Photochemical Reactions of Aromatic Compunds. XXXI.[1] Exciplex Quenching by Pyridine, Methylated Pyridines, and Methylated Imidazoles and Termolecular Interaction in the Excited Singlet State

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Pyridine, methylated pyridines, and methylated imidazoles quenched the exciplexes of aromatic nitrile–2,5-dimethylfuran or 2,5-dimethyl-2,4-hexadiene, and the rate constants for the exciplex quenching were obtained. The exciplex quenching by 2-methyl- and 2,6-dimethylpyridines was much less efficient than that by the other quenchers. The exciplex quenching was discussed in terms of the interaction of the n-orbital of the quenchers with the positive charge developed on the electron-donor side of the exciplexes. Curved Stern-Volmer plots were obtained in the quenching of aromatic nitrile fluorescence by 1-methylimidazole and/or 1,2-dimethylimidazole. On the basis of the kinetic results, the mechanism was discussed in terms of a termolecular interaction between excited singlet aromatic nitrile, the methylated imidazole as the π-donor, and the second one as the n-donor.

Exciplex formation has been recognized to be a general mechanistic pathway in fluorescence quenching[2,3] and has been suggested to precede photocycloadditions in a variety of reaction system.[4–6] We have also extensively investigated photocycloadditions of furan and olefinic compounds to aromatic nitriles, which have been suggested to occur *via* exciplexes.[7] In some exciplex-formation systems, the increase in the concentration of a precursor results in the formation of a termolecular excited complex (triplex), which arises from the interaction of a precursor with an exciplex.[8,9] This type of termolecular interaction can be considered to be rather general and has been suggested to be important in some photoreactions.[10] Caldwell and his co-workers reported a different type of termolecular interaction in the excited singlet state which occurs by means of the interaction of exciplexes with compounds which are not the precursors of the exciplexes and which possess either an electron-donor or an electron-acceptor nature.[11] In a previous paper,[12] we reported that pyridine quenches exciplexes which emit very weakly or which are not emissive at all. The exciplex quenching by pyridine provides a convenient method for establishing the existence of the exciplex intermediacy in our reaction systems. In the exciplex quenching, however, pyridine can act as either an n-donor or a π-acceptor, since it is weakly basic as well as π-deficient. In the present paper, we wish to report that pyridine, methylated pyridines, and methylated imidazoles quench the exciplexes of aromatic nitrile–2,5-dimethylfuran or 2,5-dimethyl-2,4-hexadiene by acting as n-donors, and that 1-methyl- and 1,2-dimethylimidazoles quench the fluorescence of aromatic nitriles by way of a termolecular process.

Table 1. Characteristics of exciplexes

	Exciplex		
	1-NN–DF	2-NN–DF	9-CP–DHD
$\lambda_{\max}$[a] (nm) C_6H_6	435	413	440
$\lambda_{\max}$[a] (nm) AcOEt	445	435	460
τ_{EX}[b] (ns)	32[c] (15)	28[c] (14)	21[d] (12)
Dipole momente[e] (D)	≈10	≈10	≈10
$\gamma_0 k_e$[f] (dm^3 mol^{-1} s^{-1}) $\times 10^{-9}$	8.1	2.6	8.1

a) Emission maxima of the exciplexes; 5×10^{-4} mol dm^{-3} in aromatic nitrile and 0.3 mol dm^{-3} in DF or DHD; ±2 nm. b) Lifetimes in degassed benzene; the numbers in parentheses are the lifetimes in air-saturated benzene; ±0.5 ns. c) Oxygen-quenching method. d) Determined by an N_2 laser-flash method. e) Calculated from the solvent shifts of the emission maxima. f) Apparent rate constants for the quenching of the aromatic nitrile fluorescence by DF or DHD.

Results

Characteristics of Exciplexes. For exciplex-quenching experiments, we employed the exciplexes of 1- and 2-naphthonitriles (1- and 2-NN)–2,5-dimethylfuran (DF) and 9-cyanophenanthrene (9-CP)–2,5-dimethyl-2,4-hexadiene (DHD), since these exciplexes can be considered to be typical models of the supposed intermediates in our reaction systems and all are fairly emissive. Table 1 lists the lifetimes of the exciplexes in a benzene solution containing 0.3 mol dm^{-3} in DF or DHD, the exciplex emission maxima in benzene and ethyl acetate solutions containing 0.3 mol dm^{-3} in DF or DHD, the calculated dipole moments, and the apparent rate constants ($\gamma_0 k_e$) of the quenching of the aromatic nitrile fluorescence by DF or DHD.

The lifetime of the 9-CP–DHD exciplex was directly determined by monitoring the decay of the exciplex fluorescence at 440 nm using an N_2 laser. When the decay of the residual 9-CP fluorescence was monitored at 375 nm, two decays were observed; the lifetimes of the slow and rapid decay components were calculated to be 17 ns and less than 2 ns respectively. The slow-decay component apparently arises from the reversible dissociation of the exciplex into an excited singlet 9-CP and a ground-state DHD. However, the reversible dissociation can be considered to be not so significant, since the quenching of the 9-CP fluorescence by DHD occured at a diffusion-controlled rate. The lifetimes of

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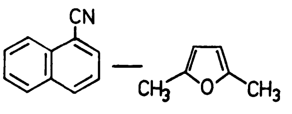
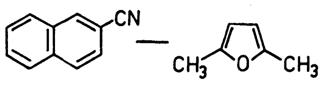
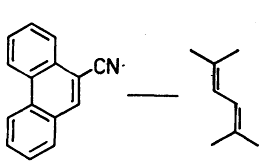
the 1-NN- and 2-NN-DF exciplexes were determined by the oxygen-quenching method proposed by Caldwell.[13]



1-NN DF



2-NN DF



9-CP DHD

These exciplexes are charge-transfer complexes in nature, as is shown by the dipole moment, which was obtained by a usual method using plots of the wave numbers of the emission maxima in various solvents *vs.* $[(\varepsilon-1)/(2\varepsilon-1)-(n^2-1)/2(2n^2-1)]$,[14] where ε and n represent the dielectric constant and the refractive index of the solvent respectively. The slopes of the plots are commonly $(10\pm1)\times10^3$ cm^{-1}, which corresponds to *ca.* 10 Debey units of the dipole moment. The 9-CP-DHD exciplex crosses over a $2\pi+2\pi$ cycloadduct,[7f] while the 1- and 2-NN-DF exciplexes do not result in the formation of any stable products at room temperature. The UV spectra showed no indication of the formation of charge-transfer complexes in the ground state.

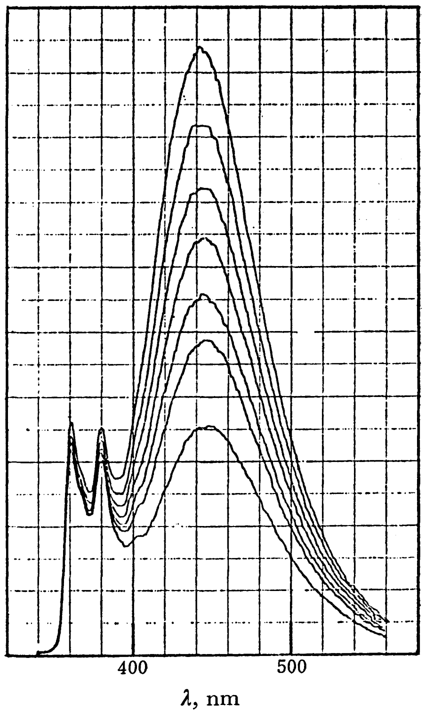
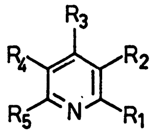
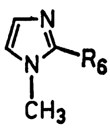


Fig. 1. Quenching of 9-CP-DHD exciplex by **1a** in deoxygenated benzene: $k_q\tau_{EX}=1.5$ dm^3 mol^{-1}.

Exciplex Quenching by Pyridine and Imidazole Compounds. For the exciplex quenching, we used pyridine (**1a**), 2-, 3-, and 4-methylpyridines (**1b**, **1c**, and **1d**), 2,6- and 3,5-dimethylpyridines (**1e** and **1f**), 1-methylimidazole (**2a**), and 1,2-dimethylimidazole (**2b**) as quenchers. The exciplex-quenching experiments were carried out as usual. Figure 1, for example, shows the spectral change in the fluorescence from a benzene solution containing 5×10^{-4} mol dm^{-3} in 9-CP and 0.3 mol dm^{-3} in DHD on the addition of **1a**. The exciplex emission with the maximum at 440 nm was significantly quenched. The plot of the relative intensities at 440 nm in the absence of and in the presence of **1a** (I^0_{EX}/I^Q_{EX}) *vs.* the concentrations of **1a** gave a linear line, the slope of which was 1.5 dm^3 mol^{-1} (Fig. 4); the rate constant (k_q) of the exciplex quenching was calculated to be 7.1×10^7 dm^3 mol^{-1} s^{-1} by applying the slope to Eq. a, where τ_{EX} and Q represent the lifetimes of an exciplex and an exciplex quencher respectively. Similarly, the rate constants of the quenching of the 1- and 2-NN-DF exciplexes by pyridine were calculated to be 3.5×10^8 and 2.6×10^8 dm^3 mol^{-1} s^{-1} respectively.

$$I^0_{EX}/I^Q_{EX} = 1 + k_q\tau_{EX}[Q] \qquad \text{(a)}$$





1a: $R_1=R_2=R_3=R_4=R_5=H$
1b: $R_1=CH_3$, $R_2=R_3=R_4=R_5=H$
1c: $R_2=CH_3$, $R_1=R_3=R_4=R_5=H$
1d: $R_3=CH_3$, $R_1=R_2=R_4=R_5=H$
1e: $R_1=R_5=CH_3$, $R_2=R_3=R_4=H$
1f: $R_2=R_4=CH_3$, $R_1=R_3=R_5=H$

2a: $R_6=H$
2b: $R_6=CH_3$

As is shown in Fig. 1, the residual 9-CP fluorescence at 360—380 nm was also slightly quenched by pyridine. Similarly, a slight quenching of the residual 1- and 2-NN fluorescence was also observed in the quenching of the 1- and 2-NN-DF exciplexes by pyridine. In contrast, the 2-NN or 9-CP fluorescence in the absence of DF or DHD was not quenched at all by pyridine, while the quenching of the 1-NN fluorescence by pyridine was relatively efficient, the rate constant being 3×10^8 dm^3 mol^{-1} s^{-1}. Therefore, the quenching of the residual 2-NN or 9-CP fluorescence can be ascribed to the decrease in the reversible dissociation of the exciplex because of the exciplex quenching. In the case of the 1-NN-DF exciplex, however, the slight quenching of the residual 1-NN fluorescence would be caused by either the exciplex quenching or the direct quenching of the excited singlet 1-NN by pyridine.

Table 2 lists the quenching constants ($k_q\tau^{air}_{EX}$) for each exciplex-quencher pair; they were obtained by the usual Stern-Volmer plots for air-saturated benzene and ethyl acetate solutions, using Eq. a but replacing τ_{EX} by τ^{air}_{EX}, the lifetime in air-saturated solutions. In order to avoid the quenching of excited-singlet aromatic

Table 2. Quenching of exciplex emission by exciplex quenchers[a)]

Quencher	$k_q\tau_{EX}^{air}$ ($dm^3\ mol^{-1}$)					
	1-NN-DF		2-NN-DF		9-CP-DHD	
	C_6H_6	AcOEt	C_6H_6	AcOEt	C_6H_6	AcOEt
1a	5.6(11.3)[b)]	9.6	3.6(7.2)[b)]	7.7	0.9(1.5)[b)]	2.6
1c	—	10.5	—	8.5	1.1	—
1d	8.0	11.0	—	9.3	1.4	3.3
1f	—	11.0	—	12.0	—	—
1b	0.8	≈1.0	—	≈0.5	<0.2	<0.2
1e	—	≈0.3	—	<0.1	<0.1	—
2a	37.5	—	20.5	—	4.9	9.0
2b	12.2	—	12.0	—	—	—

a) In air-saturated solutions; 5×10^{-4} mol dm^{-3} in aromatic nitriles and 0.3 mol dm^{-3} in DF or DHD. b) In degassed benzene.

nitrile, the concentrations of the quenchers were kept as low as the quenching of excited-singlet aromatic nitrile, which was negligible except for the exciplex quenching by **1b** and **1e**. There was no indication of the formation of any charge-transfer complexes between A or D and Q in the ground state.

*Quenching of Aromatic Nitrile Fluorescence by **2a** and **2b**.* The fluorescence of 1- and 2-NN was quenched by **2a**. Interestingly, the Stern-Volmer plots were not linear (Fig. 2). In the fluorescence quenching, very weak exciplex emissions appeared, but no isoemissive points could be observed. The 9-CP fluorescence was not quenched by **2a** at all. The quenching of the 2-NN and 9-CP fluorescence by **2b** gave, again, slightly curved Stern-Volmer plots, while that of the 1-NN fluorescence was efficient and gave a linear Stern-Volmer plot (Fig. 3). In the latter quenching, a fairly strong exciplex emission with the maximum at 408 nm appeared without an isoemissive point; it revealed its maximum intensity at the concentration of 1.8×10^{-2} mol dm^{-3} of added **2b**. A further increase in the **2b** concentration

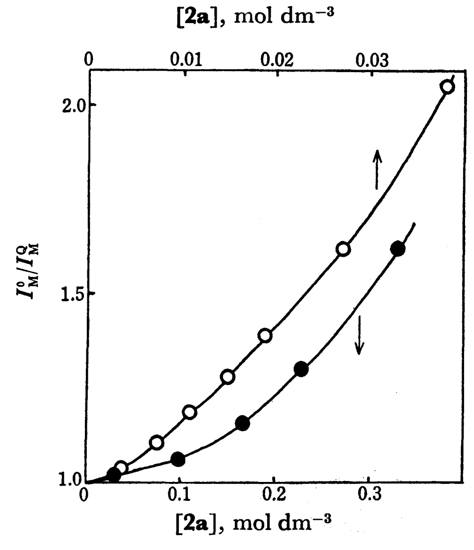


Fig. 2. Stern-Volmer plots for the quenching of 1-NN (-○-) and 2-NN (-●-) fluorescence by **2a** in air-saturated benzene, [1- and 2-NN]=5×10^{-4} mol dm^{-3}.

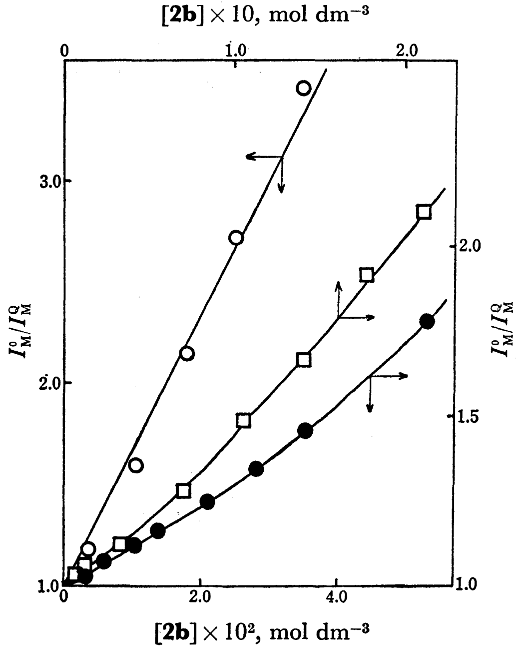


Fig. 3. Stern-Volmer plots for the quenching of 1-NN (-○-) 2-NN (-●-), and 9-CP (-□-) fluorescence by **2b** in air-saturated benzene, [Aromatic Nitrile]=5×10^{-4} mol dm^{-3}.

Table 3. Quenching of 1-NN fluorescence by **2b**[a)]

[**2b**] $\times10^2$ (mol dm^{-3})	0.36	1.1	1.8	2.5	3.6	5.4	7.2	10.8
I^0_M/I^Q_M [b)]	1.16	1.58	2.14	2.72	3.47	—	—	—
$\phi_{EX}/\phi_{EX}^{max}$ [c,d)]	0.47	0.92	1.00	0.99	0.93	0.80	0.69	0.54
L_{max}/L [d)]	0.77	0.90	1.00	1.11	1.32	1.48	1.79	2.28

a) In air-saturated benzene, 5×10^{-4} mol dm^{-3} in 1-NN. b) Relative intensities of the 1-NN fluorescence at 340 nm in the absence and in the presence of **2b**. c) Relative intensities of the exciplex emission at 408 nm. d) See the text.

resulted in a decrease in the exciplex emission. Table 3 summarizes the relative intensities of 1-NN fluorescence at 340 nm (I_M^0/I_M^Q) and those of the exciplex emission at 408 nm ($\phi_{EX}/\phi_{EX}^{max}$), the atterl of which are corrected by subtracting the intensity of the 1-NN fluorescence at 408 nm from the total intensity at this wavelength. The curved Stern-Volmer plots could be caused by the formation of charge-transfer complexes in the ground state. However, UV measurements eliminated this posibility.

Discussion

Mechanism of Exciplex Quenching. Scheme 1 shows the reaction processes involving the exciplex formation and the quenching of the exciplex, where A, D, $[A^-D^+]^*$, and Q represent the aromatic nitriles, DF or DHD, the exciplexes, and the exciplex quenchers respectively. Processes 1 and 4 involve all the unimolecular physical decays of A and $[A^-D^+]^*$ respectively. Equations b and c are the Stern-Volmer equations for the quenching of the Nonomer (A) fluorescence by D in the absence of Q and of exciplex emission at a constant concentration of D (0.3 mol dm^{-3}) by Q respectively.

$$\mathrm{A} \xrightarrow{h\nu} {}^1\mathrm{A}^*$$

$$ {}^1\mathrm{A}^* \xrightarrow{1/\tau_M} \mathrm{A} + h\nu' \text{ (or heat)} \qquad (1)$$

$$ {}^1\mathrm{A}^* + \mathrm{Q} \xrightarrow{k_q'} \mathrm{A} + \mathrm{Q} \qquad (2)$$

$$ {}^1\mathrm{A}^* + \mathrm{D} \underset{k_{-e}}{\overset{k_e}{\rightleftarrows}} [\mathrm{A}^-\mathrm{D}^+]^* \qquad (3)$$

$$ [\mathrm{A}^-\mathrm{D}^+]^* \xrightarrow{k_d} \mathrm{A} + \mathrm{D} + h\nu'' \text{ (or heat)} \qquad (4)$$

$$ [\mathrm{A}^-\mathrm{D}^+]^* \xrightarrow{k_p} \text{Product(s)} \qquad (5)$$

$$ [\mathrm{A}^-\mathrm{D}^+]^* + \mathrm{Q} \xrightarrow{k_q} \mathrm{A} + \mathrm{D} + \mathrm{Q} \qquad (6)$$

Scheme 1.

$$I_M^0/I_M^Q = 1 + \gamma_0 k_e \tau_M[\mathrm{D}] \qquad \text{(b)}$$

$$\gamma_0 = (k_d+k_p)/(k_{-e}+k_d+k_p) \approx 1$$

$$I_{EX}^0/I_{EX}^Q = \left(1+\frac{k_q'\tau_M[\mathrm{Q}]}{1+k_e\tau_M[\mathrm{D}]}\right)(1+k_q\tau_{EX}[\mathrm{Q}]) \qquad \text{(c)}$$

The value of γ_0 is nearly unity, since the fluorescence of A was quenched by D at a diffusion-controlled rate *i.e.*, $k_{-e} \ll k_d+k_p$; the exciplexes are almost irreversibly formed. In the presence of 0.3 mol dm^{-3} in D, therefore, Eq. c can be reduced to Eq. a, since $1 \gg k_q'\tau_M[\mathrm{Q}]/(1+k_e\tau_M[\mathrm{D}])$. The calculated k_q values for the quenching of the exciplexes by pyridine are one or two orders lower than the diffusion-controlled rate, showing that pyridine is an inefficient quencher for the exciplexes. Significantly, however, pyridine does not quench the 2-NN and 9-CP fluorescence at all; thus, it can be used as a selective quencher for the exciplexes involving nitriles.12) The photocycloaddition of DHD to 9-CP7f) was also quenched by pyridine; the Stern-Volmer plot gave the $k_q\tau_{EX}$ value of 1.95±0.5 dm^3 mol^{-1}, which is very similar to that obtained from exciplex-emission-quenching experiments' (Fig. 4). The results clearly demonstrate the intermediacy of the exciplex in the photocycloaddition.

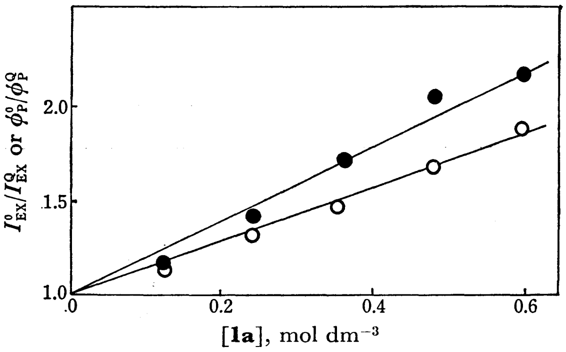
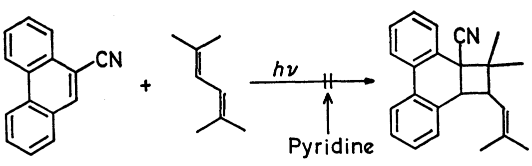
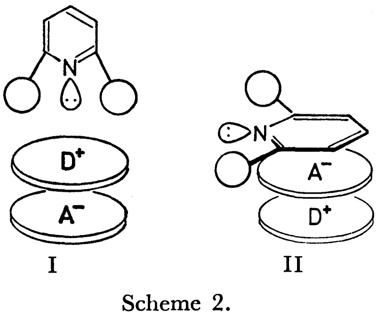


Fig. 4. Stern-Volmer plots for the quenching of 9-CP–DHD exciplex by **1a** in degassed benzene; fluorescence quenching (-○-) and product quenching (-●-) runs, [9-CP]$=5\times10^{-4}$ mol dm^{-3} and [DHD]$=0.3$ mol dm^{-3}.



According to Caldwell's generalization of exciplex quenching,11) an exciplex quencher possessing an electron-donor or electron-acceptor nature (Q_D or Q_A) interacts with an exciplex $[A^-D^+]^*$ on the D or A side *i.e.*, $A^{\delta-}\cdots D\cdots Q_D^{\delta+}$ or $Q_A^{\delta-}\cdots A\cdots D^{\delta+}$. This termolecular interaction results in exciplex quenching. Therefore, if pyridine acts as an n-donor in the exciplex quenching, the n-orbital of pyridine must perpendicularly approach to the molecular plane of the D side of exciplexes (I in Scheme 2). On the other hand, the pyridine which acts as a π-acceptor can interact with the A side of exciplexes with a sandwich type of configuration (II).



Scheme 2.

As is shown in Table 2, methyl substitution at the 2- and 2,6-positions of the pyridine ring commonly leads to a marked decrease in the quenching ability of the three exciplexes, while substitution at the other positions instead slightly enhances the quenching rate. The effect of the methyl groups at the 2- and 2,6-positions demonstrates the dominant n-donor character in the exciplex quenching. The methyl groups of **1b** and **1e** would sterically inhibit the approach of the n-orbital to the exciplexes within an effective distance for the quenching. In the cases of the other methylated pyridines, such steric hindrance can not occur in the attack of the n-orbital on the exciplexes. Moreover, this mechanism is supported by the observation that the $k_q\tau_{EX}^{air}$ values increase with the increase in the base strength of the quenchers; methyl substitution in the pyridine ring enhances the base strength, and imidazole is much more strongly basic, but less π-defficient, than pyridine.[15] In line with this mechanism, **2a** is a much more efficient quencher than **1a**. Methyl substitution at the 2-position of the imidazole ring results, again, in a decrease in the quenching efficiency to some extent, though the steric effect is much smaller than that of the methyl group of **1b**; the difference in the steric effects can be easily predicted by molecular models. In conclusion, the exciplex quenching occurs by means of the attack of the n-orbital of the quenchers on the positive charge developed on the D side because of a high degree of charge-transfer contribution to the exciplexes. The ionic or charge-transfer nature of the exciplex quenching is supported by the observation that the $k_q\tau_{EX}^{air}$ values in ethyl acetate are greater than those in benzene.

Quenching of Aromatic Nitrile Fluorescence by 2a and 2b. The quenching of the 1- and 2-NN fluorescence by **2a** gave curved Stern-Volmer plots, which, it may be suggested, occur by way of a termolecular process involving the exciplexes of 1- and 2-NN–**2a**. The termolecular mechanism is further suggested by the observation that the emission of the 1-NN–**2b** exciplex increases up to the concentration of 1.8×10^{-2} mol dm^{-3} in **2b**, but decreases upon a further increase in the concentration of **2b**. In Scheme 3, therefore, the reaction processes are shown, where A, Q, and [AQ]* denote the aromatic nitriles, **2a** or **2b**, and the exciplexes respectively. The process for the formation of stable products, [AQ]* and/or [AQ]*+Q→Products, can be discarded, since no products could be detected. Equation d represents the Stern-Volmer equation for the quenching of the aromatic nitrile fluorescence by Q, whereas Eq. e shows the quantum yield of the 1-NN–**2b** exciplex emission at a given concentration of Q.

$$\mathrm{A} \xrightarrow{h\nu} {}^1\mathrm{A}^*$$

$${}^1\mathrm{A}^* \xrightarrow{1/\tau_\mathrm{M}} \mathrm{A} + h\nu' \text{ (or heat)} \tag{7}$$

$${}^1\mathrm{A}^* + \mathrm{Q} \underset{k_{-\mathrm{e}}}{\overset{k_\mathrm{e}}{\rightleftarrows}} [\mathrm{AQ}]^* \tag{8}$$

$$[\mathrm{AQ}]^* \xrightarrow{k_\mathrm{f}} \mathrm{A} + \mathrm{Q} + h\nu'' \tag{9}$$

$$[\mathrm{AQ}]^* \xrightarrow{k_\mathrm{d}} \mathrm{A} + \mathrm{Q} + \text{heat} \tag{10}$$

$$[\mathrm{AQ}]^* + \mathrm{Q} \xrightarrow{k_\mathrm{q}} \mathrm{A} + 2\mathrm{Q} \tag{11}$$

Scheme 3.

$$I_\mathrm{M}^0/I_\mathrm{M}^\mathrm{Q} = 1 + \left\{\frac{1+k_\mathrm{q}\tau_\mathrm{EX}^0[\mathrm{Q}]}{1+(k_{-\mathrm{e}}+k_\mathrm{q}[\mathrm{Q}])\tau_\mathrm{EX}^0}\right\}k_\mathrm{e}\tau_\mathrm{M}[\mathrm{Q}] \tag{d}$$

$$\tau_\mathrm{EX}^0 = 1/(k_\mathrm{d}+k_\mathrm{f})$$

$$\phi_\mathrm{EX} = \left(\frac{I_\mathrm{M}^\mathrm{Q}}{I_\mathrm{M}^0}\right)\left\{\frac{k_\mathrm{f}\tau_\mathrm{EX}^0}{1+(k_{-\mathrm{e}}+k_\mathrm{q}[\mathrm{Q}])\tau_\mathrm{EX}^0}\right\}k_\mathrm{e}[\mathrm{Q}] \tag{e}$$

If the reversible dissociation of the exciplex into ^{1}A* and Q can be neglected (*i.e.*, $k_{-\mathrm{e}} \ll k_\mathrm{d}+k_\mathrm{f}$), Eq. d can be reduced to a usual Stern-Volmer equation; thus, the fluorescence quenching would give a linear Stern-Volmer plot. The quenching of the 1-NN fluorescence by **2b** fits the case (Fig. 3); the k_e value was calculated to be $(9.3\pm1.0)\times10^9$ dm^3 mol^{-1} s^{-1} from the slope of the Stern-Volmer plot (71.0 dm^3 mol^{-1}) and the lifetime of the excited singlet 1-NN in air-saturated benzene (7.5±0.5 ns). The occurrence of a diffusion-controlled fluorescence quenching demonstrates the negligible importance of the reversible dissociation.

If the reversible dissociation can not be neglected,

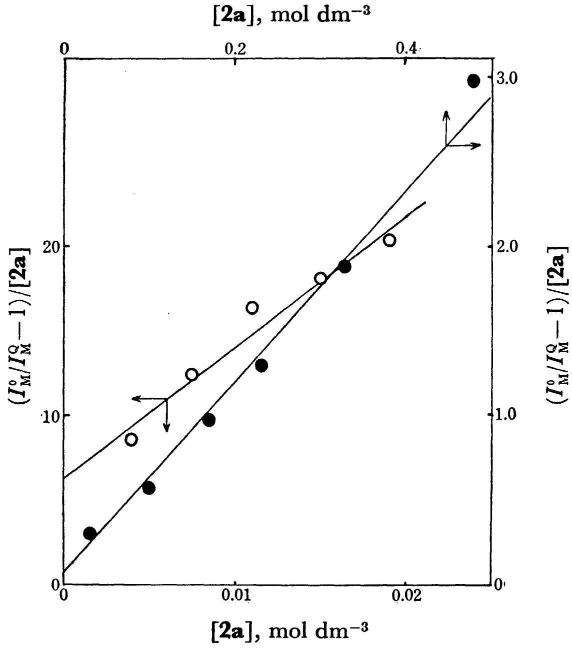


Fig. 5. Plots of $(I_\mathrm{M}^0/I_\mathrm{M}^\mathrm{Q}-1)/[\mathbf{2a}]$ *vs.* [**2a**] for 1-NN (-○-) and 2-NN (-●-) using the data in Fig. 2.

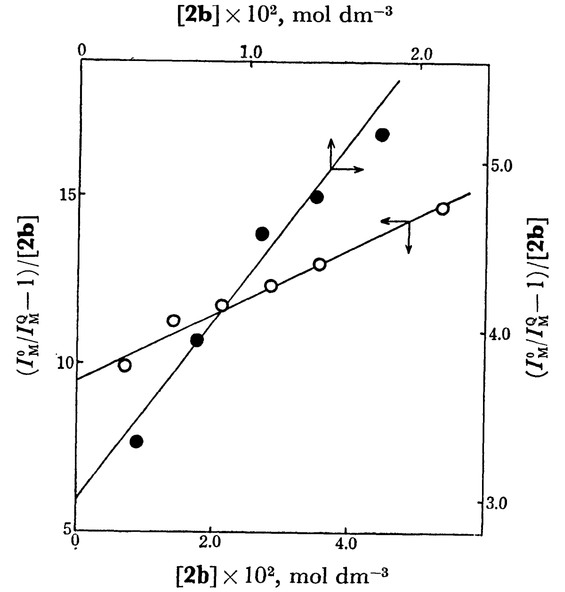


Fig. 6. Plots of $(I_\mathrm{M}^0/I_\mathrm{M}^\mathrm{Q}-1)/[\mathbf{2b}]$ *vs.* [**2b**] for 2-NN (-○-) and 9-CP (-●-) using the data in Fig. 3.

TABLE 4. RATE CONSTANTS FOR QUENCHING OF AROMATIC NITRILE FLUORESCENCE BY **2a** AND **2b**[a)]

	2a		**2b**		
	1-NN	2-NN	1-NN	2-NN	9-CP
τ_M [b)] (ns)	7.5	10.0	7.5	10.0	10.0
$\{1/(1/\tau^0_{EX}+k_{-e})\tau^0_{EX}\}k_e\tau_M$ ($dm^3\ mol^{-1}$)	6.1	0.06	71.0	9.5	3.0
$k_e/(1/\tau^0_{EX}+k_{-e})\tau^0_{EX}$ ($dm^3\ mol^{-1}\ s^{-1}$)	8.1×10^8	6×10^6	9.3×10^9	9.5×10^8	3×10^8
$k_q\tau^0_{EX}$ ($dm^3\ mol^{-1}$)	179	93.3	22.0	10.0	4.4

a) In air-saturated benzene, 5×10^{-4} mol dm^{-3} in aromatic nitriles. b) Lifetimes of excited singlet aromatic nitriles in air-saturated benzene; ±0.5 ns.

Eq. d predicts non-linear Stern-Volmer plots (Figs. 2 and 3). Equation d can be transformed into Eq. f; thus, the plots of $(I^0_M/I^Q_M-1)/[Q]$ *vs.* [Q] are shown in Figs. 5 and 6, using the data in Figs. 2 and 3. Equation f predicts that the plots will be linear at lower concentrations of Q, provided $k_q[Q]\ll k_d+k_f+k_{-e}$, while a deviation from the linearity occurs at higher concentrations of Q. The results are in good accord with this prediction.

$$(I^0_M/I^Q_M-1)/[Q] = \frac{k_e\tau_M}{1+(k_{-e}+k_q[Q])\tau^0_{EX}} + \frac{k_e\tau_M k_q\tau^0_{EX}[Q]}{1+(k_{-e}+k_q[Q])\tau^0_{EX}} \qquad \text{(f)}$$

When the slopes and intercepts in Figs. 5 and 6 applied to Eq. f, one can obtain the values of $\{1/(1/\tau^0_{EX}+k_{-e})\cdot\tau^0_{EX}\}k_e$ and $k_q\tau^0_{EX}$ listed in Table 4. The former is the apparent rate constant for the formation of the exciplex, in which the reversible dissociation of the exciplex is taken into account. In the case of the 2-NN–**2a** exciplex, the rate constant is three orders lower than the diffusion-controlled rate, suggesting the dominant dissociation; the exciplex formation must be isothermal or only slightly exothermic. In the cases of all the other exciplexes except the 1-NN–**2b** exciplex, the dissociation is also important. The curved Stern-Volmer plots arise from the quenching of the exciplexes by **2a** or **2b**. The $k_q\tau^0_{EX}$ values can be obtained by dividing the slopes by the intercepts in Figs. 5 and 6.

In the case of the 1-NN–**2b** exciplex, the $k_q\tau^0_{EX}$ value should be calculated by another method, since the Stern-Volmer plot for the quenching of the 1-NN fluorescence by **2b** gives a linear line. If Eq. g represents the maximum quantum yield of the 1-NN–**2b** exciplex emission observed in the presence of 1.8×10^{-2} mol dm^{-3} in **2b** ($[Q]_{max}$), Eq. h can be finally obtained by dividing Eq. g by Eq. e and by a subsequent transformation:

$$\phi^{max}_{EX} = \left(\frac{I^Q_M}{I^0_M}\right)_{max}\left(\frac{k_f\tau^0_{EX}}{1+k_q\tau^0_{EX}[Q]_{max}}\right)k_e[Q]_{max} \qquad \text{(g)}$$

$$L_{max}/L = \left(\frac{\phi^{max}_{EX}}{\phi_{EX}}\right)\left(\frac{[Q]}{[Q]_{max}}\right)\left\{\frac{(I^Q_M/I^0_M)}{(I^Q_M/I^0_M)_{max}}\right\} = \left(\frac{1}{1+k_q\tau^0_{EX}[Q]_{max}}\right)(1+k_q\tau^0_{EX}[Q]) \qquad \text{(h)}$$

Since the 1-NN–**2b** exciplex is almost irreversibly formed, k_{-e} was omitted in Eqs. e, g, and h. Thus, L_{max}/L was plotted *vs.* [Q] using the data in Table 3; a good linear line was thus obtained (Fig. 7). The $k_q\tau^0_{EX}$ value was calculated to be 22.0 dm^3 mol^{-1} by dividing the slope by the intercept, or 24.1 dm^3 mol^{-1} from the intercept. Although the latter must include a greater error than the former, the agreement between the calculated values is good within the limits of experimental error.

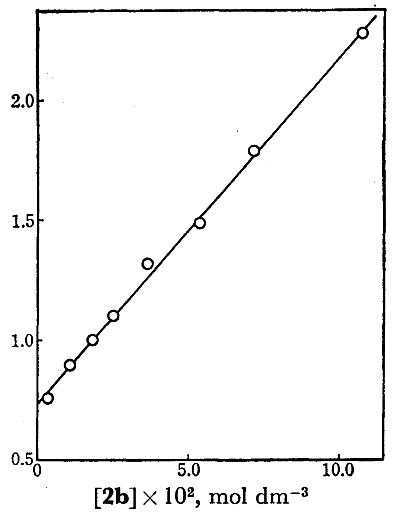
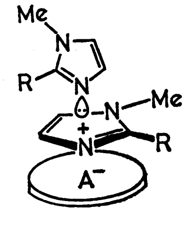


Fig. 7. Plots of L_{max}/L *vs.* [**2b**], using the data in Table 3.

The apparent rate constants for the formation of the 1- and 2-NN–**2a** exciplexes are much lower than those for the exciplexes of **2b**. This suggests that **2a** and **2b** act as π-donors in the exciplex formation, since **2b** is apparently a stronger π-donor than **2a**. In contrast, the $k_q\tau^0_{EX}$ values for 1- and 2-NN–**2a** system are about ten times greater than those for the 1- and 2-NN–**2b** system respectively. The difference between the $k_q\tau^0_{EX}$ values for **2a** and **2b** suggests that **2a** and **2b** act as n-donors in Process 11, as is illustrated as III; the methyl group at the 2-position of **2b** sterically inhibits the interaction of the n-orbital with the 1- and 2-NN–**2b** exciplexes, leading to lower k_q values than those for **2a**, as has been discussed in the foregoing section.



III

Unfortunately, the k_q values which are essential for the discussion can not be calculated, since the τ^0_{EX} values are not available. However, the participation of the n-orbital in Process 11 is further supported by the fact that DF and 1-methylpyrrole, which are strong π-donors but are very weakly basic, do not interact with the respective exciplexes of 1- or 2-NN up to 0.1 mol dm^{-3}, though they do quench the 1- and 2-NN fluorescence at a diffusion-controlled rate.[16] In summary, the termolecular interactions in the exciplex quenching and the quenching of aromatic nitrile fluorescence by **2a**, **b** occur upon the attack of **1** and **2** as n-donor, Q_n, on the exciplexes, $[A_\pi^- D_\pi^+]^*$ or $[A_\pi^- Q_\pi^+]^*$, giving rise to a purturbation of the exciplexes, by which non-radiative decays may be assisted. The interaction of triplexes, $[A_\pi D_\pi Q_n]^*$ or $[A_\pi Q_\pi Q_n]^*$, provokes an interesting speculation, though triplex emission could not be observed; the triplexes may rapidly collapse into the precursors in the ground state without emission and/or into triplet-state species. Alternatively, the interaction of Q_n with the exciplexes may cause a complete electron transfer from D_π or Q_π to A_π, leading to such ion-pairs as $[A_\pi^- \cdots (D_\pi Q_n)^+]_{solv}$ or $[A_\pi^- \cdots (Q_\pi Q_n)^+]_{solv}$; the electron reversal in the ion-pairs may exclusively occur to result in the collapse in to the precursors in the ground-state or triplet-state species because of the low polarity of the solvent. However, it should be pointed out that the decay channels are still open to question.

Experimental

The 1- and 2 naphthonitriles (Tokyo Kasei Co., Ltd.) were distilled under a high vacuum, chromatographed on silica gel, and recrystallized three times from hexane. The 9-cyanophenanthrene was prepared by a known method,[17] distilled under a high vacuum, and recrystallized three times from methanol. The 2,5-dimethyl-furan and 2,5-dimethyl-2,4-hexadine (Tokyo Kasei Co., Ltd.) were distilled from sodium under a pure nitrogen stream before use. The pyridine, methylated pyridines, 1-methylimidazole, and 1,2-dimethylimidazole (Tokyo Kasei Co., Ltd.) were all distilled from anhydrous potassium hydroxide under a pure nitrogen stream before use. The benzene and ethyl acetate (spectrograde, Nakarai Chemicals) were distilled before use.

The measurements of the fluorescence spectra and the fluorescence-quenching experiments were carried out with a Hitachi MPF-2A spectrofluorometer. The product analysis were carried out with a Shimadzu GC-2C gas chromatograph using a column of SE-30 (5% on Celite 545, 0.75 m) at 140—170 °C, a Hitachi R-24 (60 MHz) NMR spectrometer, and a Hitachi 124 UV spectrometer.

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