

QUENCHING OF EXCIPLEX WHICH EMITS VERY WEAKLY OR IS NOT EMISSIVE: EVIDENCE
FOR EXCIPLEX INTERMEDIACY IN FLUORESCENCE QUENCHING AND PHOTOCYCLOADDITION¹⁾

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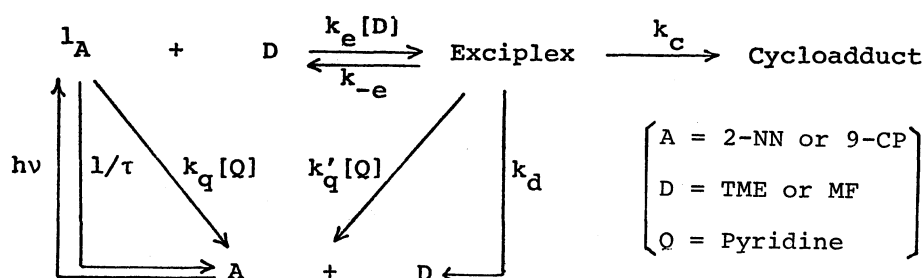
Pyridine quenched the exciplexes of 2-naphthonitrile—2-methylfuran
and —2,3-dimethylbut-2-ene which emit very weakly and that of
9-cyanophenanthrene—2,3-dimethylbut-2-ene which is not emissive.
There was provided evidence demonstrating that these exciplexes are
the intermediates in the photoreactions and reversibly formed.

Exciplex formation has been suggested to be a key mechanistic pathway in fluorescence quenching^{2,3)} and various photocycloadditions across aromatic rings.⁴⁻⁷⁾ The exciplex intermediacy requires evidence demonstrating that the intermediate is an electronically excited, stoichiometric molecular complex possessing a finite life.⁸⁾ The exciplex quenching method proposed by Caldwell and his coworkers can conveniently provide evidence for the exciplex intermediacy.^{6b,9)} However, this method has been applied to such limited exciplex systems that exciplex emission is so strong for its quenching by an exciplex quencher to be directly observed. In many cases, however, exciplex emission is very weak or absent.^{3,5,6a,7a,10-12)} Therefore, in order to apply the exciplex quenching method to these reaction systems, there must be found any other suitable method than the quenching of exciplex emission. The present communication provides evidence for the exciplex intermediacy in the fluorescence quenching and photoreactions of 2-naphthonitrile (2-NN)—2-methylfuran (MF) or —2,3-dimethylbut-2-ene (TME) and 9-cyanophenanthrene (9-CP)—TME systems, in which exciplex emission is very weak or absent.

The quenching of 2-NN fluorescence by MF and TME in air-saturated ethyl acetate¹³⁾ was inefficient, the Stern-Volmer slopes ($\gamma_0 k_e \tau$) being 3.0 and 1.8 M⁻¹, respectively, and very weak, new emissions appeared with the respective isoemissive

points at 402 and 396 nm,¹⁴⁾ thus showing exciplex formation. The quenching of 9-CP fluorescence by TME was again very inefficient ($\gamma_0 k_e \tau = 0.16 \text{ M}^{-1}$) but no new emission could be observed.

The inefficiency of the fluorescence quenching would be caused by reversible formation of an exciplex in equilibrium with its excited and ground state precursors 1A and D.^{3,10b,12)} If this is the case, the selective quenching of the exciplex by an exciplex quencher Q leads to increasing efficiency in the quenching of the fluorescence of A by D with increasing amount of added Q, as is shown in the reaction scheme and equation (1), where ϕ_f^O and ϕ_f^{DQ} represents the fluorescence yields of A in the absence and presence of both D and Q, respectively.



$$\phi_f^O / \phi_f^{DQ} = 1 + k_q \tau [Q] + \gamma k_e \tau [D] \quad (1)$$

$$\gamma = (k_c + k_d + k'_q [Q]) / (k_{-e} + k_c + k_d + k'_q [Q])$$

$$[Q] = 0, \gamma_0 = (k_c + k_d) / (k_{-e} + k_c + k_d)$$

In fact, when the fluorescence quenching was carried out in the presence of an exciplex quencher, pyridine, the quenching efficiency increased remarkably with the amounts of pyridine added (see the Table). Since pyridine does not significantly quench the fluorescence of A ($k_q \tau = 0.1 \text{ M}^{-1}$ for 2-NN fluorescence and 0.0 M^{-1} for 9-CP fluorescence), the effect of added pyridine would demonstrate the quenching of exciplexes formed in equilibrium with 1A and D. In this regard, it should be noted that the quenching of 2-NN fluorescence by MF and TME in neat pyridine was not accompanied by appearance of any new emission, showing the complete quenching of the exciplexes. Moreover, that pyridine can act as an exciplex quencher was confirmed by the quenching of exciplex emission from the other emissive exciplexes involving 2-NN and 9-CP (Figure 1).^{15,16)} Alternatively, the effect of pyridine could be interpreted in terms of increasing solvent polarity owing to added pyridine.¹⁷⁾ However, the fluorescence quenching in the presence of

6.2 vol% of t-butanol which is more polar than pyridine gave only ca. 10% greater Stern-Volmer slope than that in ethyl acetate in each case. Therefore, the solvent effect of added Q is not important.

The $\gamma k_e \tau$ values are listed in the Table, each of which was obtained from the Stern-Volmer plot with varying [D] in the presence of a fixed amount of Q in an air-saturated solution. The plots of $\gamma k_e \tau$ values vs. [Q] are shown in Figure 2. At lower [Q], the plots would be linear, provided $k'_q[Q] \ll (k_{-e} + k_c + k_d)$. With increasing [Q], however, $k'_q[Q]$ in denominator of γ can not be neglected, leading to departure from the linearity. This accords with the observation. At very high [Q], γ would reach unity, if $k'_q[Q] \gg (k_{-e} + k_c + k_d)$. The γk_e values in air-saturated pyridine were calculated to be $2 \sim 3 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}$ from the Stern-Volmer slopes (14 and 23.5 M^{-1}) and the estimated life time of 2-NN(S_1) and 9-CP(S_1) in air-saturated pyridine,¹⁸⁾ which reveal the occurrence of a diffusion-controlled quenching of the fluorescence of A by D in neat pyridine, i.e. $\gamma \approx 1$ and $k_e \approx 2 \sim 3 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}$. In ethyl acetate, therefore, exciplex formation can be believed to occur in a diffusion-controlled rate, i.e. $k_e \approx 10^{10} \text{ M}^{-1}\text{sec}^{-1}$, and hence the values of γ_0 must be much lower than unity, i.e. $k_{-e} \gg (k_c + k_d)$, suggesting reversible formation of the exciplexes.

Table. $\gamma k_e \tau$ Values (M^{-1}) for Fluorescence Quenching in the Presence of Pyridine^a

A	D	[Pyridine], M							
		0.0 ^b	0.04	0.08	0.12	0.2	0.4	0.8	Neat
2-NN	MF	3.0	-	4.4	-	5.5	8.5	12.6	14.0 ^c
	TME	1.8	3.0	4.4	5.4	8.0	13.0	18.0	14.0 ^c
9-CP	TME	0.16	-	-	-	0.28	0.47	0.77	23.5 ^c

^a [2-NN and 9-CP] = $5 \times 10^{-4} \text{ M}$ in air-saturated ethyl acetate at $17 \pm 1^\circ \text{C}$.
 Precision $\pm 5\%$. ^b $\gamma k_e \tau$ ^c Stern-Volmer slopes in pyridine.

The photocycloadditions of MF¹⁹⁾ and TME²⁰⁾ to 2-NN and of TME to 9-CP^{6a)} which occurred even in t-butanol were also quenched by pyridine. When pyridine was used as solvent, the photoreactions of 2-NN with MF and TME were completely quenched, whereas the photocycloaddition of TME to 9-CP was almost but not completely quenched. The latter photoreaction in pyridine which occurred at a rate only less than one-tenth that in ethyl acetate was completely quenched by adding 1.0 M isoprene to the pyridine solution, indicating partial participation of a triplet mechanism.^{6a,6b)}

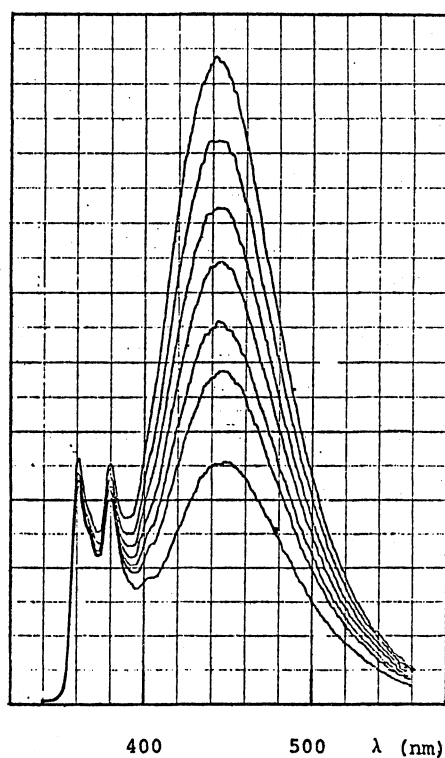


Figure 1. Quenching of 9-CP—2,5-dimethylhexa-2,4-diene exciplex by pyridine in deoxygenated benzene: $k'_q\tau_{ex} = 1.5 \text{ M}^{-1}$.

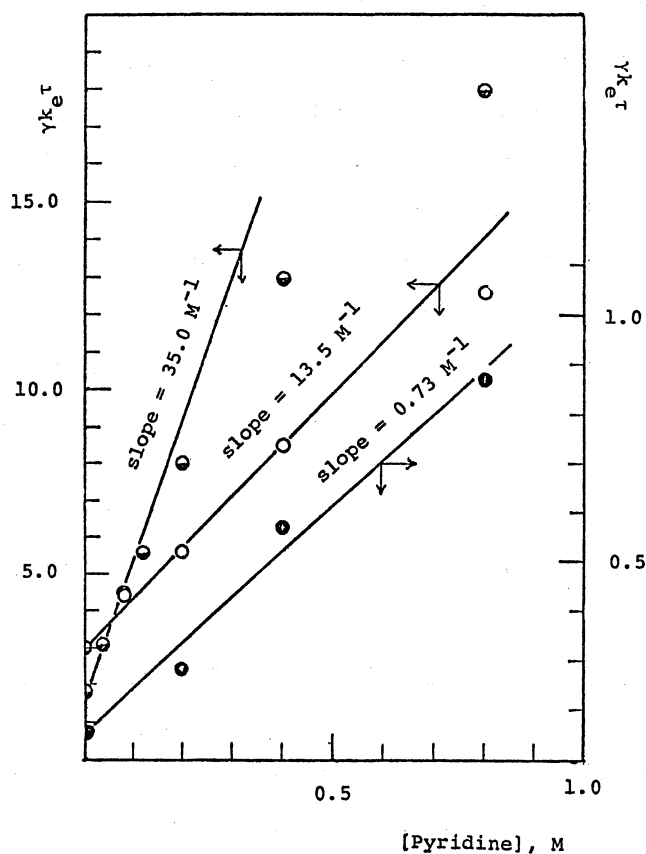


Figure 2. Plots of $\gamma k_e\tau$ vs. [Pyridine] for 2-NN—MF (—○—), 2-NN—TME (—◐—) and 9-CP—TME (—●—) systems.

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- 13) Unless otherwise specified, fluorescence measurements were carried out in air-saturated ethyl acetate solutions using a Hitachi MPF-2A spectrofluorometer.
- 14) McCullough et al. reported that no exciplex emission could be observed in the quenching of 2-NN fluorescence by TME.^{5b)}

- 15) The exciplex emissions from 2-NN— or 9-CP—2,5-dimethylhexa-2,4-diene and 2-NN—2,5-dimethylfuran exciplexes which are fairly strong were quenched by pyridine. Details will be published in a full paper.
- 16) Professor M. G. Kuzmin kindly suggested to us that pyridine quenches 9,10-dihaloanthracene—aliphatic amine exciplexes.
- 17) The quenching of 1- and 2-NN fluorescence by olefins and furan is usually more efficient in more polar solvents.^{5a,5b,7a,10a-c)}
- 18) (a) The lifetimes of 2-NN(S_1) in air-saturated cyclohexane, ethyl acetate and pyridine were estimated to be 11 ± 1 , 14 ± 1 and 5 ± 1 nsec, respectively, from the reported lifetime in degassed cyclohexane (26 nsec)^{18b)} and the ratios of fluorescence yields in corresponding solvent to that in degassed cyclohexane. In a similar way, the lifetime of 9-CP(S_1) was estimated to be 14 ± 1 nsec in air-saturated ethyl acetate and 9 ± 1 nsec in air-saturated pyridine.
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