October, 1988] Bull. Chem. Soc. Jpn., 61, 3461—3466 (1988) 3461

Phosphorescence Properties of Pyridine and Its Methyl Derivatives in the Vapor Phase

Masayuki Suzuki, Masahisa Fujita, Takeshi Takemura,* and Hiroaki Baba
Division of Chemistry, Research Institute of Applied Electricity, Hokkaido University, Sapporo 060
(Received June 3, 1988)

The phosphorescence spectra, lifetimes, and quantum yields of pyridine and its methyl derivatives, 2-picoline, 3-picoline, and 2,6-lutidine in the vapor phase have been measured with the aid of a specially designed circuit by means of control of the voltage imposed on the photomultiplier. The phosphorescence spectrum shifts to shorter wavelengths with increasing methylation. The phosphorescence lifetimes and quantum yields of pyridine and the picolines are of the order of 1 μs and 10^{-7} both values being one order of magnitude smaller than the corresponding values for the lutidine. These observations are explained by assuming that (1) the lowest triplet state (T_1) and the next lowest triplet (T_2) are of $^3(\pi,\pi^*)$ and $^3(n,\pi^*)$ types respectively, (2) the energy gap between T_1 and T_2 is small, especially in the unsubstituted pyridine, and (3) the potential energy curve for T_1 is distorted according to the energy gap, as the result of a pseudo-Jahn-Teller type of interaction between T_1 and T_2.

The phosphorescence spectrum from the pyridine molecule was first observed in the vapor phase by the present authors in 1983.[1,2] The phosphorescence properties of pyridine vapor are as follows: (a) In spite of the high intersystem crossing quantum yield,[3] the phosphorescence quantum yield is as anomalously low as 10^{-6}; (b) the phosphorescence spectrum has an onset near 350 nm, which is similar in position to the one of the benzene phosphorescence, but shows an anomalously red-shifted intensity maximum near 450 nm; and (c) the phosphorescence lifetime is anomalously short (1.2 μs) compared with those for vapors of other azines such as pyrazine (63 μs) and pyrimidine (50 μs).

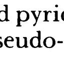
These anomalous characteristics of the phosphorescence of pyridine were attributed to strong vibronic coupling between the lowest triplet state (T_1) of $^3(\pi, \pi^*)$ type and a close-lying $^3(n, \pi^*)$ state which is assigned to the second lowest triplet state (T_2).[4,5] It was supposed that the coupling may be strong enough to give rise to a pseudo-Jahn-Teller type of interaction between the two states.[2,6,7] Such an interaction would cause distortion of the potential surface of the $T_1(\pi, \pi^*)$ state and enhance the radiationless decay from T_1,[8,9] resulting in the extremely weak phosphorescence of pyridine.

Weisman et al.[10,11] have reported recently the decay of the triplet-triplet absorption in pyridine vapor at various pressures and explained the nonradiative behavior of the triplet pyridine in terms of the strong pseudo-Jahn-Teller interaction between the $T_1(\pi,\pi^*)$ and $T_2(n, \pi^*)$ states.

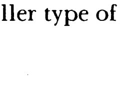
With pyridine in the vapor phase, the lowest triplet state, thus, is supposed to be of a (π, π^*) type. This assignment has received further supports from the experimental results of absorption measurements on pyridine.[12,13]

On the other hand, Schmidt et al.[14,15] have studied the lowest triplet state of pyridine in a single crystal of benzene by using electron-spin-echo spectroscopy, and reached the conclusion that the pyridine molecule is nonplanar in this state owing to the pseudo-Jahn-Teller coupling between the $T_1(n, \pi^*)$ state and a close-lying $^3(\pi, \pi^*)$ state. Thus, although the properties of the lowest triplet state of pyridine could be interpreted in terms of a pseudo-Jahn-Teller interaction, there is still a controversy about the character of the lowest triplet state.

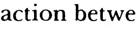
For understanding fully the phosphorescence properties of pyridine, we attempted in this study to investigate the changes of the phosphorescence properties caused by introduction of the methyl group into pyridine; that is, the phosphorescence and excitation spectra, phosphorescence lifetimes, and quantum yields were measured for pyridine (**1**), 2-picoline (**2**), 3-picoline (**3**), and 2,6-lutidine (**4**) in the vapor phase.



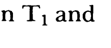
1



2



3



4

In order to obtain extremely weak phosphorescence emission of pyridine and its methyl derivatives, special care was directed to the purification of these compounds. Furthermore, a new circuit was employed which made it possible to measure time-resolved spectra in the microsecond or submicrosecond region of extremely weak emission by means of control of the voltage imposed on the photomultiplier; from now on this circuit will be called CVIPM circuit.

Experimental

Pyridine first treated after a method described in a previous paper[2] was purified by gas chromatography, and then distilled under reduced pressure. 2-Picoline, 3-picoline, and 2,6-lutidine were purified by fractional distillation under reduced pressure and were further purified by gas chromatography.

The optical experiments were carried out in the temperature range 0—40 °C and in the pressure range 2—20 Torr† with the sample vapor sealed into a 3.5 cm square quartz cell.

Absorption, emission, and excitation spectra were measured with a laser spectrophotometric system, which is essentially the same as the one described in a previous paper[16] except that a pulsed tunable dye laser (Lambda Physik FL 2002E) pumped by a XeCl excimer laser (Lambda Physik EMG 103 MSC) was used as the exciting light source in the present study. The frequency of the dye laser was doubled by a KDP crystal. The resulting UV laser pulses had an output energy of 1 mJ/pulse, a repetition rate of 20 pulses/s, a spectral bandwidth of 0.2 cm^{-1}, and a duration of 10 ns. The energy density of the pulsed UV laser beam was so high that the sample vapor was subject to chemical changes. Therefore, before reaching the sample cell, the laser beam was expanded in one direction by the use of a cylindrical lens.[17] The emission was dispersed by a Nikon G-250 monochromator and then detected by a Hamamatsu R106 photomultiplier.

Actually, the emission and excitation spectra were obtained in the form of time-resolved spectra by applying the CVIPM circuit to the laser spectrophotometric system. In the CVIPM circuit,[17] a part of the voltage imposed on the photomultiplier (PM) is pulsed so that the PM may operate (i.e., the PM may be sensitive to the incident light) only in a certain time range, e.g., 0.5—5 μs, after photoexcitation of the sample. Note that, with the present CVIPM circuit, the shorter limit of time is 0.5 μs. Under the ordinary conditions of the PM, owing to an after-effect of the irradiation of the PM by the fluorescence of pyridine, the lifetime of which is of the order of 10 ps, delayed output pulses emerge from the PM to yield a false delayed fluorescence with a lifetime of about 0.5 μs and a quantum yield comparable to that of the pyridine phosphorescence.[2] When the CVIPM circuit is used, such a delayed fluorescence does not occur. This is one of the advantages of the CVIPM circuit over the delay-and-gate circuit.[2] Thus, by measuring a time-resolved phosphorescence spectrum with the aid of the CVIPM circuit, one can eliminate the original and delayed fluorescence as well as the emissions from the cell and impurities.

Emission decays (or lifetimes) were measured by attaching a single photon counting lifetime apparatus,[16] equipped with a time-to-amplitude converter, to the laser spectrophotometric system. In this study, the delay-and-gate circuit[2] or the above-mentioned CVIPM circuit was applied to the original lifetime apparatus. For emission with a lifetime longer than 10 μs, the decay measurement was made by means of a phosphorimetric system using a circuit of a digital boxcar type.[18]

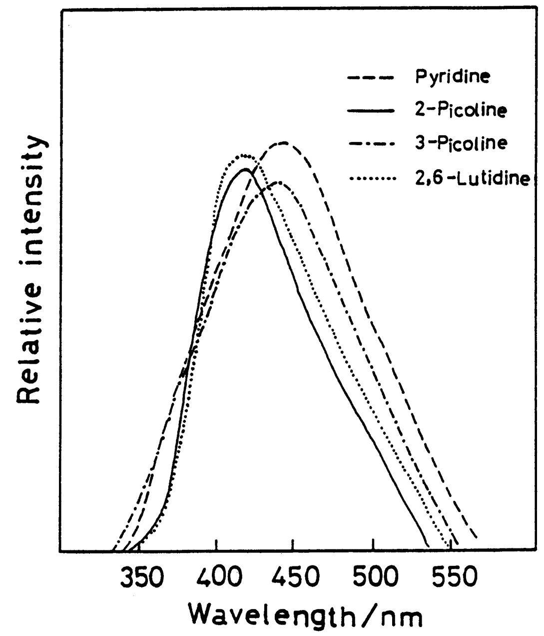


Fig. 1. Time-resolved phosphorescence spectra of pyridine and its methyl derivatives in the vapor phase. The spectra for 2 Torr of pyridine (----), 15 Torr of 2-picoline (——), and 8 Torr of 3-picoline (-·-·-) were obtained by excitation at the 0–0 band of the $S_1 \leftarrow S_0$ absorption and by observation in the time range 0.5—5 μs after pulse excitation; the spectrum for 8 Torr of 2,6-lutidine (------) was obtained by excitation at 285 nm near the onset of the $S_1 \leftarrow S_0$ absorption and by observation in the range 0.5—40 μs. The emission bandwidth is 6 nm in every case.

Table 1. Phosphorescence Characteristics of Pyridine and Its Methyl Derivatives in the Vapor Phase

Compound	$\lambda^{\mathrm{P}}_{\max}$ / nm	τ_{P} / μs	Φ_{P}
Pyridine	450	1.2	4.4×10^{-7}
2-Picoline	420	4.2	2.4×10^{-7}
3-Picoline	430	1.4	
2,6-Lutidine	415	37	2.0×10^{-6}

Results

Phosphorescence and Excitation Spectra. Figure 1 shows time-resolved phosphorescence spectra of pyridine and its methyl derivatives. These spectra were obtained with 6 nm emission bandwidth in the time range 0.5—5 μs for pyridine and the picolines and in the range 0.5—40 μs for 2,6-lutidine. The excitation of the sample vapors was carried out at the 0-0 band of the $S_1 \leftarrow S_0$ absorption for all compounds except 2,6-lutidine. With 2,6-lutidine, since the 0-0 band is not resolved, the excitation was carried out at 285 nm near the onset of the absorption.[3] The phosphorescence spectra have onsets near 350 nm for all the compounds concerned, but the intensity maximum is shifted to the blue with the increase in number of the methyl groups: The wavelengths of the phosphorescence maxima, $\lambda^{\mathrm{P}}_{\max}$ are 450 nm for the unsubstituted pyridine, 420 and 430 nm for the monomethyl derivatives 2-picoline and 3-picoline, respectively, and 415 nm for the dimethyl derivative 2,6-lutidine. These values of $\lambda^{\mathrm{P}}_{\max}$ are given in Table 1.

It should be noted here that the phosphorescence spectra of all the compounds concerned remain essentially unchanged in position and in shape upon changing the excitation wavelength and the sample vapor pressure.

---

† 1 Torr≈133.322 Pa.

It was already shown that the absorption and time-resolved phosphorescence-excitation spectra for pyridine agree reasonably well with each other.[1,2] In Figs. 2 and 3 are shown the absorption and time-resolved phosphorescence-excitation spectra in the region near the 0–0 band of the S_1–S_0 transition of 2-picoline and 3-picoline, respectively. The excitation spectrum of each of the compounds agrees very well with the corresponding absorption. This confirms that the observed phosphorescence spectra are attributable to the ones originating from the picolines. For 2,6-lutidine vapor also, the absorption and time-resolved phosphorescence-excitation spectra were measured and found to be in agreement with each other, though both spectra were completely structureless.

Figure 4 shows the phosphorescence spectrum of 2,6-lutidine in a rigid glass of 2-methylpentane (2-MP) at 77 K, together with the same spectrum in the vapor phase for the sake of comparison. The onset of the spectrum in the rigid glass is not very different from the one in the vapor phase, but the spectral maximum is shifted to the blue by about 15 nm in passing from the vapor phase to the rigid glass.

Phosphorescence Lifetimes. Figure 5 shows the phosphorescence decay curves for pyridine, 2-picoline, 3-picoline, and 2,6-lutidine vapors. The decay measurements were carried out using the delay-and-gate circuit for pyridine and 2-picoline, the CVIPM circuit for 3-picoline, and the digital boxcar type of circuit for 2,6-lutidine. The observed lifetimes τ_P are given in Table 1. The lifetime seems to become longer with increasing number of the methyl groups; i.e., the values of τ_P are 1.2 μs for pyridine, 4.2 μs for 2-picoline, 1.4 μs for 3-picoline, and 37 μs for 2,6-lutidine.

Phosphorescence Quantum Yields. Since there is a

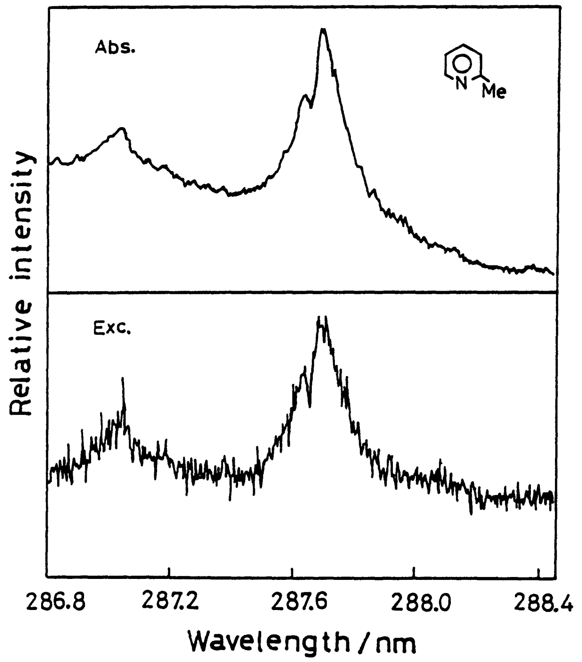


Fig. 2. Spectra near the 0–0 band of the $S_1 \leftarrow S_0$ absorption of 2-picoline vapor. (Abs.), absorption spectrum with the relative intensity representing the relative absorbance. (Exc.), time-resolved phosphorescence-excitation spectrum in the time range 0.5—5 μs after pulse excitation, obtained by monitoring the total emission.

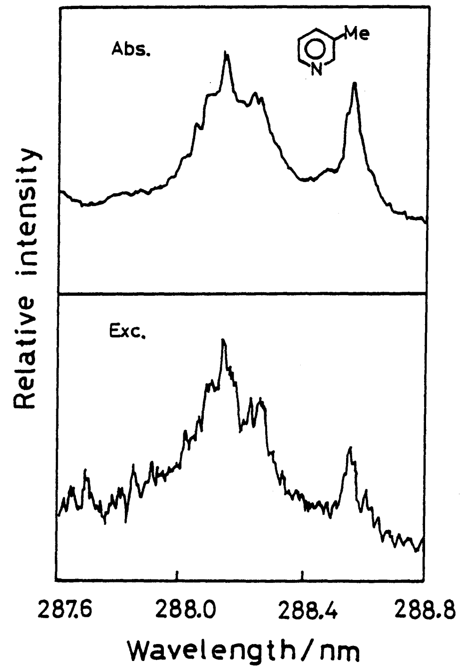


Fig. 3. Spectra near the 0–0 band of the $S_1 \leftarrow S_0$ absorption of 3-picoline vapor. (Abs.), absorption spectrum with the relative intensity representing the relative absorbance. (Exc.), time-resolved phosphorescence-excitation spectrum in the time range 0.5—5 μs after pulse excitation, obtained by monitoring the emission at 430 nm with 12 nm band width.

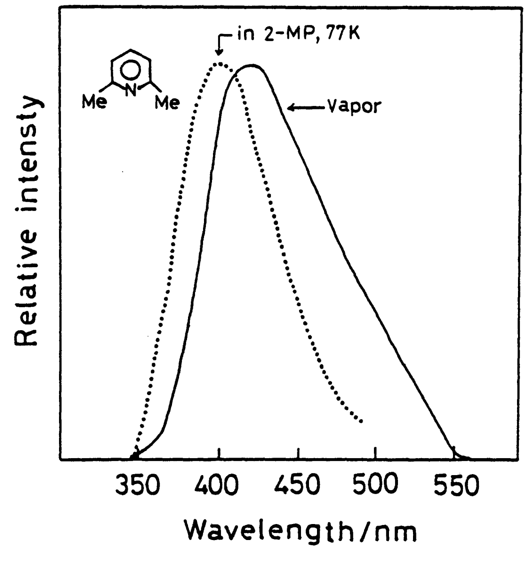


Fig. 4. Phosphorescence spectra of 2,6-lutidine in 2-methylpentane (2-MP) at 77 K and in the vapor phase. The vapor spectrum is the same as that in Fig. 1.

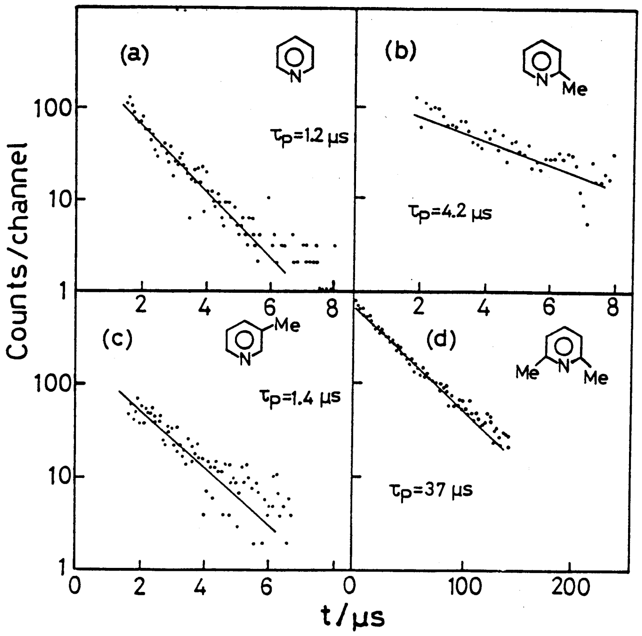


Fig. 5. Phosphorescence decays of pyridine and its methyl derivatives in the vapor phase obtained by monitoring the emission at the intensity maxima. (a) Pyridine; (b) 2-picoline; (c) 3-picoline; (d) 2,6-lutidine. For each compound, the excitation position is the same as that in Fig. 1.

little excitation-wavelength dependence of the fluorescence quantum yield for 2,6-lutidine compared with pyridine and picolines, the phosphorescence quantum yield (Φ_P) of 2,6-lutidine was first determined in the same way as that described in Ref. 2, by combining the known value of its fluorescence quantum yield (Φ_F) and the ratio of Φ_P to Φ_F. The resulting value of Φ_P for 2,6-lutidine along with the relative Φ_P values that were obtained for pyridine, 2-picoline, and 2,6-lutidine enabled us to determine the absolute values of Φ_P for pyridine and 2-picoline. In these experiments, to obtain desirable absorbance values, the pyridine vapor was cooled to 0 °C (pressure, 2 Torr), while the 2-picoline and 2,6-lutidine vapors were warmed to 40 °C (pressures, 15 and 8 Torr, respectively). The Φ_P values thus determined are shown in Table 1. It may be noted that Φ_P of pyridine given in Table 1 is about one third of that reported in our previous paper.[2]

Discussion

As is seen in Fig. 1, the phosphorescence spectra of pyridine and its methyl derivatives are similar in shape to each other. Further, it is seen from Fig. 4 that the phosphorescence spectrum of 2,6-lutidine vapor is also similar to the one in 2-MP at 77 K, which has been confirmed to originate from the $^3(\pi, \pi^*)$ state.[19] In addition, roughly speaking, all the spectra given in Figs. 1 and 4 are located in the same wavelength region. These observations suggest that the phosphorescent states for these four compounds, the unsubstituted, monomethyl-substituted, and dimethyl-substituted pyridines, are of $^3(\pi, \pi^*)$ type; in other words, T_1 is the $^3(\pi, \pi^*)$ state and T_2 is the $^3(n, \pi^*)$ in these pyridines.

The radiative phosphorescence lifetime ($\tau_\mathrm{P}^\mathrm{R}$) of a molecule is given by $\tau_\mathrm{P}^\mathrm{R}=\Phi_\mathrm{ISC}\tau_\mathrm{P}/\Phi_\mathrm{P}$, where Φ_ISC is the $S_1 \rightsquigarrow T$ intersystem crossing quantum yield. The experimental values of Φ_ISC are 0.30 and 0.6 for pyridine[20] and 2-picoline,[3] respectively. Although Φ_ISC for 2,6-lutidine has not been determined, one may tentatively assume it to be about 0.5. Then $\tau_\mathrm{P}^\mathrm{R}$ is 0.82 s for pyridine, 10 s for 2-picoline, and about 10 s for 2,6-lutidine. These values are one to two orders of magnitude larger than the values of $\tau_\mathrm{P}^\mathrm{R}$ for other azabenzenes the T_1 state of which is known to be of (n, π^*) character. In fact, $\tau_\mathrm{P}^\mathrm{R}\approx 70$ ms for pyrazine and pyrimidine in rigid-glass solution,[21] and $\tau_\mathrm{P}^\mathrm{R}=30$ ms for pyrazine vapor;[22] in any of these three cases, it has been established that T_1 is of $^3(n, \pi^*)$ type. Thus, the data concerning $\tau_\mathrm{P}^\mathrm{R}$ support the view described above that the T_1 states in pyridine and its derivatives under study are $^3(\pi, \pi^*)$ states.

It is known, on the other hand, that the excitation energies of singlet and triplet (π, π^*) states in aromatic compounds are generally lowered by methyl substitution. We then have to explain the reason why the methyl substitution shifts the pyridine phosphorescence, which has been assigned to $T_1(\pi, \pi^*) \rightarrow S_0$, toward the blue (see Table 1). We shall discuss this problem in terms of the pseudo-Jahn-Teller interaction which is likely to occur between the two nearby triplet states, $T_1(\pi, \pi^*)$ and $T_2(n, \pi^*)$.

If T_1 in pyridine is essentially of $^3(\pi, \pi^*)$ nature, it is to be assigned to ^3L_a in Platt's notation.[23] It is here desirable to know effects of the methyl substitution on the zero-order $^3L_a(\pi, \pi^*)$ state which is hypothetically supposed to be free from the pseudo-Jahn-Teller interaction. For aromatic hydrocarbons, there is correlation between molecular-size dependence of the energy of the ^1L_a state and that of the ^3L_a state. Thus, as the molecular size increases the ^1L_a-^3L_a interval monotonically decreases and approaches a limiting value; the interval seems to be primarily size-dependent and virtually structure-independent.[23]

In view of the above fact, we examined the effects of methyl substitution on the excitation energies of the

Table 2. Data on the Energies of the ^1L_a and ^3L_a states of Benzene and Its Methyl Derivatives

Compound	^1L_a		^3L_a	
	$\tilde{\nu}_\mathrm{max}$[a)]	ΔE	$\tilde{\nu}_\mathrm{0\text{-}0}$[b)]	ΔE
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
Benzene	49000	0	29500	0
Toluene	48100	−900	28900	−600
m-Xylene	47300	−1700	28700	−800

a) From absorption spectra in hexane. b) From phosphorescence spectra in cyclohexane at 77 K.

Table 3. Data on the Energies of the $^1(n,\pi^*)$, ^1L_a, and ^3L_a states of Pyridine and Its Methyl Derivatives in the Vapor Phase

Compound	$^1(n,\pi^*)$	^1L_a		^3L_a [c)]
	$\tilde{\nu}_{0\text{-}0}$ [a)]	$\tilde{\nu}_{max}$	ΔE	ΔE [d)]
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
Pyridine	34769	51900	0	0
2-Picoline	34753	50400	−1500	−1000
3-Picoline	34684	50400	−1500	−1000
2,6-Lutidine	35100 [b)]	49100	−2800	−1300

a) Taken from Ref. 3. b) The position at which the absorption intensity is comparable to that of the 0-0 band of the $^1(n,\pi^*)\leftarrow S_0$ absorption spectrum of 2-picoline; the same absorption spctrum of 2,6-lutidine is structureless. c) Zero-order state. b) Estimated energy shift.

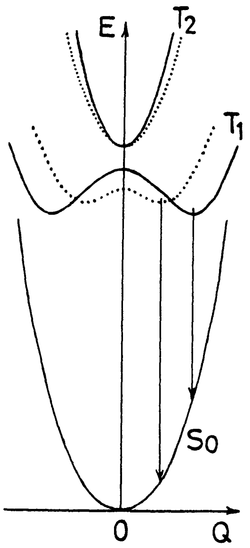


Fig. 6. Schematic potential energy curves resulting from the pseudo-Jahn-Teller interaction between T_1 and T_2: ——, pyridine; ……, 2,6-lutidine.

^1L_a and ^3L_a states of benzenes, i.e., the parent hydrocarbon of pyridine, to guess the energies of the zero-order ^3L_a states of the substituted pyridines. The results are summarized in Table 2, where ΔE denotes the energy shift caused by methyl substitution. In Table 3 are shown the observed excitation energies of the $^1(n, \pi^*)$ and ^1L_a states of pyridine and its mono- and dimethyl-derivatives. The values of ΔE for the zero-order ^3L_a states were estimated by comparing the data given in Tables 2 and 3; the results are also shown in Table 3.

As is seen in Table 3, on introducing the methyl group(s) into pyridine, the energy of the $^1(n, \pi^*)$ state remains almost unchanged. It may then be assumed that practically no change is produced in the $^3(n, \pi^*)$ state energy by the methyl substitution.

The $^3L_a(\pi, \pi^*)$ and $^3(n, \pi^*)$ states in pyridine (and also in 2,6-lutidine) belong to the irreducible representations A_1 and B_1 of the symmetry group C_{2v}, respectively, so that the vibronic coupling will be induced by a non-totally symmetric, out-of-plane bending vibration of b_1 symmetry, such as ν_{16b}.[11)] The potential energy curves distorted by the vibronic coupling of the pseudo-Jahn-Teller type are illustrated schematically in Fig. 6, with pyridine and 2,6-lutidine taken as examples. Here, Q represents the cordinate of the coupling vibrational mode. It is assumed that, especially in the case of pyridine, the coupling is so strong that the potential curve for the T_1 state takes the form of a distinct double minimum. The phosphorescence is considered to be emitted, with the highest probability, from the potential minimum that corresponds to a nonplanar structure of the molecule concerned. It should be noted that the energy of the zero-order ^3L_a state corresponds to the energy of T_1 at $Q=0$ in Fig. 6.

Inspection of Fig. 6 will reveal the following: The T_2-T_1 energy gap at $Q=0$ is larger and the energy of T_1 at $Q=0$ is lower, but the $T_1 \rightarrow S_0$ transition energy is larger, in 2,6-lutidine than in pyridine. The situation in 2- and 3-picolines may be understood in a similar way, though the molecular symmetry deviates from C_{2v} owing to the presence of the methyl group. Thus, the potential curve for T_1 (and also for T_2) of the picolines would become intermediate, with respect to the form and location, between the corresponding curves of pyridine and 2,6-lutidine. To sum up, the $T_1 \rightarrow S_0$ transition energy increases, and hence the phosphorescence spectrum shifts toward shorter wavelengths, in going from pyridine to 2- or 3-picoline and then to 2,6-lutidine, in general agreement with the experimental results.

The experimental results shown in Fig. 4 can also be explained by the same reasoning. On account of the general solvent effect, the $^3L_a(\pi, \pi^*)$ state energy (relative to the ground state energy) of 2,6-lutidine in the rigid glass is expected to be lower than that in the vapor phase. At the same time, however, this lowering of the state energy will give rise to an additional increase in the T_2-T_1 energy gap as measured at $Q=0$, so that little distortion will occur in the potential energy curve in the rigid glass. This explains the observation that the phosphorescence spectrum of 2,6-lutidine shifts further toward shorter wavelengths on changing the phase from the vapor to the rigid glass solution.

The observed phosphorescence lifetimes τ_P of pyridine and its derivatives, shown in Table 1, are only 10^{-6} times the radiative lifetimes τ_P^R mentioned previously. This means that in each case the rate constant for the decay of the phosphorescent triplet state, given by $1/\tau_P$, is practically equal to the rate constant for the nonradiative decay of that triplet state. In the case of pyridine, owing to the great distortion of the potential curve (Fig. 6), the frequency of the coupling vibration and the equilibrium nuclear configuration should be changed considerably on changing the electronic state from $T_1(\pi, \pi^*)$ to S_0.[6,9)] As a result, the vibrational factor[9)] for the $T_1 \rightsquigarrow S_0$ radiationless transition increases to reach an extent that $1/\tau_P$ for pyridine is exceptionally large, and hence Φ_P as well as τ_P is exceptionally small.[2] As has been mentioned, the methyl substitution will reduce the degree of the potential distortion, resulting in an increase in τ_P in conformity with the experimental results (Table 1). This is particularly true of 2,6-lutidine, the τ_P value of which is 30 times as large as that of pyridine.

In the foregoing descriptions, the triplet states T_1 and T_2 have been expressed simply as $T_1(\pi, \pi^*)$ and $T_2(n, \pi^*)$. However, owing to the vibronic coupling, the $^3(\pi, \pi^*)$ and $^3(n, \pi^*)$ states are to be mixed with each other. Actually, therefore, the T_1 state partly has the character of $^3(n, \pi^*)$. This accounts for the observation that the values of τ_P^R for the pyridines given in Table 1 are smaller than τ_P^R for aromatic hydrocarbons,[24] the T_1 state of which can be regarded as a pure $^3(\pi, \pi^*)$ state. Furthermore, since the vibronic coupling should be strongest in the unsubstituted pyridine, one may readily understand the fact that the value of τ_P^R is smallest in pyridine.

We should here refer to recent reports by Schmidt and his co-workers,[14,15] who performed an electron paramagnetic resonance study of the triplet state of pyridine present as a guest in a single crystal of benzene at 1.2 K by using electron-spin-echo spectroscopy. According to these authors, the lowest triplet state (T_1 in our notation) of pyridine is the $^3B_1(n, \pi^*)$ state considerably admixed with the close-lying $^3A_1(\pi, \pi^*)$ state, the lifetime of T_1 being of the order of 1 ms, and the pyridine molecule is nonplanar in T_1 owing to the pseudo-Jahn-Teller coupling between the two triplet states mentioned above. Obviously their assignment of T_1 as the $^3B_1(n, \pi^*)$ state disagrees with our assignment of T_1 in pyridine vapor as $^3A_1(\pi, \pi^*)$; the latter assignment is supported by some other authors.[10–13] We are here not in a position to explain the reasons for the disagreement between the two assignments. Probably, however, one of the reasons would be that there is a large difference between the experimental conditions adopted. We used pyridine vapor at room temperature for our phosphorescence study, while Schmidt et al. used pyridine in a crystal at 1.2 K for their magnetic resonance study. The relative positions of the close-lying $^3(\pi, \pi^*)$ and $^3(n, \pi^*)$ levels in question will vary, depending upon the environment in which the pyridine molecule is placed.

In connection with the above problem, mention should be made of a very recent theoretical study by Kitao and Nakatsuji.[25] These authors have applied the SAC (symmetry-adapted cluster) and SAC-CI theories to ab initio calculations of the valence excitations and ionizations of pyridine. The results of their calculations indicate that (1) the lowest triplet state of pyridine is the $^3A_1(\pi, \pi^*)$ state, and (2) the second lowest is the $^3B_1(n, \pi^*)$ state, which exists higher by 0.15 eV than the $^3A_1(\pi, \pi^*)$ state.

References

1) K. Sushida, M. Fujita, T. Takemura, and H. Baba, *J. Chem. Phys.*, **78**, 588 (1983).

2) K. Sushida, M. Fujita, T. Takemura, and H. Baba, *Chem. Phys.*, **88**, 221 (1984).

3) I. Yamazaki, K. Sushida, and H. Baba, *J. Chem. Phys.*, **71**, 381 (1979).

4) H. Baba and T. Takemura, *Bull. Chem. Soc. Jpn.*, **40**, 2215 (1967).

5) H. Baba, I. Yamazaki, and T. Takemura, *Spectrochim. Acta*, **27A**, 1271 (1971).

6) R. M. Hochstrasser and C. A. Marzzacco, "Molecular Luminescence," ed by E. C. Lim, Benjamin, New York (1969), p. 631.

7) A. J. Duben, L. Goodman, and M. Koyanagi, "Excited States," Vol. 1, ed by E. C. Lim, Academic Press, New York (1974), p. 295.

8) W. A. Wassam, Jr. and E. C. Lim, *J. Chem. Phys.*, **68**, 433 (1978).

9) E. C. Lim, "Excited States," Vol. 3, ed by E. C. Lim, Academic Press, New York (1977), p. 305.

10) R. B. Weisman, P. L. Holt, and J. I. Selco, *J. Chem. Phys.*, **77**, 1600 (1982).

11) J. I. Selco, P. L. Holt, and R. B. Weisman, *J. Chem. Phys.*, **79**, 3269 (1983).

12) D. F. Evans, *J. Chem. Soc.*, **1957**, 3885.

13) S. Japar and D. A. Ramsay, *J. Chem. Phys.*, **58**, 5832 (1973).

14) F. C. Bos, W. J. Buma, and J. Schmidt, *Chem. Phys. Lett.*, **117**, 203 (1985).

15) W. J. Buma, E. J. J. Groenen, and J. Schmidt, *Chem. Phys. Lett.*, **127**, 189 (1986).

16) H. Baba, M. Fujita, N. Ohta, and Y. Shindo, *J. Spectrosc. Soc. Jpn.*, **29**, 387 (1980).

17) M. Fujita, T. Takemura, and H. Baba, *Tech. Rep. Res. Inst. Appl. Elec. Hokkaido Univ.*, No 8, 1 (1987).

18) T. Takemura, K. Uchida, M. Fujita, Y. Shindo, N. Suzuki, and H. Baba, *Chem. Phys. Lett.*, **73**, 12 (1980).

19) A. G. Motten and A. L. Kwiram, *J. Chem. Phys.*, **75**, 2608 (1981).

20) K. Sushida, M. Fujita, I. Yamazaki, and H. Baba, *Bull. Chem. Soc. Jpn.*, **56**, 2228 (1983).

21) R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," Wiley-Interscience, New York (1969), p. 168; the values of Φ_{ISC} are assumed to be unity.

22) I. Yamazaki, M. Fujita, and H. Baba, *Chem. Phys.*, **57**, 431 (1981).

23) S. P. McGlynn, T. Azumi, and M. Kinishita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs (1969), Chap. 3.

24) S. K. Lower and M. A. El-Sayed, *Chem. Revs.*, **66**, 199 (1966).

25) O. Kitao and H. Nakatsuji, *J. Chem. Phys.*, in press (private communication).