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LETTERS

Exciton Coupling and Binding Behaviour of β -Cyclodextrin Substituted by One 2-Naphthoyl Moiety

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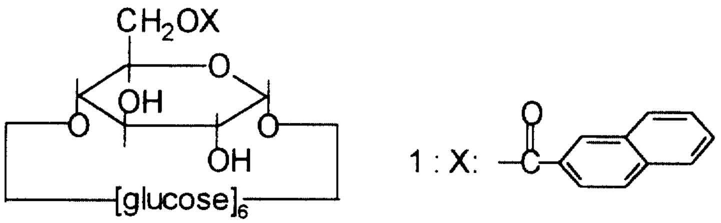
Abstract: Host-guest complexation of β -cyclodextrin substituted by one 2-naphthoyl moiety (**1**) has been studied by the circular dichroism method. The exciton coupling band suggests that two naphthoyl moieties are partly included in one β -CD cavity (forming a dimer). Both solvent-induced and guest-induced circular dichroism variations are examined. © 1999 Elsevier Science Ltd. All rights reserved.

Cyclodextrins (CDs) have been widely utilized for various purposes because of their remarkable property of forming inclusion complexes with a variety of molecules.[1,2] This property of CDs forms a basis for using CDs as molecular flasks which facilitate reactions.[3,4,5]

A. Ueno et al have described the exciton coupling and binding behaviours of γ-CD substituted by one or two naphthylacetyl moieties.[6] It has long been thought that β -CD cannot bind two molecules of benzene or naphthalene units in its smaller cavity.[7] An exciton coupling band in its circular dichroism spectrum is direct evidence for two-guest inclusion of β -CD.[8] In this paper, we report the exciton coupling and unique binding behaviour of β -CD substituted by one 2-naphthoyl moiety (**1**).



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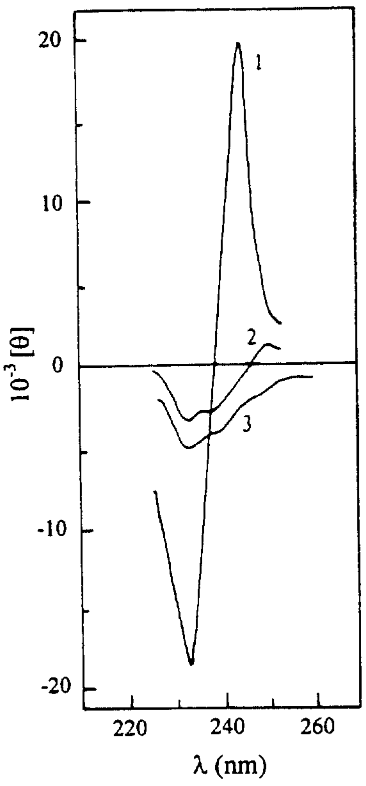


Fig. 1. Circular dichroism spectra of **1** (2.54×10^{-5} mol dm^{-3}) at various methanol contents (1, 30; 2, 60; 3, 100 v.%)

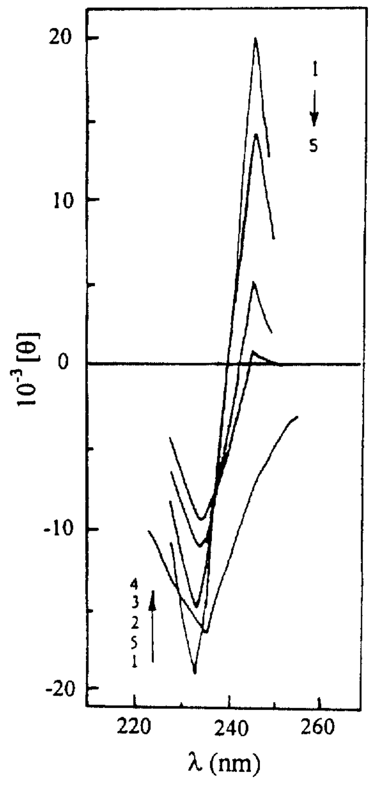
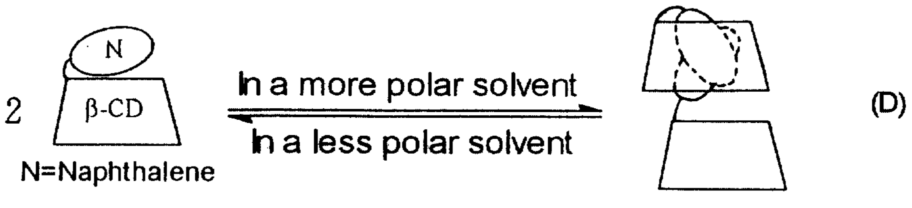


Fig. 2. Circular dichroism spectra of **1** in water-methanol (7:3, v/v) solutions (2.54×10^{-5} mol dm^{-3}) at various cyclohexanol concentrations (1, 0.0; 2, 1.88×10^{-4}; 3, 7.52×10^{-4}; 4, 1.50×10^{-3}; 5, 3.01×10^{-3} mol dm^{-3})

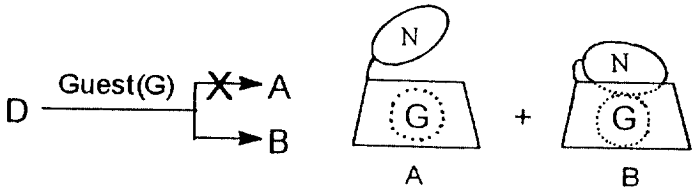
The solubility of **1** in pure water is poor, so a mixed solvent of water-methanol was used for spectroscopic measurement. We have examined solvent-induced circular dichroism variations for **1**. Figure 1 shows the circular dichroism spectrum of **1** at 18℃. Methanol was found to influence the circular dichroism pattern of **1**. When the volume ratio of water to methanol is 7 to 3, 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 spectral pattern at shorter wavelengths (^1B_B transition region) is a decisive indicator for determining the direction of the chirality since the ^1B_b transition occurs along the long axis of the naphthalene ring.[9] 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.

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.



Scheme 1

We used a mixed solvent of water-methanol (7:3 by volume) to measure the c.d. spectrum of **1** with different guest concentrations. Figure 2 shows variation of the circular dichroism pattern at 18℃ 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 243nm, we found that the binding constant (K) at 18℃ of 1 for a cyclohexanol guest is 1430 $mol^{-1}dm^3$, a large value. 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 is observed in c.d. spectrum when cyclohexanol is in large excess, indicating that 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.



Scheme 2

Although a series of modified γ-CDs have been studied as flexible hosts, γ-CD is very expensive. As shown by the above data and discussion, **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. Various modified β-CDs can be designed as enzyme models and reactions may occur with the catalysis of appended moieties.

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