

## MODIFICATION OF THE PHOTOCHEMICAL BEHAVIOUR OF ORGANIC MOLECULES BY CYCLODEXTRIN: GEOMETRIC ISOMERIZATION OF STILBENES AND ALKYL CINNAMATES

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### Summary

The photochemical behaviour of stilbenes and alkyl cinnamates complexed to cyclodextrin has been investigated in aqueous media. In benzene, on direct excitation, the photostationary state of stilbene, *p*-methylstilbene, *p*-methoxystilbene and *p*-fluorostilbene contains predominantly the *cis* isomer (greater than 85%); excitation of cyclodextrin complexes of either *cis*- or *trans*-stilbene in aqueous media resulted in a photostationary state enriched in *trans* isomers. Furthermore, the cyclization product of *cis*-stilbene, *i.e.* phenanthrene, which is formed in detectable amounts in benzene solution was found to be absent during aqueous  $\beta$ -cyclodextrin irradiation. However, for cinnamate esters the behaviours in solution and in cyclodextrin are identical. Irradiation in organic solvents such as benzene and methanol and irradiation in aqueous  $\beta$ -cyclodextrin solution result in the same 1:1 mixture of *cis* and *trans* isomers. The above results have been rationalized on the basis of the influence of the cyclodextrin cavity on the decay ratio of the twisted olefins.

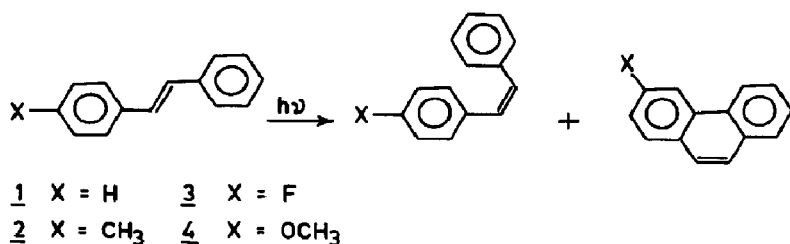
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### 1. Introduction

Modification of photoreactivity by incorporation of molecules into organized assemblies is an area of growing potential. Encapsulation of guest molecules in cavities of a host has been demonstrated to alter the reactivities of the guests in an impressive manner [1]. Cyclodextrins have excited much interest as host molecules; these are cone-shaped chiral oligosaccharides consisting of six to eight glucose units arranged in a cyclic array forming a hydrophobic cavity.  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrins consisting of six, seven and eight glucose units have cavity dimensions of 4.2 - 8.8 Å, 5.6 - 10.8 Å and 6.8 - 12.0 Å respectively, all having a depth of about 7.8 Å. Cyclodextrins are readily available, and in water or in polar organic solvents they bind hydrophobic organic segments of appropriate geometry with high affinities. The biomimetic catalysis of a variety of reactions by encapsulation of the

molecules into the cyclodextrin cavity has stimulated considerable interest in the study of cyclodextrin inclusion compounds [2]. Although the potential of cyclodextrins as "reaction vessels" for thermal reactions has been widely acknowledged, their use in photochemical reactions is yet to be fully explored. During the last few years, our group has investigated perturbations in the cyclodextrin cavity which occur on photochemical reaction. The goal is to achieve selectivity in photochemical reactions using this unusual environment and to understand the features controlling such selectivity. Such studies have concerned aryl alkyl ketones, dibenzyl ketones, phenyl esters and  $\beta$ -ionyl derivatives [3]. In continuation of such studies we have investigated the photochemical behaviour of stilbenes and cinnamates complexed to cyclodextrin. It was anticipated that the cyclodextrin cavity might impose certain constraints on the geometric isomerization of these olefins. Indeed, a significant difference in the photobehaviour of stilbenes was observed between isotropic solvents and anisotropic aqueous cyclodextrin media.

The photoisomerization of stilbenes has been extensively investigated [4] and has been an area of considerable interest. *cis*- and *trans*-stilbene on excitation in organic solvents are known to undergo isomerization as one of the major photoprocesses; cyclization of *cis*-stilbene to dihydrophenanthrene is a minor process. Another mode of decay of the singlet state of *trans*-stilbene is fluorescence decay. Owing to the sensitivity of the isomerization of *trans*-stilbenes and its fluorescence quantum yield to environmental constraints, their photobehaviour has been studied in a variety of media [5]. We have investigated the photobehaviour of stilbene (1), *p*-methylstilbene (2), *p*-fluorostilbene (3) and *p*-methoxystilbene (4) in aqueous cyclodextrin solution.



The photostationary state distributions and the emission intensity from the *trans*-stilbenes were monitored. The results of such a study are presented below.

## 2. Results

Direct excitation of aqueous solutions of cyclodextrin complexes of *cis*- and *trans*-stilbene (1 - 4) and of stilbenes 1 - 4 in benzene was conducted using a 450 W medium pressure mercury lamp with a Pyrex filter. The results

TABLE 1

Photostationary state product distribution on photolysis of stilbenes<sup>a, b</sup>

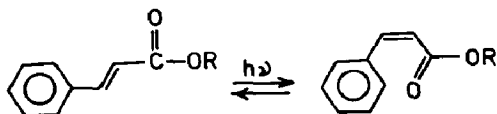
Substrate <sup>c</sup>	Medium <sup>d</sup>	Product distribution <sup>e</sup> (%)		
		Cis	Trans	Phenanthrene
Stilbene	Benzene <sup>f</sup>	91	5	4
Stilbene (cis)	$\beta$ -Cyclodextrin: water (10:1)	29	71	—
Stilbene (trans)	$\beta$ -Cyclodextrin: water (10:1)	22	78	—
<i>p</i> -Methylstilbene	Benzene <sup>f</sup>	88	9	3
<i>p</i> -Methylstilbene (cis)	$\beta$ -Cyclodextrin: water (10:1)	20	80	—
<i>p</i> -Methylstilbene (trans)	$\beta$ -Cyclodextrin: water (10:1)	17	83	—
<i>p</i> -Fluorostilbene	Benzene <sup>f</sup>	91	7	2
<i>p</i> -Fluorostilbene (cis)	$\beta$ -Cyclodextrin: water (10:1)	19	81	—
<i>p</i> -Fluorostilbene (trans)	$\beta$ -Cyclodextrin: water (10:1)	19	81	—
<i>p</i> -Methoxystilbene	Benzene <sup>f</sup>	83	14	3
<i>p</i> -Methoxystilbene (cis)	$\beta$ -Cyclodextrin: water (10:1)	7	93	—
<i>p</i> -Methoxystilbene (trans)	$\beta$ -Cyclodextrin: water (10:1)	5	95	—

<sup>a</sup>Analysed by means of gas chromatography; error limit,  $\pm 2\%$ .<sup>b</sup>Irradiated in Pyrex tubes using a 450 W medium pressure mercury lamp. The values represent those obtained after 24 h of irradiation. These values do not change after 6 h of irradiation.<sup>c</sup>Concentration of stilbene in all cases,  $5 \times 10^{-4}$  M.<sup>d</sup> $\beta$ -Cyclodextrin: stilbene ratio, 10:1; cyclodextrin was used in excess to suppress reactions from uncomplexed stilbene.<sup>e</sup>No dimer was obtained; material balance, greater than 85%.<sup>f</sup>The same product distribution is obtained whether the starting isomer is cis or trans.

are presented in Table 1. Perusal of the table reveals that there is a significant difference between the behaviour of these molecules in benzene solution and that when complexed to cyclodextrin. In benzene, on direct excitation, the photostationary state of 1 - 4 is predominantly the cis isomer (about 85%); the excitation of cyclodextrin complexes of either cis or trans 1 - 4 in aqueous media results in a photostationary state enriched in the trans isomers. Another interesting observation is that the cyclization product of *cis*-stilbene, *i.e.* phenanthrene, which is formed in detectable amounts in benzene solution, was found to be absent during aqueous  $\beta$ -cyclodextrin irradiation. Furthermore, gas chromatography and <sup>1</sup>H nuclear magnetic resonance (NMR) analysis of the product mixtures did not reveal any other products and the mass balance was excellent (greater than 85%). The results reported in Table 1 correspond to the condition under which cyclodextrin has been used in excess (ten equivalents). Irradiation with smaller amounts of cyclodextrin present resulted in dimerization as a result of association of stilbene in the aqueous phase [6]. Since dimerization was not observed under our experimental conditions, we believe that the photostationary state measured does not have any contributions from the uncomplexed stilbenes.

The following experiments provided information regarding formation of the inclusion complex between stilbenes 1 - 4 and cyclodextrin. Addition of 1 - 4 to saturated aqueous solutions of  $\beta$ -cyclodextrin precipitated a white solid which dissolved in excess water. The X-ray powder pattern of the precipitated solid differed from that of  $\beta$ -cyclodextrin. The solid state  $^{13}\text{C}$  NMR spectra of the isolated solid precipitate exhibited peaks corresponding to stilbenes in addition to those corresponding to  $\beta$ -cyclodextrin. Both these results indicate complexation of  $\beta$ -cyclodextrin to 1 - 4. Conclusive  $^1\text{H}$  NMR evidence in favour of the existence of a true inclusion complex in aqueous solution could not be obtained because of the poor solubility of these complexes.

To generalize the above-observed behaviour and to explore the effect of size of the substituents present at the olefinic double bond on the geometric isomerization, the photochemical behaviour of *trans*-cinnamates was investigated. Extensive structural [7, 8] and electrochemical [9] studies on ethyl cinnamate complexed to cyclodextrin have been carried out. A 1:1 complex has been isolated and identified by  $^1\text{H}$  NMR in aqueous media. Further, the electrochemical study provided strong support for the existence of the 1:1 complex in solution. Therefore, we did not pursue any structural studies on cinnamate-cyclodextrin complexes. On the basis of literature reports, we assume that cinnamates 5 - 7



5 R =  $-\text{CH}_2\text{CH}_3$

6 R =  $-(\text{CH}_2)_3\text{CH}_3$

7 R =  $-(\text{CH}_2)_5\text{CH}_3$

also form stable 1:1 complexes with cyclodextrin in aqueous solution and the observed photochemistry originates from them. The results for irradiation of *trans*-cinnamates in benzene, methanol and aqueous cyclodextrin solution are provided in Table 2. The direct irradiation of *trans*-cinnamates 5 - 7 in aqueous  $\beta$ -cyclodextrin solution led to behaviour totally different from that of the stilbenes. Irradiation of aqueous solutions of the  $\beta$ -cyclodextrin complexes of 5 - 7 in quartz vessels with 254 nm light gave rise to a photostationary state consisting of a 1:1 mixture of *trans* and *cis* isomers. The behaviour of *trans*-cinnamates is very similar to that in benzene solution under identical conditions.

### 3. Discussion

Interesting observations made in this study include the following. While the *trans*  $\rightarrow$  *cis* isomerization takes place in a facile manner in organic sol-

TABLE 2

Photostationary state product distribution on irradiation of alkyl cinnamates

Medium <sup>a</sup>	Ethyl cinnamate <sup>b,c</sup>		Butyl cinnamate <sup>b,c</sup>		Hexyl cinnamate <sup>b,c</sup>	
	Trans	Cis	Trans	Cis	Trans	Cis
Benzene	50	50	54	45	54	45
Methanol	50	50	53	46	56	44
SDS micelle	52	48	46	54	53	47
$\beta$ -Cyclodextrin <sup>d</sup>	49	51	51	49	51	49

SDS, sodium dodecylsulphate.

<sup>a</sup>All solutions were irradiated under identical conditions using a Rayonet reactor fitted with 254 nm lamps.<sup>b</sup>The product distribution is based on gas chromatography analysis; error limit,  $\pm 2\%$ .<sup>c</sup>The concentrations of alkyl cinnamates were  $3 \times 10^{-3}$  M; at higher concentrations dimerization occurred.<sup>d</sup>Two equivalents of  $\beta$ -cyclodextrin were used to suppress reactions from uncomplexed cinnamates.

vents to give a photo-equilibrium mixture containing about 90% of the *cis*-stilbene, the photoisomerization of *trans*-stilbene is largely restricted in the  $\beta$ -cyclodextrin cavity and the *cis*  $\rightarrow$  *trans* isomerization proceeds uninhibited. Similar remarkable effects of cyclodextrin encapsulation are also found for substituted stilbenes. However, for cinnamate esters the behaviours in solution and in cyclodextrin are identical. Irradiation in organic solvents such as benzene and methanol and that in  $\beta$ -cyclodextrin aqueous solution results in the same 1:1 mixture of *cis* and *trans* isomers. Any microheterogeneous chemical reaction which differs from its solution counterpart raises questions as to how and at what stage the medium influences the course of the reaction. In a cyclodextrin-mediated reaction, an essentially "cage-controlled" process can be envisaged where all molecular changes occur within the cavity. An alternative view would be that molecules must diffuse out of the cavity into less encumbered locations for reaction to take place and that then clathration occurs with the photoproduct. We favour, on the basis of the observed dimerization in the aqueous medium and the absence of dimerization in the presence of excess cyclodextrin, the "photoisomerization in the cavity" pathway.

Before ascribing this significant difference in the photostationary state composition between organic solvents and cyclodextrins to the influence of the cyclodextrin cavity, the following alternatives were considered.

(1) The observed reaction might occur from a suspension of undissolved complexes rather than from the dissolved complexes.

(2) The observed differences could be due to differences in the absorption spectra of the *cis* and *trans* isomers between those in benzene and those in the complexed state.

(3) The *trans*-enriched photostationary state may be due to either electron transfer or a radical-induced process.

(4) The isomerization is the result of a secondary process, *i.e.* the overall process might involve photohydration followed by dehydration to a thermodynamically more stable isomer.

The following observations, however, negated these possibilities. Irradiation of solid complexes of stilbenes 1 - 4 did not result in any isomerization. The solubility of the stilbene complexes in water was found to be about  $10^{-5}$  M. The UV absorption spectra for *cis*- and *trans*-stilbene displayed in Fig. 1 illustrate that they show identical absorption properties both in benzene and in aqueous cyclodextrin. The isomer compositions for stilbene during electron transfer and radical-initiated reactions have been reported [10] to be *trans* enriched by about 99%. Therefore the observed ratio (80% *trans*) cannot be due to these processes. Photohydration products, if formed, should be stable. However, attempts to identify them by both gas chromatography and  $^1\text{H}$  NMR analysis were not successful. Therefore, we have concluded that the remarkable difference could only be rationalized on the basis of the effect of the cyclodextrin cavities on the stilbenes included in them.

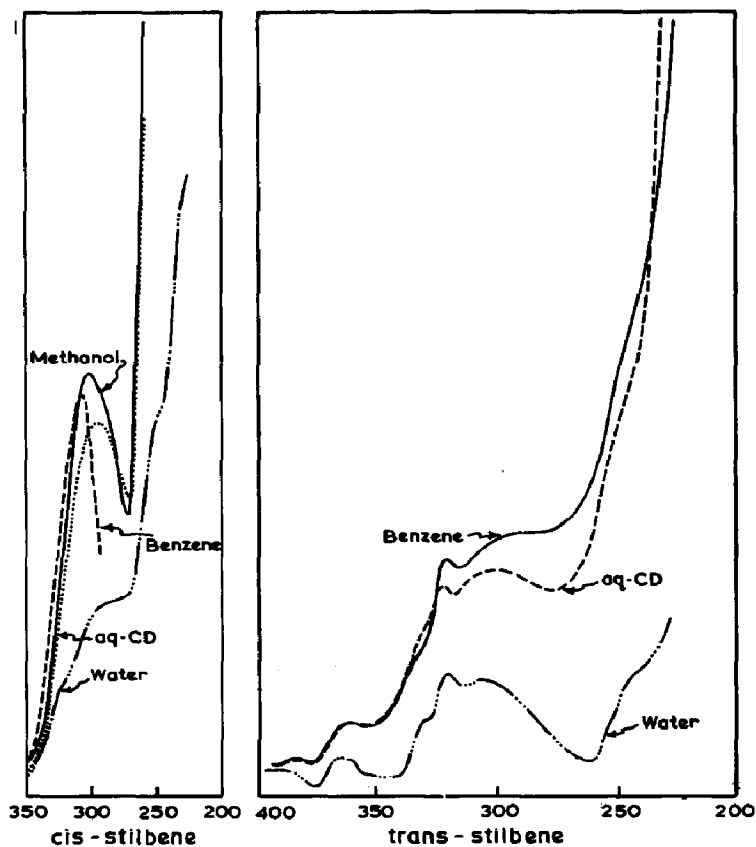


Fig. 1. UV absorption spectra of *cis*- and *trans*-stilbene in benzene and water.

The photostationary state composition of a two-isomer system is a function of the product of the excitation and decay ratios [4]:

$$\left(\frac{[\text{trans}]}{[\text{cis}]}\right)_{\text{pss}} = \left(\frac{k_e}{k_t}\right)_{\text{excit}} \left(\frac{k_t}{k_e}\right)_{\text{decay}}$$

For direct excitation, the excitation ratio is the ratio  $C_c\epsilon_c/C_t\epsilon_t$  of the extinction coefficients of the two isomers at the irradiation frequency. The decay ratio is unique to a given system and is normally independent of the reaction conditions. Thus the effect of the cyclodextrin cavity has to be understood only in terms of its influence on either the decay or the excitation ratio. Owing to identical extinction coefficients for stilbenes in benzene and aqueous cyclodextrin (Fig. 1) the excitation ratio is expected to be the same in both media. Therefore, we believe that the cyclodextrin cavity alters the decay ratio. Such an alteration can arise by two pathways. First, the environment may slow down the motion of stilbene to the twisted state to the extent that radiationless and radiative decay occur before it has reached the totally twisted configuration. This would favour decay to the trans isomer. Alternatively, the excited stilbene may reach the twisted configuration, but then be forced back to the trans form by the cavity.

On the basis of CPK molecular models and the reported structures for related azo compounds [11] the structure of the cyclodextrin complexes of *cis*- and *trans*-stilbenes can be visualized as shown in Fig. 2. Structures for the cinnamate complexes based on NMR and X-ray studies [7, 8] are also shown in Fig. 2. It is inferred from the *trans*-stilbene-cyclodextrin model that the rotation about the C=C bond to form the *cis* isomer will be restricted by the cavity. This effect arises because of the interaction between the phenyl ring and the rim of the cyclodextrin cavity. While in most of the organized media investigated the restriction for *trans* → *cis* conversion is accompanied by the enhancement of fluorescence, in the present study the intensities of fluorescence of *trans*-stilbene are comparable in water and in aqueous cyclodextrin. Therefore, we conclude that the effect of the cavity occurs at the twisted p state. The decay of the p state to the *cis*

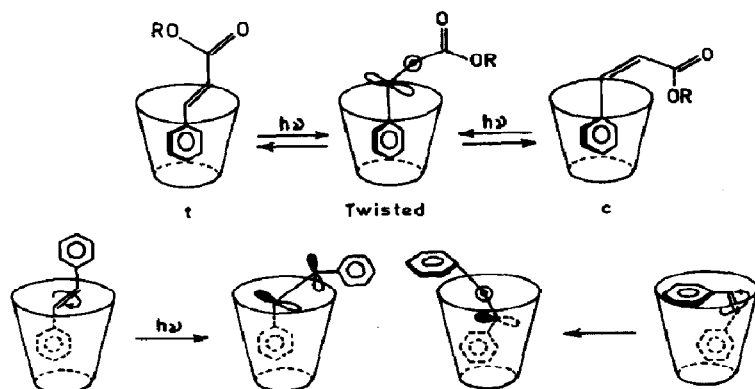


Fig. 2. Schematic representations of the isomerization of olefins in cyclodextrins.

isomer is inhibited by the cavity while that to the trans isomer occurs unabated. The facile isomerization of *cis*-stilbene to the trans form can also be explained by this model although the structure of the *cis*-stilbene-cyclodextrin complex is different (Fig. 2). Additional support for this postulate comes from the cinnamates which show behaviour in the  $\beta$ -cyclodextrin cavity identical with that in organic solvents (Table 2). This can be easily explained from the fact that the ester group of the cinnamates is smaller than the phenyl group of the stilbene. Thus, because of the smaller size of the ester group, the rotation about the C=C bond to form the *cis* isomer is not expected to be restricted by the cyclodextrin cavity.

#### 4. Experimental details

##### 4.1 Materials

*trans*-Stilbene (Aldrich) was used as received. *p*-Methylstilbene, *p*-methoxystilbene and *p*-fluorostilbene (trans isomers) were prepared by reported procedures [12]. The *cis* isomer in each case was prepared in benzene by irradiation (Rayonet reactor, RPR 300 nm lamps) of the respective trans isomer for 16 h and separation by column chromatography (alumina with hexane-benzene). *trans*-Ethyl, *trans*-butyl and *trans*-hexyl cinnamates were prepared by following literature methods [13].  $\beta$ -Cyclodextrin (Aldrich) was used as received. Doubly distilled water was used for irradiation and for the absorption spectral measurements.

##### 4.2. Preparation of $\beta$ -cyclodextrin complexes

Addition of one equivalent of stilbenes 1 - 4 (*cis* or *trans*) and *trans*-cinnamates 5 - 7 to saturated aqueous solutions of  $\beta$ -cyclodextrin (one equivalent) resulted in the precipitation of the inclusion complex as a white solid. The solutions were magnetically stirred for 24 h for complete complexation. Then the complexes were filtered, washed with ether and dissolved in excess water. The resulting solutions were used for photolysis. For stilbenes, excess cyclodextrin (ten equivalents) was required to arrest reactions occurring from uncomplexed stilbenes in the aqueous phase. However, with the cinnamates about two equivalents of cyclodextrin were sufficient to complex the substrate completely.

The molar ratio of the host to the guest was determined as follows. The solid complex, which was dried to constant weight at about 60 °C after washing with water and ether, was redissolved in water. The guest olefin was extracted thoroughly with chloroform and the amount of the olefin present in the known amount of the complex was estimated by gas chromatography. The molar ratio thus estimated was found to be in the range 1:0.9 (olefin). However, this does not provide conclusive information regarding the stoichiometry of the complexes in aqueous solution.

##### 4.3. Identification of cyclodextrin complexes

X-ray powder diffraction photographs for guest-free  $\beta$ -cyclodextrin and for  $\beta$ -cyclodextrin complexes were recorded for olefins 1 - 7 using a



Phillips powder diffractometer employing monochromated Cu K $\alpha$  radiation. The powder patterns for the  $\beta$ -cyclodextrin complexes were significantly different from the pattern for guest-free  $\beta$ -cyclodextrin. Therefore, it was concluded that microcrystalline complexes are formed between  $\beta$ -cyclodextrin and olefins 1 - 7.

The solid state  $^{13}\text{C}$  NMR spectra of the  $\beta$ -cyclodextrin complexes of the stilbenes were recorded at the National Research Council of Canada, Ottawa, by Dr. J. Ripmeester using a Bruker FT CXP-200 instrument. Signals corresponding to the guest could be observed together with those of the cyclodextrin carbon atoms.

The low solubility of the cyclodextrin complexes of stilbenes 1 - 4 in water and the low equilibrium constants prevented studies of the effect of the guests on the  $^1\text{H}$  NMR of cyclodextrin in solution. Structural details have already been reported [7] from  $^1\text{H}$  NMR spectroscopy of the ethyl cinnamate- $\beta$ -cyclodextrin complex in aqueous solution. The X-ray crystallographic structure of the ethyl cinnamate- $\beta$ -cyclodextrin complex has also been determined [8].

#### 4.4. Absorption and emission measurements

The absorption and emission spectra were recorded using a Shimadzu (UV-180) double-beam spectrophotometer and a Shimadzu spectrofluorometer (RF-540) respectively. Absorption and emission spectral studies were carried out only for the stilbene complexes. The absorption spectra of *cis*- and *trans*-stilbene showed no significant spectral shift on complexation with cyclodextrin. However, there was a slight rise in optical density OD with added  $\beta$ -cyclodextrin and this change  $\Delta\text{OD}$  in optical density at a fixed wavelength was utilized to estimate the dissociation constants of the cyclodextrin complexes. Stock solutions of *cis*-stilbene ( $10^{-3}$  M) and *trans*-stilbene ( $10^{-4}$  M) were prepared in methanol and 100  $\mu\text{l}$  of each were added to 10 ml standard flasks to which various amounts of  $\beta$ -cyclodextrin were added from a stock solution ( $10^{-3}$  M). The concentrations of *cis*- and *trans*-stilbenes used in the measurements were  $1.67 \times 10^{-5}$  M and  $1.1 \times 10^{-6}$  M respectively. The cyclodextrin concentrations were varied in the range ( $8 \times 10^{-5}$ ) - ( $4 \times 10^{-4}$ ) M. The dissociation constants were estimated from plots of  $a_0 b_0 / \Delta\text{OD}$  against  $(a_0 + b_0)$ , where  $a_0$  and  $b_0$  represent the concentrations of stilbene and cyclodextrin respectively. The values of the dissociation constants for the *cis*- and *trans*-stilbene complexes with cyclodextrin were  $4.3 \times 10^{-3}$  and  $1.4 \times 10^{-3}$  respectively. The dissociation constants for the cinnamate complexes were not measured as it has been reported that ethyl cinnamate forms a stable 1:1 complex with  $\beta$ -cyclodextrin in aqueous solution [7].

#### 4.5. Photolysis

The typical irradiation procedure for stilbenes 1 - 4 was as follows. Aqueous solutions of *trans*-stilbene- $\beta$ -cyclodextrin complexes (20 mg stilbene plus 1.25 g  $\beta$ -cyclodextrin in 200 ml water) were irradiated in Pyrex tubes using a 450 W medium pressure mercury lamp after oxygen-free

nitrogen had been bubbled through for 30 min. The products of photolysis were extracted with warm chloroform and analysed by gas chromatography. A Chemito gas chromatograph (model 3800) was used and an 8 ft  $\times$  1/8 in 5% SE-30 column was employed for analysis. The duration of irradiation required for obtaining the photostationary state ranged between 3 and 6 h. In all cases the photostationary state was measured starting from both pure cis and pure trans isomer complexes. The ratio of cis to trans isomer was monitored every hour until there was no further change. In each case a final ratio was measured after 24 h of irradiation. For comparison, stilbenes 1 - 4 in benzene were irradiated under identical conditions (concentration, volume of solution and photolysis set-up). During benzene irradiation phenanthrenes were obtained in addition to the cis and trans isomers. However, on irradiation of the aqueous solution of the complexes, no products other than the cis and trans isomers were obtained. The mass balance was excellent (greater than 85%) in all the stilbenes investigated.

The typical irradiation procedure for cinnamates consisted of the following. The photostationary states were measured starting from only the *trans*-cinnamate complexes. An aqueous solution of the *trans*-ethyl cinnamate complex (25 mg ethyl cinnamate, 165 mg  $\beta$ -cyclodextrin and 300 ml water) was irradiated in quartz tubes using a Rayonet reactor fitted with 254 nm lamps after oxygen-free nitrogen had been bubbled through. The products of photolysis were extracted with warm chloroform and analysed by gas chromatography (5% SE-30, 8 ft  $\times$  1/8 in column at 150 °C). The typical duration of photolysis required for achieving the photostationary state was between 3 and 6 h. In all cases the mass balance was good (greater than 85%) and no products other than the geometric isomers were detected by high resolution  $^1\text{H}$  NMR (270 MHz Fourier transform NMR) and by gas chromatography.

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