Picosecond Fluorescence and Two-Step LIF Studies of the Excited-State Proton Transfer in Methanol Solutions of 7-Hydroxyquinoline and Methyl-Substituted 7-Hydroxyquinolines

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Abstract: The methanol solutions of 7-hydroxyquinoline (7-HQ) and 6-methyl-substituted 7-HQ (6-Me-7-HQ) exhibit UV (λ_{max} 370−390 nm) and large Stokes shifted (λ_{max} 510−520 nm) fluorescence spectra. The former and latter were ascribed to the normal (1:1 and 1:2 H-bonded complexes) and tautomer fluorescence spectra. Picosecond fluorescence and nanosecond/picosecond two-step LIF demonstrated that the tautomer fluorescence was generated by the excited-state proton transfer (ESPT) in the 1:2 H-bonded complexes of these compounds. The methanol solution of 7-hydroxy-8-methylquinoline (8-Me-7-HQ) shows a considerably broad UV fluorescence (λ_{max} ~400 nm) without the tautomer fluorescence. Concentration dependence (methanol/hexane) of absorption spectra and pK_a determination of these compounds indicated that 7-HQ and 6-Me-7-HQ probably form 1:2 H-bonded complexes leading to the ESPT, while 8-Me-7-HQ forms only 1:1 H-bonded complex exhibiting no significant ESPT. Taking account of the steric factor of the 6- and 8-methyl groups, the *cis* conformation of the 7-OH group and the ring nitrogen atom seems to be required for 1:2 H-bonded complex formation leading to the ESPT in alcohol solutions of 7-HQ and its methyl-substituted compounds.

Introduction

Numerous investigations on the inter- and intramolecular excited-state proton transfer (ESPT) have been reported in last two decades.[1,2] We have reported the transient absorption and two-step laser-induced fluorescence (TS-LIF) for the first time for studies of the ESPT and relaxation of several hydrogen bonding systems[3−5] in addition to nanosecond time-resolved fluorescence.[6] Since we have demonstrated that two methanol molecules are required in the intermolecular ESPT in methanol solution of 7-hydroxyquinoline (7-HQ),[7] several studies on a number of methanol molecules required for the ESPT and structure of H-bonded 7-HQ have been reported in solutions,[8−11] in solid methyl methacrylate,[12] and also in Argon matrices at 10 K.[13] Further, there is a debate as to whether the solvent is a dynamic participant or a static spectator in the ESPT of not only 7-HQ but also other bifunctional H-bonding molecules such as 7-azaindole.[14−16] Recently, Lahmani *et al.*[17] have reported fluorescence studies on bare molecule and solvent effects of jet-cooled 7-HQ. They have suggested the presence of *trans* and *cis* conformers of the 7-OH group with respect to a ring nitrogen atom in jet-cooled bare 7-HQ and that the *cis* conformer was more stable than the *trans* in a 1:1 complex of this compound with water and methanol. However, no significant ESPT was observed in water and methanol clusters of 7-HQ in the jet-cooled condition.

This paper presents picosecond fluorescence and nanosecond/picosecond (ns/ps) TS-LIF studies on the ESPT in methanol solutions of 7-HQ and 6- and 8-methyl-substituted 7-HQ (6- and 8-Me-7-HQ). 6-Me-7-HQ exhibits very similar features of the ESPT and ground-state reverse proton transfer (GSRPT) to those of 7-HQ, while no significant tautomer fluorescence was observed in the methanol solution of 8-Me-7-HQ. The methanol concentration dependence of absorption spectra of these compounds in the methanol/hexane mixed system indicated that 1:2 H-bonded complex was generated in 6-Me-7-HQ as well as in 7-HQ. However, only 1:1 H-bonded complex was formed in the methanol solution of 8-Me-7HQ. Taking account of the steric factor of 6- and 8-methyl groups, two CH_3-OH H-bonded complexes of the *cis* conformer of the 7-OH group with respect to the ring nitrogen atom were confirmed to be essential to the intermolecular ESPT in 7-HQ and the related compounds, as shown in the schematic illustration of Figure 1.

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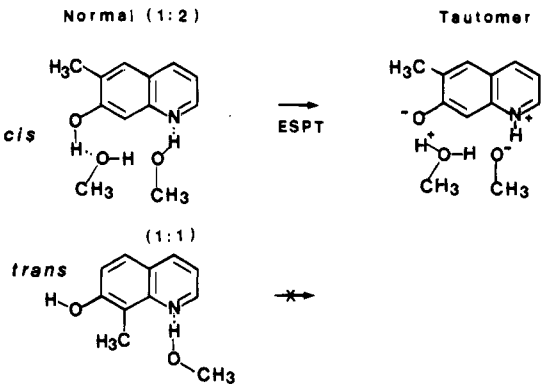

Figure 1. The schematic illustration of the 1:2 methanol H-bonded complex of 6-Me-7-HQ (*cis* conformer) leading to the ESPT and of the 1:1 H-bonded complex of 8-Me-7-HQ (*trans* conformer).

Experimental Section

Materials. 7-HQ was obtained from Eastman Kodak and purified by vacuum sublimation. Methyl-substituted 7-hydroxyquinolines (6- and 8-Me-7-HQ) were prepared from corresponding methyl-substituted aminophenols by the conventional Skraup reaction and purified by column chromatography (silica gel, Wako C-200 with appropriate solvents), recrystallization, and further vacuum sublimation. Structure and purity of these compounds were confirmed by elementary analysis and NMR (270 and/or 500 MHz) and mass spectroscopies.

6-Methyl-7-hydroxyquinoline. This compound was synthesized from 2-methyl-5-aminophenol, which was obtained from hydrogenation of 2-methyl-5-nitrophenol, by the conventional Skraup reaction and purified by column chromatography (5% dichloromethane/ethanol) and recrystallization from ethanol and further vacuum sublimation: mp 226−227 °C. ^{1}H NMR (500 MHz, CD_3OH) δ 2.38 (3H, s), 7.26 (2H, m), 7.61 (1H, s), 8.13 (1H, d, J = 8 Hz), 8.60 (1H, d, d, J = 2, 4 Hz). MS (*m/z*) 159 (M^+). Anal. Calcd for $C_{10}H_9ON$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.53; H, 5.76; N, 8.74.

7-Hydroxy-8-methylquinoline. 8-Me-7-HQ was synthesized from 2-methyl-3-aminophenol, which was obtained by hydrogenation of 2-methyl-3-nitrophenyl, by the Skraup reaction, and purified by a method similar to that described above: mp 177−178 °C. ^{1}H NMR (500 MHz, CD_3OD) δ 2.57 (3H, s), 7.20 (1H, d, J = 9 Hz), 7.28 (1H, d, d, J = 8.4 Hz), 7.61 (1H, d, J = 9 Hz), 8.16 (1H, d, d, J = 2.8 Hz), 8.74 (1H, d, d, J = 4.2 Hz). MS (*m/s*) 159 (M^+). Anal. Calcd for $C_{10}H_9ON$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.56; H, 5.63; N, 8.83.

Hydrogen Bonded Complex Formations in Equilibrium. The equilibrium of methanol H-bonded complex formations is expressed as follows;[18,19]

$$\text{7-HQ} + \text{MeOH} \overset{K_1}{\rightleftharpoons} \text{(1:1 complex)}$$

$$\text{7-HQ} + 2(\text{MeOH}) \overset{K_2}{\rightleftharpoons} \text{(1:2 complex)}$$

where K_1 and K_2 are corresponding equilibrium constants. These constants are obtained by the following equations:

$$1/C = K_1[\text{7-HQ}]_0(\epsilon_1 - \epsilon)/A_1 - K_1 \quad (1)$$

$$1/C^2 = K_2[\text{7-HQ}]_0(\epsilon_2 - \epsilon)/A_2 - K_2 \quad (2)$$

where $[\text{7-HQ}]_0$ is an initial concentration of 7-HQ; ϵ_1 and ϵ_2 are apparent extinction coefficients of the 1:1 and 1:2 complexes, respectively; and A_1 and A_2 are absorbances of 1:1 and 1:2 H-bonded complexes in low and considerably high concentrations of CH_3OH (C) in CH_3OH/hexane, respectively. If $1/C$ is plotted vs the reciprocal of absorbance of the 1:1 complex (abs^{-1}) at the wavelength region of ϵ = 0, and 1:1 equilibrium constant, K_1, can be obtained from eq 1.[18,19] The 1:1 complex equilibrium constant K_1 for 8-Me-7-HQ was obtained in considerably high methanol concentration (CH_3OH/hexane), as will be mentioned later. The equilibrium constants of 1:2 complex formation, K_2, for 7-HQ and 6-Me-7-HQ were obtained from plots of $1/C^2$ vs abs^{-1}, as shown in eq 2.[18,19] However, the 1:1 and 1:2 complex formations were indistinguishable in intermediate methanol concentrations (methanol/hexane) of 7-HQ and 6-Me-7-HQ. Therefore, the plots of these compounds in the intermediate concentration of methanol in CH_3OH/hexane were removed in this paper.

General Experimental Procedures. The spectral grade methanol (Nakarai Tesque) was distilled after refluxing 5 h over CaO, and further distilled after refluxing 3 h over magnesium oxide for absorption and fluorescence spectroscopies. The spectral grade hexane (Nakarai Tesque) was used for absorption spectroscopy. The deaeration of sample solution for fluorescence and other experimental procedures were almost the same as described in previous papers.[20,21]

A mode-locked Nd:YAG laser (Coherent Antares 76-s) and a synchronously pumped dye laser were used. The picosecond pulses were amplified by a Nd:YAG regeneratively amplified dye laser system (Continuum RGA 60 and PTA 60). A dye laser beam (pyridine I/II) with a pulse energy of approximately 0.5 mJ at 10 Hz was used. The pulses were frequency doubled with angle-tuned crystal. The fluorescence was observed through a Jobin Yvon polychromator HR250. The time-resolved detection was performed with a photon counting streak camera (Hamamatsu Photonics C2050/M1952/CCD temporal analyzer 3140-69) system. The overall instrument response was observed to be approximately 10 ps (fwhm). The rise and decay data were corrected for the temporal response function by an iterative nonlinear least-squares algorithm. The serial correlation coefficient of the residuals (R) was used to judge the quality of the fit. The transient intensities of the normal fluorescence (1:1 and 1:2 H-bonded complexes, double exponential decays) and the large Stokes shifted tautomer fluorescence (a rise and decay) were analyzed by the conventional equations mentioned previously.[21,22]

Nanosecond transient absorption and TS-LIF spectra of methanol solutions of 6- and 8-Me-7-HQ were measured by the same method as described previously. The excimer laser (Lambda Physik EMG 53 MSC, 308 nm) and the excimer laser pumped dye laser (Lambda Physik EMG 50E/FL 2002) were used as pump and probe lasers of TS-LIF. A pulsed Xe lamp was used as a monitoring light source for transient absorption spectra. Nanosecond/picosecond TS-LIF was measured by the same method as described in previous papers.[21,22]

Results and Discussion

Hydrogen Bonding Complex Formations with Methanol. The hexane solutions of 7-HQ and methyl-substituted 7-HQ exhibit similar UV absorption spectra (λ_{max} 312−316 and 325−330 nm), while these hexane solutions are almost nonfluorescent. Figure 2 shows absorption and fluorescence spectra of methanol solutions of these compounds at room temperature (300 K). The methanol solutions of 7-HQ and 6-Me-7-HQ exhibit UV and large Stokes shifted fluorescence spectra, though fluorescence intensity ratios of the former and latter are considerably different. The large Stokes shifted fluorescence was ascribed to the tautomer fluorescence generated by the intermolecular ESPT, and two hydrogen bonded methanol molecules were required for the ESPT,[7] as mentioned in the introduction. However, no significant tautomer fluorescence was observed in the methanol solution of 8-Me-7-HQ, as shown in Figure 2. Therefore, the intermolecular interactions between 7-HQ and methyl-substituted 7-HQ, and methanol were investigated at room temperature (~300 K).

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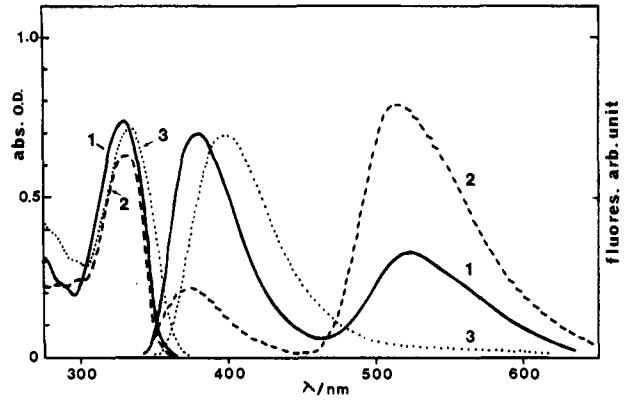

Figure 2. Electronic absorption and fluorescence spectra of methanol solutions of (1) 7-HQ, (2) 6-Me-7-HQ, and (3) 8-Me-7-HQ at room temperature. Excitation wavelengths of fluorescence are 330 nm for 7-HQ and 6-Me-7-HQ and 335 nm for 8-Me-7-HQ. Concentrations of these solutions are approximately 3×10^{-4} M.

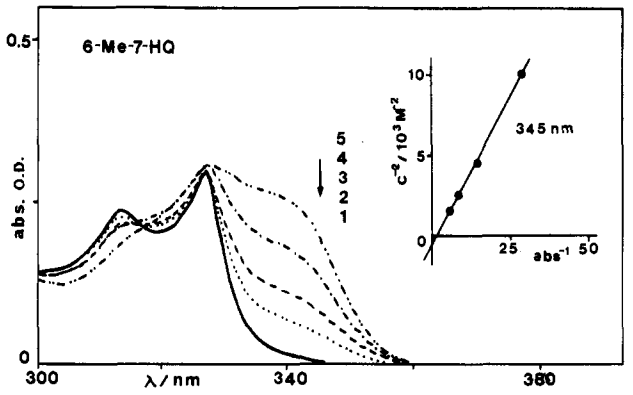

Figure 3. Absorption spectra of methanol/hexane mixed solutions of 6-Me-7-HQ (1.1×10^{-5} M and a light pathlength is 10 cm) at room temperature (~300 K) and plots of the squared reciprocal of concentration of methanol ($C^{-2}/10^{-2}$ M) vs the reciprocal of absorption intensity (abs^{-1} at 345 nm). Concentrations of methanol in the hexane mixed solution are the following: (1) 0 M; (2) 0.010 M; (3) 0.015 M; (4) 0.020 M; (5) 0.025 M.

In methanol/hexane mixed solvent systems of these compounds, considerably broad bands appeared in the 340−350-nm region and increased in intensity with increasing methanol concentration. A typical example of methanol concentration dependence of absorption spectra (6-Me-7-HQ) is shown in Figure 3. An inlet of Figure 3 shows plots of squared reciprocals of methanol concentrations (C^{-2}) vs reciprocals of absorption intensities (abs^{-1}). These plots indicate that the absorption bands at 340−350 nm which appeared in methanol solution may be attributable to the two-methanol H-bonded complex of the compound (1:2 complex), as mentioned in the Experimental Section. The equilibrium constants (K_2) of the 1:2 complex formation were estimated to be ~800 M^{-2} for 6-Me-7-HQ and ~900 M^{-2} for 7-HQ. In very low concentrations of methanol (<0.005 M) in the methanol/hexane mixed solvent, similar plots of C^{-1} vs abs^{-1} in the 345 nm region suggest 1:1 H-bonded complex formation of these compounds. Figure 4 shows the methanol concentration dependence of absorption spectra of 8-Me-7-HQ in methanol/hexane mixed solvents, whose spectra do not exhibit so significant absorption band in the 340−350-nm region as those of 7-HQ and 6-Me-7-HQ. An inset in Figure 4 shows plots of C^{-1} vs reciprocals of absorption intensities (abs^{-1}) at 345 nm. The plots of Figure 4 indicate 1:1 methanol complex formation in 8-Me-7-HQ, though a trace amount of 1:2 complex might be involved in the methanol solution of this compound. The very small equilibrium constant (K_1) of the 1:1 complex formation of 8-Me-7-HQ was roughly estimated to be 3−5 M^{-1} at room temperature (~300 K).

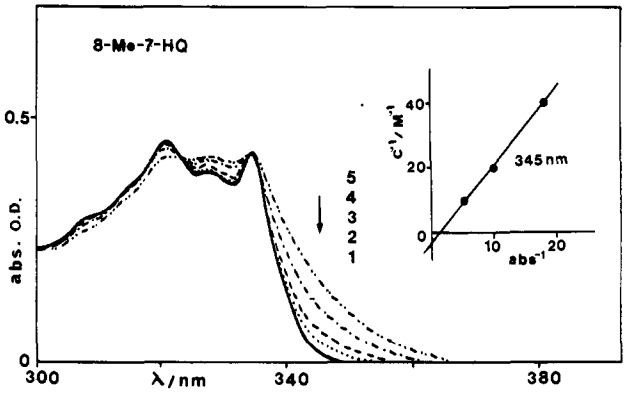

Figure 4. Absorption spectra of methanol/hexane mixed solutions of 8-Me-7-HQ (1.3×10^{-5} M, and a light pathlength is 10 cm) at room temperature and plots of the reciprocal of methanol concentration (C^{-1}/M^{-1}) vs the reciprocal of absorption intensity (abs^{-1} at 345 nm). Concentrations of methanol in the hexane mixed solution are the following: (1) 0 M; (2) 0.025 M; (3) 0.050 M; (4) 0.075 M; (5) 0.100 M.

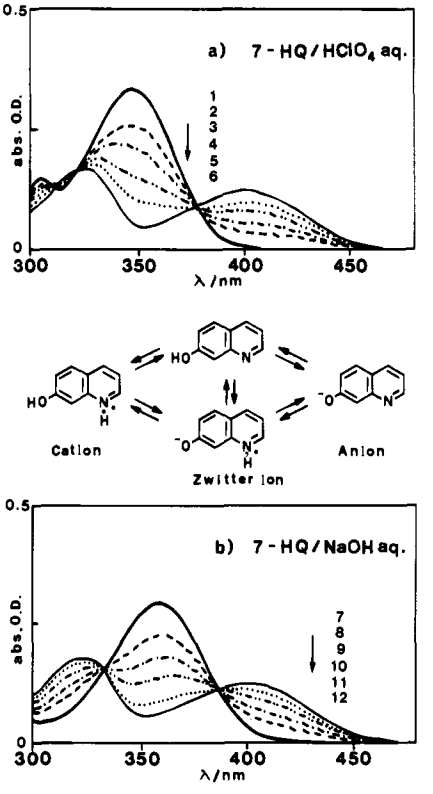

Figure 5. Absorption spectra of various forms of 7-HQ (4.7×10^{-5} M) in aqueous acid/base solutions: (a) (1) pH = 2.9, (2) 5.0, (3) 5.3, (4) 5.7, (5) 6.0, (6) 7.5; (b) (7) pH = 7.9, (8) 8.3, (9) 8.7, (10) 9.0, (11) 9.3, (12) 11.5.

In order to investigate the different H-bonding features between 8-Me-7-HQ and the other compounds (7-HQ and 6-Me-7HQ) in the ground state, a basicity of the ring nitrogen atom and an acidity of the 7-OH group of these compounds were obtained by conventional titration of absorption spectra of various pH/H_2O solutions. Figure 5 shows absorption spectra of various pH solutions of 7-HQ. Two absorption bands (λ_{max} 325 and 405 nm) may be ascribed to the zwitterion form. A band (λ_{max} 350 nm) at pH = 2.9 and a band of λ_{max} 360 nm at pH 10−11 were ascribed to the cation (N^+H) and anion ($-O^-$)

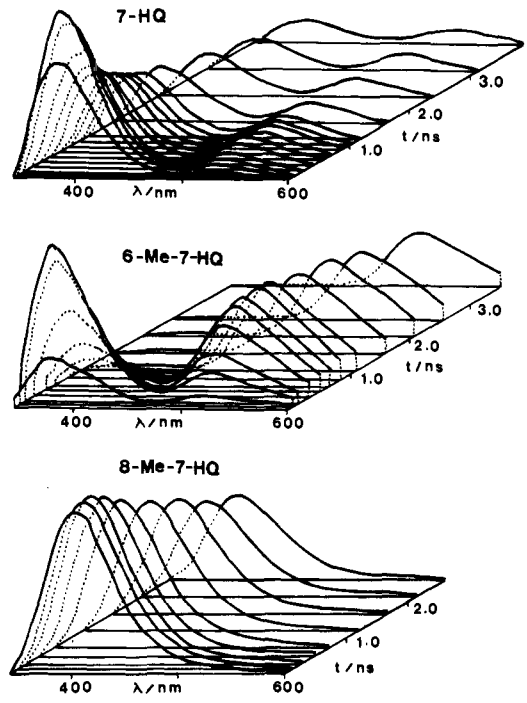

Figure 6. Picosecond time-resolved fluorescence spectra of methanol solutions of 7-HQ (excitation, 300 nm), 6-Me-7-HQ (excitation, 340 nm), and 8-Me-7-HQ (excitation, 300 nm) at room temperature; concentrations are $3-4 \times 10^{-4}$ M.

forms of this compound, respectively. From titration curves of the pH dependent absorption spectra, two pK_a (H_2O) values of 7-HQ in aqueous solution were obtained to be 5.4 and 9.0. Two pK_a (MeOH) values of cation (N^+H) and $-OH$ forms in methanol solution were estimated by the following conventional equation:[23]

$$pK_a(\text{MeOH}) = pK_a(H_2O) + \text{constant(MeOH)}$$

$$\text{constant(MeOH)} = 1.3\ (\text{AH}) \text{ and } 4.9\ (A^+H)$$

The obtained $pK_a(N^+H)$ values in methanol are 6.7 for 7-HQ, 7.0 for 6-Me-7-HQ, and 6.9 for 8-Me-7-HQ, and pK_a(OH) values are 13.9 for 7-HQ, 14.1 for 6-Me-7-HQ, and 14.4 for 8-Me-7-HQ. Taking account of these data, the first methanol molecule seems to bond to a nitrogen atom (1:1 complex) and the second methanol may bond to the 7-OH group of 7-HQ and 6-Me-7-HQ (1:2 complex) in equilibrium. However, it is noteworthy that no significant 1:2 H-bonded complex formation was observed in 8-Me-7-HQ as mentioned above (Figure 4), though the estimated pK_a(OH) value (14.4) of this compound is not so different from those of the other compounds. The fact seems to suggest that the *cis*-7-OH conformation is required for H-bonding formation with the second CH_3OH molecule, as will be mentioned later.

Picosecond Time-Resolved Fluorescence. Figure 6 shows picosecond time-resolved fluorescence spectra of methanol solutions of 7-HQ, 6-Me-7-HQ, and 8-Me-7-HQ at room temperature (300 K). The normal form fluorescence of 7-HQ shows a double exponential decay with decay times of 0.17 and 1.70 ns (detected at 375 nm), while the tautomer fluorescence shows a rise and decay with a rise time of 0.17 ns and a decay time of 3.80 ns. Since the decay time of 0.17 ns in the normal form is very consistent with the rise time of the tautomer, the short and long decay times of the normal form may be ascribed to those of the 1:2 and 1:1 H-bonded methanol complexes of 7-HQ, respectively. These decay times coincide unexpectedly with those (0.2 and 2.05 ns) obtained by nanosecond fluorescence spectroscopy reported previously.[7] Figure 7 exhibits picosecond fluorescence decay curves of the methanol solution of 6-Me-7-HQ. The normal form fluorescence shows a double exponential decay with decay times of 0.17 and 1.60 ns, though the long decay component is only 3%, as shown in Figure 7a. The tautomer fluorescence shows a rise (0.17 ns) and decay (4.10 ns). Therefore, the decay time of 0.17 ns of the normal form may be attributable to the 1:2 H-bonded complex leading to the ESPT of the tautomer formation. The steady-state (Figure 2) and picosecond time-resolved fluorescence spectra and decay curves (Figures 6) suggest that the fluorescent species of the normal form may be mostly attributable to the 1:2 methanol complex of this compound. Taking account of the steric factor of the 6-methyl group, the *cis* position of the 7-OH group with respect to the ring nitrogen atom may be favorable for the two-methanol H-bonding formation (1:2) and for the ESPT in 6-Me-7-HQ. These rise and decay times at several temperatures are summarized in Table 1.

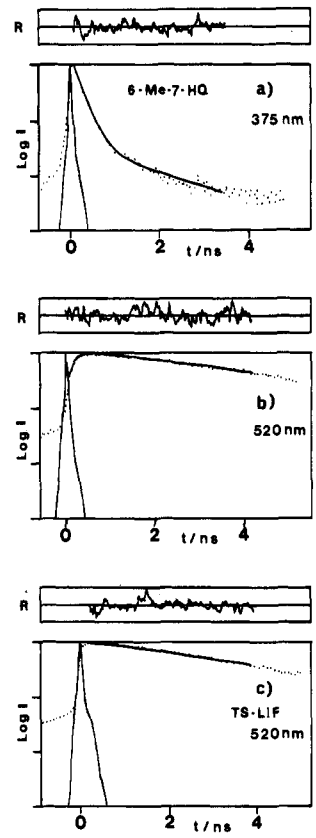

Figure 7. Fluorescence rise and decay curves of 6-Me-7-HQ/methanol: (a) the normal form fluorescence detected at 375 nm, τ = 170 ps (97%) and 1600 ps (3%); (b) rise and decay curve of the tautomer fluorescence detected at 520 nm, a rise time = 170 ps, τ = 4.10 ns; (c) ns/ps (308/436 nm) TS-LIF decay curve without rise of the tautomer fluorescence detected at 520 nm, τ = 3.90 ns.

Figure 6 shows picosecond time-resolved fluorescence spectra of the methanol solution of 8-Me-7-HQ. The normal form fluorescence exhibits a single exponential decay with a decay time of 3.50 ns throughout 370−500 nm (Figure 8a) and no tautomer fluorescence. The normal form fluorescence was ascribed to the 1:1 H-bonded complex with methanol, as mentioned above. However, a very weak transient absorption spectrum (λ_{max} 440−450 nm) with decay time of approximately 40 μs and also a very weak ns/ps TS-LIF spectrum (τ_{530nm} = 600−700 ps) were observed, as will be mentioned later. The

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Table 1. Fluorescence Decay Times of the Normal and Tautomer Forms in ESPT of Methanol Solutions of 7-HQ and 6-Me-7-HQ[a]

	normal form decay/ns			tautomer form rise and decay/ns	
	temp/K	1:1	1:2	rise	decay
7-HQ	294	1.70	0.17	0.17	3.80
	273	1.90	0.24	0.24	4.30
	251	2.00	0.38	0.38	4.70
	231	2.60	0.62	0.60	4.80
	206	3.00	1.30	1.20	5.00
6-Me-7-HQ	291		0.17	0.17	4.10
	273		0.23	0.25	4.30
	251		0.31	0.30	4.30
	231		0.60	0.61	4.70
	206		0.93	1.02	4.41

[a] The data were averaged from several experimental runs (errors approximately ±15%). The decay time of the 1:1 methanol complex of 6-Me-7-HQ was removed, because of a trace amount of decay component (<2−3%).

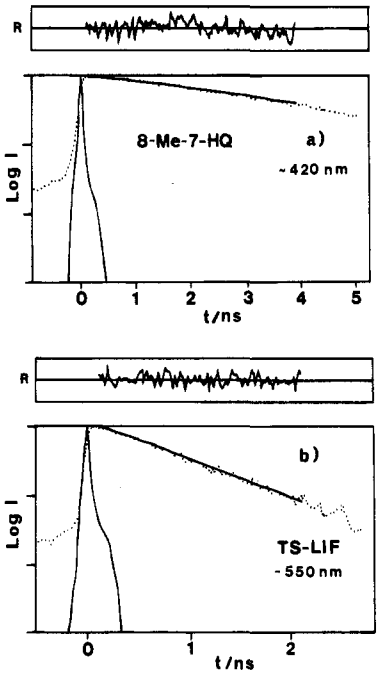

Figure 8. Fluorescence decay curves of 8-Me-7-HQ/methanol: (a) the normal form fluorescence detected at 420 nm, τ = 3.50 ns; (b) ns/ps (308/436 nm) TS-LIF decay curve detected at ~550 nm, τ = 780 ps.

facts suggest that a trace amount of 1:2 methanol complex leading to the ESPT may be involved in the methanol solution of 8-Me-7-HQ. These experimental features demonstrate that almost no significant ESPT takes place in the methanol solution of 8-Me-7-HQ and it may be attributable to the *trans* conformer of the 7-OH group of this compound, as shown in the schematic illustration of Figure 1. Almost identical picosecond time-resolved fluorescence features of these compounds in methanol were observed in the other alcohol solutions such as ethanol and propanol.

Transient Absorption and TS-LIF Spectra. Transient absorption spectra (λ_{max} ~420 nm) of methanol solutions of 6-Me-7-HQ are very similar to that of 7-HQ, as shown in Figure 9. Since the first observation of the transient absorption of the ground-state tautomer in the ESPT of 7-HQ[7] and 7-hydroxyflavone[5] by us, several research groups reported the transient absorption spectra in the ESPT. Further, Terazima and Azumi[24] confirmed by a thermal lensing effect that our transient

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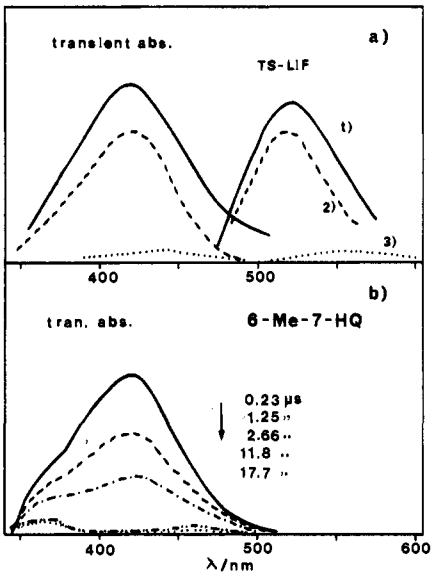

Figure 9. (a) Transient absorption (concentration and delay time in parentheses) and TS-LIF spectra of methanol solutions of (1) 7-HQ (7 × 10^{-5} M, 1.2 μs), (2) 6-Me-7-HQ (2−3 × 10^{-4} M, 0.8 μs), and (3) 8-Me-7-HQ (2−3 × 10^{-4} M, 5 μs); wavelengths of the second laser pulse (delay times from the first one in parentheses) were 440 nm for 7-HQ (1.2 μs) and 8-Me-7-HQ (5 μs) and 436 nm for 6-Me-7-HQ (0.8 μs). (b) Time-resolved transient absorption spectra of 6-Me-7-HQ/methanol (2−3 × 10^{-4} M) at several indicated delay times.

absorption in the methanol solution of 7-HQ was really attributable to the ground-state tautomer in the ESPT and no triplet state absorption band was involved. In a deaerated methanol solution of 6-Me-7-HQ, however, very weak absorption bands (τ = 30 μs) with a long delay time were observed in the 370- and 460-nm regions in addition to the transient absorption (λ_{max} ~ 420 nm, τ = 1.8 μs) due to the ground-state tautomer, as shown in Figure 9b. Since the long lived transients disappeared in the aerated methanol solution of 6-Me-7-HQ, these bands were ascribed to the triplet−triplet (T−T) absorption. It is not obvious whether these T−T absorption bands are attributable to the triplet state of normal or tautomer forms at the present stage.

The second laser excitations of transient absorptions due to the ground-state tautomer demonstrated the same tautomer fluorescence as the steady-state and picosecond time-resolved fluorescence spectra in methanol solutions of 7-HQ and 6-Me-7-HQ, as shown in Figure 9a. The TS-LIF decay times of the tautomer were identical with those of the respective tautomers, while the TS-LIF decay curves lack the fluorescence rise. The typical ns/ps TS-LIF tautomer decay curve of 6-Me-7-HQ is shown in Figure 7c, together with ps time-resolved profiles of the normal and tautomer fluorescence. The ns/ps TS-LIF decay curve without rise of the tautomer really demonstrates the involvement of the ground-state tautomer and the conventional double minimum potential energy curves in the ESPT of these compounds.

As mentioned in the last section, the methanol solution of 8-Me-7-HQ showed a very weak transient absorption band (λ_{max} 440−450 nm), whose intensity was less than 1/10 of those of 7-HQ and 6-Me-7-HQ, as shown in Figure 9. The transient absorption band of this compound seems attributable to the ground-state tautomer generated by the ESPT from a trace amount of 1:2 H-bonded methanol complex. Further, no significant absorption band due to the triplet state was observed. A very weak TS-LIF spectrum (λ_{max} 550−560 nm) was observed by the second laser excitation of the weak transient absorption band as shown in Figure 9a. The ns/ps TS-LIF decay

curve without fluorescence rise of the tautomer in 8-Me-7-HQ ($\tau = 0.78$ ns, Figure 8b) was obtained by ps pulse excitation of the transient absorption band, though no significant tautomer fluorescence was detected in a single ps pulse excitation fluorescence, as mentioned above (Figure 6c). Therefore, the major part of this compound may be the *trans* conformer of the 7-OH group dictated by the steric effect of the 8-methyl group. The *trans* conformer makes only the 1:1 H-bonded methanol complex, which exhibits no tautomer fluorescence but only normal form fluorescence, as mentioned above (Figure 1). Therefore, the *trans* or an out-of-plane conformer of the 7-OH group in 8-Me-7-HQ might be responsible to a trace amount of 1:2 H-bonded complex exhibiting very weak transient absorption and TS-LIF spectra (Figure 9).

On the other hand, Chou's group and others reported that the second laser excitation of the triplet state ($t_n' \leftarrow t_1'$) of the tautomer generated in the intramolecular ESPT exhibits the tautomer fluorescence.[25-27] They suggested that the fast reverse intersystem crossing, $t_n' \rightarrow s_1'$, is responsible for the TS-LIF in the ESPT (*the triplet mechanism*), where t_1', t_n', and s_1' are the lowest and higher triplet state tautomers and the singlet fluorescent tautomer, respectively.[27] However, we have further demonstrated the involvement of the ground-state tautomer in the intra-[4,20] and intermolecular ESPT[21] by TS-LIF and microsecond time-resolved infrared spectroscopies.[28] As mentioned above, the T−T absorption spectra in the 370- and 460-nm region ($\tau = 40$ μs) were observed in the deaerated methanol solution of 6-Me-7-HQ. However, no significant tautomer fluorescence was observed in the second laser excitation of the T−T absorption bands in the methanol solution of 6-Me-7-HQ. Therefore, the triplet state contribution was removed in the TS-LIF spectra in these compounds.

Concluding Remarks

The methanol H-bonded complex formations of 7-HQ and methyl-substituted 7-HQ were investigated by methanol concentration dependence of absorption spectra in methanol/hexane mixed systems. The effective 1:2 methanol H-bonded complex formation was observed in 6-Me-7-HQ/methanol solution, while the mostly 1:1 H-bonded complex was observed in 8-Me-7-HQ/methanol. Taking account of the steric factor of 6- and 8-methyl groups, the *cis* conformer of the 7-OH group with respect to the ring nitrogen atom was suggested to be required for the 1:2 complex formation of 7-HQ with methanol molecules. The picosecond time-resolved fluorescence and TS-LIF demonstrated that the ESPT takes place from the 1:2 H-bonded complexes of 7-HQ and 6-Me-7-HQ with methanol molecules, and that no significant ESPT occurs in the 1:1 H-bonded complex of the *trans* conformer of 8-Me-7-HQ with methanol. Figure 1 shows schematic illustrations of the ESPT in methanol solutions of 6-Me-7-HQ (*cis* conformer) and no ESPT in 8-Me-7-HQ (*trans* conformer). Therefore, it is likely that some weak molecular interaction between two methanol molecules in the 1:2 H-bonded state is essential for the ESPT of 7-HQ (the *cis* conformer) in a methanol solvent cage.

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