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Picosecond Laser Photolysis Studies of Hydrogen Atom Transfer Reaction via Heteroexcimer State in Pyrene–Primary and Pyrene–Secondary Aromatic Amine Systems: Role of "Hydrogen-Bonding" Interaction between Amino Group of Donor and π Electrons of Acceptor in the Heteroexcimer

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Abstract: The mechanism of charge transfer followed by proton transfer in the hydrogen atom transfer reaction of excited pyrene–primary and –secondary amine systems has been directly demonstrated by means of a picosecond laser photolysis method. In the case of the pyrene–*N*-ethylaniline heteroexcimer system in hexane, for example, it has been observed that the 1-hydro-1-pyrenyl radical and the pyrene triplet state are produced simultaneously in the time region of subnanosecond to nanosecond. The deuteration of the NH group of the amine affects considerably the rate of formation of the 1-hydro-1-pyrenyl radical but not the rate of intersystem crossing from the heteroexcimer. On the basis of the results obtained for various pyrene–primary and –secondary aromatic amine heteroexcimer systems, the nature of the interaction between donor and acceptor in these heteroexcimers and their conformations in relation to the mechanism of the hydrogen atom transfer reaction via heteroexcimer have been elucidated.

The formation of 1-hydro-1-pyrenyl and amino radicals was observed by means of nanosecond and microsecond flash photolysis, when pyrene fluorescence was quenched by secondary or primary amines in nonpolar solvents.[1] This result has been explained by assuming a mechanism of charge transfer (CT) followed by proton transfer on the basis of the results of systematic studies upon hydrocarbon–amine heteroexcimer systems.[1] The direct experimental evidence for the charge-transfer mechanism in the photoinduced hydrogen atom transfer reaction has been obtained in the case of the excited-singlet pyrene–diphenylamine system by means of a picosecond laser photolysis method.[2]

The charge-transfer mechanism of the photoinduced hydrogen atom transfer reaction, that is, the formation of a charge-transfer complex or an ion pair followed by proton transfer, was proposed for the first time by Cohen et al. for the benzophenone–amine system.[3] However, in the case of the triplet state of 2,6-diphenyl-1,4-benzoquinone and aromatic amine systems, Kuzmin et al.[4] concluded that the hydrogen atom transfer occurs from the encounter complex competing with the formation of triplet heteroexcimer.

In the present paper, we show directly by means of picosecond laser spectroscopy that the heteroexcimer state is a real reaction intermediate in the photoinduced hydrogen atom transfer in the excited pyrene–secondary amine systems and that the deuteration of the NH group affects considerably the proton-transfer rate in the heteroexcimer state but not the rate of intersystem crossing from the heteroexcimer-producing pyrene triplet.

The conformation of the heteroexcimer undergoing the proton transfer from the amine cation moiety to the pyrene anion moiety in the heteroexcimer has been discussed on the basis of its fast intersystem crossing and its characteristic band shape of absorption spectra. Moreover, it has been proposed that the "hydrogen-bonding" interaction between the $2p\pi$ AO at C_1 of the pyrene anion and the N–H of the secondary amine cation in the heteroexcimer plays an important role in determining the conformation of the heteroexcimer and the rate of proton transfer.

Experimental Section

Methods. Transient absorption spectra in picosecond and nanosecond time regions were obtained by a picosecond laser photolysis system using a single pulse of secondary harmonics (347 nm) from a mode-locked ruby laser to excite the solution and multichannel photodiode arrays to detect the probe light pulse. Details of the picosecond apparatus are described elsewhere.[5] A pulsed N_2 gas laser (1.5 mJ, 8 ns) set up in this laboratory was used for the measurement of the transient absorption spectra in the microsecond time region. The induced transient absorbance was averaged by a Kawasaki Electronica Transient Memory M-50E.[6] The calibrated fluorescence spectra were measured with an Aminco-Bowman spectrophotofluorometer. The fluorescence lifetimes were measured with an apparatus composed of a Bausch and Lomb high-intensity monochromator, 1P21 photomultiplier, Tektronix 661 sampling oscilloscope, and a pulsed N_2 gas laser of about 1-kW peak power.

Materials. *N*-Ethylaniline-*d*. Freshly distilled *N*-ethylaniline was shaken four times with deuterium oxide of 99.75% isotopic purity and once with that of 99.9% isotopic purity for more than an hour. The NH absorption peak of the NMR spectrum completely disappeared. Obtained *N*-ethylaniline-*d* (NEA-*d*) was dried over molecular sieves (4A) for 5 days and distilled twice under vacuum ($\sim 10^{-4}$ torr). Diphenylamine-*d* (DPA-*d*) was synthesized in an analogous way.

Di-*tert*-butylbenzene. To a mixture of *tert*-butylbenzene (100 g) and *tert*-butyl chloride (55 g) was added aluminum chloride (4.5 g) in small portions over a 20-min interval with vigorous stirring at room temperature. After 19 h, the reaction mixture was decomposed with dilute hydrochloric acid and was washed with water. A mixture of *m*- and *p*-di-*tert*-butylbenzene (43 g, 38%) was obtained by distillation (87–120 °C, 8 mmHg).

1,3,5-Tri-*tert*-butylbenzene (TBB). A mixture of *m*- and *p*-di-*tert*-butylbenzene (41 g) was dissolved in *tert*-butyl chloride (180 mL), and aluminum chloride (14 g) was added. The reaction mixture was decomposed in cold water, and the organic layer was extracted with ether. After removal of the solvent, the residue was recrystallized from methanol to give TBB: colorless, 24.9 (47%), mp 71–74 °C; ^{1}H NMR (CD-

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Cl_3) δ 1.29 (s, *tert*-butyl), 7.07 (s Ar H of phenyl).

2,4,6-Tri-*tert*-butylnitrobenzene (TBN). To a mixture of TBB (8.0 g), acetic anhydride (20 mL), and glacial acetic acid (12 mL, 99%) was added fuming nitric acid dropwise with stirring at room temperature. After 50 min, the solution was poured out in water and the product was filtered. Recrystallization from ethanol gave colorless needles of TBN (6.3 g, 67%): mp 201–203 °C; IR 1525 cm^{-1} (NO_2); ^1H NMR (CCl_4) δ 1.30 (s, *p-tert*-butyl), 1.36 (s, *o-tert*-butyl), 7.32 (s, Ar H of phenyl).

Anal. Calcd for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. Found: C, 74.42, H, 10.14; N, 4.76.

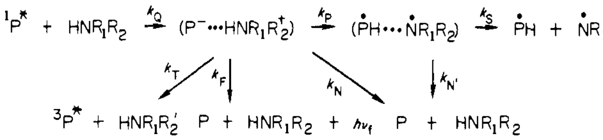
2,4,6-Tri-*tert*-butylaniline (TBA). A mixture of TBN (2.0 g) and absolute methanol (50 mL) was refluxed for 5 h over 5% sodium amalgam (50 g). After filteration, the solution was poured out in water. The product was chromatographed on silica gel with benzene, and recrystallization from methanol gave colorless plates of TBA (1.0 g, 56%): mp 145–146 °C; IR 3430, 3500 cm^{-1} (NH_2); ^1H NMR (CCl_4) δ 1.24 (s, *p-tert*-butyl), 1.43 (s, *o-tert*-butyl), 6.98 (s, Ar H of phenyl).

Aniline (AN), *N*-ethylaniline (NEA), and diphenylamine (DPA) were purified by standard methods. Aniline-d_7 (AN-d_7) (Carl Roth, 99 atom %) was distilled under vacuum. Spectrograde hexane and GR-grade ethyl ether were distilled over sodium wire. Spectrograde toluene was used as received. Pyrene and 2,7-di-*tert*-butylpyrene (DBP) were the same samples as used before in this laboratory.[7]

All solutions were degassed by freeze–pump–thaw cycles. Measurements were carried out at room temperature.

Results

In the following, we assume the reaction scheme of eq 1 for



(1)

the analysis of the obtained results, where R_1 is H, C_2H_5, or phenyl and R_2 is phenyl. P is pyrene or 2,7-di-*tert*-butylpyrene. Since the amine concentration in the present work is very high (1 M), the formation of the heteroexcimer is very rapid (completed within tens of picoseconds). Therefore, the decay processes from $^1P^*$ to $^3P^*$ and P can be neglected.

(A) Pyrene–NEA and Pyrene–NEA-*d* in Hexane Solution. Time-resolved absorbance spectra of pyrene–NEA and pyrene–NEA-*d* in hexane solution are indicated in Figure 1, where the absorbance was corrected for the shot-to-shot variations of the exciting laser power (±10%). The absorption bands with a maximum at 500 nm observed at the delay time of 500 ps are assigned to the heteroexcimer in both the pyrene–NEA and –NEA-*d* systems, since their decay times were estimated from the analysis of the time dependence of absorbance to be 3,4 ns (for pyrene–NEA) and 6.8 ns (for pyrene–NEA-*d*), respectively, which are in a good agreement with those obtained from the measurement of the heteroexcimer fluorescence decay times. The most characteristic feature of these absorption spectra is the fact that they are quite different from the very broad absorption spectra of pyrene–*N*,*N*-dimethylaniline (DMA) or pyrene–*N*,*N*-diethylaniline (DEA) heteroexcimers in nonpolar solvent[8] and very similar to the superposition of absorption bands of pyrene anion and amine cation produced by photoinduced electron transfer in acetonitrile solution.[8] At delay times longer than 1 ns, new transient absorption bands appear, one of which is due to the triplet state of pyrene with maximum at 415 nm and the other to the 1-hydro-1-pyrenyl radical ($\dot{P}H$) with maximum at 405 nm.[1,2]

It should be noted that in the case of pyrene–NEA-*d*, the lifetime of the heteroexcimer state is longer and the yield of the pyrene triplet state is much larger compared with the pyrene–NEA system. The fluorescence quantum yield of the pyrene–NEA-*d* heteroexcimer is measured to be ca. 10^{-2}, which is about two times as large as that of the pyrene–NEA heteroexcimer (5×10^{-3}), in agreement with the results of lifetime measurements.[9]

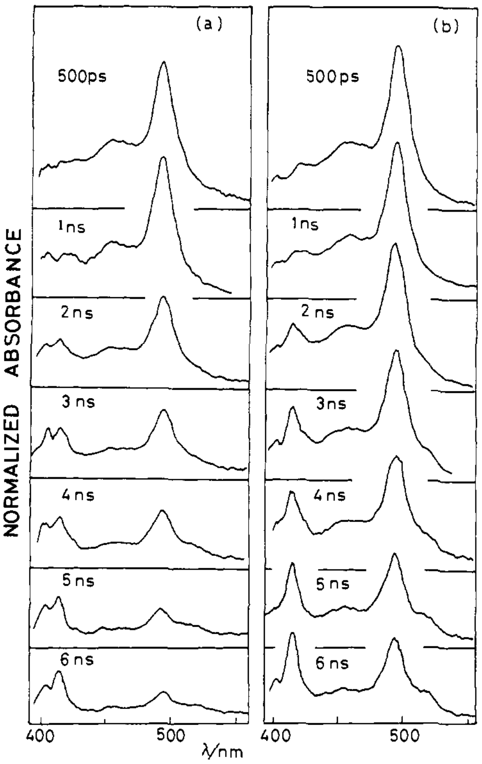


Figure 1. Time-resolved absorbance spectra of (a) pyrene-NEA and (b) pyrene–NEA-*d* systems in hexane solution. Delay times after excitation are denoted in the figure. [Pyrene] = 10^{-3} M, [NEA] = 1 M, [NEA]-*d*] = 1 M.

Some of the rate constants indicated in eq 1 may be evaluated by using the following relations:

$$\Phi_F = k_F\tau_F \qquad \Phi_T = k_T\tau_F \qquad \tau_F^{-1} = k_F + k_N + k_P + k_T \quad (2)$$

where Φ_F, Φ_T and τ_F are the fluorescence quantum yield of heteroexcimer, quantum yield of the pyrene triplet formation from the heteroexcimer, and the lifetime of the heteroexcimer, respectively. Values of Φ_F and τ_F for pyrene–NEA and pyrene–NEA-*d* are given above, and Φ_T were estimated to be 0.35 (NEA) and 0,72 (NEA-*d*), respectively, by assuming that the molar extinction coefficient of the heteroexcimer at 495 nm is equal to that of pyrene anion (ϵ = 49 200 M^{-1} cm^{-1} [10]) and by using the extinct coefficient of pyrene T–T absorption at 415 nm (ϵ = 48 200 M^{-1} cm^{-1} [11]).

Although no isotope effect upon k_F (1.5×10^6 s^{-1}) and k_T (1×10^8 s^{-1}) was observed for NEA and NEA-*d*, $k_P + k_N$ decreased remarkably by deuteration, namely, 1.9×10^8 s^{-1} for NEA and 0.4×10^8 s^{-1} for NEA-*d*. From the absorbance of hydropyrenyl radicals observed with the nanosecond N_2 laser photolysis system, the ratio of the quantum yields of $\dot{P}H$ and $\dot{P}D$ formation was obtained to be $\Phi_{\dot{P}H}/\Phi_{\dot{P}D} = 10 \pm 3$.

(B) Pyrene–DPA and Pyrene–DPA-*d* in Toluene Solution. Time-resolved absorbance spectra of pyrene-DPA and –DPA-*d* in toluene solution are shown in Figure 2. The absorption spectra of the heteroexcimer state of these systems are rather broad compared with those of the pyrene–NEA heteroexcimers. In the systems of pyrene–DPA's, proton transfer in the heteroexcimer occurs efficiently but the absorption band due to the triplet state of pyrene was not detected, as one can see from Figure 2.

The spectra observed at 0 ps may be ascribed to the absorption band of the heteroexcimer with a little contribution from the $S_n \leftarrow S_1$ band of pyrene. Many of the excited pyrene molecules form

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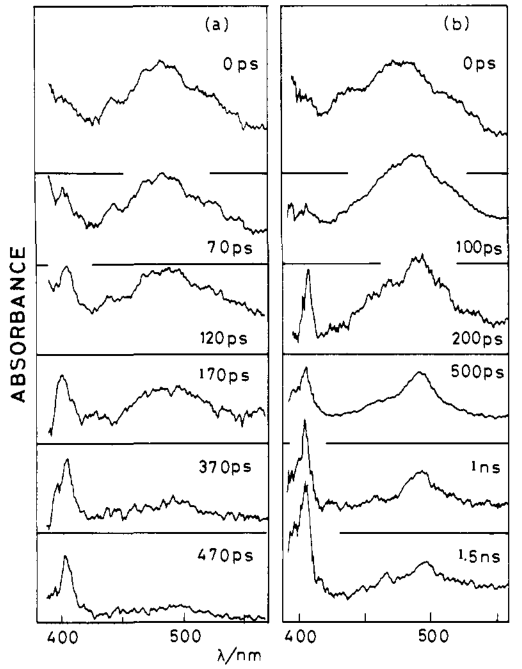

Figure 2. Time-resolved absorbance spectra of (a) pyrene–NEA and (b) pyrene–DPA-*d* systems in toluene solution. Delay times after excitation are denoted in the figure. The absorbance is not corrected for the shot-to-shot variations of exciting laser pulse. [Pyrene] = 6.6 × 10^{-4} M, [DPA] = 1 M, [DPA-*d*] = 0.94 M.

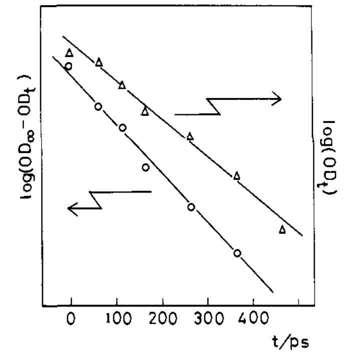

Figure 3. Decay curve of heteroexcimer state (△) and rise curve of $\dot{P}H$ (○) observed in the toluene solution of pyrene–DPA system. [Pyrene] = 6.6 × 10^{-4} M, [DPA] = 1 M.

heteroexcimers immediately after excitation, because weak collisional complexes are formed already in the ground state at such high concentrations of amines as used here.[12,13] The absorbance of the heteroexcimer decreases with the increase of that of $\dot{P}H$ or $\dot{P}D$. Under the condition that $k_Q[\mathrm{DPA}] \gg \tau_F^{-1}$, the time dependence of the absorbance of $\dot{P}H$ or $\dot{P}D$ and that of the heteroexcimer may be written approximately as shown in eq 3.

$$\begin{gathered}[\text{heteroexcimer}(t)] \approx C_1 \exp(-t/\tau_F) \\ [\dot{P}H(t)] \text{ or } [\dot{P}D(t)] \approx C_2[1 - \exp(-t/\tau_F)]\end{gathered} \tag{3}$$

The experimental results of the pyrene–DPA system corresponding to eq 3 are indicated in Figure 3. τ_F of the heteroexcimer was estimated to be about 200 ps, and this value was in good agreement with that obtained from the analysis of the rise curve of $\dot{P}H$. In contrast to this small τ_F value of the pyrene–DPA heteroexcimer, that of pyrene–DPA-*d* was obtained to be 1.1 ns. Thus, a remarkable effect of deuteration upon the decay time of heteroexcimer as well as the rise time of the hydropyrenyl radical was observed also in the pyrene–diphenylamine systems. The ratio of the quantum yields of $\dot{P}H$ and $\dot{P}D$ formation measured with nanosecond N_2 laser photolysis system was, however, about 1.0, in contrast to the value of about 10 in the case of the pyrene–NEA and –NEA-*d* systems.

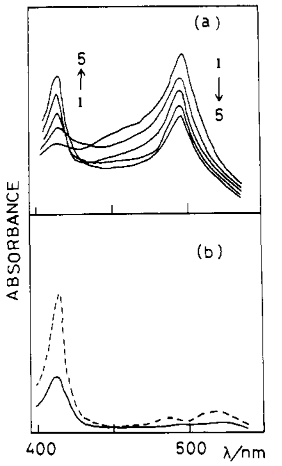

Figure 4. Transient absorbance spectra of DBP–TBA system in hexane observed by means of (a) picosecond laser photolysis system and (b) N_2 gas laser photolysis system. Delay times after excitation: (a) 1,500 ps; 2, 1 ns; 3, 2 ns; 4, 3.7 ns; 5, 5 ns; (b) --- 400 ns, — 5 μs. [DBP] = 3.6 × 10^{-4} M.

(C) Pyrene in Aniline and Aniline-d_7. In the case of pyrene in aniline solution, neither the band due to the hydropyrenyl radical nor the triplet state of pyrene was detected. The decay times of heteroexcimers were almost the same in both AN and AN-d_7 solutions. Since k_F is much smaller compared with k_N, the decay time of the heteroexcimer is determined by k_N. The observed k_N values were 1 × 10^9 s^{-1} in AN and 8 × 10^8 s^{-1} in AN-d_7. It seems that there is almost no deuteration effect upon the radiationless process of the heteroexcimers to the ground state.

(D) DBP–TBA System in Hexane Solution and DBP–DPA System in Toluene Solution. In order to investigate the steric effect upon the proton transfer in the heteroexcimer, we employed 2,7-di-*tert*-butylpyrene (DBP) and 2,4,6-tri-*tert*-butylaniline (TBA). In the heteroexcimer systems of these molecules, bulky substituent groups would prevent the donor–acceptor pair from taking a preferable geometry. Fluorescence quenching rate constants (k_Q) of pyrene–TBA and DBP–TBA systems in hexane solution were obtained to be 6.4 × 10^9 M^{-1} s^{-1} 4.2 × 10^9 M^{-1} s^{-1}, respectively. Taylor et al. have examined the pyrene-3,5-di-*tert*-butyl-*N*,*N*-dimethylaniline system and determined the k_Q value to be 6.4 × 10^9 M^{-1} s^{-1}.[14] These k_Q values indicate that the quenching reaction is diffusion controlled. DBP forms a fluorescent heteroexcimer with TBA in hexane solution, and the fluorescence quantum yield and lifetime at room temperature were obtained to be 2 × 10^{-2} and about 8 ns, respectively.

The transient absorbance spectra of the DBP–TBA system in hexane solution obtained by means of picosecond and nanosecond laser photolysis methods are given in Figure 4. The absorption band of the heteroexcimer with a maximum at ca. 500 nm decreases with the increase of the absorption band with maximum at 415 nm. The latter absorption band may be assigned to the superposition of the $T_n \leftarrow T_1$ band of DBP and the band due to the DB$\dot{P}$H radical because the ratio of the absorbance measured at 415 nm to that at 520 nm was 6.6 for the DBP–TBA system in hexane at the delay time of 2.5 μs, while that ratio in the spectrum of the triplet state of DBP in hexane was 4.2.

In case of the DBP–DPA system in toluene solution, the proton transfer in the heteroexcimer takes place much more rapidly and efficiently compared to the case of the DBP–TBA system.[2] The lifetime of the DBP–DPA heteroexcimer in toluene was about 1.4 ns.

(E) Photoreaction of Pyrene in NEA-*d*. In order to investigate the overall reaction scheme, we irradiated a solution of pyrene

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(4.3×10^{-3} M) in NEA-*d* with a 300-W high-pressure mercury lamp through a filter containing 5 mL of *N*,*N*-dimethylaniline and 1 mL of triethylamine in 150 mL of methanol. After 9 days of irradiation, although the solution turned brown, the amount of pyrene did not decrease very much and almost no pyrene adducts were found. Pyrene-d_x was obtained after the photoreaction, and the proportion of D's in pyrene was found to be $d_0 = 37\%$, $d_1 = 42\%$, $d_2 = 18\%$, and $d_3 = 3\%$. This result indicates that the 1-hydro-1-pyrenyl and aminyl radicals formed by proton-transfer reactions in the heteroexcimer state recombined with each other by a "reverse hydrogen atom transfer reaction" and did not form any photoadducts as in the case of the anthracene–amine system.[15]

Discussion

(I) Geometrical Structures of Pyrene–Primary and Pyrene–Secondary Aromatic Amine Heteroexcimers. Generally speaking, the band shape of the absorption spectrum of heteroexcimer may be expected to change corresponding to the change of the conformation of the donor and acceptor pair. Concerning the dependence of the absorption spectrum of heteroexcimer upon its geometry, the picosecond time-resolved absorption spectra[1c,5] of p-$(CH_3)_2NC_6H_4$–$(CH_2)_n$–1-pyrenyl (P_n; $n = 1, 3$) in 2-propanol seem to be typical. In the case of P_3, a loose-structure heteroexcimer is produced by the photoinduced electron transfer at first and is followed by a structural change to a tighter one. The absorption spectrum of the loose heteroexcimer is rather similar to the superposition of the absorption bands of free pyrene anion and DMA cation. The spectrum of the tighter one is very broad and is similar to that of the intermolecular pyrene–DMA heteroexcimer in nonpolar solvent. Although this type of spectral change of P_3 is detected also in acetone, no such spectral change is observed in the case of P_1, where the structural change similar to that of P_3 is not expected and which shows a spectrum similar to the superposition of the absorption bands of free pyrene anion and the DMA cation corresponding to its nonparallel conformation. Therefore, it seems to be probable that the heteroexcimer with parallel sandwich-type structure shows a quite broad absorption spectrum and the heteroexcimer with loose structure or nonparallel conformation shows a sharp absorption spectrum similar to the superposition of the absorption bands of donor cation and acceptor anion,

The absorption spectra of pyrene–NEA and pyrene–NEA-*d* heteroexcimers as shown in Figure 1 are similar to the superposition of pyrene anion and NEA cation bands. This result indicates nonparallel conformation of pyrene–NEA heteroexcimers, where the N–H bond of NEA or N–D bond of NEA-*d* might be almost perpendicular to the pyrene plane at C_1. Contrary to the spectra of pyrene–NEA heteroexcimers, those of pyrene–DPA and pyrene–DPA-*d* are very broad. However, in the case of these heteroexcimers, even in the conformation where the N–H or N–D bond is almost perpendicular to the pyrene plane, one of the two benzene rings of the diphenylamine may not be perpendicular to the pyrene plane but may be placed more closely to it, making sandwich structure.

There is another experimental result that seems to favor the above assumption that the N–H or N–D bond is almost perpendicular to the pyrene plane at the C_1 position. As it is described already, the rate constant of the intersystem crossing (k_T) of pyrene–NEA and pyrene–NEA-*d* heteroexcimers is 1×10^8 s^{-1} compared with the much smaller value (10^6 s^{-1}) of pyrene–DMA or pyrene–DEA heteroexcimers. Moreover, we have found fast intersystem crossing similar to that of the pyrene–NEA heteroexcimer as well as much faster ones in the case of some intramolecular heteroexcimer systems such as[16] 1-pyrenyl–CH_2–N$(CH_3)C_6H_4$ (PN-1), 9-anthryl–CH_2–N$(CH_3)C_6H_4$ (AN-1), 1-pyrenyl–$(CH_2)_n$–$C_6H_4N(CH_3)_2$ (P-*n*) and 1-pyrenyl–$(CH_2)_2$–N$(CH_3)_2$ (PNA-1). For example, in the case of PN-1, $k_T > 2.5 \times 10^{10}$ s^{-1} in hexane, $k_T \sim 4 \times 10^9$ s^{-1} in ethyl ether, and $k_T \sim 7 \times 10^8$ s^{-1} in acetonitrile. Very rapid intersystem crossing similar to that of PN-1 was observed also for AN-1. Fairly rapid intersystem crossing was observed also in the case of P-1 (1×10^8 s^{-1} in ethyl ether) and PNA-1 (8×10^8 s^{-1} in ethyl ether). However, the intersystem crossing in the case of P-2 and P-3 is much slower compared to those compounds with only one CH_2 chain.

The above results indicate that the rapid intersystem crossing of those intramolecular heteroexcimer systems is very sensitive to the mutual configuration of the donor and acceptor groups and the k_T value becomes much enhanced in the configuration where the nodal plane for the 2pπ AO's of the acceptor is perpendicular to that of the donor. Namely, the matrix element of the spin–orbit interaction, $\langle {}^1(A^- \cdots D^+) | \mathcal{H}_{SO} | ({}^3A \cdots D) \rangle = \langle \psi_D{}^{HOMO} | \mathcal{H}_{SO} | \psi_A{}^{HOMO} \rangle$, that is responsible for the intersystem crossing may be much larger in the perpendicular configuration compared with the parallel configuration.[16] This is based on the same reasoning as in the case of the large spin–orbit interaction matrix element between π–π^* and n–π^* states,

The above mechanism of fast intersystem crossing suggests rather strongly that, contrary to the plane-parallel sandwich configuration of the pyrene–DMA heteroexcimer, the donor and acceptor in pyrene–NEA heteroexcimer may not be plane-parallel but NEA will be oblique to the pyrene plane, which may be favorable also for the proton transfer from the donor cation to the acceptor anion in the heteroexcimer,

Usually, the sandwich configuration may be favorable for the Coulombic as well as resonance interaction between the donor and acceptor in the heteroexcimer. We assume here that the hydrogen-bonding interaction between the 2pπ AO at C_1 of the pyrene anion and the N–H of NEA cation in the heteroexcimer is responsible for keeping the oblique configuration of the pyrene–NEA heteroexcimer. The circumstance may be quite analogous also in the case of pyrene–DPA heteroexcimers. It was observed by means of vibrational spectroscopy that the π orbital of a benzene ring can act as a proton acceptor in the hydrogen-bonding interaction even in the ground electronic state.[17] Such a hydrogen-bonding interaction may become much stronger between an aromatic hydrocarbon anion and an amine cation in the heteroexcimer, which is favorable also for the proton transfer.

It should be noted here that, when two conjugate π-electronic systems are directly combined by hydrogen-bonding interaction, fluorescence of proton donor or acceptor is strongly quenched.[18-22] Possible mechanisms assumed for this quenching were charge-transfer interaction between proton donor and acceptor π-electron systems via hydrogen bonds[18,19,20] and hydrogen atom transfer[20a,22] from proton donor to acceptor. In relation to this problem, we have observed by means of a picosecond laser photolysis method that charge transfer from proton donor to acceptor occurs actually in the excited hydrogen-bonded pairs such as the 2-naphthylamine–pyridine, 1-aminopyrene–pyridine, and dibenzocarbazole–pyridine systems.[23-25] Therefore, it has been established that the hydrogen-bonding quenching of fluorescence in the case of these systems is due to the formation of a short-lived nonfluorescent charge-transfer state with a lifetime of several hundred picoseconds. Even the formation of aminyl radicals that appear to be produced by the charge-transfer followed by proton-transfer

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mechanism was detected, e.g., in the 2-naphthylamine–pyridine system,[23] but no fast intersystem crossing from the charge-transfer state has been detected.[23-25] The latter result will probably be due to the approximately planar structure and relatively short lifetime of the charge-transfer state, in contrast to the pyrene-NEA heteroexcimer with oblique configuration.

(II) Proton-Transfer Processes. According to the reaction scheme of eq 1, it is not possible in general to obtain k_P value separately, and only the combined value ($k_P + k_N$) can be obtained from the experimental results. However, the fact that τ_F of the heteroexcimer with an aromatic tertiary amine such as the pyrene–DMA or pyrene–DEA systems is much longer than that of the present systems indicates rather strongly that their τ_F values are determined mainly by k_P and/or k_T.

Therefore, the much smaller τ_F value of the pyrene–DPA heteroexcimer compared with that of the pyrene–NEA system may be ascribed to the difference of proton-transfer rate. The much faster proton transfer in the pyrene–DPA heteroexcimer compared with the pyrene–NEA heteroexcimer seems to be ascribed to the larger acidity of the DPA cation due to the more extensive migration of nitrogen 2pπ electrons to benzene rings compared with that of the NEA cation,

However, the circumstance is somewhat different in the case of pyrene dissolved in aniline, where the value of k_N is much larger than k_P and k_T. Presumably, stabilization of heteroexcimer owing to solvation by aniline and quenching of the heteroexcimer state due to the interaction with the surrounding aniline molecules are contributing to this result. In a hexane solution of the pyrene–aniline system, absorption bands due to the triplet state of pyrene and $\dot{\mathrm{P}}$H have been detected by means of microsecond flash photolysis as well as a nanosecond laser photolysis method.[1b] Owing to the small value of k_Q (5.7×10^8 M^{-1} s^{-1} in hexane), however, it was difficult to examine the pyrene–aniline system in hexane solution by means of picosecond laser spectroscopy.

The remarkable effect of deuteration upon τ_F has been observed in both pyrene–DPA and pyrene–NEA heteroexcimers. In contrast to the τ_F values of 3.4 ns and 200 ps for pyrene–NEA and pyrene–DPA heteroexcimers, those of deuterated systems were 6.8 ns and 1.1 ns, respectively. In view of the fact that, even in the case of the charge-transfer interaction with AN-d_7, k_N is approximately the same as that obtined with AN, the above results of the deuteration effect may be mainly due to the decrease of k_P by deuteration. It is already confirmed in the case of the pyrene–NEA system that k_T is not affected by deuteration. If the k_T value of the pyrene–DPA system is nearly the same as that of the pyrene–NEA system (1×10^8 s^{-1}), the formation of the pyrene triplet state from the heteroexcimer may be hardly recognized in the former system because its τ_F is 1 ns. This is actually the case. Moreover, it is possible that k_T of the pyrene–DPA heteroexcimer is a little smaller than that of the pyrene–NEA system, since the matrix element of the spin-orbit interaction responsible for the intersystem crossing, $\langle {}^1(\mathrm{A}^- \cdots \mathrm{D}^+)|\mathcal{H}_{\mathrm{SO}}|({}^3\mathrm{A} \cdots \mathrm{D})\rangle = \langle \psi_{\mathrm{D}}{}^{\mathrm{HOMO}}|\mathcal{H}_{\mathrm{SO}}|\psi_{\mathrm{A}}{}^{\mathrm{HOMO}}\rangle$, seems to depend significantly upon the π-electronic charge density on nitrogen, which will be smaller in DPA than NEA due to the more extensive charge migration from the nitrogen 2pπ orbital to the benzene rings.

On the basis of the above discussion, the remarkable effect of deuteration upon τ_F can be ascribed to the fact that the proton-transfer process in the heteroexcimer becomes much slower by deuteration. This is the well-known kinetic isotope effect of a proton-transfer reaction.[26] The much smaller yield of $\dot{\mathrm{P}}$D compared with $\dot{\mathrm{P}}$H in the pyrene–NEA system ($\Phi_{\dot{\mathrm{P}}\mathrm{H}}/\Phi_{\dot{\mathrm{P}}\mathrm{D}} = 10 \pm 3$) seems to be ascribed to the decrease of k_P by deuteration. However, whether k_N' is affected by deuteration or not and whether the contribution of k_N' is large or negligible are not very clear at the present stage of the investigation. Contrary to the case of the pyrene–NEA system, the yields of $\dot{\mathrm{P}}$D and $\dot{\mathrm{P}}$H were almost the same in the pyrene–DPA system. This result indicates that k_P and k_S are much larger than other processes in both deuterated and nondeuterated systems and not only k_T and k_N but also k_N' are not affected by deuteration even if k_N' is not small.

The proton-transfer process is affected not only by deuteration but also by the steric hindrance due to the existence of a bulky substituent or the restriction on the motions of donor and acceptor groups with methylene chains.

The heteroexcimer formation process of the DBP–TBA system in hexane solution is diffusion controlled in spite of the existence of bulky substituents. However, the proton transfer in the heteroexcimer becomes much slower compared with the case of the pyrene–NEA system. Analogous results were obtained also in the DBP–DPA system, in comparison with the pyrene–DPA system. These results indicate clearly that the proton-transfer process is more sensitive to the steric factors compared with the charge transfer. Moreover, it should be noted here that the oblique configuration of the heteroexcimer that seems to be favorable for proton transfer as discussed in I will be favorable also for the proton transfer in these heteroexcimers with bulky substituents.

Concerning the steric effects on the proton transfer via heteroexcimer, we have examined also some intramolecular model compounds of the pyrene–secondary amine heteroexcimer system (1-pyrenyl–$(\mathrm{CH_2})_n$–$\mathrm{NHC_6H_5}$, PNH$_n$, n = 1, 2, 3, 4).[27] In the case of these systems, the proton transfer in the heteroexcimer was not observed probably because the activation energy necessary to take a favorable conformation is very large due to the existence of the methylene chain substituted at C$_1$ of the pyrene moiety. For example, PNH$_2$ and PNH$_3$ in ethyl ether solution form stable heteroexcimers that have much longer lifetimes and show very broad absorption bands compared with those of the intermolecular pyrene–NEA heteroexcimer.

PNH$_1$ in ethyl ether solution, however, shows a free ionlike sharp absorption spectrum. This result may be ascribed to its nonparallel conformation as discussed in I for the P-n compounds. Moreover, PNH$_1$ shows fast intersystem crossing from the heteroexcimer state ($k_T = 2.7 \times 10^8$ s^{-1} in ethyl ether) similar to the one discussed in I, instead of the proton-transfer reaction.

Probably the proton-transfer reaction is prevented due to the large activation energy necessary for the N–H proton to approach an appropriate carbon in the pyrene moiety from a preferable direction while the fast intersystem crossing may be feasible owing to its nonparallel conformation as discussed in I for similar intramolecular heteroexcimer systems.

In conclusion, on the basis of the present results of picosecond laser photolysis studies, the nature of the interaction between donor and acceptor in the pyrene–primary and pyrene–secondary aromatic amine heteroexcimers as well as the conformations of those heteroexcimers in relation to the mechanism of hydrogen atom transfer reaction via heteroexcimer have been elucidated.

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Registry No. NEA, 103-69-5; NEA-d_1, 83365-31-5; DPA, 122-39-4; DPA-d_1, 14915-28-7; TBA, 961-38-6; TBB, 1460-02-2; TBN, 4074-25-3; pyrene, 129-00-0; *m*-di-*tert*-butylbenzene, 1014-60-4; *p*-di-*tert*-butylbenzene, 1012-72-2.

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