REGIOSELECTIVE PHOTODIMERIZATION OF 9-METHYLANTHRACENE IN HOMOGENEOUS AND MICELLAR SOLUTIONS[†]

THOMAS WOLFF, NORBERT MÜLLER and GÜNTHER VON BÜNAU

Physikalische Chemie, Universität Siegen, D-5900 Siegen (F.R.G.)

(Received September 17, 1982; in revised form November 1, 1982)

Summary

The fluorescence and dimerization quantum yields of the photodimerization of 9-methylanthracene were measured in cyclohexane, benzene, diethyl ether, methanol and aqueous solutions of cetyltrimethylammonium bromide, cetyltrimethylammonium chloride and sodium dodecylsulphate. The dependence of the quantum yields and of the ratio of head-to-head to head-to-tail photodimers (the two products of photodimerization) on solvent polarity and on the educt and surfactant concentrations was investigated. Preferred formation of head-to-tail dimers was observed in polar solvents and in micellar solutions. The heavy atom effect of the bromide counter-ions of cetyltrimethylammonium micelles reduces the photodimerization quantum yield. The activation energies of the thermal back reactions were determined.

1. Introduction

The photodimerization of 9-methylanthracene (A) is known to yield two isomeric dimers (Fig. 1), the head-to-tail photodimer (Dht) and the corresponding head-to-head dimer (Dhh). Until recently [1], the latter photodimer had escaped detection because of its fast thermal back reaction. Also the few known head-to-head photodimers of other 9-substituted anthracenes cleave much more readily than the head-to-tail isomers [2, 3] which are stable compounds at room temperature.

In the case of 9-hydroxymethylanthracene selective head-to-head photodimerization was found to prevail when carried out in aqueous sodium dodecylsulphate (SDS) solutions containing micelles [3]. This result was ascribed to preorientation of the polar 9-hydroxymethylanthracene molecules in the micelles and prompted us to study the regioselectivity of the photodimerization of the non-polar derivative A in different homogeneous and micellar solutions. Since photodimerizations of anthracene derivatives

---

[†]Dedicated to Professor Albert Weller on the occasion of his 60th birthday.
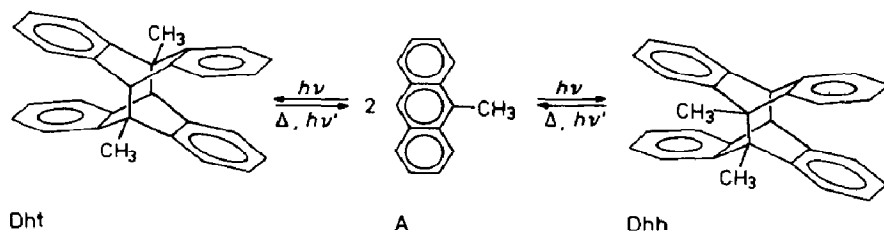
Fig. 1. The photodimerization of A.

are known to proceed via the singlet state, information on relative reaction rates of excited A is expected from quenching data. Recent studies of excited aromatic molecules in solutions containing cetyltrimethylammonium micelles have shown that the triplet quantum yield increased at the expense of the fluorescence quantum yield when cetyltrimethylammonium chloride (CTAC) micelles were replaced by cetyltrimethylammonium bromide (CTAB) micelles. These data could be interpreted as a heavy atom effect of the bromide counter-ions on micellarly solubilized excited aromatic molecules [4 - 6]. Similar effects were observed on the photodimerization yields of A and will be described in this paper.

2. Experimental details

2.1. Materials

A (Ega; minimum purity, 98%), ethanol (Merck; minimum purity, 99.5%), cyclohexane, diethyl ether and methanol (all Merck, Uvasol) were used as supplied. CTAC, CTAB and SDS were available from previous investigations [3, 4]. Tetralin was passed through Al_2O_3 (activity I). The preparation of the micellar solutions has been described elsewhere [4].

2.2. Fluorescence quantum yields

Quinine bisulphate in 1 N H_2SO_4 was used as a standard for the determination of fluorescence quantum yields [7]. Integrated fluorescence spectra of deaerated solutions not exceeding an optical density (OD) of 0.015 at the excitation wavelength (350 nm) were measured on a Spex Fluorolog spectral fluorometer. At this OD the concentration of A in 0.1 M CTAC is 3×10^{-6} M, 0.25% of the micelles are occupied and double occupation is excluded.

2.3. Irradiations

400 ml samples of solutions of A at various concentrations in the solvents cyclohexane, benzene, diethyl ether and methanol and in micellar solutions of CTAB, CTAC and SDS at various surfactant concentrations were deoxygenated by bubbling nitrogen through for 1.5 h and were irradiated for 8 min at 25 ± 0.5 °C in a falling film apparatus through a filter tube which

allowed the 365.5 nm line of a high pressure mercury lamp to be the effective wavelength. The filter tube prevented the photodimers from undergoing a photochemical back reaction. Longer irradiation times were avoided because of precipitation of the photoproducts. Between 20% and 50% of the starting material was converted in the experiments.

2.4. Analyses

The photochemical quantum yields were determined according to the method of Hatchard and Parker [8]. The intensity of the light absorbed by the irradiated solution was $(4.78 \pm 0.08) \times 10^{-5}$ einsteins s^{-1}. The disappearance of the absorption intensity at $\lambda > 300$ nm, where the products do not absorb, was taken as a measure of the consumption of the educt. This allowed evaluation of the dimerization quantum yield since photodimers are the only photoproducts under our conditions. The ratio of Dhh to Dht was determined by measuring the absorption intensity that reappeared at $\lambda > 300$ nm after thermal splitting of the unstable Dhh (see ref. 3). Absorption spectra were measured using a Beckman Acta M VII spectrometer.

The activation energies of the thermal back reactions of the Dhhs were determined as described earlier [3].

3. Results

The absorption spectra of A were measured in the solvents used. The wavelengths and extinction coefficients of the absorption maxima depend only slightly on the solvent as shown in Table 1. No dependence on the concentration of A could be detected between 10^{-4} and 10^{-2} M. It follows that ground state interactions of A need not be considered.

The fluorescence quantum yields of A were measured in 0.1 M CTAB, 0.1 M CTAC and, for comparison with a published value (0.33 [9]), in ethanol. The values found were 0.32 in ethanol, 0.65 in CTAC and 0.54 in CTAB. The ratio of the fluorescence quantum yields ϕ_f ($\phi_{f,CTAB}/\phi_{f,CTAC}$) in the two surfactants is 0.83.

TABLE 1

Extinction coefficients ϵ and wavelengths λ of the absorption maximum around 368 nm of 9-methylanthracene in various solvents

Solvent	λ_{max} (nm)	ϵ ($\times 10^3$ M^{-1} cm^{-1})
Cyclohexane	366.5	10.1
Diethyl ether	366.0	9.7
Benzene	369.5	9.2
Methanol	366.0	9.6
0.2 M CTAB	369.5	9.4
0.2 M CTAC	369.0	9.2
0.2 M SDS	368.5	9.2

TABLE 2

Photodimerization quantum yields $\phi_D = \phi_{Dhh} + \phi_{Dht}$ and ratios ϕ_{Dht}/ϕ_{Dhh} of head-to-tail to head-to-head photodimerization of 9-methylanthracene in various solvents at various educt concentrations C_A at 25 ± 0.5 °C

Solvent	C_A (M)	ϕ_D	ϕ_{Dht}/ϕ_{Dhh}
Cyclohexane	1.40×10^{-3}	0.0108	1
	2.95×10^{-3}	0.0183	1
	9.27×10^{-3}	0.0467	1
Benzene	1.01×10^{-3}	0.0100	1.6
	1.05×10^{-2}	0.0505	1.4
Diethyl ether[a]	1.44×10^{-3}	0.0112	1.5
	2.45×10^{-3}	0.0208	1.5
Methanol	9.81×10^{-4}	0.0088	2

[a] At 20 ± 0.5 °C.

The quantum yields ϕ_D of photodimerization (the sum for Dht and Dhh) were determined in four homogeneous solvents: cyclohexane, benzene, diethyl ether and methanol for several concentrations C_A of A. The values are listed in Table 2. Published values for ϕ_D at different concentrations of A in cyclohexane are available [10 - 12], the majority of which [10, 12] agree with our values. Another published value obtained in benzene ($\phi_D = 0.15$ at $C_A = 0.01$ M [13]) disagrees with our corresponding value ($\phi_D = 0.05$). However, our value is in accord with the others given in Table 2. The ratios ϕ_{Dht}/ϕ_{Dhh} of the quantum yields of Dht and Dhh are also listed in Table 2. They increase with solvent polarity and are independent of C_A in the concentration range investigated. The ratio in benzene (1.5) coincides with that reported by Kaupp and Teufel [1].

In micellar solutions we can assume that the A molecules are associated with the micelles because of their low solubility in water. Experiments with varying concentrations C_A and C_S of A and of the surfactant respectively were made. In both cases the number of singly, doubly, triply etc. occupied micelles is varied. The mean occupation numbers $\langle S \rangle$ are given in Table 3 from which the statistical distributions of the A molecules among the micelles can be calculated [14]. Table 3 shows that ϕ_D increases with $\langle S \rangle$. Compared with homogeneous solvents (Table 2) higher quantum yields ϕ_D can be obtained when $\langle S \rangle$ is chosen suitably. Independent of the value of $\langle S \rangle$, ϕ_D is lower in CTAB solutions than in CTAC solutions. The ratio $\phi_{D,CTAC}/\phi_{D,CTAB}$ is 0.75 (Table 3). We attribute this to the heavy atom effect of bromide counter-ions which convert some of the excited A molecules to the excited triplet state thereby preventing them from taking part in the photodimerization.

More Dht is formed in solutions containing SDS micelles (micellar weight, 17 200 [17]) than in those containing the larger CTAB micelles

TABLE 3

Photodimerization quantum yields $\phi_D = \phi_{Dhh} + \phi_{Dht}$ and the ratio ϕ_{Dht}/ϕ_{Dhh} of head-to-tail to head-to-head photodimerization of 9-methylanthracene in micellar solutions at various educt concentrations C_A and micelle concentrations C_{Mi} at 25 ± 0.5 °C

Surfactant	C_A ($\times 10^3$ M)	C_{Mi} [a] ($\times 10^3$ M)	ϕ_D	ϕ_{Dht}/ϕ_{Dhh}	$\langle S \rangle$ [b]	$\phi_{D,CTAB}/\phi_{D,CTAC}$
CTAC	1.30	4.5	0.0103	1.7	0.29	0.40[c]
CTAB	1.33	4.5	0.004[c]	1.5	0.30	
SDS	1.29	4.5	0.0114	1.7	0.29	
CTAC	1.27	1.5	0.0157	1.8	0.85	0.76
CTAB	1.33	1.5	0.0119	1.5	0.89	
CTAC	1.28	0.75	0.0226	1.8	1.71	0.74
CTAB	1.32	0.75	0.0167	2.3	1.76	
SDS	1.08	0.75	0.0220	4.0	1.44	
CTAC	1.02	3.0	0.0083	1.9	0.34	0.74
CTAB	1.08	3.0	0.0061	1.4	0.36	
CTAC	1.27	3.0	0.0121	2.0	0.42	0.76
CTAB	1.33	3.0	0.0092	2.0	0.44	
SDS	1.05	3.0	0.0112	2.0	0.35	
SDS	1.24	3.0	0.0162	2.0	0.41	
CTAC	3.06	3.0	0.0250	1.9	1.02	
CTAC	3.70	3.0	0.0297	2.0	1.23	0.73
CTAB	3.70	3.0	0.0216	2.0	1.23	
CTAC	5.43	3.0	0.0384	2.0	1.81	0.74
CTAB	5.43	3.0	0.0285	2.0	1.81	
CTAB	6.15	3.0	0.0297	2.5	2.05	
SDS	4.90	3.0	0.0630	4.0	1.63	

[a] $C_{Mi} = (C_s - CMC)/n_{agg}$ where n_{agg} is 80 in CTAB [15], 82 in CTAC [16] and 60 in SDS [17]; CMC is the critical micelle concentration.
[b] Average number of educt molecules per micelle.
[c] At this C_s rod-like micelles of CTAB are formed and the viscosity increases.

(micellar weight, 30 000 [17]). The ratio ϕ_{Dht}/ϕ_{Dhh} increases with $\langle S \rangle$ and reaches values of up to 2.5 in CTAB solutions and of up to 4 in SDS solutions.

The kinetic parameters of the thermal back reactions were determined in order to establish the extent to which the relative yields of Dhh and Dht can change during the irradiation time. Values for the cleavage of Dhh were measured between 15 and 40 °C in the four solvents used in the irradiation experiments. The activation energy for the cleavage of Dht (formed on irradiation in diethyl ether) was determined in tetralin between 140 and 185 °C. In this case the amount of Dhh originally formed was allowed to decay completely at 40 °C before the Dht decay constants were measured. The activation energies E_a and frequency factors F are given in Table 4. It can be estimated from these data that almost no Dht and less than 10% of

TABLE 4

Activation energies E_a and frequency factors F of the thermal cleavage of head-to-head and head-to-tail photodimers in various solvents

Solvent	E_a (kJ mol^{-1})		F (s^{-1})	
	Dhh	Dht	Dhh	Dht
Cyclohexane	82		6×10^9	
Diethyl ether	111		6×10^{14}	
0.2 M CTAC	85		2×10^{10}	
0.2 M SDS	91		3×10^{11}	
Tetralin		160		10^{16}

the Dhh can be thermally split within the reaction times of 8 min. Since on re-irradiation corresponding amounts of Dhh are formed again the error in ϕ_{Dht}/ϕ_{Dhh} due to this effect cannot be more than 3%. A published value for the E_a of Dht cleavage (about 113 kJ mol^{-1} [12]) disagrees with our value (160 kJ mol^{-1}). Since Dht is a stable substance at room temperature the published value cannot be correct unless an extraordinarily low frequency factor were to reduce the rate constants. Higher activation energies for the cleavage of Dht (about 150 kJ mol^{-1}) and of other head-to-tail photodimers of anthracene derivatives have been reported by Menter and Förster [18] and Greene [19] respectively.

4. Discussion

As expected from previous work [10 - 13], the total quantum yields of photodimerization of A were found to be much smaller than unity and to depend on the concentration of A. This dependence can be understood on the basis of the kinetic scheme shown in Fig. 2 where (A*A)hh and (A*A)ht represent the two excimer precursors of the photodimers Dhh and Dht. Excimers of A are likely to be involved in the photodimerization since (A*A)ht has been experimentally proved to be an intermediate in the photochemical splitting of Dht [20, 21]. Previously the excimer has more often been suggested [22, 23] than questioned [1] as a precursor of Dht. Under steady state conditions quantum yields according to the scheme shown in Fig. 2 are given by

$$\phi_{Dhh} = \frac{R_3}{k_1 + k_2 + R_3 + R_4} \frac{k_5}{k_5 + k_6} \phi_a \tag{1}$$

$$\phi_{Dht} = \frac{R_4}{k_1 + k_2 + R_3 + R_4} \frac{k_7}{k_7 + k_8} \phi_a \tag{2}$$

where the R_i are specific rates, the k_i are rate constants and ϕ_a is the quantum yield of the absorption process ($\phi_a = 1$ excited molecule per quantum absorbed).
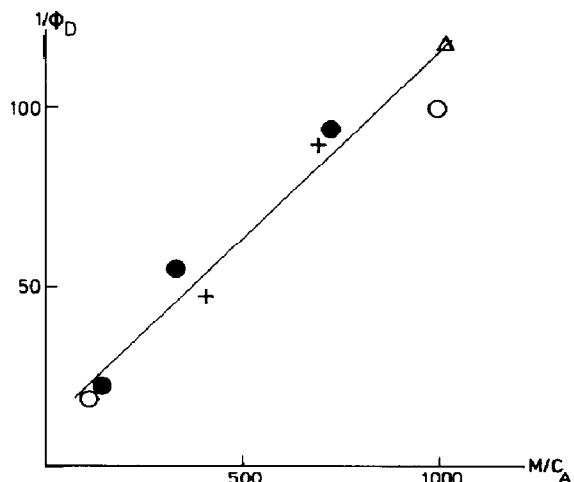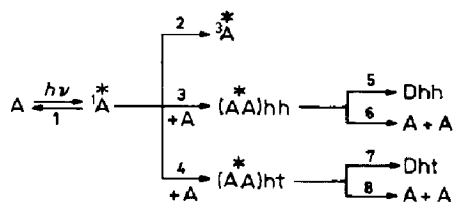
Fig. 2. Kinetic scheme for the photodimerization of A (the abbreviations are explained in the text).

Fig. 3. Dependence of the photodimer quantum yield ϕ_D on the concentration C_A of A in cyclohexane ($\bullet$), benzene ($\bigcirc$), diethyl ether (+) and methanol ($\triangle$).

In homogeneous solutions R_3 and R_4 are proportional to the concentration of A, so that a plot of $1/\phi_D$ versus $1/C_A$ gives a common straight line for all solvents (Fig. 3). In micellar solutions (provided that intermicellar diffusion of A molecules is negligible) dimer formation is only possible when some micelles are occupied by more than one molecule of A, i.e. R_3 and R_4 depend on the probability P of finding multiply occupied micelles. At low quantum flux (neglecting steric effects) the dimerization probability per unit time must be proportional to the number of A molecules which a given excited $^1A^*$ molecule may encounter within its lifetime in the same micelle. It follows that R_3 and R_4 are proportional to

$$P = p_2 + 2p_3 + 3p_4 + \ldots \tag{3}$$

where p_i designates the probability of finding i A molecules in a micelle. P can be estimated using Poisson statistics [14]. When the data of Table 3 are plotted as $1/\phi_D$ versus $1/P$ straight lines are obtained (Fig. 4). Within error limits the ratio $\phi_{D,CTAB}/\phi_{D,CTAC}$ is represented by the ratio of the slopes of these lines. The comparatively large error limits are mainly due to uncertainties in the aggregation numbers n_{agg} of the micelles. Published values for n_{agg} range from 40 to 80 for SDS and from 80 to 95 for CTAB [15]. Moreover, additives to micellar solutions are known to alter the aggregation numbers [17, 24] so that n_{agg} may vary with C_A or $\langle S \rangle$.

It follows from the kinetic scheme that the ratio of the ϕ_D values in CTAB and in CTAC solutions should be determined essentially by the magnitudes of k_1 and k_2 since these are always large in comparison with R_3 and R_4, at least in the concentration range investigated. When the rate constants of the fluorescence transition and of quenching of $^1A^*$ are given by k_1 and k_2 respectively, it is seen that
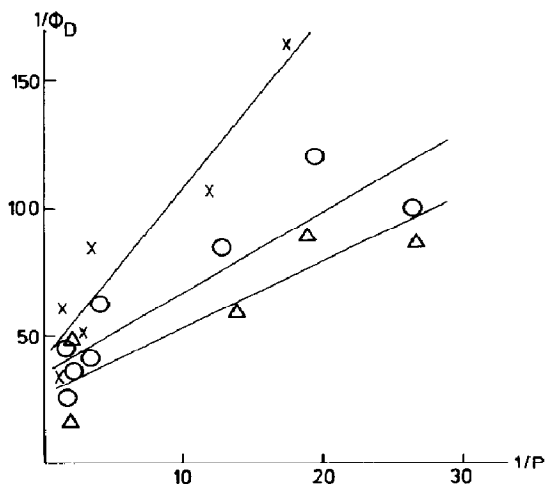
Fig. 4. Concentration dependence of the photodimer A in micellar solutions (P is calculated from eqn. (3)): $\times$, CTAB; $\bigcirc$, CTAC; $\triangle$, SDS.

$$\frac{\phi_{D,CTAB}}{\phi_{D,CTAC}} \approx \frac{k_1 + k_{2,CTAC}}{k_1 + k_{2,CTAB}} \tag{4}$$

The same expression holds for the ratio of the fluorescence quantum yields in the two surfactant solutions. Therefore the two ratios should be identical and independent of the concentration of A. This is very nearly confirmed by the results. The fluorescence quantum yield ratio (0.83) and the photochemical quantum yield ratio (0.75) do not differ significantly. However, a systematic difference may arise because both fluorescence transitions and dimerization compete with the intersystem crossing induced by the heavy atom effect of the bromide counter-ions. The rate constant k_2 depends on the distance between the excited $^1A^*$ molecule and the quenching bromide counter-ions. Since fluorescence transitions are observed in singly occupied micelles while dimerization requires multiple occupation, a smaller average distance and a larger value of k_2 are expected for dimerization.

Micellar solutions offer the possibility of producing considerably more Dht than Dhh. This selectivity is quite surprising since no preorientational effects due to the polarity of the educts (see ref. 3) can be expected. It appears from the data of Tables 2 and 3 that this selectivity partly depends on the polarity of the microenvironment of the solubilizates. Effective dielectric constants in the region of the micelle—water interface are reported in the literature [25] for SDS and CTAB (51 and 31 respectively). These values are paralleled by the higher selectivity we have found in SDS solutions compared with CTAB solutions. However, other influences such as different micelle sizes [26], microfluidity of the micellar interior [27 - 30] or preorientation of the reacting molecules [3] may also come into play.

It should be noted that the ratio ϕ_{Dht}/ϕ_{Dhh} depends on solvent properties but the sum ϕ_D does not (see Table 2). Therefore solvent effects on reactions (3) - (8) (Fig. 2) are almost excluded. This means that the kinetic scheme must be modified to allow rapid interconversion of the excimers:

$$(A^*A)hh \underset{10}{\overset{9}{\rightleftharpoons}} (A^*A)ht \tag{5}$$

The introduction of this solvent-dependent equilibrium complicates eqns. (1) and (2) but does not affect the proportionality of R_3 and R_4 to C_A.

Finally, the thermal back reaction will be considered. In a recent paper Becker *et al.* [31] have reported an investigation of the intramolecular "photodimerization" of 10-substituted 1,2-di(9-anthryl) ethanes and have given the kinetic parameters of the thermal back reaction. The activation energies varied from 142 kJ mol^{-1} for the parent compound to 130 kJ mol^{-1} for the 10-methyl compound and to 102 kJ mol^{-1} for the 10,10'-dimethyl compound. The third value is close to the activation energy of Dhh decay while the first two are nearer to that of Dht. From this comparison it can be concluded that the rate-determining step of the thermal cycloreversion is the cleavage of the 9,9' bond of Dhh and of the 10,10' bond of the compounds investigated by Becker *et al.*

5. Conclusions

The regioselectivity of the photodimerization of A can be directed by variation in the polarity of the solvent and by performing the reaction in micellar solutions of suitable concentrations. Higher dimerization quantum yields can be achieved in the micellar solutions. Care must be taken when bromide counter-ions are present because they decrease the quantum yields as a result of the heavy atom effect and in other photoreactions proceeding via competing singlet and triplet channels will favour products formed via the triplet state.

Acknowledgments

References

1 G. Kaupp and E. Teufel, *Chem. Ber.*, *113* (1980) 3669.
2 H. Bouas-Laurent, A. Castellan and J.-P. Desvergne, *Pure Appl. Chem.*, *52* (1980) 2633.
3 T. Wolff, *J. Photochem.*, *16* (1981) 343.
4 T. Wolff and G. von Bünau, *Ber. Bunsenges. Phys. Chem.*, *86* (1982) 225.
5 T. Wolff and G. von Bünau, *Abstracts 9th IUPAC Symp. on Photochemistry, Pau, July 25 - 30, 1982*, p. 382.
6 T. Wolff, *Ber. Bunsenges. Phys. Chem.*, *86* (1982) 1132.
7 W. H. Melhuish, *J. Phys. Chem.*, *65* (1961) 229.

8 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A, 235* (1956) 518.

9 A. R. Horrocks and F. Wilkinson, *Proc. R. Soc. London, Ser. A, 306* (1968) 257.

10 J. B. Aladekomo, *J. Lumin., 6* (1973) 83.

11 A. Castellan, R. Lapouyade and H. Bouas-Laurent, *Bull. Soc. Chim. Fr.,* (1976) 201.

12 J. Bendig and D. Kreysig, *J. Prakt. Chem., 323* (1981) 471.

13 A. Castellan, *C.R. Acad. Sci., Ser. C, 281* (1975) 221.

14 N. J. Turro, M. Grätzel and A. M. Braun, *Angew. Chem., 92* (1980) 712.

15 J. E. Leibner and J. Jacobus, *J. Phys. Chem., 81* (1977) 130.

16 F. Reiss-Husson and V. Luzzati, *J. Phys. Chem., 68* (1964) 3504.

17 P. H. Elworthy, A. T. Florence and C. B. Mcfarlane (eds.), *Solubilization by Surface-active Agents,* Chapman and Hall, London, 1968, pp. 41, 71.

18 J. Menter and T. Förster, *Photochem. Photobiol., 15* (1972) 289.

19 F. D. Greene, *Bull. Soc. Chim. Fr.,* (1960) 1356.

20 S. Yamamoto, K.-H. Grellmann and A. Weller, *Chem. Phys. Lett., 70* (1980) 241.

21 S. Yamamoto and K.-H. Grellmann, *Chem. Phys. Lett., 85* (1982) 73.

22 J. B. Birks and J. B. Aladekomo, *Photochem. Photobiol., 2* (1963) 415.

23 A. Castellan, R. Lapouyade and H. Bouas-Laurent, *Bull. Soc. Chim. Fr.,* (1976) 210.

24 H. W. Offen, D. R. Dawson and D. F. Nicoli, *J. Colloid Interface Sci., 80* (1981) 118.

25 K. A. Zachariasse, N. V. Phuc and B. Kozankiewicz, *J. Phys. Chem., 85* (1981) 2676.

26 T. Wolff, *J. Photochem., 18* (1982) 269.

27 K. A. Zachariasse, *Chem. Phys. Lett., 57* (1978) 429.

28 J. Emert, C. Behrens and M. Goldenberg, *J. Am. Chem. Soc., 101* (1979) 771

29 N. J. Turro, M. Aikawa and A. Yekta, *J. Am. Chem. Soc., 101* (1979) 772.

30 N. J. Turro and T. Okubo, *J. Am. Chem. Soc., 103* (1981) 7224.

31 H.-D. Becker, T. Elebring and K. Sandros, *J. Org. Chem., 47* (1982) 1064.