Formation of Unstable Photodimers of Anthracene in Regioisomers of Bis(anthracene-9-carbonyl)-γ-cyclodextrins

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Two anthracene-9-carbonyl moieties attached to AB, AC, AD, and AE glucose units of γ-cyclodextrin undergo intramolecular photodimerization, giving unstable photodimers for AB and AC regioisomers and stable photodimers for others.

γ-Cyclodextrin, which consists of eight glucose units, has been shown to be capable of including two guest molecules in its large cavity.[1] On this basis, γ-cyclodextrin has been used as a molecular flask, in which two species gather together to achieve specific interactions[1—3] or reactions.[4] When two reactive moieties are covalently linked to γ-cyclodextrin at desired positions, they may be expected to be enforced to interact with each other in particular mutual orientations in the γ-cyclodextrin cavity and then to result in stereospecific products. From this viewpoint, we have attempted to produce the *cis*-photodimer of 9-anthracenecarboxylate, which cannot usually be obtained in solution, by using the template of A,B-bis(anthracene-9-carbonyl)-γ-cyclodextrin (AB isomer). Now we report the unique photochemistry of the AB isomer together with the properties of other regioisomers.

A,B-, A,C-, A,D-, and A,E-bis(anthracene-9-carbonyl)-γ-cyclodextrins shown in Figure 1 were prepared by reactions of sodium 9-anthracenecarboxylate and the corresponding regioisomers of bis(2-naphthylsulphonyl)-γ-cyclodextrins† in dimethyl sulphoxide at 80 °C for 5 h. The products were purified by high performance liquid chromatography with an ODS column (20 × 250 mm) and characterized by n.m.r., u.v., and i.r. spectroscopy, fast atom bombardment mass spectrometry (f.a.b.m.s.), and elemental analysis.

Photoirradiation of the regioisomers dissolved in an aqueous 10% ethylene glycol solution or methanol was

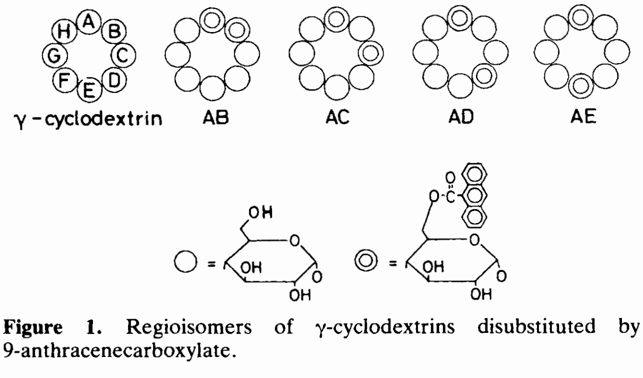

Figure 1. Regioisomers of γ-cyclodextrins disubstituted by 9-anthracenecarboxylate.

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† Preparation and assignment of A,X-bis(2-naphthylsulphonyl)-γ-cyclodextrins will be reported elsewhere.

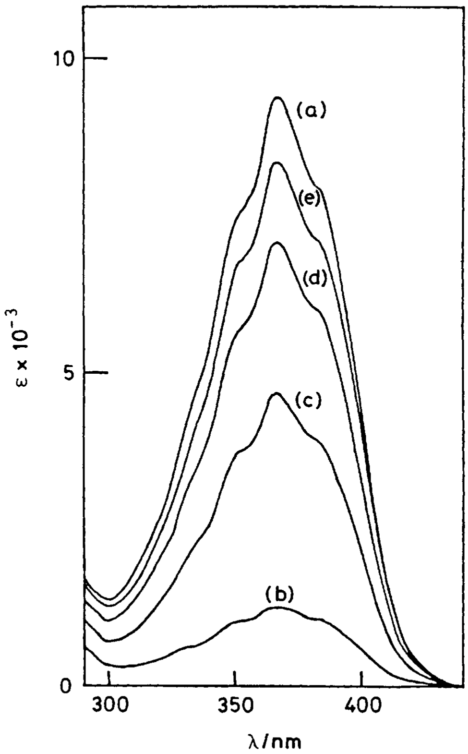

Figure 2. Absorption spectra of AB isomer in an aqueous 10% ethylene glycol solution (2.5 × 10^{-5} M) before (a) and after (b—e) photoirradiation. The spectra (b—e) were obtained 0, 10, 25, and 45 min after photoirradiation.

performed with a 500 W xenon lamp using an appropriate cut-off filter for isolating the light greater than 300 nm. All regioisomers decreased the absorption around 365 nm by photoirradiation until its intensity became negligible for AD and AE isomers or steady with the values of *ca.* 15% of the original absorptions for AB and AC isomers. When the photoirradiated solutions were placed in the dark, it was found that the absorption spectra of AB and AC isomers return to the original ones, while those of AD and AE isomers are unchanged. Figure 2 shows the spectral changes of AB isomer caused by photoirradiation and those occurring in the dark along the course of dissociation of its photodimer. This spectral behaviour indicates that the photoirradiated AB and AC isomers have unstable photodimers, which dissociate into the starting anthracene moieties thermally. The half-lives of dissociation of the photodimers measured in solution are summarized in Table 1. Dissociation occurs most rapidly for the AB isomer dissolved in an aqueous 10% ethylene glycol solution, giving a half lifetime of 12.5 min at 25 °C. In methanol, the rate of dissociation was significantly depressed with 5.6-fold larger half-life. The photodimer of AC isomer also dissociates in an aqueous 10% ethylene glycol solution with a 22-fold larger half-life than that of the AB isomer. The half-life in methanol of AC isomer is slightly smaller than that in an aqueous 10% ethylene glycol solution.

Treatment of the irradiated AC, AD, and AE isomers with an alkaline solution caused hydrolysis of the ester linkages and afforded a photodimer of 9-anthracenecarboxylic acid, which was confirmed by n.m.r. spectroscopy to be the *trans* form. This photoproduct is the same as that formed by photoirradiation of 9-anthracenecarboxylic acid in methanol. On the other hand, the same treatment of the irradiated AB isomer gave no photodimer due to the complete dissociation of the photodimer. The examination of molecular models indicates that the AB isomer cannot form the *trans* photodimer because of the stereochemical arrangement of the two 9-anthracenecarboxylate moieties; in other words, the only possible product of AB isomer is the *cis* photodimer. Figure 3 shows the different photochemistry and stereochemistry of AB and AE regioisomers.

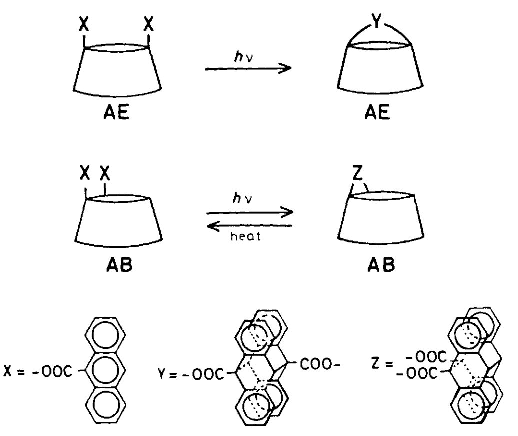

Figure 3. Photochemistry and stereochemistry of AB and AE regioisomers.

Table 1. Half-lives of regioisomers of bis(anthracene-9-carbonyl)-γ-cyclodextrins at 25 °C.[a]

Regioisomer	Solvent[b]	Half-life/min
AB	10% EG	12.5
AB	MeOH	70.5
AC	10% EG	275
AC	MeOH	206
AD	10% EG, MeOH	stable
AE	MeOH	stable

[a] The concentration of regioisomers was 2.5 × 10^{-5} M. [b] 10% EG: aqueous 10% ethylene glycol solution.

Usually photoirradiation of 9-substituted anthracenes gives only *trans* photodimers,[5] but in this study the *cis* photodimer was formed by using the AB isomer as template although it is markedly unstable. The photodimer of AC isomer is also unstable in spite of its *trans* form. This may be due to the strain existing in the photodimer, which arises from the unfavourable positions in the γ-cyclodextrin framework. These regioisomers might be used as molecular switches with which host–guest complexation can be regulated by light. This is now being studied.

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