Interactions of β-Naphthol and β-Naphthylamine in Their Excited Singlet States with Triethylamine

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(Received January 24, 1974)

Proton donor-acceptor interactions in excited states were studied by measuring mainly time-resolved fluorescence spectra for β-naphthol–TEA in toluene and in acetonitrile, and for β-naphthylamine–TEA in nonpolar mixed solvents. The Stern-Volmer relation was found to be satisfied for β-naphthol–TEA in toluene. The rate constant and activation energy of hydrogen bond formation in the excited state of this system were obtained to be 2.2×10^9 M^{-1} s^{-1} at 30 °C and 1.6 kcal/mol, respectively, indicating that the process is diffusion-controlled. The time dependences of the intensities of the fluorescence bands due to the free and complexed β-naphthol were measured with the solutions containing various concentrations of triethylamine in acetonitrile. From the analysis of the result, it is shown that this system is led to the ion-pair formation *via* the hydrogen-bonded species in the excited state. For β-naphthylamine–TEA in nonpolar mixed solvents, the bands due to hydrogen-bonded species in the ground and excited states were observed at 370 and ~390 nm in the absorption and fluorescence spectra, respectively.

One of the present authors (S.N.) and Gouterman[1)] studied the hydrogen bonding effect upon the electronic absorption spectra of α- and β-naphthols and obtained the results that the hydrogen bonding has the chargetransfer character to some extent. Förster[2)] found ion-pair formation in the excited states of β-naphthol and other compounds through proton transfer. Weller *et al.*[3–5)] and Stryer[6)] have studied the proton-transfer reaction in the excited state of β-naphthol in aqueous solution by measuring its fluorescence and have determined several kinetic and thermodynamic constants. Mataga *et al.*[7–9)] measured the fluorescence spectra of ternary solutions containing β-naphthol or other proton donors and acceptors in organic solvents. They showed that a hydrogen-bonded complex and an ion-pair exist in the excited state of the system containing β-naphthol and triethylamine in benzene. Baba *et al.*[10,11)] measured fluorescence and excitation-polarization spectra with some hydrogen bonding systems including α-naphthol as proton donor and discussed the nature of their lowest excited singlet states. Hirota[12)] investigated the behaviors of 3-hydroxy-2-naphthoic acid and its derivatives in their excited states by measuring relative fluorescence intensities of the free and hydrogen-bonded species as a function of temperature.

The above-mentioned studies have been made by measuring mainly fluorescence spectra, excitation polarization spectra, and quantum yields. In other words, they have been done under steady-state conditions. Recently, however, the fast transient technique has been applied to the study of proton transfer in the excited state. Ware[13)] studied the intramolecular proton transfer of 2-hydroxy-3-naphthoic acid in the excited state by measuring the fluorescence decay. Furthermore, Ofran and Feitelson[14)] studied the proton dissociation of β-naphthol in the excited state with the aid of fluorescence decay measurements.

In the present study, we have undertaken to study the interaction of β-naphthol or β-naphthylamine in the excited state with triethylamine by measuring nanosecond time-resolved fluorescence spectra and by analyzing the decays of fluorescence bands due to the free and complexed proton donors.

Experimental

β-Naphthol and β-naphthylamine were purified by vacuum sublimation after repeated recrystallizations from water. Triethylamine (TEA) was refluxed with acetic anhydride and thereafter distilled under reduced pressure. The purified TEA was degassed and stored in a refrigerator. Spectrograde toluene was distilled from sodium. Methylcyclohexane and isopentane were distilled after passing through a 1 m silica gel column. Acetonitrile was distilled from phosphorus pentoxide and thereafter from calcium hydride.

Samples used for fluorescence measurements were degassed by the freeze-thaw method. In order to protect them from moisture, they were prepared in a dry-box filled with dry nitrogen gas.

Absorption spectra were measured with a Cary recording spectrophotometer model 14. Fluorescence spectra were measured with a Spex 0.75 m grating monochromator, excitation being effected by an Ushio USH-102D high pressure mercury lamp and an EMI 9558QB photomultiplier being used as a detector. β-Naphthol and β-naphthylamine were excited at 313 nm by using an aqueous solution of $NiSO_4\cdot 6H_2O$–$CoSO_4\cdot 7H_2O$ as a solution-filter. The monochromator was used with a slit width of $\lesssim$0.5 mm. Fluorescence lifetimes and nanosecond time-resolved spectra were measured by the method described previously[15)] which used a coaxial nitrogen gas laser as an excitation source.

Results and Discussion

Hydrogen Bond Formation between β-Naphthol and TEA in Toluene. Time-resolved fluorescence spectra observed with the β-naphthol–TEA–toluene system are shown in Fig. 1. The steady-excitation fluorescence spectrum of β-naphthol in toluene is also shown in this figure for the purpose of comparison. The time-resolved fluorescence spectrum measured with the ternary system immediately after excitation (t=0) has a new band at 410 nm in addition to the band due to the free β-naphthol molecule at 355 nm. The former corresponds to the band found in the steady-excitation fluorescence spectrum of the β-naphthol–TEA–benzene system and ascribed to the ion-pair by Mataga and

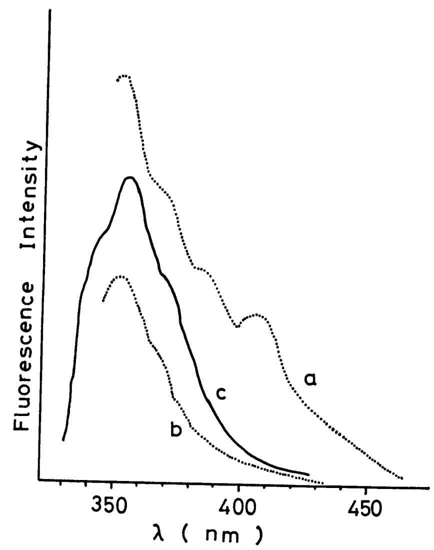
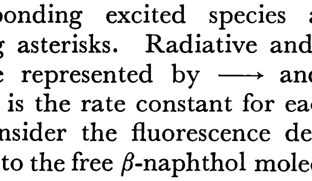


Fig. 1. Fluorescence spectra of β-naphthol under various conditions. The time-resolved spectra of the β-naphthol–TEA system in toluene at 25 °C observed 0 ns (curve a) and 10 ns (curve b) after the fluorescence of free β-naphthol reached the maximum intensity. The concentrations of β-naphthol and TEA are 1.2×10^{-4}M and 0.705×10^{-2}M, respectively. Curve c is the steady-state fluorescence spectrum of the toluene solution of β-naphthol (0.705×10^{-4}M).

Kaifu.[7] This band decays more rapidly than the band at 355 nm, as clearly seen from the comparison between curves a and b in Fig. 1. This means that the excited β-naphthol molecule complexed with TEA decays more rapidly than the excited free molecule.

Since the system under consideration has only one complexed species in the excited state, the following scheme can be considered:



$$\begin{tikzcd}
D^* + A \arrow[r, shift left, "k_3"] \arrow[d, shift left, "k_1"] \arrow[d, squiggly, "k_2"'] & (DA)^* \arrow[l, shift left, "k_4"] \arrow[d, shift left, "k_5"] \arrow[d, squiggly, "k_6"'] \\
D + A \arrow[u, shift left, "I_D"] \arrow[r, shift left, "K_{eq}"] & (DA) \arrow[l, shift left] \arrow[u, shift left, "I_{DA}"]
\end{tikzcd}$$

Scheme 1.

Here, D, A, and (DA) are β-naphthol, TEA, and the complexed species in the ground state, respectively, and the corresponding excited species are represented by putting asterisks. Radiative and nonradiative processes are represented by ⟶ and ⇝, respectively, and k_i is the rate constant for each process.

First let us consider the fluorescence decay of the 355 nm band due to the free β-naphthol molecule on the basis of the above scheme. The fluorescence lifetime, τ, measured at 360 nm with the β-naphthol–TEA–toluene system changes with the concentration of TEA, [A], as shown in Fig. 2. The observed relation between τ and [A] is represented by the Stern-Volmer equation;[17]

$$\tau^{-1} = \tau_0^{-1} + k_3[A] \qquad (1)$$

$$= k_1 + k_2 + k_3[A] \qquad (2)$$

$$I_F \propto [D^*] = [D^*]_0 \exp(-t/\tau) \qquad (3).$$

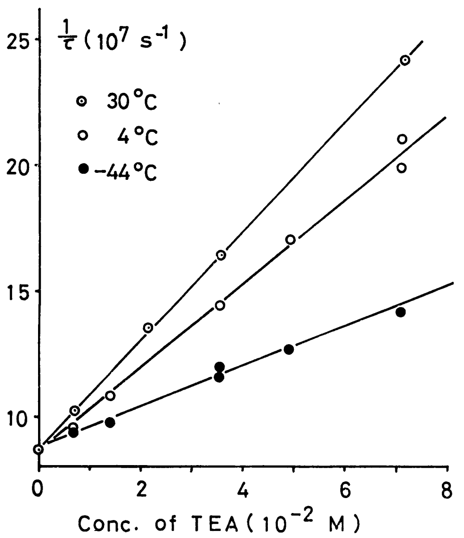


Fig. 2. The plots of decay rates at 360 nm *vs.* the concentrations of TEA for the β-naphthol–TEA system in toluene. The concentrations of β-naphthol is 1.3×10^{-4}M.

Here, I_F is the fluorescence intensity at 360 nm, $[D^*]$ and $[D^*]_0$ represent the concentrations of D^* at $t=t$ and $t=0$, respectively, and τ_0 is the fluorescence lifetime of β-naphthol at $[A]=0$. Equations (1) and (2) are derived from the above scheme for the case of $k_4 \ll k_5 + k_6$. This condition means that the dissociation process of the complexed species in the excited state is negligibly slow.

The straight line given in Fig. 2 was used for the determination of the intrinsic lifetime of β-naphthol, τ_0, and the rate constant for the complex formation in the excited state, k_3. From its intercept with the ordinate and its slope, τ_0 and k_3 were determined at 30 °C to be 11.6 ns and $(2.17\pm0.01)\times10^9$ M^{-1} s^{-1}, respectively. Plots of τ^{-1} *vs.* [A] at different temperatures between 49 and −44 °C also showed linear relationships. A plot of $\log k_3$ *vs.* T^{-1} gave a straight line, as shown in Fig. 3, and an activation energy E_a and a frequency factor A were determined as follows:

$$E_a = 1.64\pm0.11 \text{ kcal/mol}$$

$$A = (3.05\pm0.12)\times10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

The E_a value is comparable to the activation energy for the diffusion of toluene as estimated from the

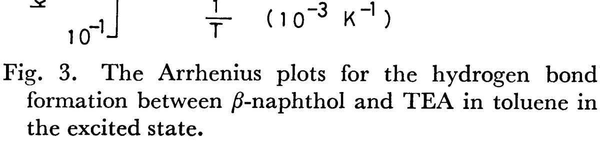


Fig. 3. The Arrhenius plots for the hydrogen bond formation between β-naphthol and TEA in toluene in the excited state.

temperature coefficient of the viscosity.[18]

The k_3 value obtained by the present authors is very close to that obtained by Weller *et al.*[4,5] ($k_3=2\sim3\times10^9\ \mathrm{M^{-1}\,s^{-1}}$) for the systems containing β-naphthol and several carboxylate ions from the analysis of the fluorescence quantum yield. Furthermore, the value obtained is reasonable in view of the fact that k_3 is calculated to be $3\sim8\times10^9\ \mathrm{M^{-1}\,s^{-1}}$ with the help of Smoluchowski's equation:[19,20]

$$k_3 = \frac{4\pi R_0(D_\mathrm{A}+D_\mathrm{B})}{R_0\int_{R_0}^{\infty} e^{U(r)/kT}\frac{\mathrm{d}r}{r^2}}\,\frac{N_\mathrm{A}}{1000} = 4\pi R_0(D_\mathrm{A}+D_\mathrm{B})\left(\frac{N_\mathrm{A}}{1000}\right) \quad [\mathrm{M^{-1}\ s^{-1}}] \tag{4}$$

Here, R_0, the sum of collision radii is taken to be 3 Å,[21] D_A and D_B are individual diffusion coefficients, N_A is Avogadro's number, and $U(r)$ is the interaction energy between the reactants. The k_3 value was evaluated to be $3\text{—}8\times10^9\ \mathrm{M^{-1}\,s^{-1}}$ by taking $U(r)$ to be zero or $-kT$.

Here let us turn to the time dependence of fluorescence of the hydrogen-bonded species measured at 410 nm for the β-naphthol–TEA–toluene system. The rise process was not observed since the rise time is too fast to be observed by the present detecting system. The decay process is almost single exponential and the fluorescence decay time of the hydrogen-bonding system decreases from ~6 to ~4 ns with the increasing concentration of TEA from 10^{-2} to 10^{-1} M.

Judging from the K_eq value, which is $60\ \mathrm{M^{-1}}$ in benzene at room temperature,[7] the concentrations of D and (DA) are almost equal to each other in the ground state for the concentrations used. Therefore the direct excitation of (DA) to (DA)* must be taken into account in addition to the process $\mathrm{D^*+A\rightarrow(DA)^*}$. In this case, the time dependence of the fluorescence due to (DA)* is represented by Eq. (5).

$$[(\mathrm{DA})^*] = \frac{k_3[\mathrm{A}][\mathrm{D}^*]_0}{(k_5+k_6)-(k_1+k_2+k_3[\mathrm{A}])}\left(e^{-(k_1+k_2+k_3[\mathrm{A}])t} - e^{-(k_5+k_6)t}\right) + [(\mathrm{DA})^*]_0 e^{-(k_5+k_6)t}. \tag{5}$$

Here, $[(\mathrm{DA})^*]$ and $[(\mathrm{DA})^*]_0$ represent the concentrations of the complexed species in the excited state at $t=t$ and $t=0$, respectively. As is expected from the experimental results, the pre-exponential factor of the first term on the right-hand side of Eq. (5) is positive. Therefore, Eq. (5) shows that the decay lifetime of (DA)* is determined by the two terms $1/(k_5+k_6)$ and $1/(k_1+k_2+k_3[\mathrm{A}])$. This is a reason why the observed decay lifetime is slightly dependent on [A].

Hydrogen Bond Formation between β-Naphthol and TEA in Acetonitrile. The absorption spectra were measured for acetonitrile solutions containing a fixed concentration of β-naphthol and various concentrations of TEA, with the result shown in Fig. 4. The equilibrium constant, K_eq, in the ground state at 25 °C was obtained to be $19\ \mathrm{M^{-1}}$ by analyzing the dependence of the absorption intensity at a fixed wavelength upon the TEA concentration.[1]

Figure 5 shows the fluorescence spectra measured for an acetonitrile solution containing β-naphthol and TEA with steady-state excitation, the intensities of which are normalized at 340 nm. From this figure, it is revealed that, besides the fluorescence band at 355 nm due to the free β-naphthol molecule, two bands appear at ~370 and ~450 nm and increase their intensities with the increasing concentration of TEA, though the latter two bands are weak compared with the former band. The band at ~370 nm can be ascribed to hydrogen bonded β-naphthol[8] and the largely redshifted band at 450 nm to either of the ion pair or the β-naphtholate ion.

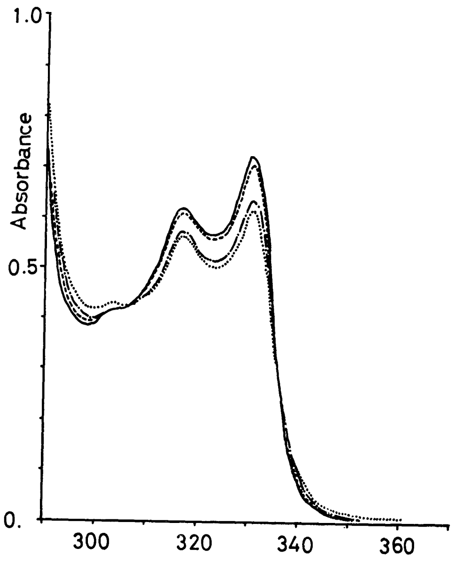


Fig. 4. Absorption spectra of the β-naphthol–TEA system in acetonitrile at 25 °C. The concentrations of TEA are 0, 0.705×10^{-2}, 2.11×10^{-2}, and 2.82×10^{-2}M for curves ——, ------, —·—, and ······, respectively. The concentrations of β-naphthol are commonly 3.46×10^{-4}M.

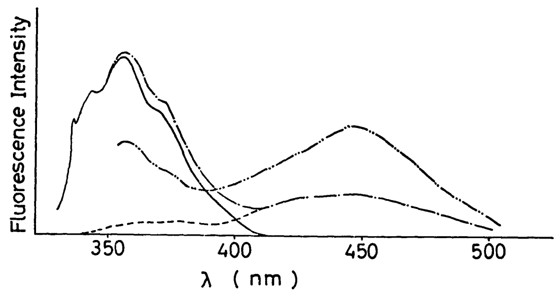
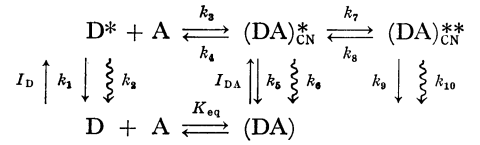


Fig. 5. The fluorescence spectra of the β-naphthol-TEA system in acetonitrile at 25 °C. The concentrations of TEA are 0, 0.705×10^{-2}, and 3.52×10^{-2}M for curves ——, —·—, and —··—, respectively. Curve ---- is a difference between curves —— and —·— normalized at 340 nm. The scattering of the excitation light prevented us from measuring the spectrum for the solution containing 3.52×10^{-2}M TEA below 355 nm.

The above-mentioned spectral data show the existence of two different kinds of hydrogen-bonded or complexed species, $(\mathrm{DA})^{*}_{\mathrm{CN}}$ and $(\mathrm{DA})^{**}_{\mathrm{CN}}$, in the excited state of the system involving β-naphthol and TEA in acetonitrile. Therefore the following scheme may be applied to this system:



Scheme 2.

According to Scheme (2), the following equations can be obtained:

$$\frac{d[D^*]}{dt} = -(k_1+k_2+k_3[A])[D^*] + k_4[(DA)^*_{CN}] \tag{6.1}$$

$$\frac{d[(DA)^*_{CN}]}{dt} = k_3[A][D^*] - (k_4+k_5+k_6+k_7)[(DA)^*_{CN}] + k_8[(DA)^{**}_{CN}] \tag{6.2}$$

$$\frac{d[(DA)^{**}_{CN}]}{dt} = k_7[(DA)^*_{CN}] - (k_8+k_9+k_{10})[(DA)^{**}_{CN}] \tag{6.3}$$

These equations are solved as follows:

$$[D^*] = \sum_{i=1}^{3} a_i e^{-\mu_i t} \tag{7.1}$$

$$[(DA)^*_{CN}] = \sum_{i=1}^{3} b_i e^{-\mu_i t} \tag{7.2}$$

$$[(DA)^{**}_{CN}] = \sum_{i=1}^{3} c_i e^{-\mu_i t} \tag{7.3}$$

The pre-exponential factors are related with each other by

$$a_i = \frac{k_4}{K_1 - \mu_i} b_i \tag{8.1}$$

$$c_i = \frac{k_7}{K_3 - \mu_i} b_i \tag{8.2}$$

$-\mu_i$'s (i=1,2,3) are roots of the following cubic equation:

$$\mu^3 + \alpha\mu^2 + \beta\mu + \gamma = 0 \tag{9}$$

where

$$\alpha = K_1 + K_2 + K_3 \tag{10.1}$$

$$\beta = K_1K_2 + K_2K_3 + K_3K_1 - k_3k_4[A] - k_7k_8 \tag{10.2}$$

$$\gamma = K_1K_2K_3 - k_3k_4[A]K_3 - k_7k_8K_1 \tag{10.3}$$

$$K_1 = k_1 + k_2 + k_3[A] \tag{11.1}$$

$$K_2 = k_4 + k_5 + k_5 + k_7 \tag{11.2}$$

$$K_3 = k_8 + k_9 + k_{10} \tag{11.3}.$$

According to the above scheme, the time dependences of $[D^*]$, $[(DA)^*_{CN}]$, and $[(DA)^{**}_{CN}]$ can be represented by the sum of three exponential terms with time constants of $\tau_1 = 1/\mu_1$, $\tau_2 = 1/\mu_2$, and $\tau_3 = 1/\mu_3$.

In order to check experimentally the above consideration, the fluorescence lifetimes of free β-naphthol and $(DA)^{**}_{CN}$ were measured at 360 and 450 nm, respectively. The measurement of the lifetime for $(DA)^*_{CN}$ was complicated by the overlapping of the fluorescence band of D*. Furthermore, it was found that the Stern-Volmer relation concerning the effect of the TEA concentration upon the fluorescence lifetime of free β-naphthol was not satisfied. This means that the dissociation reaction of the hydrogen-bonded species $(DA)^*_{CN}$ into free β-naphthol and TEA must be taken into account for this system.

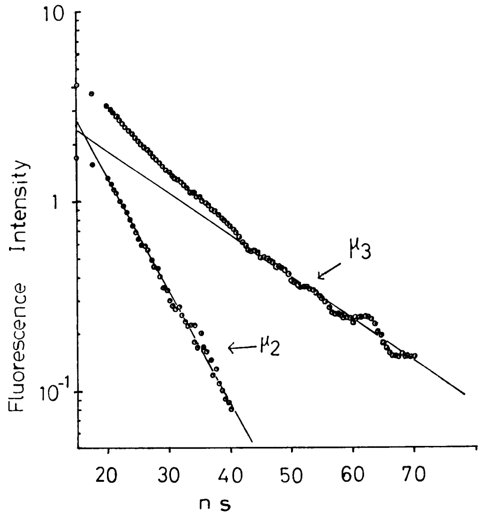


Fig. 6. Semilogarithmic plot of fluorescence intensity $I(t)$ observed at 450 nm *vs.* time for the system containing 3.46×10^{-4}M β-naphthol and 3.52×10^{-2}M TEA in acetonitrile. N_2 gas laser pulse starts at time t=0.

The decay curves observed at 450 nm for the systems with various concentrations of TEA consists of two singlet exponential curves, as is clearly seen in Fig. 6 which shows an example of the observed curves. This may be explained by considering that the exponential component with the greatest μ_i, say μ_1, rises too fast to be observed. Thus the greater and smaller decay components observed at 450 nm correspond to μ_2 and μ_3, respectively.

Let us turn to the fluorescence decay at 360 nm. The decay curve at 360 nm observed for each solution is separated into two components which are assigned to μ_1 and μ_3, or μ_2 and μ_3.[22] Thus the μ_1, μ_2, and μ_3 values were obtained from the decay curves observed

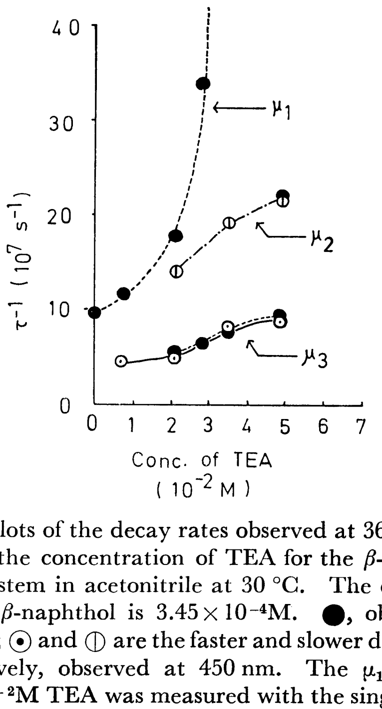
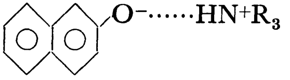


Fig. 7. Plots of the decay rates observed at 360 and 450 nm *vs.* the concentration of TEA for the β-naphthol–TEA system in acetonitrile at 30 °C. The concentration of β-naphthol is 3.45×10^{-4}M. ●, observed at 360 nm; ⊙ and ⦶ are the faster and slower decay rates, respectively, observed at 450 nm. The μ_1 value at 2.8×10^{-2}M TEA was measured with the single photon counting method.[22]

at 450 and 360 nm for the solutions containing a fixed concentration of β-naphthol and various concentrations of TEA. The results are summarized in Fig. 7.

Figure 7 shows that the μ_2 or μ_3 values obtained at both wavelengths agree well with each other for the respective solutions and therefore the decay curve observed with each of the solutions consists of the three exponential components. This gives experimental evidence for the validity of Eq. (7) and therefore an experimental support for the reaction mechanism shown by scheme (2) that $(\mathrm{DA})^{**}_{\mathrm{CN}}$ is produced *via* $(\mathrm{DA})^{*}_{\mathrm{CN}}$.[23]

The fluorescence peak of $(\mathrm{DA})^{**}_{\mathrm{CN}}$ appears at 450 nm and is far removed from that of D* (355 nm). This indicates that $(\mathrm{DA})^{**}_{\mathrm{CN}}$ is an ion-pair



or a solvated β-naphtholate ion. In view of the fact that process 8 in reaction scheme (2), namely, the back reaction from $(\mathrm{DA})^{*}_{\mathrm{CN}}$ to $(\mathrm{DA})^{**}_{\mathrm{CN}}$, can not be disregarded,[24] $(\mathrm{DA})^{*}_{\mathrm{CN}}$ is regarded as the ion-pair. This is because the process from the solvated β-naphtholate ion to $(\mathrm{DA})^{*}_{\mathrm{CN}}$ is too slow to occur within the lifetime of $(\mathrm{DA})^{**}_{\mathrm{CN}}$.[25]

Hydrogen Bond Formation between β-Naphthylamine and TEA. The hydrogen bond formation was studied for the solution containing β-naphthylamine and TEA in the 1:1 mixed solvent of isopentane and methylcyclohexane (PM). The absorption spectra observed with the system at room temperature changed only slightly with an increase in the concentration of TEA. At −30 °C, as is seen in Fig. 8, the absorption spectra change somewhat remarkably owing to the hydrogen bond formation and exhibit an isosbestic point. From the observed spectra, the equilibrium constant was found to be 7 M^{-1} at −30 °C. Thus it is obvious that at low temperature a hydrogen bond is formed between β-naphthylamine and TEA in the mixed solvent. At room temperature the spectrum of β-naphthylamine is not changed by the addition of TEA and hydrogen bond formation is negligibly small.

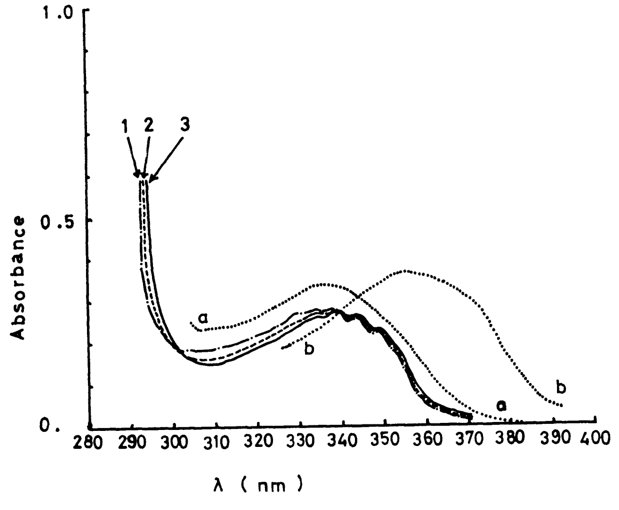


Fig. 8. Absorption spectra of β-naphthylamine in a 1:1 mixed solvent of methylcyclohexane and isopentane. Curves 1, 2, and 3 were measured at −30 °C, for solutions with the TEA concentrations of 0, 0.705×10^{-1}, and 1.41×10^{-1}M, respectively. Curves a and b were measured at 77 K for solutions with the TEA concentrations of 0 and 0.705×10^{-1}M, respectively. The concentrations of β-naphthylamine are 1.04×10^{-4}M and 0.92×10^{-4}M for curves 1∼3 and curves a∼b, respectively.

Fluorescence spectra observed with the β-naphthylamine–TEA system at 25 °C and −50 °C are shown in Fig. 9. They are insensitive to the concentration of TEA until it becomes 0.0705 M at which condition a remarkable change occurs in the spectra. This implies that, at this concentration of TEA, k_3[A] is comparable with the intrinsic decay rate constant of excited β-naphthylamine and hydrogen bond formation occurs within its lifetime. From this consideration, the order of magnitude of k_3 was obtained to be $10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ by taking the critical value of [A] to be 0.1 M. This k_3 value seems to be reasonable.

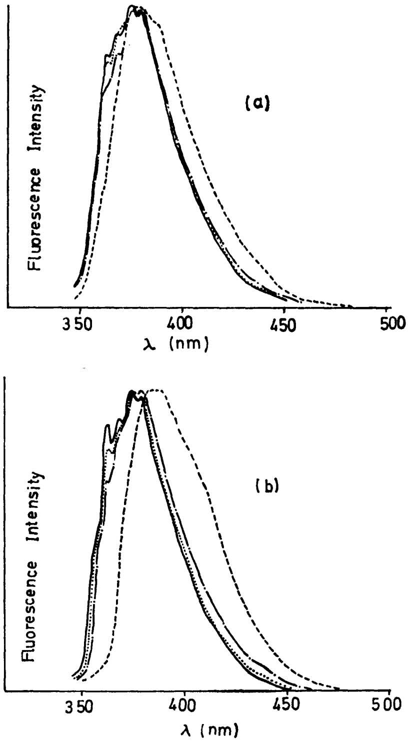


Fig. 9. Fluorescence spectra of β-naphthylamine in the 1:1 mixed solvent of methylcyclohexane and isopentane. The concentrations of TEA are 0, 0.705×10^{-4}, 0.705×10^{-2}, and 0.705×10^{-1}M for curves (1) ——, (2) ······, (3) —·—·, and (4) ------, respectively. The concentration of β-naphthylamine is 0.92×10^{-4}M. (a) at 25 °C, (b) at −50 °C.

Fluorescence decay curves were measured at room temperature for the β-naphthylamine solutions containing various concentrations of TEA and single exponential curves were obtained. The lifetimes obtained at 360 and 420 nm are 15∼14 ns for the solutions containing 0∼0.7×10^{-1} M TEA. Hence they are almost independent of the concentration of TEA. One of the reasons for this is that the ratio of the hydrogen-bonded β-naphthylamine molecule in the excited state to the total excited molecules is small, as revealed from the observed fluorescence spectra shown in Fig. 9.

We should like to express their thanks to Professor E. Lippert, Technical University of Berlin, Professor Ichiro Hanazaki, Osaka University and Dr. Takayoshi Kobayashi, The Institute of Physical and Chemical Research for their helpful discussions.

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16) The present study does not exclude the possibility that there exist some precursors to (DA)*, which decay too fast to be observed by the present time-resolving fluorescence technique.

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18) "Handbook of Chemistry and Physics," ed. by C. Hodgmon, Chemical Rubber, Cleveland, Ohio (1962), pp. 2258—2264.

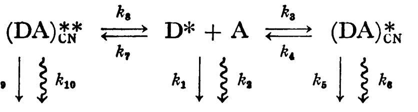
19) M. V. Smoluchowski, *Z. Phys. Chem.*, (Leipzig), **92**, 129 (1917).

20) W. R. Ware and J. S. Novros, *J. Phys. Chem.*, **70**, 3246 (1966).

21) This value seems to be reasonable in view of the fact that N—O distances of hydrogen-bonded systems are usually 2.6—2.9 Å.

22) We are indebted to Dr. Nobuyuki Wakayama, Mitsubishi-Kasei Institute of Life Sciences for his kindness in measureing the decay time constant, μ_1, with the aid of the single photon counting method.

23) Another possible mechanism for the formation of $(\mathrm{DA})^{*}_{\mathrm{CN}}$ and $(\mathrm{DA})^{**}_{\mathrm{CN}}$ is the following competitive one:



Scheme 3.

This process can be disregarded from the concentration of the observed dependence of μ_i's upon the concentration of TEA.

As is seen in Fig. 7, the observed rises and decays are represented by $\sum_{i=1}^{3} a_i e^{-\mu_i t}$ and $\sum_{i=1}^{3} c_i e^{-\mu_i t}$ for D* and $(\mathrm{DA})^{**}_{\mathrm{CN}}$, respectively. The pre-exponential factors a_1, a_3, and a_2 successively become more predominant with the increasing concentration of TEA. From this observation the following relation is obtained:

$$\Delta a_2 > \Delta a_3 > \Delta a_1 \qquad \text{relation (1)}$$

A similar relation is obtained concerning the pre-exponential factors c_i's; among these c_1 is the factor for the rise component:

$$\Delta c_2 > \Delta c_3 \qquad \text{relation (2)}$$

Here, Δ means the increment of the corresponding quantity due to the increase in the concentration of TEA. Furthermore, the relation, $\Delta\mu_1 > \Delta K_1 \gtrsim \Delta\mu_2 > \Delta\mu_3$ can be obtained from the experimental result shown in Fig. 7 and Eq. (11.1). From this relation and initial conditions of Eq. (6), say

$$\sum_{i=1}^{3} a_i = [D^*]_0,\ \sum_{i=1}^{3} b_i = [(\mathrm{DA})^{*}_{\mathrm{CN}}]_0 \sim 0, \text{ and } \sum_{i=1}^{3} c_i = [(\mathrm{DA})^{**}_{\mathrm{CN}}]_0 \sim 0,$$

the following relation concerning b_i's can be derived for scheme (2):

$$\Delta b_1 < \Delta b_2 < \Delta b_3 \qquad \text{relation (3)}$$

Similarly, relation (3) is also obtained for scheme (3).

According to the process shown by scheme (2), the pre-exponential factors for the decay and rise components are expressed by Eq. (8). Since a_1, a_2, a_3, b_2, b_3, c_2, and c_3 are positive and b_1 and c_1 are negative, the relation $\mu_3 < \mu_2 < K_1 < \mu_1 < K_3$ is obtained, and Δa_1's are represented by $\Delta a_1 = \{1/\Delta(\mu_1 - K_1)\} \times (-\Delta b_1)$, $\Delta a_2 = \{1/\Delta(K_1 - \mu_2)\} \times (\Delta b_2)$, and $\Delta a_3 = \{1/\Delta(K_1 - \mu_3)\} \times (\Delta b_3)$. Therefore, relation (3) is consistent with relations (1) and (2) only for the case of $1/\Delta(K_1 - \mu_2) > 1/\Delta(K_1 - \mu_3)$ and $1/\Delta(K_3 - \mu_2) > 1/\Delta(K_3 - \mu_3)$, respectively. These relations on $\Delta\mu_i$'s and ΔK_1 are satisfied. Thus, the observed dependence of the pre-exponential factors on the concentration of TEA can be explained in term of Scheme (2).

According to Scheme (3), the pre-exponential factors are expressed as follows:

$$a_i = \frac{k_4(c - \mu_i)}{(a - \mu_i)(c - \mu_i) - k_7 k_8[\mathrm{A}]} b_i, \text{ and}$$

$$c_i = \frac{k_7 k_8[\mathrm{A}]}{(a - \mu_i)(c - \mu_i) - k_7 k_8[\mathrm{A}]} b_i,$$

where $\mu_1 > c > \mu_2 > \mu_3$ or $\mu_1 > a > \mu_2 > \mu_3$ in this case. Furthermore, $\Delta a_1 = (\Delta Q_1) \times (-\Delta b_1)$ and $\Delta a_{2,3} = (-\Delta Q_{2,3}) \times (\Delta b_{2,3})$, and $\Delta c_{2,3} = (\Delta R_{2,3}) \times (\Delta b_{2,3})$ For this case, relation (3) is consistent with relations (1) and (2) only when $\Delta Q_2 > \Delta Q_3$ and $\Delta R_2 > \Delta R_3$ hold. In actuality, however, the examination of $\Delta\mu_i$'s and Δa_i shows that the reverse is the case. Thus, scheme (3) can safely be disregarded.

24) On the assumption of disregarding process 8, the fluorescense of D* and $(\mathrm{DA})^{**}_{\mathrm{CN}}$ are to be represented by decay curves with the two time constants of $\lambda_1{}^{-1}$ and $\lambda_2{}^{-1}$ and of $\lambda_2{}^{-1}$ and $(k_9 + k_{10})^{-1}$, respectively, where $\lambda_{1,2} = 1/2\{(K_1 + K_2) \pm \sqrt{(K_1 - K_2)^2 + 4k_3 k_4[\mathrm{A}]}\}$. The expectation conflicts with the findings that the fluorescence decay of D* is repesented by three time constants and that the two decay constants obtained for $(\mathrm{DA})^{**}_{\mathrm{CN}}$ are dependent on the concentration of TEA.

25) From the rate constant of the association between solvated ions, 10^{10} M^{-1}s^{-1}, and the concentration of proton ($<10^{-4}$M), it is revealed that the association reaction between the solvated β-naphtholate ion and triethylammonium ion possibly proceeds with a rate smaller than 10^6 s^{-1} and is too slow to occur within the intrinsic lifetime of a solvated β-naphtholate ion (*e.g.* 10^8 s^{-1} in aqueous solution).[4,14]