May, 1982] © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***55***, *1605—1616 (1982)* 1605

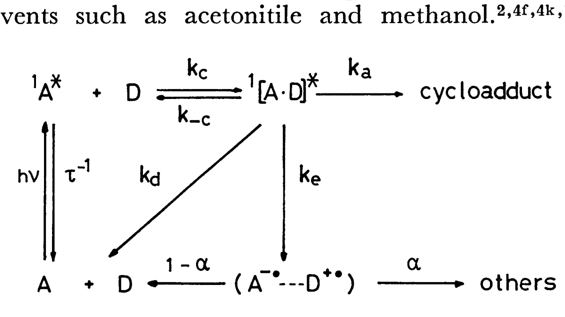
Photochemical Reactions of Aromatic Compounds. XXXVII.1) Solvent Effects on Fluorescence Quenching and Photoreactions of Naphthonitrile-Olefin and Furan Systems. Qualitative Consideration on Electronic Structures and Reactivities of Nonemissive Exciplexes

Chyongjin PAC,* Masahide YASUDA, Kensuke SHIMA,†
and Hiroshi SAKURAI
Department of Chemical Process Engineering, Faculty of Engineering,
Osaka University, Suita, Osaka 565
†*Department of Industrial Chemistry, Faculty of Engineering, Miyazaki University, Miyazaki 880*

(Received October 29, 1981)

Solvent effects on the fluorescence-quenching rate constants (γk_c) as well as on the quantum yields ($\phi^{\infty}_{-\mathrm{A}}$) of photoreactions have been investigated for the nonemissive exciplex systems in which 1- or 2-naphthonitrile is the electron acceptor whereas the donors are some enol ethers, a few simple alkenes, furan, 2-methylfuran, and ethyl phenyl ether. On the basis of the assumption of the solvent as a continuous dielectric medium, the relationships between electronic structures and reactivities of nonemissive exciplexes have been qualitatively estimated from the plots of log γk_c and log $[\phi^{\infty}_{-\mathrm{A}}/(1-\phi^{\infty}_{-\mathrm{A}})]$ *vs.* $(\varepsilon-1)/(2\varepsilon+1)$. In nonpolar and moderately polar aprotic solvents, the nonemissive exciplexes have low charge-transfer contributions but relatively high reactivities in the cycloaddition while much larger charge-transfer contributions are induced in more polar alcoholic solvents; the reactivities in the protic solvents decrease with the increase of solvent polarity. For some exciplexes, the occurrence of complete electron transfer in very polar solvents such as ethanol, methanol, and acetonitrile is strongly suggested from the product distributions. The possible availability of $E_T(30)$ or Z value as a scale of solvent polarity has been tested for the solvent effects on the processes from the nonemissive exciplexes.

It is now widely accepted that the exciplex formation is a general mechanistic pathway for interactions between electronically excited and ground-state molecules involving luminescence quenching2) as well as photoreactions,3) especially photocycloadditions.3—5) We have extensively investigated photocycloadditions of aromatic nitriles to olefinic and furan compounds,4) most of which proceed *via* totally or virtually nonemissive exciplexes.4f—k,6) Scheme 1 shows the major mechanistic pathways for the photoreactions of aromatic nitriles (electron acceptors, A) with olefinic and furan compounds (electron donors, D), where $^1[\mathrm{A\cdot D}]^*$ and $(\mathrm{A}^{-\cdot}\cdots\mathrm{D}^{+\cdot})$ represent an exciplex and an ion-radical pair respectively. The complete electron-transfer process (k_e) is negligeble in nonpolar solvents but may be important in very polar solvents such as acetonitile and methanol.2,4f,4k,7)



Scheme 1.

These dynamic processes probably depend on the electronic nature of exciplexes that can be simply represented by

$$^1[\mathrm{A\cdot D}]^* \equiv {}^1\mathrm{A}^*\mathrm{D} \leftrightarrow \mathrm{A}^-\mathrm{D}^+.$$

A stimulating problem in the chemistry of exciplex is to establish the relationships between reactivities and electronic structures of exciplexes.2b,5) Although exciplex emissions can provide a direct clue to the estimation of the electronic structures,2c—e,8) the exciplex intermediates postulated in numerous photoreactions are very often nonemissive. In these cases, the charge-transfer (CT) nature of nonemissive exciplexes has been usually discussed from the linear correlations between the logarithm of luminescence-quenching rate constants and ionization potentials of D or electrochemical reduction potentials of A for a family of similar A-D pairs.9—12) However, the linear correlations can reveal only the linear free-energy relationships in the quenching process.11,13)

In order to establish structure-reactivity relationships in the chemistry of nonemissive exciplexes, therefore, it is required to find suitable phenomena that allow us to estimate their electronic structures. Since exciplexes are more or less polar, their physical and chemical consequences should be affected by the sorrounding medium, depending on the CT nature. Therefore, solvent effects on kinetics may be diagnostic for the estimation of the CT nature of nonemissive exciplexes. We have found that the naphthonitrile-olefin and furan systems reveal remarkable solvent dependences of both fluorescence-quenching rate constants and quantum yields of the photoreactions. In the present work, we have performed qualitative, steady-state analyses of the solvent effects on the basis of the dielectric continuum model14) and have tested the applicability of E_T (30),15) an empirical scale of solvent polarity.

Results

Reaction Systems. Chart 1 lists the electron acceptors (A) and the donors (D) employed in the present work. Table 1 shows the selected A-D pairs that

TABLE 1. SELECTED EXCIPLEX-FORMING SYSTEMS

Classification	A[a)]	D[b)]	Cycloadduct (isomer ratio)[c),d)]	Reference
Case I	**1a**	**2a**	**3a** : **4a** ($\approx 1:1$)	4c
		2c	**3c** : **4c** ($\approx 1:1$)	Present work
	1b	**2a**	**5a**	4i, 4j
		2c	n.d.[e)]	
Case II	**1a**	**2b**	**3b** : **4b** ($\gtrsim 95 : \lesssim 5$)	4e
		2f	**7**	4a
	1b	**2d**	**5d**	f)
		2g	**8** : **9** (1 : 4)	g)
Case III	**1a**	**2e**	**3e** : **4e** ($\approx 1:1$)	h)
Case IV	**1a**	**2h**	No adduct	

a) **1a** : 1-Naphthonitrile and **1b** : 2-naphthonitrile. b) **2a** : Ethyl vinyl ether, **2b** : phenyl vinyl ether, **2c** : 2-methyl-2-butene, **2d** : 2,3-dimethyl-2-butene, **2e** : 2,3-dihydropyran, **2f** : furan, **2g** : 2-methylfuran, and **2h** : ethyl phenyl ether. c) See abbreviations in Scheme 1. d) In benzene solutions. e) Not determined. f) T. S. Cantrell, *J. Am. Chem. Soc.*, **94**, 5929 (1972). g) C. Pac, T. Sugioka, and H. Sakurai, unpublished results. See also Ref. 4b. h) C. Pac, K. Mizuno, and H. Sakurai, unpublished results. See also Ref. 4c.

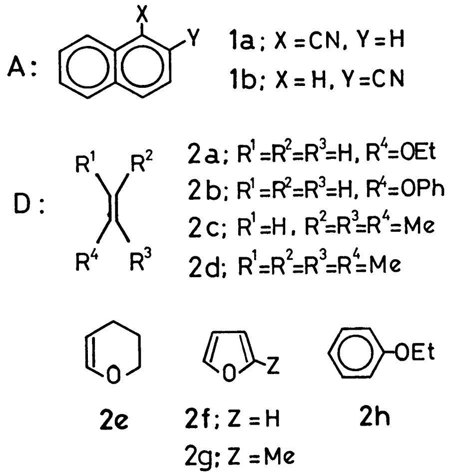


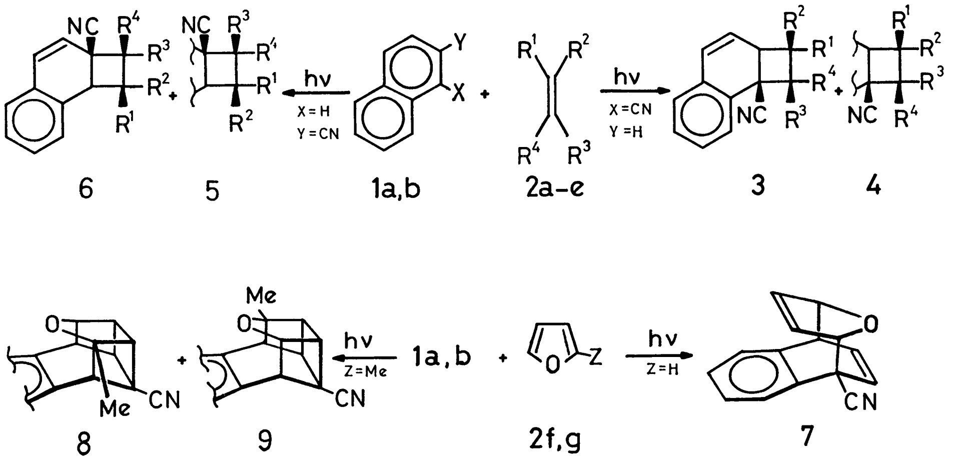
Chart 1.

are classified into the four cases. Case I is the reaction system that gives only the cycloadduct(s) irrespective of solvent polarity when photoreactions occur. The photoreactions of case II give again the cycloadducts in nonpolar and moderately polar solvents while other products are formed in very polar solvents (*vide infra*). In both cases, exciplex emissions

TABLE 2. SCALES OF SOLVENT POLARITY AND FLUORESCENCE LIFETIMES OF 1- AND 2-NAPHTHONITRILES (**1a** AND **1b**) IN VARIOUS SOLVENTS

	Solvent										
	CH[a)]	BZ[b)]	BE[c)]	DO[d)]	THF[e)]	EA[f)]	TB[g)]	IP[h)]	ET[i)]	ME[j)]	AN[k)]
ε[l)]	2.02	2.28	3.08	2.21	7.58	6.02	12.47	19.92	24.55	32.7	37.5
$f(\varepsilon)$[m)]	0.20	0.23	0.29	0.22	0.41	0.39	0.44	0.46	0.47	0.48	0.48
$E_T(30)$/kcal mol^{-1}	31.2	34.5	33.4	36.0	37.1	38.1	43.9	48.6	51.9	55.5	46
τ_F[n)]/ns; **1a**	18.5	12.3	12.7	11.3	11.1	12.3	10.2	9.7	9.4	8.4	9.3
τ_F[n)]/ns; **1b**	30.3	24.9	17.7	24.3	21.9	22.9	21.8	21.4	20.6	19.7	21.8
τ_F^{air}[o)]/ns; **1a**	11.1	8.8	7.7	9.3	8.4	7.6	8.1	7.4	7.0	6.3	6.8
τ_F^{air}[o)]/ns; **1b**	13.6	12.4	10.0	16.4	16.7	10.4	14.0	12.6	11.6	10.3	10.6

a) Cyclohexane. b) Benzene. c) Di-*n*-butyl ether. d) Dioxane. e) Tetrahydrofuran. f) Ethyl acetate. g) *t*-Butyl alcohol. h) 2-Propanol. i) Ethanol. j) Methanol. k) Acetonitrile. l) Dielectric constant. m) $f(\varepsilon) = (\varepsilon-1)/(2\varepsilon+1)$. n) Fluorescence lifetimes in degassed solutions; ±0.3 ns. o) Fluorescence lifetimes in aerated solutions; ±0.5 ns.



Scheme 2.

TABLE 3. LOGARITHM OF FLUORESCENCE-QUENCHING RATE CONSTANTS FOR NAPHTHONITRILE-OLEFIN AND -FURAN PAIRS[a)]

A	D	log γk_e[b)] CH	BZ	BE	DO	THF	EA	TB	IP	ET	ME	AN
1a	**2a**	8.95	9.10	9.07	9.08	9.23	9.30	9.05	9.45	9.64	9.82	9.83
	2b	8.88	8.75	8.81	8.93	9.02	9.14	9.21	9.37	9.57	9.95	9.82
	2c	8.02	8.27	8.21	8.62	8.69	8.60	9.11	9.26	9.63	9.89	9.58
	2f	7.40	7.96	7.86	8.18	8.38	8.42	9.24	9.48	9.83	10.31	9.45
	2h	8.61	8.73	8.90	8.93	9.11	9.30	9.72	9.77	10.0	10.05	10.09
1b	**2a**	7.28	7.57	7.38	7.62	7.58	7.70	8.11	8.20	8.32	8.53	8.39
	2c	7.22	7.47	7.32	7.44	7.45	7.69	8.10	8.34	8.56	8.96	8.81
	2d	8.35	8.66	8.62	8.84	8.69	8.50	9.04	9.16	9.49	9.83	10.09
	2g	7.91	8.13	8.12	8.41		8.52	9.09	9.33	9.74	10.14	9.89

a) For aerated solutions; [**1a** and **1b**] $=3$—6×10^{-4} mol dm^{-3}. See abbreviations in Chart 1 and Table 2. b) Averaged values for three or four runs; uncertainties ±0.05.

TABLE 4. SOLVENT EFFECTS ON ISOMER RATIOS OF [2+2] PHOTOCYCLOADDUCTS OF **1a-2a** AND **1a-2c** PAIRS[a),b)]

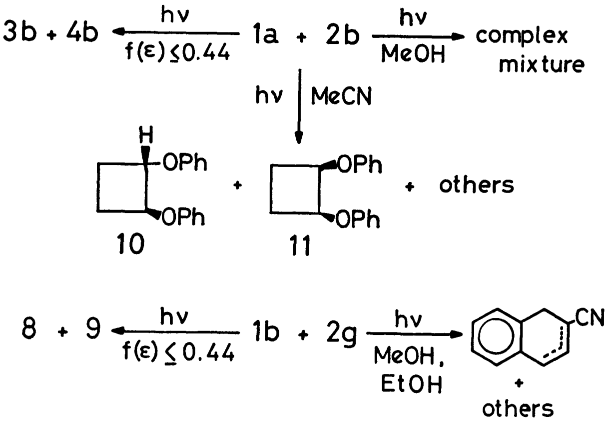
A-D pair	**3**/**4**[c)] BZ	EA	TB	IP	ET	ME	AN
1a-2a	0.96	1.11	1.33	1.23	1.22	1.23	1.11
1a-2c	1.30	1.29	1.26	1.45	1.45	1.41	1.42

a) Solutions containing $\approx$0.05 mol dm^{-3} in **1a** and $\approx$1.0 mol dm^{-3} in the olefins were irradiated at 313 nm under cooling with water; conversions were 10—30%. b) See abbreviations in Chart 1, Scheme 1, and Table 2. c) *Endo*-to-*exo* isomer ratios determined by GLC and NMR.

are not detectable or, if any, negligebly weak in any solvent at room temperature. The **1a-2e** pair (case III) was employed as a typical reactive exciplex that is emissive in measurable intensities at room temperature. The **1a-2h** pair (case IV) is a reference exciplex that is fairly emissive but undergoes no net photoreaction. The types of photocycloadditions are shown in Scheme 2. Most of the cycloadducts are known compounds,[4)] and the structures of a few unknown adducts were readily determined by comparison of their spectroscopic data with those of similar known compounds.

The obligatory intermediacy of singlet exciplexes in these photocycloadditions has been established by the oxygen-quenching method for the **1a-2a** and **1a-2e** pairs,[16)] by negative temperature effects on the photoreaction of **1a** and **2f**,[6a)] and by exciplex quenching by pyridine for the **1b-1a**, **1b-2d**, **1b-2e**, and **1b-2g** pairs.[4j,6b,6c)] The *endo* selective nature of the photocycloaddition of **1a** to **2b** strongly suggests the intervention of an exciplex intermediate which determines the stereoselectivity.

Fluorescence Quenching in Various Solvents. Table 2 lists fluorescence lifetimes of **1a** and **1b** in deaerated and aerated solutions (τ_F and τ_F^{air}) and the parameters of solvent polarity including dielectric constant (ε), its function [$f(\varepsilon)=(\varepsilon-1)/(2\varepsilon+1)$], and the $E_T(30)$ values in kcal mol^{-1}. Quenching of the fluorescence of **1a** or **1b** by **2a**—**h** was performed for air-saturated solutions, the quenching rate constants (γk_e) being thus determined from the linear Stern-Volmer plots using Eq. 4. Table 3 summarizes the logarithm of γk_e for the selected A-D pairs.



Scheme 3.

Solvent Effects on Product Distribution. Table 4 lists the *endo*/*exo*-isomer ratios (**3**/**4**) of the cycloadducts in the photoreactions of the **1a-2a** and **1a-2c** pairs (case I) in various solvents. There can be seen a tendency that the ratios in the alcoholic solvents are slightly, but significantly, higher than those in the less polar aprotic solvents. Other products than the cycloadducts were not formed even in acetonitrile and methanol.

On the other hand, irradiation of the A-D pairs of case II commonly gave complex mixtures of other products than the cycloadducts in the solvents of $f(\varepsilon)>0.46$; an increase of solvent polarity results in an increase of formation of complex mixtures. In the case of the **1a-2f** pair, irradiation of ethanol, methanol, and acetonitrile solutions gave complex mixtures involving oligomeric and polymeric compounds and a small amounts of **7**, as demonstrated by GLC, GPC, and NMR (see Fig. 8). In contrast the photoproduct in ethyl acetate and *t*-butyl alcohol is exclusively **7**.

The photoreaction of **1a-2b** pair in either *t*-butyl alcohol or ethyl acetate gave exclusively the cyclo-

TABLE 5. QUANTUM YIELDS FOR DISAPPEARANCE OF 1-NAPHTHONITRILE IN THE PHOTOREACTIONS WITH ETHYL VINYL ETHER (**2a**), 2-METHYL-2-BUTENE (**2c**), 2,3-DIHYDROPYRAN (**2e**), AND FURAN (**2f**)

	ϕ_{-A}[b)] (ϕ^{∞}_{-A})[c)]									
D	CH	BZ	BE	DO	EA	TB	IP	ET	ME	AN
2a	0.47 (0.52)	0.50 (0.55)	0.44 (0.49)	0.47 (0.51)	0.37 (0.40)	0.34 (0.38)	0.19 (0.20)	0.22 (0.23)	0.14 (0.14)	0.30 (0.30)
2c	0.34 (0.64)	0.58 (0.93)	0.35 (0.62)	0.52 (0.66)	0.52 (0.69)	0.79 (0.87)	0.30 (0.35)	0.13 (0.13)	0.08 (0.08)	0.25 (0.25)
2e[d)]	0.57	0.46	0.53	0.40	0.06	0.03	0.014	<0.01	<0.01	<0.01
2f	0.21 (0.50)	0.39 (0.58)	0.37 (0.62)	0.40 (0.51)	0.34 (0.41)	0.22 (0.23)	0.15[c)] (0.15)	0.14[e)] (0.14)	0.08[e)] (0.08)	0.08[e)] (0.08)

a) See abbreviations in Chart 1 and Table 2. b) Determined at 313 nm for aerated solutions containing 3.5—4.5×10^{-4} mol dm^{-3} in **1a** and 1.0 mol dm^{-3} in the olefins or 2.6 mol dm^{-3} in furan; averaged values for three runs with uncetainties of ±(8—15)%. c) Calculated by multiplying ϕ_{-A} by $(1+K_{SV}[D])/K_{SV}[D]$; see text. d) It is assumed that $\phi_{-A}\simeq\phi^{\infty}_{-A}$, since $K_{SV}[D](=51—95)\gg1$ in all the solvents. e) Other products than the cycloadduct (**7**) were formed.

adduct (**3b**), while the dimers of **2b** (**10** and **11**)[17)] were formed in acetonitrile as the major detectable products. The irradiation of a methanolic solution gave complex mixtures involving **3b**, **10**, and **11** in small amounts. The photoreaction of the **1b**-**2g** pair in *t*-butyl alcohol or in less polar solvents gave again the cage compounds (**8** and **9**) in >80% yields while the irradiation in methanol or ethanol gave complex mixtures from which 1,2- and 1,4-dihydro-2-naphthonitriles were obtained. Scheme 3 summarizes the photoreactions of the **1a**-**2b** and **1b**-**2g** pairs in different solvents.

Quantum Yields in Various Solvents. Table 5 shows the quantum yields (ϕ_{-A}) for disappearance of **1a** and the calculated limiting quantum yields (ϕ^{∞}_{-A}) for some selected A-D pairs in aerated solutions. The ϕ^{∞}_{-A} values were calculated by multiplying ϕ_{-A} by $(K_{SV}[D]+1)/K_{SV}[D]$; K_{SV} and [D] represent, respectively, the slopes of the Stern-Volmer plots for the fluorescence quenching and the concentration at which ϕ_{-A} was determined. This method was confirmed to be approximately valid since the calculated values of ϕ^{∞}_{-A} in cyclohexane for the **1a**-**2a** and **1a**-**2f** pairs are almost identical to the observed values (0.51 and 0.49 respectively) obtained from the intercepts of the usual plots of ϕ_{-A}^{-1} *vs.* $[D]^{-1}$. In cases where $K_{SV}[D]\gg1$, it was assumed that $\phi_{-A}\simeq\phi^{\infty}_{-A}$. In the quantum-yield measurements, concentrations of **1a** were set very similar to those used in the fluorescence-quenching experiments.

Discussion

Kinetic Representation and Free-energy Relationships. On the basis of Scheme 1, steady-state analysis gives the Stern-Volmer equation for fluorescence quenching (Eq. 3) and the rate equation for ϕ_{-A} (Eq. 4); Eq. 5 represents the rate equation of the limiting quantum yield for disappearance of A. In these equations, the quenching of both $^1A^*$ and $^1[A{\cdot}D]^*$ by molecular oxygen (Eqs. 1 and 2) has been taken into consideration since both the fluorescence-quenching and quantum-yield measurements were performed for aerated solutions. However, both $k_q[O_2]$ and $k^c_q[O_2]$ are probably almost constant independently on solvent polarity since the reported solubilities of O_2 upon air saturation into the solvents employed are in the rage of $(2—3)\times10^{-3}$ mol dm^{-3} at 25 °C[18)] and since it is reasonable to assume that $k_q\simeq k^c_q\simeq2\times10^{10}$ dm^3 mol^{-1} s^{-1}.[16b,c,19)] Moreover, it was confirmed that the presence of O_2 diminishes ϕ_{-A} in cyclohexane and ethyl acetate for the A-D pairs employed in the quantum-yield measurements; the irradiation in these solvents under air saturation gave no other products than the cycloadducts in significant amounts. Therefore, chemical processes involving O_2 can be safely neglected.

$$^1A^* + O_2 \xrightarrow{k_q} A + O_2 \tag{1}$$

$$^1[A{\cdot}D]^* + O_2 \xrightarrow{k^c_q} A + D + O_2 \tag{2}$$

$$\frac{I^0_F}{I^D_F} = 1 + K_{SV}[D] = 1 + \gamma k_c \tau_F{}^{air}[D] \tag{3}$$

$$\frac{1}{\phi_{-A}} = \frac{1}{\phi^{\infty}_{-A}}\left(1+\frac{1}{\gamma k_c \tau_F{}^{air}[D]}\right) \tag{4}$$

$$\frac{1}{\phi^{\infty}_{-A}} = \frac{k_a+\alpha k_e}{k_a+k_d+k_e+k^c_q[O_2]} \tag{5}$$

$$\frac{1}{\tau_F{}^{air}} = \frac{1}{\tau_F} + k_q[O_2] \tag{6}$$

$$\gamma = \frac{k_a+k_d+k_e+k^c_q[O_2]}{k_a+k_d+k_e+k^c_q[O_2]+k_{-c}} \tag{7}$$

It is well established that $k_c\simeq(1—2)\times10^{10}$ dm^3 mol^{-1} s^{-1} for a variety of exciplex-forming systems.[2,6b,20,21)] In cases where $\gamma k_c\ll10^{10}$ dm^3 mol^{-1} s^{-1}, therefore, it is reasonable to assume that $\gamma\ll1$, *i.e.* $(k_a+k_d+k_e+k^c_q[O_2])\ll k_{-c}$. If this is the case, γk_c can be simplified to Eq. 8 which is then rewritten as Eq. 9; ΔG_c is the free-energy change associated with exciplex formation.

$$\gamma k_c \simeq \frac{k_c}{k_{-c}}(k_a+k_d+k_e+k^c_q[O_2]) \tag{8}$$

$$\log\gamma k_c \simeq -\frac{\Delta G_c}{2.3RT} + \log(k_a+k_d+k_e+k^c_q[O_2]) \tag{9}$$

If an exciplex is a solute that has a dipole moment

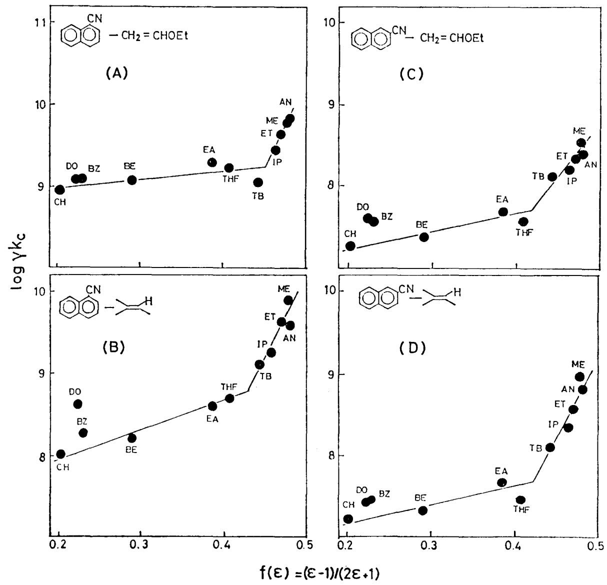


Fig. 1. Plots of $\log \gamma k_c$ *vs.* $f(\varepsilon)$ $[=(\varepsilon-1)/(2\varepsilon+1)]$ for A-D pairs of case I; (A) **1a-2a**, (B) **1a-2c**, (C) **1b-2a**, and (D) **1b-2c** pairs; see abbreviations in Chart 1 and Table 2.

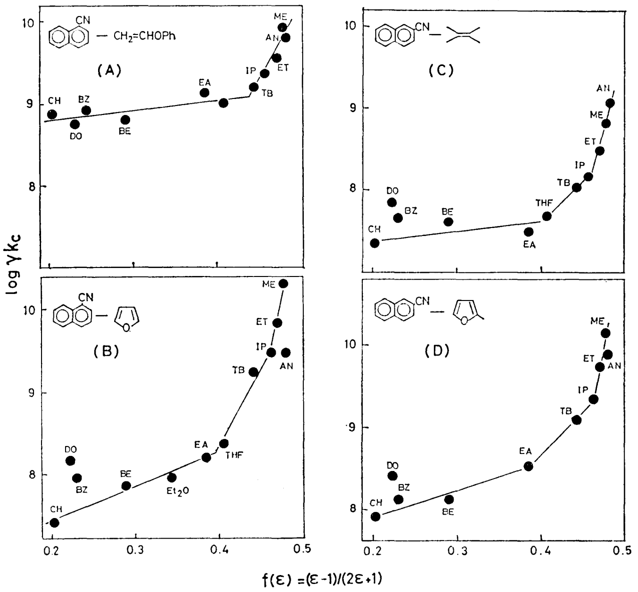


Fig. 2. Plots of $\log \gamma k_c$ *vs.* $f(\varepsilon)$ $[=(\varepsilon-1)/(2\varepsilon+1)]$ for A-D pairs of case II; (A) **1a-2b**, (B) **1a-2f**, (C) **1b-2d**, and (D) **1b-2g** pairs; see abbreviations in Chart 1 and Table 2.

of μ_c with a separation of R_c Å, the treatment of the solvent as a continuous dielectric medium gives Eq. 10 for the difference of ΔG_c between the reference solvent (*e.g.* cyclohexane) and the medium of dielectric constant ε.[14,22] Thus Eq. 9 coupled with Eq. 10 gives Eq. 11, predicting that the slope of the plot of $\log \gamma k_c$ *vs.* $f(\varepsilon)$ may reflect the dipole moment of an exciplex, if the solvent dependence of k_{-c} is much greater than that of the other rate constants.[20]

$$\Delta\Delta G_c = -\frac{\mu_c^2}{R_c^3}f(\varepsilon) + \text{constant} \tag{10}$$

$$\Delta\log \gamma k_c = \frac{1}{2.3RT} \times \frac{\mu_c^2}{R_c^3}f(\varepsilon) + \Delta\log(k_a+k_d+k_e+k_q^c[O_2]) + \text{constant} \tag{11}$$

$$\left[f(\varepsilon) = \frac{\varepsilon-1}{2\varepsilon+1}\right]$$

Equation 7 can be rewritten as Eq. 12. It has been reported that the complete electron-transfer process is negligeble in the decay pathways of **1a**——1,2-dimethylcyclopentene exciplex in ethyl acetate,[20] *i.e.* $(k_a+k_d+k_q^c[O_2]) \gg k_e$. This is probably true for the present nonemissive exciplexes in the solvents of $f(\varepsilon) \leq 0.44$, since the cycloadducts are commonly the exclusive products in these solvents and since the ionization potentials of the present donors are higher than that of 1,2-dimethylcyclopentene(7.84 eV);[23] see Table 7. In this case, therefore, Eq. 12 can be reduced to Eq.13.

$$\frac{\phi^{\infty}_{-A}}{1-\phi^{\infty}_{-A}} = \begin{cases} \dfrac{k_a+\alpha k_e}{k_d+(1-\alpha)k_e+k_q^c[O_2]} & (12) \\[2ex] \dfrac{k_a}{k_d+k_q^c[O_2]} & (13) \end{cases}$$

TABLE 6. SLOPES OF THE PLOTS OF $\log \gamma k_c$ *vs.* $(\varepsilon-1)/(2\varepsilon+1)$ FOR THE NAPHTHONITRILE-OLEFIN, FURAN, AND ETHYL PHENYL ETHER PAIRS[a,b)]

	A	D	Slopes	
			$f(\varepsilon)^{c)} < \approx 0.4$	$f(\varepsilon)^{c)} > \approx 0.4$
Case I	**1a**	**2a**	1.0	20
		2c	1.4	21
	1b	**2a**	0.9	13
		2c	1.0	17
Case II	**1a**	**2b**	1.2	18
		2f	2.3	$\gtrsim 21$
	1b	**2d**	0.6	$\gtrsim 10$
		2g	1.3	$\gtrsim 10$
Case IV	**1a**	**2e**	2.9	11.2

a) Values obtained by a rough estimate from the plots in Figs. 1, 2, and 3(B). b) See abbreviations in Chart 1. c) $(\varepsilon-1)/(2\varepsilon+1)$.

If the cycloaddition occurs from an exciplex of dipole moment μ_c to a transition state of dipole moment $\mu_{\ddagger}$ in the medium of dielectric constant ε, the dielectric continuum assumption gives Eq. 14 where $\Delta G_{\text{sol}}^{\ddagger}$ is the electrostatically induced free-energy change for the cycloaddition process.

$$\log\left(\frac{\phi^{\infty}_{-A}}{1-\phi^{\infty}_{-A}}\right) = -\frac{\Delta G_{\text{sol}}^{\ddagger}}{2.3RT} - \log(k_d+k_q^c[O_2]) + \text{constant}$$

$$\left[\Delta G_{\text{sol}}^{\ddagger} = \left(\frac{\mu_c^2}{R_c^3} - \frac{\mu_{\ddagger}^2}{R_{\ddagger}^3}\right)f(\varepsilon)\right] \tag{14}$$

Solvent Effects on Fluorescence Quenching. Estimation of Electronic Nature of Nonemissive Exciplex: As can be seen in Table 3, the fluorescence-quenching rate constants are much lower than the diffusion-controlled limits except for those in very polar solvents for

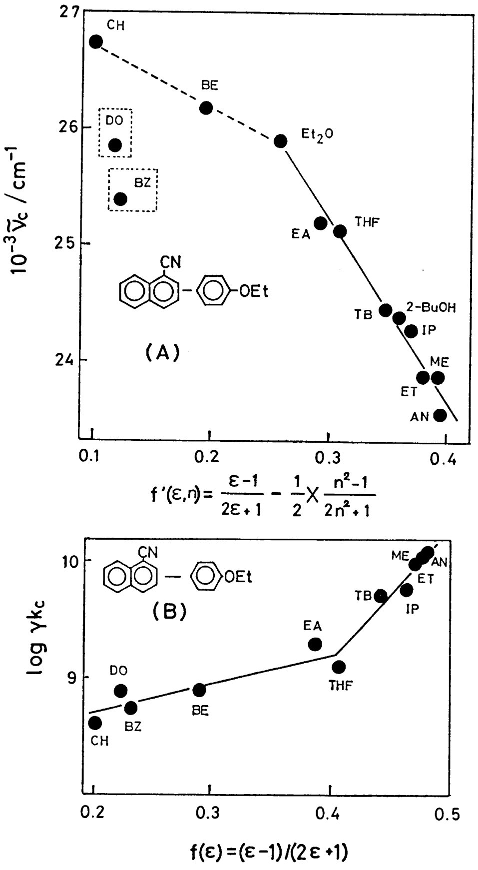


Fig. 3. (A) Plot of $\tilde\nu_c$ *vs.* $f'(\varepsilon,n)$ $[=(\varepsilon-1)/(2\varepsilon+1)-(n^2-1)/2(2n^2+1)]$ and (B) plot of $\log \gamma k_c$ *vs.* $f(\varepsilon)$ $[=(\varepsilon-1)/(2\varepsilon+1)]$ for **1a-2h** pair; see abbreviations in Chart 1 and Table 2.

TABLE 7. REDUCTION POTENTIALS OF 1- AND 2-NAPHTHONITRILES, OXIDATION POTENTIALS, AND IONIZATION POTENTIALS OF ELECTRON DONORS (D), AND CALCULATED FREE-ENERGY CHANGES FOR COMPLETE ELECTRON TRANSFER$^{a)}$

	A	$-E^{red}_{p/2}$ $^{b)}$ V	D	$E^{ox}_{p/2}$ $^{b)}$ V	*IP* eV	$-\Delta G_{ET}$ $^{c)}$ kcal mol^{-1}
Case I	**1a**	2.06	**2a**	1.35	8.49$^{d)}$	10.5
			2c	1.47	8.85$^{e)}$	7.7
	1b	2.18	**2a**			5.2
			2c			2.5
Case II	**1a**		**2b**	1.37		10.0
			2f	1.40	8.89$^{f)}$	9.3
	1b		**2d**	1.13	8.30$^{g)}$	9.7
			2g	1.14	8.39$^{f)}$	10.1
Case III	**1a**		**2e**	1.12	8.34$^{f)}$	15.8

a) See abbreviations in Chart 1. b) Determined by cyclic voltammetry for dry acetonitrile solutions *vs.* Ag/AgNO$_3$. c) Calculated according to the following equation; $\Delta G_{ET}=23.06[E^{ox}_{p/2}-E^{red}_{p/2}-e^2/\varepsilon a]-E_{0-0}(^1A^*)$. For $E_{0-0}(^1A^*)$, see Ref. 18, p. 19. d) N. E. Shore and N. J. Turro, *J. Am. Chem. Soc.*, **97**, 2482 (1975). e) W. C. Price, R. Bralsford, and P. V. Harris, *Spectrochimica Acta*, **14**, 45 (1959). f) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962). g) W. C. Price, *Chem. Rev.* **47**, 257 (1947).

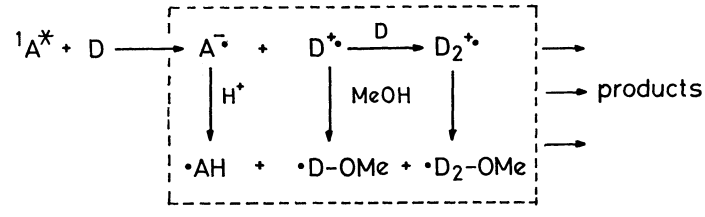
some A-D pairs. Therefore, Eqs. 8 and 9 hold for the fluorescence quenching of the present A-D pairs in most solvents. Figures 1 and 2 show the plots of log γk_c *vs.* $f(\varepsilon)$ for the 8 A-D pairs; the following common features should be noted. (1) The plots give, at least, two linear lines with a break at $f(\varepsilon)\simeq 0.4$. It is therefore suggested that the simple dielectric continuum approximation (Eq. 11) is applicable to the fluorescence-quenching process *via* the nonemissive exciplexes within the limited regions of solvent polarity, *i.e.* at $f(\varepsilon)<0.4$ (nonpolar and moderately polar solvents) and at $f(\varepsilon)>0.4$ (polar alcoholic solvents and acetonitrile). (2) The slopes of the plots at the lower region of $f(\varepsilon)$ are much smaller than those at the higher region (Table 6). On the basis of Eq. 11, therefore, μ_c^2/R_c^3 is much greater in the polar solvents of $f(\varepsilon)>0.4$ than that in the less polar solvents, suggesting that the electronic structures of the nonemissive exciplexes are changed from minor CT contributions in the nonpolar and moderately polar solvents to much larger CT contributions in the polar solvents. Such solvent-induced changes in the electronic nature have been demonstrated for a few emissive exciplexes.[20,24,25] (3) Benzene and dioxane which are nonpolar but polarizable are the out-of-line solvents in most cases. The nonemissive exciplexes would be specifically solvated by these solvents.

In order to obtain further insight into solvent effects on the electronic nature of exciplexes, we have investigated both the solvent-induced shifts of the emission maximum ($\tilde\nu_c$, cm^{-1}) and the solvent dependence of γk_c for the emissive **1a-2h** exciplex (case IV). The dipole moment (μ_c) of the exciplex was estimated as usual using Eq. 15. As is shown in Fig. 3A, the plot of $\tilde\nu_c$ *vs.* $f'(\varepsilon,n)$ gives a linear correlation at $f'(\varepsilon,n)>0.25$ with a slope of -1.3×10^4 cm^{-1} which corresponds to >10D of μ_c taking $R_c=4.5$—5 Å. This large dipole moment demonstrates the dominant CT contributions in the solvents of $f'(\varepsilon,n)>0.25$. Unfortunately, the plot at $f'(\varepsilon,n)<0.25$ is poorly cor-

$$\tilde\nu_c = -\frac{2\mu_c^2}{hcR_c^3}\left(\frac{\varepsilon-1}{2\varepsilon+1}-\frac{n^2-1}{4n^2+2}\right)+\text{constant}$$
$$= -\frac{2\mu_c^2}{hcR_c^3}f'(\varepsilon,\ n)+\text{constant} \qquad (15)$$

related because of the substantial deviations of $\tilde\nu_c$ in benzene and dioxane, though a smaller value of μ_c in the less polar solvents might be suggested (*vide infra*).

Figure 3B shows a plot of $\log \gamma k_c$ *vs.* $f(\varepsilon)$ that again consists of two linear lines with a break at $f(\varepsilon)\simeq 0.4$. From these slopes calculations based on Eq. 11 taking $T=298$ K give the values of μ_c^2/R_c^3 that are 1.5×10^4 J mol^{-1} at $f(\varepsilon)<0.4$ and 6.3×10^4 J mol^{-1} at $f(\varepsilon)>0.4$. The latter value is similar to that separately calculated from the linear portion in Fig. 3A (7.8×10^4 J mol^{-1}). Since the slope at $f(\varepsilon)<0.4$ is only one-fourth that at $f(\varepsilon)>0.4$, the CT contributions are perhaps much lower in the less polar solvents. It is thus suggested that Eq. 11 can be used as a convenient basis for qualitative estimation of electronic



Scheme 4.

structures of nonemissive exciplexes, though other physical and chemical properties of solvent should be taken into consideration for sophisticated interpretations of the solvent effects. At any rate the electronic nature of the nonemissive exciplexes seems to be inherently sensitive to the sorrounding medium.

Occurrence of Complete Electron Transfer in Very Polar Solvents: Complete electron transfer from D to $^1A^*$ may occur in very polar solvents as has been established for a variety of exciplex-forming systems.[2,5f,5k,7] Table 7 lists the observed anodic half-peak potentials ($E_{P/2}^{ox}$) and reported ionization potentials of D, the cathodic half-peak potentials of A, and the calculated free-energy changes (ΔG_{ET}) in acetonitrile associated with the complete electron-transfer process. According to the Rehm-Weller treatment,[26] the net rate constant for complete electron transfer reaches the diffusion-controlled limits in cases where $\Delta G_{ET} < -5$—-6 kcal mol^{-1}, *i.e.* $k_{-e} \ll k_e$. Since the calculated values of ΔG_{ET} are substantially negative in most cases, complete electron transfer can, but not necessarily, occur in acetonitrile and probably also in methanol.

In particular, the occurrence should be taken into consideration for the A-D pairs of case II in the polar solvents of $f(\varepsilon) > 0.44$ as indicated by the photoproducts in these solvents. The photoreaction of the **1a-2b** pair in acetonitrile clearly indicates the occurrence of complete electron transfer since the photodimerization of **2b** *via* the cation radical has now been well established.[27] The attenuation of the dimerization of **2b** in methanol can be interpreted in terms of the nucleophilic addition of methanol to the cation radical of **2b** since it is now well-known that alcohols can attack on cation-radical species of olefinic and furan compounds.[4k,28] Therefore, formation of complex mixtures in the photoreactions of methanolic solutions of the **1a-2b**, **1a-2f**, and **1b-2g** pairs can be considered to be initiated by complete electron transfer from D to $^1A^*$ followed by complex reactions involving a variety of reactive species such as $A^{\overline{\cdot}}$, its protonated species, $D^{\dot{+}}$, dimer cation radicals of D, and methoxylated species of the cation radicals (Scheme 4).[4k] Moreover, McCullough *et al.* reported that the photoreactions of **1a** and **1b** with **2d** in such very polar solvents as acetonitrile and methanol proceeds by way of complete electron transfer.[7]

In this regard, it should be noted that sharp increases of log γk_e can be seen at $f(\varepsilon) > 0.46$ in the plots for the **1a-2f**, **1b-2d**, and **1b-2g** pairs, presumably arising from increasing contributions of k_e to γ. In case I, however, the occurrence of complete electron transfer is questionable even in acetonitrile since the cycloadditions exclusively occurred in any solvent.

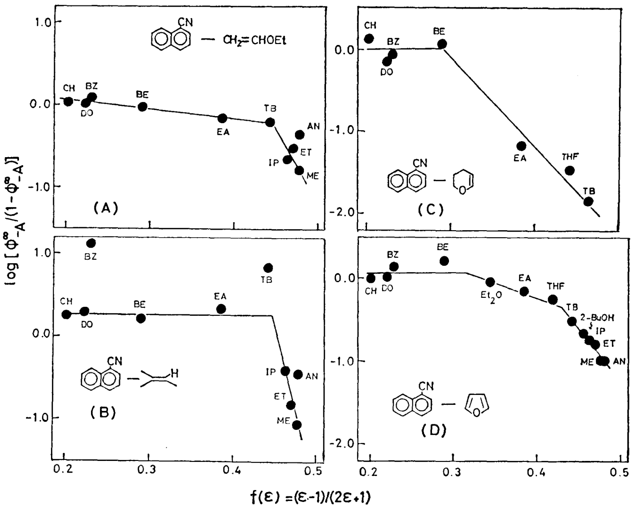


Fig. 4. Plots of log$[\phi^{\infty}_{-\mathrm{A}}/(1-\phi^{\infty}_{-\mathrm{A}})]$ *vs.* $f(\varepsilon)$ [$=(\varepsilon-1)/(2\varepsilon+1)$] for (A) **1a-2a**, (B) **1a-2c**, (C) **1a-2e**, and (D) **1a-2f** pairs; see abbreviations in Chart 1 and Table 2.

Solvent Effects on Reactivities of Nonemissive Exciplexes. Figure 4 shows the plots of log$[\phi^{\infty}_{-\mathrm{A}}/(1-\phi^{\infty}_{-\mathrm{A}})]$ *vs.* $f(\varepsilon)$ for the **1a-2a**, **1a-2c**, **1a-2f**, and **1a-2e** pairs. Since the complete electron-transfer process (k_e) can be neglected for these A-D pairs, at least, in solvents of $f(\varepsilon) < 0.44$, Eq. 13 can be used for analyses of the plots as a basis for the estimation of exciplex reactivities. In case of the **1a-2f** pair (case II), however, Eq. 12 should be used at $f(\varepsilon) > 0.44$ where complete electron transfer may occur as a competitive or dominant pathway.

For the **1a-2a** pair, k_a and k_d in cyclohexane have been determined by the oxygen-quenching method to be $\approx 10^8$ s^{-1} and $\approx 5 \times 10^7$ s^{-1} respectively.[16d] Since $k_q^c[O_2]$ approximately equals $(4$—$6) \times 10^7$ s^{-1} independently on solvent polarity, Fig. 4A suggests that both k_a and k_d do not greatly depend on solvent polarity at $f(\varepsilon) < 0.44$. On the other hand, the increase of solvent polarity at $f(\varepsilon) > 0.44$ leads to a decrease of k_a and/or an increase of k_d. A similar conclusion appears to be obtainable from Fig. 4B for the **1a-2c** pair, though the ϕ^{∞}_{-A} values in benzene and *t*-butyl alcohol are unusually high relative to those in the other solvents. On the other hand, the plot for the **1a-2e** pair (Fig. 4C) demonstrates drastic changes of k_a and/or k_d at $f(\varepsilon) > 0.3$.

Lewis and Hoyle reported that the k_a values for the diphenylvinylene carbonate–2,5-dimethyl-2,4-hexadiene exciplex remarkably decrease with solvent polarity.[24] This solvent dependence of k_a has been interpreted on the basis of the Michl's theory;[29] this theory predicts that k_a is the rate constant for the adiabatic process of avoided crossing from the polar exciplex minimum on the singly excited hypersurface to the less polar or nonpolar doubly excited state. Activation barriers for the adiabatic process should therefore be higher in more polar solvents since an exciplex of polar CT nature is more stabilized by solvation than the less polar transition state. A similar conclusion was put forth by Caldwell and Creed who observed the dependence of k_a and the independence of k_d on the degrees of CT contributions for some emissive cyanophenanthrene–styrene exciplexes.[5f,30]

On the basis of the Michl's theory, therefore, the solvent-dependent changes in ϕ^{∞}_{-A} can be expected to arise mainly from the changes in k_a.[31] If this is the case, the plots of $\log[\phi^{\infty}_{-A}/(1-\phi^{\infty}_{-A})]$ *vs.* $f(\varepsilon)$ are thus diagnostic for the elucidation of the observed solvent effects on reactivities of the nonemissive exciplexes. For example, the large negative slope of the plots at $f(\varepsilon)>0.3$ in Fig. 4C for the **1a-2e** exciplex can be interpreted to reflect large electronic changes in the cycloaddition process which presumably occur from the very polar exciplex state to the much less polar transition state. The very polar nature of the **1a-2e** exciplex was confirmed by the plot of $\tilde{\nu}_e$ *vs.* $f'(\varepsilon,n)$ that gives a linear correlation with a slope of $-(1.5\pm0.2)\times10^4\ \mathrm{cm}^{-1}$ at $f'(\varepsilon,n)>0.2$.[32a] The adiabatic process in which large electronic changes occur probably requires larger reorganization of the surrounding slovent molecules in more polar solvents at $f(\varepsilon)>0.3$, thus leading to greater ΔG_{sol}^{*}. In the much less polar and nonpolar solvents ($f(\varepsilon)<0.3$), however, solvation shells round the exciplex would be so weak that ΔG_{sol}^{*} might not significantly contribute to the total activation energies of the cycloaddition process.

Thus the plots in Figs. 4A and 4B suggest that electronic changes are only minor in the adiabatic process from the **1a-2a** or **1a-2c** exciplex to the transition state even in the moderately polar solvents of $f(\varepsilon)\leq0.44$. In other words, these nonemissive exciplexes seem to be almost nonpolar in these less polar solvents. On the other hand, substantial CT nature might be induced by specific solute-solvent interactions in the polar solvents of $f(\varepsilon)>0.44$, thus leading to greater ΔG_{sol}^{*} with higher solvent polarity. Moreover, conformational changes of the exciplexes would also occur on going from the aprotic solvents to the protic solvents since the *endo*/*exo*-isomer ratios are changed; the increase of solvent polarity at $f(\varepsilon)>0.44$ would make conformations of the exciplexes less favorable for the cycloaddition; solvent-dependent changes in R_c have been suggested.[20,25]

The **1a-2f** exciplex (case II) reveals different behaviors in the solvent dependence of ϕ^{∞}_{-A} as shown in Fig. 4D. Since the plot gives a linear line with a low negative slope at the region of $f(\varepsilon)$ from 0.3 to 0.44, this exciplex seems to be significantly, but slightly, ionic in these solvents. On the other hand, the greater negative slope at $f(\varepsilon)>0.44$ presumably arises from changes in the electronic and steric configuration of the exciplex as well as from the participation of complete electron transfer. Since both k_e and α probably increase with the increase of solvent polarity, the decrease of k_a would be, at least in part, cancelled out. In the extreme case where complete electron transfer is dominant, ϕ^{∞}_{-A} should be α, probably the value in acetonitrile or methanol that is very low (≈0.08). Since k_a is comparable with or much smaller than αk_e at $f(\varepsilon)>0.44$, the decrease of k_a with the increase of solvent polarity might be much more remarkable than that expected from the slope of the plot at $f(\varepsilon)>0.44$.

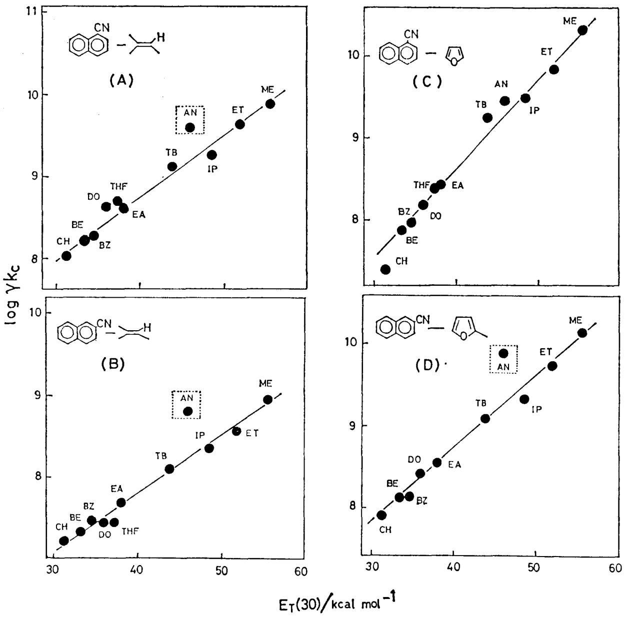


Fig. 5. Plots of log γk_c *vs.* $E_T(30)$ for (A) **1a-2c**, (B) **1b-2c**, (C) **1a-2f**, and (D) **1b-2g** pairs; see abbreviations in Chart 1 and Table 2.

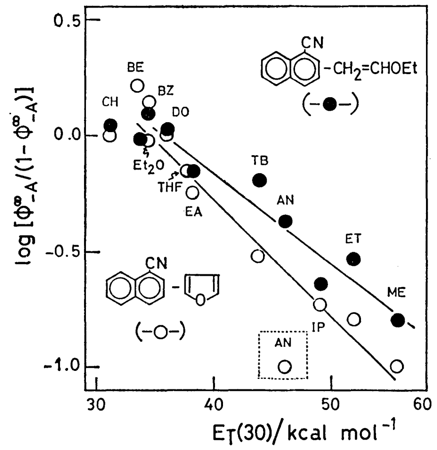
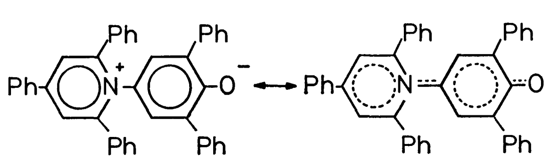


Fig. 6. Plots of $\log[\phi^{\infty}_{-A}/(1-\phi^{\infty}_{-A})]$ *vs.* $E_T(30)$ for **1a-2f** (—O—) and **1a-2a** (—●—) pairs; see abbreviations in Chart 1 and Table 2.

Applicability of $E_T(30)$ to the Solvent Effects on the Nonemissive Exciplexes. Kosower recomended the use of the $E_T(30)$ or Z value as a suitable scale of solvent polarity for exciplex systems.[33] In keeping this in mind, moreover, the finding that the logarithmic values of product ratio are linearly correlated with the Z scale for the naphthalene–acrylonitrile system in protic media[34] prompts us to investigate the availability of

$E_T(30)$ for elucidation of solvent effects on the processes from the exciplexes. Figure 5 shows typical plots of $\log \gamma k_c$ *vs.* $E_T(30)$ for the four selected A-D pairs; similar plots which are not shown here were also obtained for the other A-D pairs. Each plot gives a single linear line with a relatively good correlation irrespective of the solvent nature throughout the full range of solvent polarity employed; acetonitrile is the only out-of-line solvent. Figure 6 shows the plots of $\log[\phi^{\infty}_{-\mathrm{A}}/(1-\phi^{\infty}_{-\mathrm{A}})]$ *vs.* $E_T(30)$ for the **1a-2a** and **1a-2f** pairs, both of which reveal linear correlations with negative slopes at $E_T(30) > 38$ kcal mol^{-1} but tend to level off at the lower region of $E_T(30)$; a remakable deviation can be observed for the value of **1a-2f** pair in acetonitrile.

The $E_T(30)$ scale is based on the solvatochromic shifts of the longest absorption band of *p*-(1-pyridinio)-phenoxide **30** whose electronic structures are more polar like **30a** in the ground state and less polar like **30b** in the excited state;[15,35] the increase of solvent polarity causes stabilization of the ground state and destabilization of the excited Franck-Condon state, thus leading to the increase in the excitation energies. Therefore, the linear plots in Figs. 5 and 6 indicate the involvement of consequential changes from a less polar state to a more polar one in the fluorescence-quenching pocess and from a more polar intermediate to a less polar transition state in the cycloaddition process.



30a 30b

From these plots alone, however, it is hard to perceive any solvent-induced changes in the electronic structures of the exciplexes or in the mechanisms of the fluorescence quenching and photoreactions, an observation which is inconsistent with the discussions based on the dielectric continuum assumption. Since **30** is a polar solute of the mobile π electronics, the excitation energies, $E_T(30)$, may be perturbed by a variety of solute-solvent interactions involving hydrogen bonding in protic solvents. Taft, Abboud, and Kamlet recently reported that the $E_T(30)$ scale can be expressed by a multiple linear regression equation of the solvent dipole moment and $(n^2-1)/2(2n^2+1)$ for nonhydrogen-bonding solvents;[36] combined contributions of dipole-dipole interactions and solvent polarizability are involved in this scale unlike the electrostatic model. Therefore, the linear plots in Figs. 5 and 6 can not be simply interpreted but should be regarded to reflect only the parallel relationships in the solvent dependencies between the excitation energies of **30** and the free-energy changes in the fluorescence-quenching and cycloaddition processes.

Finally the plot of $\tilde{\nu}_c$ *vs.* $E_T(30)$ for the **1a-2h** exciplex is shown in Fig. 7, which gives two linear lines with a break at $E_T(30) \approx 38$ kcal mol^{-1}, suggesting a solvent-induced change in the electronic nature of the exciplex. A similar plot which is not shown here was also obtained for the **1a-2e** exciplex.[32b] Since the linearity is strikingly good, the solvatochromic shifts of the exciplex emission is probably again very similar to those of the absorption band of **30** in the origin. At any rate, it should be emphasized that solvent effects on the processes from exciplexes involving reversible dissociation, cycloaddition, and emission parallel those on the electronic excitation of **30**. The good linearity of the plots using $E_T(30)$ as a scale of solvent polarity seems to indicate something essential though detailed discussions can not be made because of the lack of information concerning the physical and chemical entities involved in $E_T(30)$.

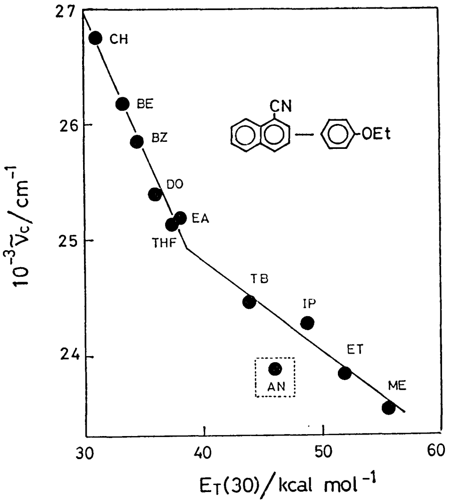


Fig. 7. Plot of $\tilde{\nu}_c$ *vs.* $E_T(30)$ for **1a-2h** pair; see abbreviations in Chart 1 and Table 2.

Conclusion

Solvent effects on the reversible dissociation and cycloaddition processes from the nonemissive naphthonitrile-olefin and furan exciplexes have been qualitatively analyzed by steady-state kinetics based on the assumption of the solvent as a continuous dielectric medium. The nonemissive exciplexes are commonly changed in both the electronic structures and the reactivities when the medium is changed from a nonpolar or moderately polar aprotic solvent to a polar protic solvent. In the less polar aprotic solvents, CT contributions are low but reactivities in the cycloadditions are relatively high. On the other hand, considerable degrees of CT contributions are induced in the more polar protic solvents, and the reactivities decrease with the increase of solvent polarity. Our results concerning CT contribution-reactivity relationships in either the [2+2] or [4+4] cycloaddition *via* an exciplex are in line with the Lewis[24] and Caldwell's[30] interpretations based on the Michl's theory.[29]

Dimroth and Reichardt's $E_T(30)$ has been found to be a suitable scale of solvent polarity for linear free-energy relationships associated with the solvent dependences in the reversible dissociation, cycloaddition, and emission processes from exciplexes. The good linearity in the plots with $E_T(30)$ may originate from internal correction of specific solute-solvent interactions. Unfortunately, implications of the linear relationships can not be sufficiently uncovered with regard to electronic structures and reactivities of exciplexes as well as the mechanisms in fluorescence quenching and photoreactions owing to umbiguities of the physical definition of $E_T(30)$.

The present treatments on solvent effects on fluorescence-quenching rate constants and quantum yields of photoreactions can thus provide a convenient, useful basis for qualitative estimations of electronic structures and reactivities of nonemissive exciplexes and will be applicable to other similar nonemissive exciplex systems, though the application is limited to such A-D pairs for which $\gamma k_c \ll 10^{10}$ dm^3 mol^{-1} s^{-1} in nonpolar and moderately polar solvents.

Experimental

Materials. An ethereal solution of the naphthonitriles (Tokyo Kasei) was washed three times with dilute hydrochloric acid and then with water, saturated sodium hydrogencarbonate, and water, dried, filtered, and evaporated. Pale yellow solids which had been obtained by vacuum distillation were purified by column chromatography on silica gel (Merck, 70—230 mesh) followed by repeated recrystallization from hexane; the pure 1- and 2-naphthonitriles were thus obtained as white flakes. The electron donors (**2a** and **2c**—**h**) were commercially obtained (Tokyo Kasei and Nakarai Chemicals) while **2b** was prepared according to the literature method.[37] The electron donors were distilled from sodium under a nitrogen atmosphere before use.

All the solvents were spectrograde (Tokyo Kasei and Nakarai Chemicals). Cyclohexane was used as received. Ethyl acetate and benzene were distilled. Diethyl ether, dibutyl ether, and tetrahydrofuran were distilled from lithium aluminium hydride. Dioxane, *t*-butyl alcohol, 2-butanol, 2-propanol, and ethanol were distilled from sodium. Methanol and acetonitrile were distilled from calcium hydride. All the distillations were performed under a nitrogen atmosphere before use.

Anayltical methods. A Hitachi MPF-4 spectrofluorometer equipped with a data processor (612-0085) was used for the fluorescence-quenching experiments and the measurements of emission spectra; all the fluorescence spectra were recorded after correction of specral response of the photomultiplier. The fluorescence lifetimes of 1- and 2-naphthonitriles were determined on the Hitachi MPF-4 spectrofluorometer equipped with a Hitachi time-resolved photometer. Concentrations of the naphthonitriles were set to $(3—6)\times10^{-4}$ mol dm^{-3} in all the spectroscopic measurements.

Proton nuclear magnetic resonance (NMR) spectra were recorded at 100 MHz on a JEOL JNM-PS-100 spectrometer or at 60 MHz on a JEOL JNM-60 spectrometer. Ultraviolet (UV) spectra were obtained on a Hitachi 124 spectrophotometer. Gas-liquid chromatography (GLC) was performed on a Shimadzu GC-3BF dual-column instrument with flame ionization detectors using 75 cm×4 mm columns packed with 5% SE-30 on Celite 545 and 10% PEG 20M on Shimalite W. Gel permeation chromatography (GPC) was carried out on a Toyosoda HLC-801 using a column of G-1000H6 polystyrene gel; tetrahydrofuran was used as eluant at an elution rate of 1.1 cm^3 min^{-1}.

Oxidation and reduction potentials were measured for N$_2$-saturated acetonitrile solutions ($\approx 10^{-3}$ mol dm^{-3}) *vs.* an Ag/AgNO$_3$ reference electrode by cyclic voltammetry. Tetraethylammonium tetrafluoroborate (0.1 mol dm^{-3}) was used as supporting electrolyte. The scan speed was 0.2 V s^{-1} and the temperature was kept at 23±0.1 °C. No cyclic voltammograms showed reversible peaks corresponding to oxidation of anion radicals and reduction of cation radicals. Therefore, half-peak values ($<\pm0.015$ V) were employed as oxidation and reduction potentials. Details of measurements were identical to those described previously.[38]

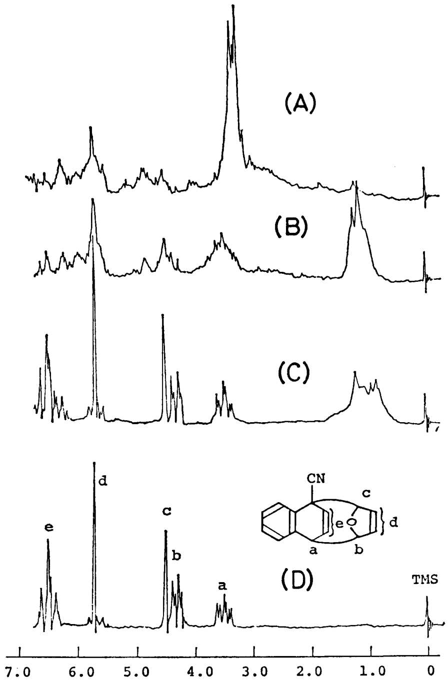


Fig. 8. NMR spectra (CDCl$_3$ solution) of photolysates of **1a**-**2f** pair in (A) methanol, (B) ethanol, (C) 2-butanol, and (D) benzene; the spectra were taken after thorough removal of both solvent and **2f** from the corresponding solutions irradiated at 313 nm; 30—40% conversions.

Determination of Quantum Yields for Disappearance of 1-Naphthonitrile. Monochromatic light at 313 nm was isolated from a high-pressure mercury lamp (Eikosha, POH-450) by passage through a Toshiba UV-D25 glass filter and an aqueous potassium chromate solution (0.2 g dm^{-3}, 10 mm path length). The intensity (I_0) of incident light was determined by potassium trioxalatoferrate(III) actinometry to be 2.01×10^{-7} einstein cm^{-3} min^{-1}. A solution (4 cm^3) containing **1a** ($(3.5—4.5)\times10^{-4}$ mol dm^{-3}) and an olefin (1.0 mol dm^{-3}) or furan (2.6 mol dm^{-3}) was introduced into an optical cell and then irradiated with the 313-nm light at 20±1 °C. The decrease in the absorbance (OD) of **1a** at 307 nm was monitored at appropriate intervals of time; $\ln(e^{OD}-1)$ was plotted against irradiation time (t, min). The plots were linear up to 20—40% conversions of **1a**. Quantum yields (ϕ_{-A}) for disappearance of **1a** were thus obtained by applying the slopes of the plots to Eq. 16, where κ is the observed molar absorption coefficient of **1a** at 307 nm for each solution in the optical cell used.

$$\ln(e^{OD}-1) = -1000\kappa I_0\phi_{-A}t + \text{constant} \qquad (16)$$

Photoreaction of 1-Naphthonitrile with Ethyl Vinyl Ether or 2-Methyl-2-butene in Various Solvents. Solutions containing **1a** (70—80 mg/10 cm^3, ≈ 0.05 mol dm^{-3}) and the olefin ($\approx$ 1.0 mol dm^{-3}) were irradiated with a high-pressure mercury lamp (Eikosha, PIH-300) through an aqueous potassium chromate solution (0.2 g dm^{-3}, 10 mm path length) under cooling with water. The progress of the photoreaction was followed by GLC, and it was confirmed that the cycloadducts (**3** and **4**) were the exclusive products without any change in the isomer ratios up to ≈50% conversion of **1a**. After ≈40% of **1a** had been consumed, the irradiated solutions were thoroughly evaporated under a high vacuum below 40 °C. The remaining oils were subjected to NMR. The isomer ratios were thus determined by both NMR and GLC and are listed in Table 4.

Photoreaction of 1-Naphthonitrile with Furan in Various Solvents. Solutions containing **1a** (70—80 mg/10 cm^3, ≈0.05 mol dm^{-3}) and **2f** (≈1.0 mol dm^{-3}) were irradiated in a similar way. The progress of the photoreaction was followed by GPC, and it was confirmed that product distributions were almost constant up to ≈40% conversion of **1a**. After 30—40% of **1a** had been consumed, the irradiated solutions were thoroughly evaporated under a high vacuum below 30 °C, and then the remaining oils were subjected to NMR. The NMR spectra are shown in Fig. 8.

Photoreaction of 1-Naphthonitrile with Phenyl Vinyl Ether in Acetonitrile. An acetonitrile solution (200 cm^3) containing **1a** (0.75 g, 0.005 mol) and **2b** (6 g, 0.05 mol) was irradiated for 20 h at 313 nm under cooling with water. After the removal of the solvent, vacuum distillation gave 2.5 g of **2b**. The distillation residue was chromatographed on silica gel (Merck, 70—230 mesh). Elution with 10% benzene in hexane gave *cis*-1,2-diphenoxycyclobutane[17] (0.42 g, 12% yield based on unrecovered **2b**) and the *trans* isomer[17] 0.42 g, 12%); 0.51 g of **1a** was recovered by elution with 30% benzene in hexane. Further elution gave untractable heavy oils.

This work was partially supported by a Grant-in-Aid No. 56550590 from the Ministry of Education, Science and Culture.

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