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Photochemistry of Transient Tautomer of 7-Azaindole H-Bonded Dimer Studied by Two-Step Laser Excitation Fluorescence Measurements[1]

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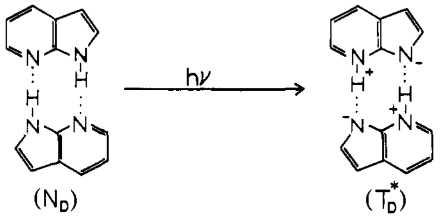
Abstract: Formation of the monomeric tautomer (7*H*-pyrrolo[2,3-*b*]pyridine) in the photodissociation of the transient ground-state dimeric tautomer, generated via excited-state double proton transfer of 7-azaindole H-bonded dimer in 3-methylpentane (MP), was confirmed by transient absorption and two-step laser excitation (TSLE) fluorescence spectroscopies. The intense XeCl laser pulse (308-nm) excitation of the H-bonded dimer in MP at room temperature produced short- (17 μs) and long-lived (47 μs) transients. The former and latter were ascribed to the dimeric and monomeric tautomers in the ground state, respectively. It is suggested that the second pulse excitation of the short-lived dimeric tautomer induces efficient dissociation to form a monomeric tautomer in the excited state together with that in the ground state. One-color (308-nm) biphotonic processes within the XeCl laser pulse are therefore responsible for the long-lived monomeric tautomer in the ground state. The decay of the monomeric tautomer in the dark is attributable to the H-transfer reaction to yield 7-azaindole. Significant deuterium isotope effects were found for H-transfer of the monomeric tautomer as well as for photodissociation of the dimeric tautomer.

Since Taylor et al.[2] had suggested the excited-state cooperative double proton transfer of H-bonded 7-azaindole (7AI) dimer, numerous steady-state[3-8] and nano- to picosecond time-resolved[7-10] fluorescence studies on the complicated phototautomerism of the H-bonded 7AI dimer (N_D) in 3-methylpentane (MP) have been reported. On the basis of detection of the slow ($\simeq$ 1 ns) and rapid (<5 ps) rise for the largely Stokes-shifted fluorescence spectrum ($\lambda_{max} \simeq 480$ nm) due to phototautomer (T_D^*) in the 263.5-nm picosecond pulse excitation of N_D in MP at 77 K, Hetherington et al.[10] directly confirmed the excited-state double proton transfer ($N_D^* \rightarrow T_D^*$) with and without an activation barrier, although it is controversial whether vibrationally relaxed and unrelaxed N_D^*[8,10] or nonplanar (singly H-bonded)[11] and planar (doubly H-bonded) N_D^*[7] are responsible for the slow and rapid $N_D^* \rightarrow T_D^*$ process.



The photochemistry and photophysics of various transient species such as the lowest excited singlet (S_1)[12] and triplet (T_1)[13,14] states, free radicals,[15-24] biradicals,[25] and carbenes[26] in solution have been studied by various two-pulse excitation techniques, in which the first pulse is employed for the generation of transient species and the second pulse for the photoexcitation of the transient speices. We have recently reported some two-step laser excitation fluoresence studies on the excited-state and ground-state proton transfer processes in intra-[27,28] and intermolecular[29-31] H-bonding systems. In these studies, the intervention of a relatively long-lived ground-state tautomer has been confirmed by detection of the transient absorption of the tautomer in the first laser pulse excitation of H-bonded normal molecule (N), and by that of the fluorescence of the tautomer in the second laser pulse excitation of the transient absorption. Such detections of absorption and fluorescence spectra due to the tautomer afford clear evidence for the formation of phototautomer in the excited-state proton transfer process. In the photoexcitation of 7AI H-bonded dimer (N_D) in MP, we recently observed[8] the transient absorption spectrum of the relatively long-lived (19 μs at 298 K; 180 μs at 172 K) ground-state dimeric tautomer (T_D), which is generated via the excited-state double proton transfer ($N_D^* \rightarrow T_D^*$) and the subsequent electronic relaxation ($T_D^* \rightarrow T_D$). However, second laser pulse excitation of T_D did not induce T_D^* fluorescence

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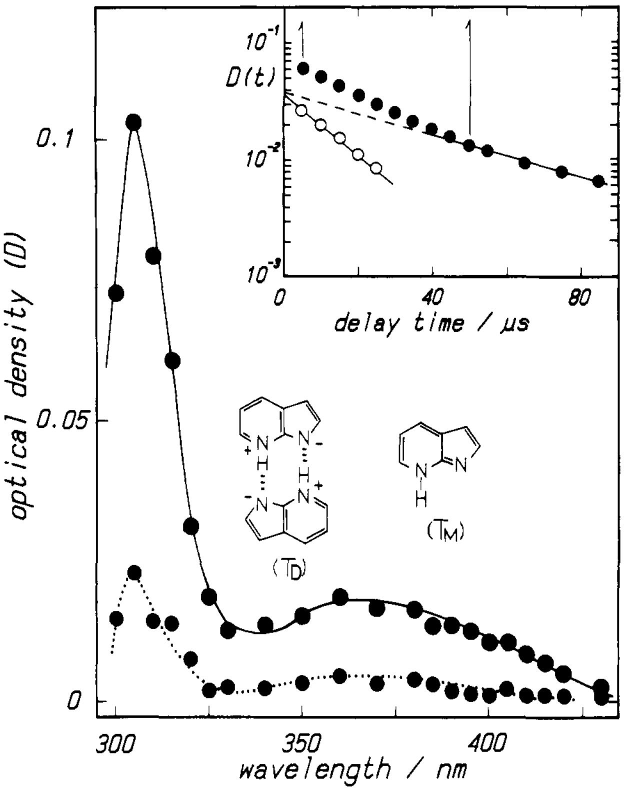


Figure 1. Time-resolved absorption spectra obtained at 5-μs (—) and 50-μs (···) delay from the XeCl laser pulse excitation of an aerated MP solution of 7AI (1.4 mM). A logarithmic plot of the transient absorption intensity, $D(t)$, at 310 nm against delay time is shown in the inset.

spectrum but slightly red-shifted fluorescence with the risetime of 1 ns at room temperature. This is the only exception where the fluoresecence spectrum observed upon the excitation of transient ground-state tautomer does not coincide with the tautomer fluorescence spectrum induced upon excitation of the H-bonded normal form. The present paper describes the transient absorption and two-step laser excitation (TSLE) fluoresence studies on the kinetics and dynamics of the photoinduced dissociation of the unstable dimeric tautomer, which is generated by the excited-state double proton transfer and subsequent electronic relaxation in the 7AI H-bonded dimer. This two-color TSLE fluorescence technique provides us with the possibility of studying the photochemical reaction of the unstable species, which is enabled by the second laser pulse excitation at selective delay times depending on the lifetimes of the transient species.

Experimental Section

7-Azaindole (7AI) from Nakarai Chemicals was purified by repeated recrystallizations from spectral grade ethanol followed by vacuum sublimation. N_1-deuterated 7AI, where the indolic hydrogen is replaced by deuterium, was obtained by dissolution of 7AI crystals in C_2H_5OD (CEA, deuterium grade = 99.0%) and subsequent complete removal of the solvent in a vacuum system. 3-Methylpentane (MP, Aldrich), purified by distillation over $LiAlH_4$, was further treated by a potassium mirror to provide a strictly anhydrous solvent. Sample solutions were prepared by transferring the anhydrous MP to the deuterated (or nondeuterated) 7AI crystals through the vacuum system. They were degassed by repeated freeze–pump–thaw cycles.

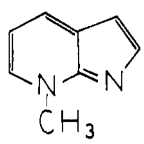
Transient absorption spectra were measured by a laser-flash apparatus consisting of an excimer laser (Lambda Physik EMG 50E) and monitoring steady-state xenon arc, the beam of which was cut by an electromagnetic shutter operating synchronously with the laser. The electric signals from a photomultiplier tube (HTV R 666) were sent to Tektronix 7904 oscilloscope with a differential comparator (7A 13 plug-in unit).

In the two-step laser excitation (TSLE) fluorescence measurements, the 308-nm pulse from the excimer (XeCl) laser was used as the first pulse to induce the excited-state tautomerization, and N_2-laser-pumped dye-laser pulses (386, 406, 421 nm) from Molectron UV 12 and DL 14 system were used as the second pulse to induce the fluorescence and/or reaction of transient tautomers. The delay time (<17 ms) between the first and the second laser pulses is variable by use of a delay circuit. The standard deviation in the delay time is within ±5%. TSLE fluorescence signals were collected by a time-correlated single-photon-counting system (Ortec) with a multichannel analyzer (Norland) after excitation of the weak pulse from a D_2 nanosecond light pulser (PRA Model 510). Temporal analyses were performed by a computer-simulated convolution. Steady-state fluorescence spectra were recorded on a Hitachi MPF-4 fluorescence spectrophotometer.

A rectangular quartz cell (1 cm) containing sample solution was placed in a compact rectangular quartz dewar, and low temperatures (>107 and 77 K) were attained by adjusting the flow rate of the cold N_2-gas stream and by keeping liquid N_2, respectively. UV steady-light, obtained by placing a UV-D33S band filter (Toshiba) in front of a super-high-pressure Hg lamp, was employed for the illumination of glassy MP solution at 77 K.

Results and Discussion

XeCl Laser Photolysis of 3-Methylpentane Solution of 7-Azaindole at Room Temperature. Figure 1 shows the time-resolved transient absorption spectra which were observed at 5- and 50-μs delay from the XeCl laser pulse (308-nm) excitation of an aerated MP solution of 7AI (1.4 mM). By removing oxygen dissolved in the solution, the decay kinetics of the spectra was not influenced, though a very long-lived ($\tau \simeq 2.6$ ms) UV transient absorption band probably due to the lowest triplet state of 7AI appeared. The transient absorption spectra at the two delay times shown in Figure 1 are very similar to each other, and they are also similar to the published absorption spectra[32,33] of stable 7-methyl-7*H*-pyrrolo[2,3-*b*]pyridine (7MPP; a model compound for a half-unit of the tautomer, T_D, of 7AI H-bonded dimer) in nonpolar solvents such as cyclohexane and heptane at room temperature, though the UV transient absorption band (λ_{max} 305 nm) is appreciably reduced in intensity by the depletion of the overlapping $S_n \leftarrow S_0$ absorptions of 7AI. Further, the decay of the transient absorption was fitted to a double exponential decay kinetics (τ = 17 and 47 μs),[34] as shown in the inset of Figure 1. Similar behavior was observed for the transient absorption of the MP solution of N_1-deuterated 7AI, and the lifetimes of the short- and long-lived transient absorptions were determined to be 41 and 130 μs, respectively. Thus, it is likely that the transient absorption spectra consist of the short- and long-lived absorption bands due to two kinds of tautomers in the ground state. It is noteworthy that the intensity ratio of the long-lived transient absorption to the short-lived one was observed to increase with the power of excitation laser. If the two transient absorption spectra observed at the short and long delay times are attributable to the dimeric and monomeric tautomers (T_D and T_M), photodissociation of the short-lived (17 μs) T_D, generated via the excited-state double proton transfer ($N_D^* \rightarrow T_D^*$) and relaxation ($T_D^* \rightarrow T_D$), may be responsible for the formation of the long-lived (47 μs) transient, T_M. If so, it is reasonable to consider that the photodissociation of T_D to form T_M significantly takes place upon one-color (308-nm) stepwise biphotonic excitation of N_D within an intense XeCl laser pulse. Since T_D exhibits a strong transient absorption band at almost the same wavelength ($\lambda_{max} \simeq 305$ nm) as that of the laser pulse (308 nm), T_D generated in the early stage of the laser pulse can be further photolyzed in the later stage. These tentative assignments will be confirmed by the two-step laser excitation (TSLE) fluoresence spectroscopy in the following section.



(7MPP)

Two-Step Laser Excitation Fluorescence Spectra of 3-Methylpentane Solution of 7-Azaindole at Room Temperature

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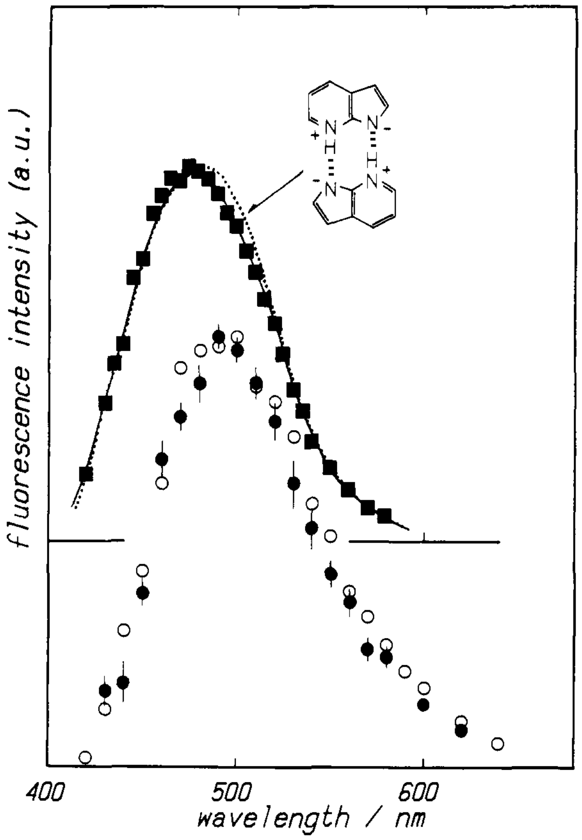


Figure 2. TSLE fluorescence spectra detected upon 406-nm pulse excitation at 2-μs (○) and 152-μs (•) delay from 308-nm pulse excitation of a degassed MP solultion of 7AI (0.74 mM) at room temperature. The spectra are normalized in intensity. Steady-state fluorescence spectrum (···) and the fluorescence spectrum (■—) induced by the attenuated first pulse (308 nm) are also shown.

(Photodissociation of Dimeric Tautomer in the Ground State). Transient absorptions ascribable to the dimeric and monomeric tautomers (T_D and T_M) were detected as described above. Then measurements of the two-step laser excitation (TSLE) fluorescence spectra were performed by selective excitations of the transient absorptions due to T_D and T_M in MP at room temperature. Figure 2 shows the TSLE fluorescence spectra detected upon the second laser pulse (406-nm) excitation delayed by 2 and 152 μs from the 308-nm pulse excitation of a deaerated MP solution of 7AI (0.74 mM). They are obviously different from the T_D^* fluorescence spectra, which were measured on a conventional fluorimeter or detected upon excitation of the unfocused and attenuated XeCl laser pulse, as seen in Figure 2. Namely, the TSLE fluorescence spectra are much more similar to the published fluorescence spectra[33,35] of the N_7-methyl tautomer (7-methyl-7*H*-pyrrolo[2,3-*b*]pyridine) than the T_D^* fluorescence spectra. These TSLE fluorescence spectra at 2- and 152-μs delay exhibit almost the same lifetime (2.1 ns) irrespective of the delay times. The lifetime is shorter than that (3.0 ns) of T_D^* fluorescence detected by a single-photon-counting system after weak D_2-pulse excitation of N_D, and it is nearly equal to the fluorescence lifetime (2.0 ns)[36] of the N_7-methyl tautomer in cyclohexane at room temperature. As shown in Figure 3, however, it is noteworthy that the fluorescence signal, detected upon nanosecond laser pulse (406 nm) excitation at 2-μs delay from the first one (308 nm) grows up more slowly than that at 152-μs delay. The latter fitted to a single exponential decay (τ = 2.1 ns) without an appreciable rise by a computer-simulated convolution analysis. Thus, the TSLE fluorescence at the long delay time may be attributable to T_M (7*H*-pyrrolo[2,3-*b*]pyridine) which already has been formed by the photodissociation of T_D within the first laser pulse. The spectrum at the short delay time may be attributable to T_M, generated via the photodissociation of T_D induced by the second laser pulse as well as by the first laser pulse. This consideration is compatible with the tentative assignment of the respective short- and long-lived transients as T_D and T_M, as described in the preceding section. The TSLE fluorescence signal at the short delay time (2 μs) from the first laser pulse exhibits a fluorescence rise, as shown in Figure 3. Dimeric and monomeric ground-state tautomers (T_D and T_M) coexist at 2-μs delay, as mentioned above. Thus, it is reasonable to consider that the second laser pulse (406-nm) excitation of T_D and T_M induces T_M^* fluorescence with and without risetime. The fluorescence signal at 2-μs delay was therefore analyzed by convolution which is based on the following equation consisting of exponential decays (τ_1 = 2.1 ns) with and without risetime (τ_2):

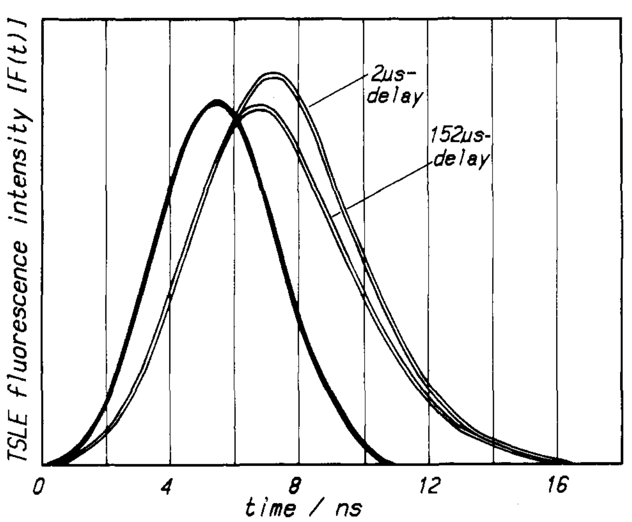
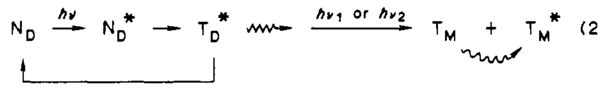


Figure 3. TSLE fluorescence signals (═) detected upon 406-nm pulse (━) excitation at 2- and 152-μs delay from 308-nm pulse excitation of a deaerated MP solution of 7AI (0.74 mM) at room temperature. These three signals are scaled so that their peak intensities are roughly comparable with each other.

$$I_F(t) = c_1 \exp(-t/\tau_1) + c_2\{\exp(-t/\tau_1) - \exp(-t/\tau_2)\} \quad (1)$$

The risetime was determined to be 0.9–1.0 ns, and the preexponential factor ratios (c_1/c_2) were 0.11 (406-nm excitation) and 0.19 (386-nm excitation). Such small values indicate the poor absorptivity of T_M compared to that of T_D at these wavelengths.[37] Furthermore, the fluorescence signal, detected upon the second laser pulse (421-nm) excitation, fitted to a simple rise and decay (c_1 = 0), suggesting nearly selective excitation of T_D. Since the photoexcitation (421 nm) of T_D induces the fluorescence due to T_M^* in place of T_D^* fluorescence, it is pointed out that an efficient photodissociation of T_D occurs to form T_M^*. The formation and decay of T_D are shown in the following scheme.


$$N_D \xrightarrow{h\nu} N_D^* \rightarrow T_D^* \rightsquigarrow \xrightarrow{h\nu_1 \text{ or } h\nu_2} T_M + T_M^* \quad (2)$$

The ground-state dimeric tautomer (T_D), formed via the excited-state double proton transfer and relaxation ($N_D^* \rightarrow T_D^* \rightarrow T_D$), is converted to N_D by transferring back two protons in the dark or to the monomeric tautomer (T_M) via photodissociation.

TSLE fluorescence measurements were performed for N_1-deutereated N_D in MP at room temperature. The transient absorption at 208-μs delay may be attributed to the long-lived (τ = 130 μs) T_M alone, since the short-lived transient absorption due to T_D does not appreciably survive. The second pulse (421-nm) excitation delayed by 208 μs from the first pulse (308 nm) ex-

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(35) Avouris, P.; Yang, Li L.; El-Bayoumi, M. A. *Photochem. Photobiol.* **1976**, *24*, 211.

(36) Waluk, J., private communication.

(37) In spite of the short delay time (2 μs) at which both T_D and T_M are alive, therefore, the nearly selective excitation of T_D can be attained at the wavelengths.

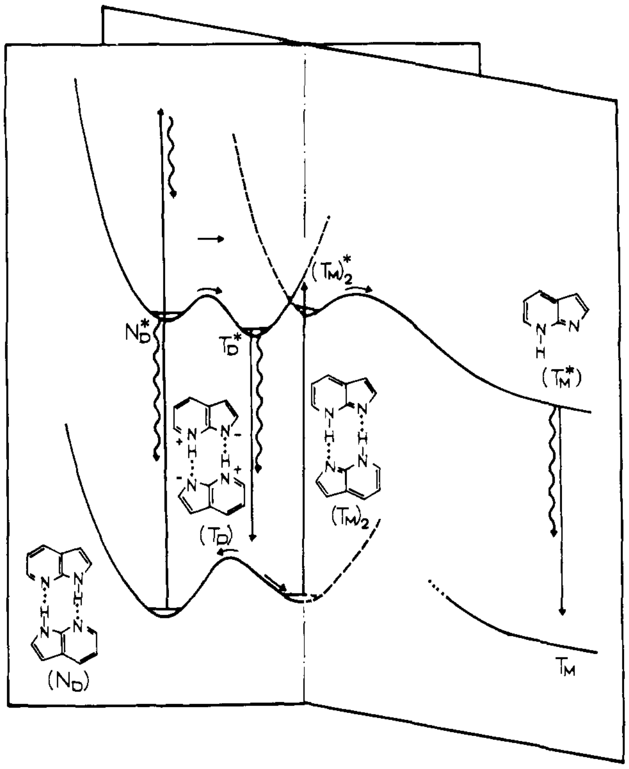


Figure 4. A schematic potential energy diagram for the adiabatic photodissociation of ground-state dimeric tautomer generated via the excited-state double proton transfer of H-bonded 7AI dimer.

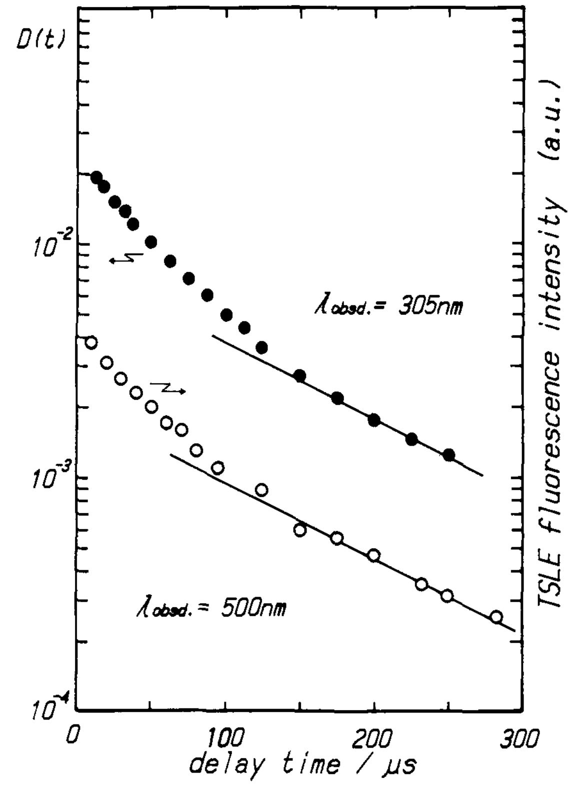
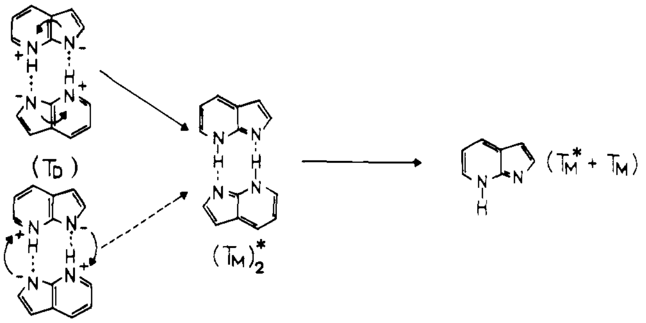


Figure 5. Logarithmic plots of transient absorption intensity (•), $D(t)$, and TSLE fluorescence intensity (○) against delay time from the 308-nm pulse excitation of a deaerated MP solution of N_1-deuterated 7AI (0.66 mM) at room temperature. The probe pulse (406 nm) was employed to induce the TSLE fluorescence.

citatioin of deuterated N_D induced the T_M* fluorescence with the lifetime of 2.2 ns, which coincides with that (2.1 ns) for nondeuterated T_M* within the experimental error. Namely, T_M* fluorescence lifetime exhibits no deuterium isotope effect. Upon weak pulsed D_2-lamp excitation of the deuterated N_D, on the other hand, the lifetime of T_D* fluorescence was determined to be 7.8 ns, exhibiting a considerable deuterium isotope effect in comparison with the lifetime (3.0 ns) for nondeuterated T_D*. A rise and decay convolution analysis was carried out for the TSLE fluorescence signal at 2-μs delay. The risetime was estimated to be 1.7 ns by using 2.2 ns of decay time. In contrast with the decay of T_M* fluorescence, the rise of T_M* as well as the decay of T_D* exhibit appreciable deuterium isotope effects. These facts clearly indicate that the isotope-dependent vibrations along a couple of N—H···N bonds play an important role for the deactivation and dissociation of the dimeric tautomer in the excited state. A slight temperature effect was also found for the rise of T_M* fluorescence. The risetimes of the TSLE fluorescence signals at 171, 202, and 247 K were evaluated to be 2.2, 2.0, and 1.8 ns, respectively. The activation energy of the dissociation of $(T_M)_2$* was roughly estimated to be 0.19 kcal/mol by the Arrhenius plot of the risetimes.

As mentioned above, it is very puzzling that the $S_1 \leftarrow S_0$ excitation of T_D results in the appearance of T_M* fluorescence with a slow rise (1–2.2 ns) in place of T_D* fluorescence. A plausible mechanism is shown by the schematic potential energy diagram in Figure 4, which may be described as follows. The dimeric tautomer (T_D*), generated via the excited state tautomerization ($N_D^* \rightarrow T_D^*$) in the first laser excitation, relaxes to the metastable (τ = 17 μs) ground state at the potential minimum by way of the Franck-Condon ground state. During the relaxation processes, a significant change in the charge distribution and conformation of the dimeric tautomer seems to occur. Then the second laser excitation of the relaxed dimeric tautomer may afford the corresponding excited state which is different from T_D*. From this excited state, the dimeric tautomer predominantly dissociates to form T_M* and T_M, surpassing fluorescent relaxation. Waluk et al.[33] pointed out that a significant charge flow from the five- to six-membered ring of 7-methyl-7*H*-pyrrolo[2,3-*b*]pyridine (a model compound for a half-unit of T_D) resulting in the inversion in the direction of dipole moment, occurs upon the $S_1 \leftarrow S_0$ transition. In each zwitterionic half-unit[38] of T_D, a similar charge flow may be expected to occur forming 7*H*-pyrrolo[2,3-*b*]pyridine (T_M). Upon the second laser pulse (386–421 nm) excitation of the relaxed T_D, therefore, such a charge flow may take place to form $(T_M)_2$*, which then slowly (≃1 ns) dissociates into monomeric tautomers ($T_M^* + T_M$).[39] Possible charge transfer processes in T_D are shown in eq 3. It is probable that the formation of $(T_M)_2$* may not be ascribed to the inter- (half-unit) charge flow but to the intra- (half-unit) charge flow upon $S_1 \leftarrow S_0$ excitation of the relaxed T_D.



(3)

Dark Reaction of the Monomeric Tautomer (T_M) *in the Ground* State at Various Temperatures. In the preceding sections, the short- and long-lived transients were reasonably assigned as the dimeric and monomeric tautomers (T_D and T_M) in the ground state, respectively. The decay of T_D in the dark was ascribed to the ground-state reverse double proton transfer process to re-

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[38] The vertical $S_1 \rightarrow S_0$ deactivation of T_D* may result in the enhanced zwitterionic character, which might be compensated to some extent by the relaxation to the potential minimum.

[39] No evidence was obtained for the emission of $(T_M)_2$* with a lifetime of ≃1 ns.

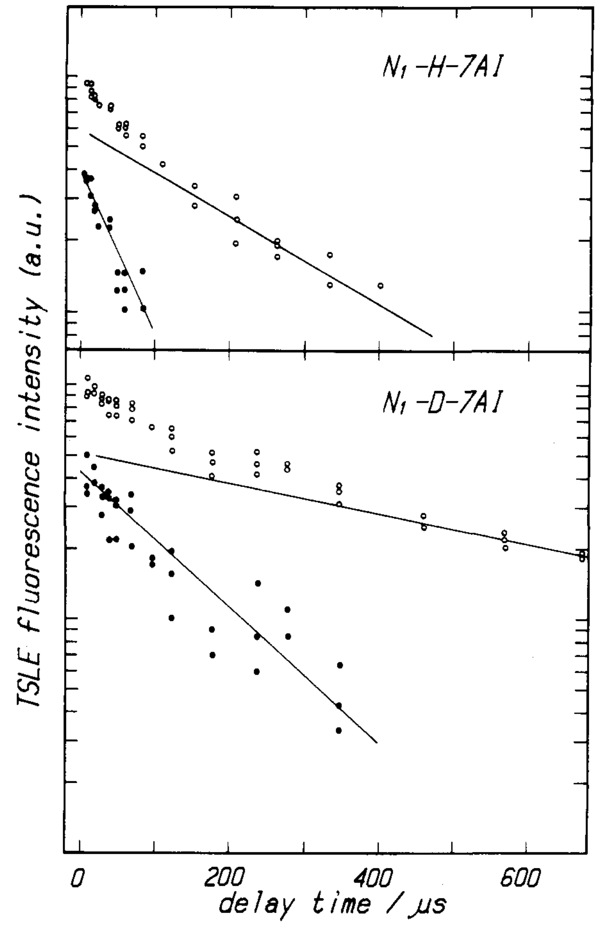

Figure 6. Resolution of double exponential decay of TSLE fluorescence intensity vs. delay time. TSLE fluorescence signals (520 nm) were detected upon 308–406-nm double pulse excitation of a deaerated MP solution of N_1-H-7AI (0.51 mM) or N_1-D-7AI (0.35 mM) at 273 K.

produce 7AI H-bonded dimer (N_D).[8] On the other hand, it is highly probable that the decay of T_M is ascribed to the ground-state H-transfer in T_M to yield 7AI monomer, although the phototautomerization of 7AI does not take place in aprotic solvents. The first band of the transient absorption spectrum due to T_M is very weak, as shown in Figure 1. Thus, it is reasonable to consider that the intensity of the TSLE fluorescence induced by the second laser pulse (406 nm) is proportional to the absorbance at this wavelength. The plot of the TSLE fluorescence intensity against the delay time between the first and second pulses (308 and 406 nm) actually exhibits decay identical with that of transient absorption, as shown in Figure 5. The decay kinetics of T_M was therefore examined by the variable delay technique of TSLE fluorescence measurements at various temperatures (247–298 K).[40]

Table I. Lifetimes (τ_M and τ_D)[a] of Monomeric and Dimeric Ground-State Tautomers Produced in the XeCl Laser Pulse (308 nm) Excitation of Deaerated MP Solution of N_1-H- and N_1-D-7AI at Various Low Temperatures

nondeuterated			deuterated	
τ_D	τ_M	T/K	τ_M	τ_D
17	47	298	130	41
35	120	290	270	59
42	230	273	770	130
		263	1100	210
59	300	247	1500	400

[a] Standard deviation ca. 30%.

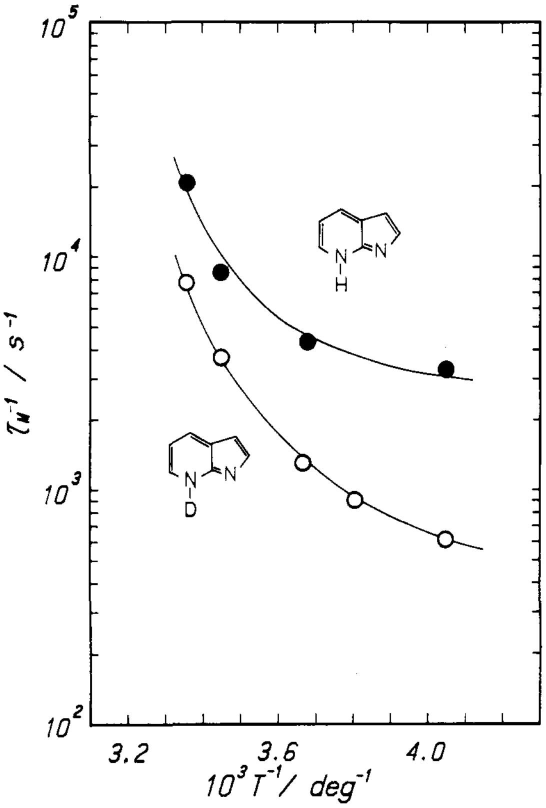

Figure 7. Arrhenius plots for the inverse of the lifetime (τ_M) of hydrogenated and deuterated monomeric tautomer (7*H*- and 7*D*-pyrrolo[2,3-*b*]pyridine) in MP.

Figure 6 shows the logarithmic plot of the double exponential decay of the TSLE fluorescence intensity[41] monitored upon the second laser pulse excitation of the MP solution of hydrogenated and deuterated 7AI at 273 K. The respective lifetimes (τ_M and τ_D) of T_M and T_D were determined from the slopes of the considerably scattered plots. Table I lists the lifetimes at various temperatures. Very weak TSLE fluorescence signals prevent us from determining reliable τ_M values at temperatures below 240 K. For the ground-state double proton transfer of T_D, we recently reported[8] the deuterium isotope effect (3.2 at 272 K; 14 at 172 K), suggesting a tunneling mechanism. Figure 7 shows the positively curved Arrhenius plots for the rate ($1/\tau_M$) of H-transfer in T_M. Since, no dark reaction of T_M (7*H*(*D*)-pyrrolo[2,3-*b*]pyridine) other than the H(D)-transfer could be detected, switching of reaction scheme may not be responsible for the curvature. The curvature of the Arrhenius plot is more pronounced for H-transfer than for D-transfer. In the intramolecular rearrangement of 2,4,6-tri-*tert*-butylphenyl radical in solution, Brunton et al.[42] have reported the pronounced temperature dependence of the deuterium isotope effect (k_H/k_D), implying that the lighter hydrogen can tunnel much more readily than deuterium. Grellmann et al.[43] also reported the signficant temperature dependence of k_H/k_D (3 at 300 K; 180 at 140 K) in the reketonization of a ground-state enol tautomer generated via the photoenolization of 2′-methylacetophenone in EPA. Although the deuterium isotope effect, k_H/k_D (2.8 at 298 K; 5.0 at 247 K), for the H-transfer rate of T_M, determined in the present study, are not signficant compared to such typical tunneling processes, a tunneling mechanism may be involved in the ground-state H(D)-transfer of 7*H*(*D*)-pyrrolo[2,3-*b*]pyridine (T_M).

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(40) It is hard to determine the accurate lifetime of weak and long-lived (>100 μs) transient absorption with the detecting system of our laser-flash apparatus.

(41) The TSLE fluorescence signals with poor S/N ratio were obtained at low temperatures.

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