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Exciton Coupling and Complexation Behaviour of *β*-Cyclodextrin Naphthoate

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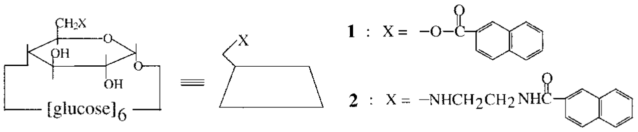
Abstract

The host–guest complexation behaviour of β-cyclodextrin 6-O-mono-2-naphthoate (**1**) and 6-[(N-2-naphthoyl-2-aminoethyl) amino]-6-deoxy-β-cyclodextrin (**2**) have been studied by the circular dichroism method. The exciton coupling band of **1** suggests that two naphthoyl moieties are partly included in one β-CD cavity. Host **1** could form a dimer in a more polar solvent and the dimer could be dissociated in a less polar solvent or by adding a guest. Solvent-induced, concentration induced, and guest-induced circular dichroism variations were examined. No exciton coupling was observed for host **2**.

Introduction

Cyclodextrins (CDs) have been widely used for various purposes because of their remarkable property of forming inclusion complexes with a variety of molecules [1, 2, 3]. This property of CDs forms a basis for using CDs as molecular flasks which facilitate reactions [4, 5]. Photochemistry and photophysics within CD cavities have attracted the attention of chemists [6]. Inoue and Tong have studied the photoisomerization of cis-cyclooctene in the presence of cyclodextrin benzoates as sensitizers [7]. In order to further study the mechanism of photoisomerization of cis-cyclooctene and provide new sensitizers, we synthesized a series of CD derivatives bearing aroyl moieties and reported the binding behaviors of β-CD bearing benzoyl moiety [8, 9, 10].

Ueno *et al.* have described the exciton coupling and binding behaviours of γ-CD substituted by one or two naphthylacetyl moieties [11, 12]. γ-CD and its derivatives could involve two molecules of naphthalene derivatives in their larger cavity. It has long been thought that β-CD cannot bind two molecules of benzene or naphthalene units in its smaller cavity [13, 14]. An exciton coupling band in its circular dichroism spectrum is direct evidence for two-guest inclusion of β-CD for the β-CD derivative in which the chromophore is connected to β-CD through a short chain [15]. In this paper, we report the exciton coupling and unique binding behaviour of β-CD substituted by one 2-naphthoyl moiety (**1**). The binding behaviour of **2** was also studied.



Experimental

Materials

β-Cyclodextrin 6-O-mono-2-naphthoate (**1**) and 6-[(N-2-naphthoyl-2-aminoethyl)amino]-6-deoxy-β-cyclodextrin (**2**) were prepared in our laboratory as reported in the previous paper [8]. Cyclohexanol, cyclohexane, decan-1-ol, and methanol were commercially available reagents (A.R.) and were used without further purification.

Measurements

The circular dichroism spectra were measured in a conventional quartz cell (light path 1 cm) at 18 °C on a JASCO J-20 spectrodichrometer. The CD spectra of **1** and **2** were measured at a concentration of 2.54×10^{-5} mol dm^{-3} in the presence of varying concentrations of the guest.

Results and discussion

The solubility of **1** in a mixed solvent of methanol-water is higher than in water, so a mixed solvent of methanol-water was used for spectroscopic measurement. Solvent-induced circular dichroism variations for **1** were examined. Figure 1 shows the circular dichroism spectrum of **1** at 18 °C. Methanol was found to influence the circular dichroism pattern

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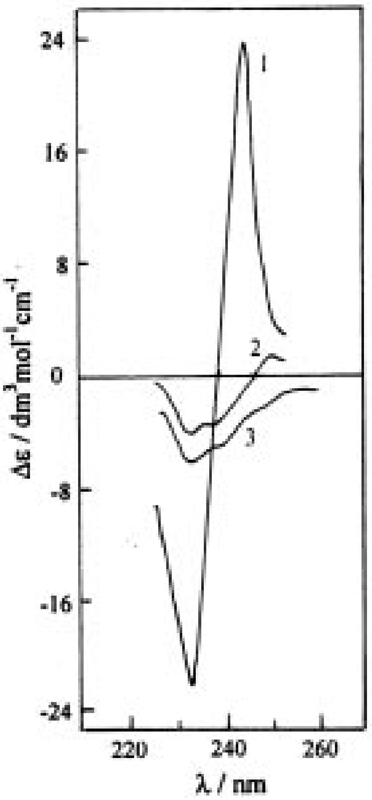


Figure 1. Circular dichroism spectra of **1** (2.54×10^{-5} mol dm^{-3}) in various methanol water solutions (MeOH/H_2O: (1) 3:7; (2) 6:4; (3) 10:0 v/v).

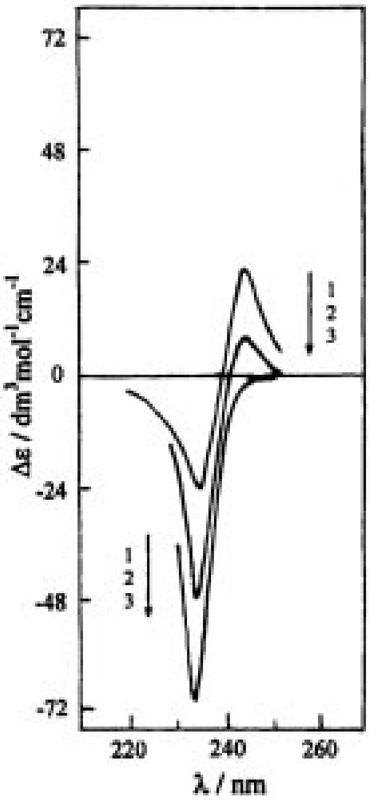
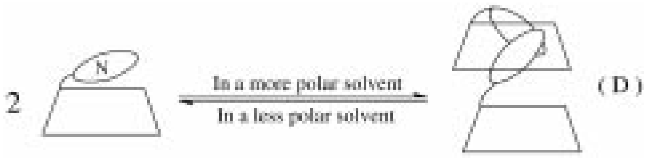


Figure 2. Circular dichroism spectra of **1** in MeOH-H_2O (3:7, v/v) solutions at its various concentrations: (1) 2.54×10^{-5}; (2) 2.54×10^{-6}; (3) 1.27×10^{-6} mol dm^{-3}.

of **1**.When the volume ratio of methanol to water is 3:7, an intense exciton coupling band is observed. The signs of the circular dichroism bands are negative in the 220–240 nm region and positive in the 240–260 nm region. The exciton coupling band was still present when the circular dichroism spectrum of **1** was measured using pure water as solvent at the concentration of 1.8×10^{-5} mol dm^{-3}. The circular dichroism spectrum of **1** in pure water was not incorporated in Figure 1 because the concentration of **1** was not the same as others.

Figure 2 shows CD spectra of **1** in MeOH-H_2O (3:7, v/v) at its various concentrations. The exciton coupling band disappears to give a negative band at the concentration of 1.27×10^{-6} mol dm^{-3}. The concentration dependence of the CD spectrum for **1** confirmed that two naphthoyl moieties formed a molecular pair at higher concentration and the molecular pair dissociated at lower concentration. Although no exact distance constraints are introduced by the observation of exciton coupling, an exciton coupling occurs only if the two naphthoyl moieties are joined together.

Two kinds of exciton coupling may occur for CD derivatives bearing chromophores. The first one is that the two chromophores are included in two CD cavities by face-to-face aggregation of the secondary sides of the CDs (see reference 13). The second one is that the two chromophores are included in one CD cavity. The naphthyl moiety in **1** was connected to the primary side of β-CD through a short chain, so it was unlikely that two nahthoyl moieties were included in two CD cavities by face-to-face aggregation of the secondary sides of β-CD. It was also unlikely that two naphthoyl moieties were included in two CD cavities by face-to-face aggregation of the primary sides of β-CD since no force let them form a stable complex. The only possible case was that the two naphthoyl moieties were included in one CD cavity (Scheme 1).



Scheme 1.

For exciton coupling, the two naphthoyl moieties must adopt a defined orientation with respect to one another and the property of chiral environments of the two naphthoyl moieties should be similar. No exciton coupling would occur if one naphthoyl moiety were simply perched on top of the β-CD cavity because of the difference of their environments. Although no empirical rule is known to elucidate the exact conformation of the two naphthoyl moieties, Corey–Pauling–Koltum (CPK) molecular models showed that it was feasible for the two naphthoyl moieties to penetrate in to the cavity (Scheme 1).

The exciton coupling pattern indicates that two 2-naphthyl moieties of **1** form a molecular pair with a chiral geometry in the cavity of **1**. The spectral pattern at shorter wavelengths (^1B_b transition region) is a decisive indicator

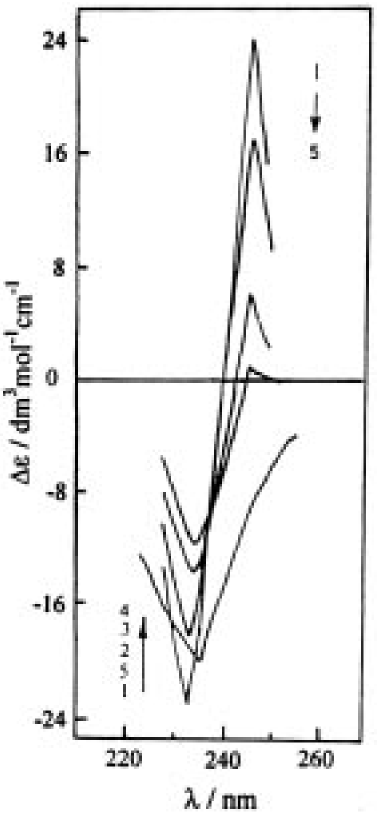
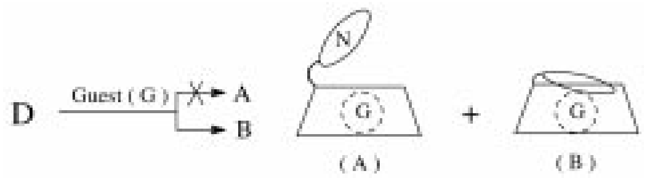


Figure 3. Circular dichroism spectra of **1** in MeOH-H_2O (3:7, v/v) solutions (2.54×10^{-5} mol dm^{-3}) at various cyclohexanol concentrations: (1) 0.00; (2) 1.88×10^{-4}; (3) 7.52×10^{-4}; (4) 1.50×10^{-3}; (5) 3.01×10^{-3} mol dm^{-3}).

for determining the direction of the chirality since the ^1B_b transition occurs along the long axis of the naphthalene ring [16]. This exciton coupling observed for the ^1B_b band demonstrates that the pair of naphthyl residues included in the β-CD cavity has R-helicity. In this system, two naphthyl units are joined together. It is noted that the intensity of the exciton coupling band in the naphthyl ^1B_b transition region diminishes with the increasing methanol content of the solvent and finally, the positive band disappears to give a negative band (Figure 1). Thus, the polarity of the solvent induces conformational change of **1** (Scheme 1). Compound **1** forms a dimer in a more polar solvent and the dimer is dissociated in a less polar solvent.

The mixed solvent of methanol-water (3:7 by volume) was used to measure the circular dichroism spectrum of **1** with different guest concentrations. Figure 3 shows variation of the circular dichroism pattern at 18 °C in the case of cyclohexanol (guest). The intensity of the positive peak of the exciton coupling band in the naphthyl ^1B_b transition region diminishes with increasing cyclohexanol concentration. By analysis of the changes of the circular dichroism intensity at 244 nm, we found that the binding constant (K_s) at 18 °C of **1** for a cyclohexanol guest is 1430 mol^{-1} dm^3. Guest binding of **1** cancels the exciton coupling. This phenomenon indicates that the chiral orientation of the naphthyl pair is lost by forming an inclusion complex between **1** and cyclohexanol. A strong negative peak at 235 nm was observed in the circular dichroism spectrum when cyclohexanol was in large excess. On the basis of the 'Sector Rule' proposed by Kajtar *et al.* [16], structure A, in which the naphthyl moiety is completely extruded outside from the cavity, is not true (Scheme 2). Structure B is supported by circular dichroism data. The naphthyl moiety as a flexible cap is likely to be in contact with the included guest molecule. The circular dichroism spectra of **1** in the presence of cyclohexane and decan-1-ol were measured. The adding of cyclohexane and decan-1-ol made the circular dichroism pattern of **1** change more rapidly than that of cyclohexanol.



Scheme 2.

Table 1. Binding constants (K_s) of **1** and **2** with different guests in MeOH/H_2O (3:7, v/v) solution at 18 °C

Hosts	Guests	K_s/mol^{-1} dm^3
1	Cyclohexanol	1430
1	Cyclohexane	20650
1	Decan-1-ol	29880
2	Cyclohexanol	368
2	Cyclohexane	2016
2	Decan-1-ol	9135

Figure 4 shows the circular dichroism of spectrum of **2** in solvent MeOH/H_2O (3:7) at 18 °C. The circular dichroism of **2** is completely different from that of **1**. A intense positive 'Cotton Effect' is observed for the ^1B_b band around 244 nm before the guest cyclohexanol is added. The 2-naphthoyl group in **2**, which is connected with a long ethylenediamine chain, could be well accommodated in the cavity of cyclodextrin. According to the 'Sector Rule', we deduce that the 2-naphthoyl moiety is deeply included in the cavity. The absolute intensity of the ^1B_b band diminishes upon addition of cyclohexanol. The analysis of the circular dichroism variations at 244 nm gave 368 mol^{-1} dm^3 as the binding constant (K_s) with cyclohexanol. The CD spectra of **2** in the presence of decan-1-ol which could form a more stable complex with β-CD were also measured. The adding of decan-1-ol in large excess decreased the CD intensity of **2** at 244 nm to almost zero. Only the CD spectra of **2** in the presence of cyclohexanol are given in this paper in order to contrast them with the CD spectra of **1**. The decrease in the circular dichroism intensity at high guest concentrations means that, as a result of the competition between the substituent and a guest molecule, the chromophoric naphthamide group is driven out of the cavity and out of the chiral field of cyclodextrin (Scheme 3). The hydrophilic ethylenediamine tether may facilitate the total exposure of the 2-naphthoyl moiety to the solvent.

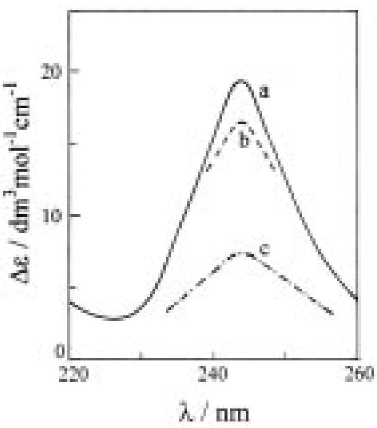
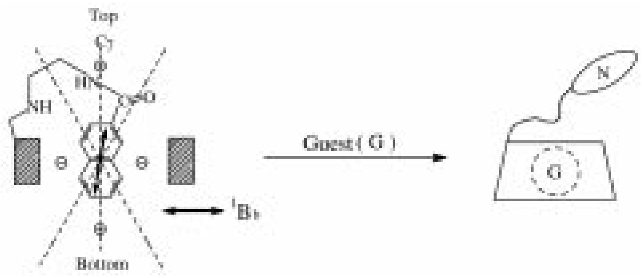


Figure 4. Circular dichroism spectra of **2** in methanol-water (3:7, v/v) solutions (2.54×10^{-5} mol dm^{-3}), (a) alone; (b) in the presence of cyclohexanol (3.01×10^{-3} mol dm^{-3}), (c) in the presence of cyclohexane (3.01×10^{-3} mol dm^{-3}).



Scheme 3.

As shown by the above data and discussion, no exciton coupling was observed for host **2** which possessed a hydrophilic flexible tether connecting the cyclodextrin and 2-naphthoyl moiety. The 2-naphthoyl moiety of **2** could be extruded out of the cavity of cyclodextrin. Conversely, an intense exciton coupling was observed for host **1** in which the 2-naphthoyl moiety was directly attached to cyclodextrin. Furthermore, host **1** afforded a much larger binding constant (K_s) than host **2**. This indicated that the 2-naphthoyl moiety perching over the rim expanded the hydrophobic cavity and greatly enhanced the binding ability of cyclodextrin. Host **1** could form a more stable complex with a guest than host **2** or native β-cyclodextrin.

Although a series of modified γ-CDs have been studied as flexible hosts, γ-CD is much more expensive than β-CD. **1** can form a dimer (partly involving two appended naphthyl units into one cavity) and bind a guest into its cavity by changing the location of the appended naphthyl unit which seems to act as a hydrophobic cap to promote binding of a guest. We are studying the photoisomerization of cis-cyclooctene using β-CD derivatives bearing aroyl moieties as sensitizers. These β-CD derivatives may be used in other field of host-guest photochemistry. Moreover, various modified β-CDs can be designed as enzyme models and reactions may occur in the hydrophobic cavity of cyclodextrin with the catalysis of appended moieties.

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