-capped β-cyclodextrin (1) exhibits chiral recognition in binding optical isomers of some guest molecules with stereoselectivity which inverts by photoirradiation.

Cyclodextrins are cyclic oligosaccharides made up of six, seven and eight glucose residues in a molecule (α-, β- and γ-CD respectively) and can include a wide variety of organic and inorganic guests in their cavities.[1] In addition, they exert catalytic action on suitable included substrate molecules, mimicking enzymes. Despite rather few restrictions other than size on the type of guest molecules incorporated, stereospecific interactions have been described in some instances.[2-16] Various chemical modifications have been applied to cyclodextrins to improve their catalytic activity,[1] but almost no effort has been invested to clarify the effect of modification on stereochemistry of CD-substrate interactions. We have recently prepared a photoresponsive capped β-CD,[17] 6,6',O,O'-(4,4'-azobenzenedicarbonyl)-cycloheptaamylose (1), which has an azobenzene cap capable of undergoing trans-cis photoisomerization



trans-1 cis-1

and accomplished photocontrolled complexation based on different binding abilities of both isomers of 1.[1,8-21] We wish to report here some features on photocontrol of chiral recognition of 1 using some chiral compounds as guests.
Both isomers of 1 exhibit induced circular dichroism of the cap azobenzene whose

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ellipticity decreases on addition of guest molecules.[18-21] On the basis of this phenomenon, the analysis of complex formation was performed using the previously reported equations,[19] and both cis- and trans-1 were found to form 1:1 and 1:2 host-guest complexes with the chiral guests (G)

$$\mathrm{CD} + \mathrm{G} \xrightleftharpoons{K_1} \mathrm{CD{-}G}$$

$$\mathrm{CD{-}G} + \mathrm{G} \xrightleftharpoons{K_2} \mathrm{CD{-}G_2}$$

where different molecular ellipticities were assumed for CD-G and CD-G_2. The formation constants for CD-G_2 were summarized in Table 1. Those for CD-G could not be determined since the values are too large to be determined definitely.

Table 1

Guest	Enantiomeric form	Host	Formation constant[a] K_2 (M^{-1})	K(L)/K(D)
Carvone	L(-)	trans-1	204	1.29
	D(+)		158	
	L(-)	cis-1	1550	0.92
	D(+)		1680	
Fenchone	L(-)	trans-1	604	1.13
	D(+)		536	
	L(-)	cis-1	1230	0.86
	D(+)		1430	
Phenylalanine	L	trans-1	1.20	0.82
	D		1.47	
	L	cis-1	45	1.22
	D		37	
α-Methylbenzyl-alcohol	L	trans-1	16.1	1.02
	D		15.8	
	L	cis-1	145	1.29
	D		112	
N-acetyl-α-methylbenzyl-amine	L	trans-1	27.5	0.73
	D		37.9	
	L	cis-1	2090	2.23
	D		939	

a) 25 °C, pH 7.2, Tris buffer; $k_2 = [\mathrm{CD{-}G_2}]/[\mathrm{CD{-}G}][\mathrm{G}]$.

We previously assumed that the first guest molecule is readily involved in the space outside the CD cavity and yet still within the azobenzene cap whereas the second one involved in the cavity.[21] The formation constants listed in Table 1, therefore, may reflect the stereoselectivity of inclusion of the second guest molecule into the CD cavity. The data indicate that (i) cis-1 binds the second guest more strongly than trans-1 and (ii) the stereoselectivity of cis-1 in binding the guest is opposite to that of trans-1 except for α-methylbenzylalcohol. These results may be derived from the changed depth of the CD cavity of 1, from shallow cavity to deep one on trans→cis photoisomerization of the cap. The light-induced enhancement in the binding ability of 1 seems to correspond to the expanded hydrophobic cavity of cis-1. The stereoselectivity observed here may arise from the interactions of the guest molecule with the CD rim or wall corresponding to the shallow or deep depth of the cavity, although the chiral guest involved first might also participate in the chiral discrimination. Thus, the results suggest that the CD wall and rim exert opposite effects with each other in recognizing the guest chirality. It should be noted that the cis form produced by photoirradiation returns to the original trans form spontaneously in the dark and the system can be regarded as a chiral discriminator controlled by light, though the extent of discrimination is not so high yet.

We are currently investigating the effect of light on the stereoselectivity in ester hydrolysis when 1 is used as a catalysis.

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