NOTES

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Fluorescence of the Proton Transferred Excited Species between 4-Amino-2-methyl-5*H*-[1]benzopyrano[3,4-*c*]pyridin-5-one and Acetic Acid. Time-Resolved Fluorescence Spectra and Solvent Effects

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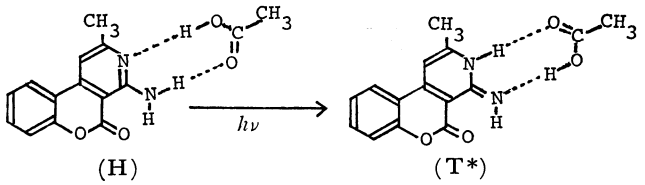
Synopsis. The nanosecond time-resolved spectra and apparent lifetime for the fluorescence of the proton transferred excited species (tautomer) between 4-amino-2-methyl-5*H*-[1]benzopyrano[3,4-*c*]pyridin-5-one (BPP) and acetic acid have been measured in isooctane (2,2,4-trimethylpentane) at room temperature. It has been established that the rising time of the tautomer fluorescence was *ca.* 15 ns and the time required for the excited hydrogen-bonded species-tautomer equilibrium was *ca.* 40 ns. Solvent effects upon the fluorescence characteristics of the tautomer have also been investigated.

Recently, El-Bayoumi *et al.*[1] and Shizuka *et al.*[2] have measured the fluorescence with large Stokes shifts for 7-azaindole (7AI) and for 6-(2-hydroxy-5-methylphenyl)-*s*-triazines (TH), respectively. It has been suggested that the fluorescence of the former originates from a tautomer formed by a fast intermolecular double proton transfer reaction of the excited hydrogen-bonded dimer of 7AI.[1] In the latter case the fluorescence has been attributed to a tautomer (keto form) formed by a fast intramolecular proton transfer reaction of the excited hydrogen-bonded species (enol form) of TH.[2]

Previous studies have reported the fluorescence with a large Stokes shift, besides the fluorescence of hydrogen-bonded species for the BPP–acetic acid system in isooctane.[3] Accordingly, from the similarity of tautomer fluorescences for 7AI and TH, it is reasonable to assume that the fluorescence of the present system with a large Stokes shift corresponds to that from the tautomer (T*) formed *via* the intermolecular double proton transfer in the excited state of the doubly hydrogen-bonded species (H) as follows:



(H) (T*)

In addition, from the absorption spectra it has been shown that substantially all BPP molecules are present as H in isooctane when the concentration of BPP is 3.5×10^{-5} M and that of acetic acid 2.0×10^{-1} M.[3] In the present study, nanosecond time-resolved fluorescence spectral techniques were applied to the problem of the double proton transfer reaction between BPP in the lowest excited singlet state and acetic acid under the conditions as stated above.

Results and Discussion

The time-resolved fluorescence spectra of the BPP–acetic acid system in isooctane solution are given in Fig. 1. As shown in Fig. 1 two fluorescence bands with peaks at *ca.* 384 nm and 458 nm appear, which correspond to the emission bands of the hydrogen-bonded and proton transferred species[3] (tautomer) respectively. The fluorescence band maxima of these two species are scarcely shifted with a delay time (t). It seems that an equilibrium between H* and T* is established in the excited state as follows:

$$\mathrm{H^*} \rightleftarrows \mathrm{T^*}$$

where H* signifies the excited hydrogen-bonded species. The tautomer fluorescence at $t\approx15$ ns has the greatest intensity as seen in Fig. 1. The rising time of T* is *ca.* 15 ns. Figure 2 shows the plot of I_2/I_1 *vs.* t for the BPP–acetic acid system, where I_1 and

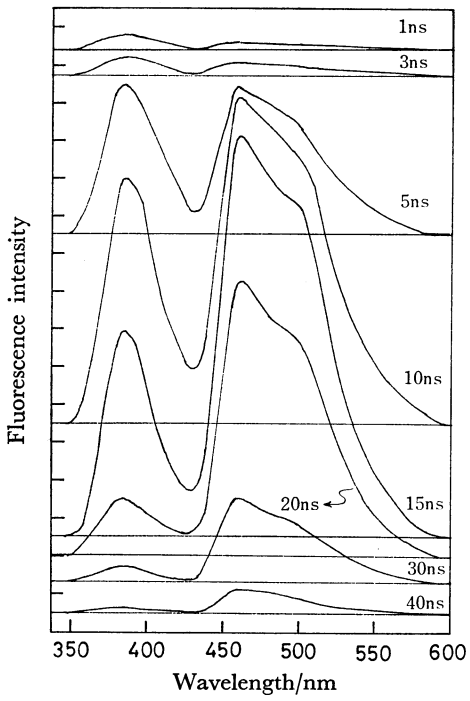


Fig. 1. Time-resolved fluorescence spectra of the BPP-acetic acid system in an isooctane solution at room temperature.

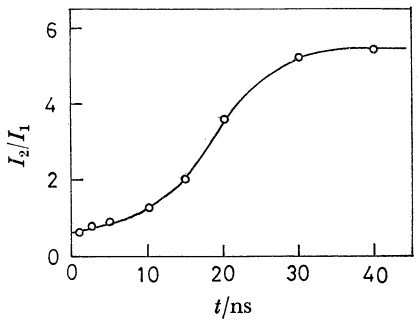


Fig. 2. The polt of I_2/I_1 *vs.* t.

I_2 represent the fluorescence intensities at 384 nm and 458 nm respectively. At first, I_2/I_1 increases with t and then is virtually invariant at $t \approx 40$ ns. Furthermore, the time-resolved fluorescence spectra at *ca.* 40 ns were the same as those in the stationary state of the BPP–acetic acid system. These results show that it takes about 40 ns to establish the H*–T* equilibrium. It should be noted that the rate of proton transfer in the excited state is generally fast,[1,2] while in the case of the system studied here that of proton transfer is relatively slow and the reaction takes time to reach the H*–T* equilibrium.

The fluorescence lifetime calculated from the integrated absorption intensity and the fluorescence quantum yield ($\Phi=0.14$[4]) of BPP in isooctane without acetic acid was estimated to be 1.0 ns. The lifetime of BPP in isooctane could not be obtained because it was shorter than the response time (few ns) of the apparatus. Nevertheless, the apparent fluorescence lifetimes (τ_T) of the tautomer T* in various solvents could be measured at room temperature. These was no wavelength effect upon the apparent lifetimes of T*. The values of τ_T at 470 nm in various solvents are listed in Table 1.

The other characteristics (the wave numbers of the band maxima and quantum yields) of the tautomer fluorescence measured in non-polar and slightly polar solvents are also given in Table 1 with dielectric constants. It is to be noted that with an incerase in the polarity of solvent the tautomer fluorescence band maximum shifted towards the red with a decrease in the fluorescence quantum yield, The apparent lifetime also decreases with an increase in the solvent polarity.

Experimental

The sample of BPP[6] was the same as reported previously.[3] The sample was recrystallized from pyridine and further purified by vacuum sublimation. Acetic acid and quinine bisulfate of extra pure grade were used without further purification. The solvent used here were commercially available and when purification was needed, they were further purified by distillation. The time-resolved fluorescence spectra and lifetimes were measured with a Hitachi MPF-4 spectrophotometer equipped with a time-resolved photometer at room temperature. An ultraviolet D_2 pulser was used for the excitation of the species. The pulse given by this lamp had a life-duration less than 5 ns. For the measurement of ordinary emission intensity, a Hitachi MPF-2A fluorescence spectrophotometer was used.

Table 1. Wave numbers (ν_T) of the band max., fluorescence quantum yields (Φ_T), and apparent fluorescence lifetimes (τ_T) of the tautomer T* in the BPP–acetic acid system measured in solvents having different polarity at room temp

Solvent	Dielectric const	ν_T $\times 10^3$ cm^{-1}	Φ_T[4]	τ_T ns
Hexane	1.88	21.8	0.088	8.1
Isooctane	1.95	21.8	0.081	8.0
Benzene	2.28	21.5	0.053	7.3
Chloroform	5.15	21.4	0.051	7.2
Chlorobenzene	5.53	21.4	0.050	7.1
Dichloromethane	8.90	21.3	0.036	6.7
Dichloroethane	10.37	21.3	0.035	6.4

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4) The fluorescence quantum yields were measured by comparison with a quinine bisulfate solution ($\Phi=0.55$ at 27 °C, see Ref. 5).

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