

# Absorption Spectra of 2, 2'-Bipyridyl, 1,10-Phenanthroline & 5-Nitro-1,10-phenanthroline in Different Solvents

C. C. DEB & D. K. HAZRA

Department of Chemistry, University of North Bengal, Darjeeling  
and

S. C. LAHIRI\*

Department of Chemistry, University of Kalyani, Kalyani 741 235

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The absorption spectra of 2,2'-bipyridyl, 1,10-phenanthroline and 5-nitro-1,10-phenanthroline have been recorded at 25°C in solvents of diverging characteristics. The spectral behaviour of 2,2'-bipyridyl has been analysed and no evidence of band at 308 nm due to covalent-hydrate formation of 2,2'-bipyridyl as reported by Henry and Hoffman is observed [*J. phys. Chem.*, 83 (1979), 625]. The transitions involved are all  $\pi \rightarrow \pi^*$  transitions. The solvent-induced shifts of  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions have been discussed in terms of ground state and excited state solvation arising from solute-solvent interactions of varied nature. It is noted that for solutes with hydrogen-bonding capability, blue shift is observed in going from non-polar to polar solvents be it  $n \rightarrow \pi^*$  or  $\pi \rightarrow \pi^*$  transitions.

THE effect of solvent-induced shifts on the absorption spectra of organics is not only useful for spectral assignments but also for understanding different factors influencing solute-solvent interactions<sup>1-3</sup>. However, lack of proper knowledge of the different factors associated with solute-solvent interactions makes such a study complicated and a clear picture is yet to come. This is particularly true for  $\pi \rightarrow \pi^*$  transitions which are characterized by small solvent-induced shifts. This prompted us to undertake the title investigation. We have also examined the anomalous spectral behaviour of 2,2'-bipyridyl reported recently by Henry and Hoffman<sup>4</sup>.

## Materials and Methods

2,2'-Bipyridyl (Bipy), 1,10-phenanthroline (phen) and 5-nitro-1, 10-phenanthroline (5-NO<sub>2</sub>-phen) were of extra pure quality (E. Merck or Sigma Chemicals). Methanol (GR, E. Merck) and isopropanol (AR, BDH) were distilled. Formamide (GR, E. Merck), dimethyl sulphoxide (Baker analyzed) and propylene carbonate (K. Light, puriss) were dried over freshly ignited quicklime for several hours and then distilled under reduced pressure. N,N'-Dimethylformamide, *n*-heptane, isooctane, cyclohexane (Uvasol grades) were used as such. Methyl cellosolve was treated with lithium hydride until the evolution of H<sub>2</sub> ceased and finally distilled. Dioxane (AR, BDH) was refluxed for 48 hr over NaOH pellets, distilled twice, kept over metallic sodium overnight and distilled again. Absolute ethanol was treated with a little excess of freshly ignited quicklime, kept overnight and distilled. It was refluxed with Zn-dust and caustic potash for

48 hr and finally distilled. In all the cases, the middle fractions were used within several hours.

HClO<sub>4</sub> (GR, E. Merck) was estimated in the usual way.

The spectra of Bipy at different acidities were noted in aqueous and DMF-water and in other mixed solvents. In order to have approximate idea regarding the basicity of the solvents, we noted the pH-meter readings (which in no way measured the H<sup>+</sup>ion activity in mixed or non-aqueous solvents) of the solvents and their acidic solutions.

The meter readings were taken using a digital pH-meter (Systronics). The spectra were recorded on a Beckman DU-2 spectrophotometer at 298K.

## Results and Discussion

*Spectra of ligands and anomalous behaviour of 2,2'-bipyridyl* -- All the ligands exhibit two intense bands in the UV region (Table 1). The longer wavelength band is ascribed to  $\beta$ -band and the short wavelength band to  $\alpha$ -band<sup>5-10</sup>. However, in the case of Bipy, in addition to 233 and 281 nm bands, Henry and Hoffman<sup>4</sup> observed a band at 308 nm in neutral solutions. They attributed the band at 308 nm to covalent hydrate formation [Bipy + H<sub>2</sub>O  $\rightleftharpoons$  Bipy. H<sub>2</sub>O], but found no evidence of Phen.H<sub>2</sub>O though Phen is known to retain water tenaciously due to its fixed coplanarity and better feasibility of hydrate formation (see Fig. 1). In the present study Bipy did not show any band corresponding to  $\alpha$ - or  $\beta$ -band of Phen (Table 2).

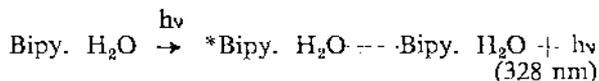
In the pH region (4.5-7.0)<sup>4</sup>, the spectra were characteristic of Bipy and protonated Bipy and the spectra of pure Bipy could only be obtained above

TABLE 1 — ABSORPTION MAXIMA OF 2,2'-BIPYRIDYL, 1,10-PHENANTHROLINE AND 5-NITRO-1,10-PHENANTHROLINE

Solvent	$\nu_{\max}$ (cm <sup>-1</sup> )					
	2,2'-Bipy		1,10-Phen		5-Nitro-1,10-phen	
<i>n</i> -Heptane	42,370	35,460	43,290	38,020	43,290	37,740
Isocetane	—	—	43,290	38,170	43,290	37,740
Cyclohexane	42,370	35,460	43,290	37,880	—	—
Isopropanol	42,370	35,340	43,480	38,020	43,290	37,590
Ethanol	—	—	43,670	37,880	—	—
Methanol	42,550	35,590	43,860	38,020	43,480	37,740
Water	42,920	35,710	44,050	37,880	43,230	37,450
Formamide	—	35,340	—	—	—	37,040
Dimethyl formamide	—	35,460	—	—	—	36,900
Dimethyl sulphoxide	—	35,090	—	37,740	—	37,450
Propylene carbonate	—	35,340	—	38,020	—	—
Methyl cellosolve	42,370	35,340	43,290	37,880	—	—
Dioxan	42,190	35,340	43,100	37,880	—	—

pH 7 ( $pK_{\text{BipyH}^+} = 4.48$ )<sup>11</sup>;  $\epsilon_{\text{BipyH}^+}$  is high and  $\epsilon_{\text{Bipy}}$  is almost zero in this region. The reason that "the disappearance of the 308 nm band on the addition of OH<sup>-</sup> is not accompanied by any change in extinction coefficient of 281 nm band of Bipy. within the experimental precision (3%)" is due to the fact that the isobestic point of Bipy and BipyH<sup>+</sup> is in the region  $282 \pm 1$  nm and is not due to the reaction  $\text{Bipy} \cdot \text{H}_2\text{O} + \text{OH}^- \rightleftharpoons \text{Bipy} \cdot \text{OH}^- + \text{H}_2\text{O}$  as conjectured by Henry and Hoffman<sup>4</sup>.

Similarly, the strong emission at 328 nm observed in the pH region 4–10 was shown<sup>4</sup> to originate due to reaction



Due to change in acid-base behaviour in the excited state ( $pK_{\text{BipyH}^+}^* = 9.5$ )<sup>12,13</sup>. Bipy should exist as  ${}^*\text{BipyH}^+$  or a mixture of  ${}^*\text{Bipy}$  and  ${}^*\text{BipyH}^+$  and not as  ${}^*\text{Bipy} \cdot \text{H}_2\text{O}$ . Obviously, similar pH dependence of intensities of the band at 328 nm (emission) and 308 nm is due to the gradual conversion of BipyH<sup>+</sup> to Bipy. DMF is highly basic and addition of water makes it comparatively acidic. This is the reason why the band at 308 nm of Bipy is observed in DMF + water but not in DMF alone. It is to be noted that the  $pK$ -values of the ligands undergo appreciable change in non-aqueous or mixed solvents due to change in electrostatic and non-electrostatic characters of the solvents. Much of the derived conclusions<sup>4</sup> arose due to neglect of

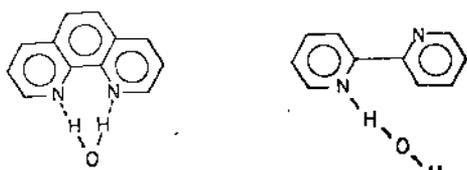


Fig. 1

TABLE 2 — ABSORPTION MAXIMA OF 2, 2'-BIPYRIDINIUM ION IN DIFFERENT SOLVENTS

Solvent*	$\nu_{\max}$ (cm <sup>-1</sup> )	
Water	41,490	33,220
MeOH-H <sub>2</sub> O	41,490	33,110
Pr <sup>t</sup> OH-H <sub>2</sub> O	41,580	33,060
Dioxane-H <sub>2</sub> O	41,150	33,000
Formamide-H <sub>2</sub> O	—	34,360
DMF-H <sub>2</sub> O	—	34,900
DMSO-H <sub>2</sub> O	—	32,790
Methyl cellosolve-H <sub>2</sub> O	41,240	32,890

\*90% (v/v) of organic solvent.

this fact. Moreover, the presence of high concentrations of H<sub>2</sub>SO<sub>4</sub> (or other acids) changes the solvent structure and the acid-base properties of the media enormously. The emission spectra is known to be susceptible to the nature of the medium. Thus the conclusions of Henry and Hoffman<sup>4</sup> are hardly justifiable.

We are not in a position to check the emission spectra. The anomalies are apparent in the reported values, e. g.  $\lambda_{\max}^{\text{em}}$  values of Phen and PhenH<sup>+</sup> are 360 nm ( $\lambda_{\max}^{\text{ab}} = 264$  nm) and 410 nm ( $\lambda_{\max}^{\text{ab}} = 272$  nm) respectively. The emission spectra of Bipy could not be detected whereas BipyH<sup>+</sup> has  $\lambda_{\max}^{\text{em}}$  at 335 nm ( $\lambda_{\max}^{\text{ab}} = 301$  nm.) The abnormally large Stokes' shifts of Phen and PhenH<sup>+</sup> compared to the Stokes' shift (3371.9 cm<sup>-1</sup>) of BipyH<sup>+</sup> require explanation and further study.

Kasha<sup>14</sup> and McConnel<sup>15</sup> have used the solvent-induced shifts as criteria for distinguishing  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. The blue shifts of  $n \rightarrow \pi^*$  transitions in the case of acetone, formaldehyde etc. are due to increasing hydrogen-bonding capabilities from non-polar to polar solvents<sup>3</sup> and can be correlated to  $Z$ -values of solvent polarities<sup>16</sup>. How-

ever, the hydrogen-bonding capabilities of the solutes are also important.

It is known that  $n \rightarrow \pi^*$  transitions usually involve less energy compared to  $\pi \rightarrow \pi^*$  transitions. Due to the presence of lone-pair of electrons having high dipole-moments, the solutes are susceptible to marked solute-solvent interactions and H-bonding making solvent shifts appreciable. Solvent shift in case of  $\pi \rightarrow \pi^*$  transitions involves a large change in energy and would be observable if  $\pi \rightarrow \pi^*$  transitions are in the long wavelength region and energy changes due to solute-solvent interactions are high.

The 'solvation energies' of solutes in different solvents are obviously different arising from the differences in energy changes<sup>27</sup> due to (i) the creation of a cavity of appropriate size in the bulk solvent, (ii) the reorganization of solvent molecules around the cavity, (iii) solute-solvent interactions (e.g. dispersion interactions, dipole-dipole and dipole-induced dipole interactions and specific interactions like H-bonding, charge-transfer and intermolecular energy transfer etc.) of different magnitude and (iv) the energy changes due to change in the standard states from gas to solution. The step (iii) is most important and the step (iv), however, vanishes for comparison.

Thus, the proper interpretation of solvent-induced shifts involves the knowledge of ground state (as well as excited state) solvation energies. It is known that

$$\Delta \nu = \nu(\text{soln}) - \nu(\text{gas})$$

In the absence of  $\nu(\text{gas})$  data, we consider  $\nu$  (heptane or hydrocarbons) roughly equal to  $\nu(\text{gas})$ , so that  $\Delta \nu_{\text{ab}}$  can be a measure of solute-solvent interactions (exothermic in the case of blue shift and endothermic in the case of red shift) or an approximate measure of the differences in the ground state solvation energies of a solute assuming the energies of the Franck-Condon (F. C.) excited states to be the same in all the solvents. Similarly,  $\Delta \nu_{\text{em}}$  is expected to give a rough estimate of the differences in the excited state solvation energies of the solute<sup>13</sup>.

The large blue-shifts observed in case of  $n \rightarrow \pi^*$  transitions of ketones or azo compounds in going from hexane to ethanol have been ascribed by Haberfeld<sup>18,19</sup> to increased ground state solvation (which is greatest in the case of H-bonding solvents) accompanied by diminished excited state solvation in going from polar to non-polar solvents.

Moreover, the observed blue shifts of nitroaromatics like 1-nitronaphthalene<sup>20</sup> etc., from DMF to MeOH cannot be correlated with the greater ground state solvation by H-bonding solvent or the greater Franck-Condon (F.C.) strain as would be apparent from the uniformly endothermic enthalpies of transfer of the F. C. excited states (or the relaxed excited states). It is clear that the blue shift does not necessarily implies  $n \rightarrow \pi^*$  transitions or greater H-bonding capability. If the H-bonding capabilities of the solutes are weakened by  $-\text{NO}_2$ ,  $-\text{Cl}$  groups etc. red-shift may also be observed.

From a study of the spectral solvent-induced shifts of Bipy and Phen Badger and Walker and others<sup>21-23</sup>

found no evidence of  $n \rightarrow \pi^*$  transitions. The solvent shift (emission) of Bipy observed and attributed to  $n \rightarrow \pi^*$  transitions by Harriman and coworkers<sup>24,25</sup> was, however, contradicted by Henry and Hoffman<sup>4</sup>. It is to be noted that all solutes are to some extent modified by the solvents. Spectral solvent shift is, thus, always probable be it  $n \rightarrow \pi^*$  or  $\pi \rightarrow \pi^*$  transitions. But the observed transitions of Bipy, Phen and 5- $\text{NO}_2$ -Phen are  $\pi \rightarrow \pi^*$  transitions as (i) these bands are located at relatively short wavelength regions characterized by high intensities, (ii) the transitions are insensitive to heteroatom substitution, (iii) the bands show large redshifts due to protonation in acid solutions contrary to the large blue shifts or disappearance of bands in case of  $n \rightarrow \pi^*$  transitions and (iv) the long-wavelength transition of Phen and 5- $\text{NO}_2$ -Phen show almost no or slight red shift in going from non-polar to polar solvents.

In spite of similar linkages, the differences in spectral behaviour of Bipy and Phen must be due to (i) fixed coplanarity and resonance stabilization of Phen compared to Bipy, (ii) capability of free-rotation of 2,2'-bipyridyl and preferred *trans*-configuration in the molecular form and slightly twisted *cis*-configuration in the ionic form (the geometry of the molecule may also be changed due to twisting of the molecule), and (iii) the dipole moments of the *trans*-Bipy, *cis*-Bipy and Phen are 0.91D, 3.80D and 4.11D<sup>23,27</sup>.

Thus, due to greater dipole-dipole interactions, H-bonding and resonance stabilization, Phen is in the lower energy level in the ground state compared to Bipy requiring much more energy for solvent-induced shift. 5- $\text{NO}_2$ -Phen will be in the higher energy state as the resonance stabilization is disturbed and the capability of H-bond formation is weakened. These are well reflected in the spectra. However, small shifts indicate little solute-solvent interactions.

In spite of anomalies, both  $\beta'$ - and  $\beta$ -bands of Bipy and  $\beta$ -band of Phen show slight blue shifts in going from non-polar (having high intensities) to polar solvents (having low intensities), an indication generally ascribed to  $n \rightarrow \pi^*$  transitions, though H-bonding solvents are also known to cause marked blue shifts of  $\pi \rightarrow \pi^*$  transitions of chromophores<sup>23,28</sup>. The blue shifts could also arise from the differences of the ground state and excited state solvation energies arising from the differences in dispersion forces, dipole-dipole, dipole-polarization forces, orientation-strain, etc.

The  $pK^* > pK$  values of Bipy, Phen and 5- $\text{NO}_2$ -Phen suggest that the electron densities on the N-atom and dipole moments of the molecules increasing in the excited states and may be due to the canonical structures like II, III, V, VI, etc. (see Fig. 2) similar those of acridine, naphthylamine etc. suggested by Jackson and Porter<sup>29</sup>. Coulson and Jacobs<sup>30</sup> from MO calculations predicted a migration of charge towards N-atom of pyridine. This is expected in the case of Bipy and Phen also. A considerable increase in the dipole moment of Phen is observed from the large Stokes' shift in aqueous solution ( $\nu_{\text{Phen}}$  is calculated to be 3.70Å). The red shift is expected in the case of non-polar solvents but a

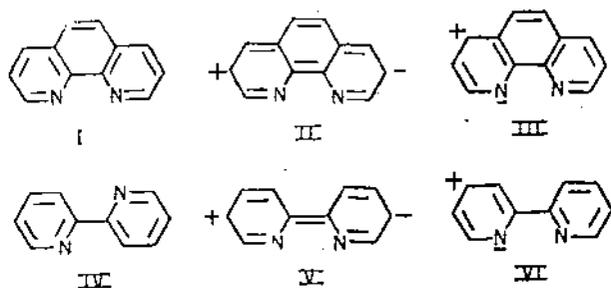


Fig. 2

resultant blue shift is expected in the case of H-bonding solvents due to greater ground state solvation and orientation strain. This is actually observed as seen from the data in Table 1. In the case of dipolar aprotic solvents wherein the polarization shift and the dipole-dipole interaction would be high in the excited state, a red shift is observed. The small blue shift or no shift, however, suggests similarity of solvation in the ground and excited states.

The introduction of nitro group (as in 5-NO<sub>2</sub>-Phen) increases the dipole-dipole and dipole-induced dipole interactions but weakens the H-bonding ability. A resultant red shift is thus observed in going from isoctane to water to DMF (Table 1).

Though the solvent effects of UV transitions are poorly correlated by the dielectric constants or functions of the dielectric constants, the transition energies have been found to be a linear function<sup>2</sup> of

$$f(D) \text{ [where } f(D) = \frac{2(D-1)}{D+1} \text{ where } D \text{ is the}$$

dielectric constant of the medium] within limitations. Deviations from linearity indicates 'specific association' like 'band specific' H-bonding. The  $\nu(\text{cm}^{-1})$  vs  $f(D)$  plots of both Bipy and Phen show band-specificity indicating H-bonding.

However, greater anomalies are observed in solvents having lone pair of electrons (H<sub>2</sub>O, dioxane, DMF, DMSO, etc.) even if there is no H-bonding.

The deviation in the case of dioxane has been ascribed<sup>31</sup> to greater effective reaction field than indicated by the macroscopic property. In DMSO, introduction of CH<sub>3</sub>-groups leads to strong solute-solvent interactions or complex formation; *d*-orbital of S may be involved in the case of DMSO which possesses polarized  $\pi$ -bonding.

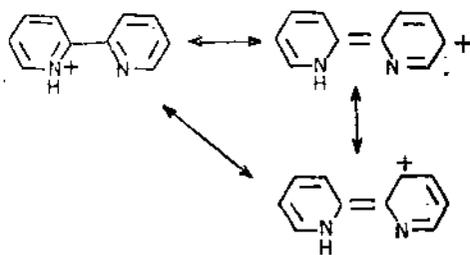


Fig. 3

The spectra of Bipy H<sup>+</sup> show some interesting features (Table 2). In this case *cis*-form predominates (see Fig. 3) and the dipole moment in the excited state is likely to be increased due to resonance stabilization<sup>32</sup> and a red shift is expected in mixed solvents (90% v/v of organic solvents) like MeOH, Pr'OH, dioxane, MC and DMSO.

The blue shift as observed in formamide + H<sub>2</sub>O and DMF + H<sub>2</sub>O mixtures are due to the presence of both Bipy and BipyH<sup>+</sup> in these solvent mixtures.

It is thus apparent that for solute molecules with H-bonding ability, the spectral shift is dependent on the type of solvents and their degree of order determined by (i) H-bonding, (ii) dipole-dipole interactions and (iii) molecular shape<sup>33</sup>. In H-bonding solvents, the blue shift is expected in  $n \rightarrow \pi^*$  or  $\pi \rightarrow \pi^*$  transitions. If the H-bonding capability of solute is weakened, red shift may also be observed. In the case of polar or dipolar aprotic solvents, the solvent shift would depend mainly on the dipole-dipole, dipole-induced dipole interactions; the blue or red shift may be expected depending on the decrease or increase in the dipole moment of the solute in the excited states.

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