Table I. ^1H NMR Spectral Data of 1,3-Butadiene-1,1,4-tricarboxylic Acids and Esters[a]

	chemical shift, δ					coupling constants, Hz		
compd[b]	$COOCH_3$	COOH	H2	H3	H4	$^3J_{2,3}$	$^3J_{3,4}$	$^4J_{2,4}$
1a	3.78	11.4	8.68	7.32	6.26	11.5	11.5	−1.0
1b[c]	3.78, 3.82, 3.86		8.53	6.97	6.08	11.5	11.5	−1.0
1c[d]			7.35	6.40	6.05	11.5	11.5	*e*
2a	3.77	11.7	7.65	7.90	6.59	11.8	15.6	−0.65
2b	3.79, 3.82, 3.90		7.49	7.55	6.55	12.1	15.5	−0.65
2c[f]		12.1	7.38	7.42	6.48	11.8	15.7	−0.8

[a] Recorded at 60 MHz. The spectra of **2a–c** were solved by ABX treatment and the solutions confirmed by computer simulation of the patterns. [b] Ca. 5%, in $(CD_3)_2CO$ unless otherwise stated. [c] In $CDCl_3$. [d] In D_2O/NaOD, generated in situ from **1a**. [e] No coupling observed. [f] In $(CD_3)_2SO$.

Table II. Electronic Spectra of 1,3-Butadiene-1,1,4-tricarboxylic Acids and Esters

compd	solvent	λ_{max}, nm	ϵ_{max}, L mol^{-1} cm^{-1}
1a	0.1 M HCl	269	20 000
1a	0.1 M phosphate buffer, pH 7	280	17 500
1b	CH_3OH	265	20 000
1c[a]	0.1 M NaOH	271	17 100
2a	0.1 M HCl	271	25 000
2b	CH_3OH	266	25 000
2c	0.1 M HCl	270	25 000
2c	0.1 M NaOH	276	21 700

[a] Generated in situ from **1a**.

ether–petroleum ether); IR (KBr) 3300–2500 (s), 1755 (s), 1730–1700 (s), 1600 (m) cm^{-1}; ^1H NMR $[(CD_3)_2CO]$ δ 3.85 (Hα), 5.64 (H2), 6.28 (H4), 7.89 (H3), 11.4 (COOH) ($^3J_{2,\alpha}$ = 8 Hz, $^3J_{2,3}$ = 1.6 Hz, $^3J_{3,4}$ = 6 Hz, $^4J_{2,4}$ = 2.1 Hz); ^1H NMR (D_2O) δ 5.80 (H2), 6.37 (H4), 7.95 (H3), Hα exchanged for deuterium ($^3J_{2,3}$ = 1.5 Hz, $^3J_{3,4}$ = 6 Hz, $^4J_{2,4}$ = 2 Hz).[13]

Anal. Calcd for $C_7H_6O_6$: C, 45.17; H, 3.25. Found: C, 44.96; H, 3.23.

Equilibrium between 1c and 3. Solutions of the trisodium salt of **1c**, prepared by hydrolysis of **1a** in 0.1 M NaOH and dilution with water, were added to 0.2 M citrate–phosphate buffers to give solutions with λ_{max} 271 nm (ϵ_{max} 14000) (pH 7.0), 272 (6000) (pH 6.0), and 274 (920) (pH 5.0). Identical ultraviolet spectra were obtained by adding a solution of **3** in 0.01 M HCl to the same buffers. Approximate equilibrium constants (see text) were calculated by assuming the absorptivity of anions of **1c** present in the equilibrium mixtures to be identical with that of the trianion in 0.1 M NaOH (Table II).

Acidification of the above equilibrium mixtures with 3 M HCl resulted in formation of **3** and thus in complete loss of ultraviolet absorption.[8] The lactonization could also be observed directly by ^1H NMR spectroscopy in D_2O solutions. Rates of approach to equilibrium at pH 5.2 and 6.0 were measured by following changes of ultraviolet absorption at 272 nm after addition of solutions of the trisodium salt of **1c** in 0.01 M NaOH or of **3** in 0.01 M HCl to 0.2 M citrate–phosphate buffers at 25 °C.

Decarboxylation of 3. The lactone **3** (0.2 g) was dissolved in 5 mL of water, the pH was adjusted to ca. 3 with 0.1 M NaOH, and the solution was boiled several minutes, acidified with 2 M HCl, saturated with NaCl, and extracted with several 20-mL portions of ethyl acetate to give 0.1 g (65%) of **4a**; mp 188–191 °C (after recrystallization from ether) (lit.[9] mp 190–191 °C); UV (0.1 M HCl) λ_{max} 262 nm (lit.[14] 263 nm in 1 M acid); IR spectrum as reported;[15] ^1H NMR $[(CD_3)_2CO]$ δ 6.10 (H5), 6.29 (H2), 6.90 (H4), 8.52 (H3), 11.5 (COOH) ($^3J_{2,3}$ = 15.5 Hz, $^3J_{3,4}$ = 11.5 Hz, $^3J_{4,5}$ = 11.5 Hz).[16] When a similar decarboxylation was performed in D_2O, the ^1H NMR spectrum of the solution corresponded to (2*E*,4*Z*)-2,4-hexadiene-2-*d*-dioic acid (**4b**): δ 6.10 (H5), 6.67 (H4), 7.98 (H3) ($^3J_{3,4}$ = 11.5 Hz, $^3J_{4,5}$ = 11.5 Hz; the signal of H3 broadened owing to coupling with deuterium).

Heating solutions of **3** at pH 5–6, where some ionized **1c** present at equilibrium gave rise to ultraviolet absorption at 272–274 nm, caused the maximum to shift to 265–267 nm with an increase of intensity as a result of formation af **4a**. Acidification of these solutions with 2 M HCl caused a further shift to λ_{max} 262 nm as the open-chain anions were removed by conversion to **3**, and the pure absorption of **4a** remained. Prolonged heating of weakly acidic solutions of **4a** caused loss of ultraviolet absorption, presumably owing to formation of **6**.

Solutions of **3** in 0.2 M citrate–phosphate buffers were heated at 100 °C during 3 min and acidified, and the amounts of **4a** formed were estimated by comparison of intensites of the UV absorption maxima at 262 nm. The amounts of decarboxylation product generated at pH 1 (0.1 M HCl), pH 4, and pH 6 were respectively about $^1/_6$, $^1/_2$, and $^1/_5$ of the amount generated at pH 3.

Heating neat **3** a few degrees above its melting point gave 2,5-dihydro-5-oxo-2-furanacetic acid (**6**); mp 108–110 °C (after recrystallization from ether–petroleum ether) (lit.[17] mp 110.5–111.5 °C); IR (KBr) 3300–2500 (m), 1790 (s), 1760 (s), 1700 (s), 1600 (w) cm^{-1}; ^1H NMR $[(CD_3)_2CO]$ δ 2.69 (HαA), 2.87 (HαB), 5.44 (H2), 6.16 (H4), 7.79 (H3) ($^2J_{\alpha A,\alpha B}$ = 16.5 Hz, $^3J_{2,\alpha A}$ = 7.5 Hz, $^3J_{2,\alpha B}$ = 5.8 Hz, $^3J_{2,3}$ = 1.5 Hz, $^3J_{3,4}$ = 5.5 Hz, $^4J_{2,4}$ = 2.0 Hz).[13,18]

Acknowledgment. This work was supported in part by a fellowship from the Danish Natural Science Research Council to J.W.J.

Registry No. 1a, 81158-33-0; **1b**, 82639-54-1; **1c**, 56549-11-2; **1c** trisodium salt, 82639-55-2; **2a**, 82639-56-3; **2b**, 82639-57-4; **2c**, 82639-58-5; **3**, 82639-59-6; **4a**, 1119-73-9; **4b**, 82639-60-9; **5**, 6666-46-2.

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Photodimerization of Coumarin in Aqueous and Micellar Media

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The photochemical and photophysical processes of many organic compounds are a function of the environment in which they are present. In this connection we have chosen to investigate the environmental perturbations on the

Table I. Photodimerization of Coumarin in Various Media

no.	medium	[coumarin], M	product dimer	quantum yield[a]	yield of dimer,[b] %
1	methanol[c]	0.02	anti head-head	$<10^{-5}$	~2
2	benzene[c]	0.02	anti head-head	$<10^{-5}$	~2
3	water[c]	0.02	syn head-head	2.0×10^{-3}	20
4	SDS (0.02 M)[c]	0.02	syn head-head	2.0×10^{-3}	21
5	CTAB (0.02 M)[c]	0.02	syn head-head	0.3×10^{-3}	3
6	Triton X-100 (0.02 M)[c]	0.02	syn head-head	1.0×10^{-3}	11
7	water[d]	0.008	syn head-head	0.8×10^{-3}	6
8	water-NaCl (1 M)[d]	0.008	syn head-head	1.7×10^{-3}	13
9	water-KCl (1 M)[d]	0.008	syn head-head	1.7×10^{-3}	13
10	water-LiCl (1 M)[d]	0.008	syn head-head	2.0×10^{-3}	15

[a] The quantum yield was monitered by following the disappearance of coumarin by its UV absorption within 10% conversion. The disappearance of coumarin and formation of the syn head-head dimer agreed within ±10%, the error limit was ±20%. [b] The dimer yield was measured gravimetrically; the error limit was ±5%. [c] All these six irradiations were conducted under comparable conditions. Samples were irradiated by using a 450-W medium-pressure mercury lamp for 22 h. [d] All these four irradiations were conducted under comparable conditions; irradiation for 20 h.

photodimerization of coumarin,[1] and the results of our study in aqueous and micellar media are presented in this paper. Coumarin has historically been the subject of intense photochemical and spectroscopic interest, mainly as a consequence of its importance in biological systems. Coumarin has been chosen for our investigation as its fascinating photochemical behavior has been fairly well explored,[2] and therefore the environmental influence, which is the subject of our concern, would be easily understandable.

Results and Discussion

Photodimerization of Coumarin in Aqueous Solution. A distinct property observed during this study is the ready dimerization of coumarin to a single dimer (syn head-head) in aqueous solutions in contrast to the poor efficiency obtained in methanol and benzene.[3] This photoreaction was noted to differ very significantly in the aqueous medium, the quantum yield being $\sim 10^{-3}$ (0.01 M) while that in methanol and benzene is $<10^{-5}$ (0.02 M) (Table I). Although the anti head-head dimer, the major product of dimerization (at low concentrations) in both polar and nonpolar solvents, has been reported, the syn head-head dimer obtained in our studies was very much unexpected, especially at the low concentrations used. Yet another interesting feature to come to light was the dimer product crystallizing out of the solution as the photoreaction proceeded, thus simplifying the isolation procedures. The enhanced reactivity and selectivity in the dimerization might be caused either by the polarity of the medium or by aggregation of coumarin molecules in water due to hydrophobic interactions.[4]

In line with the general understanding of coumarin photodimerization,[2] we suppose that the syn head-head dimer in water originates from the lowest excited singlet state (S_1) of coumarin. Assuming the lifetime of S_1 in water to be the same as that estimated in organic solvents ($\sim 10^{-12}$ s),[5] the quantum yield of dimerization in aqueous medium (10^{-3}) would require a collisional rate of 10^{11} M^{-1} s^{-1} which exceeds the diffusional limit, making it physically impossible. This anomaly can be overcome if the excited state (S_1) of coumarin in water had a longer lifetime or if excitation and dimerization of preformed ground-state complexes took place. Enhanced dimerization in aqueous medium due to ground-state aggregation has already been established during photodimerization of dimethylthymine and tetramethyluracil.[6] Failure to observe any deviation from Beer's law in the absorption spectrum of coumarin (10^{-3}–10^{-2} M) offers no substantial support in favor of the

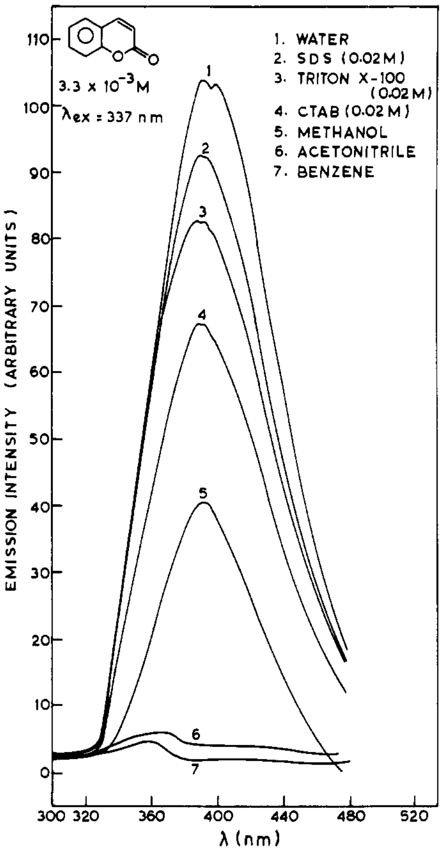

Figure 1. Fluorescence spectra of coumarin in water, organic solvents, and micellar media.

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[3] Photodimerization of coumarin has been reported to exhibit interesting features;[2] product distribution is both solvent and concentration dependent. The syn head-head dimer is the preferred product in polar media whereas the anti dimer is formed in nonpolar solvents. The syn dimer is reported to proceed via a singlet precursor whereas the anti dimer is reported to proceed via the triplet state. Dimerization of coumarin readily occurs at higher concentrations (0.3 M) to give the syn dimer in methanol and the anti dimer in benzene.

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Table II. Photodimerization of Coumarin in SDS under Various Conditions

no.	medium	[coumarin], M	quantum yield[a]	% yield of syn head-head[b] dimer
1	SDS (0.02 M)[c]	0.02	2×10^{-3}	17.0
2	SDS (0.02 M)[c] NaCl (0.95 M)	0.02	2×10^{-3}	18.0
3	SDS (0.02 M)[c] benzophenone (0.01 M)	0.02	0.2×10^{-3}	~1.5
4	SDS (0.02 M)[c] benzophenone (0.01 M) NaCl (0.95 M)	0.02	0.2×10^{-3}	~2.0
5	SDS (0.02 M)[d]	0.033	4×10^{-3}	20.0
6	SDS (0.03 M)[d]	0.033	3.6×10^{-3}	18.0
7	SDS (0.04 M)[d]	0.033	3×10^{-3}	15.0
8	SDS (0.05 M)[d]	0.033	2.5×10^{-3}	13.0

[a] The quantum yield was monitered by following the coumarin disappearance by its UV absorption; the error limit was ±20%. [b] The dimer yield was measured gravimetrically; the error limit was ± 5%. [c] All four of these irradiations were conducted under comparable conditions; irradiation for 18 h. [d] All four of these irradiations were conducted under comparable conditions; irradiation for 22 h.

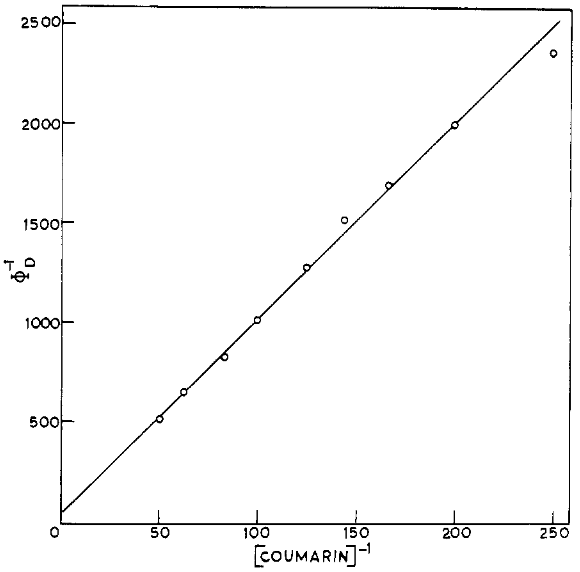
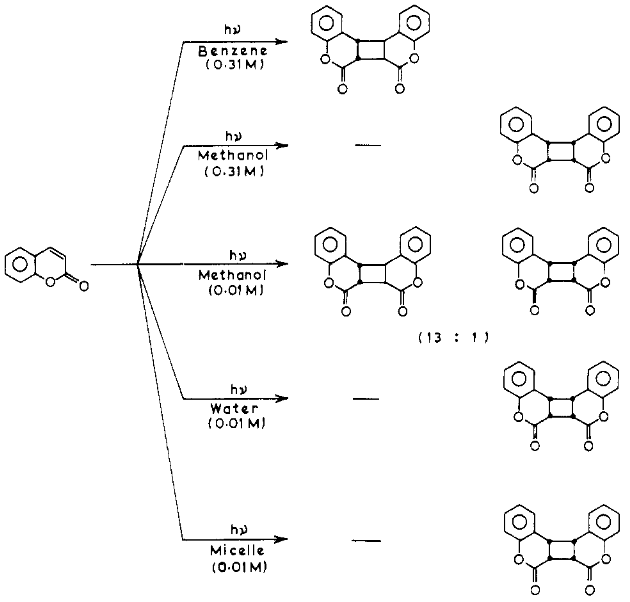


Figure 2. Plot of Φ^{-1} vs. [coumarin]$^{-1}$ for dimerization of coumarin in water.

latter argument. However, to our surprise coumarin exhibited moderate fluorescence in aqueous medium (Figure 1), although no emission was detected in benzene and acetonitrile.[7] Coincidence of the excitation and absorption spectra confirms that the emission corresponds to coumarin. This may be indicative of the longer excited-state lifetime of coumarin in water which enables fluorescence to compete effectively with other deactivating paths from S_1. If this was the case, the enhanced reactivity at lower concentrations in water is easily understood. Changes brought about in the polarity of the medium (compared to organic solvents) alter the lifetime and hence the reactivity. This is in agreement with the results observed on the addition of inorganic salts (Table I). Consistent with this proposition, a linear relationship was obtained between [coumarin]$^{-1}$ and Φ^{-1} (Figure 2). The need to explore the unique influence exerted by water on the reactivity of organic molecules is thus further justified by the results presented above.[11]

Scheme I. Products of Photodimerization of Coumarin in Various Media



Photodimerization of Coumarin in Micellar Medium. Poor solubility of coumarin in water limits photodimerization. We therefore attempted solubilizing coumarin in micelles which are also known to orient organic molecules into the hydrocarbon core.[12] The results of our study are presented in Tables I and II. Dimerization occurred smoothly to yield the syn head–head dimer as the sole product (Scheme I). The formation of this dimer was rather surprising since one would expect coumarin in the hydrocarbon-like interior of the micelle to behave as it does on excitation in nonpolar solvents (yield anti head–head dimer).[2] It might therefore be pictured that the reaction occurs in the aqueous exterior to give the same product that photodimerization of aqueous solution does, the

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(7) The literature with respect to coumarin fluorescence, at room temperature, is inconclusive. Earlier, coumarin has been reported to fluoresce in ethanol at room temperature.[8] Recent attempts to measure coumarin fluorescence at room temperature have been unsuccessful.[9] However, many of the substituted coumarins show intense solvent-dependent fluorescence at room temperature.[10]

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micelle serving as the storage site. Altering the nature of the micelle by using anionic (SDS), cationic (CTAB), and nonionic (Triton X-100) micelles affected the quantum yield of dimerization (Table I). This observation contradicts the above speculation on the reaction site and supports the contention that it occurs in the hydrophobic core of the micelle, changes in which are reflected by the quantum yield variation. The data in Table II showing an inverse relation between SDS concentration and the quantum yield of dimerization can be understood in terms of the variation in the mean occupation number. Furthermore, addition of sodium chloride, having no effect on the quantum yield of dimerization, reveals coumarin to be protected from changes in polarity that occur in the aqueous exterior. Interestingly, the dimer formation was completely abolished by the addition of benzophenone. Although this could occur through a "double energy-transfer process",[8,13] we are unable to provide convincing evidence in favor of this. This quenching can occur only if the dimerizing coumarin and benzophenone were within the micelle.

We conclude that coumarin is incorporated into the micelle and that its reactivity is directed by the micelle. Unexpected formation of the syn head–head dimer, we believe, throws light on the nature of the interior of the micelle. Formation of the syn head–head dimer may be directed by the orientational effect and/or by the polarity within the micelle. As illustrated in Figure 1, coumarin shows moderate fluorescence even in micellar media, thus suggesting that the environment wherein coumarin is present is polar, probably due to the penetration of water. Recently, evidence in favor of such water penetration into the micelle has been accumulating, and the micellar interior is suggested to be polar.[14] On the basis of this model, one would expect the formation of the syn head–head dimer, and indeed it is formed. We suggest that the variation in the quantum yield of dimerization is a reflection of the extent of water penetration into the three micellar systems investigated. Interestingly, the present results which suggest that SDS is more porous than CTAB is consistent with the recent reports.[15] The above decrease in the quantum yield of dimerization from SDS to CTAB is also reflected in the emission intensity of coumarin (Figure 1).

Conclusion

Reactivity and emission intensity of coumarin are enhanced in aqueous and micellar media. The syn head–head dimer is the sole product under these conditions. Selectivity in the formation of the dimer and enhanced reactivity are attributed to the polar environment in which coumarin undergoes dimerization. The variation in the reactivity of coumarin between the three micellar systems investigated is probably a reflection of the extent of water penetration. Interesting results observed in this system call for further investigation in utilizing aqueous and micellar media for chemical reactions.

Experimental Section

Materials. Coumarin (Aldrich) was recrystallized twice from hot doubly distilled water for fluorescence measurements and was used as received for the reaction. All solvents were distilled prior to use. Surfactants CTAB, SDS (Sigma products) were recrystallized twice from ether–methanol mixture and 95% ethanol. Triton X-100 (Sigma) was used as received.

Fluorescence Measurements. Fluorescence spectra were recorded by using Perkin-Elmer spectrofluorimeter (MPF-44 Model). A stock solution of coumarin (3.3×10^{-3} M) in water was prepared; 20 mL of this solution was pipetted out into a set of conical flasks containing known amounts of surfactants and solubilized by stirring overnight. Solutions of coumarin (3.3×10^{-3} M) in methanol, acetonitrile, and benzene were prepared by dissolution of the weighed amounts. Spectral measurements were repeated at least three times by using independent solutions, and the spectra thus obtained are displayed in Figure 1. Emission and excitation spectra were recorded in a routine manner.

Photodimerization of Coumarin. Aqueous and micellar solutions of coumarin were prepared by adding finely powdered coumarin into water and surfactant solutions of known concentrations, respectively, and stirring the solutions for 15–20 h. Salt-saturated surfactant solutions were warmed slightly before addition of coumarin. Stirred solutions were filtered through Whatman filter circles to remove the insoluble particles, if any. Micellar solutions containing benzophenone were prepared in a similar manner.

Irradiations were conducted by using a 450-W medium-pressure mercury lamp contained in a water-cooled Pyrex well. As the irradiation proceeded, dimer crystallized out of the solution. At the end of the irradiation crystals of dimer were collected by filtering the irradiated solution through a sintered crucible (G-3 or G-4). Filtrates of the aqueous reaction mixture were extracted with chloroform while filtrates of surfactant solutions were diluted well below the CMC and extracted with excess ether. The ether extract was found to contain only the unreacted coumarin. Precipitated material was identified to be the syn head–head dimer on the basis of its spectral properties and comparison with an authentic sample: mp 265–267 °C (lit.[7] mp 272–274 °C); IR (Nujol) 1745 cm^{-1} (C=O stretching); NMR ($CDCl_3$) δ 4.15 (m, 4 H), 6.77–7.24 (m, 8 H). The yields presented in Tables I and II correspond to the gravimetric estimation of the dimer after thorough washing and drying in an oven at 110 °C. All irradiations were stopped within 25% conversion (~20 h). The yields of the dimer and the recovered coumarin agreed within 10%. Careful attempts to isolate the anti head–head dimer in aqueous and micellar solutions were unsuccessful. However, control experiments showed that the anti dimer is stable in water and can be extracted with ether. As a control, 200 mg of anti head–head dimer was stirred in 100 mL of water at 35 °C for 24 h, and upon extraction with ether the above dimer was recovered quantitatively.

Quantum yield measurements were done by irradiating (450-W medium-pressure mercury lamp with Corning glass filter, CS-7.60) samples in a merry-go-round style and using potassium ferrioxalate actinometry.[16] The disappearance of the coumarin was followed by its UV absorption. Since dimerization required about 20 h, the light intensity was measured three times at regular intervals, and the average intensity was used for calculation. Since there is a mismatch in the absorption of the actinometer solution and coumarin (under the available filter conditions), the measured quantum yields are subjected to ±20% error. Since the only reaction observed was dimerization (based on the yields of isolated dimer and the recovered coumarin), the quantum yield of coumarin disappearance is taken to be that of dimerization.

Acknowledgment. We sincerely thank Dr. P. Balaram for the kind use of the spectrofluorimeter. K.M. thanks the University Grants Commission, Government of India, for a Senior Research Fellowship.

Registry No. Coumarin, 91-64-5; (α6a*H*,β6b*H*,β12b*H*,α12c*H*)-cyclobuta[1,2-*c*,4,3-c^1]bis[1]benzopyran-6,7-dione, 5248-12-4; (α6a*H*,α6b*H*,α12b*H*,α12c*H*)-cyclobuta[1,2-*c*,4-3-c^1]bis[1]benzopyran-6,7-dione, 5248-11-3; SDS, 151-21-3; CTAB, 57-09-0; Triton X-100, 9002-93-1.

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(13) Although the formation of the syn head–head dimer was arrested in the presence of benzophenone, the expected triplet product anti head-head dimer was not isolated. However, we have noticed that the anti head–head dimer can be extracted from aqueous medium by using chloroform or ether. Therefore, we assume that the anti head-head dimer was not formed during the above irradiation, but the reason for this is not clear.

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