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Proton Transfer in the Excited State of 1- and 2-Methyl-4-amino-5*H*-[1]benzopyrano[3,4-*c*]pyridin-5-one Dimers and Complexes

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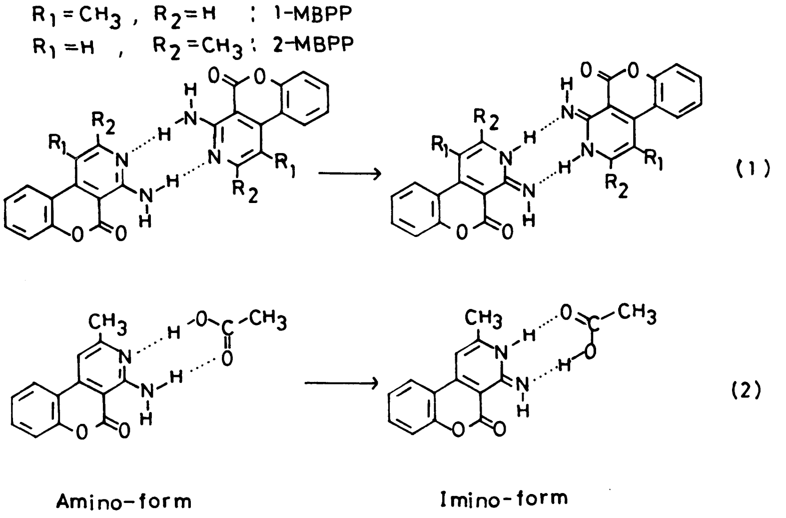
The fluorescence rise and decay times and UV absorption spectra of 1-methyl-4-amino-5*H*-[1]benzopyrano-[3,4-*c*]pyridin-5-one (1-MBPP), 2-methyl-4-amino-5*H*-[1]benzopyrano[3,4-*c*]pyridin-5-one (2-MBPP), and the 1-MBPP/acetic acid and 2-MBPP/acetic acid systems have been measured in hydrocarbon and hydroxylic solvents at room temperature and 77 K. From these data, a rapid formation of proton-transferred species (tautomers) was found to occur in an excited state for 1-MBPP (or 2-MBPP) hydrogen-bonded dimers in hydrocarbon at 77 K, and for 1-MBPP (or 2-MBPP) hydrogen-bonded complexes with acetic acid in hydrocarbon at room temperature and 77 K. The rise times of the tautomer fluorescence for the dimers and complexes were less than 65 ps. The observed fluorescence lifetimes of the 1-MBPP and 2-MBPP monomers agreed well with the lifetimes calculated using the integrated absorption intensity and fluorescence quantum yield.

El-Bayoumi *et al.*[1)] have presented the results of a time-resolved fluorescence study of an excited-state double proton transfer. The observed value of the rate constant for a deuterium transfer in a deuterated 7-azaindole dimer at 77 K was $1.9\times10^{8}\,s^{-1}$. Recently, Hetherington III *et al.*[2)] have suggested that photoexcited dimers of 7-azaindole undergo a double proton transfer in less than 5 ps at room temperature and 77 K. The proton-transfer rate in an excited state is generally as fast as reported by them[1,2)] and other workers.[3—5)]

In a previous paper[6)] we presented the emission spectra and polarization spectra of 1-methyl-4-amino-5*H*-[1]benzopyrano-[3,4-*c*]pyridin-5-one (1-MBPP), 2-methyl-4-amino-5*H*-[1]benzopyrano-[3,4-*c*]pyridin-5-one (2-MBPP), and the 2-MBPP acetic acid system (2-MBPP/AcOH) in glassy solvents at 77 K. In the course of this investigation, an anomalous fluorescence was observed with a maximum near 450 nm for 1-MBPP, near 436 nm for 2-MBPP, and near 460 nm for 2-MBPP/AcOH in hydrocarbon glassy solvents at 77 K. The anomalous fluorescence band was thought to have originated from the tautomer (imino-form) of the 1-MBPP and 2-MBPP formed by an intermolecular double proton transfer in the excited state of the doubly hydrogen-bonded dimer and complex of amino-form as shown in Schemes 1 and 2. In addition, the fluorescence spectra of the monomer, dimer (or complex) and tautomer, and the phosphorescence spectra of the monomer and dimer have been separately observed on the basis of concentration and tempera-



Schemes 1 and 2.

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ture effects on these emissions.[6] 7-Azaindole is known to show the double proton transfer in the excited state, where the phosphorescence spectrum greatly overlaps the tautomer fluorescence band.[7] 1-MBPP and 2-MBPP are, therefore, suitable for studying the dynamics of proton transfer in excited states.

In the present study, the fluorescence rise and decay times and the UV absorption spectra of 1-MBPP, 2-MBPP, 1-MBPP/AcOH, and 2-MBPP/AcOH in hydrocarbon and hydroxylic solvents at ambient temperature and 77 K were investigated in order to elucidate the proton-transfer mechanism in an excited state.

Experimental

Materials. 1-MBPP, 2-MBPP, acetic acid, and solvents were the same as in a previous paper.[6] Solvents used were as follows: (1) a mixed solvent of isopentane and methylcyclohexane (volume ratio 5:1) (IM), (2) a mixed solvent of ethanol and methanol (volume ratio 5:1) (EM), and (3) diethyl ether-isopentane-ethanol (volume ratio 5:5:2) (EPA). Concentrations of 1- and 2-MBPP were 1×10^{-4} mol dm^{-3} and that of the acetic acid was 5×10^{-4} mol dm^{-3}.

UV Absorption Measurements. The UV absorption spectra were obtained at room temperature and at 77 K with an Hitachi model 323 spectrophotometer. The UV absorption measurements at 77 K were carried out on rigid glass samples in a quartz cell of 5 mm path length placed in a glass Dewar vessel with quartz windows.

Fluorescence Time Profile Measurements. A nitrogen laser (Molectron UV24), a pumped dye laser (DL14), and a second-harmonic generator (a KDP crystal) were used for the nanosecond excitation.[8] The excitation wavelength was 305 nm (Rhodamine B/KDP, pulse duration 5 ns). A single-photon counting system (ORTEC) connected to a Spex 14 (0.75 m) monochromator and a HTV R1332 photomultiplier was used for the fluorescence lifetime measurements. More precise measurement with picosecond excitation was performed using a synchronously pumped, cavity-dumped dye laser (Spectra Physics 375 and 3445), operated with a mode-locked Ar$^+$ laser (Spectra Physics 171—18). The laser was operated with a repetition rate of 800 kHz and a pulse duration of 6 ps. The dye used was Na-fluorescein and its second harmonic (280 nm) was generated with a KDP crystal. Through a modification of the detecting systems, the apparent pulse width (fwhm) was found to be about 70 ps, and the rise and decay times were analyzed by a convolution-simulation method using the time profile of scattered laser light as a reference. Details of the experimental setup and single-photon counting systems for picosecond regions have been reported elsewhere.[9]

Results and Discussion

The UV absorption spectra of 1-MBPP in hydrocarbon[10] and hydroxylic[11] solvents at room temperature are shown elsewhere. The UV absorption spectra of 1-MBPP and 2-MBPP in IM and EM at 77 K are illustrated in Fig. 1 with those of 1-MBPP/AcOH and 2-MBPP/AcOH in IM at 77 K. The UV spectra of 1- and 2-MBPP in EPA at 77 K were similar to those in EM at 77 K. 1-MBPP and 2-MBPP in alcoholic solvents at room temperature as well as at 77 K exist as monomers, though they form hydrogen-bonded complexes with alcohols.[11] These molecules in IM at room temperature exist as monomers,[10] but at 77 K they are considered to form molecular complexes since the UV absorption spectra of 1- and 2-MBPP in IM are similar to those of hydrogen-bonded complexes of 1-MBPP/AcOH and 2-MBPP/AcOH in the same solvent at 77 K, respectively (Fig. 1). From the similarity of these UV absorption spectra, the model of the molecular complex for 1- and 2-MBPP is assumed to be the doubly hydrogen-bonded dimer of the amino-form as shown in Scheme 1.

The fluorescence lifetimes ($\tau_{\mathrm{f\,obsd}}$) were measured at fluorescence band maxima ($\lambda_{\mathrm{f\,max}}$) in various solvents at room temperature (Table 1) and 77 K (Table 2). An example of fluorescence decay curves observed by means of the single-photon counting method is presented in Fig. 2 for 1-MBPP at ambient temperature.

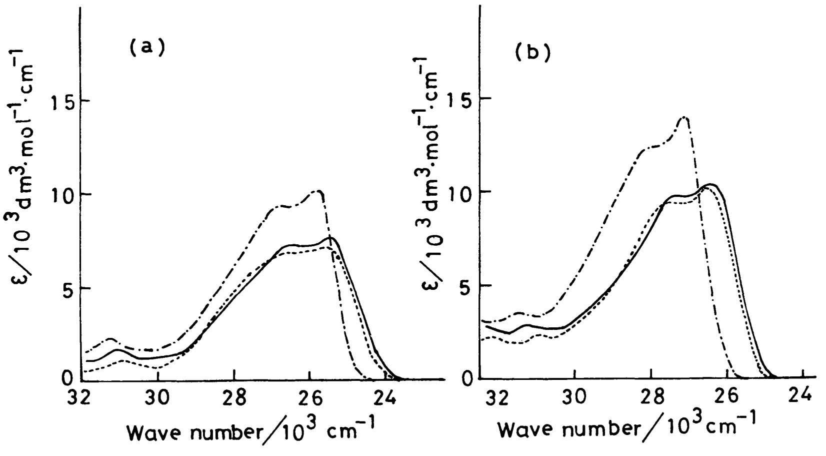

Fig. 1. UV absorption spectra of 1-MBPP (a) and 2-MBPP (b) in IM (——) and EM (—·—) at 77 K, with those of 1-MBPP/AcOH and 2-MBPP/AcOH (······) in IM at 77 K.

Table 1. Band maxima ($\lambda_{\mathrm{f\,max}}$), quantum yields ($\phi_\mathrm{f}$), observed lifetimes ($\tau_{\mathrm{f\,obsd}}$), and calculated lifetimes ($\tau_{\mathrm{f\,calcd}}$) of 1-MBPP and 2-MBPP fluorescence in various solvents at room temperature with those of 1-MBPP/AcOH and 2-MBPP/AcOH

System	Solvent	$\lambda_{\mathrm{f\,max}}$ / nm	ϕ_f	$\tau_{\mathrm{f\,obsd}}$ / ns	$\tau_{\mathrm{f\,calcd}}$ / ns	$k_\mathrm{r}\times10^{-7}$ / s^{-1}	$k_\mathrm{nr}\times10^{-7}$ / s^{-1}
1-MBPP	IM	403	0.07	0.95	1.2	7.4	98
1-MBPP	EM	420a)	0.29a)	3.75	5.6	7.7	19
1-MBPP	EPA	420	0.29	3.77	5.4	7.7	19
1-MBPP/AcOH	IM	475	0.02	1.48	0.3	1.4	66
2-MBPP	IM	373	0.09	0.79	0.9	11	120
2-MBPP	EM	400a)	0.24a)	1.56	2.6	15	49
2-MBPP	EPA	398	0.23	1.50	2.7	15	51
2-MBPP/AcOH	IM	458	0.09	6.89	1.2	1.3	13

a) See Ref. 6.

Table 2. Band maxima ($\lambda_{\mathrm{f\,max}}$), quantum yields ($\phi_\mathrm{f}$), observed lifetimes ($\tau_{\mathrm{f\,obsd}}$), and calculated lifetimes ($\tau_{\mathrm{f\,calcd}}$) for the 1-MBPP and 2-MBPP fluorescence in various glasses at 77 K with those of 1-MBPP/AcOH and 2-MBPP/AcOH

System	Solvent	$\lambda_{\mathrm{f\,max}}$a) / nm	ϕ_fa)	$\tau_{\mathrm{f\,obsd}}$ / ns	$\tau_{\mathrm{f\,calcd}}$ / ns	$k_\mathrm{r}\times10^{-7}$ / s^{-1}	$k_\mathrm{nr}\times10^{-7}$ / s^{-1}
1-MBPP	IM	450	0.15	8.88	1.3	1.7	9.6
1-MBPP	EM	405	0.48	4.05	7.5	12	13
1-MBPP	EPA	401	0.43	2.43	6.7	18	23
1-MBPP/AcOH	IM	473	0.09	8.49	0.9	1.1	11
2-MBPP	IM	435	0.13	7.71	1.7	1.7	12
2-MBPP	EM	386	0.24	1.35	2.8	17	56
2-MBPP	EPA	384	0.24	1.42	2.6	17	54
2-MBPP/AcOH	IM	460	0.09	16.08	1.3	0.56	5.7

a) See Ref. 6.

The decay curve was found to be single exponential and the lifetime was 0.95 ns (Table 1). In Tables 1 and 2, the fluorescence quantum yields (ϕ_f) and the calculated fluorescence lifetimes ($\tau_{\mathrm{f\,calcd}}$), deduced from the integrated UV absorption intensity and ϕ_f, are also shown together with the radiative (k_r) and nonradiative (k_nr) rate constants calculated from the fluorescence characteristics in several solvents at room temperature and 77 K, respectively.

The values of $\lambda_{\mathrm{f\,max}}$ for 1- and 2-MBPP in IM glassy matrices and those for 1-MBPP/AcOH and 2-MBPP/AcOH are appreciably longer wavelengths than those in an alcoholic glass.[6] The values of $\tau_{\mathrm{f\,obsd}}$ of 1-MBPP/AcOH and 2-MBPP/AcOH in nonpolar glass were greater than those of $\tau_{\mathrm{f\,calcd}}$ estimated from the integrated absorption intensity of the hydrogen-bonded complex of amino-form and the fluorescence quantum yields observed at the band maxima (473 nm for 1-MBPP and 460 nm for 2-MBPP). This tendency was also seen for the cases of 1- and 2-MBPP in IM at 77 K. The results described above and the resemblance of the fluorescence characteristics of 1-MBPP and 2-MBPP in IM at 77 K indicate that the tautomer (imino-form) formation from the 1-MBPP and 2-MBPP hydrogen-bonded dimers (amino-form) occurs in the excited state, as given in Scheme 1, just as in the case of acid complexes in Scheme 2.[6] On the other hand, the values of $\tau_{\mathrm{f\,obsd}}$ in alcoholic matrices at 77 K agreed with those of $\tau_{\mathrm{f\,calcd}}$. This result is compatible with the assumption that 1-MBPP and 2-MBPP in an alcoholic solvent at 77 K (as well as at room temperature) behave like monomers, though they make hydrogen-bonded complexes with alcohol.

The tautomerization from benzopyranopyridine hydrogen-bonded dimers (amino-form) to imino-form was investigated with the picosecond laser induced fluorescence technique. The fluorescence rise times were observed at the tautomer fluorescence band at room temperature and 77 K. It is noted that there are fast and slow rise components in the tautomer fluorescence for 1-MBPP and 2-MBPP at 77 K, and for 1-MBPP/AcOH and 2-MBPP/AcOH at room temperature and 77 K, as summarized in Table 3. As described by Hetherington III *et al.* in the study on the proton

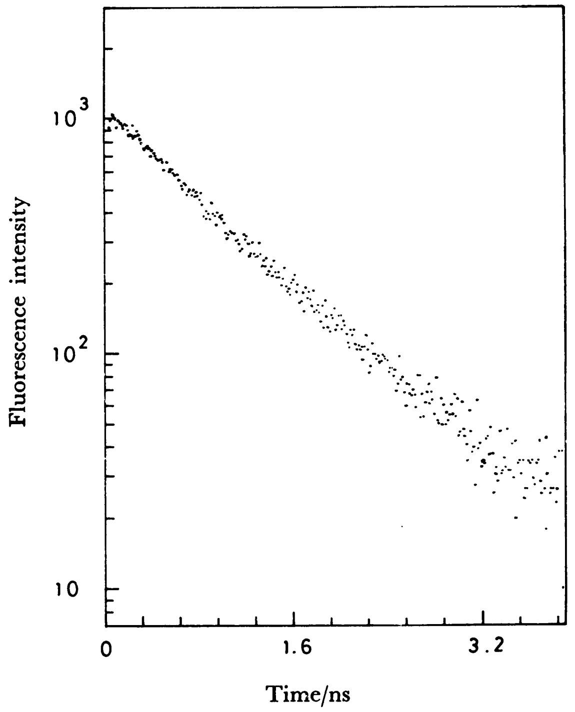

Fig. 2. Logarithmic plot of a fluorescence decay of 1-MBPP in IM at room temperature.
Excitation wavelength; 280 nm, Emission wavelength; 403 nm.

Table 3. Rise times of tautomer fluorescence for different systems in IM at room temperature and 77 K

System	Fast component ps	Slow component ps
1-MBPP at 77 K	<20	$\sim$40
1-MBPP/AcOH at room temp	<20	$\sim$45
1-MBPP/AcOH at 77 K	<20	$\sim$65
2-MBPP at 77 K	<20	$\sim$35
2-MBPP/AcOH at room temp	<20	$\sim$45
2-MBPP/AcOH at 77 K	<20	$\sim$65

transfer of the 7-azaindole dimer,[2] the presence of fast and slow rise components in the tautomer fluorescence for 1- and 2-MBPP and their acetic acid complex systems suggests that there are two different pathways for the formation of the tautomer in an excited state: (a) the rapid proton transfer from the excited Franck-Condon state and (b) the relatively slow proton transfer from the excited state generated by energy relaxation from the excited Franck-Condon state.

The slow fluorescence rise times for 1-MBPP/AcOH and 2-MBPP/AcOH at room temperature were shorter than those for the same systems at 77 K. This result indicates that tautomer formation *via* pathway (b) at room temperature is more favored than at 77 K because proton transfer at room temperature occurs effectively across the barrier by thermal activation. In addition, the rise time of the dimer was shorter than that of heterogeneous systems such as 1-MBPP/AcOH. This result means that the barrier height in proton transfer in the excited state for homogeneous complexes is lower than that for heterogeneous complexes.

The intensity ratio of the fast and slow rise components in the tautomer fluorescence is thought to depend on the excitation wavelength. In the present case the excitation wavelength was 280 nm, about 9500—11700 cm^{-1} above the absorption edge of the complexes. A red edge excitation and time profile observation will give further information on the energy and proton transfer in an excited state.

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