Association of Naphthalene-appended γ-Cyclodextrin with β-Cyclodextrin

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γ-Cyclodextrin derivatives appended by a naphthyl moiety associate with β-cyclodextrin using the moiety as a connector.

We have recently prepared naphthalene-appended γ-cyclodextrins [(**1**): 6-*O*-(2-naphthylsulphonyl)cyclo-octa-amylose, (**2**): 6-*O*-(2-naphthylacetyl)cyclo-octa-amylose] as a new series of host compounds.[1] This communication presents a new aspect of the chemistry of modified CDs, an appended moiety of a CD serving as a connection between two CD units (Figure 1).

Sample solutions of (**1**) or (**2**) (7.5×10^{-6} mol l^{-1}) and various concentrations of β-CD were used for spectroscopic measurements (25 °C). Both (**1**) and (**2**) exhibit enhanced fluorescence on addition of β-CD, indicating a change in the environment around the naphthyl moiety from the polar medium to less polar one,[2] and showing that the appending naphthalene fits into the hydrophobic β-CD cavity. Analyses of the fluorescence behaviour of the peak intensities of (**1**) (350 nm) and (**2**) (335 nm) by the modified Benesi–Hildebrand equation[3] gave association constants of 98 and 217 mol^{-1} l for (**1**) and (**2**), respectively. Similar enhancement by β-CD was observed in the c.d. spectra in the ^1B_b transition region of the naphthyl moiety [228 and 224 nm for (**1**) and

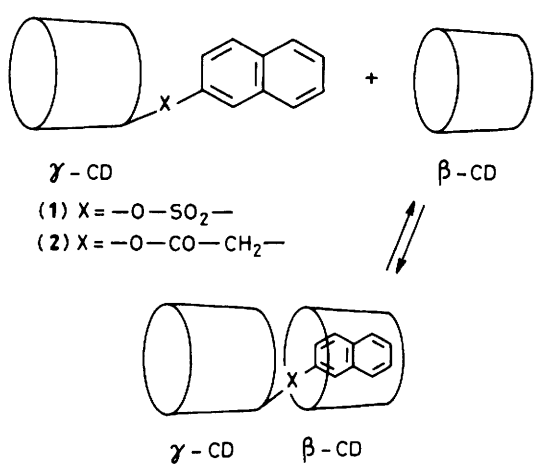

Figure 1. Association of two cyclodextrin units, using an appended moiety as the linking element.

(**2**), respectively], indicating the involvement of the naphthyl moiety in the chiral β-CD cavity. Analyses of the c.d. data[4] afforded almost the same results as obtained by the fluorescence method, revealing that the appending naphthyl moiety prefers to be included in the cavity of β-CD rather than in the γ-CD cavity of (**1**) or (**2**). This is consistent with the fact that the large γ-CD cavity of (**1**) and (**2**) does not allow the naphthyl moiety to be held tightly in its own cavity.

Association constants with β-CD of sodium 2-naphthylsulphonate and sodium 2-naphthylacetate obtained by the fluorescence method are 541 and 628 mol^{-1} l, respectively, which are much greater than those of (**1**) and (**2**). The smaller binding abilities of (**1**) and (**2**) for β-CD suggest that it is difficult for two bulky CD units to come close enough to allow the naphthyl moiety to be included completely in the cavity of β-CD. The extent of the steric hindrance can be related to the length of the naphthyl arm: *i.e.* the longer arm of (**2**) results in the greater association constant.

Fluorescence measurements have also shown, by the absence of fluorescence enhancement, that α-CD is incapable of associating with (**1**) or (**2**). This result is consistent with the fact that the cavity size of α-CD is too small to accommodate a naphthyl unit.

Hirotsu *et al.* recently reported the crystal structure of β-CD appended by a t-butyl moiety, which is accommodated in the cavity of another β-CD unit.[5] The present study demonstrates that a similar phenomenon occurs in solution, and shows also that the association between two different kinds of cyclodextrins, one as the donor and another as the acceptor of a linking group, is possible.

Received, 31st August 1983; Com. 1170

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