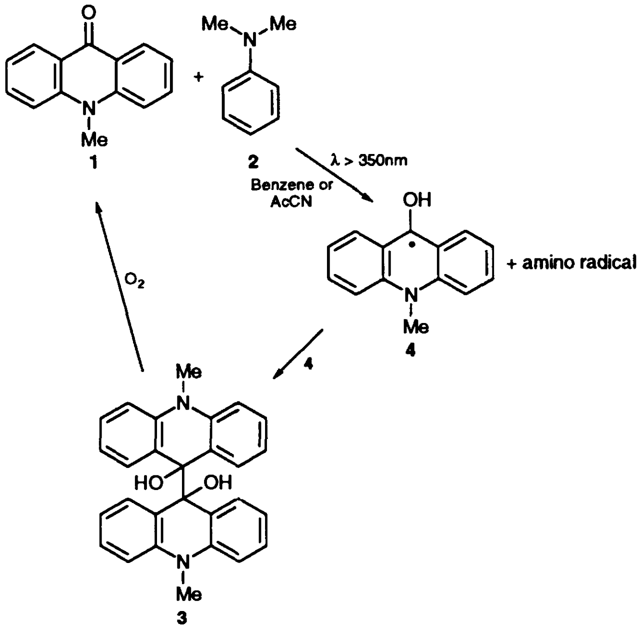
Mechanism of Photodimerization Reaction of 10-Methylacridone in Polar and Non-polar Solvents

Hiroki Kawata*,[a] **Kazuaki Shimada**,[b] **Tsutomu Kumagai**[c] **and Shigeya Niizuma**[a]
[a] *College of Humanities and Social Sciences, Iwate University, Ueda, Morioka 020, Japan*
[b] *Department of Applied Chemistry, Faculty of Engineering, Iwate University, Ueda, Morioka 020, Japan*
[c] *Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan*

The photodimerization reaction of 10-methylacridone (**1**) in the presence of *N,N*-dimethylaniline (**2**) was investigated both in deaerated benzene and acetonitrile solutions by a continuous light irradiation ($\lambda > 350$ nm) method and a flash photolysis. The photoreaction proceeds *via* the triplet state of **1** (^{3}**1***) and results in electron transfer followed by proton transfer from **2** to **1** to give the dimer, 9,9′-dihydroxy-10,10′-dimethyl-9,9′-biacridan (**3**).

Photodimerization reactions of acridine derivatives are classified into two groups; one is those initiated by the hydrogen abstraction from solvents[1] and the other by the photoinduced electron transfer[2] reactions. Compound **1** undergoes the electron transfer reaction followed by a proton transfer from **2** by photoirradiation ($\lambda > 350$ nm), yielding the dimer, the pinacol, in deaerated non-polar (benzene) and polar (acetonitrile) solvents, as shown in Scheme 1. This photoreaction is similar to that of benzophenone in alcoholic solutions.[3] We also found that acridone partly showed the same reaction as that of **1**. In connection with this, it is reported that the excited acridone abstracts a hydrogen from the ground state acridone to yield radicals.[4] Thus, as the circumstances of acridone appear to be complicated in the kinetic analysis, we shall limit our attention to the photoreaction of **1**.



Scheme 1

The present study[5] is designed to clarify the photodimerization reaction mechanism of **1** in polar and non-polar solvents using continuous light irradiation and conventional flash photolysis techniques.

Results and Discussion

Absorption and Fluorescence spectra.—When **2** was added to **1** in benzene solution, neither an absorption shift of **1** nor a new absorption band was seen even at a high concentration (~2.0 mol dm^{-3}) of **2**. This indicates that no complex formation between **1** and **2** occurs in the ground state. On the other hand, spectral changes in **1** were observed when aniline was added. The absorption spectra of **1** with various concentrations of aniline are shown in Fig. 1. Isosbestic points appeared at 380, 390 and 398 nm. It is clear that **1** and aniline are in equilibrium with their hydrogen bonded complex in the ground state. The equilibrium constant was evaluated to be 0.17 dm^3 mol^{-1} at 23 °C by analysing Fig. 1. No new bands appeared in the fluorescence spectrum of **1** for the addition of concentrations of **2** or aniline up to 2.0 mol dm^{-3}. Instead, decrease in fluorescence intensity was observed and it was found to fit the Stern–Volmer kinetics very well, as shown in Fig. 2. The plot is linear throughout the concentration of **2** or aniline used. The fluorescence lifetime (τ_f) of **1** was determined as 1.5 ns when measured at 410 nm (the fluorescence maximum wavelength) in benzene. τ_f is the same as that observed at another wavelength. Using this τ_f and the Stern–Volmer constants and assuming that the hydrogen bonded species is not fluorescent in the aniline system, we obtained the fluorescence quenching rate constants, k_q^f's in **2** and aniline systems, as 1.0×10^{10} dm^3 mol^{-1} s^{-1} and 7.5×10^9 dm^3 mol^{-1} s^{-1}, respectively. These k_q^f's values indicate that the quenching reaction is diffusion controlled. The fluorescence quenching of **1** by **2** is probably caused by the electron transfer from the nitrogen in the dimethylamino group, which is electron rich due to the two electron donating methyl groups, while the delocalization of π electrons through the

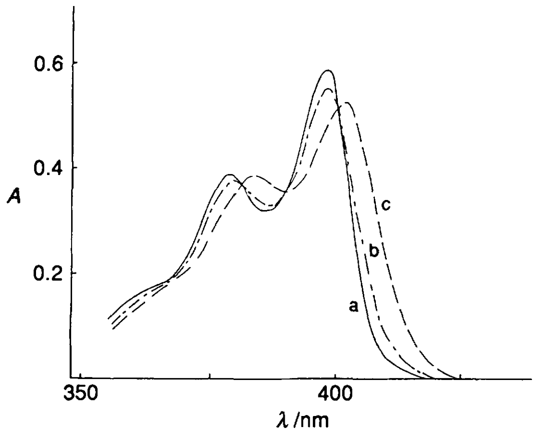


Fig. 1 Absorption spectra of **1**. [Aniline]: (a) 0 mol dm^{-3}, (b) 0.5 mol dm^{-3}, (c) 3.0 mol dm^{-3}.

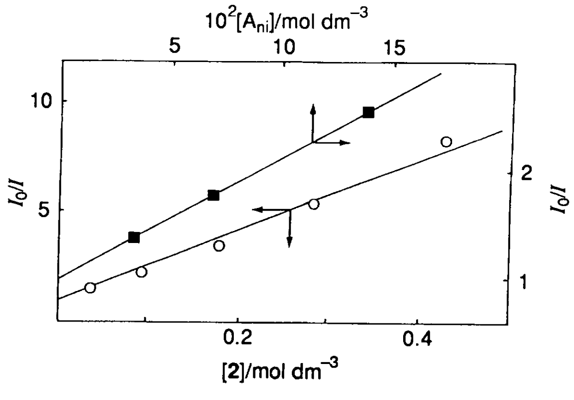


Fig. 2 Effects of [2] (○) and [Aniline] (■), as a quencher, on the fluorescence intensity of 1: [1] = 1.4×10^{-5} mol dm^{-3}

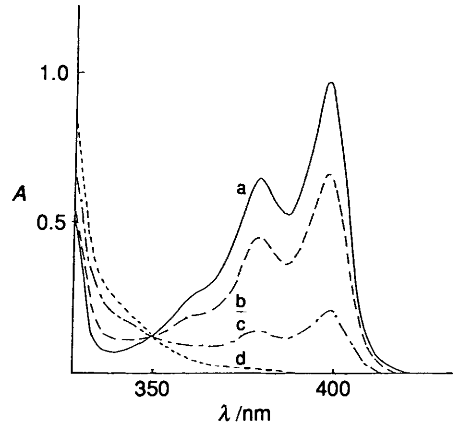


Fig. 3 Spectra of a solution of 1 containing 4.0×10^{-3} mol dm^{-3} of 2 on irradiation at 365 nm for various times ([1] = 7.1×10^{-5} mol dm^{-3}): curve a, 0 min; curve b, 3 min; curve c, 8 min; curve d, 15 min.

hydrogen bond in excited state between the two π electronic systems,[6] 1 and aniline, quenches the fluorescence of 1.

Continuous Light Irradiation.—Irradiation of a deaerated benzene solution of 1 (7.1×10^{-5} mol dm^{-3}) and 2 (4.0×10^{-3} mol dm^{-3}) gave the dimer, 3, under conditions such that only 1 was able to absorb the light. The analysis for confirmation of 3 was successfully performed, though it partly decomposed during TLC, column chromatography and/or recrystallization to form 1. Compound 1 is recovered up to 60% when the aerated benzene solution of 3 is allowed to stand in the dark for three days at room temperature, while 1 is rarely re-formed in the deaerated system. Compound 3 is relatively sensitive to oxygen. Spectral changes with irradiation are shown in Fig. 3. An isosbestic point appeared at 351 nm. The absorption band of 1 disappeared completely and that of the adduct appeared at the wavelength shorter than that of 1. This indicates that the conjugated system of aromaticity is broken at >C=O.[7] The same reaction occurs in the presence of 2 in deaerated acetonitrile solution. Under aerated conditions, the photoreaction occurs neither in benzene nor acetonitrile even in the presence of 2. Furthermore, without 2, no photoreaction occurs in deaerated hydrogen donating solvents such as propan-2-ol and ethanol, unlike the case of benzophenone.

The quantum yield (Φ) for the disappearance of 1 with 365 nm irradiation in benzene increases with increasing concentration of 2. The effects of the concentration of 2 as well as ferrocene on the quantum yield are listed in Table 1. Clearly, ferrocene quenches the photoreaction. More precisely, it quenches $^{3}1^{*}$ and its quenching rate constant, k_q, was 7.3×10^{9} dm^{3} mol^{-1} s^{-1} (see flash photolysis). However, in the 1-aniline system, the photoreaction occurred in neither aerated nor deaerated benzene solution.

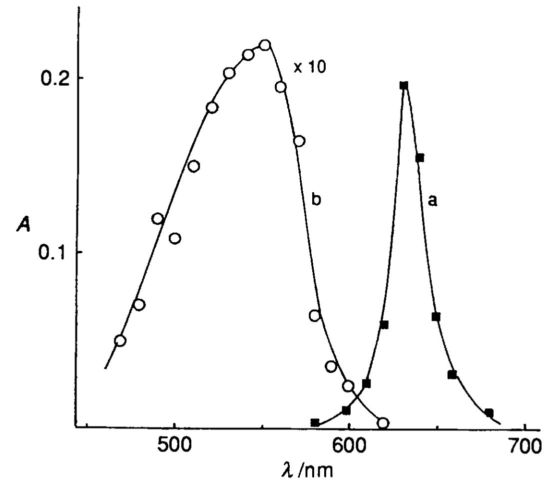


Fig. 4 Transient absorption spectra in nitrogen saturated benzene solution: (a) [2] = 0 mol dm^{-3}, 50 μs after flash; (b) [2] = 4.0×10^{-3} mol dm^{-3}, 100 μs after flash. The concentration of 1 is 7.1×10^{-5} mol dm^{-3} in both (a) and (b).

Flash Photolysis.—Fig. 4(a) is the transient absorption spectrum observed at 50 μs after flashing in the benzene solution containing 1 (7.1×10^{-5} mol dm^{-3}). The transient with a very sharp absorption maximum at 630 nm decays as a first-order process. Its decay rate constant, k_n, was 7.1×10^{4} s^{-1}. The absorption spectrum of this transient resembles the T-T absorption of 1 reported by Abdullah.[8] This transient is quenched by anthracene, ferrocene and oxygen. When anthracene was added, triplet energy transfer occurred from 1 to anthracene and the T-T absorption of anthracene (λ_{max} 430 nm in benzene) was observed. Hence, the transient spectrum is attributed to that of T-T absorption of 1. The quenching rate constant for $^{3}1^{*}$ by ferrocene, k_q, was determined to be 7.3×10^{9} dm^{3} mol^{-1} s^{-1}. Flash photolysis of a benzene solution of 1 (7.1×10^{-5} mol dm^{-3}) containing 2 (4.0×10^{-3} mol dm^{-3}) generated a transient absorption. The spectrum at 100 μs after flashing is shown in Fig. 4(b). The decay of this transient was a second-order process with the rate constant $k\varepsilon^{-1}$ (560 nm) = 4.7×10^{6} cm s^{-1}. No transient was observed when the solution was air saturated. When 2 was omitted, only T-T absorption was observed. This transient is unequivocally formed from $^{3}1^{*}$ since its yield decreases with the addition of ferrocene. Thus, we interpret this transient as a precursor of 3, 9-hydroxy-10-methylacridan C-radical (4). Compound 4 was also observed in acetonitrile solution under the same conditions as that in benzene solution, but the amount of 4 was small compared to that in benzene, resulting in the low quantum yield for the formation of 3 (discussed later). As in benzene, 4 was not observed without 2 but only T-T absorption of 1 was observed in acetonitrile. Judging from the above results and discussion, it is not necessary to take into account the hydrogen atom abstraction from the solvent.

Reaction Scheme.—On the basis of the above results, we can summarize the reactions in deaerated benzene or acetonitrile in Scheme 2, from which eqns. (9), (10) and (11) are derived.

$$1 \xrightarrow{h\nu} {}^{1}1^{*} \qquad (1)$$

$$^{1}1^{*} \xrightarrow{k_d} 1 \qquad (2)$$

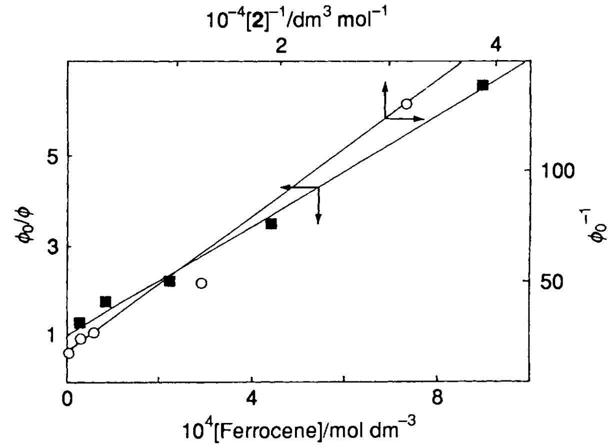


Fig. 5 Stern–Volmer plots for the quantum yield quenching by ferrocene (■) ([**2**] was fixed to be 4.0×10^{-3} mol dm^{-3}) and the effect of [**2**] on the quantum yield (○)

$$^1\mathbf{1}^* \xrightarrow{k_f} \mathbf{1} + h\nu' \tag{3}$$

$$^1\mathbf{1}^* + \mathbf{2} \xrightarrow{k_q^f} \mathbf{1} + \mathbf{2} \tag{4}$$

$$^1\mathbf{1}^* \xrightarrow{k_{isc}} {}^3\mathbf{1}^* \tag{5}$$

$$^3\mathbf{1}^* \xrightarrow{k_n} \mathbf{1} \tag{6}$$

$$^3\mathbf{1}^* + \mathbf{2} \xrightarrow{k_r} \mathbf{3} \tag{7}$$

$$^3\mathbf{1}^* + Q \xrightarrow{k_q} \mathbf{1} + Q^* \tag{8}$$

Scheme 2

$$k_{obs} = k_n + k_r[\mathbf{2}] \tag{9}$$

$$\varphi_0/\varphi = 1 + k_q[Q]/\{k_r[\mathbf{2}] + k_n\} \tag{10}$$

$$\varphi_0^{-1} = \varphi_{isc}^{-1}\{1 + k_n/k_r[\mathbf{2}]\} \tag{11}$$

Here, $^1\mathbf{1}^*$ is the singlet state of **1**. k_{obs} is the decay rate constant of $^3\mathbf{1}^*$ in the presence of **2**. φ_0 and φ are the quantum yield for the disappearance of **1** in the absence and in the presence of quencher Q, ferrocene, respectively. φ_{isc} is the quantum yield of the intersystem crossing of $^1\mathbf{1}^*$.

The quenching of dimer formation by ferrocene indicates that $^3\mathbf{1}^*$ is involved in the photoreaction. If the mode of formation of **3** comprises only process (7) then quenching of $^3\mathbf{1}^*$ should give a linear Stern–Volmer type plot. This is indeed the case and is shown in Fig. 5. k_n, k_r and k_q in eqns. (9) and (10) were respectively determined as 7.1×10^4 s^{-1}, 3.8×10^8 dm^3 mol^{-1} s^{-1} and 7.3×10^9 dm^3 mol^{-1} s^{-1} from the flash photolysis. k_r was obtained using eqn. (10) as 2.8×10^8 dm^3 mol^{-1} s^{-1} when the concentration of **2** was fixed at 4.0×10^{-3} mol dm^{-3}. In a similar manner, the plots of φ_0^{-1} *vs.* $[\mathbf{2}]^{-1}$ gave φ_{isc} and k_r in eqn. (11) as 0.07 and 2.4×10^8 dm^3 mol^{-1} s^{-1}, respectively (see Fig. 5). On the other hand, Bendig and Siegmund[9] have reported φ_{isc} as 0.96, which is much larger than the value obtained in this study. The values of k_r reasonably agree with those obtained using eqns. (9) and (10), demonstrating the validity of Scheme 2.

Mechanism of the Dimerization Reaction.—Scheme 3 is plausible for the reduction mechanism of $^3\mathbf{1}^*$ by **2**. Since the

$$\begin{tikzcd}
{}^3\mathbf{1}^* + \mathbf{2} \arrow[r] & \begin{array}{c}(\mathbf{1}^{\bullet -}\cdots\mathbf{2}^{\bullet +})\\ \text{Contact radical ion pair}\end{array} \arrow[r, shift left] \arrow[d] & \mathbf{4} + \text{Amino radical} \arrow[l, shift left] \arrow[d, "\mathbf{4}"] \\
& \mathbf{1} + \mathbf{2} & \mathbf{3}
\end{tikzcd}$$

Scheme 3

photoreaction occurs neither in benzene in the presence of aniline which makes a hydrogen bond with **1** nor in the hydrogen donating solvents, the electron transfer mechanism is therefore, involved in the formation of **4** in the **2** system which has two electron donating methyl groups. Thus, **4** may be produced by electron transfer followed by proton transfer from **2**. The first step is likely to be the formation of a contact radical ion pair between $^3\mathbf{1}^*$ and **2**. The contact radical ion pair may give **4** and the amine radical and/or the anion radical of **1** and the cation radical of **2** according to the polarity of the solvents. It supports Scheme 3 in that the yields of **3** and **4** depend on the solvent polarity. The quantum yield of **3** in acetonitrile is one-third of the value in benzene. In accordance with eqn. (11), plots of φ_0^{-1} *vs.* $[\mathbf{2}]^{-1}$ are found to be linear in acetonitrile solution. From the intercept, φ_{isc} is calculated to be 0.05. k_n and k_r in acetonitrile were determined as 3.5×10^4 s^{-1} and 1.4×10^8 dm^3 mol^{-1} s^{-1}, respectively from the flash photolysis. Using these values for calculating the quantum yield and assuming $^3\mathbf{1}^*$ in acetonitrile decays through the same processes as those in benzene, we obtain the value as 0.031 when [**2**] was fixed to be 4.0×10^{-4} mol dm^{-3}. Indeed, the quantum yield observed is 0.013. It is about a factor of 0.4 as small as that calculated. On the contrary, in the case of benzene, the quantum yield calculated, 0.042, is fairly in agreement with the experimental value, 0.043. This suggests the existence of other reaction pathways to suppress the formation of **3** in acetonitrile solution. In non-polar solvents, the deactivation process of the contact ion pair may be mainly the formation of **4**. In polar solvents, there may exist the formation of the anion radical besides that of **4**. This is likely to decrease the yield of **4** and consequently decreases that of **3**.

Picosecond flash photolysis of benzophenone–aromatic amine systems was performed by Simon and Peters.[10] They observed the formation process of the anion radical of benzophenone and showed there exists an equilibrium between the contact ion pair and the ketyl radical. The equilibrium constant decreases with an increase in the relative permittivity of the solvent which results in a smaller yield of the ketyl radical. In our case, the direct measurement of the formation of **4** is the problem in future. At present, however, it is evident that the yield of **4** and/or **3** depends on the polarity of the solvents, which strongly supports the existence of charged intermediates.

As to the fate of the α-amino radical, it most likely undergoes dimerization or disproportionation reactions.[11]

Experimental

Materials.—Compound **1** (Aldrich Chem. Co.) was recrystallized twice from ethanol with active carbon, **2** (special grade, Wako Junyaku) was purified by distillation under reduced pressure. Benzene (spectral grade, Wako Junyaku) and acetonitrile (spectral grade, Wako Junyaku) were used without further purification.

Apparatus.—Absorption and fluorescence spectra were

Table 1 The effects of concentrations of **2** and ferrocene on the quantum yields for disappearance of **1**

[**2**][a] $\times 10^4$ mol dm^{-3}	Quantum Yield $\varphi \times 10^2$	[Ferrocene][b] $\times 10^4$ mol dm^{-3}	φ_0/φ
0	0	0.4	1.30
0.3	0.8	0.9	1.75
0.8	2.7	2.2	2.20
4.0	4.3	4.5	3.42
8.0	4.8	9.0	6.50
40	6.9		
80	7.1		

[a] [**1**] was fixed to 7.1×10^{-5} mol dm^{-3}. [b] [**1**] and [**2**] were 7.1×10^{-5} and 4.0×10^{-3} mol dm^{-3}, respectively.

measured with a Hitachi ERI-G3 spectrophotometer and a JASCO FP-777 fluorometer, respectively. Fluorescence lifetime of **1** was measured by means of the time-correlated single photon counting method using a synchronously pumped, cavity dumped dye laser and a Hamamatsu R2809U MCP-PMT for detecting fluorescence. The response time of the apparatus was typically 50 ps.

Quantum Yield.—A Toshiba SHL-100 UV high pressure mercury lamp, equipped with Toshiba UVD-35 and L-1A filters, was used for the 365 nm irradiation (only **1** was excited). A sample cell was of a 1 × 1 × 4 cm quartz. The quantum yield of the photoreaction was determined at 23 °C using an aerated ethanol solution of acridine as an actinometer.[12] Unless otherwise noted, the sample solutions were degassed by the freeze-pump-thaw cycles or by flushing with argon. This latter technique gave the same results as the degassing procedure.

Flash Photolysis.—Flash photolysis was carried out using a conventional flash photolysis system. The flash energy was 60 J and full width at half-maximum was about 10 μs. A 135 W a xenon short arc lamp was used as the monitoring lamp with a L-42 filter. A Toshiba-UV 35 filter was usually used for excitation. The concentration of **1** was 7.1×10^{-5} mol dm^{-3} both in benzene and acetonitrile. The sample solutions were always new for every flashing. All the measurements were carried out at 23 °C.

Photochemical Preparation of **3**.—The solution of **1** in benzene (260 mg in 600 cm^3) was irradiated with a 400 W high pressure mercury lamp (Riko-400) in the presence of **2** (2.0 g) under argon for 15 min at 15 °C. After irradiation, benzene was removed by evaporation. Unreacted **2** was evaporated using a vacuum line system. One hundred fifty mg of crude **3** was obtained (yield 58%). It was washed with 10 cm^3 of cold benzene and 50 mg of pure **3** was obtained. **3**: Pale yellow powder, m.p. 184–188 °C. Found: C, 79.7; H, 5.9; N, 6.8%; Calc. for $C_{28}H_{24}N_2O_2$: C, 79.97; H, 5.75; N, 6.66%, HRMS ($M^+ - 17$) Found: 403.1801; Calc. for $C_{28}H_{22}NO_2$ 403.1810; IR (KBr) ν/cm^{-1} 3490, 1580, 1475 and 1358. δ_H(600 MHz, 23 °C, [$^2H_6$] acetone) 2.85 (Me), 5.20 (s, OH), 6.75 (H_2, dd, *J** 8.1, 0.9), 6.85 (H_4, t, *J* 7.2), 7.27 (H_3, ddd, *J* 8.1, 7.2, 1.9) and 7.79 (H_5, m); δ_C(150 MHz, 23 °C [$^2H_6$] Acetone) 33.88 (N-Me), 77.30 (C-OH), 111.68 (C_2), 119.48 (C_4), 126.31 (C_6), 128.79 (C_3), 128.88 (C_5) and 142.68 (C_1). Compound **3** is stable in crystalline form, but in solutions it decomposes slowly to **1**. This makes the identification of structure **3** difficult.

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* *J* values are given in Hz.