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Picosecond Laser Spectroscopy of Intramolecular Heteroexcimer Systems. Time-resolved Fluorescence Studies of p-$(CH_3)_2NC_6H_4$-$(CH_2)_n$-(9-Anthryl), p-$(CH_3)_2NC_6H_4$-$(CH_2)_n$-(1-Pyrenyl) Systems and 9,9′-Bianthryl

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In order to elucidate the details of elementary processes of photochemical charge transfer and heteroexcimer formation processes, and also in order to compare the obtained results with those of transient absorption spectral measurements, we have examined the following intramolecular heteroexcimer systems by means of ps time-resolved fluorescence measurements with a mode-locked Nd^{3+}: YAG laser and a streak camera: p-$(CH_3)_2NC_6H_4$-$(CH_2)_n$-(9-anthryl) (n=0, 1, 2, 3), p-$(CH_3)_2NC_6H_4$-$(CH_2)_n$-(1-pyrenyl) (n=1, 2, 3) and 9,9′-bianthryl. Effects of methylene chain length, solvent polarity and viscosity upon the intramolecular charge transfer processes have been clearly demonstrated. It is concluded that molecules with sandwich configuration in the ground state are not recognized in both n=3 compounds, and it takes a few ns for the heteroexcimer formation in hexane because of an extensive conformation change necessary to take sandwich configuration. Both conformation change and solvent reorientation are involved in the heteroexcimer formation processes in polar solvents, and heteroexcimer formation becomes faster with increase of solvent polarity and decrease of its viscosity. Moreover, two step conformation changes are observed in the case of the heteroexcimer formation of n=3 compounds in polar solvents, *i.e.* a heteroexcimer with loose structure is formed first, and then follows a structural change to the one of sandwich type. In acetonitrile, a strongly polar solvent, formation of heteroexcimer is very fast, occurring within the time-resolution of the picosecond apparatus.

The nature of CT (charge transfer) interactions in electronically excited states is a subject under lively investigation at present,[1] and the results appear to be important from the viewpoint of photochemical as well as photobiological reaction mechanisms.

In order to clarify the details of photo-induced CT and HE (heteroexcimer) formation processes, we have been examining intramolecular HE systems such as p-$(CH_3)_2NC_6H_4$-$(CH_2)_n$-(9-anthryl) (A_n, n=0, 1, 2, 3), p-$(CH_3)_2NC_6H_4$-$(CH_2)_n$-(1-pyrenyl) (P_n, n=1, 2, 3) and 9,9′-bianthryl (Bian), by means of ns time-resolved fluorescence and ns as well as ps time-resolved absorption spectral measurements.[2–10,12,14,16] It has been demonstrated that fluorescence spectra of A_1, A_2 and P_1 in nonpolar solvents can be ascribed to the anthracene or pyrene part (LE (locally excited state) fluorescence), and they show HE fluorescences only in polar solvents due to the solvent-induced change of electronic state during the excited state lifetime. Analogous results have been observed also for A_0. For A_3, P_3, and P_2 HE fluorescences can be observed not only in polar solvents but also in nonpolar solvents, due to a conformation change from an extended form to the sandwich or a similar structure during the excited state lifetime. Moreover, it has been demonstrated that the HE formation process is affected considerably by solvent polarity. By means of ps transient absorption measurements of P_3 in 2-propanol photoinduced CT has been found to produce at first a loose HE followed by a structural change to the more compact one.

In the present study, by means of ps time-resolved fluorescence measurements we have made direct observations of CT fluorescence rise curves as well as LE fluorescence decay curves of the above intramolecular exciplex systems in various solvents of different polarity, and have provided a systematic interpretation of photoinduced CT processes in solution.

Experimental

Apparatus and Measurements. The third harmonic (355 nm, 15 ps, 1 mJ) of a passively mode-locked Nd^{3+}:YAG laser was used as an exciting light source. The ps pulse repeated at 1 Hz. Fluorescence rise and decay curves were measured with a streak camera (HTV C979), the streak being digitized by a TV camera/microcomputer system (HTV C1000). Measurements in a few ns region were made also by a high speed tandem microchannel plate photomultiplier (HTV R1294X) connected to a transient digitizer (Tektronix R7912). All solutions for the measurements were de-aerated by freeze-pump-thaw cycles.

Materials. All solvents used were Merck spectrograde. Hexane, acetone and acetonitrile were used without further purification. 2-Propanol and butyronitrile were distilled before use. Bian was the same sample as used previously.[12] A_n (n=0, 1, 2, 3) and P_n (n=1, 2, 3) were synthesized and purified as described below.

All melting points are uncorrected. The NMR and MS spectra were recorded with a Hitachi Perkin-Elmer R-20 or a Varian XL-100 and a Hitachi RMU-7, respectively.

p-*(9-Anthryl)*-N,N-*dimethylaniline* (A_0). To a Grignard reagent prepared from p-bromo-*N,N*-dimethylaniline (20 g, 0.1 mol) and magnesium flake (2.4 g, 0.1 mol) in tetrahydrofuran, a solution of anthrone (5.82 g, 0.03 mol) in tetrahydrofuran was added with stirring over a period of 30 min at 0 °C under nitrogen atmosphere. After stirring for additional 1 h, the reaction mixture was worked up. The crude product was chromatographed on alumina and recrystallized from benzene.

A_0: yelloe granulars, 1.1 g (12.3%), mp 260—260.5 °C, NMR ($CDCl_3$) δ 3.11 (s, CH_3), 7.0—8.4 ppm (m, ArH).

Found: C, 88.94; H, 6.23; N, 4.72%; MS (*m/e*) 297 (M^+). Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71%; M, 297.38.

p-*Arylmethyl*-N,N-*dimethylaniline* (*A_1, P_1*). A mixture of *N,N*-dimethylaniline (2 ml) and 9-(bromomethyl)anthracene[19] (500 mg, 1.9 mmol) was stirred overnight at room temperature and at 40—50 °C for 30 min. After adding 10 ml of methanol to the reaction mixture, resulting precipitate was collected and washed with methanol. Recrystallization of the precipitate from acetone gave pale yellow plates of A_1 (180 mg, 30%), mp 133—134 °C. NMR ($CDCl_3$) δ 2.75 (s, CH_3), 4.82 (s, CH_2), 6.68 (m, ArH of phenyl), 7.0—8.3 ppm (m, ArH of Anthryl). Found: C, 88.45; H, 7.06; N, 4.50%, MS (*m/e*), 311 (M^+). Calcd for $C_{23}H_{21}N$: C, 88.70; H, 6.80; N, 4.50%; M, 311.41.

In a similar manner, P_1 was prepared. P_1: colorless needles from acetone, mp 103—105 °C. NMR ($CDCl_3$) δ 2.86 (s, CH_3), 4.62 (s, CH_2), 6.85 (m, ArH of phenyl), 7.7—8.4 ppm (m, ArH of pyrenyl). Found: C, 89.30; H, 6.23; N, 4.06%; MS (*m/e*), 335 (M^+). Calcd for $C_{25}H_{21}N$: C, 89.51; H, 6.31; N, 4.18%; M, 335.43.

p-*(2-Arylvinyl)*-N,N-*dimethylaniline* (*$I_{A,P}$*). To a stirred suspension of phosphonium salt (2.7 g, 5 mmol) in benzene, prepared from 9-(bromomethyl)anthracene[19] and triphenylphosphine, was added an ethereal solution of phenyllithium (1 mol dm^{-3}, 5 mmol) under nitrogen. To this mixture a solution of *p*-dimethylaminobenzaldehyde (0.75 g, 5 mmol) in benzene was added dropwise for 5 min. Stirring was continued overnight at room temperature. After working up in the usual manner the crude product was recrystallized from acetone to afford yellow needles of I_A (500 mg, 31%), mp 178—180 °C. Found: C, 88.89; H, 6.37; N, 4.26%. Calcd for $C_{24}H_{21}N$: C, 89.12; H, 6.55; N, 4.33%.

The synthesis of I_P was done in the same manner. I_P: yellow granulars from benzene–acetone, mp 193.5—195 °C. Found: C, 89.90; H, 6.08; N, 3.91%. Calcd for $C_{26}H_{21}N$: C, 89.87; H, 6.09; N, 4.03%.

p-*(2-Arylethyl)*-N,N-*dimethylaniline* (*A_2, P_2*). Catalytic hydrogenation of I_A (3.23 g, 10 mmol) in benzene was carried out by stirring with 5% Pd–C (200 mg) for 30 h. The reaction mixture was worked up and chromatographed on silica gel to afford yellow solid A_2 (1.97 g, 60.6%). A_2: yellow needles from acetone, mp 119.5—120.5 °C. NMR ($CDCl_3$) δ 2.92 (s, CH_3), 2.8—4.0 (m, CH_2), 6.9 (m, ArH of phenyl), 7.1—8.4 ppm (m, ArH of anthryl). Found: C, 88.50; H, 7.11; N, 4.26%; MS (*m/e*), 325 (M^+). Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30; M, 325.43.

The preparation of P_2 was accomplished in a similar manner. P_2: pale yellow granulars from acetone, mp 118—120 °C. NMR ($CDCl_3$) δ 2.92 (s, CH_3), 2.9—3.7 (m, CH_2), 6.94 (m, ArH of phenyl), 7.8—8.4 ppm (m, ArH of pyrenyl). Found: C, 89.41; H, 6.64; N, 3.99%, MS (*m/e*) 349 (M^+). Calcd for $C_{26}H_{23}N$: C, 89.36; H, 6.63; N, 4.01%; M, 439.45.

p-*(3-Aryl-3-oxo-1-propenyl)*-N,N-*dimethylaniline* (*$II_{A,P}$*). A mixture of 9-acetylanthracene (27.5 g, 125 mmol), *p*-dimethylaminobenzaldehyde (18.5 g, 125 mmol), and potassium cyanide (3 g, 45 mmol) in ethanol was heated under reflux for 4 h. The resulting precipitate was collected and recrystallized from toluene to yield ketone II_A (39 g, 90%), orange granulars, mp 188—189 °C. Found: C, 85.64; H, 5.76; N, 3.81%. Calcd for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99%.

The preparation of II_P was done in the same manner. II_P: orange plates from acetone–benzene, mp 171.5—172.5 °C. Found: C, 86.12; H, 5.32; N, 3.63%. Calcd for $C_{27}H_{21}NO$: C, 86.37; H, 5.64; N, 3.73%.

p-*(3-Aryl-3-oxopropyl)*-N,N-*dimethylaniline* (*$III_{A,P}$*). The ketone II_A (20 g, 57 mmol) was reduced with lithium aluminium hydride (4 g, 110 mmol) in boiling diethyl ether for 20 h using an extractor of Soxhlet-type. After removal of the solvent, the residue was recrystallized from acetone to give pure III_A, yellow granulars, 17.4 g (87%), mp 103—103.5 °C. Found: C, 84.79; H, 6.41; N, 3.92%. Calcd for $C_{25}H_{23}NO$; C, 84.95; H, 6.56; N, 3.96%.

In the same manner III_P was prepared. III_P: yellow plates from acetone, mp 142—143 °C. Found: C, 86.09; H, 6.09;, N. 3.72%. Calcd for $C_{27}H_{23}NO$: C, 85.91; H, 6.14; N, 3.71%.

p-*(3-Arylpropyl)*-N,N-*dimethylaniline* (*A_3, P_3*). The dihydroketone III_A (2 g, 5.6 mmol) was added to a stirred suspension of lithium aluminium hydride (0.38 g, 9.8 mmol) and aluminium chloride (2.66 g, 19.6 mmol) in diethyl ether (50 ml). After stirring for 2 h under reflux, ethyl acetate, water, and 5% aq sodium hydroxide were successively added to the reaction mixture. It was extracted with diethyl ether, and the organic layer was worked up in the usual manner. The residual yellowish brown solid was chromatographed on silica gel to give A_3 (34 mg, 18%). A_3: colorless granulars from acetone, mp 105—106 °C. NMR ($CDCl_3$) δ 2.92 (s, CH_3), 1.9—3.8 (m, CH_2), 6.95 (m, ArH of phenyl), 7.3—8.3 ppm (m, ArH of anthryl). Found: C, 88.65; H, 7.29; N, 4.10% MS (*m/e*), 339 (M^+). Calcd for $C_{25}H_{25}N$: C, 88.45; H, 7.42; N, 4.13%; M, 339.46.

In the same manner P_3 was prepared. P_3: pale yellow powder, mp 97—97.5 °C. NMR ($CDCl_3$) δ 2.9 (s, CH_3), 2.0—3.5 (m, CH_2), 6.89 (m, ArH of phenyl), 7.1—8.2 ppm (m, ArH of pyrenyl). Found: C, 89.12; H, 6.95; N, 3.90%, MS (*m/e*), 363 (M^+). Calcd for $C_{27}H_{25}N$: C, 89.21; H, 6.93; N, 3.85%; M, 363.48.

Results

A_3 and P_3 in Hexane Solution. Fluorescence spectra of A_3 and P_3 in hexane are shown in Fig. 1. Decay times (τ_d) of LE fluorescence measured in the wavelength region of 390—420 nm and rise time (τ_r) of HE fluorescence observed through a filter transparent for the region longer than 550 nm are listed in Table 1. Both τ_d and τ_r values of each compound agree within experimental error.

It should be noted here that the rise curve of the HE fluorescence measured at 540 nm contains a considerable amount of the rapid component. However, the rapid component is negligible if the fluorescence is observed through a filter which is transparent above 550 nm (Fig. 2).

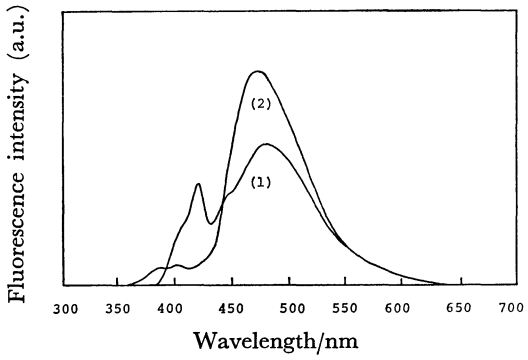

Fig. 1. Fluorescence spectra of A_3 and P_3 in hexane. (1): A_3, (2): P_3.

Table 1. Decay times of LE fluorescence and rise times of HE fluorescence of A_3 and P_3 in hexane

	τ_d/ns	τ_r/ns
A_3	2.3±0.1	2.6±0.4
P_3	4.6±1.0	3.9±0.6

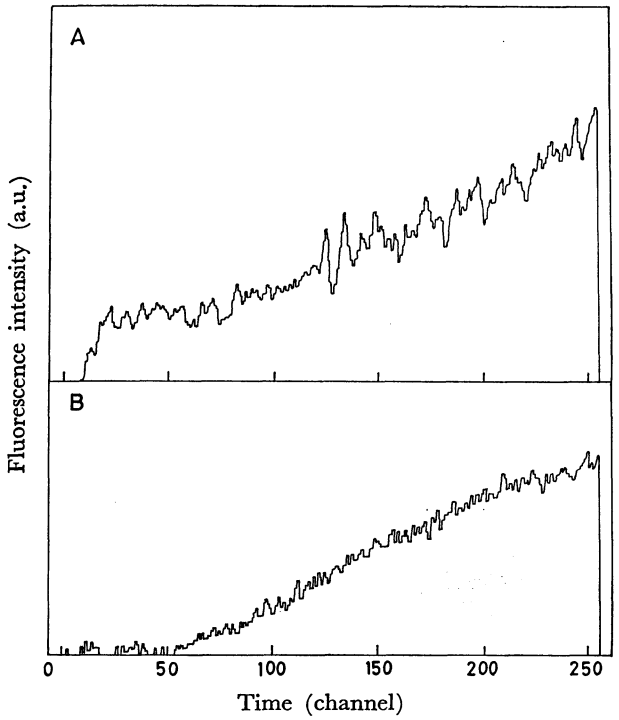

Fig. 2. Fluorescence rise curves of A_3 in hexane measured by means of ps streak camera.
A: Observed at 540 nm, B: observed through a filter which passes the wavelength region longer than 550 nm.

A_n and P_n in 2-Propanol Solution. Fluorescence spectra of A_n and P_n in 2-propanol solution are shown in Fig. 3. The HE band is shifted to considerably longer wavelength compared to that in hexane solution. Decay times of LE fluorescence observed in the region of 390—420 nm and rise times of HE fluorescence observed through a filter which is transparent above 520 nm are given in Table 2 for A_1, P_1, A_2, and P_2. The τ_d and τ_r values of each compound approximately agree, although there is a tendency that τ_r value is a little longer than that of τ_d for A_1 and P_1. As a typical example, the observed decay curve and also the rise curve of P_1 are shown in Fig. 4.

For A_3 and P_3, circumstances are somewhat complicated. By detailed observation of P_3 at 401 nm, we detected clearly a two-component decay of fluorescence as shown in Fig. 5A, from which decay times were estimated to be $\tau_d^1=340\pm20$ ps and $\tau_d^2=1.1\pm0.2$ ns.

We examined dynamic features of the HE fluorescence at several different wavelength regions. The measurement through a filter which is transparent above 680 nm indicated clearly rise and two-component decay curves (Fig. 5B). By analyzing this result, the

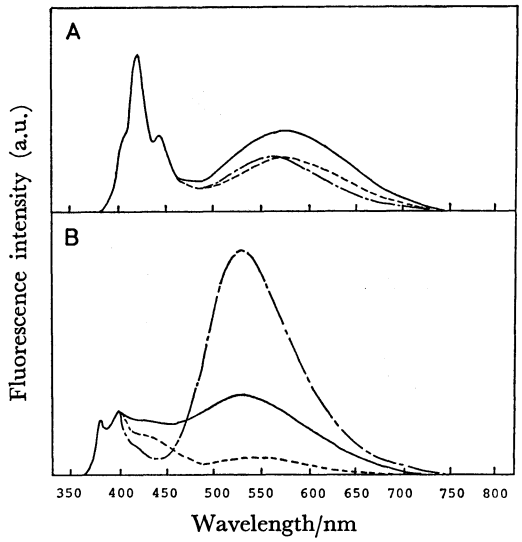

Fig. 3. Fluorescence spectra of A_n and P_n in 2-propanol.
A: A_n, B: P_n, (normalized at LE band maxima).
——: A_1, P_1, - - -: A_2, P_2, — - —: A_3, P_3.

Table 2. Decay times of LE fluorescence and rise times of HE fluorescence of A_1, P_1, A_2, and P_2 in 2-propanol solution

	τ_d/ps	τ_r/ps
A_1	40± 9	54± 9
A_2	98± 5	93±23
P_1	62± 6	93±20
P_2	170±39	192±39

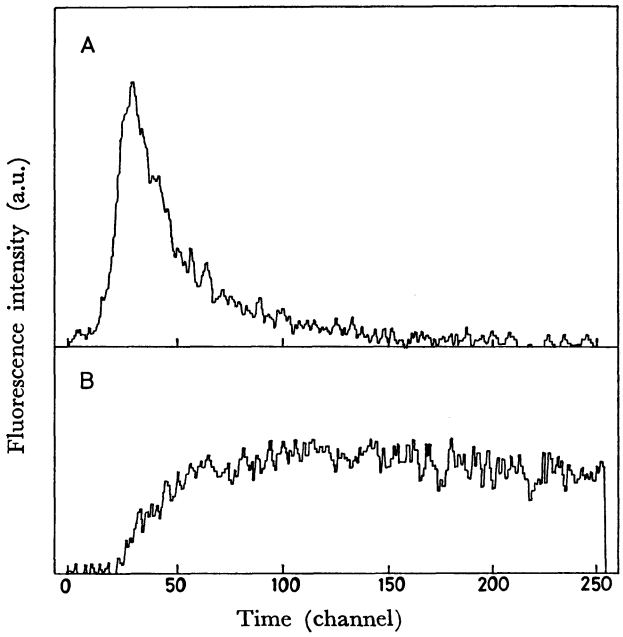

Fig. 4. Decay curve of LE fluorescence (A) and rise curve of HE fluorescence (B) of P_1 in 2-propanol.

fluorescence rise time and the decay time of the fast component of the two-component decay curve were estimated to be $\tau_r^{HE}=345\pm50$ ps and $\tau_d^{HE}=1.1\pm0.1$ ns, respectively. We can see a good agreement be-

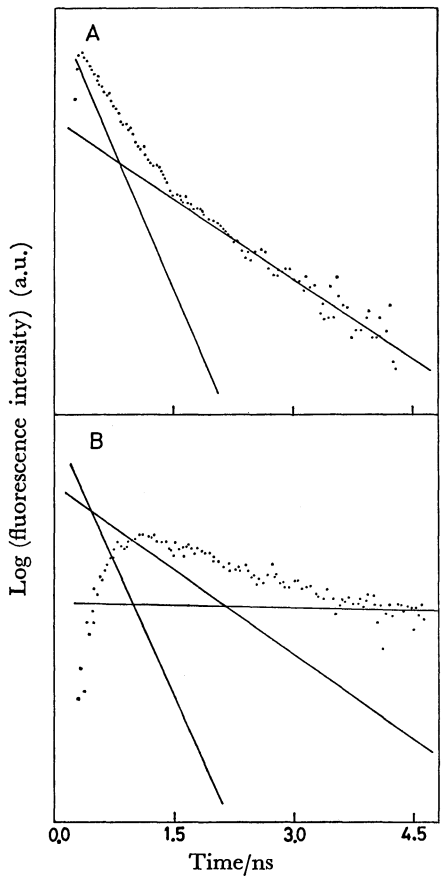

Fig. 5. Decay curve of LE fluorescence observed at 401 nm (A) and rise and decay curve of HE fluorescence observed through a filter which passes the wavelength region longer than 680 nm (B) in the case of 2-propanol solution of P_3. The observed results were calibrated for variations in the value of ps/channel in the following way. Conversion of n-th channel to the delay time $t(n)$ was made according to: $t(n)=\sum_{i=0}^{n}\Delta t(i)$, where $\Delta t(i)$ is the value of ps/channel of the i-th channel, and the observed intensity $I(i)$ at i-th channel was corrected according to: $I_{corr}(i)=I(i)/\Delta t(i)$.

tween τ_r^{HE} and τ_d^1 as well as between τ_d^{HE} and τ_d^2. Therefore, the results in Fig. 5 satisfy the ordinary kinetics of HE formation and decomposition. However, the measurement of HE fluorescence in the region including shorter wavelengths gave rather complicated results due to the contribution from the LE fluorescence.

Although we have not made such a detailed study for A_3 in 2-propanol, the circumstance seems to be analogous to P_3, since we have observed two component decay of the HE fluorescence by observing in the region longer than 650 nm and obtained the approximate τ_d^{HE} value of the fast component to be 1.5 ns.[16]

P_3 in an Acetone Solution. The results were similar to those in 2-propanol. However, the observed τ_d^1 value was much shorter (60 ps), while the τ_d^{HE} value was not so much different ($\approx$1 ns).

P_2 and P_3 in Acetonitrile Solutions. Both LE fluorescence decay and HE fluorescence rise times of P_2 in acetonitrile were shorter than 20 ps, the response time of the apparatus. The LE fluorescence decay time of P_3 was also shorter than 20 ps. Thus, the CT or HE formation becomes very fast in acetonitrile, a strongly polar and less viscous solvent. However, the ordinary kinetics for HE formation and decomposition as observed for P_3 in 2-propanol was not recognized clearly in this case.

A_0 and Bian in Polar Solvents. In the fluorescence spectra of these compounds in polar solvents, the LE and HE bands are not so distinct as those of A_n and P_n (n=1, 2, 3). One can recognize, however, that the vibrational structure of the LE band superposed upon the broad CT (HE) fluorescence band for Bian.[11,12] In accordance with this result, the decay curve of LE fluorescence in the region, 390—420 nm and the rise curve of CT fluorescence in the region above 520 nm for Bian were observed in 2-propanol (Fig. 6). In Fig. 6A, the fluorescence observed at longer delay times is due to the CT fluorescence band superposed upon the LE band. The decay time (τ_d) of the LE fluorescence and the rise time (τ_r) of the CT fluorescence of Bian in 2-propanol were estimated to be τ_d=80±17 ps and τ_r=80±20 ps. These values are in good agreement with each

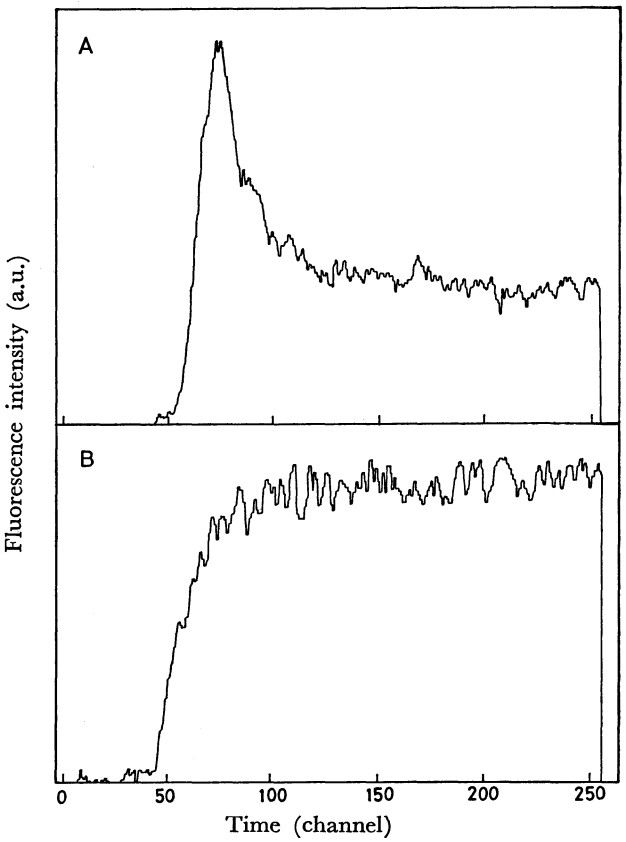

Fig. 6. Fluorescence decay and rise curves of Bian in 2-propanol.
A: Decay curve of LE fluorescence observed in the wavelength region of 320—420 nm. The long life tail is due to the CT fluorescence extending to this wavelength region, B: rise curve of CT fluorescence observed through a filter which passes the wavelength region above 520 nm.

other. Both the LE fluorescence decay and CT fluorescence rise times of Bian in acetone and acetonitrile were shorter than the response time of the apparatus (≈20 ps).

For A_0, the fluorescence spectra in polar solvents are more broad, and one cannot recognize clearly the LE fluorescence band.[2,6] In 2-propanol solution, we observed a decay curve in the region, 320—420 nm with the apparent decay time of approximately ≈70 ps, and a rise curve in the region longer than 520 nm with the apparent rise time of approximately ≈110 ps. Just as for Bian, both LE fluorescence decay and CT fluorescence rise times of A_0 in less viscous or more polar solvents like acetone, butyronitrile and acetonitrile were shorter than the response time of the apparatus (≈20 ps).

Discussion

HE Formation in Nonpolar Solvents. It is well established now that intramolecular HE formation is not possible for A_1, A_2, and P_1 in nonpolar solvents, while it is possible for A_3 and P_3 even in nonpolar solvents.[1-7] It has been confirmed already for P_3 in decalin solution that the rise time of the HE formation at room temperature is about 8 ns.[4,7] The fully slow formation process is ascribed to the internal rotations around CH_2–CH_2 bonds necessary for the conformation change and somewhat high viscosity of decalin. Both internal rotaions and solvent viscosity are affected by temperature, and the rise time becomes much longer by lowering temperature. For example, for P_3 in decalin, τ_r is 25 ns at −10 °C and 58 ns at −50 °C.[4,7]

Even if a less viscous solvent, hexane, is used, the rise of intramolecular HE fluorescence still takes a few ns for both A_3 and P_3, which indicates an important role of internal rotation for slowing down the HE formation process. Assuming the reaction mechanism of Eq. 1, where k_2 and k_3 are sum of radiative and non-radiative rate constants, the well-known Eq. 2 representing time dependence of each species is obtained.

$$\mathrm{S(A^*\ /\backslash/\backslash\ D)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{HE_s}\begin{bmatrix}\text{sandwich}\\ \\ \text{heteroexcimer}\end{bmatrix} \quad (1)$$

$$\downarrow k_2 \qquad\qquad \downarrow k_3$$

$$[\mathrm{S}] = C_1 \exp(-\lambda_1 t) + (C_0 - C_1)\exp(-\lambda_2 t)$$
$$[\mathrm{HE_s}] = C_2[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)]. \quad (2)$$

The values of λ_2^{-1} were determined as shown in Table 1, and these of λ_1^{-1} in hexane were given by the previous study as 130 ns and 87 ns for A_3 and P_3, respectively.[7]

The rapid component in the fluorescence rise curve observed at 540 nm (Fig. 2A) is indicative of the existence of ground state A_3 molecules in a sandwich configuration, which give HE fluorescence immediately after excitation as reported by Gnädig and Eisenthal.[13] However, this possibility is rejected, because no rapid component is found when the rise curve was observed only for the region longer than 550 nm (Fig. 2B).

Although the $S_n \leftarrow S_1$ spectrum of anthracene itself does not show any appreciable absorbance at 694 nm where Gnädig and Eisenthal monitored the transient absorbance of A_3 HE, we have confirmed by ps transient absorbance measurements on A_3 that the $S_n \leftarrow S_1$ spectra of anthracene are affected by alkyl substitution, and there arises some absorbance around 694 nm.[16] Thus, the rapid component observed in the ps transient absorption of A_3 can be ascribed to $S_n \leftarrow S_1$ spectra, and that shown in Fig. 2A must be ascribed to LE fluorescence.

Photo-induced CT and HE Formation of A_n and P_n (n=1, 2, 3) in Polar Solvents. In general, the wave equation and the Hamiltonian operator for the solute–solvent system may be given by

$$\mathscr{H}\Psi = E\Psi,\ \mathscr{H} = \mathscr{H}_0 + \mathscr{H}',\ \mathscr{H}' = -\vec{\mu}_{op}\cdot\vec{F}, \quad (3)$$
$$\vec{F} = \vec{\mu}\cdot f_\varepsilon/a^3,\ f_\varepsilon = 2(\varepsilon-1)/(2\varepsilon+1),\ \vec{\mu} = \langle\Psi|\vec{\mu}_{op}|\Psi\rangle,$$

where, $\mathscr{H}'$ represents the solute–solvent interaction, $\vec{\mu}_{op}$ is the dipole operator, $\vec{F}$ is the Onsager's reaction field and ε is the dielectric constant of solvent.

For an excited CT system, a simplified wavefunction may be given by

$$\Psi = C_1\Psi_{CT} + C_2\Psi_{LE}, \quad (4)$$

where Ψ_{CT} represents the CT structure A^-D^+, and Ψ_{LE} the LE structure A*D. By using Eqs. 3 and 4, the following matrix elements are defined:

$$\vec{\mu} = C_1^2\langle\Psi_{CT}|\vec{\mu}_{op}|\Psi_{CT}\rangle = C_1^2\cdot\vec{\mu}_0$$
$$\langle\Psi_{CT}|\mathscr{H}|\Psi_{CT}\rangle = \langle\Psi_{CT}|\mathscr{H}_0|\Psi_{CT}\rangle + \langle\Psi_{CT}|\mathscr{H}'|\Psi_{CT}\rangle$$
$$= E_c - \langle\Psi_{CT}|\vec{\mu}_{op}\cdot\vec{F}|\Psi_{CT}\rangle$$
$$= E_c - C_1^2(\mu_1^2/a^3)f_\varepsilon$$
$$\langle\Psi_{CT}|\mathscr{H}|\Psi_{LE}\rangle = \alpha,\ \langle\Psi_{LE}|\mathscr{H}|\Psi_{LE}\rangle = E_e. \quad (5)$$

With these matrix elements, the secular equations are written as

$$C_1(E_c - C_1^2(\mu_0^2/a^3)\cdot f_\varepsilon - E) + C_2\alpha = 0$$
$$C_1\alpha + C_2(E_e - E) = 0. \quad (6)$$

By solving these nonlinear equations and by adding the polarization energy of the solvent to the solution of Eq. 6, the energies of the states relevant to the fluorescence transition can be obtained.[1]

For A_1 and P_1, for example, α which is due to the electronic delocalization interaction between electron donor and acceptor groups may be negligibly small. Therefore, the energy of the CT state relaxed with respect to solvation may be given by,

$$E_{CT} = E_c - (1/2)(\mu_e^{eq2}/a^3)\cdot f_\varepsilon, \quad (7)$$

where $\vec{\mu}_e^{eq}$ is the dipole moment of the relaxed CT state. E_{CT} is higher than E_e in nonpolar solvents for A_1, P_1, and A_2. With increase of the solvent polarity, E_{CT} becomes lower than E_e. At the inversion point, there arises the orientational destabilization energy δE^{FC} in the Franck-Condon ground state of the fluorescence transition.

$$\delta E_g^{FC} = (1/2)\cdot(\mu_e^{eq2}/a^3)\cdot(f_\varepsilon - f_n)$$
$$f_n = 2(n^2-1)/(2n^2+1). \quad (8)$$

Therefore, in more polar solvents than that giving the inversion point, the frequency of the CT fluorescence is given by Eq. 9.

$$h\nu_e = \text{Const.} - (\mu_e^{eq2}/2a^3)(2f_s - f_n). \quad (9)$$

We have actually observed, for A_1, P_1, and A_2, especially large red shifts of the HE fluorescence at the inversion point due to δE^{FC},[3-5] and have confirmed that Eq. 9 holds not only for the HE fluorescence of A_n and P_n ($n=1$, 2) but also for A_3 and P_3.[3-5]

In the present work, we are investigating the dynamic processes of appearance of the HE state. The simple picture described above seems to be especially suitable to the cases of A_1 and P_1. Thus, the time-resolved fluorescence measurements of these systems will reflect directly the solvation process in the CT state.

The results indicated in Table 2 and Fig. 4 for A_1 and P_1 in 2-propanol solution show that the relaxation processes of the decay of LE and appearance of the CT state take about 50—100 ps. These values, however, are considerably longer than the shorter reorientational relaxation time[15] (<30 ps) of 2-propanol liquid. This result seems to indicate two possibilities: (a) the relaxation process of the CT state formation involves not only the rapid reorientational relaxation of 2-propanol but also slower ones covering a wider region around the solute molecule and involving hydrogen bond breaking and formation; (b) the relaxation process involves not only the solvent reorientation and solvent-induced change in the electronic structure as outlined by Eqs. 3—7 but also the geometrical change *i.e.* internal rotations of the solute molecule around single bonds connecting the CH_2 group with two aromatic groups, and the relaxation time is inherent in this conformation change.

However, the fact the relaxation times for the CT state formation of Bian and A_0 in 2-propanol are likewise 50—100 ps indicates that this relaxation time is inherent in reorientation of 2-propanol molecules around the bichromophoric molecule in the excited CT state formation rather than its conformational change.

A little longer τ_r value than that of τ_d for A_1 and P_1 may be due to the time-dependent red shift of HE band during the rise of HE fluorescence.

The considerably longer relaxation times of A_2 and P_2 compared with those of A_1 and P_1 may be explained as due to more extensive conformational change necessary for the photo-induced CT and for taking the stable HE configuration.

The behavior of P_3 in 2-propanol is a good example of enhancement of photo-induced CT process in polar solvent, and also of the control or slowing down of the CT reaction by internal rotations which are necessary to bring A* and D to the mutual distance and orientation where the CT is possible. The latter effect of the internal rotations makes it possible to elucidate photo-induced CT processes in solution which are difficult to study in detail even by ps laser methods for free A* and D. This difficulty is caused by very rapid and mutually combined translational and rotational diffusions, and they make the result complicated.

The faster decay of LE fluorescence and the faster rise of HE fluorescence of P_3 in 2-propanol solution than in hexane solution despite the higher viscosity of 2-propanol suggest that the photo-induced CT in polar solvent is possible, even if A* and D are somewhat separated, because the energy of the CT state is lowered by the interaction with the polar solvent, and loose HE is formed. Moreover, our previous semi-quantitative studies of ps transient absorption spectra of P_3 in 2-propanol indicated a two step change of spectra which is probably due to loose HE formation followed by a conformational change into the one of sandwich-type.[8,10]

The double exponential decay of LE fluorescence observed at 401 nm and the rise as well as decay of HE fluorescence observed in the region longer than 680 nm can be well reproduced by assuming the reaction scheme of Eq. 10 and by Eq. 11 derived from it.

$$\begin{array}{ccccc} S(A^* \,/\backslash/\backslash\, D) & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & HE_l \left[\begin{array}{l}\text{loose}\\ \\ \text{heteroexcimer}\end{array}\right] & \xrightarrow{k_2} & HE_s \left[\begin{array}{l}\text{sandwich}\\ \\ \text{heteroexcimer}\end{array}\right], \\ \downarrow k_3 & & \downarrow k_4 & & \downarrow k_5 \end{array} \quad (10)$$

where k_3, k_4, and k_5 are sums of rate constants of radiative as well as radiationless deactivations, respectively.

$$\begin{aligned} [S] &= C_1' \exp(-\lambda_1' \cdot t) + (C_0' - C_1') \exp(-\lambda_2' \cdot t) \\ [HE_l] &= C_2'[\exp(-\lambda_1' \cdot t) - \exp(-\lambda_2' \cdot t)] \\ [HE_s] &= C_3[(\lambda_1' - k_5) \exp(-\lambda_2' \cdot t) - (\lambda_2' - k_5) \exp(-\lambda_1' \cdot t) \\ &\quad - (\lambda_2' - \lambda_1') \exp(-k_5 \cdot t)]. \end{aligned} \quad (11)$$

In view of the good correspondence between the τ values, the time-dependences of fluorescence observed at 401 nm and those observed in the region longer than 680 nm are assigned to S and HE_l, respectively, from which $\tau_d = \tau_r^{HE} = \tau'^{-1}_2 \approx 350$ ps and $\tau_d = \tau_d^{HE} = \tau'^{-1}_1 \approx 1.1$ ns were obtained. The assignment of the long wavelength band to the loose HE may be supported also by the fact that the ordinary (time-integrated) fluorescence spectra of P_1 and P_2 in 2-propanol are somewhat red-shifted compared to those of P_3 in the same solvent. The latter spectra can be attributed almost completely to HE_s because of its much longer lifetime ($\approx$100 ns) compared with HE_l. Moreover, our recent results of accurate ps time-resolved absorption measurements on the same system can be explained quantitatively assuming the same scheme (10), and they give the same λ' values.[16]

The results of similar measurements in acetone solution can be interpreted by the same scheme as Eq. 10, with $\lambda'^{-1}_2 \approx 60$ ps and $\lambda'^{-1}_1 \approx 1$ ns. Since the polarity of acetone is close to that of 2-propanol, it is necessary to have a similar conformation (HE_l) for

the photo-induced CT to occur. Therefore, the much shorter value of $\lambda'_2{}^{-1}$ might be due to the considerably lower viscosity of acetone compared to 2-propanol, resulting in faster conformation change. However, the reason why the value of $\lambda'_1{}^{-1}$ is not so much different from that in 2-propanol solution is not so clear at the present stage of investigation. Presumably, the HE_1 formation may occur by solvent reorientation and a small rotation of two chromophore groups with only a slight internal rotation around CH_2–CH_2 bonds, while the HE_s formation involves extensive internal rotations which seem to determine the velocity of the process irrespective of the solvent viscosity.

The photo-induced intramolecular CT process becomes much faster in acetonitrile, a strongly polar and less viscous solvent, since CT may be possible at longer mutual distance between A* and D due to the rapid and stronger solvation. In other words, the extent of the conformation change necessary for the photo-induced CT may be much smaller in acetonitrile than in 2-propanol.

Thus, both the LE fluorescence decay time and HE fluorescence rise time of P_2 are shorter than 20 ps, the response time of the apparatus. The LE fluorescence decay time of P_3 is also shorter than 20 ps, but the corresponding rise of the HE fluorescence was not observed. The fluorescence from the loose HE formed immediately after the rapid photo-induced CT may not be detectable in the case of P_3 because of the very small fluorescence yield due to strong solvation of the ion-pair state.

Behaviors of Bian and A_0 in Polar Solvents. Interestingly Bian shows in the excited state intramolecular CT from one anthracene nucleus to another, which is caused by the interaction with polar solvent molecules.[11] This is a solvent-induced "broken symmetry" phenomenon, *i.e.* the lowering of the symmetry of the solute molecule due to the interaction with polar solvent molecules, resulting in the CT state even if the molecule is composed of two identical chromophores.[12] Direct confirmation of the intramolecular CT was made by transient absorption spectral measurements in polar solvent.[12]

In the present work, we have directly demonstrated the CT state formation process and decay of the corresponding LE state in 2-propanol. Both the CT state rise and the LE state decay times are *ca.* 80 ps, which are considerably longer than the shorter reorientational relaxation time of 2-propanol liquid at room temperature. Just as in the cases of A_1 and P_1 in 2-propanol, two interpretations might be possible. One is the relaxation process which includes some contribution from slower processes involving solvent hydrogen bond breaking and formation. The other involves not only the solvent reorientation but also the geometrical structural change of Bian, *i.e.* the rotation around the 9–9′ bond which determines the observed relaxation time.

The two π-electronic systems of Bian are oriented perpendicular to each other because of a strong steric hindrance in the relaxed ground state as well as the Franck-Condon excited state. It was suggested that the stable conformation in the excited state may not be the perpendicular one but the oblique one.[11] Since the CT fluorescent state of excited Bian may be considered as a resonance hybrid of the CT configuration mixed with the LE configuration, its solvation by polar solvents will oppose the electronic delocalization between two chromophores, because the solvation energy increases with increasing charge separation in the CT system. When the conformation is the perpendicular one, the electronic delocalization will become very small. Therefore, the excited equilibrium conformation in polar solvents will be very close to that of the excited Franck-Condon state.

The above considerations lead to the conclusion that the rate of the photo-induced CT state formation of Bian will be determined by the solvent reorientation relaxation time and will become faster in a less viscous polar solvent. Actually, we have found that the LE fluorescence decay and the CT fluorescence rise times of Bian in acetone as well as in acetonitrile are much shorter (<20 ps) than those in 2-propanol.

Although the fluorescence spectra of A_0 are quite broad, we were able to observe the LE fluorescence decay in 2-propanol solution at the shorter wavelength edge of the fluorescence band, and the CT fluorescence rise process in the longer wavelength region. This result is somewhat analogous to those of A_1, P_1, and Bian. Although the CT character of S_1 state seems to be evident from the very large red shift of fluorescence with increase of solvent polarity, another evidence comes from the measurement of the effect of solvent polarity upon the $S_n \leftarrow S_1$ spectra.[6] It has been confirmed that the $S_n \leftarrow S_1$ spectra in moderately or strongly polar solvents are comparable to the superposition of those of anthracence anion and DMA cation.[6,17]

In this case too, the LE fluorescence decay time (≈ 70 ps) as well as the CT fluorescence rise time (≈ 110 ps) in 2-propanol are considerably longer than the shorter reorientation relaxation time of 2-propanol liquid at room temperature. A little larger value of the latter compared with the former can be explained as due to the time-dependent red shift of the CT fluorescence band occuring during the CT state rise process just as for A_1 and P_1. The fact that the CT fluorescence rise time agrees approximately with the LE fluorescence decay time for Bian in 2-propanol may be explained as due to the much smaller solvent-induced red shift of the CT fluorescence band of Bian compared with A_0. Namely, the wavenumber difference between the fluorescence band maxima of Bian in hexane and 2-propanol is *ca.* 1.4×10^3 cm^{-1}, smaller compared with the corresponding value of A_0, 5.3×10^3 cm^{-1}.

Thus, there arises a similar problem with A_1, P_1, and Bian concerning the mechanism of CT state formation in 2-propanol, *i.e.* the relaxation process includes some contribution from the slower process of solvent rearrangements involving hydrogen bond breaking and formation, or it involves structural changes of A_0. The possibility of an excited equilibrium structure of A_0 in polar solvents where molecular planes of two moieties are perpendicular to each other has been discussed already.[6,18] Moreover, we have also

confirmed that the LE fluorescence decay time as well as the CT fluorescence rise time of A_0 in less viscous and polar solvents, like acetone, butyronitrile and acetonitrile are much shorter than the response time (20 ps) of the apparatus. Analogously to the cases of A_1, P_1, and Bian, the rate of the CT state formation in polar solvents for A_0 seems to be determined by the solvent reorientations.

Summary

We have observed directly by means of ps time-resolved fluorescence measurements the intramolecular HE formation process and its solvent dependence for typical hydrocarbon–amine systems and have confirmed our prediction of the enhancement of intramolecular CT process with increase of solvent polarity. Existence of loose HE's as an intermediate during sandwich type HE formation in polar solvents has been demonstrated for three methylene-chain compounds and we have found that the loose HE emits at longer wavelength than sandwich type one. Moreover, it has been found that the loose HE in strongly polar solvents is non-fluorescent. These results demonstrate clearly the effect of solvent polarity upon the photo-induced CT and HE formation processes as well as upon the electronic and geometrical structures of the formed HE's.

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References

1) See for example: N. Mataga and M. Ottolenghi, "Molecular Association," ed by R. Foster, Academic Press, London (1979), Vol. 2.

2) T. Okada, T. Fujita, M. Kubota, S. Masaki, N. Mataga, R. Ide, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, **14**, 563 (1972).

3) N. Mataga, "The Exciplex," ed by M. Gordon and W. R. Ware, Academic Press, New York (1975).

4) N. Mataga, T. Okada, H. Masuhara, N. Nakashima, Y. Sakata, and S. Misumi, *J. Luminescence*, **12/13**, 159 (1976).

5) S. Masaki, T. Okada, N. Mataga, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **49**, 1277 (1976).

6) T. Okada, T. Fujita, and N. Mataga, *Z. Phys. Chem. N. F.*, **101**, 57 (1976).

7) T. Okada, T. Saito, N. Mataga, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **50**, 331 (1977).

8) M. Migita, M. Kawai, N. Mataga, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, **53**, 67 (1978).

9) J. Hinatu, H. Masuhara, N. Mataga, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **51**, 1032 (1978).

10) N. Mataga, M. Migita, and T. Nishimura, *J. Mol. Struct.*, **47**, 199 (1978).

11) F. Schneider and E. Lippert, *Ber. Bunsenges. Phys. Chem.*, **72**, 1155 (1968).

12) N. Nakashima, M. Murakawa, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **49**, 854 (1976).

13) K. Gnädig and K. B. Eisenthal, *Chem. Phys. Lett.*, **46**, 339 (1977).

14) M. Migita, T. Okada, N. Mataga, N. Nakashima, K. Yoshihara, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, **72**, 229 (1980).

15) L. A. Hallidy and M. R. Topp, *Chem. Phys. Lett.*, **48**, 40 (1977).

16) T. Okada, M. Migita, N. Mataga, Y. Sakata, and S. Misumi, *J. Am. Chem. Soc.*, **103**, 4715 (1981).

17) T. Okada, M. Kawai, N. Mataga, Y. Sakata, S. Misumi, and S. Shionoya, unpublished.

18) A. Siemiarczuk, Z. R. Grabowski, A. Krowczynski, M. Asher, and M. Ottolenghi, *Chem. Phys. Lett.*, **51**, 315 (1977).

19) J. S. Meek, W. B. Evans, V. Godefroi, W. R. Benson, M. F. Wilcox, W. G. Clarks, and T. Tiedeman, *J. Org. Chem.*, **26**, 4281 (1961).