Chirality of the Two Pyrene Molecules included in γ-Cyclodextrin

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Induced circular dichroism has revealed that β-cyclodextrin accommodates one pyrene molecule with axial inclusion but that γ-cyclodextrin includes two pyrene molecules with *S*-helicity.

Cyclodextrins (CDs), which are torus-shaped oligosaccharides, form inclusion complexes with various substrates.[1] In contrast to α- and β-CDs which form one host–one guest complexes with small arenes, recent fluorescence studies have suggested that γ-CD can include two molecules of napthalene derivatives owing to the large size of its cavity.[2–4] However details of the two-guest inclusion have not been clarified. An important problem is the configuration of the two arene molecules trapped in γ-CD. We describe here results for the induced circular dichroism (i.c.d.) of pyrene in the presence of β- or γ-CD, from which the configuration of the two pyrene molecules included in γ-CD has been determined.

Sample solutions were prepared by adding 5×10^{-3} M of β- or γ-CD to 10^{-5} M of pyrene suspended in distilled water with stirring.† After ageing for 24 h, the intensity ratios of excimer/monomer fluorescence (ratio of emission at 472/392 nm) were 0.012 and 2.153 for β-CD (system I) and γ-CD (system II), respectively, thus suggesting a 1 : 1 complexation for system I[6] and 1 : 2 complexation for system II (the predominant species is a 1 : 2 complex of γ-CD with pyrene).‡ These solutions were used for i.c.d. measurements. The results are shown in Figure 1. In system I, the signs of the i.c.d. spectra were positive in the 240—270 and 290—360 nm regions and negative in the 275—290 nm region. The positions of the peaks and troughs were in complete agreement with those of the absorption peaks. It has already been substantiated, on the basis of the Kirkwood–Tinoco coupled oscillator expression, that a plus sign in the i.c.d. spectra of arenes included in β-CD is produced by electronic transitions parallel to the

† The solubility of pyrene in water is 1.6×10^{-6} M.[5] The solution became homogeneous and transparent after ageing for 24 h.

‡ By analysis of the computer simulation of the excimer intensity *vs.* [γCD] plots, concentrations of the γCD–pyrene (Py) complexes in the present system were estimated (the details will be published in *Bull. Chem. Soc. Jpn.* shortly): [Py·γCD] = 2.53×10^{-7} M, [Py·Py·γCD] = 2.89×10^{-6} M, [γCD·Py·γCD] = 3.80×10^{-7} M, and [γCD·Py·Py·γCD] = 5.15×10^{-7} M.

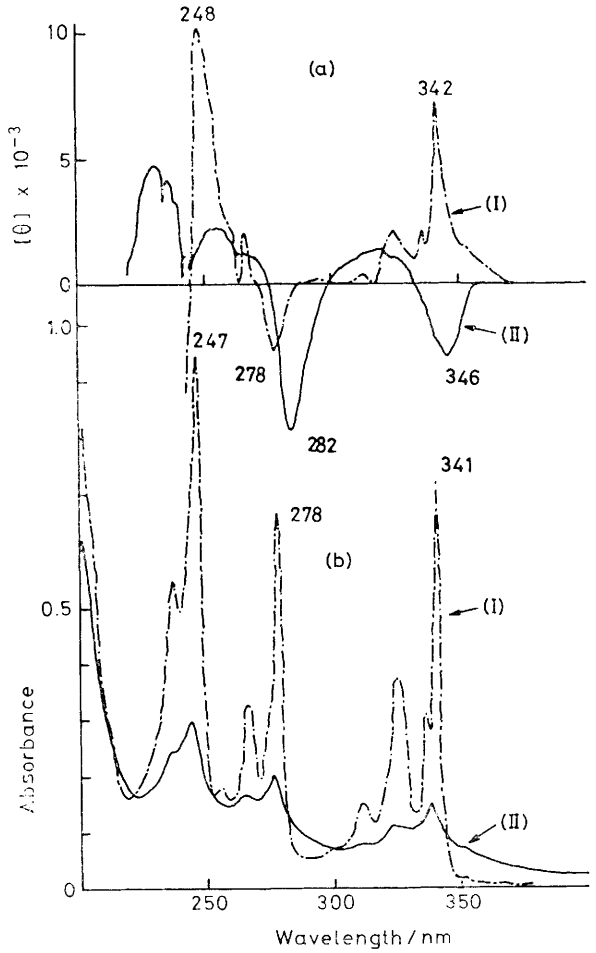

Figure 1. (a) Circular dichroism and (b) absorption spectra of 10^{-5} M pyrene in distilled water in the presence of 5×10^{-3} M β-CD (I) or γ-CD (II). The temperature was *ca.* 20 °C. Path lengths were 100 mm and 10 mm for i.c.d. and absorption spectra, respectively.

molecular axis of the CD.[7,8] Since the spectrum of pyrene is polarized along the long axis at 290—360 nm and the short axis at 275—290 nm,[9] the i.c.d. spectra indicate an axial inclusion in which the long axis of pyrene is parallel to the axis of β-CD. In system II, however, two sinusoidal i.c.d. curves with a change in sign from minus to plus from the longer wavelength side were observed, associated with ^1L_a and ^1B_b transitions, suggesting inclusion of more than one pyrene molecule. Since a Corey–Pauling–Koltun molecular model effectively eliminates the possibility of inclusion of more than two pyrene molecules, the above i.c.d. spectrum must be that of γ-CD including two pyrene molecules.‡ The two pyrene molecules included must have *S*-helicity owing to the change of sign of the i.c.d. spectrum at the ^1L_a band.

Thus we have shown that β-CD accommodates one pyrene molecule with axial inclusion but that γ-CD includes two pyrene molecules with *S*-helicity.

We have confirmed separately that two acridine orange molecules can also be accommodated by γ-CD with *S*-helicity.

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