

SELECTIVITY IN THE PHOTOCHEMISTRY OF β -IONYL AND β -IONYLIDENE DERIVATIVES IN β -CYCLODEXTRIN: MICROSOLVENT EFFECT

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Summary

The photochemical behaviour of β -ionone, β -ionylidene acetaldehyde, β -ionylidene acetonitrile and ethyl- β -ionylidene acetate has been investigated in β -cyclodextrin as the host. They all form a fairly stable and water-soluble complex with β -cyclodextrin. An impressive difference in the behaviour of β -ionone and β -ionylidene acetaldehyde was observed between solution (in benzene and methanol) and as a cyclodextrin complex (in water). While in organic solvents β -ionone gives rise to products arising from geometric isomerization and 1,5-hydrogen migration, in cyclodextrin only 1,5-hydrogen migration occurs. Similarly, while in solution β -ionylidene acetaldehyde gives only geometric isomers as the final products; in cyclodextrin it gives *retro- γ* product derived via 1,5-hydrogen migration as the final product. No difference in the behaviour of β -ionylidene acetonitrile and ethyl β -ionylidene acetate was observed between solution and cyclodextrin complex. The variation in the photochemical behaviour of these compounds has been rationalized on the basis of the effect of cyclodextrin on the $n\pi^*-\pi\pi^*$ character of the lowest excited state.

1. Introduction

The control and modification of reactivity through incorporation of molecules into organized assemblies remain areas of considerable interest. A specific subarea that has attracted recent interest concerns the reactivity of molecules incorporated into "host-guest" complexes [1]. These studies have paved the way to an intriguing number of possibilities by which photo-reactivity can be modified. Cyclodextrins are naturally occurring doughnut-shaped chiral macrocyclic oligomers. It has been established that they encapsulate organic molecules in their molecular cavities [2]. Internal diameters and depths of cyclohexaamylose or α -cyclodextrin (4.2 - 8.8 Å and 7.8 Å), cycloheptaamylose or β -cyclodextrin (5.6 - 10.8 Å and 7.8 Å)

and cyclooctaamylose or γ -cyclodextrin (6.8 - 12.0 Å and 7.8 Å) provide cavities for appropriately sized guest molecules. The recognized potential of cyclodextrin-guest interactions as models for enzyme active sites has prompted the numerous investigations of these systems. 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.

Ohara and Watanabe [3] were the first to report the para selectivity during the photo-Fries rearrangement of phenyl acetate in β -cyclodextrin. Similar selectivity has recently been reported for phenyl benzoate [4]. These ortho-para selectivities are attributed to the geometry of the inclusion complex. Nucleophilic photosubstitution reactions of 2-fluoro- and 4-fluoroanisoles in cyclodextrins have recently been investigated by Liu and Weiss [5]. The photoreactivity of α - and β -cyclodextrin-complexed fluoroanisoles towards nucleophilic substitution with cyanide or water is suppressed. This is suggested to be the net result of a combination of factors: intrinsic solute photoreactivity, steric constraints to reactivity imposed by cyclodextrin and special water structure near the positions of substitution in cyclodextrin complexes. Other reactions in which the steric constraints and cavity size play a crucial role are the photo-oxidation and dechlorination of chloropromazine [6] and the photo-oxidation of oxime derivatives [7]. Another feature of the γ -cyclodextrin cavity, namely its ability to include two molecules, has been exploited to bring about quantitative dimerization of substituted anthracenes even in dilute solution (less than 10^{-4} M) [8]. Optical induction has also been observed during the photoisomerization of complexed tropolone derivatives [9]. However, it has not yet been demonstrated that the microsolvent effect of cyclodextrins is photochemically useful. The results presented below on β -ionyl and β -ionylidene derivatives in β -cyclodextrin are relevant in this context.

The solvent-dependent photoisomerization of retinal and other members of the series is a well-known phenomenon which has received considerable attention in terms of both its synthetic value and mechanistic understanding [10]. From a combination of the results of photoisomerization of the polyenals and polyenones in the retinal series and the photophysical data obtained by Das and Becker [11], it has been suggested that the well-known solvent-dependent photoisomerization of retinal was due to switching of the role of the reactive states: the $n\pi^*$ state in non-polar solvents and the $\pi\pi^*$ state in polar solvents [12]. A study on shorter-chain aldehydes and ketones in the above series revealed that the solvent dependence is chain-length dependent, occurring only in compounds with more than four double bonds [12]. It is hoped that the reactive states ($n\pi^*$ and $\pi\pi^*$) of even the lower members of the retinal series can be reversed, leading to variation in their photochemical behaviour by using a highly polar medium such as water. The results presented below suggest that β -cyclodextrin can expose organic molecules to a highly polar environment by incorporating them in a specific geometry.

2. Experimental details

2.1. Materials

β -Ionone (Eastman) was distilled twice and the centre fraction was used. All *trans*- β -ionylidene acetonitrile, β -ionylidene acetaldehyde and ethyl- β -ionylidene acetate (Fig. 1) were obtained as gifts from Professor R. S. H. Liu and Dr. V. J. Rao. They were passed once through a silica gel column (hexane-benzene) prior to use. 7-*cis* isomers of β -ionylidene acetonitrile were prepared by Rose Bengal sensitization of the corresponding 7-*trans* isomers. β -Cyclodextrin (Aldrich) was used as received. Doubly distilled water was used for all the experiments.

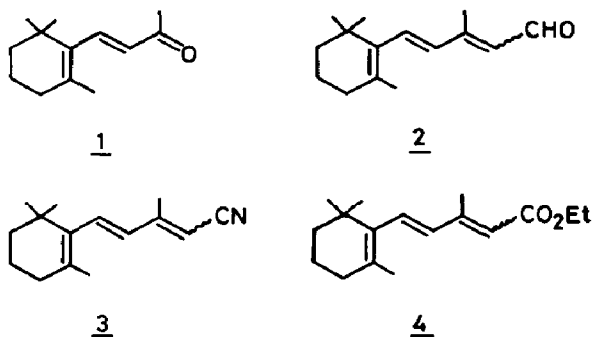


Fig. 1. β -Ionyl and β -ionylidene derivatives investigated.

2.2. Preparation of the cyclodextrin complexes

Addition of the β -ionyl derivatives (Fig. 1, 1 - 4; 1 equivalent) to saturated solutions of cyclodextrin (1 or 2 equivalents) resulted in precipitation of the inclusion complex. The solutions were magnetically stirred for completion of complexation and then dissolved in excess water (about 50 ml). These solutions were used for photolysis.

2.3. Identification of cyclodextrin complexes

2.3.1. Powder diffraction of the solid complexes

X-ray powder photographs of β -cyclodextrin and β -cyclodextrin complexes with 1 - 4 were taken using a Phillips powder diffractometer employing monochromated Cu K α radiation. Powder patterns of β -cyclodextrin and of the complexes were significantly different and it could be concluded that microcrystalline complexes have been formed between β -cyclodextrin and β -ionyl derivatives.

2.3.2. ¹³C nuclear magnetic resonance of the solid complexes

The solid state ¹³C nuclear magnetic resonance (NMR) spectrum of the complex of β -ionone with β -cyclodextrin was run at the National Research Council of Canada, Ottawa, by Dr. J. Ripmeester on a Bruker FT CXP-200 instrument. The spectra revealed the presence of peaks corresponding to

both cyclodextrin and β -ionone. Most of the peaks were broad, possibly owing to disorder in the crystal structure.

2.3.3. ^1H nuclear magnetic resonance of the aqueous cyclodextrin complex

^1H NMR spectra of β -cyclodextrin and its complex with β -ionone in D_2O solution were recorded using a Bruker HW-270 FT NMR spectrometer. About 6 - 7 equivalents of β -ionone were added to solutions of β -cyclodextrin (2 mg) in 1 ml of D_2O . The solution was stirred well and transferred to an NMR tube and the spectrum was recorded.

2.3.4. UV spectral measurements

0.01 M stock solutions of β -ionyl derivatives 1 - 4 were prepared in methanol and 50 μl portions of these were added to 10 ml standard flasks containing various amounts of β -cyclodextrin solutions (0.5 - 5 ml of 10^{-3} M). The solutions were made up to 10 ml and stirred well for 2 - 3 h. The UV spectra of these solutions were recorded using a Shimadzu UV-180 spectrophotometer. In the case of β -ionone and β -ionylidene acetaldehyde a clear red shift in the spectra was seen. The spectra are reproduced in Fig. 2. The optical density values were measured at a wavelength where the maximum shift is noticed. Plots of $a_0 b_0 / \Delta\text{OD}$ versus $(a_0 + b_0)$ (where a_0 and b_0 are the concentrations of cyclodextrin and substrate respectively) were linear. The stability constants K_s were determined from the slopes and intercepts of these plots.

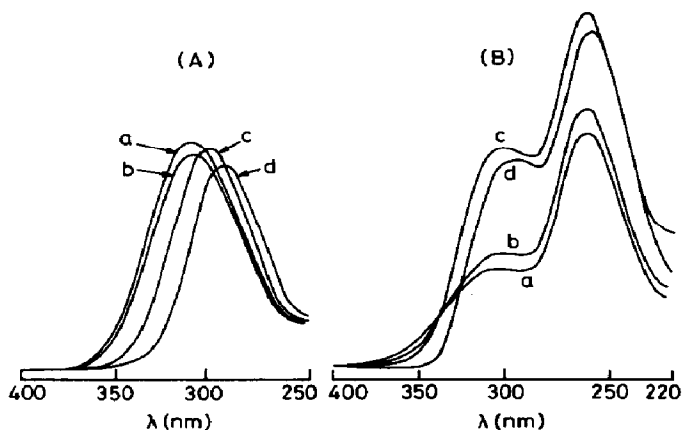


Fig. 2. UV absorption spectra for (A) 1 and (B) 3: curves a, in H_2O ; curves b, in aqueous β -cyclodextrin; curves c, in methanol; curves d, in cyclohexane.

2.4. Photolysis of the β -cyclodextrin complexes

The aqueous solutions of the β -cyclodextrin complexes were irradiated in Pyrex tubes after oxygen-free dry nitrogen had been bubbled through for 20 min. A Rayonet photochemical reactor with 300 nm lamps or 450 W

medium pressure mercury arc lamps were used for irradiation. The products were extracted with warm chloroform and analysed by ^1H NMR (60, 100 and 270 MHz). Progress of the reaction was monitored every 15 min. The product ratios were estimated by integrating the appropriate ^1H NMR signals. For comparison, β -ionyl compounds were irradiated in benzene and methanol under identical conditions.

3. Results

3.1. Complexation with β -cyclodextrin

Addition of β -ionyl derivatives 1 - 4 to saturated aqueous solutions of β -cyclodextrin precipitated a white solid which dissolves in excess water. The X-ray powder pattern of the precipitated solid differed from that of β -cyclodextrin. The solid state ^{13}C NMR spectra of the isolated solid precipitate exhibited peaks corresponding to the β -ionyl derivatives in addition to those corresponding to β -cyclodextrin. Both these results indicate complexation of β -cyclodextrin with β -ionyl derivatives. The complex of β -cyclodextrin with β -ionone was taken as the model for structural analysis in aqueous solution. The 270 MHz ^1H NMR spectra of aqueous solutions of β -cyclodextrin and its complex with β -ionone were recorded. The cyclodextrin protons were identified in the 270 MHz spectra by their specific coupling pattern [13]. The chemical shifts of β -cyclodextrin protons in the uncomplexed and in the complexed forms were utilized for comparison and are given in Table 1. The H(3), H(5) and H(6) protons present in the interior of the cyclodextrin were shifted most. The H(1) and H(4) protons are almost unaffected, supporting the contention that the complexation occurs at the interior of the ring. The upfield shift of these protons is attributed to the magnetic anisotropic effect of the π cloud of the double bond.

3.2. Stability of the complexes

It has been observed by several groups of workers that there is a change in the UV absorption spectra of substrates on complexation [14]. The UV absorption spectra of 1 - 4 in aqueous solutions with various amounts of β -cyclodextrin were recorded. The spectra for 1 - 4 in cyclohexane, methanol, water and β -cyclodextrin complex in water were recorded and those of 1 and 3 are shown in Fig. 2. A red shift (with respect to the organic solvents) in the spectra of 1 and 2 in water and aqueous cyclodextrin was noticed. However, 3 and 4 showed no change in the absorption maxima. Increased amounts of β -cyclodextrin in water resulted in an increase in the optical density of 1 - 4 without much change in the absorption maxima. The differences ΔOD in optical densities were noted at a wavelength where the maximum shifts were observed on addition of β -cyclodextrin. The plots of $a_0 b_0 / \Delta\text{OD}$ versus $(a_0 + b_0)$ were linear for all compounds. From the slopes and intercepts of these linear plots the stability constants were estimated

TABLE 1

¹H nuclear magnetic resonance spectral data for β -cyclodextrin protons and the β -cyclodextrin- β -ionone complex in D₂O

β -Cyclodextrin proton	Chemical shift (Hz) in uncomplexed β -cyclodextrin	Chemical shift (Hz) in the β -cyclodextrin- β -ionone complex		Difference in chemical shift (Hz) between the complexed and uncom- plexed β -cyclodextrin
		1:0.7 ^a	1:1 ^a	
H(1)	1359.6	1360.0 (+0.4)	1360.6 (+1.0)	+0.3
H(2)	975.7	972.9 (-2.8)	971.0 (-9.7)	-4.2
H(3)	1059.9	1046.7 (-13.2)	1045.5 (-14.4)	-13.9
H(4)	958.4	963.1 (+4.7)	963.7 (+5.3)	+3.9
H(5)	1030.0	1011.0 (-19.0)	1009.0 (-21.0)	-20.4
H(6)	1039.1	1046.7 (+7.6)	1046.5 (+7.4)	+7.2
			1359.0 (0.6)	
			970.5 (-5.2)	
			1045.8 (-14.1)	
			961.1 (+2.7)	
			1008.7 (-21.3)	
			1045.8 (+6.7)	

^aMolar ratio of β -ionone to β -cyclodextrin in aqueous solution.

on the basis of the method of Benesi and Hilderbrand [15]. The dissociation constants were as follows: 1, $2.8 \times 10^{-4} \text{ M}^{-1}$; 2, $1.4 \times 10^{-4} \text{ M}^{-1}$; 3, $1.1 \times 10^{-4} \text{ M}^{-1}$; 4, $1.7 \times 10^{-4} \text{ M}^{-1}$. The low values of the dissociation constants imply that the complexes are fairly stable.

3.3. Photolysis

Four β -ionyl derivatives 1 - 4 were chosen for investigation in β -cyclodextrin. Singlet state reactions of polyenes in the vitamin A series are quite limited. Other than geometric isomerization only two types of unimolecular reactions are known for these systems. They are sigmatropic hydrogen migration and electrocyclicization. While sigmatropic hydrogen migration and electrocyclicization have their origin in the excited singlet state, geometric isomerization comes from both excited singlet and triplet states. In this study β -ionone, β -ionylidene acetaldehyde, β -ionylidene acetonitrile and ethyl- β -ionylidene acetate were photolysed in benzene, methanol and aqueous cyclodextrin. The products were characterized by comparing their spectral properties with reports given in the literature [16]. Product distributions were monitored by ^1H NMR.

Direct photolysis of β -ionone 1 in benzene and methanol leads to the formation of *retro*- γ -ionone 5 and the α -pyran 6 (Fig. 3): prolonged irradiation (Pyrex vessel) of β -ionone for about 24 h resulted in 15% *retro*- γ -ionone and 85% α -pyran. Further irradiation did not result in any change. Under

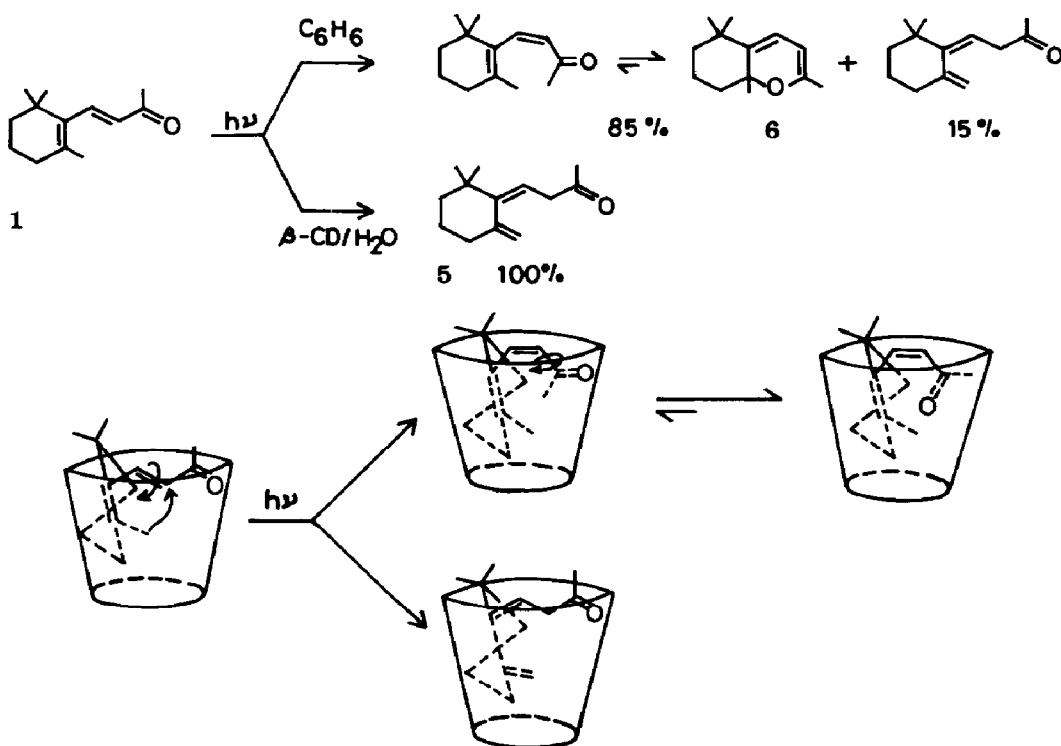


Fig. 3. Direct photolysis of β -ionone in benzene and in cyclodextrin.

the conditions of irradiation (450 W Hanovia medium pressure mercury lamps or Rayonet RPR-3000 lamps with Pyrex filters) α -pyran did not absorb the light. Surprisingly, irradiation of the aqueous solution of cyclodextrin complex of β -ionone gave only *retro- γ* -ionone; no α -pyran is to be found. This is remarkable considering the fact that the initial product distribution in benzene and methanol is heavily in favour of α -pyran.

Irradiation (RPR-3000 lamps) in benzene and methanol of the *7-cis* or *7-trans* isomers of β -ionylidene acetaldehyde in the region where both isomers absorb the light gave a photostationary state mixture consisting of *7-cis* and *7-trans* isomers and a small amount of *retro- γ* isomers (Fig. 4). However, most interestingly, irradiation of the cyclodextrin complex of *7-trans*- β -ionylidene acetaldehyde in aqueous media gave *retro- γ* -ionylidene acetaldehyde **7** as the only final product. Examination of the initial product distribution showed the presence of *7-cis* isomers, suggesting that isomerization is not inhibited by the cyclodextrin cavity. Formation of *retro- γ* -ionylidene derivatives is indeed surprising considering the fact that they were obtained only in trace amounts in benzene and methanol on photolysis.

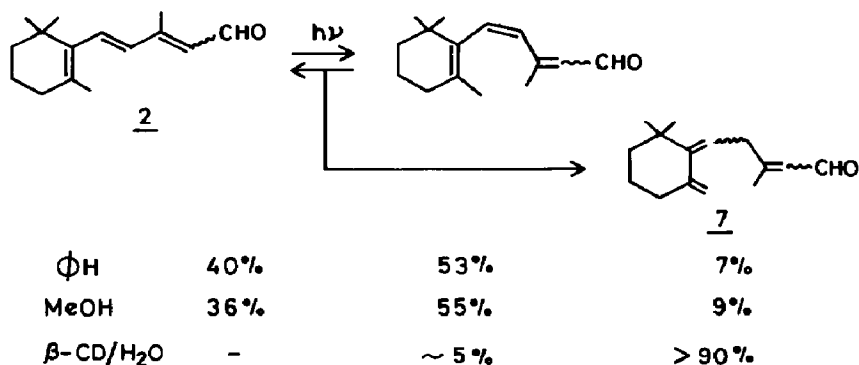


Fig. 4. Photolysis of β -ionylidene in benzene, methanol and in cyclodextrin.

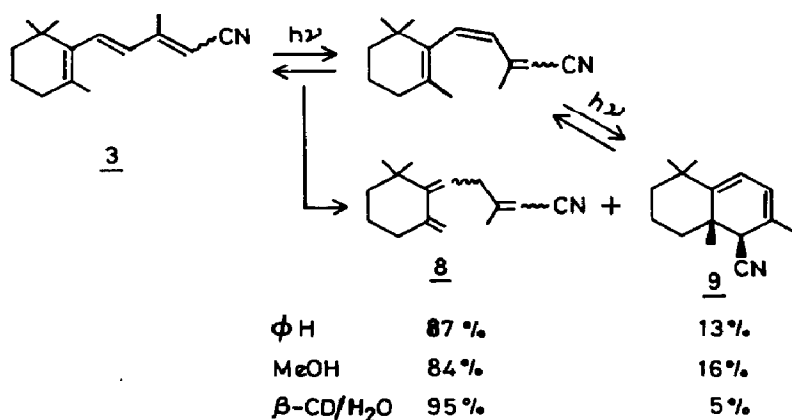


Fig. 5. Photolysis of **3**.

Direct irradiation of the trienes **3** and **4** was examined. The end products were the corresponding *retro-γ* products **8** and **10** and the electrocyclic products **9** and **11**. Photolysis of either 7-*cis* or 7-*trans* isomers of **3** and **4** in benzene, methanol and in aqueous cyclodextrin gave closely similar product mixtures. Time *versus* product distribution revealed that **3** and **4** undergo both hydrogen migration and isomerization around 7–8 and 9–10 double bonds simultaneously. Furthermore, product distribution at all stages of irradiation in cyclodextrin was similar to that in benzene and methanol (Figs. 5 and 6). Thus while β -ionone and β -ionylidene acetaldehyde show remarkably different photochemical behaviour in β -cyclodextrin, the behaviours of β -ionylidene acetonitrile and ethyl- β -ionylidene acetate in β -cyclodextrin are identical with those in organic solvents. The photochemical behaviours of **1** - **4** observed in organic solvents in this study are identical with those reported in the literature [17].

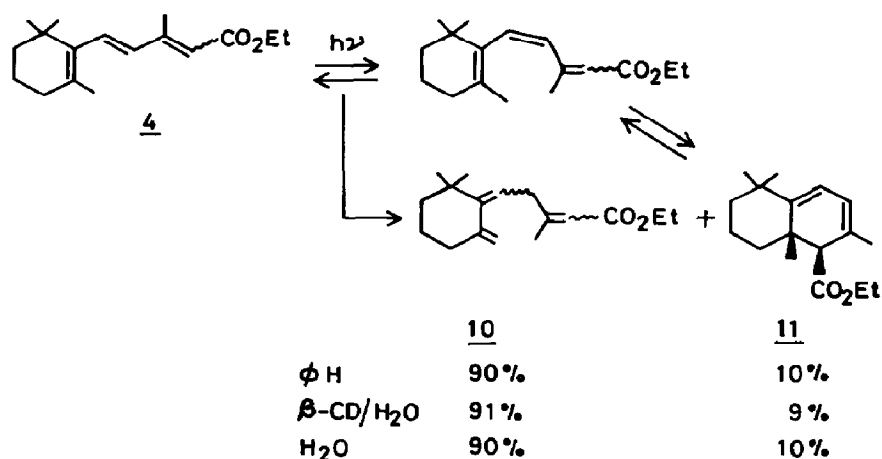


Fig. 6. Photolysis of **4**.

4. Discussion

An impressive difference in the behaviour of β -ionone and β -ionylidene acetaldehyde was observed between solution and cyclodextrin complexes. While in organic solvents β -ionone gives rise to products arising from geometric isomerization and 1,5-hydrogen migration, in cyclodextrin (aqueous medium) only 1,5-hydrogen migration occurs. Similarly, while in solution β -ionylidene acetaldehyde gives only geometric isomers as the final products, in cyclodextrin it gives *retro-γ* product derived from 1,5-hydrogen migration as the final product. One of the simple explanations for these results is the restriction imposed by the cavity on the rotation of the double bond. CPK molecular models of the β -ionone–cyclodextrin complex as shown in Fig. 3 indeed suggest that the rotation of the 7–8 double bond may be hindered in the cavity of cyclodextrin. In contrast, 1,5-hydrogen migration requiring minimal motion of atoms would proceed uninhibited by the cavity.

However, this reasoning does not hold good for β -ionylidene derivatives 2 - 4. Although β -ionylidene acetaldehyde gives the *retro- γ* product 7 as the final product, isomerization around both the 7-8 and the 9-10 double bonds occurs at the initial stages of the irradiation. Therefore, it is clear that rotation of the double bonds is not fully restricted by the cavity. However, the ability of 1,5-hydrogen migration to compete with geometric isomerization in the case of β -ionylidene acetaldehyde could mean that either the rotation about the double bonds is at least partially slowed down by the cavity or the rate of 1,5-hydrogen migration is enhanced. In order to ascertain this, the photochemical behaviour of β -ionylidene acetonitrile and ethyl β -ionylidene acetate, molecules that possess a closely similar molecular structure, was investigated. As mentioned earlier, no difference in their behaviour was observed between solution and cyclodextrin. This clearly suggested that the cyclodextrin cavity is not offering any restriction for isomerization of the double bonds. Although the variation in the geometry of complexation of 2 - 4 could contribute to the difference in the photo-behaviour of 2 - 4, we prefer to visualize that all three β -ionylidene derivatives (2 - 4) would possess similar geometry in the complex. Furthermore, we attribute the preference for *retro- γ* products in the case of β -ionone and β -ionylidene acetaldehyde in cyclodextrin and the absence of cavity influence in the case of β -ionylidene acetonitrile and ethyl β -ionylidene acetate to a microsolvent effect; steric constraints to isomerization by the cavity are suggested to be minimal.

In organic solvents, β -ionone and β -ionylidene acetaldehyde possess a low-lying $n\pi^*$ state and a closely higher-lying $\pi\pi^*$ state. However, β -ionylidene acetonitrile and ethyl β -ionylidene acetate are not expected to have low-lying $n\pi^*$ states. These states are expected to lie in a higher energy region. Therefore, while the former two compounds can be expected to show a medium dependent photochemical behaviour due to dual participation of the $n\pi^*$ and $\pi\pi^*$ states, the latter two β -ionylidene derivatives are not. The solvent effect on the absorption and emission properties of β -ionone and β -ionylidene acetaldehyde has been extensively investigated [11]. Although these compounds are non-emitting both in 3-methylpentane and EPA, they become moderately intensely fluorescent in the presence of trichloroacetic acid, a hydrogen bonding agent. The dramatic change in the fluorescence quantum yield on hydrogen bonding is attributed to the $n\pi^*-\pi\pi^*$ state reversal. The strong hydrogen bonding agent is thought to raise the energy of the $n\pi^*$ state and lower that of the $\pi\pi^*$ by a comparable magnitude. Even in our case, β -ionone is found to show a weak emission in the region 340 - 500 nm in aqueous β -cyclodextrin solution. Influenced by these studies, we suggest that the energies of $n\pi^*$ and $\pi\pi^*$ states are altered by β -cyclodextrin either through hydrogen bonding or by allowing the molecule to face a highly polar aqueous medium. This is supported by the red shift observed in the absorption maxima of β -ionone and β -ionylidene acetaldehyde in β -cyclodextrin media (even compared with methanol (Fig. 2)). We believe that the change in photochemical behaviour for β -ionone

and β -ionylidene acetaldehyde in β -cyclodextrin is due to approach of the $\pi\pi^*$ and $n\pi^*$ states. In organic solvents the $n\pi^*$ character dominates and in β -cyclodextrin the $\pi\pi^*$ character begins to play a role. This change in character of the lowest excited state allows the 1,5-hydrogen migration to compete effectively with geometric isomerization. The absence of the cyclodextrin effect in the case of β -ionylidene acetonitrile and ethyl β -ionylidene acetate must then be due to the fact that either the energy gap between the $n\pi^*$ and $\pi\pi^*$ states is too large to be affected or the $\pi\pi^*$ state is of lower energy. This is also in accordance with the absorption spectra wherein no change is noticed in the absorption maxima. The results presented here are consistent with the view that all four compounds 1 - 4 complex with β -cyclodextrin and that the excited state character of the β -ionones and β -ionylidene acetaldehyde is altered either through hydrogen bonding or by exposing the guest molecules to a highly polar aqueous exterior. Several reported examples of the use of fluorescence have demonstrated that organic substrates can observe an environment less polar than water when bound to cyclodextrins [18]. It is to be noted, however, that the polarity sensed by the guest will be dependent on the binding geometries and the exact location of the chromophore inside the host [19].

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