J. Am. Chem. Soc. **1981**, *103*, 4715–4720

Picosecond Laser Spectroscopy of Intramolecular Heteroexcimer Systems. Time-Resolved Absorption Studies of p-$(CH_3)_2NC_6H_4(CH_2)_n$(1-pyrenyl) and -(9-anthryl) Systems

Tadashi Okada,*[†] Masahito Migita,[†] Noboru Mataga,*[†] Yoshiteru Sakata,[‡] and Soichi Misumi[‡]

Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan, and the Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan. *Received August 13, 1980*

Abstract: The time-resolved absorption spectra of p-$(CH_3)_2NC_6H_4(CH_2)_n$(1-pyrenyl) (P_n: $n = 1$, 3) and p-$(CH_3)_2NC_6H_4(CH_2)_3$(9-anthryl) (A_3) in various solvents at room temperature have been measured with high accuracy and reliability by using a mode-locked ruby laser. It is found that the photoinduced electron transfer in P_n depends upon the number of methylenes in the chain as well as the solvent polarity and viscosity. Although the distance between donor and acceptor moieties of P_n is shorter than the critical distance obtained by quenching experiments of intermolecular systems in polar solvents, solvent reorientations and a little rotational relaxation of two moieties with a slight internal rotation around CH_2–CH_2 bonds are necessary to induce the intramolecular charge transfer generating a heteroexcimer. The rise time of the P_1 heteroexcimer in 2-propanol is measured to be about 65 ps. On the other hand, the time-resolved absorption spectra of P_3 in 2-propanol show that a loose structure heteroexcimer is produced with a rise time of 350 ps at first, followed by a structural change during 1.2 ns to a tighter one. The absorption spectrum of the loose structure heteroexcimer is rather similar to that of a free pyrene anion, and that of the tighter one is very broad and is similar to that of an intermolecular pyrene–dimethylaniline heteroexcimer in nonpolar solvent. Although this type of spectral change is detected also in the case of P_3 in acetone as well as A_3 in 2-propanol, no such spectral change is observed in acetonitrile where rapid electron transfer takes place immediately after excitation. In the case of P_3 in nonpolar solvent, hexane, the formation of heteroexcimer is possible only in the sandwich-type conformation. The apparatus used here to obtain the wide-band (380–950 nm) picosecond transient spectra is described in detail.

Introduction

Studies on the structure and dynamical behavior of electron donor–acceptor systems in the excited state are important for understanding primary processes of photochemical and photobiological reactions. Many intramolecular exciplex (heteroexcimer (HE) and excimer) systems have been examined in order to elucidate the geometrical requirements for exciplex formation as well as the dynamical aspects of charge-transfer interaction.[1-7] For example, in the case of the compounds p-$(CH_3)_2NC_6H_4(CH_2)_n$(1-pyrenyl) (P_n) and p-$(CH_3)_2NC_6H_4(CH_2)_n$(9-anthryl) (A_n) studied in this paper, the results obtained from the measurements of solvent effects upon fluorescence spectra and quantum yields as well as fluorescence rise and/or decay curves are summarized as follows.[2] (1) Not only compounds with $n = 3$ but also those with $n = 1$ and 2 can emit HE fluorescence when the charge-transfer state is stabilized owing to interaction with the surrounding solvent molecules. Therefore, the two aromatic planes of donor and acceptor need not be parallel for fluorescent heteroexcimer formation. (2) The intramolecular systems show a quite large red shift of HE fluorescence including a solvent-induced electronic structure change in poalr solvents in which fluorescence of the intermolecular HE cannot be observed because of ionic dissociation. (3) The rise time of HE fluorescence of P_3 and A_3 in polar solvents is much faster than in nonpolar solvents. This result suggests that orientational fluctuations of the surrounding polar solvent molecules and an approach of the two moieties may induce charge transfer, generating a HE with loose structure in polar solvents.

Thus, by restricting the geometrical structure of donor and acceptor by connecting the two moieties with a methylene chain, we expect that important problems which cannot be studied directly in the case of the intermolecular systems in polar solvents, such as the mechanism of the charge-transfer (electron-transfer) interaction in polar solvents and dynamical behavior of the geminate ion pair as a dissociative state into the solvated ions or as a reaction intermediate, etc., may be elucidated.

In order to clarify these dynamical phenomena, the transient absorption measurement using a picosecond spectrometer is one of the most useful methods. The time-resolved wide-band absorption spectra following the optical excitation with a picosecond laser pulse provides new structural and dynamical information that was not available from studies of the time evolution of the absorbance at one or two wavelengths.

In this paper a detailed description of our picosecond laser spectrometer system is presented. Then the dependence of photoinduced charge-transfer processes and structures of transient charge-transfer states of intramolecular HE systems upon solvent polarity and viscosity are discussed.

Experimental Section

Measurement of Picosecond Transient Absorption Spectra. A single optical pulse generated by a mode-locked ruby laser system was used as

---

[†] Faculty of Engineering Science.

[‡] Institute of Scientific and Industrial Research.

(1) (a) B. R. G. Brimage and R. S. Davidson, *J. Chem. Soc., Chem. Commun.*, **1385** (1971); (b) E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, **9**, 393 (1971); (c) E. J. Land, J. T. Richards, and J. K. Thomas, *J. Phys. Chem.*, **76**, 3805 (1972); (d) P. J. Wagner, *J. Am. Chem. Soc.*, **98**, 4515 (1976).

(2) (a) T. Okada, T. Fujita, M. Kubota, S. Masaki, N. Mataga, R. Ide, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, **14**, 563 (1972); (b) R. Ide, Y. Sakata, S. Misumi, T. Okada, and N. Mataga, *J. Chem. Soc., Chem. Commun.* 1009 (1972); (c) S. Masaki, T. Okada, N. Mataga, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **49**, 1277 (1976); (d) T. Okada, T. Saito, N. Mataga, Y. Sakata, and S. Misumi, *ibid.*, **50**, 331 (1977).

(3) (a) M. Migita, M. Kawai, N. Mataga, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, **53**, 67 (1978); (b) N. Mataga, M. Migita, and T. Nishimura, *J. Mol. Struct.*, **47**, 199 (1978); (c) J. Hinatu, H. Masuhara, N. Mataga, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **51**, 1032 (1978).

(4) (a) M. Itoh, T. Mimura, H. Usui, and T. Okamoto, *J. Am. Chem. Soc.*, **95**, 4388 (1973); (b) M. Itoh and T. Mimura, *Chem. Phys. Lett.*, **24**, 551 (1974); (c) M. Itoh, *ibid.*, **26**, 505 (1974).

(5) (a) Y. Hatano, M. Yamamoto, and Y. Nishijima, *J. Phys. Chem.*, **82**, 367 (1978); (b) T. Kanaya, Y. Hatano, M. Yamamoto, and Y. Nishijima, *Bull. Chem. Soc. Jpn.*, **52**, 2079 (1979).

(6) G. E. Johnson, *J. Chem. Phys.*, **63**, 4047 (1975).

(7) (a) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965); (b) M. Yamamoto, K. Goshiki, T. Kanaya, and Y. Nishijima, *Chem. Phys. Lett.*, **56**, 333 (1978); (c) K. A. Zachariasse, W. Kühnle, and A. Weller, *ibid.*, **59**, 375 (1978); (d) A. M. Halpern, M. W. Legenza, and B. R. Ramachandran, *J. Am. Chem. Soc.*, **101**, 5736 (1979).

0002-7863/81/1503-4715$01.25/0

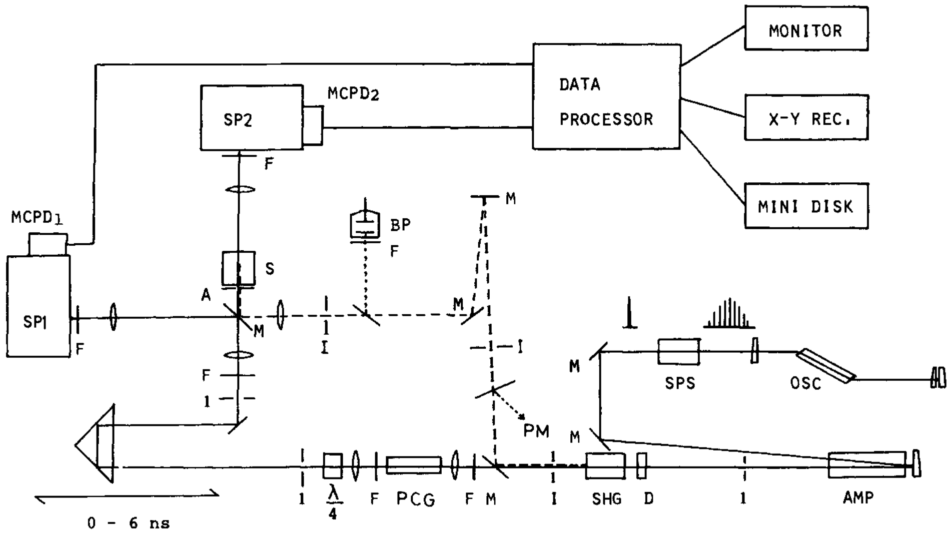


Figure 1. Experimental arrangement for picosecond laser spectroscopy. OSC: a mode-locked ruby laser oscillator; SPS: single pulse selector; AMP: amplifier; D: cryptocyanine dye; SHG: second harmonic generator; M: dichroic mirror; F: filter; PCG: picosecond continuum generator (polyphosphoric acid or quartz block); BP: biplanar phototube; S: sample cell; A: aperture; SP: spectrograph; PM: integrated power meter.

a light source for our picosecond transient absorption measurement. The oscillator and amplifier were similar to that described previously,[8] except for improvements in the stabilization of laser oscillation. A type I angle phase matched KDP crystal generates the 347-nm second harmonic of the amplified laser fundamental. The transverse structure of the beam is close to Gaussian and the energy of ultraviolet light is typically 10 mJ.

The experimental arrangement of the picosecond laser spectrometer is illustrated in Figure 1. The fundamental laser beam through a dichroic beam splitter, which reflects the second harmonic used as the excitation pulse, is focused by a lens (17-cm focal length) into a 15-cm cell of heated polyphosphoric acid (Wako, approximately represented by $H_6P_4O_{13}$) or a 10-cm quartz block used as a picosecond continuum generator. The generated continuum used as a probe pulse is spectrally filtered by a 694-nm blocking filter and recollimated by a lens, passes through a $\lambda/4$ plate, and has an optical delay line arranged to permit 0–6-ns time delay from the excitation UV pulse. Then, it is divided into two beams by a dichroic beam combiner which serves also to reflect the excitation UV pulse in the direction collinear with the continuum beam. The diameter on the aperture placed in contact with the cell is 1.2 mm. The F number of the continuum beam is larger than that of the exciting beam. After passing the sample cell, the continuum beam is focused onto the entrance slit of a spectrograph, SP2 ($F = 4$, 300 lines/mm grating), while another continuum beam reflected by a dichroic beam combiner and used as a reference of the spectral distribution is also focused onto the slit of another spectrograph, SP1. The spectra are detected by multichannel photodiode arrays, MCPD1 and -2 (Matsushita Model MEL512K), and transferred to a microcomputer system for storage and analysis.

The combination of the spectrograph and MCPD system described here provides a spectral resolution of approximately 2 nm and can measure transient spectra covering a wavelength band width of 200 nm. The transient absorption spectrum is obtained in principle by two laser shots with and without an excitation pulse:

$$A(\lambda) = \log \frac{I_1^E(\lambda)}{I_2^E(\lambda)} - \log \frac{I_1(\lambda)}{I_2(\lambda)}$$

where $A(\lambda)$ is the absorbance of transient species at the wavelength λ, and I_i^E and I_i are the intensities of the continuum beam detected by MCPDi with and without excitation UV pulse, respectively. The resulting absorbance spectra are averaged several times, and data smoothing can be applied if necessary. For every shot, the excitation laser pulse is monitored with a biplanar phototube (Hamamatsu, R-1193) and a storage oscilloscope (Tektronix 7834). The excitation energy is digitally detected using a photodiode and peakhold circuit.

Two types of measurements were made for a stringent test of the accuracy and stability of the transient spectrometer. By blocking the exciting pulse, ground-state absorption of naphthacene and Rhodamine 6G solutions showed a linear relation up to the absorbance value of 1.7 with the value measured by a conventional spectrophotometer. Next the $S_n \leftarrow S_1$ absorption of pyrene in hexane solution was taken under various exciting energies and delay times. No spectral distortion was observed over the absorbance range up to 1.5, and furthermore the effect of pyrene fluorescence could be removed satisfactorily under all exciting pulse energies examined.

In order to obtain the time dependence of absorption intensity, a quantitative measurement was carried out. The relationship between the transient absorbance vs. the intensity of the exciting laser pulse was measured at each delay time from the exciting pulse. The obtained relations were used to calibrate the observed absorbance of the intermediates and to estimate the amount of the two-photon ionization of the pyrene or anthracene moiety. In the case of P_3 in acetonitrile, the quantitative measurements were carried out under conditions where the contribution of the radical cation of the pyrene moiety produced by the two-photon absorption of the exciting laser pulse to the observed absorbance spectrum was less than 10%. In other solvents, the effect of two-photon ionization was negligible. The origin of the time scale, which is defined as the delay time giving maximum overlap of excitation and probe pulse at the domain exciting the sample, was determined by measuring the buildup of $S_n \leftarrow S_1$ absorption of pyrene in hexane solution.

Materials. The preparation of P_n and A_n compounds used will be reported elsewhere.[9] A quartz cell with a 1-cm optical path was used for the measurements. The concentrations of P_n were $2.5 \sim 6.8 \times 10^{-5}$ M which give absorbance of $0.8 \sim 2.3$ at the wavelength of excitation laser pulse. Spectrograde hexane, acetone, and acetonitrile were used without further purification. Spectrograde 2-propanol was carefully distilled.

All solutions for the measurement were deaerated by freeze–pump–thaw cycles. Measurements were carried out at room temperature (26 ± 1 °C). Absorption and fluorescence spectra were carefully measured before and after laser excitation and it was ascertained that the amount of photochemical decomposition of P_n was less than 1% in all solutions.

Results

Time-resolved absorption spectra of P_1 in 2-propanol are shown in Figure 2. No smoothing and averaging of the data have been applied. The broad transient absorption spectra observed at early time after excitation can be ascribed to superposition of the absorption spectrum of the locally excited (LE) state of the pyrene part and that of the intramolecular HE state. The latter is characterized by the bands similar to those of the dimethylaniline cation and pyrene anion. With increase of delay time, the spectra become more and more similar to the HE band. At delay times longer than 200 ps, no spectral changes were observed.

The time dependence of the absorbance at the peak wavelength, 495 nm, of excited P_1 in 2-propanol is indicated in Figure 3. The dashed curve in the figure shows the buildup curve of $S_n \leftarrow S_1$

---

[8] (a) N. Nakashima and N. Mataga, *Chem. Phys. Lett.*, **35**, 487 (1975); (b) N. Nakashima, M. Murakawa, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **49**, 854 (1976).

[9] M. Migita, T. Okada, N. Mataga, Y. Sakata, S. Misumi, N. Nakashima, and K. Yoshihara, to be published.

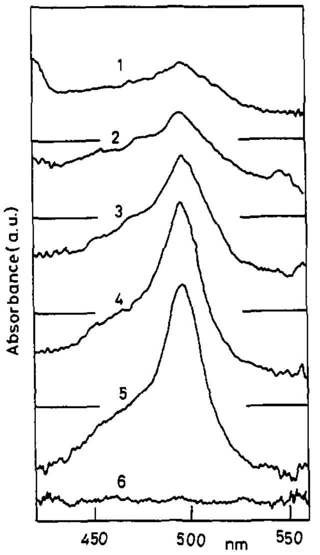


Figure 2. Time-resolved absorbance spectra of P_1 in 2-propanol. Delay times (ps) after excitation: (1) 0, (2) 33, (3) 70, (4) 200, (5) 400, (6) typical baseline spectrum.

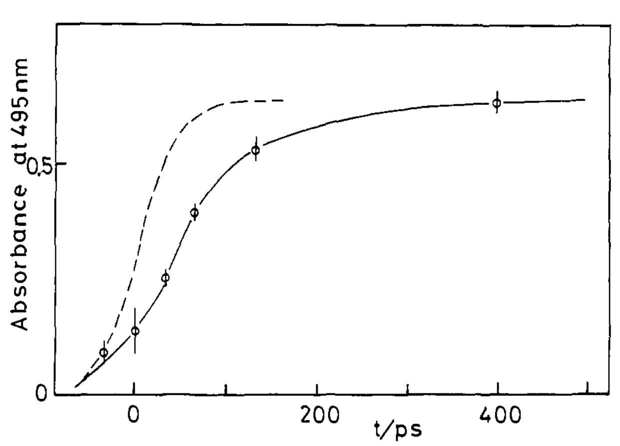


Figure 3. Time dependence of absorbance at 495 nm of P_1 in 2-propanol. Broken curve denotes the buildup of the pyrene $S_n \leftarrow S_1$ absorbance.

absorption of pyrene in hexane. In order to estimate the rise time of the P_1 HE state, the response function $F(t)$ of our optical circuit was determined by using the observed buildup curve of the pyrene $S_n \leftarrow S_1$ absorption $G(t)$:

$$G(t) = \int_0^t p(t-t')F(t)\,dt' \tag{1}$$

where $p(t)$ is a step function. Then one obtains

$$F(t) = dG(t)/dt \tag{2}$$

Assuming

$$HE(t) = C\{1 - \exp(-t/\tau_r)\}$$

the risetime τ_r of P_1 HE in 2-propanol was determined by the deconvolution of $R(t)$ by

$$R(t) = \int_0^t F(t-t')HE(t')\,dt' \tag{3}$$

where $R(t)$ is the observed time dependence of HE absorbance. The value of τ_r was estimated to be about 65 ps.

Figure 4 gives the transient absorbance spectra at several delay times of P_3 in 2-propanol (a) and in acetone (b). The behavior of the excited state of P_3 in these solvents are very similar to each other except for the time scale. The spectra may be characterized by three different absorption bands, one of which, observed at early time after excitation, may be mainly due to the absorption of the lowest excited singlet state localized in the pyrene moiety, LE. With increase of delay time, the band shape becomes rather similar to that of the pyrene anion. This absorption band may be ascribed to the loose HE, HE_l, which is formed owing to the charge transfer induced by a slight approach of the two moieties from the stretched form. With further increase of delay time, the HE_l band changed to a broad one, indicating a structural change from HE_l to a sandwich HE, HE_s.

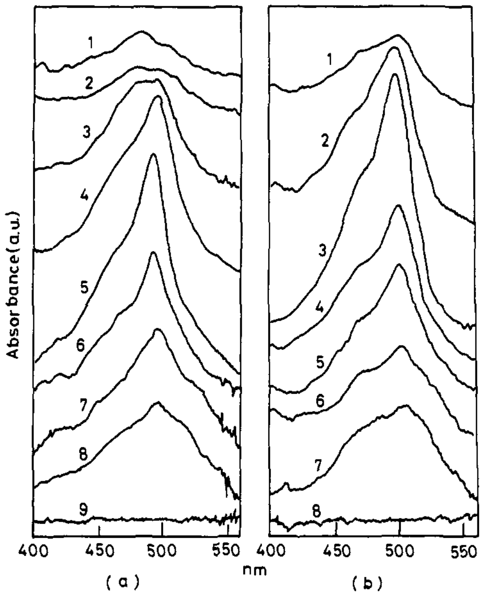


Figure 4. Time-resolved absorbance spectra of P_3 in 2-propanol (a) and in acetone (b). Delay times after excitation: (a) (1) −30 ps, (2) 0 ps, (3) 140 ps, (4) 400 ps, (5) 900 ps, (6) 1.8 ns, (7) 2.3 ns, (8) 3.3 ns, (9) typical baseline spectrum. (b): (1) 0 ps, (2) 30 ps, (3) 160 ps, (4) 500 ps, (5) 1.5 ns, (6) 2.5 ns, (7) 3.5 ns, (8) typical baseline spectrum.

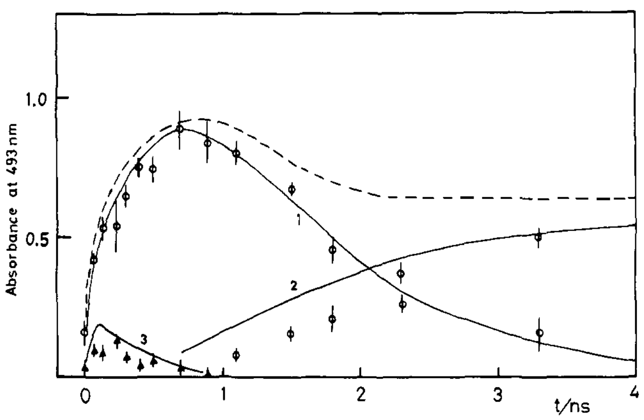


Figure 5. Time dependence of calculated absorbances at 493 nm of LE (1), HE_l (2), and HE_s (3) of P_3 in 2-propanol. Broken curve denotes the total time profile detected at 493 nm, and solid curves are simulated ones by eq 5, 6, and 7, respectively, using obtained $\lambda_{1,2}$ and k_5 values. See text.

The spectra indicated in Figure 4 can be well separated into those three components under the following reasonable assumption. That is, the absorption spectra of LE, HE_l, and HE_s correspond to the spectra of $S_n \leftarrow S_1$ absorption of 1-ethylpyrene, spectra obtained at 900 ps in 2-propanol and 160 ps in acetone, and that measured by means of the nanosecond laser photolysis apparatus,[3c] respectively. The time dependence of the absorbance at 493 nm of excited P_3 in 2-propanol is shown in Figure 5, where each point at every delay time represents absorbance values of three species at 493 nm estimated according to the assumption described above.

The reaction scheme of P_3 in 2-propanol and in acetone may be written as shown in eq 4, where k_3, k_4, and k_5 represent

$$\begin{tikzcd} LE \arrow[r, shift left, "k_1"] \arrow[d, "k_3"'] & HE_l \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2"] \arrow[d, "k_4"] & HE_s \arrow[d, "k_5"] \\ {} & {} & {} \end{tikzcd} \tag{4}$$

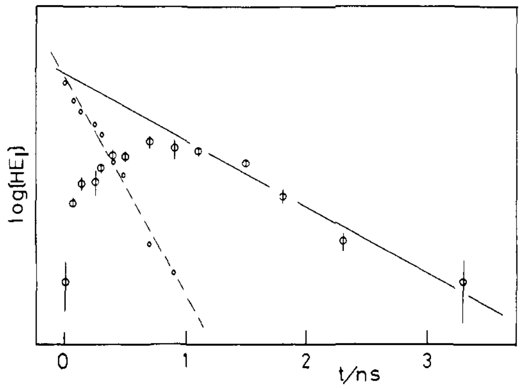


Figure 6. Semilogarithmic plot of HE$_l$ absorbance.

deactivation processes of each species. The time dependence of LE, HE$_l$, and HE$_s$ may be given by the following equations.

$$[\mathrm{LE}(t)] = C_1 \exp(-\lambda_1 t) + C_2 \exp(-\lambda_2 t) \quad (5)$$

$$[\mathrm{HE}_l(t)] = C_3\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \quad (6)$$

$$[\mathrm{HE}_s(t)] = C_4\{(k_5 - \lambda_2)\exp(-\lambda_1 t) - (k_5 - \lambda_1)\exp(-\lambda_2 t) + (\lambda_2 - \lambda_1)\exp(-k_5 t)\} \quad (7)$$

where

$$\lambda_{1,2} = \tfrac{1}{2}[(k_1 + k_{-1} + k_2 + k_3 + k_4) \mp \{(k_1 + k_3 - k_{-1} - k_2 - k_4)^2 + 4k_1k_{-1}\}^{1/2}]$$

$$C_1 = \frac{k_1 + k_3 - \lambda_2}{\lambda_1 - \lambda_2}[\mathrm{LE}]_0$$

$$C_2 = \frac{\lambda_1 - (k_1 + k_3)}{\lambda_1 - \lambda_2}[\mathrm{LE}]_0$$

$$C_3 = \frac{(k_1 + k_3 - \lambda_1)(k_1 + k_3 - \lambda_2)}{k_{-1}(\lambda_1 - \lambda_2)}[\mathrm{LE}]_0$$

$$C_4 = \frac{c_3k_2}{(k_5 - \lambda_1)(k_5 - \lambda_2)} \quad (8)$$

From semilogarithmic plot of [HE$_l$(t)] against delay time as shown in Figure 6, λ values were obtained to be $\lambda_2^{-1} \simeq 350$ ps and $\lambda_1^{-1} \simeq 1.2$ ns. The solid curves in Figure 5 were time dependences of each species simulated by eq 5–7 using obtained λ values and $k_5 = 2 \times 10^7$ s^{-1}. We also have examined fluorescence rise and decay curves of P$_3$ in 2-propanol at several different wavelengths. A double exponential decay has been observed at the LE fluorescence band, 410 nm, and fluorescenc rise and decay have been detected at wavelengths longer than 680 nm.[10] The time constants λ_1^{-1} and λ_2^{-1} obtained by analysis of the fluorescence decay curves agree completely with the values obtained from the transient absorption measurements.

In the case of P$_3$ in acetone, λ_1^{-1} and λ_2^{-1} values were determined to be about 900 and 45 ps, respectively, by the same procedure as in the case of 2-propanol solution.

Similar behavior has been observed also in the case of A$_3$ in 2-propanol. Figure 7 shows a two-components decay curve of HE fluorescence of A$_3$ in 2-propanol detected at wavelengths longer than 650 nm. The rapid component of the decay curve can be assigned to the term with λ_1 of eq 6 for HE$_l$ fluorescence because the fluorescence band of HE$_l$ seems to appear in the longer wavelength region than that of HE$_s$ owing to the large destabilization energy in the Franck-Condon ground state. Actually, the steady-state fluorescence spectra of A$_1$ and A$_2$ in considerably polar solvents such as 2-propanol and acetone are red shifted compared to those of A$_3$.[2c] Time-resolved absorption spectra of A$_3$ in 2-propanol are shown in Figure 8. The absorption band ascribed to HE$_l$ is observed at first with an increase of delay time, and the HE$_l$ band changes to a broad and red shifted one suggesting a structural change to HE$_s$. The values of λ_1^{-1} and λ_2^{-1} for this system were estimated to be about 1.5 ns and 200 ps, respectively.

Figure 9 shows results obtained with P$_3$ in acetonitrile. The absorption spectra of the HE state are sharper compared with those of 2-propanol solution. In addition, the band did not show

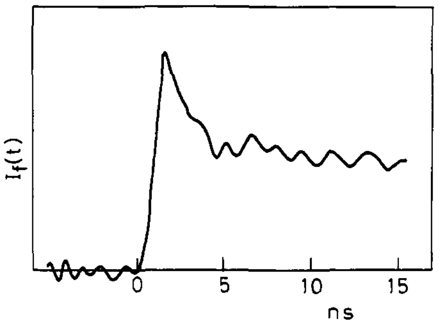


Figure 7. Decay curve of HE fluorescence of A$_3$ in 2-propanol observed through a filter which passed the wavelength region longer than 650 nm. A$_3$ was excited with the second harmonic of the mode-locked ruby laser, and the fluorescence was detected by a high-speed microchannel plate photomultiplier (HTV R1194UX) connected to the storage oscilloscope (Tektronix 7834).

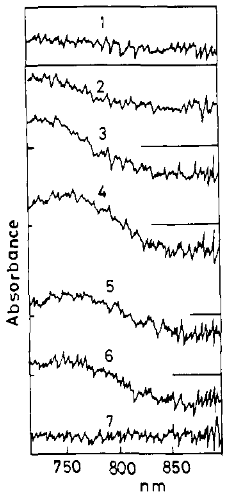


Figure 8. Time-resolved absorbance spectra of A$_3$ in 2-propanol. Delay times after excitation: (1) 33 ps, (2) 100 ps, (3) 300 ps, (4) 1 ns, (5) 2 ns, (6) 2.5 ns, (7) typical baseline spectrum.

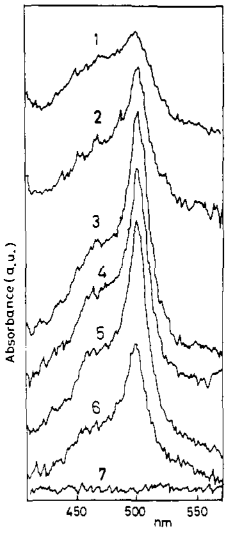


Figure 9. Time-resolved absorbance spectra of P$_3$ in acetonitrile. Delay times after excitation: (1) –37 ps, (2) 17 ps, (3) 33 ps, (4) 97 ps, (5) 163 ps, (6) 300 ps, (7) typical baseline spectrum.

---

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

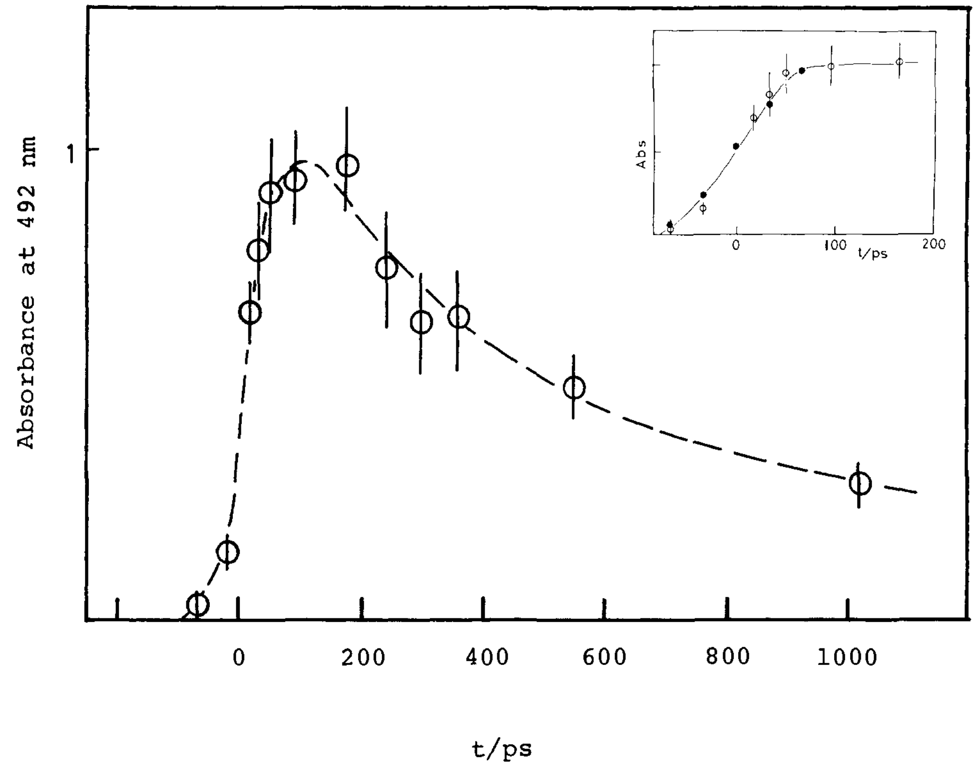


Figure 10. Time dependence of absorbance at 492 nm of P_3 in acetonitrile. Inset: buildup of absorbance of P_3 heteroexcimer (○) and of $S_n \leftarrow S_1$ absorbance of pyrene (●).

any broadening with increase of delay time. This result may be ascribed to the stronger solvation of the HE state in acetonitrile, which may not allow the formation of the compact sandwich intramolecular HE. The rise and decay curve of the HE-state absorption observed at 495 nm is indicated in Figure 10. The obtained rise curve of the ion band was identical with that of the optical circuit measured by pyrene $S_n \leftarrow S_1$ absorption as one can see in the insert of the figure.

Next, we examined P_3 in a nonpolar solvent, hexane, as shown in Figure 11. The transient spectrum at 200-ps delay time was due to the pure LE state of P_3, being identical with the $S_n \leftarrow S_1$ spectrum of ethylpyrene. Moreover, even at the delay time of 4 ns, the spectrum can be ascribed to the superposition of the absorption bands of LE and HE. Therefore, no rapid HE formation immediately after excitation with the picosecond pulse as reported by Gnädig and Eisenthal[11] was detected in the case of P_3 in hexane. The rise time of HE fluorescence was obtained to be 4.5 ns.[2d,10]

Discussion

Intramolecular Heteroexcimer Formation of P_3 in Hexane Solution. Rate constants for intramolecular excimer formation and dissociation in 1,3-bis(*N*-carbazolyl)propane (1,3-BCP) were measured in a number of solvents using the time-resolved fluorescence decay technique by Johnson.[6] According to his results, it is evident that there was no simple correlation of the rate constants with viscosity among dissimilar solvents, although the overall predominant trend was toward smaller values with increasing viscosity. However, there was a definite correlation among two homologous series of solvents, alkanes and alcohols. In these solvents, rate constants obey a relationship originating from the concept of free volume requirements for intramolecular conformational change. It may be reasonable to consider that the same situation prevails also in the case of the intramolecular heteroexcimer formation process of P_3 in hexane solution. In fact, the obtained rise time for the P_3 heteroexcimer in hexane, 4.5 ns, is in good agreement with the rate constant for the 1,3-BCP excimer in hexane, 2.2×10^8 s^{-1}.[6] This result indicates that in nonpolar solvents P_3 heteroexcimer formation involves rotation about the carbon–carbon bonds of the linking methylene groups to achieve a conformation in which the two moieties overlap in a sandwich-like arrangement.

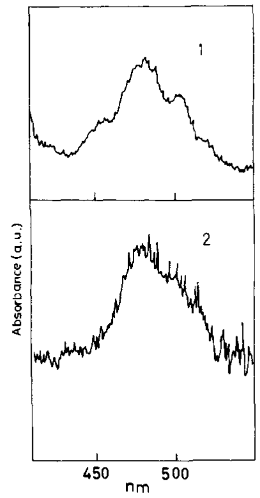


Figure 11. Transient absorbance spectra of P_3 in hexane taken at delay times 160 ps (1) and 4 ns (2).

Dynamical Aspects of Photoinduced Intramolecular Electron-Transfer Interaction in Polar Solvents. In general, the charge-transfer (electron-transfer) process depends upon various factors such as the distance between the electron donor–acceptor pair and molecular configurations as well as the polarity of solvent. The intramolecular exciplex systems which consist of two chromophores bonded to the ends of an insulating alkane group are expected to separate to some extent these various factors affecting the charge-transfer process, because the process is unimolecular and does not depend on the translational diffusion of reactive species. One of the main objects of the present work has been to make clear the dependencies of heteroexcimer formation processes in polar solvents upon the above factors.

The results obtained for P_1, P_3, and A_3 in polar solvents may be summarized as follows.

---

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

(1) The charge-transfer process depends upon the number of methylene chains. It becomes slower with increase of methylene chains (Figures 3 and 5).

(2) The charge-transfer process of excited P_3 depends strongly upon solvent polarity as well as solvent viscosity. It becomes faster with increase of solvent polarity (Figures 4 and 9) and decrease of solvent viscosity (Figure 4).

(3) Two kinds of heteroexcimer states are observed in the cases of P_3 in 2-propanol and acetone and A_3 in 2-propanol. HE_l, which shows a sharp ion-like absorption band, is formed at first and HE_s with broad absorption band is formed from HE_l.

(4) Time-dependent spectral change, indicating the change in the conformation of the HE state, is not detected in the case of P_3 in acetonitrile.

Kanaya et al. calculated the equilibrium distribution of conformations of the series of compounds, (9-carbazolyl)-$(CH_2)_nO_2CC_6H_4COOCH_3$ in the ground state.[5b] The end-to-end distance, *r*, where *r* was defined as the distance between the center of the five-membered ring of carbazole and the center of the benzene ring of methyl terephthalate, was localized at ca. 6.3 Å for $n = 1$ and was distributed between 7.5 and 9.1 Å for $n = 3$. In the case of $n = 3$, the fraction of the most extended conformation with $r = 9.1$ Å was about 20%, and short-distance configurations with $\sim 7.8 < r < 8.7$ Å were more than 60%.

By using the structural parameters of pyrene and dimethylaniline instead of those of carbazole and methyl terephthalate, we have estimated the values of *r* to be about 6.7 Å for P_1 and ~8–9 Å for P_3. Although these values of the intramolecular distance between two moieties are smaller than or almost the same as the approximate values of encounter distance estimated from studies of intermolecular fluorescence quenching in polar solution, the observed rate constants for charge transfer are 65 ps for P_1 in 2-propanol and 45 and 350 ps for P_3 in acetone and 2-propanol, respectively. This result clearly shows that some fluctuational motion of surrounding solvent molecules and those of donor and acceptor moieties are necessary for the charge transfer to occur even in the case of P_1 where two moieties sit within the quenching sphere. Therefore, the value of the quenching distance deduced from theory of diffusion-controlled kinetics may be in error, especially at short separations.

The direct observation of molecular orientational relaxation, as a function of the solvent properties, can clarify how solvent–solute forces affect overall molecular motions. Many investigations were made concerning the orientational relaxation times in a variety of solvents using transient measurement techniques.[12] According to these investigations, the orientational relaxation times of dyes in protic solvents depend upon solvent viscosity and are distributed between more than a hundred picoseconds to a nanosecond, while in aprotic solvents, the values are considerably smaller although they depend also upon solvent viscosity. For example, orientational relaxation times of Rose Bengal in acetone and 2-propanol are 70 ± 10 and 840 ± 70 ps, respectively.[12d] Of course, the rotational diffusion times depend also upon molecular structure. Fleming et al. have investigated the molecular rotation of 3,3′-diethyloxadicarbocyanine iodide (DODCI) in 2-propanol. The stable form of DODCI, the cis,cis-1,5 conformation, has a rotational correlation time of 320 ± 40 ps, whereas that of the photoisomer (all-trans isomer) formed by irradiating DODCI is longer than 700 ps.[12b]

In view of the above results, our observed λ_2 values for P_3 in acetone and 2-propanol may be explained as follows on the basis of the orientational relaxation. Namely, the solvent reorientations and rotational relaxation of two moieties with only a slight internal rotation around the CH_2–CH_2 bonds in the extended form of P_3 may induce the intramolecular charge-transfer interaction in the excited state. Then the resulting ion pair, HE_l, forms a sandwich-type heteroexcimer, HE_s, by extensive internal rotation about the CH_2–CH_2 bonds similar to the case of the intramolecular excimer formation process except for the assistance of coulombic attractive forces. In relation to this problem, one should note here that the ratio of the rate constants in acetone and 2-propanol for excimer formation of 1,3-BCP was measured to be about 1.2 in spite of large differences in solvent viscosity. This result is very similar to our observation that the λ_1^{-1} values for P_3 in acetone and 2-propanol are about 900 ps and 1.2 ns, respectively, and their ratio is very close to 1.2.

In the case of P_3 in acetonitrile, the photoinduced charge-transfer process occurs within the resolution time of our picosecond spectrometer, probably because of the stronger stabilization of the charge-transfer state by the solvent orientational fluctuations as well as to the rapid rotational relaxation of the donor–acceptor moieties without internal rotations around the CH_2–CH_2 bonds.

Since we cannot recognize any broadening of the absorption band with increase of the delay time and the spectra are very similar to those of free ion radicals in acetonitrile solution, the formation of a more compact sandwich-type HE such as formed in nonpolar as well as moderately polar solvents may not be possible in acetonitrile because of the strong solvation of the charge-transfer state.

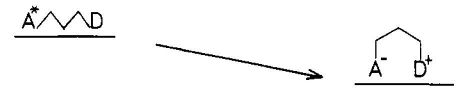
Conclusion

The studies of time-resolved absorption spectra of P_n in various solvents provide important information about the microscopic mechanisms of the charge-transfer interaction in excited donor-acceptor systems especially in polar solvents. This information may be useful for understanding the chemical reactions, including formation of ionic states in solution.

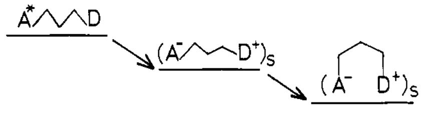
The mechanism of the intermolecular heteroexcimer formation in nonpolar solvents may be similar to that of the intramolecular excimer formation, and the sandwich-type configuration is probable in the case of the P_3 heteroexcimer.

In polar solvents the charge-transfer interaction seems to be induced by the rotational orientation relaxation of the two moieties, which depends strongly upon the solvent polarity as well as solvent viscosity.

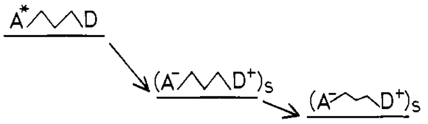
The mechanisms of intramolecular heteroexcimer formation of P_3 may be illustrated as follows: In non-polar solvents



In polar solvents



In strongly polar solvents



It should be noted here that the above result is also a clear experimental demonstration of the original idea[13] that the structure (electronic as well as geometrical) of an exciplex changes depending upon the solvent polarity.

Acknowledgment. The authors wish to thank Mr. M. Kawai for preparing the programs for data processing used in this study. N. M. and T. O. acknowledge the support by the Toray Science Foundation and Mitsubishi Foundation, and N. M. also acknowledges the support by a Grant-in-Aid for Special Project Research on Photobiology from the Japanese Ministry of Education, Science, and Culture.

---

(12) (a) H. E. Lessing, A. von Jena, and M. Reichert, *Chem. Phys. Lett.*, **36**, 517 (1975); H. E. Lessing and A. von Jena, *ibid.*, **42**, 213 (1976); A. von Jena and H. E. Lessing, *Chem. Phys.*, **40**, 245 (1979); (b) G. R. Fleming, A. E. W. Knight, J. M. Morris, R. J. Robbins, and G. W. Robinson, *Chem. Phys. Lett.*, **49**, 1 (1977); **51**, 399 (1977); (c) G. Porter, P. J. Sadkowski, and C. J. Tredwell, *ibid.*, **49**, 416 (1977); (d) K. G. Spears and L. E. Cramer, *Chem. Phys.*, **30**, 1 (1978).

(13) N. Mataga, T. Okada, and N. Yamamoto, *Chem. Phys. Lett.*, **1**, 119 (1967).