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N heteroatomic effect on the photophysics of a polyphenyl system: 2,2′-dipyridylamine

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Abstract

A detailed investigation of the absorption and emission characteristics of 2,2′-dipyridylamine (DPyA) and diphenylamine (DPA) has been carried out in different polar and non-polar solvents at room temperature (300 K) and at 77 K. A dramatic change in both the characteristics has been observed in DPyA in comparison with DPA. Measured fluorescence and phosphorescence lifetimes and critical study of the absorption and emission spectral data suggest that DPyA is more planar than DPA and its lowest-energy singlet state is of ^1L_a type containing a little charge transfer character. Evidence of the presence of a $^1n\pi^*$ state has been found in DPyA on protonation in the binary mixture of water and sulphuric acid at room temperature.

Keywords: Heteroatomic effect; Photophysics; Polyphenyl system

1. Introduction

Azaaromatics have attracted many researchers in connection with their elusive photophysical [1–9] and photochemical [10–12] properties, excited state phototautomerization [13], biological and pharmacological significances [14]. Because of the presence of $n\pi^*$ and $\pi\pi^*$ states, the proximity effect has long been recognized as an important characteristic of azaaromatic systems. Another interesting and exciting feature of this system has been explored in relation to the important role of the N heteroatom in modulating their photophysical properties through a change in molecular geometry. Polyphenyl molecules are well known to exhibit different conformers depending on the nature of substituent in the phenyl rings and also on the environmental conditions [9,15,16]. For 4-[4-(dimethylamino)phenyl] pyridine [3], the lowest energy singlet state has been assigned as ^1L_a, and moderately strong fluorescence occurs from this state. Recently we have studied the N heteroatomic effect on the photophysics of a polyphenyl system [9]. From detailed analysis of experimental data it is shown that 2,6-diphenylpyridine (DPP) provides an intense long-wavelength absorption band of ^1L_a type, and strong fluorescence is observed from this state. Interaction of non-bonding electrons of N atom and π electrons of the outer phenyl rings is held responsible for the dramatic absorption and emission characteristics of this DPP molecule. This seems to be important in the search for an effective fluorescent compound, which could be used as a very effective laser-active medium and also as a fluorescent probe for the study of the structure and dynamics of nucleic acid. Another interesting system is aromatic amines. The photophysics of these compounds are highly sensitive to molecular geometry changes [17–22]. Spin–orbit coupling (SOC) in aromatic amines is enhanced relative to their relevant aromatic hydrocarbons, which results in increased phosphorescence-to-fluorescence-quantum-yield ratio and shorter phosphorescence lifetimes. Both experimental and theoretical studies of a series of aromatic amines, from a distinctly non-planar molecule diphenylamine (DPA) to a planar molecule carbazole indicate that the charge transfer character of the excited electronic states gradually decreases from non-planar to planar molecules, being a maximum for DPA and a minimum for carbazole [20,21]. It is well established that intramolecular charge transfer transitions play an important role in the SOC of aromatic amines.

In view of our earlier attempt to understand the N heteroatomic effect on the photophysics of aromatic molecules and the highly molecular geometry-dependent photophysical

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behaviour of the aromatic amines, a detailed investigation of the absorption and emission characteristics of 2,2′-dipyridylamine (DPyA) in different environments has been carried out. Studies on a structurally similar molecule DPA are also made under identical experimental conditions for comparison. In fact, we have obtained through the present study a dramatic change in the absorption and emission characteristics of DPyA in relation to those of DPA.

2. Experimental details

The samples DPyA ($(C_5H_4N)_2NH$) and DPA ($(C_6H_5)_2NH$), supplied by Aldrich Chemical Company, USA, were used after vacuum sublimation. Spectroscopic grade ethanol (EtOH) supplied by E. Merck, Germany, was used fresh from the package. Methylcyclohexane (MCH) obtained from E. Merck was purified in the usual way. For aqueous solution, a stock solution was prepared in spectroscopic grade methanol (MeOH) (E. Merck) and then diluted by water in such a way that final solutions contained less than 1% (v/v) of MeOH [23]. Triply distilled water further purified by a Milli Q plus water purification system having a resistivity of 18.2 M was used. The sulphuric acid (95–98%) used was GR grade supplied by E. Merck, India. Before use, each solvent was tested and no impurity emission was detected.

The absorption spectra were recorded with a Shimadzu UV–visible spectrophotometer model 210A and the emission and excitation spectra were recorded with a Perkin–Elmer model MPF 44A fluorescence spectrophotometer, equipped with a corrected spectra unit, model CSU. The concentration of the solutions was maintained in the range 10^{-6}–10^{-5} M. The quantum yields were measured considering DPA as the standard. The long-wavelength tail part of fluorescence spectrum extending well into the phosphorescence region was taken into account in the calculation of quantum yields. It was presumed that the spectral shape of fluorescence at 77 K was identical with that at 300 K where no phosphorescence was present. A photoselection technique was used for the measurement of the degree of polarization which was corrected following Azumi and McGlynn [24].

To study the phosphorescence decay, the emission wavelength was chosen at 400 nm. To obtain dark decay, the exciting radiation was cut off after the phosphorescence intensity achieved a steady state.

Fluorescence decays were recorded using a single-photon-counting set-up. The excitation was done at 620 nm using a synchronously pumped cavity-dumped rhodamine 6G dye laser (coherent 702) pumped by a continuous-wave mode-locked Antares Nd-doped yttrium aluminium garnet laser. For room-temperature emission decay measurements the solutions were purged with N_2 for 30 min to make them free from molecular oxygen.

3. Discussion

3.1. Absorption spectra

Room-temperature absorption spectra (Fig. 1) of DPyA exhibit two strong bands at 312 and 265 nm in EtOH solution with f values of 0.35 and 0.42 respectively. The higher energy absorption band shows a marginal change in energy position in going from the non-polar solvent MCH to the polar solvent EtOH while the lowest energy absorption band system in MCH shows a peak maximum at 311 nm and a prominent shoulder at 319 nm which is found to be almost smeared out in EtOH. The characteristics of this lowest energy absorption appear to be quite similar to those of DPA. In DPA an intense absorption band is observed at 284 nm with a weak shoulder at 292 nm in MCH whereas in EtOH it displays a broad band with a peak at 285 nm (Fig. 2). It is reported [20,21] that for DPA this higher energy band at 284 nm, with an f value of 0.44, corresponds to the ^1L_a band ($^1S_2$–$^1S_0$ transition) and the lower energy band at 292 nm, with an f value of 0.07, is assigned as the ^1L_b band ($^1S_1$–$^1S_0$ transition). However, in the case of the title compound, it was not possible to separate these two bands conveniently, even with the utmost effort. So the f value (0.35) of this first band system is supposed to be the sum of f values of the ^1L_a and ^1L_b bands. From the studies of a series of aromatic amines [20,21], it is concluded that the f value of the ^1L_a band decreases gradually from 0.44 in the case of the distinctly non-planar molecule DPA, down to 0.15 in the case of the distinctly planar molecule carbazole. However, the f value of the ^1L_b band remains more or less unchanged ($f = 0.07$ for DPA and $f = 0.05$ for carbazole). The large change in the oscillator strength of the second band system (^1L_a) is attributed to the significant variation in the charge transfer character in this transition in the aromatic

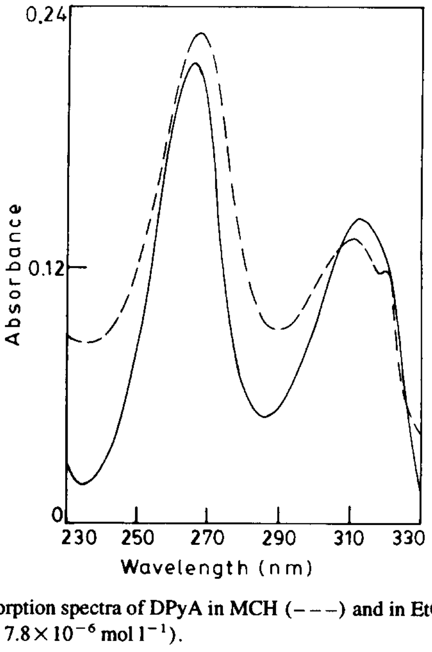


Fig. 1. Absorption spectra of DPyA in MCH (– – –) and in EtOH (——) at 300 K ($C = 7.8 \times 10^{-6}$ mol l^{-1}).

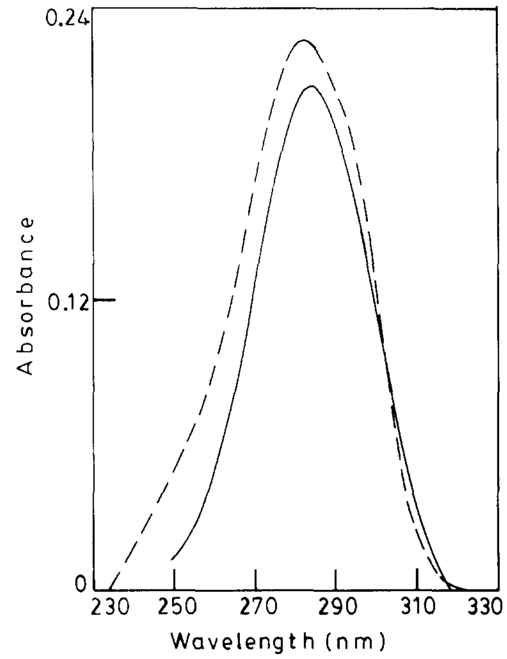


Fig. 2. Absorption spectra of DPA in MCH (- - -) and in EtOH (——) at 300 K ($C = 7.8 \times 10^{-6}$ mol l^{-1}).

amines. If we assume that, for DPyA, the *f* value of the ^1L_b band remains more or less the same as that of DPA, the oscillator strength of the ^1L_a band is found by subtracting $f(^1L_b) \approx 0.07$ from the total *f* value (0.35). The *f* value of the ^1L_a band thus calculated as 0.28 indicates that DPyA is more planar than DPA but not to the extent of carbazole. The other higher energy strong band at 265 nm seems to be related to the K band as already reported in the case of some aromatic molecules [9]. It is note worthy that a similar type of absorption band is also observed at 257 nm in carbazole [20]. As the ^1L_a and ^1L_b bands of DPyA could not be separated from the studies of the absorption spectra, the fluorescence lifetime has been measured to provide some information about their relative positions and to determine which is the lowest state. The fluorescence lifetime τ_f of DPyA measured in EtOH at room temperature is 0.45 ns. The *f* value calculated from the fluorescence quantum yield ($\phi_f = 0.12$) and the measured fluorescence lifetime τ_f using the formulae

$$\phi_f = \frac{k^0}{k_f^0 + k_{ISC} + k_{IC}} = k^0\tau \qquad (1)$$

and

$$\tau_f^0 = \frac{1}{k_f^0} = \frac{1.5}{nf\nu_{max}^2} \qquad (2)$$

(where all the symbols have the usual significance) [25] is found to be 0.38 for DPyA. This *f* value is close to that predicted from the absorption spectra and adds credence to the assignment of the lowest excited singlet state as ^1L_a type. Similar observations were also made for some other aromatic molecules [9]. However, it seems that the measurements of steady state emission and its polarization spectra of the DPyA molecule might be helpful to assign more conclusively the lowest excited state.

3.2. Emission spectra

With excitation into the ^1L_a band, DPyA exhibits intense and weakly structured fluorescence and phosphorescence spectra in the EtOH glass matrix at 77 K (Fig. 3). The fluorescence and absorption spectra at 300 K are also found to display mirror symmetry (Fig. 4). Similar observations were also made with some other planar and rigid molecules [26]. In contrast, DPA yields strong phosphorescence but very weak fluorescence in the same environment (Fig. 3). The phosphorescence lifetime τ_p of DPyA is of the order of seconds, characteristics of the $\pi\pi^*$ triplet state. Moreover, with excitation into the ^1L_a band, negative polarizations were obtained not only with the band origin but also with other vibronic bands in the weakly structured phosphorescence of DPyA. This also adds further evidence to the above assign-

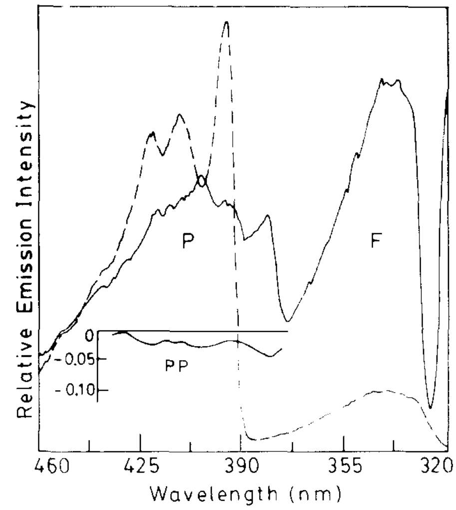


Fig. 3. Emission spectra of DPyA (——) and DPA (- - -) in EtOH at 77 K: F, fluorescence; P, phosphorescence; PP, polarized phosphorescence.

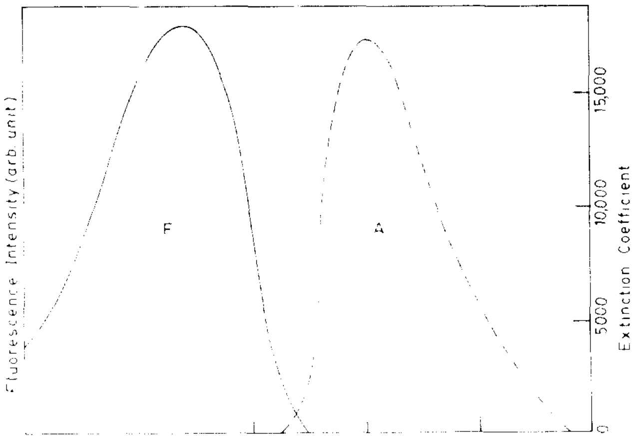
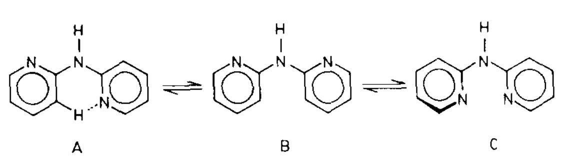


Fig. 4. Fluorescence (——) and absorption (- - -) spectra of DPyA in EtOH at 300 K: F, fluorescence; A, absorption.

ment of the lowest triplet state. The fluorescence and phosphorescence quantum yields, phosphorescence lifetime and the other derived parameters of both DPA and DPyA are shown in Table 1. It is note worthy that for both DPA and DPyA the total quantum yield $\phi_p + \phi_f$ accounts for 80–90% of the adsorbed light. In the EtOH matrix at 77 K, the fluorescence quantum yield increases but ϕ_p/ϕ_f decreases in going from DPA to DPyA, indicating that either the fluorescence deactivating pathway becomes more efficient or the intersystem crossing rate becomes less efficient or both. In order to obtain a better understanding of all these behaviours, we felt the need to examine the rate constants, which determine the various relaxation processes of the excited states.

A comparative study of the rate constants (Table 1) shows that in EtOH matrix the intersystem crossing (ISC) rate k_{ISC} decreases while the radiative fluorescence rate constant k_f^0 and non-radiative triplet decay constant k_{nr} increase significantly in going from DPA to DPyA. It is reported that the ISC rate of aromatic amines decreases in going from the non-planar molecule DPA to the planar molecule carbazole [21]. This behaviour is generally explained on the basis of reduction in the charge transfer character of the ^1L_a band in the more planar molecule, which diminishes the spin-orbit interaction between the ^1L_a state and the lowest triplet state. The observed k_{ISC} (27.4×10^7 s^{-1}) in DPyA, which is certainly much less than that (49.2×10^7 s^{-1}) of DPA, indicates that charge transfer character of the ^1L_a band of DPyA is less than that in DPA. The increased planarity in the molecular geometry of DPyA with respect to DPA is thought to be responsible for the considerable decrease in the charge transfer character. In this context the following molecular conformations of DPyA (Scheme 1) may be considered. Since CH bonds are very weak contributors to hydrogen bonding, structure **A** (Scheme 1) is less possible, especially in EtOH solutions because of greater and more efficient intermolecular hydrogen bonding. Probably the structure **C** is more planar than the structure **B** because steric interaction between the H atoms is expected to be less in the former case. Similar evidence for the planarity of the molecule was also found from the absorption data. Although the phosphorescence lifetimes of both the molecules are of the order of seconds, it is worth mentioning that the τ_p value for DPyA is almost half that for DPA and the radiative phosphorescence rate k_p^0 is higher in DPyA. This characteristic can be explained in the following way.



Scheme 1.

The phosphorescence radiative rate depends chiefly on two factors: firstly the amount of mixing between the lowest triplet and the excited singlet states and secondly on the f value of the lowest S_0–S_1 transition which causes the intensity of the S_0–T_1 transition to increase. It has already been mentioned that the lowest triplet and the singlet states are both of $\pi\pi^*$ type. Moreover the lowest singlet state in DPyA contains less charge transfer character than that of DPA. Therefore the mixing cannot be efficient until and unless there is certain intervening triplet state of $n\pi^*$ character in DPyA. In N heterocyclic compounds [1,4] with lowest $^1\pi\pi^*$ and $^3\pi\pi^*$ states, it is reported that the intervening $n\pi^*$ triplet state has a significant effect on the phosphorescence intensity, lifetime and polarization character. Since the lowest ^1L_a band of DPyA has an f value equal to 0.28 which is greater than that of the ^1L_b band of DPA by about one order and $\Delta E(S_1$–$T_1)$ does not change appreciably, it is likely that the transition dipole moment $M(T_1$–$S_0)$ increases in DPyA compared with DPA. It is note worthy that the measured phosphorescence lifetime in the EtOH rigid matrix is found to decrease in going from DPA ($\tau_p = 2.3$ s) to DPyA ($\tau_p = 1.1$ s). The phosphorescence polarization curve recorded in polar glassy media (Fig. 3) with ^1L_a excitation shows negative polarization of the 0–0 band of DPyA as -0.05 while the polarization of the corresponding band in DPA is reported to be -0.07. These results together with variation in the degree of polarization outside the band origin imply the occurrence of vibronic interaction between close-lying $^3\pi\pi^*$ and $^3n\pi^*$ states. Indeed this is the general behaviour of N heterocyclic compounds with lowest $^3\pi\pi^*$ state [27].

3.3. Solvent effect

In both DPA and DPyA, the peak positions of the fluorescence band do not undergo any significant change in going

Table 1

Emission quantum yields and different excited-state depletion rate parameters in EtOH at 77 K

Molecules	ϕ_f	ϕ_p	τ_p (s)	k_f^0 [a] ($\times 10^7$ s^{-1})	$k_s \equiv 0$ [b]			$k_{nr} \equiv 0$ [c]		
					k_p^0 (s^{-1})	k_{nr} (s^{-1})	k_{ISC} ($\times 10^7$ s^{-1})	k_s ($\times 10^7$ s^{-1})	k_p^0 (s^{-1})	k_{ISC} ($\times 10^7$ s^{-1})
DPyA	0.40	0.50	1.1	18.3	0.76	0.15	27.4	4.5	0.91	22.9
DPA	0.10	0.73	2.3	5.47	0.35	0.08	49.2	9.3	0.43	39.9

[a] k_f^0 has been calculated taking $f = 0.28$ for DPyA and $f = 0.07$ for DPA.

[b] $\tau_p = 1/(k_p^0 + k_{nr})$; $k_{nr} = 1/\tau_p - 1/\tau_p^0$; $k_{ISC} = k_f^0 (1 - \phi_f)/\phi_f$; $k_p^0 = \phi_p/(1 - \phi_f)\tau_p$.

[c] $k_{ISC} = k_f^0 \phi_p/\phi_f$; $k_s = k_f^0(1/\phi_f - 1) - k_{ISC}$.

from a low temperature to room temperature in MCH solution, around 332 nm at 77 K and 330 nm at 300 K, whereas in EtOH solution the peak positions are red shifted by significant amounts, around 337 nm at 77 K and 353 nm at 300 K. This may be attributed to the conformational change of the two molecules at higher temperatures in EtOH solution. The fluorescence intensity changes observed in different environments are very interesting. In DPA, the fluorescence intensity is greater in alcoholic solution at both temperatures compared with that in MCH. However the intensity patterns of DPyA in the polar and non-polar solutions are just reversed at these two temperatures; at low temperatures the fluorescence is found to be stronger in EtOH whereas at room temperature it is more intense in MCH. This can be explained in the following manner. In EtOH at 77 K, all the three N atoms of DPyA (one with the amino group and the other two in the rings) are hydrogen bonded with the solvent molecules in the rigid matrix. This reduces the possibility of different types of non-radiative deactivation promoted through the lone pair electrons associated with these nitrogen atoms and consequently enhances the fluorescence intensity. However, in the non-polar rigid matrix (MCH) there is no possibility of such hydrogen bonding. The proximity effect arising owing to the presence of $\pi\pi^*$ and $n\pi^*$ states in the singlet manifold leads to a greater possibility of non-radiative processes conducted through the N atoms (ring) which in turn quenches fluorescence in this non-polar matrix. These are the general characteristics of azaaromatic and aromatic amines in non-polar solvent [27,28]. However, the photochemical reactions are reported to be increased in azaaromatic molecules in the polar solvent at high temperatures [29]. Phototautomerizations [13] may also have some effect on the non-radiative pathways in azaaromatics. All these factors account for the reduction in fluorescence intensity of DPyA in EtOH at room temperature. However, in the case of DPA in EtOH, the nitrogen atom in the amino group is hydrogen bonded with the solvent molecules at both room temperature and a low temperature (77 K). This closes the non-radiative channels connected with this N atom and as a result the fluorescence intensity of DPA in EtOH is found to be greater than that of MCH solutions where the free lone pair electrons in the nitrogen atoms increase the possibilities of non-radiative deactivations of the singlet state.

3.4. Protonation effect

From the room temperature absorption spectra (Fig. 5) of DPA in the binary mixture of water and sulphuric acid, it is found that the intensity of the ^1L_a band (at $\lambda_{max}=280$ nm) in pure water decreases with gradual increase in acid concentration and a much weaker and broad band, shifted significantly to the red side, gradually appears. At very high acid concentrations the pure water band (at $\lambda_{max}=280$ nm) completely disappears and the new red-shifted broad band becomes prominent at $\lambda_{max}=320$ nm. The intensity of the band is, however, much less than that of the original band (in pure water). This new band (320 nm) seems to correspond to the new species where the proton is transferred to the nitrogen atom associated with the amino group of the molecule and the disappearance of the original band indicates the saturation with the proton-transferred molecules. The fluorescence intensity is found to decrease with increase in acid concentration. This kind of reduction of the fluorescence intensity was found by Hidalgo et al. [23] in 7-azaindole in H_2SO_4 solutions. This reduction in fluorescence intensity may be attributed to the characteristics of the new species for which the K_f value and hence the fluorescence quantum yield decreases because of its significant reduction in the f value as appeared from Fig. 5. These effects are complicated but more interesting in DPyA. In the room-temperature absorption spectra (Fig. 6) of the molecule in the binary mixture of water and sulphuric acid, the lowest band (^1L_a) at $\lambda=307$ nm in pure water is shifted towards red at $\lambda=321$ nm and on it a new weak band appears as a shoulder on the blue side of this band ($\lambda=290$ nm) whereas the K band ($\lambda_{max}=261$ nm) is blue shifted (with $\lambda_{max}=250$ nm) in the binary mixture. As the H_2SO_4 concentration gradually increases, all the above

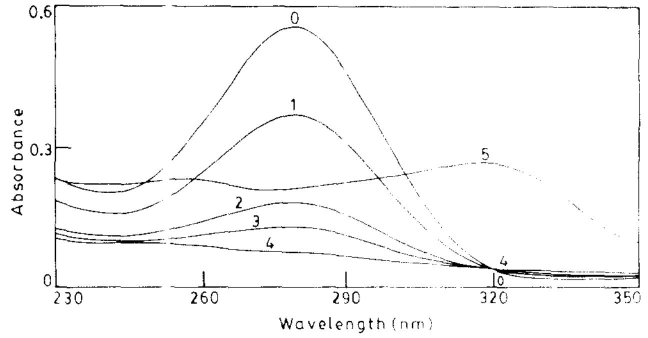


Fig. 5. Absorption spectra of DPA in H_2O at 300 K: concentration of 36 N H_2SO_4 in 0 N (curve 0), 0.02 N (curve 1), 0.2 N (curve 2), 0.96 N (curve 3), 4.8 N (curve 4) and 30 N (curve 5).

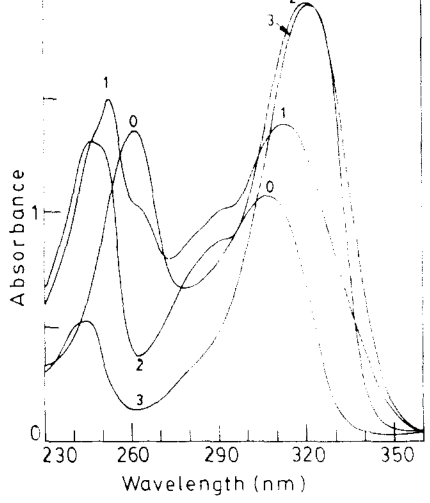


Fig. 6. Absorption spectra of DPyA in H_2O at 300 K: concentration of 36 N H_2SO_4 in 0 N (curve 0), 0.2 N (curve 1), 4.8 N (curve 2) and 30 N (curve 3).

bands first grow in intensity and the shoulder at $\lambda = 290$ nm on the blue side of the ^1L_a band becomes more prominent. However, at and above a certain acid concentration, this shoulder disappears first and then the K-band intensity decreases significantly at very high acid concentrations. In the binary mixture, the fluorescence intensity is rather peculiar. At first, with increase in H_2SO_4 concentration, the fluorescence intensity is found to decrease but, with further increase in acid concentration, the fluorescence intensity increases again. These absorption and emission characteristics may be explained as follows.

At lower acid concentrations, because of the higher basicity of the nitrogen atom in the amino group with respect to the ring nitrogen atoms in ground state DPyA, the proton is preferably transferred at the nitrogen atom in the amino group. This changes the amino group from a more planar to a less planar structure (i.e. the hybridization of the amino group nitrogen atom changes from more sp^2 to more sp^3). This makes the two pyridyl rings more non-planar. Possibly as a result of this conformational change, at first an $^1n\pi^*$ band (associated with the lone pair electrons of the ring nitrogen atoms) appears in the absorption spectra at lower H_2SO_4 concentrations. However, at higher concentrations of sulphuric acid, proton transfer occurs not only at the amino nitrogen but also at the N atoms in the rings, leading to the disappearance of the weak band at $\lambda = 290$ nm, assigned as the $^1n\pi^*$ band. So at lower acid concentrations the fluorescence intensity decreases so long as this $^1n\pi^*$ band is present very close to the ^1L_a band which increases the non-radiative rate from the emitting state through vibronic interaction. At higher acid concentrations, where this $^1n\pi^*$ band disappears, it is possible that owing to lack of the proximity effect between $^1n\pi^*$ and ^1L_a states the fluorescence intensity again increases. Investigations with similar systems are now under way in our laboratory to corroborate the propositions made above.

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