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Kinetics of Dissociation of the Hydrogen Bond in the (n, π^*) Singlet State of 9,10-Diazaphenanthrene

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Synopsis. Changes of fluorescence properties with temperature have been examined for 9,10-diazaphenanthrene (DAP) in proton-donating solvents. From a kinetic analysis, the rate constant for dissociation of the hydrogen bond in the (n, π^*) singlet state of DAP is evaluated to be 4.3×10^8 s^{-1} at 113 K, and the activation energy of the dissociation is 10.0 kJ/mol.

In proton-donating solvents the n$\rightarrow\pi^*$ absorption spectrum of 9,10-diazaphenanthrene (DAP) exhibits a large blue shift which is attributable to formation of a hydrogen bond between solute and solvent molecules.[1] On the contrary, the n$\leftarrow\pi^*$ fluorescence shows only a small shift, indicating that the hydrogen bond is broken in the (n, π^*) excited singlet state within its lifetime.[1]

Baba and Mugiya[2] reported that a large blue shift occurs in the fluorescence spectrum of DAP in an aprotic polar solvent at low temperature. They interpreted the blue shift as due to the fact that the relaxation process from the Franck-Condon excited to the equilibrium excited state, with respect to the orientation of solvent dipoles, is inhibited at such a low temperature that the solvent becomes rigid. For DAP in proton-donating solvents at low temperature, Rau and Bisle[3] suggested that the dissociation of the hydrogen bond in the excited state is more or less inhibited owing to an increase in solvent viscosity with lowering temperature.

In this study, the fluorescence spectrum and lifetime have been examined for DAP in a mixture of alcohols at temperatures ranging from 300 to 77 K with a view to obtaining quantitative information as to the kinetic behavior of the hydrogen bond in the ^{1}(n, π^*) state.

Experimental

A mixture of methanol and ethanol (volume ratio, 1: 1) and that of isopentane and methylcyclohexane (volume ratio, 4: 1) were used as a proton-donating solvent and a nonpolar reference solvent, respectively. These mixtures, hereafter referred to as ME and PM, respectively, give good rigid glasses at 77 K. A DAP concentration of less than 10^{-4} M was adopted to prevent the formation of a dimer of DAP in PM at low temperature.[4]

Fluorescence decay measurements were made with a single-photon counting apparatus using a time-to-amplitude converter.[5] The lifetime could be determined quantitatively down to 0.5 ns on the basis of the deconvolution method.

Results and Discussion

Table 1 gives the frequencies of n$\rightarrow\pi^*$absorption and n$\leftarrow\pi^*$ fluorescence maxima, denoted by ν_a and ν_f respectively, and the fluorescence lifetimes τ_f for DAP in PM and proton-donating solvents at 300 and 77 K. The table gives also the frequency shifts, $\Delta\nu_a$ and $\Delta\nu_f$, relative to the frequencies in PM at 300 K. The values of ν_a in proton-donating solvents were estimated on the assumption that the shape and half-width of the n$\rightarrow\pi^*$ absorption curve are the same as those in PM. When the solvent is changed from PM to ME at 300 K, the absorption spectrum is greatly displaced to the blue, whereas the fluorescence shows only a small blue shift, *i.e.*, $\Delta\nu_a=1550$ cm^{-1} and $\Delta\nu_f=220$ cm^{-1}. On the contrary, at 77 K the fluorescence shift in ME is almost as large as the absorption shift, *i.e.*, $\Delta\nu_f=1330$ cm^{-1}. It should be emphasized that the absorption and fluorescence spectra in PM containing a small amount (0.5% by volume) of ethanol are essentially the same as those in ME. The fluorescence in PM has a constant lifetime of about 4 ns irrespective of temperature. In ME the fluorescence lifetime varies distinctly according to the temperature; the lifetime in ME at 300 K is comparable to the one in PM, whereas it is 1.2 ns at 77 K. All these results indicate that at 300 K the hydrogen-bonded complex between solute and solvent molecules dissociates in the ^{1}(n, π^*) state of DAP, but that at 77 K the breakage of the hydrogen bond is inhibited owing to the high viscosity of the solvent. Thus the fluorescence spectra in ME at 77 and 300 K originate from the hydrogen-bonded complex and the free DAP molecule, respectively.

Table 1. Frequencies of absorption and fluorescence maxima and fluorescence lifetimes of DAP in different solvents

Solvent	ν_a / cm^{-1}	ν_f / cm^{-1}	$\Delta\nu_a$ / cm^{-1}	$\Delta\nu_f$ / cm^{-1}	τ_f / ns
PM					
300 K	24630	19940	0	0	4.9
77 K[a]	24950	20280	320	340	3.6
PM+ethanol (0.5%)					
300 K	26050[b]	20120	1420	180	4.9
77 K	26110[b]	21280	1480	1340	1.2
ME					
300 K	26180[b]	20160	1550	220	3.5
77 K	26180[b]	21270	1550	1330	1.2

a) A small amount of ethyl ether (5% by volume) was added to prevent the formation of DAP dimer.
b) Estimated values (see text).

The changes of the fluorescence spectrum and lifetime in ME with temperature occur in the range 150—77 K. The spectrum shifts rapidly to the blue as the temperature is lowered from 150 K, as is seen in Fig. 1. Furthermore, at the intermediate temperatures, the fluorescence lifetimes were found to exhibit different values depending on the wavelength where the fluorescence was monitored. Therefore, each of the fluorescence spectra obtained at temperatures between 150 K and 77 K is regarded as a superposition of two kinds of spectra: one originating from the hydrogen-bonded complex and the other from the free DAP molecule. On the assumption that

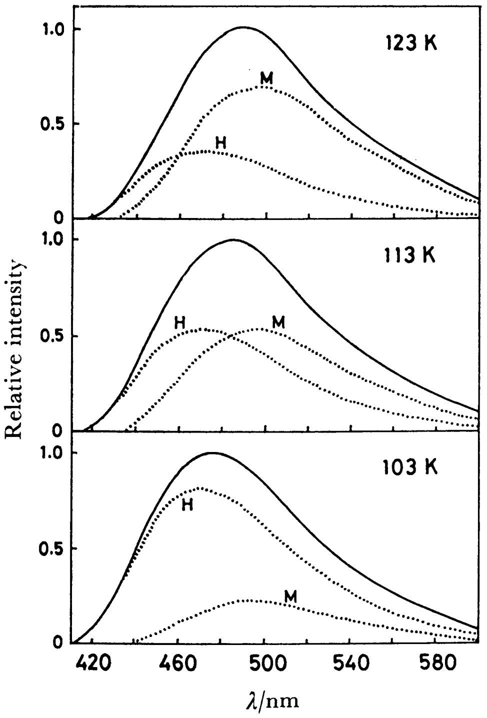

Fig. 1. Fluorescence spectra of DAP in ME at different temperatures (solid lines), and analysis of the individual spectra into the components (dotted lines) of the hydrogen-bonded complex (H) and the free DAP molecule (M). For each of the observed spectra the maximum fluorescence intensity is normalized to a unit relative intensity.

the spectral shape of each fluorescence component is independent of temperature in this temperature range, one can analyze the whole spectrum into separate components; the results are shown in Fig. 1 for three temperatures. It is seen that, as the temperature is lowered, the contribution from the fluorescence component of the hydrogen-bonded complex increases, while that from the component of the free DAP molecule decreases. This means that on lowering the temperature the solvent becomes rigid and the dissociation of the hydrogen bond is inhibited in varying degrees, depending upon the viscosity of the solvent.

The deactivation processes in the excited state involving the dissociation of the hydrogen bond are represented by the following kinetic scheme:

$$\begin{tikzcd} \mathrm{DAP}^*\cdots\mathrm{H} \arrow[rr, "k_d(T)"] \arrow[d, "k_{fH}"'] \arrow[d, squiggly, shift left=3, "k_{qH}"] & & \mathrm{DAP}^* \arrow[d, "k_{fM}"'] \arrow[d, squiggly, shift left=3, "k_{qM}"] \\ {} & & {} \end{tikzcd}$$

where DAP* and DAP*···H denote the excited singlet states of the free DAP molecule and hydrogen-bonded complex, respectively; k_{fH}, k_{qH}, k_{fM}, and k_{qM} are the radiative (f) and radiationless (q) decay constants for the hydrogen-bonded complex (H) and free molecule (M); $k_d(T)$ is the rate constant for the dissociation of the hydrogen bond as a function of temperature, T. The rate constants other than $k_d(T)$ are assumed to be independent of T in the range concerned here (150—77 K). Then the ratio of the fluorescence quantum yield of the free molecule to that of the hydrogen-bonded complex, $\Phi_M(T)/\Phi_H(T)$, is expressed as

$$\Phi_M(T)/\Phi_H(T) = (k_{fM}/k_{fH})k_d(T)/(k_{fM}+k_{qM}). \qquad (1)$$

In this equation, $k_{fM}+k_{qM}\simeq 1/\tau_f(150\text{ K})=3\times10^8\text{ s}^{-1}$ and $k_{fM}/k_{fH}=0.69$; these values are obtained by using the ratio (0.5) of $\Phi_H(77\text{ K})$ to $\Phi_M(150\text{ K})$ and the lifetimes at 77 and 150 K (1.2 and 3.5 ns, respectively). The quantum yield ratio $\Phi_M(T)/\Phi_H(T)$ can be evaluated from the analysis of the spectrum as shown in Fig. 1. Thus, the rate of the hydrogen-bond dissociation, $k_d(T)$, can be calculated from Eq. 1. At 113 K where the two quantum yields Φ_M and Φ_H are nearly equal (Fig. 1), $k_d=4.3\times10^8\text{ s}^{-1}$, which value is comparable to $k_{fH}+k_{qH}\simeq 1/\tau_f(77\text{ K})=8.3\times10^8\text{ s}^{-1}$. The k_d value becomes smaller at lower temperatures and negligible at 77 K compared with $k_{fH}+k_{qH}$, while at higher temperatures k_d becomes larger and at 150 K it dominates over $k_{fH}+k_{qH}$. This means that, within the lifetime of the $^1(n, \pi^*)$ state, the dissociation of the hydrogen bond is completed at temperatures higher than 150 K, but that practically no dissociation occurs at 77 K.

In the previous study by Baba and Mugiya[2] concerning the Franck-Condon blue shift of the fluorescence of DAP in an aprotic solvent, it was noted that the reorientation of solvent dipoles occurs with the rate which follows an equation of the Arrhenius type, and that the activation energy for the reorientation process is about 17 kJ/mol. The rate constants at different temperatures obtained in the present study for the hydrogen-bond dissociation were found to be well described in terms of the Arrhenius equation with an activation energy of 10.0 kJ/mol. This somewhat small value of activation energy is consistent with the view that in the case of hydrogen-bonding interaction in the $^1(n, \pi^*)$ state a repulsive force is operative between the proton donor and acceptor. Furthermore, the smaller activation energy is favorable for the expectation that the hydrogen bonding interaction would be localized at a limited portion of the donor–acceptor system concerned.

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