

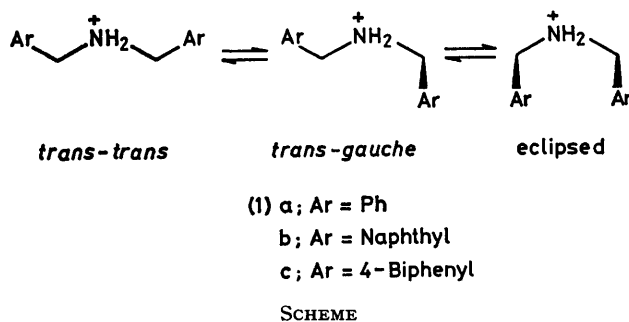
Enhanced Intramolecular Excimer Formation of Guest Molecules included in the Cavity of γ -Cyclodextrin

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Summary Whereas both α - and β -cyclodextrin significantly inhibit intramolecular excimer formation of bis-(4-biphenylmethyl)ammonium chloride, γ -cyclodextrin enhances it considerably, indicating its ability to induce a conformational change in a molecule by forming an inclusion complex.

THOUGH the cyclodextrins have been shown to catalyse a variety of reactions of included aromatic guests,¹ little attention has been paid to the possibility that they could influence the conformations of bound substrates.² Recently, enhanced excimer fluorescence of α -naphthylacetate in the presence of γ -cyclodextrin (γ -CD) was used as evidence that host-guest complexes with a stoichiometry of 1:2 can be formed.³ Thus, the possibility arises that with compounds containing two aryl moieties such as (1), γ -CD might be able to induce a conformational transition to the eclipsed state (Scheme) which could be readily detected by monitoring the fluorescence spectrum of (1).



Dilute solutions of (1) normally exhibit two emission bands in their fluorescence spectra, a monomer band characteristic of the aryl moiety and a long wavelength excimer band resulting from the intramolecular interaction of an excited aryl group with a ground state aryl group.⁴ Inclusion of one of the aromatic rings into a cyclodextrin cavity could lead to one of two possibilities. If the cavity were too small to accommodate the second aromatic ring, excimer formation should be inhibited by complexation. On the other hand, if the cavity were large enough to bind both moieties, excimer formation should be facilitated because it would lead to a 'tighter' inclusion complex.

Addition of α -, β -, or γ -CD (5×10^{-3} M) had no effect on the fluorescence spectrum of aqueous dibenzylammonium chloride (2×10^{-4} M) at 26 °C. Models suggest that for α - and β -CD, the presence of the second aryl moiety as well as the positively charged nitrogen prevent deep penetration of the guest into the host, resulting in inefficient binding. Though these adverse interactions are reduced in γ -CD because of the larger size of the cavity (8.5 \AA), the latter complex is too 'loose', again causing poor binding.

The fluorescence spectrum of bis-(α -naphthylmethyl)-ammonium chloride (10^{-4} M) was also unaffected by

5×10^{-3} M α - and β -CD at 26 °C. In the α -case, the cavity size (4.5 \AA) is too small to accommodate the naphthyl group whereas in the β -case (7.0 \AA) models again indicate steric crowding of the second aryl moiety and the positively charged nitrogen with the rim of the toroid. γ -CD, however, whose large cavity should permit binding of the naphthyl group, caused a 40% increase in the intensity ratio of excimer to monomer. The conformational transition of the included molecule to the eclipsed state upon irradiation is facilitated by γ -CD probably because it fills up the cavity resulting in a better fit.

These effects should be magnified with better binding probes. Bis-(4-biphenylmethyl)ammonium chloride (1c) has a longer hydrophobic residue which should allow efficient binding of at least the bottom phenyl ring without bringing the cationic nitrogen and the other bulky aryl group near the rim of the toroid. Indeed, in the presence of β -CD (5×10^{-3} M), no excimer peak at all could be observed from 10^{-4} M solutions of (1c) at 26 °C. However, in the presence of γ -CD, the monomer peak almost disappeared, as shown in the Figure. The smaller cavity of β -CD which can only accommodate one aryl residue completely inhibits excimer formation, whereas the larger cavity of γ -CD, which can host two aryl moieties, facilitates excimer formation dramatically. Though it has an even smaller cavity than β -CD, α -CD permits some excimer fluorescence to be observed because it is a poor binder for this substrate.

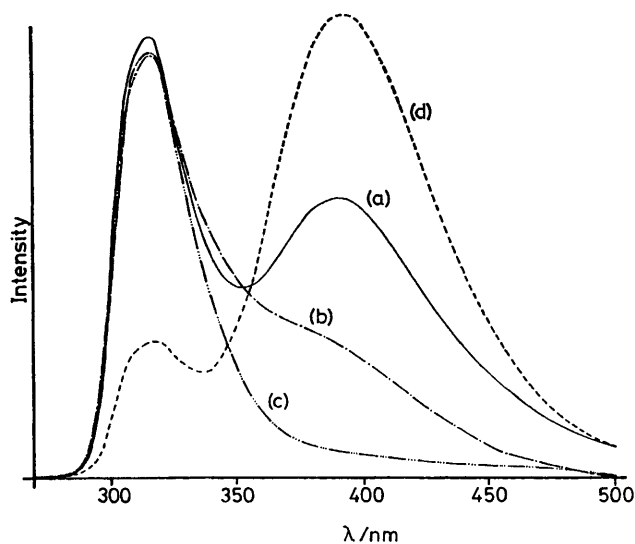


FIGURE. Fluorescence spectra of bis-(4-biphenylmethyl)-ammonium chloride (10^{-4} M) (a) in ethanol, (b) in water with 5×10^{-3} M α -CD, (c) β -CD, and (d) γ -CD.

It should be noted that the absorption spectrum of (1c) is largely unperturbed by the presence of γ -CD. If inclusion complex formation induces the eclipsed state in the ground state of (1c), significant shifts in the absorption spectra of

the type reported for 3,3-paracyclophanes would be expected.⁵ It therefore appears that this effect can thus far only be observed in the excited state where interactions between the rings are attractive.

These results clearly indicate that with carefully tailored geometries even crude binding sites such as those of the cyclodextrins are capable of profoundly influencing the

conformations of included guests. Such effects have also been observed in aqueous micellar systems.⁶

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