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# Phosphorescence Emission of 2,6-Diacetylpyridine: Role of *N*-Heteroatom and Effect of Hydrogen-Bonding

S. K. Sarkar† and T. Ganguly*
Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India

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The absorption, excitation, and luminescence spectra of 2,6-diacetylpyridine (DAP) and acetophenone (ACP) are investigated in nonpolar methylcyclohexane (MCH) and polar ethanol (EtOH) matrices at 300 K and 77 K. The emitting state of DAP is found to be the lowest triplet state of essentially nπ* nature. In the emitting lowest triplet nπ* states of DAP and ACP the carbonyl group is observed to be the chromophore. The comparative studies on the photophysical properties of DAP and ACP reveal that the introduction of a pyridinic nitrogen atom in the phenyl nucleus of ACP leads to large nonradiative transitions from the lowest $^3n_O\pi^*$ due to vibronic interaction between this state and the pyridinic $n_N\pi^*$ state. In the case of ACP a weak ππ* fluorescence, in addition to phosphorescence is observed in EtOH glass matrix at 77 K. On the other hand in EtOH no such fluorescence is detected for DAP. The phosphorescence decay profile of DAP in presence of EtOH is found to be of single exponential indicating emission from a particular excited electronic state. It is suggested that due to comparatively much weaker hydrogen-bonding interaction between DAP molecule and EtOH solvent both intersystem crossing and internal conversion rates are little affected.

Studies on the photophysical properties of pyridyl ketones and their parent carbonyl molecules in different solvents of varying polarity has been the subject of increasing interest.(1–5) The photophysical behaviors of these compounds are mainly governed by the relative energy positions of nπ* and ππ* states and the vibronic interaction between them in the singlet and triplet manifolds. It was demonstrated by several authors(6–9) that the radiative and nonradiative properties of aromatic compounds are markedly modified with the introduction of a nitrogen atom in the phenyl nucleus of these molecules. Moreover, interest in the characterization of the lowest emitting states of such type of molecules is always high.(10–16) Generally these compounds exhibit only phosphorescence in nonpolar rigid matrix. In polar solvent a weak fluorescence, in addition to phosphorescence, has been observed in a few cases. Even though a few works were done to assign unambigously the nature of the lowest triplet states of some pyridyl ketones, controversy in characterizing the nature of the emitting states still remains.

In the present paper our attention is directed to study the photophysical properties of 2,6-diacetylpyridine and to compar these properties with those of acetophenone which may be treated as a parent carbonyl compound of DAP. This investigation is done to reveal how the photophysical properties of the parent carbonyl compound are modified with the introduction of a pyridinic nitrogen atom. The DAP molecule having both acyl groups and an N-atom in the phenyl nucleus possesses biological importance.(17) The hydrogen-bonding nature in both ground and excited electronic states of pyridyl ketone molecule is expected to differ significantly from the parent aryl ketone due to the presence of pyridinic nitrogen atom in the former molecule. It is well-known that electron-withdrawing substituents generally decrease hydrogen-bonding ability both in the electronic ground and excited states. The pyridinic nitrogen atom can be considered as an electron-withdrawing substituent. It can also produce additional electronic excited states of nπ* character. The role of this heteroatom is thought to be of very much important in the mechanism of intermolecular hydrogen-bonding interaction particularly in the excited electronic states through which radiative and nonradiative processes of the excitational energy occur. Keeping this in view the absorption, excitation, and emission spectra, triplet lifetimes and polarization data of DAP and ACP are recorded both in nonpolar methylcyclohexane and polar protic ethanol rigid glass matrices at 77 K. In this paper the results are described.

## Experimental

2,6-Diacetylpyridine purchased from Aldrich Chemical Company (USA) was purified first by repeated crystallization and subsequently by zone refining. Acetophenone (EGA Chemie, West Germany) was purified by repeated fractional distillation till no impurity could be detected with a flame ionization detector column (Hewlett Packard, Model 5730A). Spectrograde ethanol, methylcyclohexane, and acetonitrile of E. Merck, West Germany were distilled under reduced pressure and tested for residual impurity phosphorescence emission at a sensitivity level at least one order of magnitude greater than that used for recording of the spectra of the compounds under investigation. Freshly prepared and deoxygenated solutions of concentration $10^{-4}$ M (1 M=1 mol dm$^{-3}$) were used for recording absorption and emission spectra. Emission, excitation, and polarization data were obtained with a Perkin-Elmer MPF 44A spectrophotometer equipped with a compensating spectral unit model ESU while absorption data were recorded with a Shimadzu UV-Vis spectrophotometer model 210A. Phosphorescence life-

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† Present address: Department of Physics, Vidyasager College, Calcutta 700006, India.

times were measured using ECIL 05769 10 MHZ oscilloscope in conjunction with the rotating can phosphorescence accessory. Phosphorescence quantum yields of DAP were determined relative to that of acetophenone.[18)]

## Results and Discussion

In nonpolar MCH and in polar protic solvent EtOH at 300 K both ACP and DAP are found to exhibit two systems of π-electronic absorption bands corresponding to $^1L_b \leftarrow S_0$ and $^1L_a \leftarrow S_0$ transitions in the wavelength regions of 300—260 and 250—220 nm, respectively (Table 1). The phosphorescence excitation spectra of both these molecules in MCH glassy matrix at 77 K clearly exhibit these two band systems (Fig. 1). Besides these ππ* bands the phosphorescence excitation spectrum of DAP displays a very weak band system in the spectral region of 320—380 nm as shown in Fig. 1. Such a band system in the same spectral region is also observed in the case of ACP (Fig. 1). By analogy this band system observed in the case of DAP may be designated as singlet $n_O\pi^*$ band arising due to transition involving the n-electrons on the oxygen atom of carbonyl group (the subscript "O" stands for oxygen atom). In the protic solvent EtOH these $^1n_O\pi^*$ bands are observed to be broadened (Fig. 1). It is noteworthy that in the case of DAP in which a pyridinic nitrogen atom is present, no band system associated with $^1\pi^* \leftarrow n_N$ transition due to the excitation of n-electrons on the *N*-heteroatom could be observed. Moreover, the band systems corresponding to $^3\pi^* \leftarrow \pi$ and $^3\pi^* \leftarrow n_O$ transitions could not be detected in the case of DAP, though such band systems were observed by Kastha et al.[18)] in the absorption and excitation spectra of ACP. It may be presumed that the very weak absorption and phosphorescence emission of DAP as compared to that of ACP prevent us from detecting such $^3n_O\pi^*$ and $^3\pi\pi^*$ bands. However, it may be assumed that the $^3n_O\pi^*$ and $^3\pi\pi^*$ states of DAP molecule lie nearly in the same energetic positions as observed in the case of ACP molecule.

When excited with 280 nm wavelength which corresponds to the $^1L_b \leftarrow S_0$ transition, both ACP and DAP exhibit fairly intense phosphorescence emission in MCH rigid glassy matrix at 77 K. The lack of fluorescence emission is observed from both the molecules in MCH matrix. The measured phosphorescence lifetimes ($\tau_p$) of ACP and DAP are found to be of 2.5 and 2 ms, respectively (Table 2). In polar protic EtOH glassy matrix large blue shifts of phosphores-

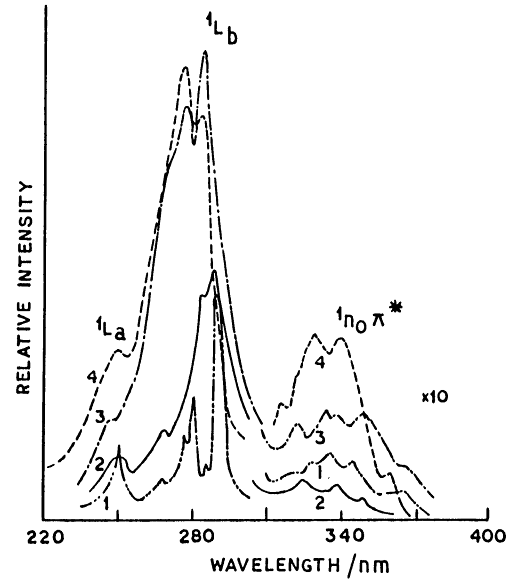

Fig. 1. Phosphorescence excitation spectra of ACP in MCH (1) and EtOH (2), and DAP in MCH (3) and in EtOH (4) at 77 K.

Table 1. Observed Singlet ππ* and $n_O\pi^*$ States and Triplet $n_O\pi^*$ States of ACP and DAP from Room Temperature Absorption and 77 K Phosphorescence Excitation and Emission Spectra in Different Solvents

| Molecules | $^1L_a(\pi\pi^*)$ $\nu_{00}$/cm$^{-1}$ | | $^1L_b(\pi\pi^*)$ $\nu_{00}$/cm$^{-1}$ | | $^1n_O\pi^*$ $\nu_{00}$/cm$^{-1}$ | | $^3n_O\pi^*$ $\nu_{00}$/cm$^{-1}$ | |
|---|---|---|---|---|---|---|---|---|
| | MCH | EtOH | MCH | EtOH | MCH | EtOH | MCH | EtOH |
| ACP | 42092[a)] | 41395 | 34954 | 34712 | 27692 | 28000 | 25819[c)] | 26007 |
| | (39892)[b)] | (39749) | (34675) | (34532) | (27776) | (28240) | | |
| DAP | 42735 | 42194 | 35398 | 35398 | 27313 | 27800 | 24420 | 24753 |
| | (40322) | (40000) | (35211) | (35211) | (27397) | (28011) | | |

a) From absorption spectra. b) From phosphorescence excitation spectra. c) From phosphorescence emission spectra.

Table 2. Measured Phosphorescence Quantum Yield ($\Phi_p$) and Lifetime ($\tau_p$), Derived Radiative Lifetime ($\tau_p^0$) and Phosphorescence Radiative ($k_p$) and Nonradiative ($k_{np}$) Rate Constants at 77 K

| Molecules | $\Phi_p$ | | $\tau_p$/ms | | $\tau_p^0$/ms | | $k_p$/s$^{-1}$ | | $k_{np}$/s$^{-1}$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | MCH | EtOH | MCH | EtOH | MCH | EtOH | MCH | EtOH | MCH | EtOH |
| ACP | 0.65 | 0.60 | 2.5 | 5 | 3.9 | 8.3 | 260 | 120 | 140 | 80 |
| DAP | 0.14 | 0.35 | 2 | 4 | 14.3 | 11.4 | 70 | 90 | 430 | 160 |

cence spectra of these molecules are observed and $\tau_p$ values are found to be increased by two folds (Table 2). In EtOH glass a very weak fluorescence emission band appears in the case of ACP[18] but DAP exhibits no detectable fluorescence emission in the same solvent. It was reported by several authors[18] that intersystem crossing (ISC) and internal conversion (IC) in some aromatic carbonyls are substantially decreased in hydrogen-bonding solvents relative to nonpolar solvents and fluorescence emission becomes detectable in the hydrogen-bonding solvent. The lack of fluorescence of DAP in the polar solvent, therefore, needs clarification. Before that the nature of the emitting state is to be examined.

Figure 2 reproduces phosphorescence spectra of DAP both in MCH and EtOH rigid glassy matrices at 77 K and the degree of polarization of the same spectra as obtained by photoselection technique. As seen in Fig. 2, the phosphorescence 0,0 band of DAP is polarized highly positive with respect to the excitation into the $^1L_a$ band at about 240 nm both in MCH and EtOH glassy matrices. The observation of short phosphorescence lifetimes (2.5 ms) as it was described earlier, polarization behavior both in MCH and EtOH glasses, and the blue shift of the phosphorescence spectra in going down from MCH to polar protic solvent EtOH strongly suggest that the emitting state is the lowest triplet state which is essentially of $n\pi^*$ nature. Further, from the phosphorescence spectra exhibiting the vibrational progression of carbonyl stretching frequency it is apparent that the phosphorescence bands are attributable to transitions involving the n-electrons on the oxygen atom of the carbonyl group and have been designated as $^3n_O\pi^*$ bands. So in the triplet $n\pi^*$ state of DAP, the carbonyl group is the chromophore, as it is for ACP molecule.[18] The relative dispositions of the $n_O\pi^*$ and $\pi\pi^*$ singlet and triplet energy levels of DAP indicate that the excitational energy corresponding to $^1L_b \leftarrow S_0$ transition is transferred to the lowest $^3n_O\pi^*$ state through $^1\pi\pi^*(^1L_b) \rightarrow {}^1n_O\pi^*$ IC, $^1n_O\pi^* \rightarrow {}^3\pi\pi^*$ ISC, and $^3\pi\pi^* \rightarrow {}^3n_O\pi^*$ IC processes as in the case of ACP molecule. To observe the effect of pyridinic nitrogen atom in an aromatic ketone like molecule on the energetic positions of its different excited electronic states and also on the radiative and nonradiative depletion processes, the phosphorescence quantum yields ($\phi_p$), triplet lifetime ($\tau_p$) of both ACP and DAP are measured in MCH and EtOH rigid glassy matrices at 77 K for comparative study. Moreover, the other photophysical parameters e.g., radiative ($k_p$) and nonradiative ($k_{np}$) rate constants and the radiative lifetimes ($\tau_p{}^0$) are evaluated for these compounds using the well-known relations given below and they are listed in the Table 2.

$$\tau_p{}^0 = \tau_p/\phi_p \text{ (considering triplet yield } \phi_T = 1),$$
$$k_p = 1/\tau_p{}^0;\ k_{np} = 1/\tau_p - 1/\tau_p{}^0.$$

It is generally believed that an electron-withdrawing substituent stabilizes the $n\pi^*$ states of the carbonyls. If the pyridinic nitrogen is considered to be an electron-withdrawing substituent, the energy positions of the $^1n_O\pi^*$ and $^3n_O\pi^*$ states of DAP will be lowered with respect to ACP. The observed red shifts of the $^1n_O\pi^*$ and $^3n_O\pi^*$ band systems of DAP as compared to ACP are in accord with this expectation (Table 1). As DAP molecule has two carbonyl groups one can also expect that the interaction between the nonbonding electron pairs leads to the splitting of carbonyl $n_O$ molecular orbitals into the $n_O{}^+$ and $n_O{}^-$ orbitals and there are two possible excited electronic states of $n_O\pi^*$ nature resulting from $n_O{}^+ \rightarrow \pi^*$ and $n_O{}^- \rightarrow \pi^*$ orbital transitions.[19] Such splitting of carbonyl $n_O$ molecular orbitals may give another reason of the red shifted $n_O\pi^*$ states of DAP as compared to ACP. It is noteworthy that the presence of N-atom may hinder the conjugation effect of the accepting acyl group, leading to destabilization of the $\pi\pi^*$ states of DAP relative to ACP. The large blue shifts of the $^1L_a(\pi\pi^*)$ and $^1L_b(\pi\pi^*)$ bands observed in the case of DAP relative to ACP (Table 1) support this view.

In MCH glassy matrix at 77 K, $\phi_p$ of DAP (0.14) is found to be lower in magnitude in comparison to that of ACP (0.65), as shown in Table 2. It is also seen from this table that the $k_{np}$ of DAP is larger nearly by three times relative to that of ACP molecule. On the other hand the $k_p$ of DAP is approximately one fourth

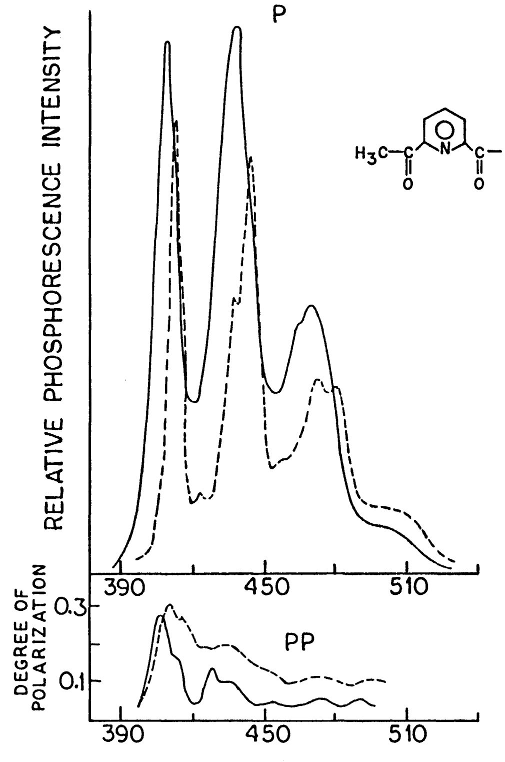

Fig. 2. Phosphorescence (P) and phosphorescence polarization (PP) spectra of DAP in MCH (....) and EtOH (——) at 77 K.

of that value observed for ACP. The larger value of the $\tau_p{}^0$ further supports the proposition that the phosphorescence radiative rate from the emitting triplet state, $^3n_O\pi^*$ of DAP is reduced considerably. It is apparent that large changes in the values of $\phi_p$, $\tau_p$ and other photophysical parameters are brought about due to the introduction of a pyridinic nitrogen atom in ACP type of molecule. Wassam and Lim[20] pointed that in many nitrogen heterocyclic compounds the lowest emitting triplet state is distorted due to vibronic interaction between the closely lying $^3n_N\pi^*$ and $^3\pi\pi^*$ states which enhances the nonradiative rate from the emitting state. The magnitude of the vibronic interaction depends on the proximity of the interacting states. Because of the close proximity, the lower state may acquire some characteristics of the upper state. In the case of DAP, the predominantly in-plane polarization of phosphorescence emission and very short triplet lifetime indicate that the emitting state is essentially of $^3n_O\pi^*$, but it may be the case that the lowest triplet state acquires a small amount of $\pi\pi^*$ character, due to closely lying $^3\pi\pi^*$ state. Since our observed phosphorescence lifetime is very much like that of $^3n\pi^*\rightarrow S_0$ emission it seems reasonable to regard such vibronic mixing to be less important. Because of the presence of N-atom in DAP it is expected that there is a possibility of $^3n_N\pi^*$ state lying close to the $^3n_O\pi^*$ state and the vibronic interaction between these states may lead to the mixing of the emitting state with $^3n_N\pi^*$ state. Following the emission characteristics of N-heterocyclic compounds it is presumed that the vibronic interaction between the closely lying upper $^3\pi\pi^*$ state and the lowest triplet state having a small amount of $^3n_N\pi^*$ character may enhance the nonradiative transition which is manifested by the reduction in $\phi_p$ and $\tau_p$ values for DAP as compared those in ACP. It is to be pointed in this context that there is another possibility of photochemical reaction in the $^3n_O\pi^*$ state which may be considered to account for the large reduction in the $\phi_p$ and $\tau_p$ values for DAP. The occurrence of photochemical reaction in the $^3n_O\pi^*$ state of some pyridyl ketones has been reported by some earlier authors.[21–25]

In EtOH rigid glass at 77 K it is observed that the $\phi_p$ and $\tau_p$ values of DAP increase as compared to those in MCH glass. On the other hand for ACP molecule $\tau_p$ increases with the change of solvents from normal hydrocarbon glass to polar protic EtOH glass but a little lowering in the $\phi_p$ value is observed (Table 2). The increased $\phi_p$ and $\tau_p$ values of DAP in protic solvent can be accounted for in terms of decreased vibronic interaction between $^3n_O\pi^*$ and $^3n_N\pi^*$ states. It is seen from Table 1 that the $^3n_O\pi^*$ state of DAP is blue shifted by 333 $\mathrm{cm}^{-1}$ in changing the matrix from MCH to EtOH whereas for ACP this shift is found to be 188 $\mathrm{cm}^{-1}$. Unfortunately, we could not find the position of $^3n_N\pi^*$ state of DAP in any solvent. However, in the case of pyridine derivatives like cyanopyridines it is reported that the $^3n_N\pi^*$ state undergoes large blue shift (846 $\mathrm{cm}^{-1}$) in going from MCH to EtOH glass.[9] In view of the above facts it is expected that the energy gap between the $^3n_N\pi^*$ and $^3n_O\pi^*$ states of DAP increases in protic solvent as a result of which the vibronic interaction between these states is considerably decreased. This reduction in the vibronic interaction in the triplet manifold causes a substantial decrease in $^3n_O\pi^*\rightarrow S_0$ nonradiative deactivation leading to the increase in $\phi_p$ and $\tau_p$ values of DAP in EtOH glass. As regards to fluorescence activation it is important to note that ACP molecule exhibits a weak $\pi\pi^*$ fluorescence band in EtOH glassy matrix whereas DAP molecule is nonfluorescent in both the polar and nonpolar matrices. It is apparent that for ACP molecule $^1\pi\pi^*\rightarrow{}^1n_O\pi^*$ IC and $^1n_O\pi^*\rightarrow{}^3\pi\pi^*$ ISC rates are hindered a little in polar matrix as a result of which a weak fluorescence is observed. The nonfluorescence behavior of DAP suggests that the IC and ISC rates are not affected appreciably in EtOH. It is generally known that hydrogen-bonding effect in the electronic excited states may hinder IC and ISC rates.[18] Keeping this in view a systematic study has been made to reveal the fact that hydrogen-bonding interaction does really occur between DAP and EtOH solvent. Existence of hydrogen-bonding between ACP and EtOH has been confirmed previously by some authors from the observation of lowering in IC and ISC rates. As seen from the Fig. 1, the sharp vibronic bands in the excitation spectra of DAP corresponding to $^1n_O\pi^*\leftarrow S_0$ observed in MCH glass at 77 K become broadened in EtOH. Such broadening of the excitation spectra was not observed in acetonitrile solvent which may be treated as a nonhydrogen-bonding solvent. These observations suggest that there may be hydrogen-bonding interaction between C=O group of DAP and EtOH solvent in the ground state. To examine the occurrence of such interaction in the excited state the following experiment has been performed.

As EtOH of low concentration is gradually added to the binary mixture of DAP and MCH, the phosphorescence band of DAP is found to be gradually shifted to higher energy region with the increase in intensity (Fig. 3). The observed blue shift of phosphorescence spectrum is certainly characteristic of $\pi^*\leftarrow n$ transition. As MCH solution can be treated as the bulk of the ternary solution in which the relative concentration of EtOH is low, the effect of change of polarity will not be of any great significance and the observed spectral changes should presumably be attributed to intermolecular hydrogen-bonding involving C=O group of excited DAP and EtOH molecules. In order to get corroborative evidence for the occurrence of hydrogen-bonding interaction in the excited state the phosphorescence spectrum of DAP is also recorded in acetonitrile which is a nonhydrogen-bonding solvent having a higher dielectric constant ($\varepsilon\approx38$) than EtOH ($\varepsilon\approx25$). It can be seen from the Fig. 3 and Table 1

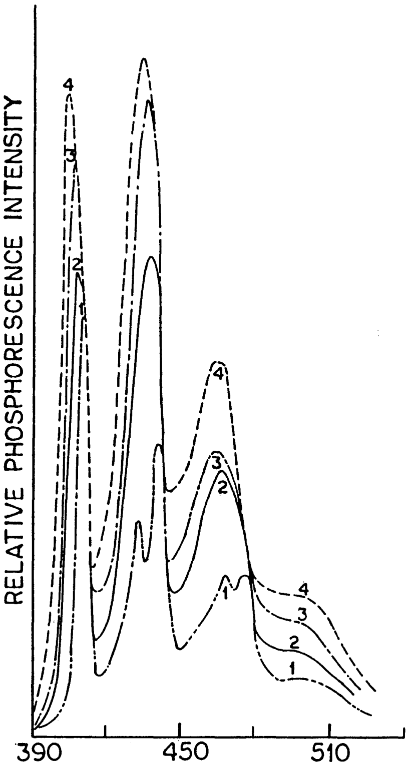

Fig. 3. Phosphorescence spectra of DAP in MCH at 77 K (excitation wavelength: 280 nm). Concentration of DAP is $1\times10^{-4}$ M and that of EtOH in 1, 0M, 2, 0.04M; 3, 0.08M; 4, 0.12M.

that a blue shift of 271 $cm^{-1}$ is produced with acetonitrile while a larger blue shift (333 $cm^{-1}$) is observed with EtOH having lower dielectric constant value. Invariably hydrogen-bonding interaction has a significant role for this blue shift. These blue shifts observed in the cases of both DAP and ACP molecules in changing the environment from MCH to EtOH matrix may be ascribed to the formation of C=O...H-OEt type hydrogen-bonding. The broadening of phosphorescence vibrational structure with gradual addition of EtOH in binary mixture of DAP and MCH as well as the decrease of C=O stretching frequency from 1680 $cm^{-1}$ in MCH to 1631 $cm^{-1}$ in pure EtOH provide the evidences for the occurrence of intermolecular hydrogen-bonding interaction in the ground state. (The observed blue shifts and the augmentation of the phosphorescence bands support the formation of intermolecular hydrogen-bonds in the triplet state of DAP with EtOH.)

From the above observations it may be concluded that hydrogen-bonding interaction between C=O group of DAP in the ground and excited states and EtOH is largely responsible for the broadening of phosphorescence excitation and emission spectra and large blue shifts of phosphorescence band origin. However, the effect of hydrogen-bonding interaction is found to be different in the cases of ACP and DAP molecules. In the case of former molecule, the magnitude of $\phi_p$ is observed to be slightly lowered due to hydrogen-band formation with EtOH with the appearance of a very weak $\pi\pi^*$ fluorescence band system. Moreover, both $k_{np}$ and $k_p$ values are seen to be considerably reduced (Table 2). But in the case of the latter molecule $\phi_p$ value increases due to hydrogen-bonding interaction with EtOH with the significant reduction of $k_{np}$ and increment of $k_p$ (Table 2). It is well-known that hydrogen-bonding interactions in the excited states of some aromatic and pyridyl ketones hinder the ISC and IC processes resulting a weak fluorescence emission from these molecules in EtOH solvent. In the case of DAP no such fluorescence has been detected in EtOH. It is reported that in the presence of pyridinic nitrogen atom C=O group loses its basic properties mostly. As a result hydrogen-bonding interaction of DAP with EtOH becomes much weaker than that of ACP where no pyridinic nitrogen atom is present. Therefore, in the case of DAP it is probable that hydrogen-bonding interaction is not sufficient enough to decrease ISC and IC rates significantly leading to the observation of $\pi\pi^*$ fluorescence emission and lowering in $\phi_p$ value. It is already pointed that in contrast to acetophenone, the splitting of carbonyl $n_o$ molecular orbitals of DAP gives rise to two $^1n_O\pi^*$ states. As the $n_O\pi^*$ states generally undergo blue shift in EtOH it is possible that the vibronic interaction between the $^1\pi\pi^*$ ($^1L_b$) state and the nearby $^1n_O\pi^*$ state increases in the protic solvent. This phenomenon may provide another reason of the nonfluorescence behavior of DAP in EtOH. Such vibronic interaction in the singlet manifold seems to have a correlation with the observation that the relative intensity of $^1n_O\pi^*\leftarrow S_0$ excitation spectrum of DAP is considerably enhanced in the higher frequency region in EtOH compared to that in MCH. The progressive enhancement of phosphorescence intensity with the addition of hydrogen-bonding solvent EtOH in the MCH solution of DAP also finds its explanation from the decrease of vibronic interaction in the triplet manifolds. It is described earlier that in EtOH matrix $^3n_N\pi^*$ state may be largely destabilized so that the energy gap between the interacting $^3n_N\pi^*$ and $^3n_O\pi^*$ states in the protic medium becomes larger than that in MCH. As EtOH is gradually added to the solution of DAP in MCH, it is expected that the energy separation between the interacting states increases and the vibronic interaction between them decreases. This leads to the decrease in the nonradiative rate from the emitting state, which is manifested as the gradual enhancement of phosphorescence intensity with the addition of EtOH in MCH solution of DAP.

It is observed that both in MCH and EtOH glass matrices at 77 K a single exponential of phosphorescence decay profile is observed for DAP. On the other hand in case of ACP dual phosphorescence emission was observed in EtOH.[18] This phenomenon was interpreted in the light of strong hydrogen-bonding interaction between ACP and EtOH due to which IC process between the two closely lying $^3\pi\pi^*$ and $^3n\sigma\pi^*$ states is lowered.[26,27] This makes the radiative processes from $^3\pi\pi^*$ to some extent competent with the IC process leading to the observation of dual phosphorescence emission in case of ACP. It may be presumed that due to comparatively much weaker hydrogen-bonding interaction in the case of DAP, IC between $^3\pi\pi^*$ and $^3n\sigma\pi^*$ states would not be much affected leading to single exponential nature of the triplet decay curve of hydrogen-bonded DAP.

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