

Effect of ring aza substitution on the luminescence of aromatic ketones. Luminescence of isomeric acetylpyridines

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Abstract. The absorption and luminescence characteristics of 2-, 3- and 4-acetyl-pyridines (ACP) and acetophenone have been examined in polar and nonpolar media at room temperature and low temperature (77 K). All the ACP exhibit intense and structured phosphorescence emission of $n\pi^*$ character. Though the triplet yields of these ketones are very high, the phosphorescence quantum yield and lifetime of ACP decrease significantly in the order 4-ACP > 3-ACP > 2-ACP > acetophenone. The distinctive differences in the spectral properties and the luminescence characteristics of ACP from their phenyl analogue have been interpreted in terms of the perturbing influences of the inductive effect of the pyridinic nitrogen, the vibronic interaction between the $n\pi^*$ and $\pi\pi^*$ states and the photochemical reaction occurring from the lowest triplet state.

Keywords. Isomeric acetylpyridines; absorption; emission; inductive effect; vibronic interaction; photochemical reaction; luminescence.

1. Introduction

The luminescence properties of many aromatic carbonyl compounds *viz* benzaldehyde, acetophenone, benzophenone and their derivatives have been extensively studied (Shimada and Goodman 1965; Takemura and Baba 1969; Olmsted and El-Sayed 1971; Cheng and Hirota 1974; Ghoshal *et al* 1981). Unlike their hydrocarbon counterparts the photophysical behaviours of this system are primarily determined by the relative energy positions of $n\pi^*$ and $\pi\pi^*$ states and the interaction between them in the singlet and triplet manifolds. It is also known that the radiative and nonradiative properties of aromatic molecules are markedly altered when a N-hetero atom is introduced in the phenyl ring of these molecules (Hotchandani and Testa 1973; Babiak and Testa 1976; Hotchandani and Testa 1977; Sarkar *et al* 1982a) because of the presence of additional $n\pi^*$ states arising from the non-bonding electrons of nitrogen atom in the singlet and triplet manifolds of the parent molecules. It is therefore surprising that except for a preliminary study on the location of the lowest triplet states (Arnold 1968), no attention has been given to a systematic study of the luminescence of the simple N-heterocyclic carbonyls. Moreover, though it is known that in suitable media many of the carbonyl compounds undergo photochemical reaction in their lowest $n\pi^*$ triplet states (Yang *et al* 1967; Arnold 1968; Turro 1978) no such investigation appears to have been made with their N-heterocyclic counterparts. The object of the present work is to study how the photophysical properties of the parent carbonyl molecules are modified with the introduction of a nitrogen atom in

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the phenyl nucleus of these molecules. With this in view, the absorption and luminescence characteristics of three isomeric pyridylketones (or acetylpyridines) in the vapour phase and in polar as well as nonpolar solvents at room temperature and low temperature (77 K) have been studied and compared with those of acetophenone reported earlier (Ghoshal *et al* 1981).

2. Experimental

2.1 Materials

All the isomeric acetylpyridines procured from Schuchardt, Munchen (Germany) were subjected to repeated fractional distillation under reduced pressure till no impurity could be detected with a flame ionization detector column (Hewlett-Packard, Model 5730A). Spectrograde solvents were further purified by fractional distillation. Freshly prepared and deoxygenated solutions of concentrations 10^{-4} – 10^{-5} M were used for recording all the spectra except for $T \leftarrow S_0$ absorption where solutions of higher concentration (*ca* 10^{-3} M) were employed.

2.2 Spectroscopic measurements

The solution and vapour phase absorption spectra at room temperature (300 K) were recorded with a Shimadzu 210A UV-VIS absorption spectrophotometer. Low temperature (77 K) emission, excitation and polarization spectra were obtained with a Perkin-Elmer model MPF 44A fluorescence spectrophotometer. The phosphorescence lifetimes were determined by using a Molecron UV-1000 N₂-Laser as the excitation source (337 nm) in conjunction with an EC storage oscilloscope. The energy in the laser beam was 3 mJ with a pulse duration of 5 nsec and a repetition frequency of 5/sec.

The triplet yields (Φ_T) of these acetylpyridines in methylcyclohexane were estimated following the method described by Favaro (1973). Assuming unitary triplet yield for benzophenone, the Φ_T values of the isomeric acetylpyridines were determined by their efficiency in sensitizing biacetyl phosphorescence.

3. Results

3.1 Absorption spectra and phosphorescence excitation spectra

Like acetophenone each of the three isomeric acetylpyridines (ACP) shows two systems of singlet $\pi\pi^*$ absorption bands corresponding to $^1L_a \leftarrow S_0$ and $^1L_b \leftarrow S_0$ transitions in the spectral region 200–300 nm in the vapour phase and in ethanol and *n*-hexane solutions at room temperature (figures 1 and 2). The phosphorescence excitation spectra of these compounds in *n*-hexane at 77 K reproduced in figure 3 also clearly display these two bands with their associated vibronic structures. A comparison of the absorption and excitation spectra of the acetylpyridine molecules with those of acetophenone reveals that: (i) While the 1L_b bands of acetophenone are sharp and structured, the corresponding bands in the ACP are broad and structureless. (ii) The band origins of this system in 2- and 3-ACP are located at frequencies higher than that of acetophenone and their intensities are significantly larger while in the 4-isomer the O,O band is shifted towards lower frequencies by a small amount. (iii) The 1L_a bands of all the ACP molecules, on the other hand, appear with markedly reduced intensity and are considerably blue shifted with respect to acetophenone. This shift is largest in the 4-isomer.

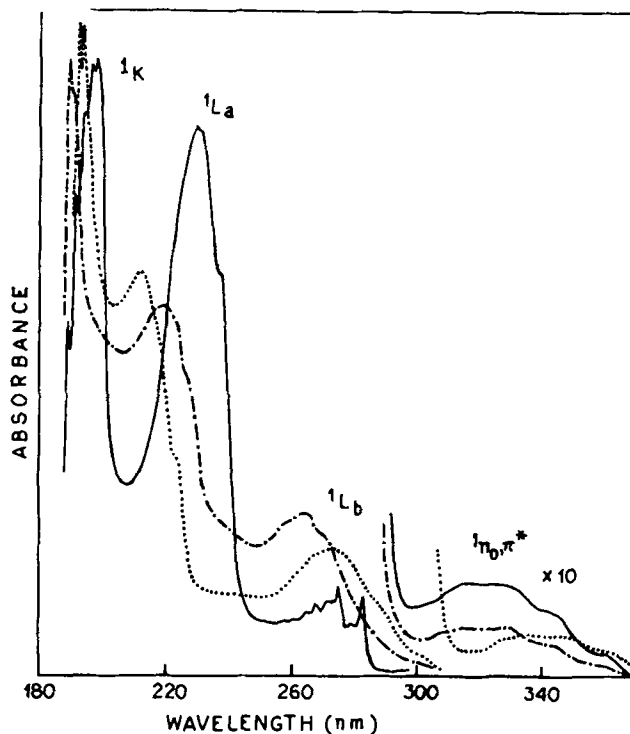


Figure 1. Vapour phase absorption spectra of acetophenone (—), 2-ACP (---) and 4-ACP (.....) at 330 K and 0.1 torr. ${}^1n_{\text{O}}, \pi^*$ corresponds to singlet-singlet $\pi^* \rightarrow n$ transition due to n electrons on carbonyl oxygen atom.

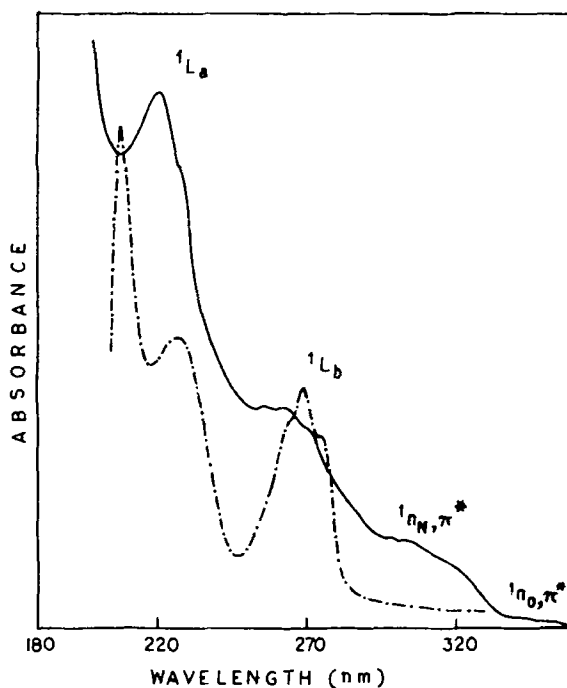


Figure 2. Absorption spectra of 3-ACP: (—) in vapor phase at 330 K and 0.1 torr; (---) in 1% HCl at 300 K. ${}^1n_{\text{N}}, \pi^*$ and ${}^1n_{\text{O}}, \pi^*$ correspond to singlet-singlet $\pi^* \rightarrow n$ transitions due to n electrons on the pyridinic nitrogen and carbonyl oxygen atom, respectively.

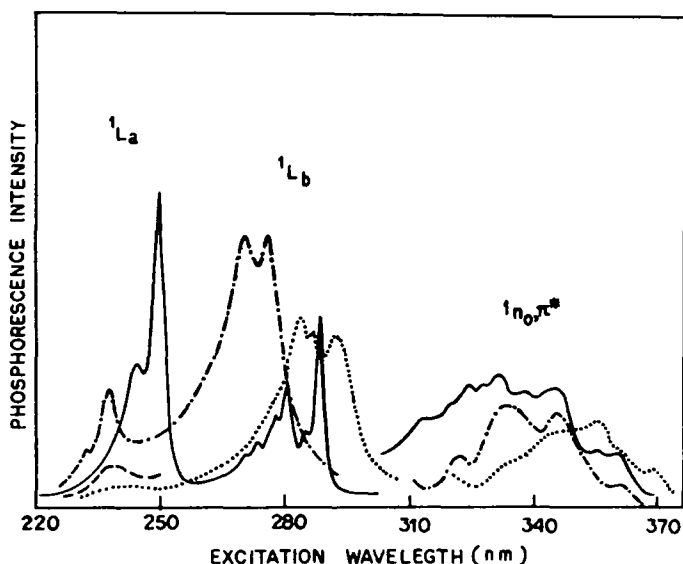


Figure 3. Phosphorescence excitation spectra of acetophenone (—), 2-ACP (---) and 4-ACP (....) in *n*-hexane at 77 K. Only a part of the spectrum corresponding to 3-ACP (---) is shown in the figure for the sake of clarity of the diagram. ${}^1n_0\pi^*$ corresponds to singlet-singlet $\pi^* \rightarrow n$ transition due to *n* electrons on carbonyl oxygen atom.

Besides these distinctive features of the $\pi\pi^*$ bands, the absorption spectrum of each of the ACP exhibits weak band system in the spectral region 300–370 nm as in acetophenone (figure 1). They are also evident from the excitation spectra (figure 3). By analogy these bands are attributed to transitions involving the *n*-electrons on the oxygen atom of the carbonyl group and have been designated as ${}^1n_0\pi^*$ bands. Comparison of the vapour phase absorption spectra of the ACP molecules with that of acetophenone (figure 1) reveals that there exists another region of absorption between the 1L_b and ${}^1n_0\pi^*$ band systems. Though these bands are not clearly separated because of the overlapping by the tail of the much stronger 1L_b bands, their occurrence can reasonably be inferred from the fact that in the same spectral region such absorption bands appear distinctly in the case of pyridylaldehydes which have also been studied in this laboratory. The relevant spectral data are shown in table 1.

In strongly hydrogen bonding and acidic media (*e.g.* 1% HCl in ethanol) both the weak absorption bands at the tail part of 1L_b bands and the more distinct ${}^1n_0\pi^*$ bands disappear completely as is seen from the spectra of 3-ACP (figure 2). It is also observed that in the absorption spectrum of acidic solution the 1L_b bands appear with more resolved vibronic structure presumably because of the disappearance of the overlapping $\pi\pi^*$ bands. This observation is similar to that reported in the case of pyridine and some of its derivatives (Sarkar *et al* 1982a). By comparison the weak absorption region has been associated with the singlet-singlet $\pi^* \rightarrow n$ transition due to the excitation of *n*-electrons on the pyridinic nitrogen atom and is henceforth referred to as ${}^1n_N\pi^*$ band to distinguish them from the ${}^1n_0\pi^*$ band. Unfortunately the ${}^1n_N\pi^*$ bands could not be detected in the phosphorescence excitation spectra of the acetylpyridine molecules.

In addition to the bands arising from the singlet-singlet transitions described above, the solution phase absorption spectra of all the isomeric acetylpyridines display weak

Table 1. Observed singlet $\pi\pi^*$ and $n_0\pi^*$ energy levels of acetophenone and acetylpyridines (ACP) and ${}^1n_0\pi^*$ energy levels of pyridinealdehydes (PAD) from room temperature absorption and 77 K phosphorescence excitation spectra.

Molecules	${}^1L_a (\pi\pi^*) \nu_{00}$ in cm^{-1}			${}^1L_b (\pi\pi^*) \nu_{00}$ in cm^{-1}			${}^1n_0\pi^* \nu_{00}$ in cm^{-1}			${}^1n_1\pi^* \nu_{00}$ in cm^{-1}		
	Vapour	EtOH	<i>n</i> -hexane	Vapour	EtOH	<i>n</i> -hexane	Vapour	EtOH	<i>n</i> -hexane	Molecules	Vapour	<i>n</i> -hexane
Aceto-phenone ^c	42997	41395 (39749)	42092 (39892)	35387	34712 (34532)	34954 (34675)	27886	31736 (28240)	27692 (27776)			
2-ACP	45647	43654 (42003)	44234 (42058)	36885	36286 (36051)	36485 (36194)	27769	31075 (27548)	27886 (27464)	2-PAD	33547	33888 (33774)
3-ACP	45337	43846 (41481)	44039 (41500)	36889	36415 (36345)	36485 (36352)	27784	31873 (27700)	27900 (27624)	3-PAD	33103	33323 (32885)
4-ACP	47154	45143	45234	34591	34109 (34160)	34203 (34178)	27720	—	27880 (27322)	4-PAD	—	32885 (32777)

^aFigures in paranthesis indicate the positions of the band origins of the respective transitions as determined from phosphorescence excitation spectra at 77 K

^bStudied in the present investigation.

^cFrom Ghoshal *et al* 1981.

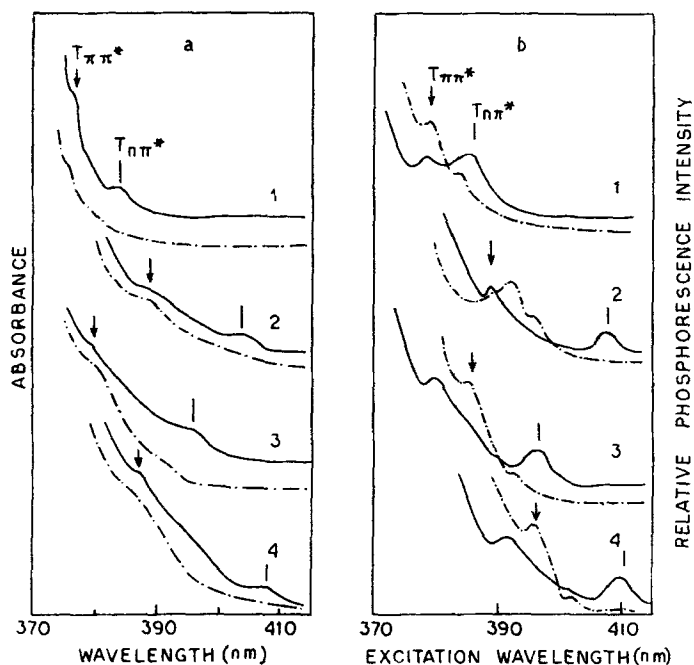


Figure 4. Singlet-triplet absorption and phosphorescence excitation spectra of acetophenone (1), 2-ACP (2), 3-ACP (3) and 4-ACP (4) in *n*-hexane (—) and ethanol (---). **a.** Absorption at 300 K. **b.** Excitation at 77 K.

Table 2. Observed triplet $\pi\pi^*$ and $n_0\pi^*$ energy levels of acetophenone and acetylpyridines (ACP) from room temperature absorption and 77 K phosphorescence excitation and emission spectra^a

Molecules	Absorption				Phosphorescence			
	$^3\pi\pi^*$	ν_{00} in cm^{-1}	$^3n_0\pi^*$	ν_{00} in cm^{-1}	$^3n_0\pi^*$	ν_{00} in cm^{-1}	$\Delta E(^3\pi\pi^* - ^3n_0\pi^*)^c$ in cm^{-1}	
	EtOH	<i>n</i> -hexane	EtOH	<i>n</i> -hexane	EtOH	<i>n</i> -hexane	EtOH	<i>n</i> -hexane
Acetophenone ^b	26510 (26377)	26517 (26383)	— (26034)	26000 (25933)	26007	25819	360	507
2-ACP	25600 (25470)	25666 (25568)	— (25213)	24745 (24502)	24899	24538	414	1048
3-ACP	26308 (25966)	26329 (26200)	— (25438)	25245 (25181)	25633	24899	430	1160
4-ACP	25765 (25245)	25799 (25568)	— (24868)	24502 (24383)	24654	24235	484	1259

^aFigures in parenthesis indicate the positions of band origins of the respective transitions as determined from phosphorescence excitation spectra at 77 K.

^bFrom Ghoshal *et al* 1981.

^cIndicates average of the values of $^3n_0\pi^*$ energy positions obtained from the position of band origins in the phosphorescence excitation and emission spectra.

bands in the spectral region 370–410 nm. Inspection of the spectra (figure 4a) reveals, that as in acetophenone, each of the ACP exhibits a weak but distinct band and a barely resolved band to the higher energy side of the former. These bands are more distinctly observed in the excitation spectra shown in figure 4b. In analogy with acetophenone (Ghoshal *et al* 1981) and on the basis of the spectral positions and solvatochromic effects the lower and higher energy bands are assigned to triplet singlet π^*-n_0 and $\pi^*-\pi$ transitions respectively. In neither of the room temperature absorption nor 77 K phosphorescence excitation spectra could the bands due to ${}^3n_N\pi^* \leftarrow S_0$ transition be detected. However, their approximate energy positions have been inferred in the following way.

We have already shown that the energy positions of ${}^1n_N\pi^*$ states should be similar to that in 2-, 3- and 4- pyridinealdehydes, at least in hydrocarbon solvents at 77 K. Further, the singlet-triplet separations in some substituted pyridines is *ca* 2000 cm^{-1} . In cyanopyridines the position of ${}^3n_N\pi^*$ state is at about 28,000 cm^{-1} (Sarkar *et al* 1982a) and in 4-aminopyridine it is located at *ca* 29000 cm^{-1} (Sarkar *et al* 1982b). So the ${}^3n_N\pi^*$ state in the ACP is expected to lie between 31000-30000 cm^{-1} which is at least 3000 cm^{-1} above the respective ${}^3\pi\pi^*$ level in these substituted pyridine molecules. In ethanol solvents the ${}^3n_N\pi^*$ states will be shifted to higher energy region. Table 2 shows all the relevant experimental data.

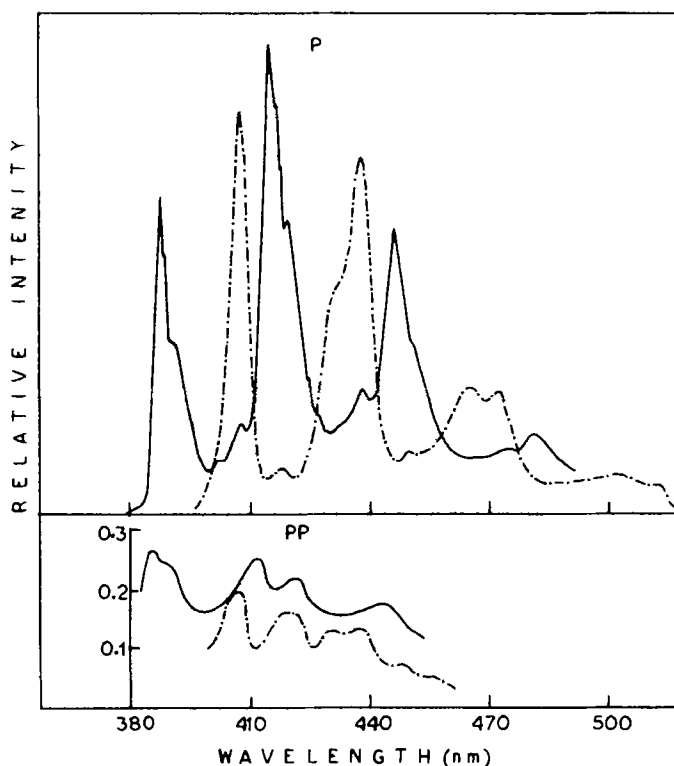


Figure 5. Phosphorescence (P) and phosphorescence polarization (PP) spectra of acetophenone (—) and 2-ACP (---) in 3-methylpentane glass at 77 K.

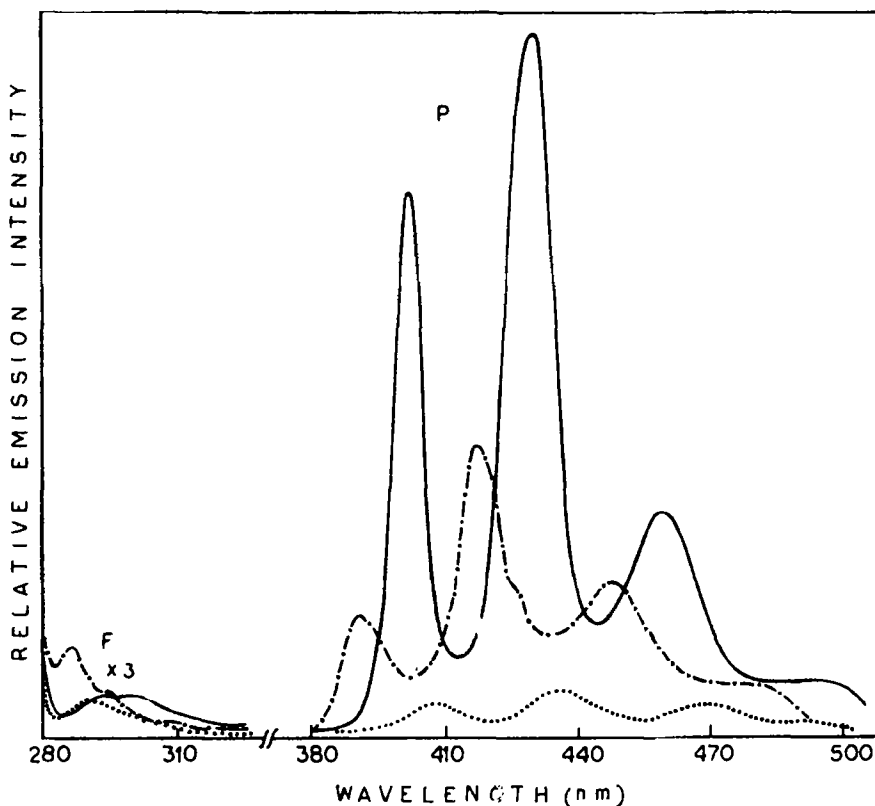


Figure 6. Fluorescence (F) and Phosphorescence (P) spectra of 2-ACP (—), 3-ACP (---) and 4-ACP (.....) in ethanol glass at 77 K.

3.2 Luminescence spectra

All the isomeric acetylpyridines exhibit fairly strong ketone like phosphorescence in rigid nonpolar and moderately polar glassy solvents at 77 K. Moreover, all of them are nonfluorescent in hydrocarbon solvent but emit a very weak fluorescence in protic media at low temperature. Despite close resemblance in the appearance of the phosphorescence spectra of the pyridylketones and acetophenone, several distinguishing features are revealed from careful examination of the spectra presented in figures 5 and 6.

- (i) In contrast to the moderately sharp and structured phosphorescence spectrum of acetophenone, the spectra of ACP are markedly broader and less structured. Also, these spectra are considerably red-shifted relative to acetophenone.
- (ii) The phosphorescence spectra of all the ACP exhibit a vibrational progression of carbonyl stretching frequency which is found to be reduced significantly in comparison with that of acetophenone.
- (iii) The phosphorescence intensity is observed to decrease in the order acetophenone > 2-ACP > 3-ACP > 4-ACP (figure 6).

As in acetophenone, the degree of phosphorescence polarization (P) for all the isomeric ACP in 3-methylpentane glass at 77 K is positive with respect to $^1L_a \leftarrow S_0$ excitation and this indicates a predominantly in-plane polarization of the phosphores-

Table 3. Measured phosphorescence yield (Φ_p) and lifetime (τ_p), triplet yield (Φ_T) and carbonyl stretching frequency ($\nu_{C=O}$) in the phosphorescence emission spectra of acetophenone and acetylpyridines (ACP) at 77 K

Molecules	τ_p (ms)		Φ_p		Φ_T		$\nu_{C=O}$ in cm^{-1}	
	EtOH	Methylcyclohexane	EtOH	Methylcyclohexane	Methylcyclohexane	EtOH	Methylcyclohexane	
Acetophenone ^d	5.0	2.5	0.6	0.65	0.90	1666	1710	
2-ACP	0.9	0.8	0.3	0.42	0.90	1657	1698	
3-ACP	0.7	0.6	0.16	0.24	0.85	1631	1666	
4-ACP	0.4	0.3	0.04	0.06	0.80	1605	1617	

From Ghoshal *et al* (1981)

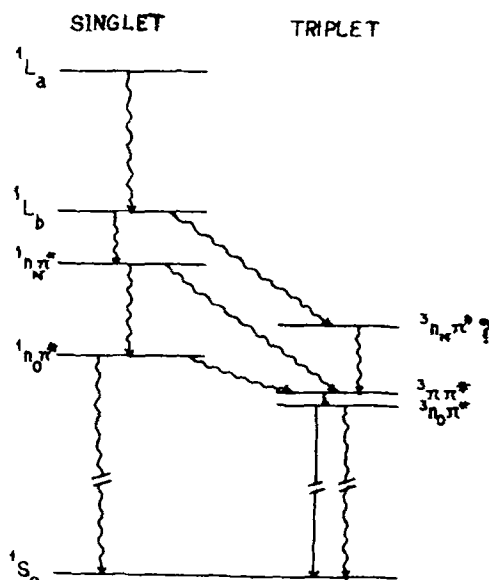


Figure 7. Schematic energy level diagram and probable radiative and nonradiative processes of acetylpyridines. Radiative and nonradiative transitions are shown by the vertical solid line and wavy curves respectively.

cence emission from these compounds. Further, the (P) value outside the band origin shows significant alteration (figure 5), which is attributable to the occurrence of a nontotally symmetric out-of-plane vibronic activity arising from vibronic interaction between the closely spaced triplet states in these molecules.

It is also observed that the decay nature of the phosphorescence emissions from all the pyridyl ketones are almost nonexponential even in protic media in contrast to the markedly exponential nature observed in the case of acetophenone in such media (Ghoshal *et al* 1981). Further, the phosphorescence lifetimes (τ_p) of all the ACP are significantly shorter than that of acetophenone, the τ_p values are found to decrease in the order acetophenone > 2-ACP > 3-ACP > 4-ACP, which is parallel to the change in Φ_p -values. Incidentally, the triplet yields (Φ_T) of acetophenone and acetylpyridines in methylcyclohexane glass at 77 K (determined by the usual method) do not show large

variations. The luminescence data for all the ketones are presented in table 3.

The short phosphorescence lifetime, significant blue shifts of the phosphorescence bands in protic media, the vibrational structure and the predominantly in-plane polarization of the phosphorescence emission strongly suggest that the lowest triplet state in each of the pyridylketones is $n_0\pi^*$ in nature. The approximate energy level scheme and the various probable radiative and nonradiative processes may be sketched as in figure 7.

4. Discussion

The distinctive differences in the spectral properties of acetylpyridines and acetophenone and the observed trends in the luminescence characteristics among the isomers clearly point to the influence of the pyridinic nitrogen atom. Moreover, these perturbations are found to vary from one isomer to the other depending on the relative positions of the acetyl group and the pyridinic nitrogen atom.

4.1 Inductive effect

It is known that an electron withdrawing substituent stabilizes the $n\pi^*$ states of the carbonyls. If the pyridinic nitrogen atom is considered to be an electron withdrawing substituent, the energy positions of the singlet and triplet $n_0\pi^*$ states of the acetylpyridines will be lowered with respect to those of acetophenone. The observed bathochromic shifts (tables 1 and 2) are found to be consistent with that expected from the inductive effect of the pyridinic nitrogen atom. Moreover, the red shifts suffered by either the band origin of $^1n_0\pi^* \leftarrow S_0$ or $^3n_0\pi^* \leftarrow S_0$ transitions of the isomeric acetylpyridines are different for the different isomers.

4.2 Vibronic interaction

Pyridinic nitrogen atom manifests its influence somewhat indirectly. It is seen from table 1 that $^1L_b(\pi\pi^*)$ state in the ACP are fairly close to the inferred position of the $^1n_N\pi^*$ state in each of the molecules. It is known that such proximity of energy states of the same multiplicity gives rise to vibronic interactions between the two states and its magnitude depends on their energy separation. The noticeable broadening of the 1L_b bands observed in the absorption spectra (figure 1) and in the excitation spectra (figure 3) of the ACP relative to that of acetophenone is a clear indication of the occurrence of such vibronic interactions. This observation thereby points to the perturbation caused by the pyridinic N atom.

4.3 Conjugative effect

The conjugation effect of the strongly electron accepting acyl group leads to a large stabilization of the 1L_a and $^3L_a(\pi\pi^*)$ states of benzene. As a result the energy positions of these bands in acetophenone are lowered by *ca* 7130 and 2790 cm^{-1} respectively relative to the corresponding bands of benzene. In the ACP one of the CH groups has been replaced by the strongly electronegative nitrogen atom and this renders the migration of electrons towards the carbonyl group difficult. The aza substitution tends to counteract the effect of conjugation due to the acyl group, which leads to some destabilization of the $\pi\pi^*$ states of ACP relative to acetophenone. The large hypsochromic shifts of the 1L_a bands of the ACP with respect to that in acetophenone support this view (table 1).

The most interesting aspects of the effect of the pyridinic nitrogen atom are observed through the variations in phosphorescence quantum yields (Φ_p) and phosphorescence lifetime (τ_p) among the ACP isomers in comparison with those of acetophenone in ethanol glass and hydrocarbon matrices at 77 K. It is seen from table 3 that the efficiency of triplet formation (Φ_T) measured in methylcyclohexane (MCH) glass at 77 K is almost unity but this also shows a slowly decreasing tendency in the order acetophenone > 2-ACP > 3-ACP > 4-ACP. This implies that a very small part ($1 - \Phi_T$) of the primary excitation is lost through $S_1 \rightsquigarrow S_0$ nonradiative process in these pyridyl ketones. Indeed, we have observed that there is some vibronic interaction between the $^1\pi\pi^*$ (1L_b) and $^1nN\pi^*$ states of these ketones which favours nonradiative process. Our data also indicate that such interaction is greatest in the 4-isomer.

The large Φ_T -values in these aromatic ketones suggest that most of the primary excitation is transferred to the lowest triplet $n_0\pi^*$ state through the various internal conversion and inter-system crossing mechanisms. On the other hand, the gradually decreasing values of Φ_p in these molecules show that a large part of this triplet excitation is lost through various deactivation processes. This is reflected in the large reduction of the observed phosphorescence lifetimes of the pyridyl ketones as compared to acetophenone. Of the various deactivation mechanisms the two probable nonradiative processes, (i) vibronic interactions and (ii) possibility of photochemical reaction in the triplet $n_0\pi^*$ state, are considered to be important.

From the 'proximity effect' on radiationless transition (Wassam and Lim 1978) it is known that distortion of the potential surface of the lowest emitting triplet state due to vibronic interaction with a close lying upper triplet level favours nonradiative transitions. The magnitude of the interaction depends on the proximity of the two interacting states and as a result of vibronic mixing the lower state acquires some of the characteristics of the upper state. A perusal of the data given in table 2 shows that in each of the pyridyl ketones the energy separation between the $^3\pi\pi^*$ and $^3n_0\pi^*$ states in hydrocarbon matrices is more than twice as large as in ethanol glass while the observed phosphorescence lifetime (τ_T) in the former is slightly smaller than in the latter. This is in contrast to what is obtained with acetophenone where the value of τ_p in methylcyclohexane is only half the value in ethanol glass though the energy separation in the former is *ca* 1.5 times more than in the latter. The large energy separation between the two interacting $^3\pi\pi^*$ and $^3n_0\pi^*$ states of the acetylpyridines in *n*-hexane would lead to very little vibronic interaction and therefore to little mixing of the two states. As a result the $^3n_0\pi^*$ state would be expected to retain its pure $n_0\pi^*$ character and the lifetime would be appropriate for this state. Hence the vibronic interaction may not be mainly responsible for the decrease in the τ_p values of the acetyl pyridines, particularly for the 3- and 4- isomers.

It is seen from table 3 that both the Φ_T and τ_p values of acetophenone are considerably reduced with the introduction of a N-atom in the phenyl ring of the aromatic ketone and this reduction becomes more and more pronounced as one moves from 2-ACP to 4-ACP. It is quite reasonable that the observed decrease in the Φ_p and τ_p values is due to the effect of the pyridinic N-atom. The possibilities by which the N-atom may produce the observed modifications mainly arise from the vibronic interactions between the $^3nN\pi^*$ state and the lowest energy $^3n_0\pi^*$ state and/or from photochemical reactions occurring in the $^3n_0\pi^*$ state. We have already seen that the $^3nN\pi^*$ states are at least 3000 cm^{-1} above the $^3\pi\pi^*$ states in the pyridylketones and therefore, are less likely to produce the large decrease in τ_p -values by enhancing the nonradiative rate through vibronic interaction.

The possibility of photochemical reactions in the triplet $n_0\pi^*$ state is now considered to account for the large reductions in the Φ_p - and τ_p -values of the 3- and 4-acetylpyridines. During the measurement of phosphorescence lifetimes of the ketones in ethanol and methylcyclohexane rigid matrices at 77 K by the method described under experimental section, it was observed that in the case of acetophenone and 2-acetylpyridine neither the maximum of the phosphorescence signal nor its decay nature is altered to any appreciable extent during successive excitation flashes. In the case of 3-acetylpyridine, on the other hand, there was a measurable reduction in the maximum of phosphorescence signal after five successive flashes. With the 4-acetylpyridine this reduction was so large that during the second pulse the phosphorescence signal maximum was reduced to about one-half of the value observed with the first pulse and in the third pulse, the phosphorescence signal was barely detectable. In view of the known fact that in suitable solvents (*viz.* isopropyl alcohol) acetophenone photoreacts in the $^3n_0\pi^*$ state with the formation of pinacol (Arnold 1968; Turro 1978) the above observations may be rationalized by postulating that a part of the molecules excited to the $^3n_0\pi^*$ state of 3- and 4-ACP's is removed by photochemical reactions between the excited pyridyl ketone molecules and the solvent in which they are dispersed. The photoreaction rate in 3-ACP is larger than that in acetophenone and 2-acetylpyridine while in the 4-isomer the rate is the largest. The observed phosphorescence lifetime which is the reciprocal of the combined radiative, nonradiative and photochemical reaction rates would therefore decrease in the order 2-ACP > 3-ACP > 4-ACP among the pyridylketones as has been experimentally determined. This incidentally, would also account for the observed decrease of the experimental Φ_p -values of the pyridylketones and the order of their decrement. Though, it has not been possible to obtain quantitative values of the reaction rates from these observations, it seems probable that in the 3- and 4-ACP, the photoreaction rate constant would be comparable with the phosphorescence rate constant.

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