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Luminescence of Aminopyridines and Related Molecules

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Synopsis. Quantum yields and lifetimes of fluorescence and phosphorescence were measured for 2-, 3-, 4-aminopyridines, 2-, and 4-(dimethylamino)pyridines in ethanol–methanol, in an acidic ethanol–methanol mixture, and in a mixture of triethylamine and 2-methyltetrahydrofuran at 300 K and at 77 K. Quantum yields of fluorescence of 2- and 3-substituted pyridines are appreciable, while those of 4-substituted pyridines are as low as or less than 0.01 at 77 K. In view of the significant quantum yields of fluorescence for 2- and 3-substituted pyridines in the aprotic solvent, it may be concluded that the higher excited $^1(n\pi^*)$ or $^3(n\pi^*)$ states are not so close in energy to the lowest excited $^1(\pi\pi^*)$ states.

Quantum yields of fluorescence (Φ_f) of aminopyridines measured by Weisstuch and Testa[1] at room temperature suggest that the lowest excited singlet states (S_1) of 2- and 3-aminopyridines are assigned to ($\pi\pi^*$), in contrast with that of 4-aminopyridine, which is assigned to ($n\pi^*$) in nonpolar solvents or to the charge transfer type ($\pi\pi^*$) in polar solvents. However, in view of the significant temperature dependence of Φ_f's for some nitrogen–heterocyclics,[2] measurements of Φ_f's and lifetimes of fluorescence (τ_f) at low temperature are desirable.

Φ_f's, τ_f's, quantum yields (Φ_p), and lifetimes (τ_p) of phosphorescence for 2-, 3-, 4-aminopyridines, 2-, and 4-(dimethylamino)pyridines are summarized in Tables 1 and 2. Solvents used were ethanol–methanol (A), an acidic (0.05 M H_2SO_4) ethanol–methanol mixture (H^+), and a mixture of triethylamine and 2-methyltetrahydrofuran (B). The first absorption bands of 2- and 3-substituted pyridines correspond fairly well to their fluorescence bands, as judged by the mirror symmetry relationship to each other. S_1's and the lowest excited triplet states (T_1) of 2- and 3-substituted pyridines are assigned unambiguously to ($\pi\pi^*$) from Φ_f's and τ_p's in Table 1. The rate constants of the radiative transition (k_f) from S_1 are fairly independent of temperature and of protonation, while those of the radiationless deactivation (k_{nr}), which are composed of the rate constants of the internal conversion and the intersystem crossing from S_1, depend significantly on temperature and on protonation. If it is presumed that the k_f's are constant irrespective of the presence or absence of protons in solvents, then k_{nr}'s are estimated from Φ_f's without the observed τ_f's. k_{nr}'s at 77 K, designated in parentheses in Table 1, are calculated on this assumption, and those at 300 K on the assumption of the temperature-independent k_f's. As the Φ_p's of 2- and 3-substituted pyridinium cations used in this work are as low as or less than 0.01 at 77 K, their k_{nr}'s correspond

TABLE 1. QUANTUM YIELDS AND LIFETIMES OF FLUORESCENCE AND PHOSPHORESCENCE FOR 2-, 3-AMINOPYRIDINES, AND 2-(DIMETHYLAMINO)PYRIDINE

	$\lambda_{f\,max}$ (nm)	Φ_f	τ_f (ns)	$k_f\times10^{-7}$ (s^{-1})	$k_{nr}\times10^{-7}$ (s^{-1})	$\lambda_{p\,max}$ (nm)	Φ_p	τ_p (s)
300 K								
2AMP(H^+)	366	0.63	14.8	4.3	2.5			
(A)	348	0.28			(12)			
(B)	338	0.06			(70)			
2DMAMP(H^+)		<0.01						
(A)	370	0.36	12.2	3.0	5.3			
(B)	351	0.23			(11)			
3AMP(H^+)	402	0.44	18.8	2.3	3.0			
(A)	352	0.24			(10)			
(B)	344	0.06			(52)			
77 K								
2AMP(H^+)	349	0.71	16.2	4.4	1.8	482	<0.01	1.8
(A)	346	0.52	11.7	4.4	4.1	441	0.10	2.0
(B)	341	0.35			(8)	435	0.19	1.4
2DMAMP(H^+)	389	0.47	15.0	3.1	3.5	472	<0.01	1.4
(A)	355	0.44	13.6	3.2	4.1	441	0.16	1.7
(B)	346	0.29			(8)	431	0.18	1.1
3AMP(H^+)	377	0.70	20.5	3.4	1.5	452	<0.01	1.3
(A)	352	0.54	16.3	3.3	2.8	465	0.33	3.0
(B)	344	0.15			(19)	442	0.41	2.7

2AMP, 3AMP, and 2DMAMP represent 2-, 3-aminopyridines, and 2-(dimethylamino)pyridine, respectively.
k_f's and k_{nr}'s are deduced from the following equations: $k_f=\Phi_f/\tau_f$ and $k_{nr}=(1-\Phi_f)/\tau_f$.

Table 2. Quantum yields and lifetimes of phosphorescence for 4-aminopyridine and 4-(dimethylamino)pyridine at 77 K

	$\lambda_{p\,max}$ (nm)	Φ_p	τ_p (s)
4AMP(H^+)	359	0.45	2.0
(A)	359	0.51	1.9
(B)	373	0.32	0.7
4DMAMP(H^+)	401	0.12	1.6
(A)	392	0.42	1.6
(B)	388	0.24	0.5

approximately to the rate constants of the internal conversion from S_1. However, the estimated k_{nr}'s in an aprotic solvent at 77 K are fairly large, and suggest a significant contribution of the rate constants of the intersystem crossing from S_1, in view of decrease in Φ_f's and the corresponding increase in Φ_p's. An increase in k_{nr}'s for 2- and 3-aminopyridines in the aprotic solvent at 300 K may arise from the temperature dependence of the rate constants of the intersystem crossing[3] as well as those of the internal conversion, in marked contrast with the almost temperature-independent k_{nr} of 2-(dimethylamino)pyridine in the same solvent. However, the fairly large k_{nr} for a 2-(dimethylamino)pyridinium cation might be deduced from the scarcely observed Φ_f at 300 K, which is quite opposed to the change in Φ_f's found in 2- and 3-aminopyridinium cations. In view of the large Φ_f's even in the aprotic solvent at 77 K, the singlet or triplet ($n\pi^*$) states of 2- and 3-substituted pyridines are not so close in energy to the S_1's.

The Φ_f's of 4-substituted pyridines are smaller than 0.01 at 77 K, irrespective of the solvents used in this work. The phosphorescence spectra of 4-aminopyridine show vibrational structures, in which a characteristic vibration at 850 cm^{-1}, indicative of the C–H out-of-plane deformation mode of aromatic rings, may be found, while those of 4-(dimethylamino)pyridine are without vibrational structures.[4] As is summarized in Table 2, the large Φ_p's and the long τ_p's suggest that the T_1's of 4-substituted pyridines are ($\pi\pi^*$) irrespective of solvents used. The small Φ_f's of 4-substituted pyridines in the aprotic and the acidic solvents at 77 K are consistent with the assignment of S_1's proposed by Weisstuch and Testa.[1]

Experimental

2-, 3-, 4-Aminopyridines, and 4-(dimethylamino)pyridine were recrystallized three times from ethanol-ligroin, then purified through a basic alumina column, and finally sublimed *in vacuo*. 2-(Dimethylamino)pyridine was distilled through a spinning band column, then purified through a basic alumina column, and finally distilled twice *in vacuo*. Triethylamine and 2-methyltetrahydrofuran were stored over sodium-potassium alloy after distillation through a stainless steel helices packed column, and used without exposure to air. The methods of purification of other solvents and reagents were described elsewhere.[5]

Measurements of Φ_f's, Φ_p's, τ_f's, and τ_p's were the same as those described elsewhere.[5] The concentrations used in the measurements of Φ_f's and Φ_p's and those of τ_f's and τ_p's were 10^{-2}—10^{-3} M and 10^{-4}—10^{-5} M, respectively. In the former case, the correction of concentration quenching, if necessary, was made by the use of the Stern-Volmer equation. All the samples were evacuated by the repeated cycles of freezing, pumping, and thawing. Then, the sample cells were sealed off from the evacuation system.

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