Luminescence Characteristics of 2-Amino-4,6-Diphenylpyrimidine in Different Solvents and at Various pH

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Abstract

The absorption and fluorescence spectral properties of 2- amino-4,6 - diphenylpyrimidine(ADP) have been investigated in a series of organic solvents of different polarity and in aqueous solutions with Ho / pH /H_ in the range -10 to 17 . The largely red shifted fluorescence maximum observed in hydrogen bonding solvents can be attributed to dual intermolecular hydrogen bonding interaction between ADP and the solvents. The correlation between the Stokes shifts and the solvent polarity parameters, is better with ET(30) than with BK values. The low value of correlation coefficient may be due to the presence of both intra- and dual intermolecular hydrogen bonding in polar solvents.The acidity constants for various prototropic reactions in So and S1 states are determined and discussed.

Keywords: 2- amino-4,6 – diphenylpyrimidine, hydrogen bonding interactions, prototropic reaction, solvent polarity parameters, acidity constant values.

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1. Introduction

The comparison of solvent effects on absorption and emission spectra, gives valuable information regarding the nature of the electronically excited state in contrast to the ground state and also the nature of interaction between the solute and solvent molecules in the ground and excited states. The absorption and fluorescence characteristics [1-4] of a large number of aromatic compounds in solution have been studied extensively.

Acid- base properties of aromatic compounds in their excited states are of great interest in chemistry and biochemistry. They are closely related to the corresponding electronic structures. The ground state pKa values have been used to draw information concerning the structure, electronic charge distribution and chemical reactivity of molecules in the ground states. The pKa* values are used to get similar inferences of the molecules in excited singlet state.

Photophysical characteristics of fused aromatic systems like naphthalene, phenanthrene, fluorene, pyrene and anthracene [5-12] and non-fused aromatic systems like diphenyls[13-18], diphenyl sulphones [19-23] and diphenylamines [24-26] with one or more functional groups have been studied extensively. Spectral characteristics of some of the bifunctional molecules possessing electron donating functional groups revealed interesting features [12-15, 27].

Several pyrimidines were found to possess antifungal and antileigumanial activity as well as biological properties particularly being calcium channel blockers. In recent years pyrimidine derivatives received significant attention owing to their diverse range of biological properties. Structural studies on

bioactive derivatives of 2-amino-4,6-disubtituted pyrimidine derivatives have been studied. These bioactive compounds are immunological agents with anticancer and interferon-inducing properties.

In this study we have analysed the luminescence characteristics of 2-amino-4,6-diphenylpyrimidine in different solvents and at various pH.

2. Experimental Setup

2.1 Instruments used

The absorption spectra were recorded using a JASCO UNIDEC-7800 spectrophotometer and fluorescence measurements were made using a JASCO FP-550 spectrofluorimeter. pH values in the range 1.5–12.0 were measured on ELICO pH meter model LI-IOT.

2.2 Reagents

2-amino-4,6-diphenylpyrimidine was prepared by adopting the general procedure[28]. The purity of the compound was checked by its sharp melting point and similar fluorescence spectra with different excitation wavelengths. All the solvents used were of highest grade(Spectrograde or AnalaR) commercially available. The purity of solvents has been verified by taking UV spectra. Triply distilled water was used for the preparation of aqueous solutions. Solutions in the pH range 1.5–12 were prepared by adding appropriate amount of NaOH and H_3PO_4. A modified Hammett's acidity scale(Ho) [29] for solutions below pH 1.5(using H_2SO_4–H_2O) and Yagil's basicity scale(H_-) [30] for solutions above pH12(usingNaOH–H_2O) were employed. The concentration of the solutions were of the order10^{-4} to10^{-5} M. The isosbestic wavelengths were used as the excitation wavelength for measuring the fluorescence intensities at any analytical wavelength. The experimental solutions were prepared just before taking measurements.

3. Results and Discussions

3.1 Effect of Solvents

The absorption and fluorescence spectra of 2-amino-4,6-diphenylpyrimidine(ADP) have been recorded in various solvents and the relevant data are compiled in Table 1. Relative to cyclohexane, the absorption maxima of ADP are red shifted in all the solvents. Compared to methanol a slight blue shift is observed in water. In water ADP behaves as a proton acceptor since proton donating capability of water is reported to be more[15]. Hence a slight blue shift is observed in water when compared to methanol.

The fluorescence maximum of ADP is regularly red shifted as polarity and hydrogen bonding capacity of the solvent increases ie., from cyclohexane to water. The red shifts observed in hydrogen bonding solvents are due to interaction of solvents with hydrogen atom of the $–NH_2$ group. The Stokes shifts of ADP in various solvents are compared with solvent polarity parameters ET (30) [31] and BK (32) values (Table 4.1.2). The absorption and fluorescence solvatochromic shifts reveal that the solvent interaction of hydrogen bonding solvents is predominant. This is confirmed by the better correlation of the Stokes shifts of ADP with ET (30) than BK values. The low value of correlation coefficient with ET (30) parameter may be due to the presence of both intra- and intermolecular hydrogen bonding in polar solvents.

So, in all hydrogen bonding solvents a large deviation is observed and the deviation is more in water and methanol. The largely red shifted fluorescence maximum observed for these two solvents can be attributed to dual intermolecular hydrogen bonding interaction

Table 1: Absorption and fluorescence maxima(nm) of 2-Amino-4,6-diphenyl - pyrimidine in different solvents and at various pH.

No	Solvents	abs	flu
1.	Cyclohexane	328.0 250.0	375
2	Dioxane	37.0 254.8	395
3.	Ethyl acetate	335.0 254.2	391
4	Dichloromethane	329.0 258.0	381
5.	*ter*-Butyl alcohol	334.0 252.0	398
6	Acetonitrile	334.7 254.4	396
7	Isopropyl alcohol	335.8 258.1	395
8	n- Butyl alcohol	335.0 250.6	397
9.	Methanol	335.4 254.3	398
10.	Water	330.0 254.0	399
11.	Monocation	347.0 283.2 235.0	---
12.	Dication	386.0 305.2 250.0(s)	430
13.	Monoanion	350.0 262.1	---

ADP and the solvents. Such type of dual intermolecular hydrogen bonding with 1:1 stoichiometry was reported for 2-amino-4,6-dimethylpyrimidine with acetic acid in cyclohexane and with water molecule [33]. The dual intermolecular hydrogen bonding interaction between ADP and water molecule is shown below.

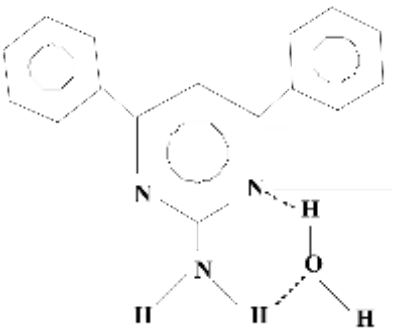


Figure 1: Dual intermolecular hydrogen bonding

Table 2: Stokes shifts(cm-1) observed for ADP in different solvents with ET(30) and BK values

No	Solvents	ET(30)	BK	Dn
1	Cyclohexane	31.2	-0.001	3820
2	Dioxane	36.0	0.043	4357
3	Ethyl acetate	38.1	-	4275
4	Dichloromethane	41.1	0.586	4149
5	ter-Butyl alcohol	43.9	0.673	4815
6	Acetonitrile	46.0	0.864	4625
7	Isopropyl alcohol	48.6	0.766	4463
8	n- Butyl alcohol	50.2	0.754	4662
9	Methanol	55.5	0.856	4691
10	Water	63.1	0.913	5241
	Correlation coefficient ET(30) = 0. 879 BK = 0. 751			

3.2 Effect of acid- base concentrations

The absorption and fluorescence spectra of ADP have been recorded in the Ho/ pH/H_ range –10 to 17.0. With the decrease of pH from 7, the absorption spectra of ADP is red shifted from pH 3.5 and the spectrum has the maxima 347, 283.2 and 235nm. The following

trend in the absorption and fluorescence spectra is generally observed during protonation or deprotonation of heterocyclic molecules if

* is the lowest energy transition. i) A blue shift in absorption and fluorescence spectra is observed on protonation of amino group [34]. ii) A red shifted absorption and fluorescence band is noticed if the tertiary nitrogen atom is protonated[35]. iii) A red shift is observed in the spectral behaviour if amino group is deprotonated[36]. In ADP first protonation shifts the absorption maxima to longer wavelength which implies that one of the ring nitrogen atoms was protonated first rather than the primary amino group. The reason is because of reduced availability of lone of electrons on –NH2 group due to the presence of two electron withdrawing ring nitrogen atoms. When the acidity is further increased, the spectrum is red shifted from Ho -2.8. The spectrum has the maxima at 386, 305.2 and 250(s) nm. Since the absorption spectrum is red shifted, the second protonation also occurs at another ring nitrogen atom. Further increase in acidity do not cause any change in absorption spectrum. The absorption and fluorescence spectral maxima of various prototropic species are presented in the Table.1 and the absorption spectra of different species are shown in Fig.1.

The absorption spectra of ADP do not change, when the basicity is increased upto H_ 14.0. But a regular red shift is noticed with further increase in basicity (H_ >14.0) with no clear isosbestic point. The red shifted spectrum may be due to the formation of monoanion which is obtained by the deprotonation of amino group.

The neutral species shows a fluorescence maximum of 399nm. When pH is decreased from 7, there is no change in the spectral maximum upto Ho-1.38. But the intensity of neutral form starts quenching from Ho +0.83 and a red shifted fluorescence spectrum with the maximum 430nm is appeared when Ho> -1.38. This maximum may be due to the simultaneous protonation of both the ring nitrogen atoms since the spectral maximum is red shifted. The excitation spectrum monitored at 430nm resembles the absorption spectrum of dication. Hence the red shifted peak may be due to dication of ADP When acidity is further increased there is no change in the fluorescence maxima till Ho-10.0. The fluorescence spectra of various prototropic species of ADP are shown in Fig 2.

When the pH is increased from 7, the quenching of fluorescence starts from pH 12.5 and this may be due to the formation of non-fluorescent monoanion. This is consistent with the earlier results that the monoanion formed by the deprotonation of aromatic amines are non-fluorescent[16, 37].

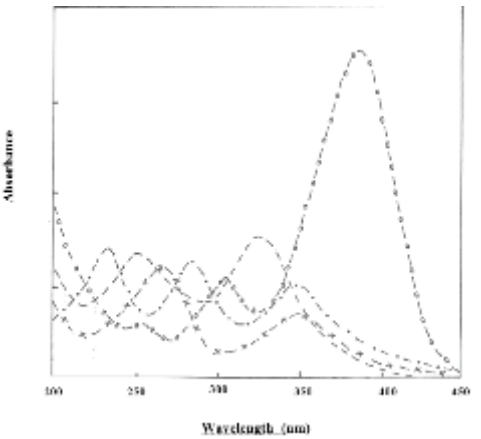
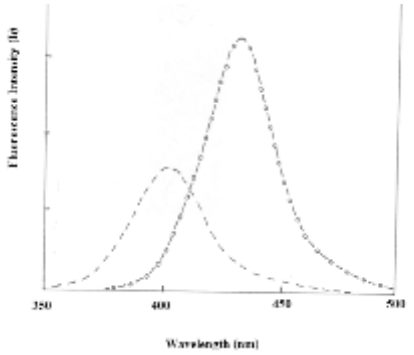


Figure 2: Absorption spectra of different prototropic species of ADP at 2981

---------- neutral, ---------- monoction
-o-o-o-o-o- neutral, -x-x-x-x-x- monoction

3.3 Acidity constants

The ground state pKa values for various prototropic reactions were determined spectrophotometrically. The pKa* values for different proton-transfer reactions of ADP were obtained with the help of fluorimetric titration(FT)(Table. 3).



Fiigure 3: Fluorescence spectra of diffrent prototropic speciess of ADP at 298K

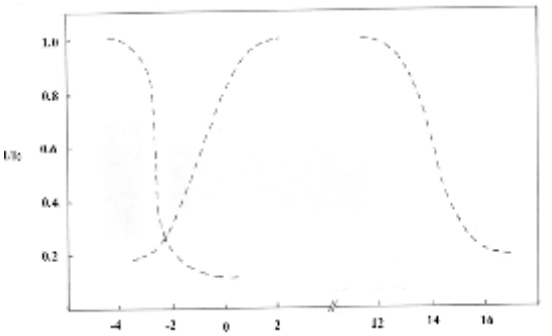
------Neutral, -o-o-o-o-o- dication

Table 3: Acidity constant values of various prototropic equilibria of ADP in the lowest excited singlet and ground states

Equilibria			pK_a	pK_a^* (FT)
Dication	⇌	Monocation	-2.7	-2.4
Monocation	⇌	Neutral	3.4	-1.1
Neutral	⇌	Monoanion	14.9	14.2

The FT curves of ADP for various equilibria are shown in Fig.3. Since the monocation of ADP is non-fluorescenct, pKa*(FT) value for monocation-neutral equilibrium is obtained from the mid -point of the quenching curve of the neutral form. The pKa*(FT) value is found to be less than that of ground state pKa value which indicates that the molecule becomes less basic in S1 state.

The pKa*(FT) value for dication-monocation equilibrium is obtained from the formation curve of the dication. This value is close to the ground state pKa value. This indicates that the rate of protonation cannot compete with rate of fluorescence. The pKa* value for the neutral-monoanion equilibrium was determined from the fluorescence quenching curve of the neutral species of ADP. The wavelength of constant absorbance is used as λexi for fluorimetric titration as the isosbestic point is not constant. The pKa* value shows that –NH2 group becomes slightly basic in the S1 state than the So state.



Ho/H/H_

Figure 4: Plot of relative fluorescence intensities (I/I_0) vs Ho/pH/H_of the various species of ADP

4. Conclusions

Solvatochromic and prototropic behavior of 2-amino-4,6-diphenylpyrimidine (ADP) has been studied in different solvents and at various pH. The absorption and fluorescence solvatochromic shifts reveal that the solvent interaction of hydrogen bonding solvents is predominant. The largely red shifted fluorescence maximum observed in hydrogen bonding solvents can be attributed to dual intermolecular hydrogen bonding interaction between ADP and the solvents. The monoanion of ADP is found to be non-fluorescent.

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