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EXCITON COUPLING, INTRAMOLECULAR SELF-COMPLEXATION, AND HOST–GUEST COMPLEX FORMATION OF $6^A,6^X$-BIS-(ANTHRACENE-9-CARBONYL) DERIVATIVES OF CYCLOMALTO-OCTAOSE

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ABSTRACT

The four regioisomers of $6^A,6^X$-bis(anthracene-9-carbonyl)cyclomalto-octaose (**1**–**4**, X = B–E) exist in solution in aqueous 10% ethylene glycol as intramolecular complexes, in which two anthracene moieties are included in the cavity of cyclomalto-octaose. Spectroscopic data suggest that the arrangement of the two anthracene rings is nearest to face-to-face in **4** and the most remote in **2**. The c.d. spectra of the regioisomers reveal excition coupling bands in the ^1B_b region with the patterns of *R*-helicity for **1**, **2**, and **4**, and *S*-helicity for **3**. The regioisomers changed the intensities and shapes of the exciton coupling bands on complexation with *l*-borneol. The host–guest association constants were in the order **4**<**3**<**1**<**2**, indicating that the intramolecular complexes stabilized by the face-to-face interaction of the anthracene moieties are difficult to convert into intermolecular complexes.

INTRODUCTION

Cyclomalto-octaose (γ-cyclodextrin, γCD) has a cavity 8.5 Å in diameter[1] that can accommodate two molecular species. This property has been substantiated by the promoted formation of excimers[2,3] and charge-transfer complexes[4] in the presence of γCD. On the other hand, γCDs with two arene groups attached were shown[5,6] to form intramolecular complexes in which the two arenes were included in the cavity. On the addition of guest substances, these intramolecular complexes were converted into intermolecular complexes by moving the arene moieties outside the cavity (Eq. *1*). Hitherto, the study of this induced-fit type of guest binding has been confined to $6^A,6^E$-disubstituted γCDs, and the behaviour of other regioisomers ($6^A,6^B$-, $6^A,6^C$-, and $6^A,6^D$-disubstituted γCDs) is unknown. The study now reported is concerned with the formation of inclusion complexes (**1**–**4**) of $6^A,6^B$-, $6^A,6^C$-, $6^A,6^D$-, and $6^A,6^E$-bis(anthracene-9-carbonyl)-γCD. Since these hosts have

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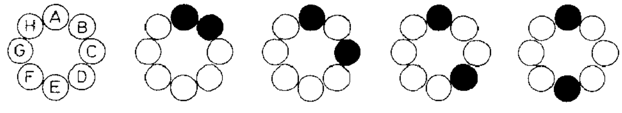
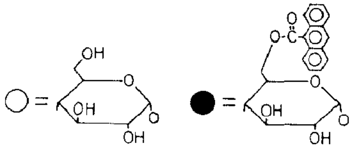


γ-cyclodextrin **1** **2** **3** **4**



(1)

two anthracene moieties included in the cavity with different mutual orientations, the geometrical differences were expected to be reflected in the absorption and c.d. characteristics.

EXPERIMENTAL

$6^A,6^X$-Bis(anthracene-9-carbonyl)-γCDs were prepared as described[7]. C.d., absorption, and fluorescence spectra were measured at 25° with a Jasco J-400X spectrodichrometer, a Shimadzu UV-250 spectrophotometer, and a Shimadzu RF-500 spectrofluorophotometer, respectively.

RESULTS AND DISCUSSION

Fig. 1 shows the absorption spectra of **1–4** in solution in aqueous 10% ethylene glycol, in which the major electronic transitions are essentially those of anthracene. The bands at 240–260 and 300–430 nm are attributed to ^1B_b and ^1L_a transitions, respectively. The patterns were different for each regioisomer and depended on the positions of the two anthracene moieties. The relative intensities ($\varepsilon_{245}/\varepsilon_{260}$) of the absorption peaks at ~245 and ~260 nm of the ^1B_b band follow the order of **2<3<1≈4**, and the resolution of the ^1L_a absorption became worse in the same order.

The spectral variation of the ^1B_b transition may be related to the selection rule for dimers of dye molecules given by Kasha[8] as follows. A spectral blue-shift for the face-to-face dimer, a spectral red-shift for the head-to-tail dimer, and band splitting for the oblique dimer. Since **1** and **4** have a predominant absorption peak at 245 nm (blue-shifted band), it seems feasible that they have the face-to-face dimer. The band splitting observed for **2** and **3** may not be due to the simple oblique

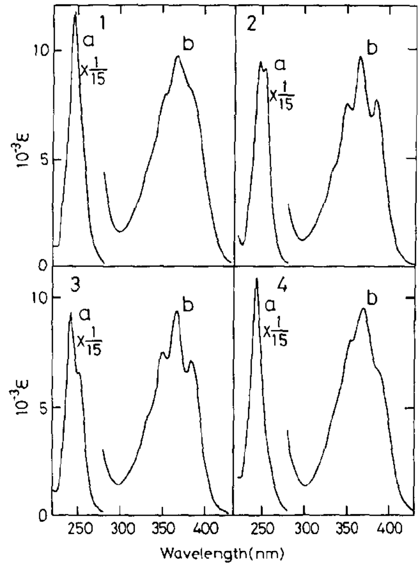


Fig. 1. Absorption spectra of solutions of **1–4** in aqueous 10% ethylene glycol: (a) 5.0 × 10^{-6}M, (b) 2.5 × 10^{-5}M.

dimers. Indeed, the anthracene moieties of **2** and **3** undergo photodimerization, so that there is no doubt that they can form face-to-face dimers. The band splitting may be due to the combination of different orientations, and the $\varepsilon_{245}/\varepsilon_{260}$ value may be used as a parameter which reflects the ratio of the face-to-face and the oblique dimers.

It is well known that a chromophore placed in a chiral environment exhibits induced c.d. Since the anthracene moieties in **1–4** are attached to the chiral γCD framework, c.d. may be induced in the absorption regions of anthracene. The results for **1–4** are summarized in Table I, and Fig. 2 shows the c.d. spectra of **1–4** in solution in aqueous 10% ethylene glycol observed in the ^1B_b transition region of anthracene. The spectra of **1**, **2**, and **4** each exhibit a peak at ~260 nm and a trough at ~245 nm, whereas that of **3** is inverted with a trough at 259 nm and a peak at 240 nm.

The sinusoidal curves were assigned to the exciton coupling bands of *R*- and *S*-helicities, respectively, that originated from the electronic interaction of the two anthracene moieties. This assignment was confirmed by the fact that the exciton coupling band of *R*-helicity is similar to that of the rigid compounds, in which two anthracene moieties are oriented clockwise[10]. The results indicate that the chiral environment of the γCD cavity forces the two anthracene moieties to be twisted in the *R*-helical orientation, except for **3**. The chirality of CDs is basically due to D-glucopyranose residues, but they have a C_n symmetrical axis (n = 8 for γCD) that makes it difficult to predict the chirality of the exciton coupling of the regioisomers. This situation is in contrast to the simple structure–helicity relationship for rigid compounds with two chromophores.

TABLE I

C.D. INTENSITIES OF **1–4** (5 × 10^{-6}M)[a]

Compound	*Solvent*[b]	*Wavelength (nm)*	*[θ] (deg.cm^2.dmol^{-1})*
1	10% EG	245 (242)	−173 000 (544,000)
		260 (257)	151 000 (−993,000)
	100% EG	244 (244)	−289 000 (−268,000)
		257 (257)	515 000 (488,000)
2	10% EG	244 (241)	−406 000 (448,000)
		258 (258)	290 000 (−791,000)
	100% EG	235 (243)	6 800 (48,800)
		256 (258)	−19 600 (−93,600)
3	10% EG	240 (241)	282 000 (199,000)
		259 (258)	−183 000 (−323,000)
	100% EG	241 (242)	39 400 (39,600)
		256 (257)	−28 000 (−45,400)
4	10% EG	245 (248)	−210 000 (−106,000)
		262 (264)	313 000 (136,000)
	100% EG	246 (246)	−938 000 (−909,000)
		261 (261)	987 000 (956,000)

[a] The values in parentheses were obtained in the presence of 1.06mM *l*-borneol. [b] EG, Ethylene glycol.

It is not clear why **1**, **2**, and **4** exhibit the exciton coupling band of *R*-helicity and **3** exhibits that of *S*-helicity. Fig. 2 also shows the exciton coupling bands observed in the presence of excess of *l*-borneol as the guest. Marked changes in c.d. were induced on addition of the guest. It is surprising that, for **1** and **2**, the helicity changes from *R* to *S* on binding of the guest as shown by the guest-induced reversion in the sign of the c.d.

The strong exciton coupling observed for the inclusion complexes was not expected, because induced c.d. of modified CDs is usually lost when associated

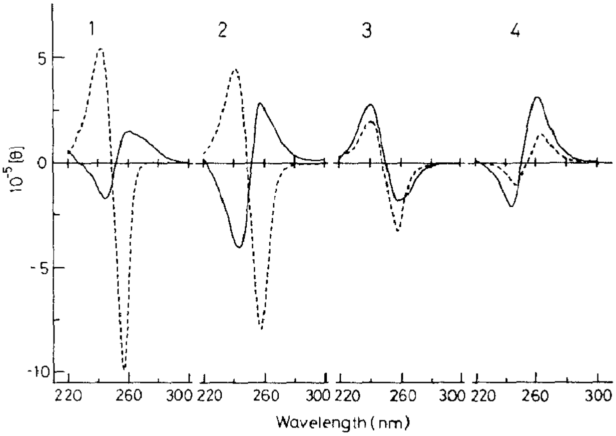


Fig. 2. C.d. spectra below 300 nm of 5.0 × 10^{-6}M solutions of **1–4** in aqueous 10% ethylene glycol alone (——) or in the presence of 1.06 × 10^{-3}M *l*-borneol (---).

with guest accommodation in the cavities[5]. The variations in guest-induced c.d. suggest that changes in the locations of the anthracene moieties occur in **1**–**4**, and the exciton coupling existing even after complexation indicates that the anthracene moieties are still mutually oriented.

Fig. 3 shows the molecular ellipticities at ~260 nm of **1**–**4** in solution in aqueous 10% and 100% ethylene glycol. The sign of the longer-wavelength region of the exciton coupling band should be positive and negative for *R* and *S* helicities, respectively. The sign and intensity of the exciton coupling should depend on the angle made by the two anthracene rings[9]. If the angles are the same, the intensity should be inversely proportional to the square of the distance between the two anthracene rings[9]. Since the two anthracene moieties of **1**–**4** in solution in aqueous 10% ethylene glycol must be folded into the cavity of γCD to contact each other, the angle is likely to be a factor that determines the sign and the intensity of the exciton coupling band. In solution in ethylene glycol, however, the anthracene moieties are unlikely to be held in the cavity because of the lack of water, which is a prerequisite for the hydrophobic driving force to become effective, and consequently the distance between the two anthracene rings may be important. This argument is substantiated by the much greater magnitude of the ellipticity of **1** in solution in ethylene glycol in comparison with the values of **2** and **3**. The large ellipticity of **4** may not be consistent with this consideration, but it seems reasonable if it is considered that the anthacene moieties of this substance still remain in the cavity, as shown by the absorption data. Similar distance-dependency may be expected for the complexes of **1**–**4**, since the anthracene moieties cannot be involved fully in the cavity when *l*-borneol is already present. Indeed, it was observed that the absolute ellipticity increased in the order **4**<**3**<**2**<**1**.

Fig. 4 shows the c.d. spectra of **1**–**4** for solutions in aqueous 10% ethylene glycol observed in the ^1L_a transition region of anthracene. The ^1L_a transition, which occurs along the short axis of anthracene, exhibits no exciton coupling band. There might be a relationship between the helicity and the sign of the c.d. band since **1**, **2**, and **4** with *R*-helicity exhibit negative bands, whereas **3** with *S*-helicity exhibits a positive band. The magnitudes of these bands may simply reflect the extent of involvement of the anthracene moieties in the cavity of the γCD. In fact, the intensities of the c.d. diminish on addition of *l*-borneol, indicating outward movement of the anthracene moieties from the cavity.

Table II shows the host–guest association constants of **1**–**4** for *l*-borneol, which were determined from the analysis of variations in the guest-induced c.d. in the ^1B_b transition region. The values are in the order **4**<**3**<**1**<**2**. Examination of CPK molecular models indicates that the parallel packing of the two anthracene moieties is most easily attained in the cavity of **4**, whereas it is almost impossible in that of **2**. If the intramolecular complex is stabilized by the face-to-face interaction of the anthracene moieties, the order of the host–guest association constants indicates that stable intramolecular complexes are difficult to convert into intermolecular complexes. The intramolecular photodimerization of anthracene in **1**–**4**

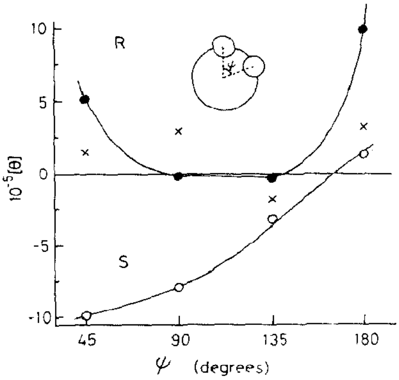


Fig. 3. Molecular ellipticities of the peak or trough at ~260 nm as a function of the angle (ψ) made by two radii projected from the center of γCD toward the glucose residues bearing an anthracene moiety (ψ = 45, 90, 135, and 180° for **1**–**4**, respectively). The values were obtained for solutions in aqueous 10% ethylene glycol alone (×) and in the presence of *l*-borneol (○) or in ethylene glycol (●).

may allow an insight into this point, since the reaction requires the face-to-face interaction of anthracene moieties. Upon irradiation, **3** and **4** gave stable photodimers, whereas **1** and **2** gave unstable photodimers[11]. The stereochemistry of the photodimers is *trans* for **2**–**4** and *cis* for **1**. The *trans* photodimer of **2** is unstable due to the strain within the structure, and it dissociates thermally into the original species. The results suggest that it is difficult for the anthracene rings to form the face-to-face dimer, so that the intramolecular complex is not stabilized. This geometrical feature may explain why **2** is a good host for *l*-borneol.

Fig. 5 shows the fluorescence spectra of **1**–**4** in solution in aqueous 10% ethylene glycol and methanol measured at 25° by excitation at 365 nm. These substances exhibit excimer-like emission with a structureless broad band, but this

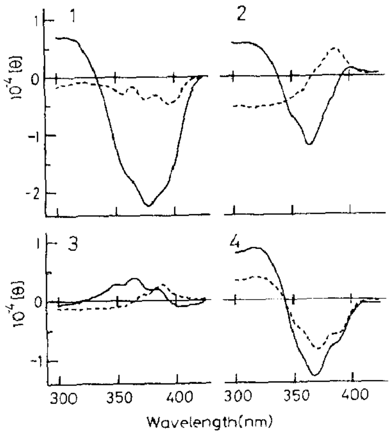


Fig. 4. C.d. spectra above 300 nm for 2.5×10^{-5}M solutions of **1**–**4** in aqueous 10% ethylene glycol alone (——) or in the presence of 10^{-3}M *l*-borneol (---).

TABLE II

HOST–GUEST ASSOCIATION CONSTANTS WITH *l*-BORNEOL IN SOLUTIONS OF AQUEOUS 10% ETHYLENE GLYCOL AT 25°

Host	K (M^{-1})
1	3400
2	12,000
3	2500
4	1400

emission should be assigned to the monomer fluorescence since the reference compound, methyl 6-*O*-(anthracene-9-carbonyl)-α-D-glucopyranoside, also exhibits a similar spectrum[6]. The fluorescence intensities of **1–4** in solution in aqueous 10% ethylene glycol were remarkably different. The intensity of **2** was much greater than that of **4**, suggesting it to be related to the ratio of the face-to-face and oblique dimers. Therefore, it seems feasible that the face-to-face dimer forms an excimer, which is readily converted into a photodimer without exhibiting any emission. On the addition of *l*-borneol, the fluorescence intensities of **1–4** were enhanced with slight shifts of the positions of the peaks to shorter wavelengths. This effect may be explained by the fact that the complexation with *l*-borneol separates the anthracene moieties which then act as monomer species. This argument is consistent with the observation that the fluorescence intensities of **1–3** are similar for solutions in methanol, in which tight inclusion of the anthracene moieties into the cavity is unlikely. The fluorescence intensity of **4** in solution in methanol is smaller than those of **1–3** and is consistent with the formation of a face-to-face dimer of **4**, even in methanol, indicated by the absorption data.

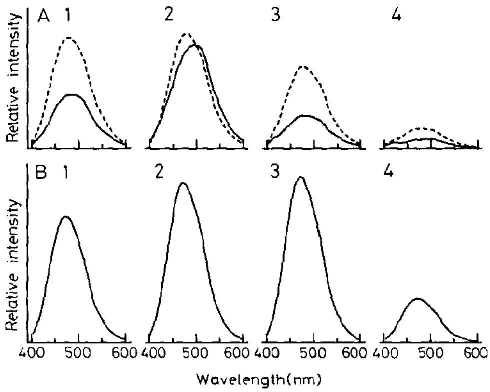


Fig. 5. Fluorescence spectra of solutions of **1–4** in aqueous 10% ethylene glycol (A, 2.5×10^{-5}M) and methanol (B, 2.5×10^{-5}M), alone (——) or in the presence of 10^{-3}M *l*-borneol (---). No effect of *l*-borneol was observed on the solution in methanol. The fluorescence intensities are comparable with each other within A or B. All spectra can be made comparable if the intensities of the spectra in B are magnified five times.

The foregoing data conclusively show that the regioisomers **1**–**4** are flexible hosts, which change the orientation and location of the anthracene moieties on complexation. In the absence of guests, the substances form intramolecular complexes by accommodating the anthracene moieties in the cavity of the γCD. In such complexes, the two anthracene moieties are oriented differently, showing exciton coupling bands of *R*- or *S*-helicity. The formation of face-to-face dimers by the anthracene moieties is likely to stabilize the intramolecular complexes, resulting in the depressed host–guest association constants. Consequently, the greatest guest binding was attained with **2**, which has a high content of the oblique dimer. The stability relationship between intra- and inter-molecular complexes could be applied to other modified CDs that contain one or two hydrophobic moieties.

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