Solvent Effects upon Dynamic Behavior of Intramolecular Heteroexcimers

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Solvent effects upon fluorescence quantum yields, fluorescence rise and/or decay curves of p-$(CH_3)_2NC_6H_4$–$(CH_2)_n$–(9-anthryl) (n=1, 2, 3) and p-$(CH_3)_2NC_6H_4$–$(CH_2)_n$–(1-pyrenyl) (n=1, 2, 3) have been investigated in detail. It is concluded that the sandwich structure is not necessary for the intramolecular charge transfer in polar solvents and that the mechanism of intramolecular heteroexcimer formation in polar solvents is different from that in nonpolar solvents.

Studies on the structures and dynamic behavior of electron donor–acceptor systems in excited states are important for understanding primary processes of photochemical reactions. We have examined the intramolecular exciplex (heteroexcimer and excimer) systems in order to clarify the electronic structures and mechanisms of the dynamic behavior of exciplex systems, such as fluorescence quenching due to the electron transfer reaction as well as the fluorescent exciplex formation. In a previous paper,[1] solvent shifts of the fluorescence bands and an analysis of results by a theoretical method were reported for the following intramolecular heteroexcimer systems: p-$(CH_3)_2NC_6H_4$–$(CH_2)_n$–(1-pyrenyl) (n=1, 2, 3, abbreviated as P_n) and p-$(CH_3)_2NC_6H_4$–$(CH_2)_n$–(9-anthryl) (n=1, 2, 3, abbreviated as A_n).

We have measured the solvent effects upon fluorescence quantum yields as well as fluorescence rise and/or decay curves of these compounds. From the results the mechanisms of intramolecular charge transfer and the fluorescent heteroexcimer formation will be discussed in the following.

Experimental

Absorption spectra were measured with a Cary 15 spectrophotometer. Fluorescence quantum spectra were measured with an Aminco-Bowman spectrophotofluorometer calibrated by using a standard tungsten lamp. The fluorescence rise and decay curves as well as the time resolved fluorescence spectra were observed on an apparatus consisting of a Bausch & Lomb high intensity monochromator, 1P28 photomultiplier, Tektronix 661 sampling oscilloscope, and a pulsed nitrogen gas laser of *ca.* 1 kW peak power.

The preparation of A_n and P_n will be reported elsewhere. Spectrograde hexane, decalin, dibutyl ether, tetrahydrofuran (THF), 2-propanol, acetone, and acetonitrile were used without further purification. Butylacetate and isobutyl alcohol (chromatographic reagents) were used without purification. GR-grade diethyl ether and methanol were used without further purification. 1-Pentanol was dried over calcium oxide and distilled. Butyronitrile was dried over calcium hydride and distilled carefully with phosphorus pentoxide. All solutions were deaerated by freeze-pump-thaw cycles. For the measurement of temperature effects upon the fluorescence rise and decay curves and the time resolved fluorescence spectra as well as the steady state fluorescence spectra, the temperature of a solution in a cuvette placed in a metal dewar with quartz windows was controlled by a constant flow of cold nitrogen gas. The temperature of the sample was measured with a thermocouple placed in the sample tube.

Results and Discussion

A. Solvent Effects upon Fluorescence Quantum Yields. Absorption spectra of A_1, A_2, A_3, P_1, P_2, and P_3 show no indication of the ground state interaction. Excitation for the fluorescence measurements was made at the absorption band of the pyrene or anthracene moiety. For the evaluation of relative fluorescence yields of A_n and P_n in various solvents, their fluorescence quantum spectra were measured using solutions with equal absorbance (0.45) at the wavelengths of the excitation, 345 nm for P_n and 368 nm for A_n. Since the LE (local excited state) fluorescence band of pyrene or anthracene moiety frequently overlaps the intramolecular HE (heteroexcimer) fluorescence band, it is necessary to subtract the LE band from the observed spectra for the evaluation of the HE fluorescence yield. For this purpose, LE fluorescence spectra of hexane solutions of A_1, A_2, 9-ethylanthracene, P_1 and 1-ethylpyrene were used, respectively, for the spectra of A_1, A_2, A_3, P_1, and P_2 as well as P_3 in various solvents. We have employed this procedure instead of using the same LE spectra throughout the P_n or A_n series, since the vibrational structures of the spectra appear to depend a little upon the number of methylene chains as indicated in Fig. 1 for A_1 and A_2. A continued ultraviolet irradiation of solutions of A_n and P_n brings out a decrease in the absorption intensity of the aromatic hydrocarbon moiety as well as an increase in the LE fluorescence intensity and a decrease in the HE fluorescence intensity. Accordingly, freshly prepared solutions were used always for quantitative measurements. Practically no change in absorption and fluorescence intensities was observed during the course of measurements. Fluorescence quantum yields were determined, using 9,10-diphenylanthracene as a standard.[2] The values obtained are given in Table 1, where Φ_{LE} is the quantum yield of the LE fluorescence and Φ_{HE} that of the HE fluorescence.

A_1, A_2, and P_1 in nonpolar solvents such as hexane and decalin show the LE fluorescence of anthracene or pyrene part, and the HE fluorescence can be observed only in polar solvents.[1,3,4] The result is explained as follows.[1] Because of the large separation between donor and acceptor groups, the stabilization energy of the charge transfer state due to the coulomb interaction between the pair in these compounds may be smaller than in the case of A_3 or P_3 where the sandwich type conformation is possible. However, since their dipole moments in the charge transfer state are much larger

Table 1. Fluorescence quantum yield of intramolecular HE systems

Solvent	P_1		P_2		P_3		A_1		A_2		A_3	
	Φ_{LE}	Φ_{HE}	Φ_{LE}	Φ_{HE}	Φ_{LE}	Φ_{HE}	Φ_{LE}	Φ_{HE}	Φ_{LE}	Φ_{HE}	Φ_{LE}	Φ_{HE}
Hexane	0.61	—	0.13	0.13_3	0.01_0	0.40_3	0.2_5	—	0.4_3	—	0.1_3	0.3_2
Decalin	0.60	—	0.09_1	0.10_3	0.007_3	0.24_4	0.1_9	—	0.5_2	—	0.2_5	0.2_5
Dibutyl ether	0.09	0.17	0.01_8	0.09_6	0.003_8	0.26_1	0.02	0.02_2	0.3_4	0.3_4	0.1_4	0.2_3
Diethyl ether	0.006	0.07_0	0.02_1	0.12_1	0.004_7	0.26_3	0.004	0.008	0.09	0.1_2	0.03_1	0.2_2
Butyl acetate	0.003	0.05_0	0.01_0	0.15_4	0.001_0	0.15_4	0.0004	0.004	0.01_3	0.06_5	0.01_6	0.1_6
THF	0.005	0.04_0	0.01_7	0.15_7			0.0005	0.001	0.01_1	0.07	0.004	0.1_1
Isobutyl alcohol	0.002	0.03_0	0.01_0	0.03_1	0.003_8	0.08_3	0.0005	0.0005	0.01_7	0.004	0.01_4	0.01_5
Acetone	0.006	0.02_0	0.01_0	0.001	0.003_5	0.03_4	0.0005	0.0008	0.009	0.003_0	0.01_7	0.003
Methyl alcohol	0.002	0.004_3	0.009		0.001_1	0.005_2						
Aceto-nitrile	0.002	0.004_0	0.008	0.0001	0.001_7	0.004_0	0.0003	0.0003	0.006	0.0004	0.007	≈ 0

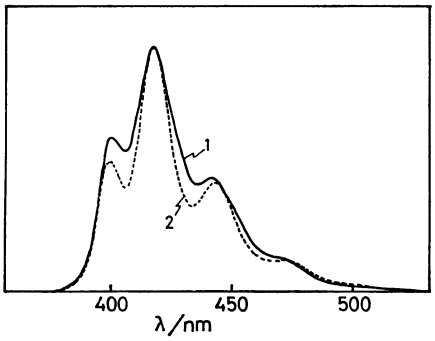

Fig. 1. Fluorescence spectra of A_1 (1) and A_2 (2) in hexane at room temperature.

than those of the sandwich type heteroexcimers, the solvation in a polar solvent may be very effective for the stabilization of the charge transfer state. Thus, the level inversion between the LE and the charge transfer state may arise and the HE fluorescence will compete with the LE fluorescence in polar solvents.

Roughly speaking, Φ_{LE} as well as Φ_{HE} decrease with increasing solvent polarity. Presumably, deactivation processes leading to the ground state or to some non-fluorescent products are considerable in strongly polar solvents. In the case of A_1, both Φ_{LE} and Φ_{HE} are much smaller than those of the other systems in polar solvents. Thus the deactivation processes competing with the HE formation are predominant in the case of A_1 in polar solvents.

Although the fluorescence yields decrease with increase in solvent polarity, Φ_{HE} values of the present intramolecular HE systems in polar solvents are much larger as compared with the intermolecular case. As an example, Φ_{HE} of P_3 in pyridine is 0.07[3] as compared with 0.015 of pyrene-*N*,*N*-dimethylaniline (DMA) intermolecular HE.[5] The observed values of P_3 in acetone and acetonitrile are 0.034 and 0.004, respectively, while no HE fluorescence can be observed in these solvents in the case of the intermolecular system.

The above results were explained[3,4] as due to the fact that it is difficult for ionic dissociation from the nonrelaxed electron transfer state, which is a dominant prccess in the case of the intermolecular HE system in polar solvents,[6,7] to occur in the case of the intramolecular HE.

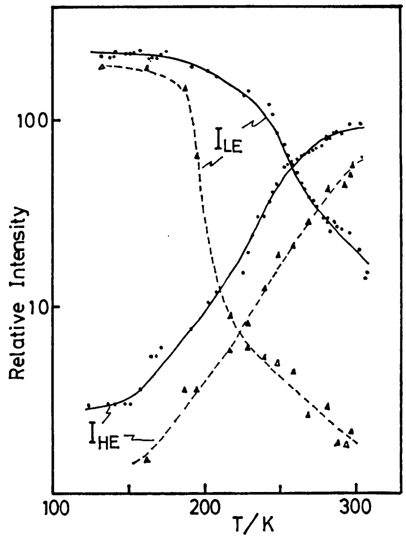

Fig. 2. Temperature dependence of I_{LE} and I_{HE} of P_3 in decalin (solid line) and 2-propanol (dotted line).

Although the ionic "dissociation" is not possible, the formation of non-fluorescent intramolecular ion-pairs from the LE state or the non-relaxed electron transfer state may not be prohibited in polar solvents. This seems to result in the decrease of HE fluorescence yield with increasing solvent polarity as described above.

For detailed studies of the intramolecular HE formation processes, it is necessary to confirm, especially in the case of the system capable of forming sandwich type of HE, whether the HE is formed by the dynamic process or not. It is possible that weak intramolecular complexes are formed at low temperature in the ground state leading to immediate formation of fluorescent HE state under excitation.[8]

For this purpose, temperature effects upon fluorescence intensity of P_3 were examined. As indicated in Fig. 2, the intensity of the LE fluorescence (I_{LE}) increases with decreasing temperature, approaching a constant value at sufficiently low temperature both in decalin and isopropanol. This suggests that the

TABLE 2. FLUORESCENCE RISE AND DECAY TIMES OF INTRAMOLECULAR HE SYSTEMS (in units of ns)

Solvent	P_1		P_2		P_3		A_1		A_2		A_3	
	τ_{LE}	τ_{HE}	τ_{LE}	τ_{HE}	τ_{LE}	τ_{HE}	τ_{LE}	τ_{HE}	τ_{LE}	τ_{HE}	τ_{LE}	τ_{HE}
Hexane	156	—	120	101	4.5 & 86	87	4.8	—	9.5	—	3.3	130
Decalin	120	—	5.6 & 92	3.3[a)], 101	7.5 & 90	7.5[a)], 90	6.7	—	12	—	4.8	130
Dibutyl ether	19.3	20.8	3.9	80	6	116	7.0	7.5	≈3 & 48	48	≈3	121
Diethyl ether	9.3	9.3	3.8 & 85	82	3	141	7.3	8.9	≈3 & 112	120	<2	200
Butyl acetate	3.1	10.8	3.8	76	4	134						
THF	4	11	4.4	72			7.5[b)]	11	51	83		150
Isobutyl alcohol	4	9	4.2	21	5	4.5, 86	3	4.5	<2	≈2		40
Acetone	3.6	10	4.3	8.5	4.4	63	7.5[b)]	4	8.5[b)]	5		9
Methyl alcohol	3	4.5	3.5	≈2	3	23.5						
Acetonitrile	4	7.5	3.9	3.5	5	≈2	8.5[b)]	≈5	8.8[b)]	≈3	9[b)]	≈3

a) Rise time of the HE fluorescene detected by the present apparatus. b) The values might be the lifetimes of the photoproducts.

intramolecular donor-acceptor interaction arises mainly by the dynamic process in the excited state. In accordance with this behavior of LE fluorescence, the intensity of the HE fluorescence (I_{HE}) decreases with temperature lowering.

B. Effects of Solvent Polarity and Temperature upon Fluorescence Rise and Decay Processes. Fluorescence rise and decay curves were measured at both wavelengths of LE and HE fluorescence bands. Typical two-component decay curve measured at the LE band and corresponding rise and decay curves measured at the HE band were confirmed in the case of several systems in nonpolar or slightly polar solvents. These kind of rise and decay curves are common in the case of intermolecular excimer and HE systems.

A possible kinetic scheme for the formation and decomposition processes of an intramolecular HE in nonpolar solvents can be written as follows.

$$\begin{tikzcd}
A^{*}\cdots D \arrow[r, shift left, "k_1"] \arrow[d, squiggly, shift right, "k_i"'] \arrow[d, shift left, "k_f"] & (A^{-}\cdot D^{+}) \arrow[l, shift left, "k_2"] \arrow[d, squiggly, shift right, "k_i'"'] \arrow[d, shift left, "k_f'"] \\
A\cdots D & (A\cdot D) \arrow[l]
\end{tikzcd} \qquad (1)$$

Assuming a δ-function excitation, the time dependences of the LE and HE fluorescence intensities are given by the following equations.

$$I_{LE}(t) = \frac{I_0}{(\lambda_2-\lambda_1)}\{(\lambda_2-X)\exp(-\lambda_1 t) + (X-\lambda_1)\exp(-\lambda_2 t)\} \qquad (2)$$

$$I_{HE}(t) = \frac{I_0 k_1}{(\lambda_2-\lambda_1)}\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \qquad (3)$$

where

$$\left.\begin{matrix}\lambda_1\\ \lambda_2\end{matrix}\right\} = 1/2[X+Y\mp\{(Y-X)^2+4k_1k_2\}^{1/2}] \qquad (4)$$

$$X = k_1 + k_f + k_i$$
$$Y = k_2 + k_f' + k_i'$$
$$I_0 = I_{LE}(0)$$

By means of Eqs. 2 and 3, the short lived component in the decay curve of the LE fluorescence and the rise time of HE fluorescence were evaluated graphically from the semilogarithmic plots of $I(t)$ as indicated in Fig. 3. However, in moderately as well as strongly polar solvents, it was difficult to observe the two-component decay of the LE fluorescence or the rise curve of the HE fluorescence. The results of fluorescence rise and decay times at room temperature are given in Table 2.

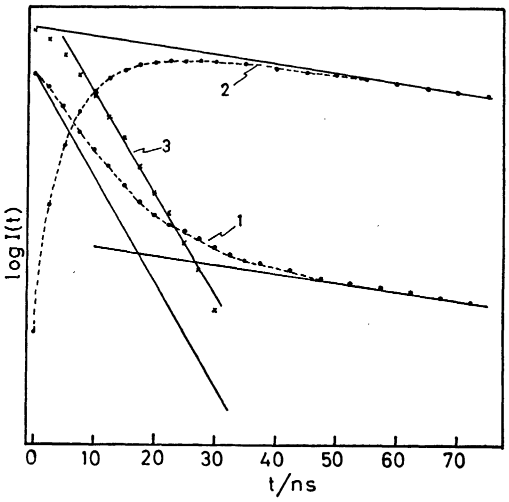

Fig. 3. Semilogarithmic plots of $I_{LE}(t)$ and $I_{HE}(t)$ of P_3 in decalin at room temperature.
(1) : $I_{LE}(t)$ (2) : $I_{HE}(t)$
(3) : $\frac{I_0 k_1}{\lambda_2-\lambda_1}\cdot\exp(-\lambda_1 t) - I_{HE}(t)$

In the case of A_1, A_2, and P_1, although the fluorescence spectrum of hexane solution is identical with that of the decalin solution, the fluorescence lifetime of hexane solution differs from that of the decalin solution. This seems to suggest that, even in the case of these systems in nonpolar solvents, the HE state is attained transiently from the thermally excited LE state, but will decompose immediately by the back charge transfer process of k_2.

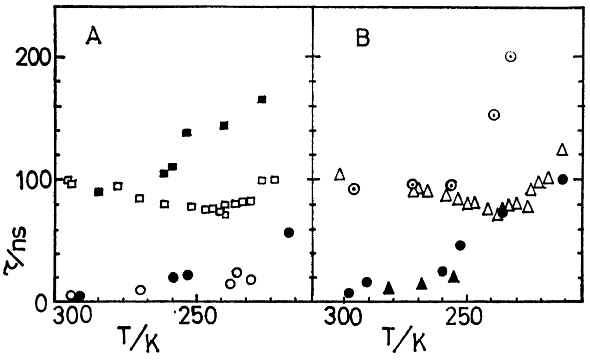

Fig. 4. Temperature effects upon fluorescence rise and decay times of P_2 and P_3 in decalin.

A. Rise and decay times of HE fluorescence.

○: Rise time of P_2, ●: rise time of P_3, □: decay time of P_2, ■: decay time of P_3.

λ_{obsd} for P_2: 500 nm, λ_{obsd} for P_3: 550 nm.

B. Decay times of two-component LE fluorescence.

△: Long life component of P_2, ⊙: long life component of P_3, ▲: short life component of P_2, ●: short life component of P_3.

$\lambda_{obsd}=400$ nm for both P_2 and P_3.

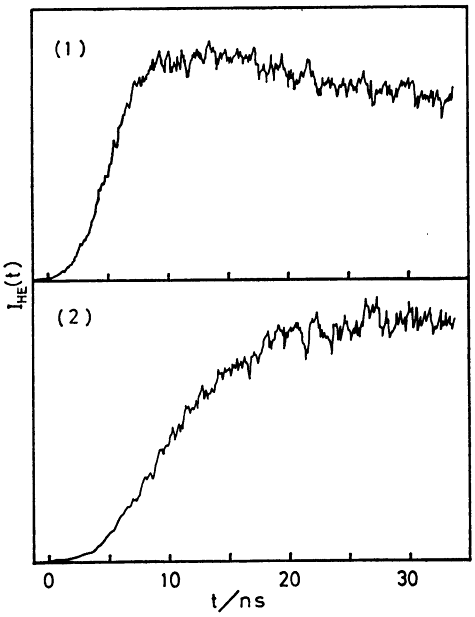

Fig. 5. Fluorescence rise curves of P_3 HE in 1-pentanol (1) and decalin (2) at room temperature.

Lewis and Ware[9] reported a special case of the HE system where the quenching process of the LE fluorescence could not be explained without assuming the transient HE formation though no HE emission was obseved as in the above case. They estimated the lifetime of the transient HE by analyzing the effect of the quencher concentration upon the decay process of the LE fluorescence. In the present case, however, it is not possible to examine such a concentration effect.

With the increase in solvent polarity, the HE state may be stabilized and the rate constant k_1 will increase. When the HE state is placed at the same energy as the LE state of pyrene or anthracene part and no extensive change of the geometrical structure is necessary, it is plausible that the HE formation and decomposition reaction becomes so rapid that the equilibrium between LE and HE state is attained approximately. If the equilibrium is attained, both the LE and HE fluorescence will show the single exponential decay with the same decay time. The behavior of A_1 as well as P_1 in ethers seems to correspond to this case.

Typical two-component decay represented by Eq. 2 was observed in cases of P_2 and P_3 in hexane as well as decalin, and A_2 in ethers at room temperature. The rise and decay times of P_3 HE in decalin were $\lambda_2^{-1}=$ 7.5 ns and $\lambda_1^{-1}=90$ ns, agreeing respectively with those obtained by measuring the two-component decay of the LE fluorescence. The temperature effect on the rise and decay curves of P_2 and P_3 in decalin was examined, the results being shown in Fig. 4. The observed decay curves can be reproduced by Eq. 2 in the temperature range 300—210 K. Thus, it has been confirmed that the HE's of P_2 and P_3 in decalin are formed by the dynamic process in the excited state even at low temperatures. Although λ_2 is a function of various rate constants, it seems to be close to k_1. Thus, the formation process of the HE state does not seem to be so fast as in the case of the intermolecular HE. The result may be due to the hindered rotations about CH_2–CH_2 bonds which are necessary to form a sandwich type HE, and also due to somewhat large solvent viscosity of decalin. As an example, values $\lambda_2^{-1}=25$ ns at 263 K, and 58 ns at 223 K were obtained in the case of P_3 in decalin. Thus, the temperature lowering makes the process of conformational change very slow. It is possible that both the hindered rotation itself and the solvent viscosity can be affected by the change of temperature. It is not clear which of these is more effective for retarding the conformational change.

In contrast to the above results, the rise time of P_3 HE fluorescence at room temperature is shorter than 2 ns (the rise time of the exciting laser pulse) both in 1-pentanol and 2-propanol, though these solvents are more viscous than decalin. The rise curve of P_3 HE in 1-pentanol is shown in Fig. 5 together with that in decalin. The result suggests that the mechanism of HE formation in polar solvents differs from that in nonpolar solvents. Presumably, orientational fluctuations of surrounding solvent dipoles and a slight approach of the two moieties of P_3 may induce the electron transfer without taking the sandwich type of structure.

In order to clarify the behavior of HE in polar solvents, temperature effects upon the fluorescence rise and decay curves of P_1, P_2, and P_3 in 2-propanol have been examined. The results are shown in Fig. 6. The rise times of HE fluorescence in the range from room temperature to *ca.* 160 K are much shorter than those of P_2 and P_3 HE's in decalin solution. Thus, the HE formation process in 2-propanol is much faster than that in decalin not only at room temperature but also at low temperatures. The decay time of the HE fluorescence of P_1 and P_2 is *ca.* 10 ns at room temperature, slightly increasing at low temperatures.

In the case of P_3 HE, the decay of HE fluorescence above 250 K can be represented by a single exponential curve, but not so below 250 K. By subtracting the slow component from the decay curve, the residual part

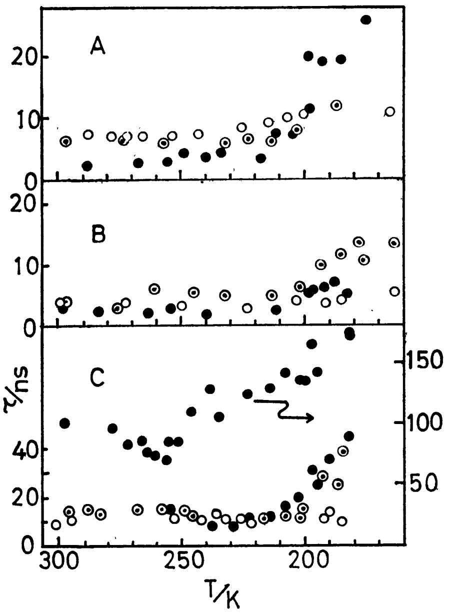

Fig. 6. Temperature effects upon fluorescence rise and decay times of P_1, P_2 and P_3 in 2-propanol.
○: P_1, ⊙: P_2, ●: P_3.
A. Decay times of LE fluorescence. $\lambda_{obsd}=400$ nm.
B. Rise times of HE fluorescence. $\lambda_{obsd}=550$ nm.
C. Decay times of HE fluorescence. $\lambda_{obsd}=550$ nm.
The time scale for the long life component of P_3 is indicated on the right hand side ordinate.

can be represented approximately by an exponential decay, as indicated in Fig. 7. Moreover, below 220 K, it was possible to observe the rise time of the HE fluorescence in 2-propanol with the present apparatus. The observed decay time of the fast component of the LE fluorescence at low temperatures does not agree with the rise time of the HE fluorescence. Similar results were obtained in 1-pentanol and butyronitrile.

As indicated in Fig. 6-C, the decay time of the fast component of the HE fluorescence of P_3 observed below 250 K shows a temperature dependence similar to that of the fluorescence decay times of P_1 and P_2 HE's. The result suggests that, at low temperatures, there are two kinds of HE's of P_3 which have decay times differing from each other, one of which seems to have a structure similar to that of P_1 or P_2 HE.

On the other hand, according to the result of recent laser photolysis studies,[10] the absorption spectrum of P_2 HE in 2-propanol was very close to the superposition of the absorption bands of pyrene anion and *N,N*-dimethylaniline cation, while a very broad absorption band with peak around 500 nm was observed in the case of the P_3 HE in 2-propanol. As regards the above argument concerning two kinds of HE's, we have measured time-resolved absorption spectra of P_3 HE in 2-propanol at 210 K. Corresponding to the result of fluorescence measurements, the short-life and long-life components of the time-resolved absorption spectra were similar respectively to the spectrum of P_2 HE and P_3 HE in 2-propanol at room temperature. Thus, the existence of two kinds of HE's of P_3 at low temperatures, one similar to P_1 or P_2 HE and the other analogous to the P_3 HE at room temperature, has been confirmed.

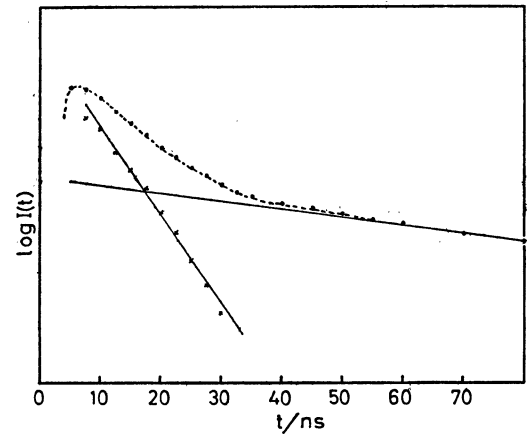

Fig. 7. Fluorescence decay function of P_3 HE observed at 550 nm in 2-propanol at 223 K.

However, according to our measurement of the time-resolved fluorescence spectra of P_3 HE, the spectrum of the slow component of the decay curve was approximately the same as that of the fast component. The result seems to indicate that these HE states with different lifetimes emit fluorescence at approximately the same wavelength region. Actually, the fact that the fluorescence band maxima of P_1, P_2, and P_3 in 2-propanol at room temperature are *ca.* 585, 585, and 590 nm, respectively,[1] indicates that a small difference in the geometrical structure of the HE does not appreciably affect the wavelength of the HE fluorescence in these polar solvents. Therefore, there seems to be a possibility that many kinds of HE's with different geometrical structures in polar solvents have similar fluorescence spectra and the HE fluorescence decay curve consists of many exponential curves with different decay times, which might be revealed by a more accurate measurement.

In the above interpretation, the non-fluorescent ion-pair does not play an important role in the formation process of the HE state. Nevertheless, it seems plausible that some non-fluorescent ion-pairs are formed in polar solvents, as discussed in *A* in relation to the solvent effect upon the HE fluorescence yield. Namely, several kinds of HE's as well as the non-fluorescent ion-pairs may be formed from the LE state or the non-relaxed CT state in polar solvents. Actually, formation of a species which might be identified with the non-fluorescent ion-pair was observed in the case of P_3 in acetonitrile.[3]

We see from the tables that both the HE fluorescence yield and decay time of the present systems decrease with increase of the solvent polarity, the extent of the decrease of the yield being a little larger. The result is comprehensible on the basis of the above discussion. The formation of the non-fluorescent ion-pair from the LE state or the non-relaxed CT state may be enhanced with increase of the solvent polarity. The result can also be interpreted by assuming the solvent-induced change of electronic and geometrical structures of the HE.[3,5] However, the interpretation does not seem to be supported by the above results of fluorescence decay curve measurements at low temperatures and their explanation.

It is described in *A* that the fluorescence yields of the present intramolecular HE's are much higher as compared with those of the intermolecular systems. However, the difference between the intra- and intermolecular systems is not restricted to the fluorescence yield. The fluorescence lifetimes of these intramolecular HE's are much longer than those of the intermolecular systems. As an example, the fluorescence lifetime of P_3 HE in pyridine is 100 ns³⁾ as compared with the value 30 ns of the pyrene-DMA intermolecular HE.⁵⁾ Although the fluorescence of the pyrene-DMA intermolecular HE cannot be observed in acetone probably due to the predominant ionic dissociation from both the non-relaxed CT state and the HE state, the HE fluorescence of P_3 with lifetime of 63 ns can be observed easily in the same solvent. Thus, once the HE of P_3 is formed, it seems to be difficult for the quenching process to the non-fluorescent ion-pair to take place even in such a strongly polar solvent as acetone. A more or less analogous circumstance can be observed in the other systems.

In view of the above results, it should be noted that the exceptionally high fluorescence quantum yield and long lifetime of the intermolecular HE systems in alcohol solutions¹¹⁾ can be ascribed to some mechanism involving the hydrogen bonding between the surrounding solvent molecules which prevents the ionic dissociation.

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