Absorption and Fluorescence Spectra of 1-Methyl-2(1*H*)-pyridinimines and 2-Methylaminopyridine–Acetic Acid Complex

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Synopsis. Upon the addition of acetic acid to 2-methylaminopyridine in isooctane, weak absorption and fluorescence bands appeared near 350 and 465 nm at the tail of the main bands, respectively. These new bands were attributed, on the basis of the spectral results of 1-methyl-, 1,3-dimethyl-, 1,4-dimethyl-, 1,5-dimethyl-, and 1,6-dimethyl-2(1*H*)-pyridinimines, and 1-methyl-2-methylimino-1,2-dihydropyridine, to have originated from 2(1*H*)-pyridinimine moiety (imino-form tautomer) in the 2-methylaminopyridine-acetic acid complex. In addition, the fluorescence quantum yields of the 1-methyl-2(1*H*)-pyridinimines in isooctane were shown to be very small.

Only a limited number of papers have been written on the amino–imino tautomerizations concerning 2-aminopyridine and its related compounds in the ground state.[1–3] In a previous investigation,[1] the UV absorption spectrum of 2-aminopyridine was measured in an acetic acid and isooctane (2,2,4-trimethylpentane) mixed solvent, and its spectrum showed a shoulder band near 335 nm as the concentration of acetic acid increased. A similar shoulder band had been observed at around 345 nm in the case of the 2,6-diaminopyridine–ethanol system; it was assigned to the π, π^* transition of 6-amino-2(1*H*)-pyridinimine.[2] On the other hand, the fluorescence spectra of the 2-aminopyridine-acetic acid system showed a new emission band at 420 nm, and another peak at 360 nm with an increase in the acetic acid concentration.[3] The latter peak was assigned to the monocation species, that is, the aminopyridinium from the fluorescence spectra of 2-aminopyridine in acidic aqueous solution and from the theoretical consideration by the molecular orbital method.[3] However, the shoulder absorption band near 335 nm and the fluorescence band at 420 nm were not clarified experimentally, though these bands had been theoretically assigned to the π–π^* transition of the 2(1*H*)-pyridinimine moiety in the 2-aminopyridine–acetic acid complex.[1,3]

It was found in the present study that the absorption band at 350 nm and the fluorescence bands at 390 and 465 nm for the 2-methylaminopyridine–acetic acid system correspond to the absorption band at 335 nm, and the corresponding bands at 360 and 420 nm for the same system of 2-aminopyridine,[3] respectively. In order to make these bands of 2-methylaminopyridine experimentally more clear the absorption and fluorescence spectra of 1-methyl-2(1*H*)-pyridinimine and its methyl derivatives were investigated by spectroscopic methods.

Results and Discussion

The UV absorption and fluorescence spectra of 2-methylaminopyridine with acetic acid in isooctane solution are shown in Figs. 1 and 2, respectively. The addition of a small amount of acetic acid to 2-methylaminopyridine in isooctane perturbs the absorption spectrum. The large band-shift to the longer wavelength and the appearance of clear isosbestic points at 257 and 305 nm are attributed to the formation of a hydrogen bonded 1 : 1 complex between 2-methylaminopyridine and acetic acid, as shown in Eq. 1.

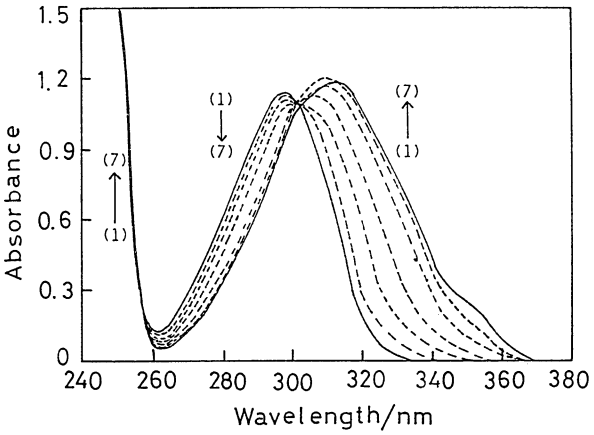


Fig. 1. Absorption spectra of the 2-methylaminopyridine–acetic acid system in isooctane at 20 °C. Concentration of 2-methylaminopyridine: 2×10^{-4} mol dm^{-3}, concentration of acetic acid (mol dm^{-3}): (1) 0, (2) 1×10^{-4}, (3) 5×10^{-3}, (4) 1×10^{-2}, (5) 5×10^{-2}, (6) 1×10^{-1}, (7) 3×10^{-1}.

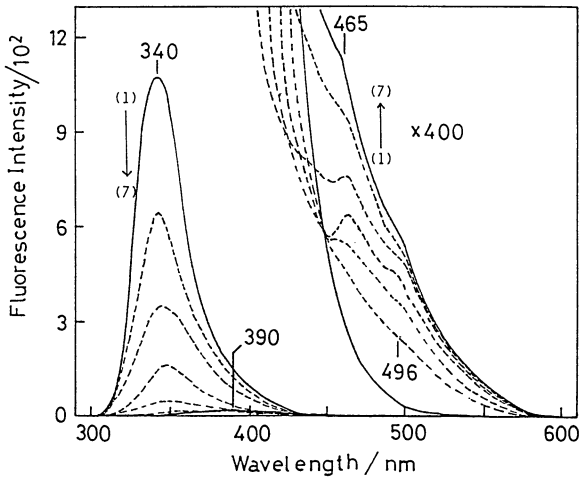
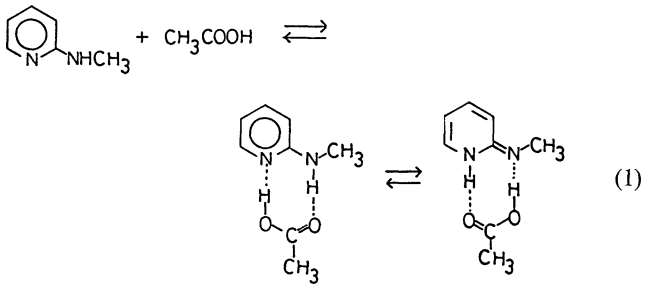


Fig. 2. Fluorescence spectra of the 2-methylaminopyridine–acetic acid system obtained by excitation at 300 nm in isooctane at room temperature. These spectra were measured at the same concentrations as those in Fig. 1.



(1)

In a previous paper,[1] similar results had been reported for 2-aminopyridine and its methyl derivatives. In Fig. 1, the absorption band at 315 nm is due primarily to the complex and can be used to determine the equilibrium constant (K) by the method of Benesi and Hildebrand.[4] The enthalpy changes ($-\Delta H$) accompanying hydrogen bond formation can be obtained from knowledge concerning of the variation of K with temperature. In the present experiment the values of K were determined for the methylaminopyridine–acetic acid system at four temperatures within the range from 15 to 40 °C. The values of K, $-\Delta H$, and $-\Delta S$ for 2-methylaminopyridine with acetic acid are 1.8×10^{3} dm^3 mol^{-1} (20 °C), 25.5 kJ mol^{-1}, and 2.5×10^{-2} J K^{-1} mol^{-1}, respectively. The $-\Delta H$ value is smaller than that of 2-aminopyridine with acetic acid (47.3 kJ mol^{-1}).[3] 2-Methylaminopyridine has two conformations with respect to the methylamino group. One of them has a steric hindrance for hydrogen bond formation with acetic acid. The other makes a hydrogen bond without this situation, as shown in Eq. 1. The smaller hydrogen bond energy may be attributed to the above-mentioned two conformations.

Furthermore, upon the addition of acetic acid to 2-methylaminopyridine in isooctane a new, weak shoulder band appeared near 350 nm at the tail of the main band of the hydrogen-bonded complex between 2-methylaminopyridine and acetic acid (Fig 1.). As is shown in Fig. 3, the absorption bands of 1-methyl-2(1*H*)-pyridinimine[5] and 1-methyl-2-methylimino-1,2-dihydropyridine (as the model of the 2(1*H*)-pyridinimine moiety (imino-form tautomer) for the 2-methylaminopyridine–acetic acid system) were observed at 345 and 372 nm. These values of 345 and 372 nm are close to the above-mentioned observed value of 350 nm. Therefore, as shown in Eq. 1, it seems reasonable that the shoulder band is due to the 2-methylimino-1,2-dihydropyridine–acetic acid complex formed from the 2-methylaminopyridine–acetic acid complex. The corresponding shoulder bands of the 2-aminopyridine–acetic acid system and the same system of its methyl derivatives had been reported in a previous paper.[1] In Fig. 4, the wavelengthes of the shoulder band of methyl-substituted 2-aminopyridine-acetic acid system and those ones of the absorption band maxima of methyl-substituted 1-methyl-2(1*H*)-pyridinimine are plotted against the position of the methyl group. Figure 4 shows the existence of a close relationship between the two systems.

On the other hand, the fluorescence spectra of 2-methylaminopyridine in isooctane changes drastically upon the addition of acetic acid (Fig. 2). On the disappearance of the emission at 340 nm with an increase in the acetic acid concentration, a new, very weak emission band appeared at 465 nm; then, with the disappearance of the new, weak emission band, another intense emis-

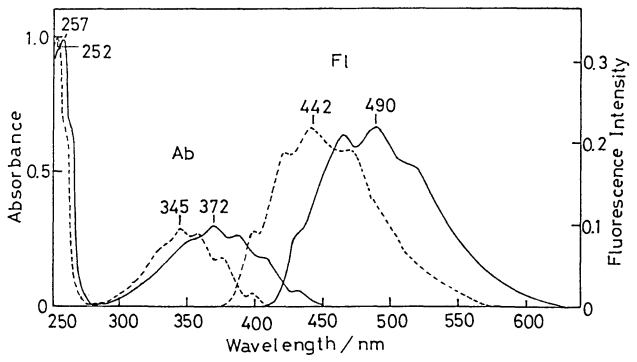


Fig. 3. Absorption (Ab) and fluorescence spectra (Fl) of 1-methyl-2(1*H*)-pyridinimine (----) and 1-methyl-2-methylimino-1,2-dihydropyridine (——) in isooctane at room temperature. The concentrations of these compounds are 2×10^{-4} mol dm^{-3}.

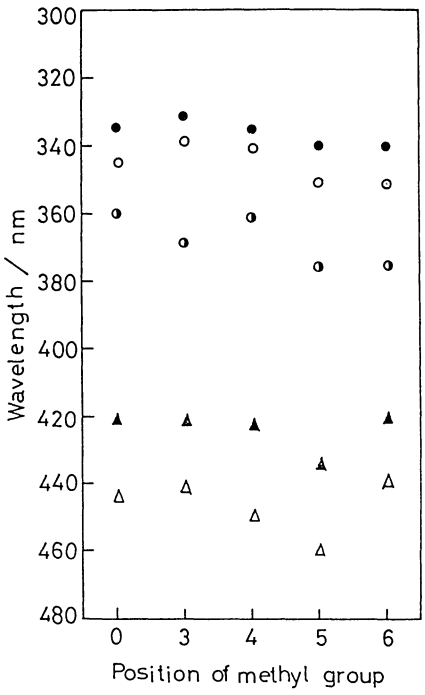


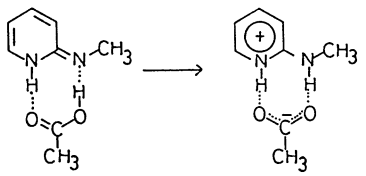
Fig. 4. Plots of the wavelengths of the absorption shoulder bands of the methyl-substituted 2-aminopyridine–acetic acid systems (●), those of the absorption band maxima of methyl-substituted 1-methyl-2(1*H*)-pyridinimines (○), those of the fluorescence band maxima near 390 nm of the methyl-substituted 2-aminopyridine–acetic acid systems (◑), those of the fluorescence band maxima near 465 nm of the methyl-substituted 2-aminopyridine–acetic acid systems (▲), and those of fluorescence band maxima of methyl-substituted 1-methyl-2(1*H*)-pyridinimines (△) vs. the position of methyl group. The zero position corresponds to the 2-aminopyridine–acetic acid system or 1-methyl-2(1*H*)-pyridinimine. The plot ◑ at the zero position is due to the fluorescence band maximum of the pyridinium form of the 2-aminopyridine–acetic acid system.

Table 1. Fluorescence Quantum Yields (ϕ_f) of 2-Methylaminopyridine, 2-Aminopyridine, and Unsubstituted and Monomethyl-Substituted 1-Methyl-2(1*H*)-pyridinimines in Isooctane at Room Temperature

Compound	ϕ_f
2-Methylaminopyridine	$(4.0\pm0.4)\times10^{-2}$
2-Aminopyridine	$(4.3\pm0.4)\times10^{-2}$
1-Methyl-2(1*H*)-pyridinimine	$(3.7\pm0.9)\times10^{-5}$
1-Methyl-2-methylimino-1,2-dihydropyridine	$(3.6\pm0.9)\times10^{-5}$
1,3-Dimethyl-2(1*H*)-pyridinimine	$(1.2\pm0.3)\times10^{-5}$
1,4-Dimethyl-2(1*H*)-pyridinimine	$(7.2\pm1.8)\times10^{-6}$
1,5-Dimethyl-2(1*H*)-pyridinimine	$(9.1\pm2.3)\times10^{-6}$
1,6-Dimethyl-2(1*H*)-pyridinimine	$(9.6\pm2.4)\times10^{-6}$

sion peak was observed at 390 nm, as the acetic acid concentration increased. In Fig. 2, a clear isoemissive point is observed at 448 nm in the fluorescence spectra. The emission near 465 nm has a band progression of ca. 1400 cm^{-1}, while that near 390 nm is a broad band. In order to ascertain an experimental interpretation of the emission bands at 465 and 390 nm, the fluorescence spectra of 1-methy-2(1*H*)-pyridinimine and 1-methyl-2-methylimino-1,2-dihydropyridine as the imino-form model of the 2-methylaminopyridine-acetic acid system were measured. As is shown in Fig. 3, emission peaks having a band progression of ca. 1400 cm^{-1} were observed at 442 and 490 nm, respectively. From the similarity of the band progression and position, the new emission band of the 2-methylaminopyridine-acetic acid system at 465 nm may be considered to correspond to the fluorescence band of the 2-methylimino-1,2-dihydropyridine-acetic acid complex (tautomer) formed through the hydrogen-bond formation of 2-methylaminopyridine with an acetic acid. The fluorescence band of the tautomer at 465 nm can be clearly observed by excitation in the region of the absorption shoulder band near 350 nm.

On the other hand, the fluorescence of 2-methylaminopyridine in 0.1 mol dm^{-3} hydrochloric acid was observed at 388 nm. The observed band of 388 nm of 2-methylaminopyridine in the acidic solution is in fair correspondence with that of 390 nm of the 2-methylaminopyridine–acetic acid system. Accordingly, the fluorescence band at 390 nm may be assigned to the 2-methylaminopyridinium produced from the tautomer in the excited states, as is shown in Eq. 2.



(2)

Both of the emission bands near 465 and 390 nm were observed for the 2-aminopyridine-acetic acid[3] and its methyl derivative–acetic acid systems. The wavelengths of the emission band maxima near 465 nm of the methyl-substituted 2-aminopyridine-acetic acid systems are compared with those ones of the fluorescence band maxima of methyl-substituted 1-methyl-2(1*H*)-pyridinimines, as given in Fig. 4. The former is closely related to the latter. Therefore, the fluorescence band near 465 nm of the methyl derivative–acetic acid systems are due to the imino-forms. On the other hand, the fluorescence bands corresponding to 390 nm for the methyl-substituted derivative–acetic acid systems would be due to the aminopyridinium already described above.

The fluorescence quantum yields (ϕ_f) of 1-methyl-2(1*H*)-pyridinimines in isooctane at room temperature are given in Table 1, with those of 2-methylaminopyridine and 2-aminopyridine. It is noted that the ϕ_f's of the pyridinimines are smaller than those of 2-methylaminopyridine and 2-aminopyridine. This result suggests that the fluorescence quantum yields of imino-form of 2-aminopyridines may be appreciably smaller than those of the amino-forms.

Experimental

Commercial 2-methylaminopyridine (Aldrich) was purified by repeated silica-gel column chromatography using ether as an eluent. 1-Methyl-2(1*H*)-pyridinimine and its methyl substituted derivatives were prepared according to a procedure of Taylar et al.[6] These compounds were purified by alumina column chromatography using isooctane as an eluent. The purification of 2-aminopyridine and its methyl derivatives, isooctane, and acetic acid has been described in the literature.[1,3] The UV absorption and fluorescence spectra were measured with Hitachi model 3410 and F-4010 spectrophotometers, respectively. The fluorescence quantum yields were normalized to a value of 0.006[7] for 1-methyl-2-pyridone in alcohol (ethanol containing 10% methanol) mixture.

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