

REACTIVE STATE SELECTIVITY IN PHOTODIMERIZATION THROUGH MICELLAR COUNTER-ION EFFECTS: PHOTODIMERIZATION OF ACENAPHTHYLENES

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Summary

Photodimerization of acenaphthylene and 5,6-dichloroacenaphthylene solubilized in sodium dodecylsulphate (SDS), cetyltrimethylammonium chloride (CTAC), dodecyltrimethylammonium chloride (DTAC), cetyltrimethylammonium bromide (CTAB) and Triton X-100 micelles gives a mixture of *cis* and *trans* dimers. The magnitude of the *cis:trans* ratio is sensitive to the type of micelle used. In CTAB micelles the heavy atom effect of the bromide counter-ions leads to an increased triplet-derived *trans* dimer yield, whereas in micelles with light atom counter-ions (CTAC, DTAC and SDS) the singlet-derived *cis* dimer predominates.

1. Introduction

Previous studies [1 - 5] have shown that the photophysical properties of excited aromatic molecules in aqueous micellar solutions are sensitive to the nature of the counter-ions. The decrease in the fluorescence quantum yield (intensity) of naphthalene [1], anthracene [2], 9-methylantracene, 9,10-dimethylantracene, fluorene, indeno[2,1-*a*]indene, *N*-methyldiphenylamine [3], azulene, ovalene [4] and fluoranthene [5] in cetyltrimethylammonium bromide (CTAB) micelles compared with that in cetyltrimethylammonium chloride (CTAC) micelles has been attributed to the external "heavy atom effect" of the bromide counter-ions. An enhancement in phosphorescence from pyrene [6, 7], naphthalene, biphenyl [8] and carbazole [9] solubilized in sodium dodecylsulphate (SDS) micelles has been achieved by the addition of thallos nitrate to the aqueous micellar solution. It is suggested that thallos ions which serve as "heavy atoms" enhance $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ radiative and radiationless intersystem crossings via intermolecular spin-orbit coupling. A recent study [3] of the external heavy atom effects of counter-ions on excited anthracenes, 9-methylantracene, 9,10-dimethylantracene, fluorene, indeno[2,1-*a*]indene and *N*-methyldiphenylamine in aqueous micellar solutions of CTAC and CTAB has revealed that by changing

the micelle from CTAC to CTAB a decrease in the fluorescence quantum yield is accompanied by an increase in the triplet quantum yields.

These observations suggest that, by using micelles with different counterions, it may be possible to attain selectivity in the reactive state of a photochemical reaction. In an effort to explore the feasibility of this, a study of the photodimerization of acenaphthylene **1** and 5,6-dichloroacenaphthylene **2** (Fig. 1) in micellar media was undertaken and the results of this investigation are presented below.

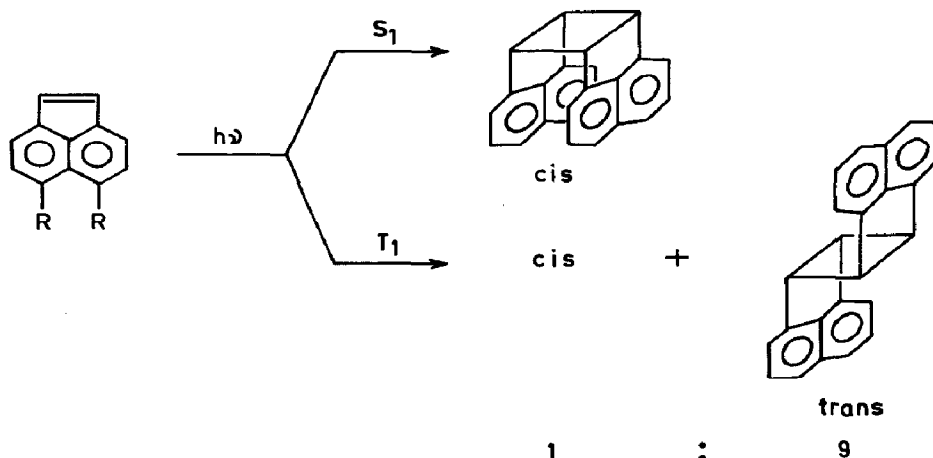


Fig. 1. Photodimerization of acenaphthylene (**1**, R = H) and 5,6-dichloroacenaphthylene (**2**, R = Cl).

2. Results and discussion

The irradiation of acenaphthylene in various organic solvents has been investigated previously [10, 11]. The excited singlet yields the *cis* dimer exclusively, whereas the triplet state yields a mixture of *trans* and *cis* dimers in the ratio 9:1 (Fig. 1). The formation of the *cis* dimer is favoured by a higher concentration of acenaphthylene, the polarity of the solvent or the presence of oxygen in the medium. Most importantly, the photodimerization is sensitive to external heavy atom perturbation [12, 13]. Heavy atom solvents and cyclohexane-ethyl iodide solvent mixtures favour formation of the *trans* dimer. Mechanistic studies [10] have revealed that in acenaphthylene the rate of $S_1 \rightarrow T_1$ intersystem crossing is more sensitive to heavy atom perturbation than that of $T_1 \rightarrow S_0$.

The results of the irradiation of acenaphthylene in SDS, CTAC, dodecyltrimethylammonium chloride (DTAC), CTAB and Triton X-100 micelles in a nitrogen atmosphere in the concentration range 8 - 0.8 mM are summarized in Table 1. The mean occupancy number $\langle S \rangle$ (calculated using a Poisson distribution) for each concentration is also included.

TABLE 1

Photodimerization of acenaphthylenes 1 and 2 in micellar media

Surfactant	Bulk concentration of acenaphthylenes (mM)	Mean occupancy number $\langle S \rangle^a$	Duration of irradiation (h)	Conversion ^b (%)	Yield of dimers (%)	[cis]/[trans] ^c
<i>Acenaphthylene (1)^d</i>						
SDS (0.05 M)	8.0	9.0	2.5	54	80	4.6
	6.0	7.0	2.5	56	76	4.6
	5.0	6.0	2.5	50	78	4.0
	2.3	3.0	5.0	75	78	3.6
	1.3	2.0	5.0	75	70	2.0
	0.8	0.1	8.5	70	65	1.7
CTAC (0.025 M)	8.0	25.0	2.5	78	83	4.4
	6.0	19.0	2.5	88	90	4.2
	1.3	4.0	5.0	90	75	1.8
DTAC (0.05 M)	8.0	—	2.5	85	78	3.8
	1.3	—	5.0	90	75	1.0
CTAB (0.025 M)	8.0	25.0	2.5	80	85	2.3
	6.0	19.0	2.5	80	78	2.1
	5.0	16.0	2.5	85	78	2.1
	2.3	8.0	5.0	90	83	1.3
	1.3	4.0	5.0	90	80	0.1
	0.8	0.3	8.5	90	65	0.1
Triton X-100	8.0	4.0	4.5	85	75	2.3
	6.0	3.0	4.5	85	72	2.0
	5.0	2.0	4.5	80	75	2.0

(continued)

TABLE 1 (continued)

Surfactant	Bulk concentration of acenaphthylenes (mM)	Mean occupancy number $\langle S \rangle^a$	Duration of irradiation (h)	Conversion ^b (%)	Yield of dimers (%)	[cis]/[trans] ^c
Triton X-100	2.3	1.0	6.5	90	63	1.0
	1.3	0.1	8.0	90	63	0.1
5,6-dichloroacenaphthylene (2) ^e						
CTAC (0.025 M)	2.0	4.0	20.0	80	—	11.5
CTAB (0.025 M)	2.0	4.0	20.0	85	—	3.0

^aCalculated using aggregation numbers 60, 80, 80 and 10 for SDS, CTAB, CTAC and Triton X-100 respectively.

^bDetermined by monitoring the acenaphthylene disappearance by its UV absorption at 390 nm.

^cAverage of three trials. The dimer ratios were determined by nuclear magnetic resonance integration of signals at $\delta = 4.9$ ppm (cis) and $\delta = 4.1$ ppm (trans) for acenaphthylene. The dimer ratios were determined by UV analysis for 5,6-dichloroacenaphthylene.

^dThe irradiations were conducted in nitrogen-purged micellar solutions.

^eThe irradiations were conducted in aerated micellar solutions.

The striking observations on the photodimerization of acenaphthylenes in micellar media are (i) a decrease in the magnitude of the *cis:trans* dimer ratio with a decrease in the bulk concentration of the solubilized reactant and (ii) for a given bulk concentration the magnitude of the *cis:trans* dimer ratio differs with the type of micelle. These observations can be rationalized as follows.

With a decrease in the bulk concentration of the reactant the mean occupancy number $\langle S \rangle$ decreases (Table 1). Since the probability for formation of the singlet-derived *cis* dimer is high at high monomer concentrations, *cis* dimer formation is favoured at concentrations where the mean occupancy number is high. As the mean occupancy number is decreased the probability for excited singlet states to encounter ground state monomers before intersystem crossing to triplet states is decreased and hence the magnitude of the *cis:trans* dimer ratio decreases.

For a given bulk concentration the *cis:trans* ratio as well as the mean occupancy number vary with the type of micelle used. For example, for a bulk concentration of 8 mM the occupancy numbers in SDS, CTAC and CTAB micelles are 9, 25 and 25 respectively. If the mean occupancy number effect alone is operative then the *cis:trans* dimer ratios are expected to be much larger in CTAB and CTAC than in SDS. However, it is observed that the *cis:trans* ratio in CTAB is about half that in CTAC and SDS. This is true for all concentrations. At a bulk concentration of 1.3 mM the photodimerization is almost exclusively via the triplet channel in CTAB, whereas in CTAC, DTAC and SDS micelles the singlet-state-derived *cis* dimer still predominates. The low *cis:trans* ratios, in spite of the high occupancy numbers in CTAB, are most probably due to the external heavy atom effect of the bromide counter-ions. The bromide counter-ions enhance the $S_1 \rightarrow T_1$ intersystem crossing via intermolecular spin-orbit coupling and the triplet-derived *trans* dimer yield is increased.

In a previous study [14] of the photodimerization of acenaphthylene in Nikkol PBC-34 and SDS micelles it was observed that the *cis:trans* ratio in PBC-34 is much smaller than that in SDS micelles. Our observation of the photodimerization of 1 in Triton X-100 micelles is similar. For a given bulk concentration, the *cis:trans* ratio in Triton X-100 is similar to that in CTAB. The low occupancy numbers for Triton X-100 compared with those for the other micelles could probably be a reason for the increase in the *trans* dimer yield as discussed above.

Koziar and Cowan [15] have observed that the photodimerization of 5,6-dichloroacenaphthylene in degassed cyclohexane yields the *cis* and *trans* dimers in the ratio 3:7. While the S_1 state yields the *cis* dimer exclusively, the T_1 state yields a mixture of *trans* and *cis* dimers. Heavy atom solvents favour the *trans* dimer whereas solvents of high polarity and the presence of oxygen favour the *cis* dimer. It has been observed that photolysis of an oxygen-saturated cyclohexane solution of 2 yields almost exclusively the *cis* dimer. A study of the photodimerization of 2 in micellar media was attempted. Unfortunately 2 is sparingly soluble in micellar media and on nitrogen purging

tends to come out of solution. Therefore, irradiation had to be conducted in aerated media. The results of the photodimerization of a 2 mM (saturation concentration) solution of **2** in CTAB and CTAC micelles are presented in Table 1.

In both CTAB and CTAC micelles the *cis* dimer is the major product. Further, as observed for **1**, the *cis:trans* ratio under identical conditions is much lower in CTAB than in CTAC. An increase in the triplet population due to the heavy atom effect of the bromide counter-ions is the probable reason for the increase in the *trans* dimer yield in CTAB compared with that in CTAC.

The present investigations of the photodimerization of acenaphthylenes **1** and **2** in micellar media suggest that, for photochemical reactions that proceed via competing singlet and triplet states, state selectivity can be achieved by utilizing heavy atom counter-ions for triplet state products and light atom counter-ions for predominantly singlet state products. However, this technique has its limitations. Firstly, the photochemical reaction should be sensitive to the heavy atom effect. Secondly, the $S_1 \rightarrow T_1$ intersystem crossing should be more sensitive to heavy atom perturbation than the $T_1 \rightarrow S_0$ crossing. If $T_1 \rightarrow S_0$ intersystem crossing is the more sensitive, then the use of micelles with heavy atom counter-ions will result in a reduction in the yield of triplet-derived products.

Indeed this has been observed [16] during the photodimerization of substituted coumarins **3**, **4** and **5** (Fig. 2). It has been established that on direct excitation 4-methoxycoumarin (**3**) dimerizes from the triplet state to yield the *anti* head-to-tail dimer, 4-methyl-7-methoxycoumarin (**4**) dimerizes

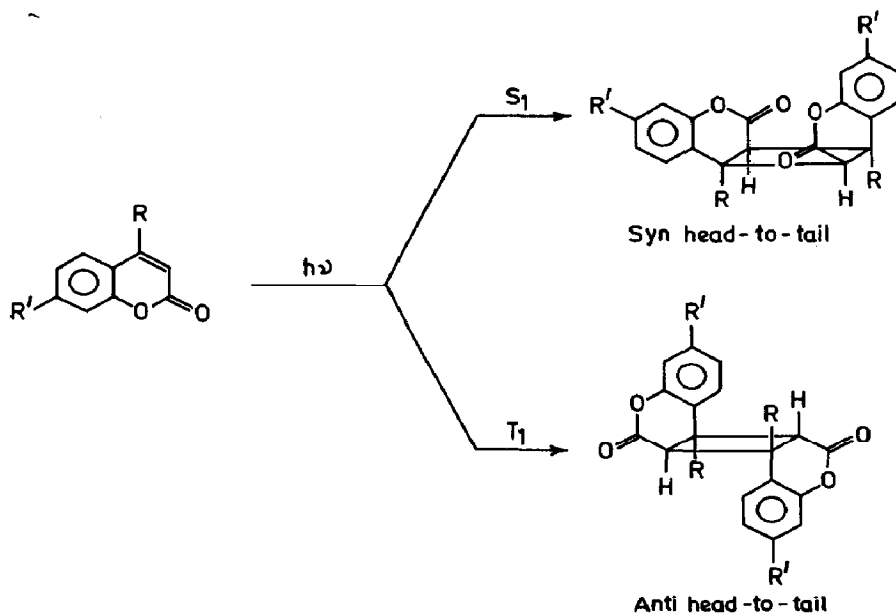


Fig. 2. Photodimerization of substituted coumarins **3** ($R' = H$; $R = OCH_3$), **4** ($R' = OCH_3$; $R = CH_3$) and **5** ($R' = R = CH_3$).

TABLE 2

Photodimerization of substituted coumarins 3 - 5 in micellar media

Compound	Surfactant	Bulk concentration of coumarins (mM)	Duration of irradiation ^a	Nature of dimer ^b	Yield of dimer ^c
3	SDS (0.03 M)	10.0	68	<i>anti</i> H-T	45
	CTAB (0.01 M)	3.3	72	<i>anti</i> H-T	30
4	SDS (0.03 M)	4.4	72	<i>syn</i> H-T	40
	CTAB (0.01 M)	4.0	72	<i>syn</i> H-T	5
5	SDS (0.03 M)	8.5	72	<i>syn</i> H-T and <i>anti</i> H-T	20
	CTAB (0.01 M)	4.3	72	<i>syn</i> H-T and <i>anti</i> H-T	5

^aThe irradiations were conducted in Pyrex tubes using a 450 W medium pressure mercury arc lamp.

^bH-T, head to tail.

^cThe dimer yield was measured gravimetrically; the error limit was $\pm 5\%$. The amount of coumarin reacted and the yield of dimer agreed to within $\pm 10\%$.

from the singlet state to yield the *syn* head-to-tail dimer and 4,7-dimethylcoumarin (5) dimerizes from the singlet and triplet states to yield *syn* and *anti* head-to-tail dimers (Fig. 2). The results of the photodimerization of 3 - 5 in SDS and CTAB micelles are summarized in Table 2. It is observed that in all cases the yields of the dimers are lower in CTAB than in SDS. These results indicate that for 3 - 5 probably both $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ intersystem crossings are sensitive to heavy atom perturbation with $T_1 \rightarrow S_0$ predominating.

3. Experimental details

SDS (Sigma) (recrystallized from 95% ethanol) and CTAB, CTAC and DTAC (Eastman Kodak) (recrystallized from a methanol-ether mixture) were used. Acenaphthylene (Aldrich) after recrystallization from 95% ethanol and Triton X-100 (Sigma) were used. 5,6-dichloroacenaphthylene was synthesized and purified following the reported procedure [15, 17]. Doubly distilled water was used to make up the micellar solutions.

3.1. Solubilization and irradiation procedure

The required amounts of 1 and 2 were added to 100 ml of surfactant solutions (SDS, 0.05 M; CTAB, 0.025 M; CTAC, 0.025 M; DTAC, 0.05 M; Triton X-100, 0.8 vol.%) and stirred for 12 h. The micellar solutions were filtered through a Whatman No. 1 filter paper to remove the insoluble reactant.

Irradiations were conducted in Pyrex tubes at room temperature using a 450 W medium pressure mercury arc lamp for time intervals indicated in Table 1. For acenaphthylene, nitrogen was bubbled through the micellar

solutions for 1 h before irradiation and as a slow stream during irradiation. For 5,6-dichloroacenaphthylene nitrogen purging was rendered impossible because of the low solubility of the compound. Hence aerated samples were irradiated in this case. The photodimers which precipitated out during irradiation were collected on a Whatman No. 42 filter paper, washed with water and dried at 60 °C. The filtrate was diluted to recover any soluble dimer but no dimer was found in the filtrate.

The *cis:trans* dimer ratio for acenaphthylene was determined [14] from nuclear magnetic resonance integration of the methine proton signals at $\delta = 4.9$ ppm (*cis* dimer) and $\delta = 4.1$ ppm (*trans* dimer). The compositions of the product dimer mixtures of 5,6-dichloroacenaphthylene were determined [15] by measuring the optical densities of benzene solutions of these dimers at 340 and 316 nm.

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