Photodimerization of Coumarins in Solid Cyclodextrin Inclusion Complexes

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Received January 16, 1992

The photodimerizations of coumarin and eight of its derivatives are found to proceed selectively in solid inclusion complexes with β- and γ-cyclodextrins (β- and γ-CD). The distribution of photodimers from these complexes is compared with those from the neat coumarin solids and their solutions in a variety of solvents. By assuming that the stereochemistry of the dimers reflects the packing arrangements of their precursors in the CD complexes, several hypotheses concerning the locations and arrangements of the coumarins in the host toruses have been made. The stoichiometries of the complexes have been assigned on the basis of the presence or absence of photodimers and from NMR integration ratios of characteristic coumarin and saccharide protons. The relative orientations of substituted coumarins within a complex are inferred from the stereochemistry of the photodimers. Depending upon the substitution pattern of the coumarin molecules and the type of CD employed, complexes whose guest-host stoichiometries are 1:1, 2:1, and 2:2 have been identified. In several instances, dimers not available from irradiation of neat solid coumarins or their solutions have been obtained from the CD complexes.

Introduction

Cyclodextrins are toroidally shaped polysaccharides comprised usually of six to eight glucose units.[1] They have been used extensively to model protein–ligand and enzyme–substrate interactions.[2-4] Their cavities have internal diameters ranging from 4.7 to 8.3 Å, permitting them to form inclusion complexes with a variety of guest molecules.[1,5] In some cases, the complexes are structurally specific and sufficiently stable to be isolated.

Complexation between cyclodextrins and substrates in solution has been exploited to induce selectivity in some unimolecular and bimolecular photochemical reactions.[6] For example, photodimerization of anthracene-2-sulfonate and anthracene-2-carboxylate has been reported to proceed regio- and stereoselectively in aqueous media containing β- or γ-cyclodextrin (β- or γ-CD).[7] Regulation of stereochemistry has also been achieved in the intramolecular photodimerization of various regio isomers of γ-cyclodextrins to which two anthryl groups have been covalently attached.[8] There are comparatively few reports concerning cyclodextrin-assisted solid-state bimolecular reactions. For example, Wernick et al. recently reported a Diels–Alder reaction between guest molecules of a solid ternary cyclodextrin complex.[9]

Surprisingly, we have been able to find few examples of bimolecular photochemical reactions of substrates conducted with solid CD inclusion complexes. Tanaka et al. examined the photodimerization of a coumarin/β-CD inclusion complex dispersed in a KBr pellet.[10a] Their interest was confined to the effect of cyclodextrin on the rates of coumarin dimerization; the distribution of photodimers was not investigated. Later, the same group reported that irradiation of coumarin/β-CD complexes yields only the syn head-to-head dimer, albeit at an attenuated rate with respect to that found upon irradiation of neat coumarin or physical mixtures of β-CD and coumarin.[10,11] Recently, several interesting examples of unimolecular photochemical reactions of solid cyclodextrin complexes have appeared.[12] In several of these, the influence of cyclodextrin in directing the course of the substrate reaction is significant.

We report here the results from a study on the photodimerizations of coumarin and several of its derivatives in solid complexes of β- and γ-CD. The stereo- and regioselectivities of these photodimerizations are compared with those from the same substrate irradiations conducted in solution[13] or in the neat solid state.[14,15] Our interest is to explore the extent to which the toruses of cyclodextrins can mediate the photodimerizations. In principle, static interactions between guest and host molecules may be greater in solid complexes than in dissolved ones; solid complexes do not dissociate as they do in solution, and motions of guest molecules in the toruses of solid complexes are expected to be attenuated. Additionally, the removal of mobile solvent molecules (usually water) around dissolved complexes probably imposes additional con-

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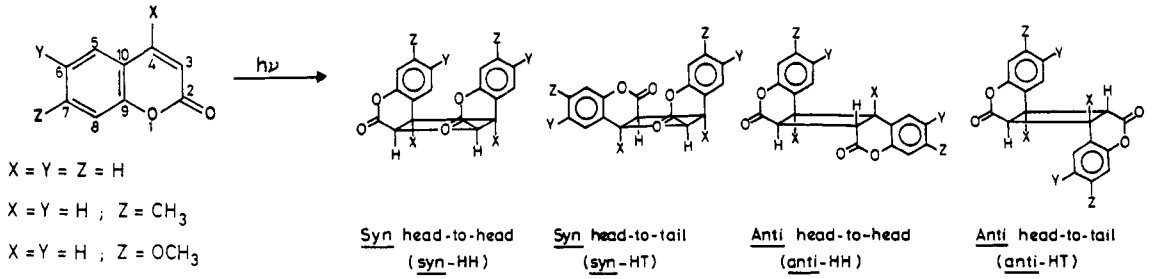
Scheme I. Coumarin and Substituted Coumarins Examined and Their Possible 2 + 2 Photodimers



X = Y = Z = H

X = Y = H ; Z = CH_3

X = Y = H ; Z = OCH_3

X = Z = CH_3 ; Y = H

X = Y = CH_3 ; Z = H

X = CH_3 ; Y = H ; Z = OCH_3

X = Cl ; Y = Z = H

X = OMe ; Y = Z = H

X = CH_3 ; Y = Cl ; Z = H

Table I. Room-Temperature Irradiation of Coumarin and Substituted Coumarins in Solution and as Neat Solids or Solid Complexes with Cyclodextrins

		solid CD complexes					neat solid phases			solutions[c]			
coumarin substituents	host CD	irradiation time (h)	dimer type	dimer yield (%)	H:G[a]	inferred complex[b] (H:G)	irradiation time (h)	dimer type	dimer yield (%)	solvent	irradiation time (h)	dimer type	dimer yield (%)
none	β	135	syn-HH	64	1:0.65–0.75	1:2 or	48	syn-HH	~20	H_2O	22	syn-HH	20
								syn-HT					
						2:2		anti-HH		CH_3OH	22	anti-HH	2
7-methyl	β	135	*d*	0	1:1	1:1	120	syn-HH	65	$CHCl_3$	72	*d*	0
	γ	140	syn-HH	80	1:1.85	1:2							
7-methoxy	β	140	*d*	0	1:0.6	1:1	15	syn-HT	90	CH_2Cl_2	72	syn-HT	40
	γ	140	syn-HH	65	1:1.7	1:2				CH_3OH	72	syn-HT	25
			syn-HT	35									
4,7-dimethyl	β	75	anti-HH	94	1:0.96	2:2	200	*d*	0	CH_2Cl_2	96	anti-HT	
	γ	140	syn-HH	57	1:1.72	1:2						syn-HT	
			syn-HT	28									
4,6-dimethyl	β	140	syn-HH	48	1:0.51	2:2	200	*d*	0				
	γ	140	syn-HH	74	1:1.52	1:2							
7-methoxy-4-methyl	β	140	syn-HH	45	1:0.96	2:2	20	syn-HH	80	C_6H_6	72	syn-HT	5
			syn-HT	25				syn-HT	20	CH_3OH	72	anti-HT	10
4-chloro	β	140	*d*	0	1:0.75	1:1	200	anti-HT	25	CH_2Cl_2	72	anti-HT	5
	γ	140	*d*	0	1:1.41	1:2		syn-HT					
4-methoxy	β	140	*d*	0	1:0.81	1:1	200	*d*	0	H_2O	20	anti-HT	65
6-chloro-4-methyl	β		*e*				140	syn-HH	50				
	γ		*e*										

[a] From NMR analyses. [b] Based upon NMR and photochemical results; see text for explanation. [c] Results taken from ref 13; [coumarin] ≃ 10^{-2}–10^{-1} M; aerated samples irradiated through Pyrex. [d] No dimers detected. [e] No solid complex isolated.

straints upon the direction of substrate inclusion in solid complexes.

Several varieties of complexes with cyclodextrins have been identified. These include 1G:1H,[3] 2G:1H,[16] and 2G:2H[7] (where G is the guest or substrate molecule and H is the host or CD). Recent studies have shown that molecular orientations within even 1G:1H complexes can be very complicated.[17,18] In fact, each substrate–CD system should be studied in detail to determine whether the complex is a discrete entity or an average of several orientations and stoichiometries. Several unimolecular photochemical reactions of guests in CD complexes have been examined in solution to address these questions.[2]

The distribution of coumarin photodimers in solution depends upon solvent polarity and the multiplicity of the excited state molecule undergoing reaction.[14,19,20] In polar solvents, the dominant isomers are syn- and anti-HH. The anti-HH is formed in a triplet-state reaction and syn-HH is derived mainly from singlet-state dimerizations. The minor solution-phase dimers, syn-HT and anti-HT, form in singlet and triplet reactions, respectively. Although the multiplicity of the excited states of the coumarins employed in our solid-state studies must play an important role in determining the *efficiency* of the photodimerizations, we believe that it influences the *types* of photodimers formed to a much smaller extent; regardless, we have no direct knowledge of the excited states which are involved. In spite of this, the photoproduct distributions can be a useful probe of the structures of their precursor solid CD complexes provided the nature of the

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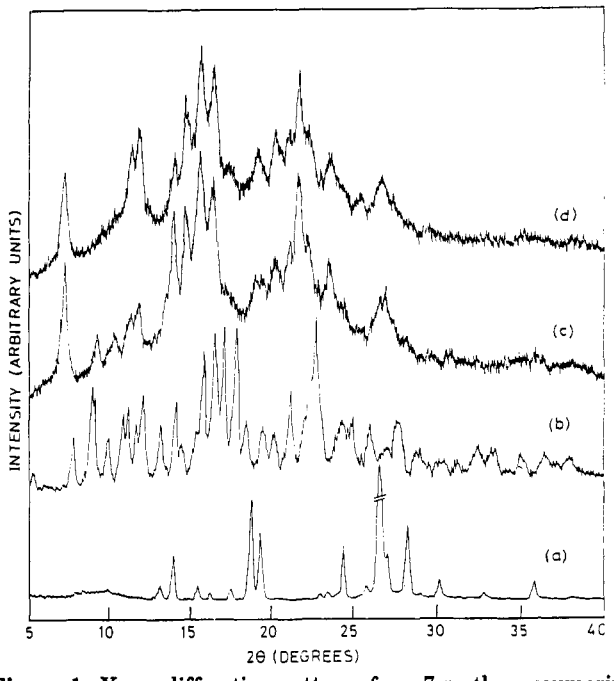

Figure 1. X-ray diffraction patterns from 7-methoxycoumarin (a), γ-cyclodextrin (b), and the 7-methoxycoumarin/γ-CD complex before (c) and after 144 h (d) of irradiation.

photodimers reflects the orientations of the coumarins in the cyclodextrin toruses. Since the mobility of coumarin molecules in the torus of a solid CD complex should be very limited during their excited state lifetimes, we believe that this crucial assumption is valid.

Results

Coumarin and the eight derivatives investigated by us (Scheme I) may, in principle, form as many as four cis-fused dimers: syn head-to-head (syn-HH), syn head-to-tail (syn-HT), anti head-to-head (anti-HH), and anti head-to-tail (anti-HT). Table I summarizes their photochemical behavior in solution,[13] in neat solid phases,[14,15] and in solid complexes with β- and γ-cyclodextrins. Yields of photodimers were calculated from high-performance liquid chromatograms assuming that no other reactions contribute to the loss of the coumarins (see Experimental Section). Since irradiations were conducted under similar but not directly comparable conditions, the combination of percent yields and irradiation times in Table I should be considered as approximate measures of reaction efficiencies. Formation of solid inclusion complexes between the coumarin derivatives and β- or γ-cyclodextrin was inferred from X-ray powder diffractograms that could not be modeled as a weighted sum of the separate diffractograms from the neat coumarin and cyclodextrin. An example of the diffractograms for 7-methylcoumarin, γ-CD, and their solid complex before and after 6 days of irradiation is displayed in Figure 1. Although coumarin in its solid state has been reported to be stable to UV radiation,[19] careful experiments conducted in Bangalore reveal that it forms three photodimers. The formation of the three photodimers must be a result of reactions occurring at crystal defect sites since the crystal packing is unfavorable for the observed reactivity in a topochemical fashion.[21] Irradiation in water or methanol yields two different photodimers in low yields.[13] However, solid β-CD inclusion complexes of coumarin form a single photodimer upon irradiation. Single-crystal X-ray analysis confirms the dimer to be syn-HH;[22] see Experimental Section for data.

From these results, it is clear that the environment of the coumarins in which they are irradiated is a major factor in both the efficiency and stereochemistry of their photodimerizations. This is demonstrated clearly by the stereochemical differences in photodimers obtained upon irradiation of β- and γ-CD complexes or upon drastic changes in the course of photochemistry which can attend subtle substituent modifications in one type of cyclodextrin complex.

No precipitated complexes could be isolated from solutions of 6-chloro-4-methylcoumarins containing either β- or γ-CD (due, possibly, to a low association constant with the former and a very "loose fit" with the latter). Irradiation of this coumarin in its solid state yielded the syn-HH photodimer. Another heterodisubstituted coumarin, the 7-methoxy-4-methyl derivative, formed solid complexes with β-CD which gave respectable yields of syn-HH and syn-HT dimers. The same two dimers are obtained upon irradiation of neat crystals of 7-methoxy-4-methylcoumarin although topological arguments (based upon one of its cell constants being short, 3.99 Å[23]) would predict that only the syn head-to-head dimer should be formed. Apparently, the syn-HT dimer forms at defect sites created during formation of the syn-HH dimer since the HH/HT ratio of dimers decreases with greater irradiation time.

The guest–host stoichiometries of the solid complexes were deduced by dissolving them in DMSO-d_6 and integrating their ^{1}H NMR signals from the C1 proton of cyclodextrins (having a distinct chemical shift near δ 5.0) and the aromatic protons of the coumarins. From these results and, especially, the stereochemistry and appearance of photoproducts, it was ascertained that the 7-methoxy and 4,7-dimethyl derivatives form at least two types of 2:1 G–H solid complexes with γ-CD.

To probe the possibility that photodimerization may induce changes in the crystallinity of the complexes, powder diffractograms of the 7-methylcoumarin–γ-CD complexes were recorded after various periods of irradiation. They showed that the reaction proceeds from one crystalline state to another without the complex becoming amorphous. Diffractograms before irradiation and after 6 days of irradiation are shown in Figure 1c and d.

Discussion

Characterization of Photodimers. Configurational assignment of the dimers is based primarily on ^{1}H NMR spectral data. The chemical shifts and splitting patterns of the cyclobutyl protons of the four coumarin photodimers have been reported;[13] they have distinct splitting patterns. The analogous dimers from substituted coumarins could be clearly associated with the ^{1}H NMR resonances of one of them. Usually, analytical samples of the individual components of dimer mixtures could be isolated by preparative thin-layer chromatography.

Cyclobutyl protons of syn dimers usually resonate >0.1 ppm downfield from the protons of their anti isomers[13] due to diamagnetic anisotropic shielding effects of the carbonyl and phenyl groups. Cyclobutyl protons of the 7-methylcoumarin dimer and one of the two 7-methoxycoumarin

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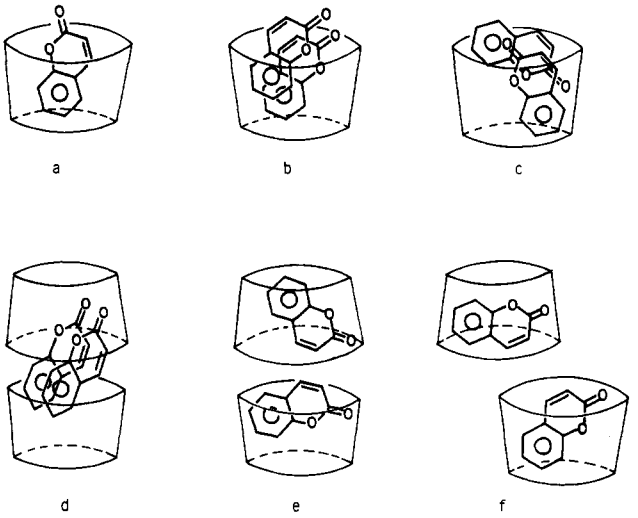

Figure 2. Models depicting possible guest locations and orientations within 1G:1H (a), 2G:1H (b, c), and 2G:2H complexes (d–f). See text for explanations.

dimers from γ-CD complexes exhibited resonances completely analogous to those of the syn-HH dimer of coumarin:[13] each possesses two sets of resonances (integrating for four protons) which are centered at δ 4.1 and 4.2. The ^{1}H NMR spectrum of the second dimer from irradiation of the 7-methoxycoumarin/γ-CD complex was the same as that of the dimer obtained from the neat solid and known from X-ray crystallographic determination to be syn-HT.[24] The H_5, H_6, and H_8 aromatic protons of this dimer make an AMX pattern which is upfield with respect to the analogous proton resonances in the monomer. The very strong shielding effect on H_8 of the dimer (>0.6 ppm) is reasonable only in the syn-HT configuration.[13c,d]

The anti dimer of 7-methoxy-4-methylcoumarin and 6-chloro-4-methylcoumarin (isolated from irradiations of methanolic solutions) are known to have cyclobutyl proton resonances near δ 3.4 and a methyl singlet at δ 1.2;[13a] the corresponding resonances of the syn dimers occur near δ 3.6 and 1.7, respectively. Analogous shielding arguments to those above can accommodate these changes. On the basis of these considerations, the configurations of the photodimers from 4,6-dimethylcoumarin and 7-methoxy-4-methylcoumarin have been assigned as indicated in Table I.

The ^{1}H NMR spectrum of the dimer from irradiation of the 4,7-dimethylcoumarin–β-CD complex corresponds to the spectrum of neither the syn-HT nor the anti-HT dimer.[13] By a process of elimination and based upon the chemical shift of its methyl and cyclobutyl protons, the dimer is assigned the anti-HH configuration. Dimers from irradiation of the γ-CD complex gave ^{1}H NMR spectra which correspond to the known isomers.[13]

Packing Considerations in CD Complexes. Space-filling molecular models (Corey–Pauling–Koltun) indicate that the cavity of a γ-CD can accommodate two coumarin molecules. If oriented appropriately, such complexes can lead to efficient dimer formation upon irradiation. Association between 1G:1H complexes can also lead to coumarin photodimerization: in solution, some 1G:1H complexes have been shown to self-associate at high concentrations, allowing photodimerization of the guest molecules;[7] we expect that only those solid 1G:1H complexes which associate so that the secondary hydroxyl groups of adjacent CD molecules are facing each other as shown in Figure 2d–f will yield photodimers since the smaller opening of even γ-CD (~7.5 Å in diameter[5]) would allow two coumarin molecules to fit through simultaneously only with difficulty.

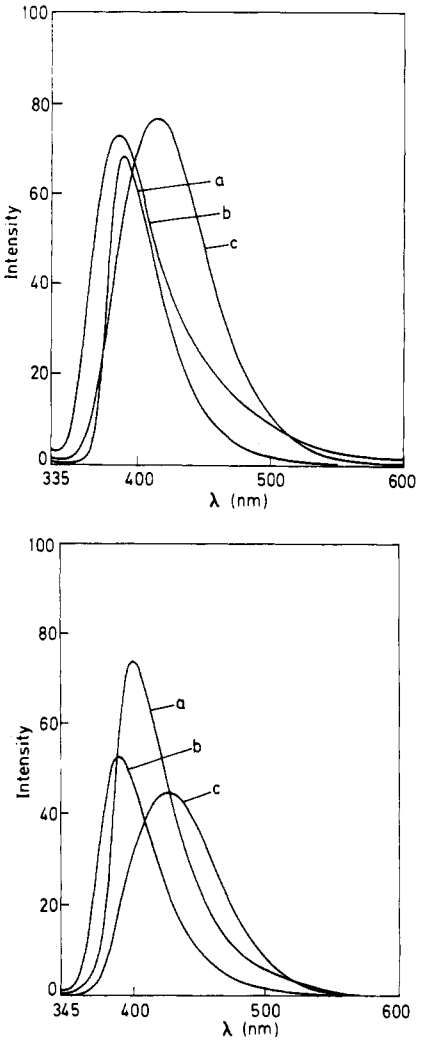

Figure 3. Solid-state fluorescence spectra from 7-methylcoumarin (top; λ_{ex} = 320 nm) and 7-methoxycoumarin (bottom; λ_{ex} = 330 nm): (a) neat coumarin; (b) β-CD complex; (c) γ-CD complex. All intensities are relative.

We have used an operational definition to distinguish 1G:1H and 2G:2H complexes since they cannot be differentiated by our NMR analyses. The assumption is that solid complexes with equal molecular quantities of coumarin and cyclodextrin are 1:1 if no photodimer is formed and 2:2 if photodimer is observed. It should be recognized that in some cases—when steric factors preclude the double bonds of coumarins in 2G:2H complexes from attaining an appropriate orientation and proximity to allow dimerization—this definition will lead to an incorrect conclusion. With this caveat in mind, the combination of NMR and photochemical results permit the stoichiometries listed in Table I for the complexes between coumarins and cyclodextrins to be assigned.

Only in the case of coumarin and β-CD was it not possible to determine precisely the nature of the solid complex. The high solubility of coumarin in water made isolation of the true complex difficult. As the crude solid was washed with aliquots of water to remove occluded β-CD, some coumarin was dissolved also; the stoichiometry of this complex varied with the amount of water used to wash it.

Complexes of 1G:1H Type. From the lack of photodimers derived from their irradiation, the β-CD complexes

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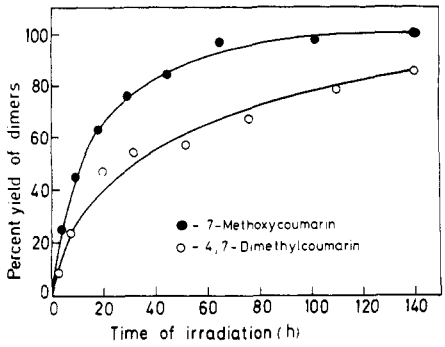

Figure 4. Percent yield of dimers versus irradiation time for two coumarin/γ-CD complexes.

with 7-methylcoumarin, 7-methoxycoumarin, 4-chlorocoumarin, and 4-methoxycoumarin are inferred to be 1G:1H (Figure 2a). Interestingly, the intensity maxima of their fluorescence spectra match those of the neat solids.

Complexes of 2G:1H Type. As shown in Figure 3, the emission maxima from 7-substituted coumarin complexes with γ-CD appear 25–30 nm to the red of the maxima detected from the neat solids or from their complexes with β-CD. Similar shifts are not observed from 4,6- and 4,7-dimethylcoumarins. Thus, the shifts may be due to water molecules (occupying excess free volume in the cavity) which hydrogen-bond to the monosubstituted coumarin guests (resulting in an environment which is of locally high polarity[24]) or to the 4-methyl groups which make the disubstituted coumarins less amenable to facile inclusion in a torus. Regardless of the source of the shifts, they may be analytically and synthetically useful if found to be present in a larger sampling of complexes.

Irradiation of the 7-methoxycoumarin/γ-CD or 4,7-dimethylcoumarin/γ-CD complex yielded two photodimers. The ratios of the dimers remained constant throughout the irradiation periods (i.e., up to the percent conversions listed in Table I) in spite of the *rate* of conversion changing with irradiation time (Figure 4). Initially, the rate of conversion to dimer from either complex was very rapid; at longer irradiation times, the rate of conversion slowed drastically as the concentration of coumarin molecules was depleted. We interpret the lack of change in the dimer ratios to an ability of neighboring coumarins within a γ-CD torus to change their orientations relative to each other fairly rapidly. Alternatively, the quantum efficiencies for photodimerization from both predimer orientations may be equal, and the coumarins remain frozen in their orientations established at the moment of complex precipitation. However, we consider the probability of the quantum yields for syn-HH and syn-HT dimer formation being equal as being improbable. If they were, solution-phase irradiations of 7-methoxycoumarin or 4,7-dimethylcoumarin should have yielded equal amounts of the syn-HH and syn-HT dimers. Clearly, they do not. The ability of coumarin molecules to reorient themselves within a γ-CD torus must be very dependent upon their substituent types and locations. Both 7-methylcoumarin/γ-CD and 4,6-dimethylcoumarin/γ-CD complexes yield only one photodimer (syn-HH). A possible arrangement of these coumarins in a γ-CD torus is shown in Figure 2b.

Complexes of 2G:2H Type. From NMR analyses, a 1/1 ratio of components is indicated for β-CD complexes with 4,6-dimethylcoumarin, 4,7-dimethylcoumarin, and 7-methoxy-4-methylcoumarin. However, the high yields of dimers isolated from irradiation of these complexes, in particular those with the latter two coumarins, lead us to conclude that their stoichiometry is 2G:2H. Remarkably, the 4,7-dimethylcoumarin/β-CD complex yields a sterically demanding anti-HH dimer; it suggests that a large portion of the 4,7-dimethylcoumarin molecules resides outside the β-CD cavities. This, in turn, should increase orientational flexibility and facilitate high dimer yields. Although irradiation of 4,7-dimethylcoumarin in methylene chloride solution yields both syn and anti dimers, neither is HH. It is tempting to hypothesize from the significantly lower yield of syn-HH dimer that 4,6-dimethylcoumarin penetrates more deeply into the β-CD torus, restricting rotational motion of the reactants to achieve favorable juxtaposition. On the basis of the stereochemistries of their photodimers, we infer that the 4,6- and 4,7-dimethylcoumarins are oriented in the β-CD complexes as shown in Figures 2d and 2e, with CDs juxtaposed as head–head channels or that the halves of the 4,7-dimethylcoumarin-/β-CD complex are offset from one another as shown in Figure 2f. Confirmation (or refutation) of these and the other models proposed in Figure 2 must await X-ray or other direct structural analyses.

Conclusions

We have demonstrated that β- and γ-cyclodextrin can form solid complexes with coumarins containing a wide variety of substituents and substitution patterns. The stoichiometry and approximate geometry of the complexes have been inferred from a combination of NMR and photodimer analyses. In several examples, the stereochemistry of the photodimers from cyclodextrin complexes does not correspond to that found upon irradiation of the same coumarins as neat solids or in dilute solutions. Some substituted coumarins which are photochemically inert as neat solids, such as 4,6- and 4,7-dimethylcoumarins and coumarin which behaves nontopochemically, give high yields of photodimers when irradiated as cyclodextrin complexes; others (7-methylcoumarin, 7-methoxycoumarin, and 4-chlorocoumarin), which dimerize readily in their neat solid state, are unreactive when precipitated with β-cyclodextrin due to the enforced isolation of the coumarin molecules in their 1G:1H complexes. Many of the topochemical considerations which apply to the photodimerizations of the neat solids[15] probably apply to neighboring pairs of coumarins held in cyclodextrin toruses. However, the details of these effects and the possible influences of hydrogen bonding from the cyclodextrins to the coumarins must await more detailed structural elucidation of the complexes. To this end, our efforts continue to produce single crystals of coumarin–cyclodextrin complexes suitable for X-ray structural analysis. Regardless of the outcome of those endeavors, the results provided thus far demonstrate that cyclodextrin complexes may be employed to produce high yields of coumarin dimers whose stereochemistry is sometimes different from that found in photodimers synethesized via other techniques.

Experimental Section

Materials. β-Cyclodextrin (Sigma) was recrystallized from doubly distilled water, and γ-cyclodextrin (Sigma) was used as received. Coumarin (Aldrich) was recrystallized from hot water: mp 68–69 °C. The substituted coumarins were synthesized and purified according to reported procedures (Table II). In those cases for which two photodimers were formed and both could not be isolated in analytical purity, their molar extinction coefficients were assumed to be equal for the purposes of calculating the yields reported in Table I. All organic solvents (>99% pure) were distilled prior to use. Double-distilled water was used throughout.

Instrumentation. UV spectra were recorded at 25 °C with a Shimadzu UV-180 double-beam spectrophotometer. NMR spectra were recorded on a Jeol-90Q FT spectrometer. HPLC analyses were performed on a Shimadzu two-pump system with

Table II. Melting Points and Molar Extinction Coefficients of Coumarins Examined

coumarin	melting points (°C) obsvd	lit.	ref	ϵ_{260} (methanol) monomer	dimer
unsubstituted	68–69	68–69	27a	7200	4000 (syn-HH)
7-methyl	128	127	27a	3900	2200 (syn-HH)
7-methoxy	117–118	119–120	13c	5750	3350 (syn-HT)
4,7-dimethyl	130–131	132	27b	4160	3320 (anti-HH)
4,6-dimethyl	146–147	148	27b	5670	3300 (syn-HH)
7-methoxy-4-methyl	161–162		13c, 27e	1750	3690 (syn-HT)
4-chloro	90–91	91	27g	1370[a]	
4-methoxy	121–122	123	27d	1320[a]	
6-chloro-4-methyl	182–183	184–185	27f		

[a] 280 nm.

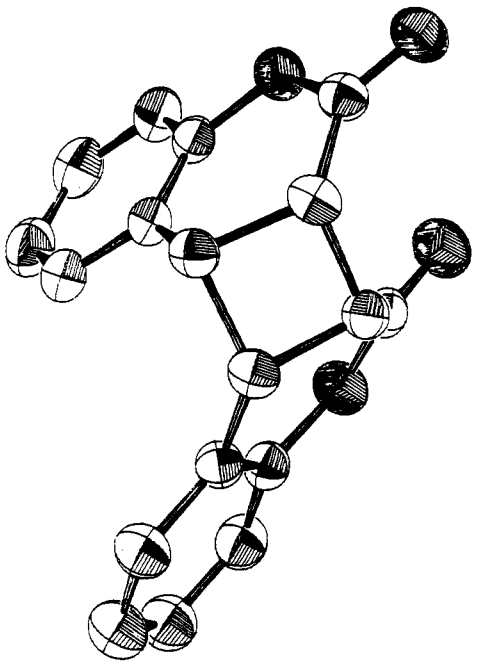

Figure 5. Perspective ORTEP drawing of syn-HH dimer of coumarin. Protons are not included, and oxygen atoms are shaded.

a Shimpack reversed-phase CLC ODS column (6 × 150 mm, 5 μm) and a UV (260 nm) detector. Methanol–water linear gradient elution was employed. Fluorescence spectra were recorded with a RF 540 Shimadzu fluorometer equipped with a DR-3 data recorder. Fluorescence from solid (powdered) samples was collected front-face. Melting points were determined on a Reichert Kofler micro heating stage with a microscope, and the values are uncorrected.

Preparation of Complexes. A methanolic solution containing 30 mg of coumarin was added to 1 molar equiv of cyclodextrin as a saturated solution in water. The methanol was slowly evaporated on a steam bath for 2 h and the remaining mixture stirred at ambient room temperature for 20 h. The precipitate was filtered and washed with 2–3 mL of cold ether and later with 3 mL of cold water to remove uncomplexed substrate and cyclodextrin, respectively, and dried in an oven at 50 °C for 10 h.

Irradiation Procedures. Irradiation ($\lambda > 300$ nm; Pyrex filter) of the powdered neat solids and complexes in Pyrex-covered Petri dishes in air at ambient temperatures was accomplished in a Rayonet reactor. The powder particles were stirred periodically to expose different surfaces directly to the radiation. After irradiation, the complexes were dissolved in water and extracted with chloroform. The product mixture, obtained after evaporation of the chloroform, was analyzed by ^{1}H NMR.

Yields of Photodimers. Product yields from irradiation of solid CD complexes were calculated from HPLC analyses. In a typical experiment, 3 mg of the irradiated solid complex was suspended in 500 μL of methanol, and 100 μL of *tert*-butyl alcohol was added. The mixture was shaken vigorously. An aliquot of the supernatant liquid was injected onto the HPLC column. The peaks in the chromatogram were identified by comparison of their retention volumes with those of authentic samples (separated by preparative thin-layer chromatography and characterized by ^{1}H NMR). From the areas of the peaks corresponding to monomer and dimer in the chromatogram, and from their molar extinction coefficients at the detection wavelength ($\lambda = 260$ nm), yields could be calculated.

The yields from irradiations of neat solids are based on integration ratios of olefinic and cyclobutyl protons in ^{1}H NMR spectra of the irradiated samples dissolved in DMSO-d_6.

X-ray Crystallographic Data for the Coumarin Dimer. Single crystals suitable for X-ray crystallographic study were obtained from chloroform solution by slow evaporation. The crystals were monoclinic, space group $P21/C$: $a = 10.481$ (1) Å, $b = 11.785$ (1) Å, $c = 10.972$ (1) Å; $\beta = 91.10$ (1)°. The calculated density is 1.43 g/cm^3 for $Z = 4$. The data were collected on an Enraf Nonius CAD4 diffractometer with Mo Kα ($\lambda = 0.7107$ Å) radiation using the $\omega/2\theta$ scan mode up to a θ limit of $\theta \leq 25°$. 2269 reflections were significant [$|F_o| \geq 3\sigma(|F_o|)$]. The structure was solved using the direct-method program MULTAN87.[25] The refinement of positional and anisotropic thermal parameters of non-hydrogens and positional and thermal parameters of hydrogens with a full-matrix least-squares method using SHELX 76[26] converged to final $R = 0.052$ and $Rw = 0.049$, where $R = \sigma$(del)/σ(F(obs)) and $Rw = \sigma$(del*sqrt(weight))/$\sigma(F$(obs)*sqrt(weight)). The weighting function used is given by the formula $w = k/(\sigma^2(F) + gF^2)$ with $k = 3.6898$ and $g = 0.000\,161$. The final difference Fourier map was featureless with $\Delta\rho_{max} = 0.16$ and $\Delta\rho_{min} = -0.17$ e/Å^3. Figure 5 shows the syn-HH configuration of the dimer in conformity with the assignment based on NMR analysis.

X-ray diffractograms of a powder aliquot of the 7-methylcoumarin/γ-CD complex were recorded on a Jeol JDX-8P diffractometer using Cu Kα radiation ($\lambda = 1.542$ Å).

Acknowledgment. We thank Prof. P. Balaram and Mr. R. Gurunath of the Molecular Biophysics Unit of I.I.Sc., Bangalore, for their generous help in performing the HPLC analyses. Also, we thank the Council of Scientific and Industrial Research and University Grants Commission of India for financial assistance. R.G.W. wishes to express his gratitude to the Fulbright Foundation for a fellowship from the Indo–U.S. Subcommission on Education and Culture which supported his sabbatical stay in India.

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