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HYDROGEN ATOM TRANSFER REACTION FROM EXCITED CARBAZOLE TO PYRIDINE

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Summary

The hydrogen bonding interaction between excited carbazole and pyridine was investigated in cyclohexane by an emission–absorption flash technique. Triplet carbazole is deactivated by pyridine with a rate constant of 4.9×10^7 M^{-1} s^{-1}, yielding the carbazyl radical with a reaction yield of unity. The triplet–triplet absorption of carbazole hydrogen bonded with pyridine was not observed. By means of the triplet energy transfer from *N*-ethylcarbazole to the hydrogen-bonded carbazole it was found that the triplet state of the hydrogen-bonded carbazole yields the carbazyl radical with a reaction yield of 0.7. Excited singlet carbazole is deactivated by pyridine with a diffusion-controlled rate, yielding the carbazyl radical with a reaction yield of 0.1. Flashing of the hydrogen-bonded carbazole does not yield carbazyl radical. The difference in the reaction yields between the free and the hydrogen-bonded species indicates that the dynamic hydrogen atom transfer reaction occurs from the encounter state in competition with hydrogen bond formation.

1. Introduction

When two conjugate π electronic systems are directly joined together by a hydrogen bond, the ability of the hydrogen-bonded species to fluoresce is diminished with the exception of the acridone–pyridine system [1 - 3]. This phenomenon has been interpreted in terms of a charge transfer interaction [1] and a hydrogen atom transfer reaction [3 - 8].

Carbazole forms an $\gtrdot N-H\cdots N\lessdot$-type hydrogen bond with pyridine and the fluorescence of carbazole is strongly quenched by the addition of pyridine [9]. In this case the very weak fluorescence from the hydrogen-bonded species was measured by Martin and Ware [10]. The fluorescence

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lifetime of the hydrogen-bonded species was evaluated to be 28 ps in cyclohexane by simulating a Stern–Volmer plot for the fluorescence quenching [10].

Masuhara *et al.* [11] tried to measure the transient absorption of the hydrogen-bonded species in acetonitrile using nanosecond laser photolysis, but they could not detect any transient. Martin and Bréhéret [12] studied the hydrogen bonding interaction in the triplet state by conventional flash photolysis and found that the carbazyl radical is formed through the interaction. Further, the triplet lifetime of the hydrogen-bonded species was estimated to be 23 μs in cyclohexane.

Recently Martin *et al.* [13] investigated the deactivation processes of excited singlet dibenzocarbazoles hydrogen bonded with pyridine by picosecond laser photolysis. They observed the formation of a charge transfer state ($D^+—H\cdots A^-$) from the hydrogen-bonded species in the excited singlet state ($(D—H\cdots A)^*$). However, no transient absorption was observed after the disappearance of $(D—H\cdots A)^*$ and ($D^+—H\cdots A^-$).

In our previous work on the hydrogen bonding interaction in the excited singlet and triplet states [3 - 8] it was found that (i) in the excited singlet state the hydrogen atom transfer reaction occurs only in a non-relaxed encounter state before hydrogen bond formation and (ii) in the triplet state hydrogen atom transfer occurs in both the non-relaxed encounter state and the hydrogen-bonded state. However, the difference in the reactivity between the non-relaxed encounter state and the hydrogen-bonded state has not been interpreted fully.

In the present work we studied the hydrogen atom transfer reaction in excited singlet and triplet states for the carbazole–pyridine system in cyclohexane. A comparison of the rate and/or yield of the hydrogen atom transfer reaction between an $\gtrdot N—H\cdots N\lessdot$-type and an $> —O—H\cdots N\lessdot$-type hydrogen bonding system is expected to give further information for the hydrogen bonding interaction in the excited states. It was found that the hydrogen atom transfer reaction of the carbazole–pyridine system occurs in a similar manner to that of the 2-naphthol–pyridine system in both excited singlet and triplet states, although the pK_a value for carbazole is much greater than that for 2-naphthol in these states.

2. Experimental details

Carbazole (Extra Pure grade, Tokyo-Kasei) and *N*-ethylcarbazole (Guaranteed Reagent grade, Nakarai) were treated by thin layer chromatography and sublimated twice under vacuum. Naphthalene (Extra Pure grade, Kanto-Kagaku) was recrystallized from ethanol and sublimated under vacuum. Ferrocene (Guaranteed Reagent grade, Tokyo-Kasei) was recrystallized from benzene, zone refined and sublimated in vacuum. Pyridine (Guaranteed Reagent grade, Nakarai) was dried over barium oxide and distilled. Cyclohexane (Extra Pure grade, Wako-Junyaku) was treated with fuming sulphuric acid diluted with concentrated sulphuric acid, washed with water, neutralized with an aqueous alkaline solution, treated with alkaline potassium permanganate, washed again with water, dried over calcium chloride and then distilled over sodium wire.

Absorption spectra were recorded on a Hitachi EPS-3T spectrophotometer. Fluorescence spectra were measured with a modified Hitachi EPU spectrophotometer. An argon–air flash-lamp (64 J; full width at half-maximum (FWHM), 20 μs) or a xenon flash-lamp (130 J; FWHM, 10 μs) was used for excitation together with Toshiba UVD 25 and UV 31 filters. The method of measuring transient absorption and time-integrated fluorescence intensity during a flash was the same as reported elsewhere [14]. A frequency-doubled *Q*-switched ruby laser (0.05 J; FWHM, 30 ns) was used for the laser experiments.

Cyclohexane solutions were degassed by freeze–pump–thaw cycles. All measurements were made at 23 °C.

3. Results and discussion

The hydrogen bonding equilibrium constant K_g in the ground state for the carbazole–pyridine system was determined to be 12 M^{-1} at 23 °C which is equal to the value given in the literature [10]. The fluorescence lifetime τ_0 and yield Φ_f were reported to be 14.8 - 16.1 ns and 0.38 - 0.40 at 24 °C [10, 15] respectively. Using these values and assuming that the hydrogen-bonded species is not fluorescent we obtained $k_q = 1.0 \times 10^{10}$ M^{-1} s^{-1} for the bimolecular quenching rate constant from the Stern–Volmer plot for the fluorescence quenching by pyridine. This value is close to that reported [10]. The triplet yield Φ_{isc} was determined to be 0.60 at 23 °C by means of an emission–absorption flash technique [16] with naphthalene ($\Phi_{isc} = 0.75$ in cyclohexane [17]) as a standard. Using $\tau_0 = 14.8$ - 16.1 ns and $\Phi_{isc} = 0.60$ we obtain $k_{isc} = (3.7 - 4.1) \times 10^7$ s^{-1} for the rate constant of intersystem crossing.

Flashing of the deaerated solution of carbazole gives two kinds of transient absorption in the visible region [18]. The transient absorption at $\lambda_{max} = 420$ nm decays as a first-order process with a rate constant k_{dt} of 6×10^3 s^{-1} and was assigned to the triplet–triplet (T–T) absorption spectrum. The other transient absorption at $\lambda_{max} = 600$ nm decays as a second-order process with a rate constant of 4.9×10^9 M^{-1} s^{-1} and was assigned to the spectrum of the carbazyl radical R·. It was confirmed that R· is formed from both higher excited singlet [19] and higher excited triplet states [18].

The interaction of triplet carbazole with pyridine was studied by Martin and Bréhéret [12] at pyridine concentrations of less than 10^{-3} M. From the non-linearity of the Stern–Volmer plot on the triplet decay they concluded that the hydrogen bonding equilibrium in the triplet state is established during the triplet lifetime. However, our result shown in Fig. 1 differs from theirs. The observed first-order decay constant k_{obs} is linear with respect to

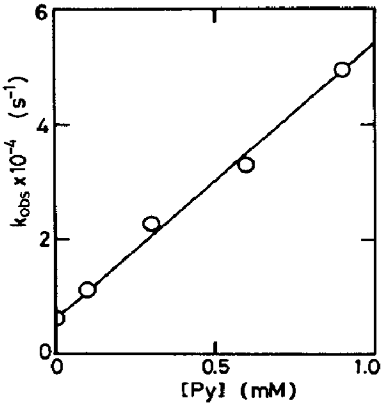


Fig. 1. The dependence of the observed triplet decay constant for carbazole on the pyridine concentration.

the pyridine concentration up to 10^{-3} M. From the slope of the plot we obtained $k_{qt} = 4.9 \times 10^7$ M^{-1} s^{-1} for the bimolecular quenching rate constant of triplet carbazole with pyridine.

To observe the T–T absorption of the hydrogen-bonded species, we measured the transient absorption at higher pyridine concentrations by using a frequency-doubled *Q*-switched ruby laser. Since carbazole has no absorption at 347 nm, *N*-ethylcarbazole was used as a triplet sensitizer. The triplet energy of *N*-ethylcarbazole (24 200 cm^{-1} [20]) is slightly lower than that of carbazole (24 600 cm^{-1} [20]), so that the triplet energy transfer between carbazole and *N*-ethylcarbazole may be reversible [21, 22]. Further it was confirmed that *N*-ethylcarbazole does not form a hydrogen bond with pyridine and that the decay rate ((5 - 6) $\times 10^3$ s^{-1}) of triplet *N*-ethylcarbazole does not depend on the pyridine concentration below 5 M. When the concentration of the hydrogen-bonded carbazole in the ground state (C···Py (Py ≡ pyridine)) is negligible, the decay of the triplet states of *N*-ethylcarbazole, carbazole and the hydrogen-bonded carbazole in the solution containing *N*-ethylcarbazole S, carbazole C and pyridine may be described as shown in the following scheme:

$$\begin{tikzcd}
{}^3\mathrm{S} + \mathrm{C} \arrow[r, shift left] \arrow[d] & \mathrm{S} + {}^3\mathrm{C} \arrow[l, shift left] \arrow[r, shift left, "+\mathrm{Py}"] \arrow[d] & {}^3\mathrm{C}\cdots\mathrm{Py} \arrow[l, shift left, "-\mathrm{Py}"] \arrow[r] \arrow[d] & \text{reaction products} \\
\mathrm{S} & \mathrm{C} & \mathrm{C}\cdots\mathrm{Py} &
\end{tikzcd}$$

When the solution containing 4×10^{-3} M *N*-ethylcarbazole, 4.2×10^{-4} M carbazole and 10^{-2} M pyridine, where hydrogen bond formation is negligible in the ground state, was irradiated with a laser pulse, the transient absorption was observed at 420 nm and it decayed as a first-order process with a rate constant of 3.3×10^5 s^{-1}. Although the T–T absorptions of *N*-ethylcarbazole and carbazole are present at 420 nm, this result means that the decay rate of triplet carbazole is greater than 3.3×10^5 s^{-1} at 10^{-2} M pyridine. Further, it was found that the decay at 420 nm is accompanied with an increase in the absorption at 600 nm where the carbazyl radical has an absorption maximum. When the pyridine concentration was increased to 5 M, where the hydrogen bond formation is almost complete in the ground state, the decay rate of the transient absorption at 420 nm increased to 1.2×10^6 s^{-1}. By conventional flash photolysis the rate constant k_{ET} of energy transfer from triplet *N*-ethylcarbazole to the hydrogen-bonded carbazole was determined to be 4×10^9 M^{-1} s^{-1} in 5 M pyridine solution. Hence the decay rate of triplet *N*-ethylcarbazole in a solution containing 4.2×10^{-4} M carbazole and 5 M pyridine is calculated to be 1.7×10^6 s^{-1}, which agrees with the decay rate obtained above. These results show that the triplet lifetime of the hydrogen-bonded carbazole is much less than 1 μs. Therefore the hydrogen bonding equilibrium in the triplet state cannot be established at a pyridine concentration below 10^{-3} M, in contrast with the result of Martin and Bréhéret [12]. This is why they could not observe the T–T absorption of the hydrogen-bonded species for the carbazole–pyridine system in contrast with the 1-anthrol–pyridine system [5]. The absorption at 420 nm immediately after laser excitation and the absorption at 600 nm after the disappearance of the absorption at 420 nm are attributed to triplet *N*-ethylcarbazole and the carbazyl radical respectively. Their absorbances $D_T'(420)$ and $D_R'(600)$ were 0.064 and 0.024 respectively in 10^{-2} M pyridine and 0.047 and 0.013 respectively in 5 M pyridine.

Flashing of the solution containing 10^{-5} M ferrocene does not give any transient absorption, because triplet carbazole is quenched by ferrocene F with a rate constant k_F of 6.0×10^9 M^{-1} s^{-1} and hence carbazyl radical formation due to the $T_1 \rightarrow T_n$ excitation is decreased. However, the solution containing 10^{-5} M ferrocene and 10^{-4} - 10^{-2} M pyridine gives the transient absorption due to the carbazyl radical. The carbazyl radical formation may be explained by the following scheme:

$$\mathrm{C} \xrightarrow{I_{\mathrm{abs}}} {}^1\mathrm{C}^*$$

$$ {}^1\mathrm{C}^* \xrightarrow{k_f + k_{ic}} \mathrm{C}$$

$$ {}^1\mathrm{C}^* \xrightarrow{k_{isc}} {}^3\mathrm{C}$$

$$ {}^3\mathrm{C} \xrightarrow{k_{dt}} \mathrm{C}$$

$$ {}^3\mathrm{C} + \mathrm{F} \xrightarrow{k_F[\mathrm{F}]} \mathrm{C} + \mathrm{F}$$

$$ {}^3\mathrm{C} + \mathrm{Py} \xrightarrow{\Phi_{rt} k_{qt} [\mathrm{Py}]} \mathrm{R}\cdot + \mathrm{PyH}\cdot$$

$$ {}^3\mathrm{C} + \mathrm{Py} \xrightarrow{(1 - \Phi_{rt}) k_{qt} [\mathrm{Py}]} \mathrm{C} + \mathrm{Py}$$

The hydrogen-bonded species gives no transient absorption and its fluorescence yield is much smaller than that of free carbazole. Therefore the carbazyl radical concentration $[\mathrm{R}]_0$ at the end of a flash is related to the total quantity $\int I_{\mathrm{abs}}\,\mathrm{d}t$ of light absorbed by free carbazole during a flash as follows:

$$[\mathrm{R}]_0 = \Phi_{\mathrm{isc}} \frac{\Phi_{\mathrm{rt}} k_{\mathrm{qt}}[\mathrm{Py}]}{k_{\mathrm{dt}} + k_{\mathrm{F}}[\mathrm{F}] + k_{\mathrm{qt}}[\mathrm{Py}]} \int I_{\mathrm{abs}}\,\mathrm{d}t \tag{1}$$

where Φ_{rt} is the reaction yield for dynamic triplet quenching. Furthermore, the time-integrated fluorescence intensity during a flash is given by

$$\int I_{\mathrm{f}}(\lambda')\,\mathrm{d}t = \alpha(\lambda')\Phi_{\mathrm{f}} \int I_{\mathrm{abs}}\,\mathrm{d}t \tag{2}$$

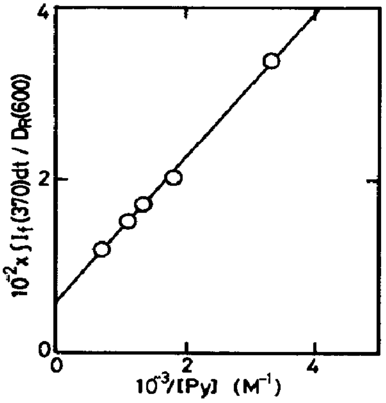
where $\alpha(\lambda')$ is a constant depending on the experimental conditions. From eqns. (1) and (2) and the relation $D_{\mathrm{R}}(\lambda) = \epsilon_{\mathrm{R}}(\lambda)[\mathrm{R}]_0 d$ we obtain

$$\frac{\int I_{\mathrm{f}}(\lambda')\,\mathrm{d}t}{D_{\mathrm{R}}(\lambda)} = \frac{\alpha(\lambda')\Phi_{\mathrm{f}}}{\epsilon_{\mathrm{R}}(\lambda) d \Phi_{\mathrm{isc}}} \frac{1}{\Phi_{\mathrm{rt}}} \left(1 + \frac{k_{\mathrm{dt}} + k_{\mathrm{F}}[\mathrm{F}]}{k_{\mathrm{qt}}[\mathrm{Py}]}\right) \tag{3}$$

where $\epsilon_{\mathrm{R}}(\lambda)$ and $D_{\mathrm{R}}(\lambda)$ are the molar extinction coefficient and the absorbance respectively of the carbazyl radical immediately after flashing and d = 10 cm is the optical path length of a sample cell. A plot of $\int I_{\mathrm{f}}(\lambda')\,\mathrm{d}t/D_{\mathrm{R}}(\lambda)$ *versus* $1/[\mathrm{Py}]$ is shown in Fig. 2. From the ratio of the slope to the intercept we obtained $k_{\mathrm{qt}}/(k_{\mathrm{dt}} + k_{\mathrm{F}}[\mathrm{F}]) = 7.1 \times 10^2\ \mathrm{M}^{-1}$. Using $k_{\mathrm{F}} = 6.0 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, $[\mathrm{F}] = 1.0 \times 10^{-5}$ M and $k_{\mathrm{dt}} = 6.0 \times 10^3\ \mathrm{s}^{-1}$ we obtain $k_{\mathrm{qt}} = 4.7 \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ which agrees very well with the value obtained from the quenching experiment on the triplet decay.

The concentration of triplet carbazole $[^3\mathrm{C}]_0$ at the end of a flash is given by

$$[^3\mathrm{C}]_0 = \Phi_{\mathrm{isc}} \int I_{\mathrm{abs}}\,\mathrm{d}t \tag{4}$$



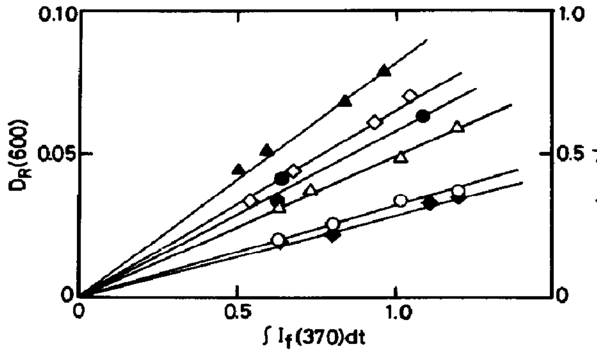


Fig. 2. A plot of $\int I_f(\lambda')\,\mathrm{d}t/D_{\mathrm{R}}(\lambda)$ *vs.* $1/[\mathrm{Py}]$ (λ = 600 nm; λ' = 370 nm).

Fig. 3. Plots of $D_{\mathrm{R}}(\lambda)$ and $D_{\mathrm{T}}(\lambda'')$ *vs.* $\int I_f(\lambda')\,\mathrm{d}t$ for various pyridine concentrations (λ = 600 nm; λ' = 370 nm; λ'' = 420 nm): ○, 0 M; ◆, 0.30 mM; △, 0.55 mM; ●, 0.75 mM; ◇, 0.90 mM; ▲, 1.5 mM.

TABLE 1

Determination of the reaction yield for dynamic triplet quenching

$[\mathrm{Py}] \times 10^4$ (M)	$D_T(420)/\int I_f(370)\,dt$	$D_R(600)/\int I_f(370)\,dt$	$1 + (k_{dt} + k_F[F])/k_{qt}[\mathrm{Py}]$	Φ_{rt}
0	0.0325	—	—	—
3.0	—	0.0029	5.75	1.0_4
5.5	—	0.0049	3.50	1.0_9
7.5	—	0.0058	2.83	1.0_3
9.0	—	0.0065	2.38	0.99
15.0	—	0.0083	1.92	1.0_1
Average				1.03

From eqns. (2) - (4) and the relation $D_T(\lambda'') = \epsilon_T(\lambda'')[^3C]d$ we obtain

$$\Phi_{rt} = \frac{D_R(\lambda)/\int I_f(\lambda')\,dt}{D_T(\lambda'')/\int I_f(\lambda')\,dt}\,\frac{\epsilon_T(\lambda'')}{\epsilon_R(\lambda')}\left(1 + \frac{k_{dt} + k_F[F]}{k_{qt}[\mathrm{Py}]}\right) \tag{5}$$

where $\epsilon_T(\lambda'')$ and $D_T(\lambda'')$ are the molar extinction coefficient and the absorbance respectively of the T–T absorption immediately after flashing. The plots of $D_T(\lambda'')$ and $D_R(\lambda)$ *versus* $\int I_f(\lambda')\,dt$ are shown in Fig. 3. The slopes of these plots are listed in Table 1. With $k_{dt} + k_F[F] = 6.6 \times 10^4$ s^{-1} at $[F] = 10^{-5}$ M and $k_{qt} = 4.9 \times 10^7$ M^{-1} s^{-1}, the values for $1 + (k_{dt} + k_F[F])/k_{qt}[\mathrm{Py}]$ were calculated for various pyridine concentrations and are listed in Table 1. The values for ϵ_T and ϵ_R have already been determined to be 14 500 M^{-1} cm^{-1} at 420 nm and 7000 M^{-1} cm^{-1} at 600 nm respectively [18]. The values for Φ_{rt} at various pyridine concentrations were calculated according to eqn. (5) and are listed in Table 1. As the average value for Φ_{rt} is unity, it is concluded that the dynamic quenching of triplet carbazole by pyridine is entirely due to the hydrogen atom transfer reaction. This result is the same as for the 2-naphthol–pyridine [4] and 1-anthrol–quinoline systems [6] as shown in Table 2. However, it is noted that the bimolecular rate constant of the carbazole–pyridine system is much smaller than those of the other two systems.

When the hydrogen bond formation is complete in the ground state, no transient absorption appeared by a direct flash excitation. In this case the reaction efficiency Φ_{rt}' of the hydrogen-bonded carbazole triplet may be determined by using *N*-ethylcarbazole as a triplet sensitizer. Since the decay of the hydrogen-bonded triplet carbazole was found to be very fast, the back energy transfer from the hydrogen-bonded carbazole to *N*-ethylcarbazole can be neglected. In this case the following scheme is adequate:

$$\mathrm{S} \xrightarrow{I_{abs}} {}^1\mathrm{S}^*$$

$$^1\mathrm{S}^* \xrightarrow{k_\mathrm{f} + k_\mathrm{ic}} \mathrm{S}$$

$$^1\mathrm{S}^* \xrightarrow{k_\mathrm{isc}} {}^3\mathrm{S}$$

$$^3\mathrm{S} \xrightarrow{k_\mathrm{dt}{}^\mathrm{S}} \mathrm{S}$$

$$^3\mathrm{S} + \mathrm{C}\cdots\mathrm{Py} \xrightarrow{k_\mathrm{ET}[\mathrm{C}\cdots\mathrm{Py}]} \mathrm{S} + {}^3\mathrm{C}\cdots\mathrm{Py}$$

$$^3\mathrm{C}\cdots\mathrm{Py} \xrightarrow{\Phi_\mathrm{rt}'k_\mathrm{dt}'} \mathrm{R}\cdot + \mathrm{PyH}\cdot$$

$$^3\mathrm{C}\cdots\mathrm{Py} \xrightarrow{(1 - \Phi_\mathrm{rt}')k_\mathrm{dt}'} \mathrm{C}\cdots\mathrm{Py}$$

TABLE 2

Summary of the hydrogen bonding interaction in the excited singlet and triplet states

System	*Triplet state*				*Excited singlet state*			$\Delta E(\mathrm{S}_1 - \mathrm{T}_1)$ (kcal mol^{-1})
	k_qt ($\mathrm{M}^{-1}\ \mathrm{s}^{-1}$)	Φ_rt	Φ_rt'	$\Delta \mathrm{p}K_\mathrm{a}$	k_q ($\mathrm{M}^{-1}\ \mathrm{s}^{-1}$)	Φ_r	$\Delta \mathrm{p}K_\mathrm{a}$	
1-anthrol*–pyridine	—	0	0	4.8	1.2×10^{10}	0	−5.3	31.7
Carbazole*–pyridine	4.9×10^7	1.0	0.7	15.9	1.0×10^{10}	0.1	6.7	15.5
1-anthrol*–quinoline	$(1.1 - 1.4) \times 10^9$	1.0	0.6	5.1	1.3×10^{10}	< 0.1	−5.0	31.7
2-naphthol*–pyridine	$(1.5 - 1.9) \times 10^9$	1.0	0.8	3.0	$(1.2 - 1.4) \times 10^{10}$	0.2	−2.4	24.4

The $\Delta \mathrm{p}K_\mathrm{a}$ values were calculated by using data from refs. 5 and 23. The $\mathrm{p}K_\mathrm{a}$ value for triplet carbazole was assumed to be equal to that for the ground state.

Under the condition that $k_\mathrm{ET}[\mathrm{C}\cdots\mathrm{Py}] \gg k_\mathrm{dt}{}^\mathrm{S}$ which is satisfied for $[\mathrm{C}\cdots\mathrm{Py}] > 10^{-5}$ M the reaction yield Φ_rt' of the hydrogen-bonded triplet carbazole is expressed by

$$\Phi_\mathrm{rt}' = \frac{D_\mathrm{R}(\lambda)/\int I_\mathrm{f}{}^\mathrm{S}(\lambda')\,\mathrm{d}t}{D_\mathrm{T}{}^\mathrm{S}(\lambda'')/\int I_\mathrm{f}{}^\mathrm{S}(\lambda')\,\mathrm{d}t}\ \frac{\epsilon_\mathrm{T}{}^\mathrm{S}(\lambda'')}{\epsilon_\mathrm{R}(\lambda)} \tag{6}$$

where $\epsilon_\mathrm{T}{}^\mathrm{S}(\lambda'')$ and $D_\mathrm{T}{}^\mathrm{S}(\lambda'')$ are the molar extinction coefficient and the absorbance of the T–T absorption of *N*-ethylcarbazole immediately after flashing and $\int I_\mathrm{f}{}^\mathrm{S}(\lambda)\,\mathrm{d}t$ is the time-integrated fluorescence intensity of *N*-ethylcarbazole during a flash. The plots of $D_\mathrm{R}(\lambda)$ and $D_\mathrm{T}{}^\mathrm{S}(\lambda'')$ *versus* $\int I_\mathrm{f}{}^\mathrm{S}(\lambda')\,\mathrm{d}t$ are shown in Fig. 4. From the slopes of these plots we obtained $D_\mathrm{R}(600)/\int I_\mathrm{f}{}^\mathrm{S}(380)\,\mathrm{d}t = 0.019$ and $D_\mathrm{T}{}^\mathrm{S}(420)/\int I_\mathrm{f}{}^\mathrm{S}(380)\,\mathrm{d}t = 0.051$. The value for $\epsilon_\mathrm{T}{}^\mathrm{S}$ was determined to be 13 500 $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ at 420 nm in the same way as the

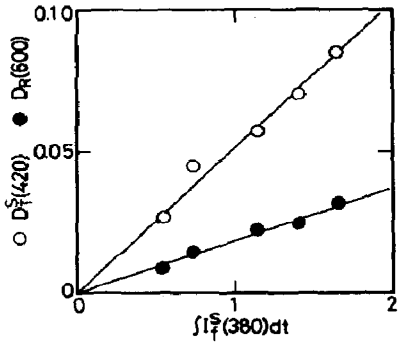
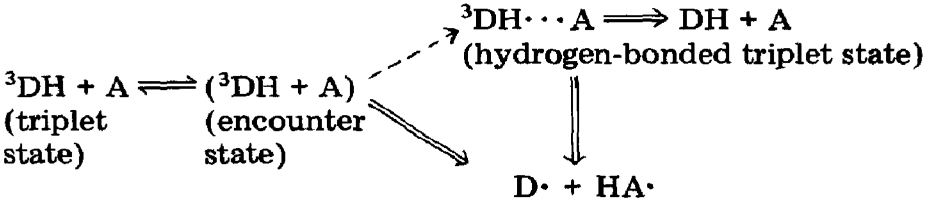


Fig. 4. Plots of $D_T^S(\lambda'')$ and $D_R(\lambda)$ vs. $\int I_f(\lambda')\,dt$ (λ = 600 nm; λ' = 380 nm; λ'' = 420 nm; *N*-ethylcarbazole (sensitizer) concentration, 0.3 mM; carbazole concentration, 0.1 mM): ○, 0 M pyridine; ●, 5 M pyridine.

determination of ϵ_T. Using these values we obtain $\Phi_{rt}' = 0.72$. This value is compared with the results of the laser photolysis described previously. Since the hydrogen bond formation is complete in 5 M pyridine and is neglected in 10^{-2} M pyridine, the ratio $D_R'(600)/D_T'(420)$ for pyridine concentrations of 10^{-2} M or 5 M is proportional to Φ_{rt} or Φ_{rt}' respectively. Therefore, if the efficiencies of the triplet energy transfer from triplet *N*-ethylcarbazole to the free and hydrogen-bonded carbazole are the same, the ratio $D_R'(600)/D_T'(420) = 0.27$ for 5 M pyridine solution to $D_R'(600)/D_T'(420) = 0.38$ for 10^{-2} M pyridine solution gives $\Phi_{rt}'/\Phi_{rt} = 0.71$. This result is consistent with that obtained by an emission–absorption flash photolysis.

It was suggested that the hydrogen atom transfer reaction is regarded as an electron transfer followed by a proton transfer [24]. This suggestion was supported by a study of the relation between k_{qt} and the reduction potential of a hydrogen atom acceptor [7]. In contrast, the hydrogen bond formation begins with the approach of the proton of a hydrogen bond donor to the non-bonding orbital of a hydrogen bond acceptor. Since the hydrogen atom transfer reaction and the hydrogen bond formation were considered to be competitive reactions from the encounter state, the difference in the values for Φ_{rt} and Φ_{rt}' has been interpreted with the following scheme [6]:



Hydrogen bond formation in the triplet state does not occur readily, so that the triplet quenching is essentially due to the hydrogen atom transfer reaction. For the 1-anthrol–pyridine system, the hydrogen atom transfer reaction does not occur whereas the T–T absorption of the hydrogen-bonded species was observed [5], and the decay rate of the hydrogen-bonded triplet species (5.8×10^3 s^{-1} in pyridine) is not very different from that of the free species (3.4×10^3 s^{-1} in cyclohexane). Therefore it is obvious that the hydrogen bonding interaction in the triplet state does not enhance the deactivation very much in contrast with that in the excited singlet state, when the hydrogen atom transfer reaction does not occur. The rate constant k_{qt} is related to the free-energy change for the hydrogen atom transfer reaction. From the k_{qt} values summarized in Table 2 it may be concluded that the hydrogen atom transfer reaction in the triplet state is energetically impossible for the 1-anthrol–pyridine system and that it is energetically more unfavourable for the carbazole–pyridine system than for the 1-anthrol–quinoline and 2-naphthol–pyridine systems.

The hydrogen bonding interaction in the first excited singlet state was investigated at pyridine concentrations of 5×10^{-3} - 10^{-1} M where the fluorescence from the hydrogen-bonded species is negligible compared with that from the free species, and triplet carbazole decays entirely through the bimolecular reaction with pyridine. The carbazyl radical formation is satisfactorily described by the following scheme:

$$\mathrm{C} \xrightarrow{I_{abs}} {}^1\mathrm{C}$$

$${}^1\mathrm{C}^* \xrightarrow{k_f + k_{ic}} \mathrm{C}$$

$${}^1\mathrm{C}^* \xrightarrow{k_{isc}} {}^3\mathrm{C}$$

$${}^1\mathrm{C}^* + \mathrm{Py} \xrightarrow{\Phi_r k_q[\mathrm{Py}]} \mathrm{R}\cdot + \mathrm{PyH}\cdot$$

$${}^1\mathrm{C}^* + \mathrm{Py} \xrightarrow{(1 - \Phi_r)k_q[\mathrm{Py}]} \mathrm{C} + \mathrm{Py}$$

$${}^3\mathrm{C} + \mathrm{Py} \xrightarrow{k_{qt}[\mathrm{Py}]} \mathrm{R}\cdot + \mathrm{PyH}\cdot$$

In this scheme the enhancement of the intersystem crossing due to the hydrogen bonding interaction in the excited singlet state was not taken into account, because it was not observed for the 1-anthrol–pyridine system for which the T–T absorption of the hydrogen-bonded species was measured [5]. According to the above scheme we obtain

$$\frac{D_{\mathrm{R}}(\lambda)}{\int I_f(\lambda')\,\mathrm{d}t} = \frac{\epsilon_{\mathrm{R}}(\lambda)d}{\alpha(\lambda')k_f}(k_{isc} + \Phi_r k_q[\mathrm{Py}]) \qquad (7)$$

Figure 5 shows the plot of $D_{\mathrm{R}}(\lambda)/\int I_f(\lambda')\,\mathrm{d}t$ *versus* [Py]. From the slope and the intercept we obtained $\Phi_r k_q/k_{isc} = 27 \pm 3$ M^{-1}. With $k_q = 1.0 \times 10^{10}$ M^{-1} s^{-1} and $k_{isc} = (3.7$ - $4.1) \times 10^7$ s^{-1}, we obtain $\Phi_r = 0.10$ - 0.11. This result is similar to that for the 2-naphthol–pyridine system. The results obtained from the present work and previous studies are summarized in Table 2.

It is interesting that Φ_{rt} is unity for all systems when bimolecular quenching occurs and that Φ_r changes widely in spite of the fact that all k_q values are of the order of the diffusion-controlled rate. The difference in the reaction yield between the excited singlet and triplet states may be interpreted in terms of the differences in the strength of the hydrogen

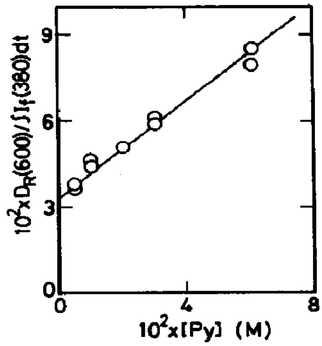
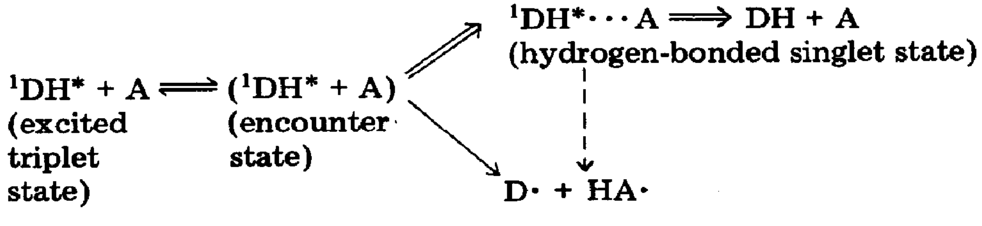


Fig. 5. A plot of $D_R(\lambda)/\int I_f(\lambda')\,dt$ *vs.* [Py] (λ = 600 nm; λ' = 380 nm).

bonding interaction and/or in the spin multiplicity of the geminate radical pair formed by the hydrogen atom transfer reaction between these states. However, when the fluorescence quenching of 1-anthrol with pyridine is completely due to the hydrogen atom transfer reaction followed by the geminate radical recombination, Φ_r is not considered to be zero because the geminate radical recombination competes more or less with the dissociation of the geminate radical pair to free radicals. Therefore the fluorescence quenching of the 1-anthrol–pyridine system is considered to be due to the rapid hydrogen bond formation from the encounter state rather than due to the geminate radical recombination following the hydrogen atom transfer reaction. It is known that the pK_a value of a hydrogen bond donor or an acceptor is a measure of their hydrogen bond ability [1]. Hence the difference in pK_a between the hydrogen bond donor and acceptor may be regarded as a measure for the facility in the hydrogen bond formation. The values for Δp$K_a \equiv$ pK_a(donor) − pK_a(acceptor) are listed in Table 2, where pK_a(donor) represents the pK_a of the donor in its excited singlet state (S_1) or corresponding triplet state. The ΔpK_a value is positive for all systems in the triplet state whereas it is negative in the excited singlet state with the exception of the carbazole–pyridine system. Therefore it seems that the difference in the strength of the hydrogen bonding interaction between the excited singlet and triplet states is the principal cause of the difference between Φ_r and Φ_{rt}, even if the Φ_r value is somewhat decreased through the geminate radical recombination. The hydrogen bond formation is faster than the hydrogen atom transfer reaction in the excited singlet state as shown in the following scheme [6]:



For the carbazole–pyridine system the ΔpK_a value is positive in the excited singlet state as well as in the triplet state. Hence it may be expected that the Φ_r value for the carbazole–pyridine system is close to unity. In contrast with this expectation, however, it is much less than unity and is close to the values for the 1-anthrol–quinoline and 2-naphthol–pyridine systems. To understand the results according to the above scheme, it is necessary to compare the rate of the hydrogen atom transfer reaction with that of hydrogen bond formation. The k_{qt} value for the carbazole–pyridine system is smaller by two orders of magnitude than those for the 1-anthrol–quinoline and 2-naphthol–pyridine systems so that the hydrogen atom transfer reaction in the triplet state is energetically more unfavourable for the carbazole–pyridine system than for the other two systems. The energy gap $\Delta E(S_1 - T_1)$ between the excited singlet and the triplet states is smaller for carbazole than for 1-anthrol and 2-naphthol. Therefore the hydrogen atom transfer reaction in the excited singlet state is also energetically more unfavourable for the carbazole–pyridine system than for the other two systems. The rate constant for the hydrogen atom transfer reaction for the carbazole–pyridine system is considered to be much smaller than those for the other two systems. This situation might not allow the Φ_r value for the carbazole–pyridine system to exceed the values for the other two systems, although the rate constant for hydrogen bond formation is considered to be smaller for the carbazole–pyridine system than for the other two systems.

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