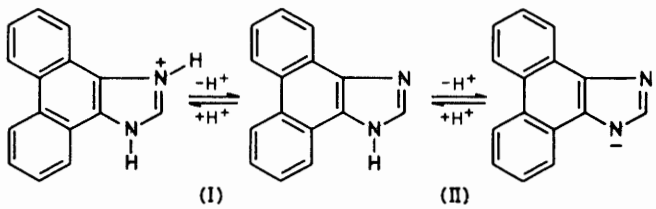
Unusual Behaviour in the Excited State Proton Transfer of 1*H*-Phenanthro[9,10-*d*]imidazole

Meenakshisunderam Swaminathan and Sneh K. Dogra *
Chemistry Department, Indian Institute of Technology, Kanpur, U.P. 208016, India

Absorption and fluorescence spectra of 1*H*-phenanthro[9,10-*d*]imidazole in different solvents and at different pH values have shown that the long wavelength bands are due to the transitions localised at the phenanthrene ring and the pyridine nitrogen atom is more acidic in S_1 than in S_0.

Detailed studies of the u.v. spectra of benzimidazole have indicated that the absorption pattern resembles that of a substituted benzene derivative, *i.e.* the short and long wavelength absorption bands correspond to transitions in the imidazole and aryl rings, respectively.[1-3] Derivatives of 1*H*-phenanthro[9,10-*d*]imidazole (PIH), which are useful anti-inflammatory drugs,[4] give a long wavelength u.v. spectrum which resemble the absorption spectrum of a substituted phenanthrene derivative.

We have chosen 1*H*-phenanthro[9,10-*d*]imidazole (PIH) as our model compound and the following studies have been carried out. (a) Absorption and fluorescence in different solvents have been studied to establish the pattern of the u.v. spectra. (b) PIH possesses two types of nitrogen atom, one of the pyrrole type and the other of the pyridine type. It is well known that pyridine nitrogen atoms become more basic and pyrrole atoms more acidic in the first excited state if there is a $\pi \longrightarrow \pi^*$ electronic transition.[5] This behaviour has been observed by us in diaza-systems (pyrazole,[6] 4,5-diphenylimidazole,[7] benzimidazole,[8] and 2-phenylbenzimidazole [9]) with both pyridine and pyrrole nitrogen atoms. The effect of pH on the absorption and fluorescence spectra was studied to calculate pK_a^* (I) and pK_a^* (II) (Scheme) to see whether similar behaviour occurs in this case or not. (c) Since most analytical measurements on biological or model biological systems are carried out in solutions containing buffers, often in high concentrations to maintain a constant pH, the effect of buffer concentration on both equilibria in the Scheme has also been studied.



Scheme.

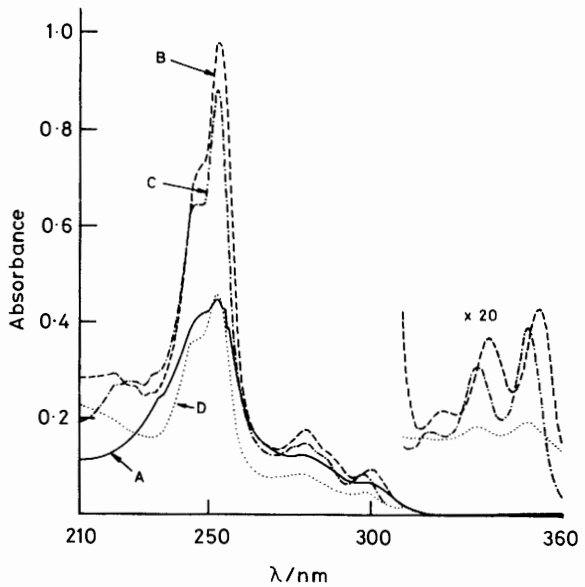


Figure 1. Absorption spectra of PIH in different solvents: A, saturated hexane; B, acetonitrile, 1×10^{-5}M; C, methanol, 1×10^{-5}M; D, water, 1×10^{-5}M

Experimental

PIH was prepared by the thermal synthesis from 9,10-phenanthroquinone and hexylamine.[10] The purity of the compound was established by the same emission maxima at different excitation wavelengths. B.D.H. spectrograde methanol and analytical grade H_2SO_4 and NaOH were used as such. Analytical grade acetonitrile (E. Merck) and hexane (B.D.H.) were further purified by literature methods.[11] Triply distilled water was used for the preparation of aqueous solutions. For absorptiometric and fluorimetric titrations, all solutions were prepared immediately before use to eliminate the decomposition errors. During fluorimetric titration in the presence of a given concentration of buffer, the total analytical concentration of phosphate ($H_2PO_4^- + HPO_4^{2-}$) was kept constant in all solutions. The concentration of PIH in all the solutions was 10^{-5}M and for fluorimetric titrations, the solutions were excited at the isosbestic point of the respective equilibria.

pH Measurements were made on a Toshniwal pH meter model CL44A. Absorption spectra were recorded with a Cary 17D spectrophotometer. Fluorescence measurements were made on a scanning spectrofluorimeter, fabricated in our laboratory.[12] Excitation and emission monochromators were calibrated using a low pressure mercury lamp.

Results and Discussion

Absorption and Fluorescence Spectra.—Due to the poor solubility of PIH in hexane and water, the longer wavelength peaks were absent in hexane and their resolution was poor in water. The absorption spectra of PIH at two different concentrations (1×10^{-4} and 1×10^{-5}M) in different solvents are shown in Figure 1 and the $\nu_{max.}$ are given in Table 1. The extinction coefficients and the band maxima have the same pattern as noticed by Hennessy and Testa [13] in ethanol as solvent. All the absorption bands, except those at 252.5 nm

Table 1. Absorption maxima (cm^{-1}) of PIH in different solvents and at different pH

Hexane	Acetonitrile	Methanol	Water	Cation	Anion
40 816	40 816	40 816	40 816	41 152	40 160
39 603	39 525	39 603	39 603	39 920	39 062
35 714	35 714	35 842	35 842	36 900	35 087
33 333	33 333	33 557	33 613	35 842	32 679
	31 007	31 446		34 423	28 169
	29 717	30 030	30 075	30 978	
	28 409	28 667	*28 735*	*29 585*	*27 322*

Table 2. Fluorescence maxima (cm^{-1}) of PIH in different solvents and at different pH

Hexane	Acetonitrile	Methanol	Water	Cation	Anion
28 368	27 548	28 011	27 777	29 455	*24 360*
26 990	26 455	26 845	*26 667*	*28 090*	
25 510	25 031	25 380		26 667	

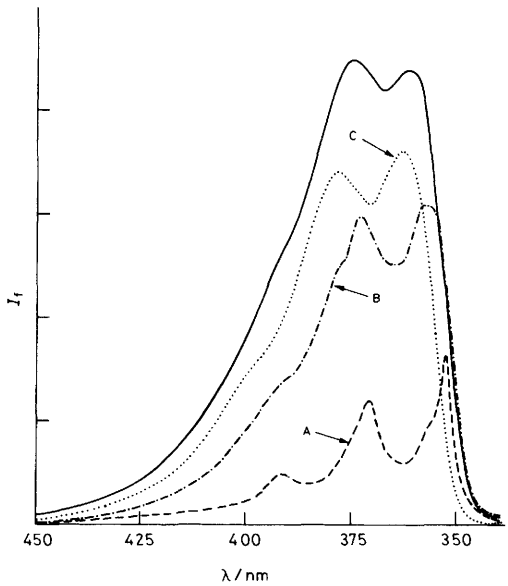


Figure 2. Fluorescence spectra of PIH in different solvents: A, saturated hexane; B, methanol, 1×10^{-5}M; C, acetonitrile, 1×10^{-5}M; D, water, 1×10^{-5}M

and below, are blue-shifted with an increase in the polarity and hydrogen bonding nature of the solvents. As the molecule is rigid, the structure of the bands is not lost in polar solvents. The respective $\nu_{max.}$ values of PIH_2^+ (phenanthroimidazole cation) are blue-shifted and resemble those of phenanthrene,[14] whereas those of PI^- (phenanthroimidazole anion) are red-shifted and are also listed in Table 1.

The fluorescence spectra of PIH in different solvents at 298 K are shown in Figure 2. The $\nu_{max.}$ of the fluorescence spectra of PIH in different solvents, PIH_2^+, and PI^- are listed in Table 2. The fluorescence spectra of PIH and PIH_2^+ are structured. When compared with the spectrum in hexane, fluorescence spectra in other solvents are broader and the maxima are red-shifted. But the fluorescence maxima in methanol and water are blue-shifted relative to that in acetonitrile and it is larger in the case of methanol. The blue shift becomes a maximum in acidic medium in which PIH_2^+ is formed.

On the basis of the results of Tables 1 and 2, the transitions could not be $n \longrightarrow \pi^*$ for the following reasons. (i) The extinction coefficients of all the bands are quite large [13] and (ii) at room temperature, fluorescence is generally observed if S_1 is a $\pi \longrightarrow \pi^*$ and phosphorescence if S_1 is an $n \longrightarrow \pi^*$ transition.[15] Thus, the blue shift observed in absorption contrary to the normal red shift noticed in the $\pi \longrightarrow \pi^*$ transition could be explained as follows. The lone pair can affect the $\pi \longrightarrow \pi^*$ transitions in two ways: (i) a resonance effect, where the lone pair is delocalised over the complete system and raises the energy of the bonding orbital more than the antibonding orbital if the lone pair is in the same plane of π electrons; (ii) an inductive effect, where charge migration takes place without delocalisation of the lone pair and affects the coulombic integral of each atom. Thus the red shift in the $\pi \longrightarrow \pi^*$ transition of the parent molecule is smaller in the latter case than in the former. Since the above processes will be opposed by the hydrogen–donor interaction of methanol and water with the lone pair on nitrogen, the absorption maxima in these solvents are blue-shifted relative to acetonitrile, which is a weak hydrogen-atom-acceptor solvent. This is further confirmed by the blue shift observed in the absorption maxima of PIH_2^+, which is an extreme case of hydrogen-bond formation.

The fluorescence spectra of PIH in different solvents can be explained on the above lines, *i.e.* fluorescence maxima will be red-shifted in the presence of hydrogen-acceptor solvents (interaction with pyrrole nitrogen atom) and blue-shifted in the presence of hydrogen-donor solvents (interaction with the lone pair of pyridine nitrogen atom). The large red shift observed in fluorescence maxima of PIH in acetonitrile relative to hexane is due to dispersive interaction and the hydrogen-atom-accepting nature of the solvent. The red shift in methanol and water relative to hexane and the blue shift relative to acetonitrile show that in addition to the dispersive interaction and hydrogen-accepting tendency, these solvents also exhibit a hydrogen-donating capability. The difference in the shifts for methanol and water is due to their preferential interactions at the pyrrole or pyridine nitrogen atom. The magnitude of each interaction cannot be determined from our study. But qualitatively one can say that water is acting here as a poor hydrogen donor compared with methanol and its hydrogen-accepting interaction with the pyrrole hydrogen atom may be stronger than that in methanol. Similar behaviour has been observed in the absorption spectra of different isomeric aminoquinolines [17] on going from hexane to ethanol to water, *i.e.* the site of hydrogen-bond formation is at a different nitrogen atom in different solvents. The maximum blue shift observed in the acidic medium, where the lone pair

Table 3. Excited-singlet-state acidity constants of PIH

Equilibrium	pK_a	pK_a* (abs)	pK_a* (flu)	pK_a* (ave)	pK_a* (FT) C 0.0	pK_a* (FT) C 0.1M	pK_a* (FT) C 1.0M
(I)	4.65	2.87	1.66	2.26	2.2	2.2	2.2
(II)	11.86	8.69	7.01	7.95	11.66	11.3	10.72

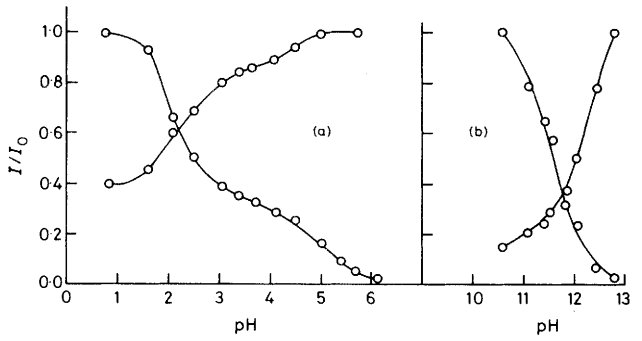


Figure 3. Plot of relative fluorescence intensities of PIH *versus* pH: (a) cation and neutral form, (b) neutral and anion form

is completely prevented from charge-transfer interaction, also supports the above conclusion.

Acidity Constants.—The ground-state dissociation constants for equilibrium (I) and (II) were determined spectrophotometrically and are listed in Table 3. These values (4.65 and 11.86) are lower than those of imidazole (6.95 and 14.52) and benzimidazole (5.53 and 13.2) and are consistent with the theory that electron-withdrawing groups, like phenyl, decrease the basicity and increase the acidity of the molecule.[18]

The pK_a* values at 25 °C are calculated using the Förster cycle method, *i.e.* $pK_a - pK_a^* = 2.3 \times 10^{-3}(\nu - \nu')$, where ν and ν' are the wave numbers of the 0–0 transition of the acid and its conjugate base. The 0–0 transition or band maxima (if it is difficult to determine the 0–0 band) can be obtained from absorption, fluorescence spectra, or the average of the absorption and fluorescence band maxima. The transitions used to calculate pK_a* (I) and pK_a* (II) are italicised in Tables 1 and 2. The values thus obtained are listed in Table 3. pK_a* Values were also calculated from the fluorimetric titrations (Figure 3) and are also listed in Table 3. The fluorimetric titration for the neutral–anion equilibrium (pH 10—14) is straightforward but that for the cation–neutral equilibrium is a little complicated. Even though both curves cross at pH 2.3, which is different from pK_a (I), these curves may be looked on as stretched sigmoid curves covering the whole of the ground- and excited-state pK_a region. Figure 4 represents the behaviour of fluorimetric titrations, carried out in the presence of different amounts of phosphate buffers. There is virtually no change in the values of pK_a* (I) but those of pK_a* (II) decrease with the increase in the concentration of the buffers as mentioned in Table 3. Figure 5 represents the fluorescence of PIH in buffered and unbuffered solution at pH 10.5.

The pK_a* (I) values obtained by different methods show the same trend in which the pyridine nitrogen atom becomes more acidic in S_1. This trend is against the normal behaviour observed in other compounds containing pyridine nitrogen atoms, but confirming our earlier conclusions that the first few excited singlet states are localised on the phenanthrene

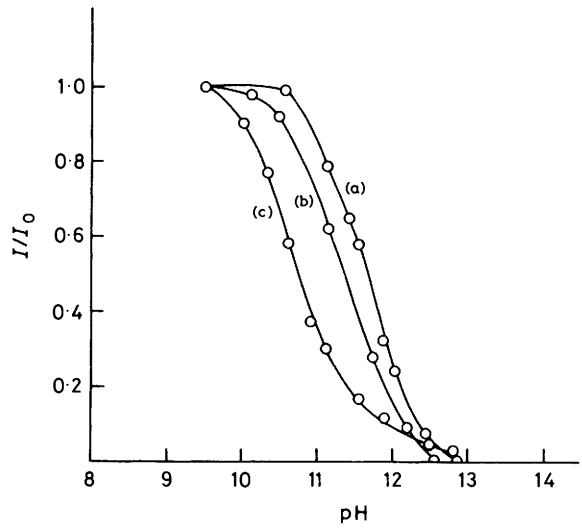


Figure 4. Plot of relative fluorescence intensities of PIH *versus* pH: (a) without buffer, (b) with 0.1M buffer, and (c) 0.5M buffer

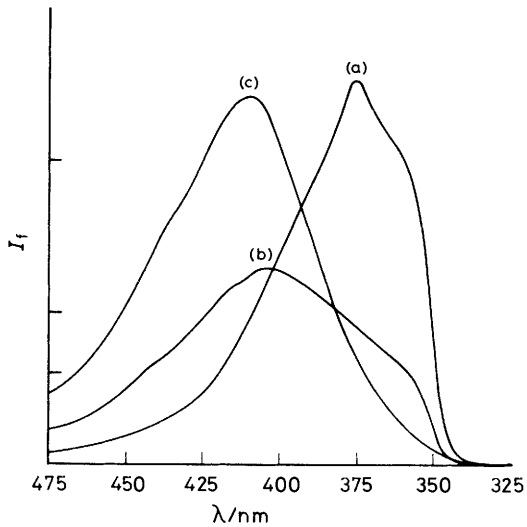


Figure 5. Fluorescence spectra of PIH: (a) pH 10.2, without buffer; (b) pH 10.2 (0.5M buffer); (c) pH 12.3, without buffer

ring and the lone pair on the nitrogen atom is behaving like that present on the amino-group.[16] The small difference of 1.21 units between pK_a* (abs) and pK_a* (flu) could be due to the unequal solvent relaxation of the conjugate pair in S_0 and S_1 states. The deviation of pK_a* (flu) from pK_a* (FT) by 0.6 units could be because of the use of fluorescence band maxima rather than the 0–0 transition. The pK_a* (ave) value agrees very nicely with that determined by fluorimetric titrations, indicating that errors due to unequal solvent relaxations,

vibrational spacings, and location of the 0–0 band of the conjugate acid–base pair cancel each other.

In the fluorimetric titration from pH 1.5 to 3 (Figure 3), the cation fluorescence intensity decreases sharply to 0.4 of its maximum intensity while the fluorescence of the neutral form rises to 0.8 of its maximum value. From pH 3 to 4, the change in fluorescence intensity is less but again a sharp change in intensity occurs from pH 4 to 5.1. The actual dependence of fluorescence intensity of acid or base with pH in S_1 is determined by the excited-state lifetimes of acid or base, their rate constants, and mechanisms of proton exchange and concentration of proton donor and acceptor species in solution. If the rate of excited-state proton transfer is much slower than the rate of fluorescence decay of acid and conjugate base, the sharp inflection points (in a narrow pH region) in the fluorimetric titration curves correspond to pK_a and if the rate of excited-state proton exchange is much faster than the rates of fluorescence decay of the conjugate acid–base pair, then the mid-point corresponds to pK_a^*. Here the stretched sigmoid curves covering a pH range of 1—7 show the partial establishment of the equilibrium in S_1. That is why there are two inflection points, one at pH = pK_a^* and the other at pH = pK_a. But the inflection point in the pH 1.5—3 region is so sharp that both curves cross here. This indicates that the proton-transfer rate is relatively faster than those of fluorescence decay of the acid–base pair, but it is not so fast as to attain complete equilibrium. Similar behaviour has been observed in β-naphthol [19] and phenanthren-9-ol [20] but in these cases the flat portion is relatively large. The absence of this large flat portion in the fluorimetric titration of PIH could be due to the small difference between pK_a and pK_a^*.

The pK_a^* (II) values clearly show that PIH is more acidic in S_1 than S_0 and this behaviour is consistent with the pyrrole type of nitrogen atom. The small difference between pK_a^* (II, abs) and pK_a^* (II, flu) can be explained along the lines for pK_a^* (I). The fluorimetric titration gives only the pK_a value. Similar behaviour has been observed in many heterocyclic compounds containing a nitrogen atom and with pK_a^* values falling in the mid-pH region (3—10).[6] In this pH range, because of the small concentration of H^+ and OH^- ions, the rate of proton exchange is slower than that of fluorescence decay, although the rate constant for the former process is large. So the addition of buffer ions, which are themselves proton donors or acceptors, may increase the rate of proton transfer in S_1. Figure 4 and the data in Table 3 clearly show that buffers have no effect on pK_a^* (I) as it is outside the mid-pH range but pK_a^* (II) is clearly shifted towards lower values. Because of the saturation limit of the buffers, the levelling effect in pK_a^* (II) could not be observed in our study but it is quite clear that the rate of proton transfer is increased in the presence of high concentrations of buffers in the mid-pH range. This is also confirmed by the fluorescence spectra of the anion at pH 10.5, noticed only in 1M buffer solution and not in unbuffered solution (Figure 5).

In conclusion, these results clearly indicate that even though the lone pair is at one of the sp^2 hybrid orbitals of the nitrogen atom, it affects the longer wavelength $\pi \longrightarrow \pi^*$ transitions and seems to be localised on the phenanthrene ring. Moreover it also appears qualitatively that it is the environment of the nitrogen lone pair which affects the coulomb integral of that nitrogen which in turn relays the effect *via* the nitrogen $2p$ orbital to the carbon skeleton of the π system rather than due to the non-planarity in the imidazole ring (*i.e.* direct or resonance effect). This is because (a) the lone pair of the pyridinic nitrogen atom is perpendicular to the plane of the π system and (b) the spectral shifts due to hydrogen-bond-formation tendency of the solvents is small. A conclusion regarding which effect is predominant can only be made from MO calculations.

Acknowledgements

M. S. acknowledges the award of a Teacher Fellowship by the University Grants Commission under the Faculty Improvement Programme.

References

1 D. J. Rabiger and M. M. Joule, *J. Org. Chem.*, 1964, **29**, 476.
2 G. Leadri, A. Mangini, F. Montanari, and R. Posserini, *Gazz. Chim. Ital.*, 1955, **84**, 769.
3 P. N. Preston, 'The Chemistry of Heterocyclic Compounds,' Wiley, New York, 1981, vol. 40, p. 64.
4 *Chem. Abstr.*, 1980, **93**, 168 269.
5 J. F. Ireland and P. A. H. Wyatt, 'Advances in Physical Organic Chemistry,' ed. V. Gold, Academic Press, London, 1976, vol. 12, p. 199.
6 M. Swaminathan and S. K. Dogra, *J. Photochem.*, 1983, **21**, 245 and references mentioned therein.
7 M. Swaminathan and S. K. Dogra, *Indian J. Chem.*, in the press.
8 T. K. Alder, *Anal. Chem.*, 1962, **34**, 685.
9 A. K. Mishra and S. K. Dogra, unpublished results.
10 V. N. R. Pillai and E. Purushothaman, *Curr. Sci.*, 1968, **47**, 627.
11 J. A. Riddick and W. Bunger, 'Organic Solvents,' Wiley-Interscience, New York, 1970.
12 M. Swaminathan, Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1982.
13 J. Hennessy and A. C. Testa, *J. Phys. Chem.*, 1972, **76**, 3362.
14 R. A. Friedel and M. Orchin, 'Ultraviolet Spectrum of Aromatic Molecules,' Wiley, New York, 1951.
15 M. Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.
16 K. Tsutsumi, K. Aoki, H. Shizuka, and T. Morita, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 3245.
17 S. G. Schulman, 'Physical Methods in Heterocyclic Chemistry,' ed. A. R. Katritzky, Academic Press, New York, 1974, vol. VI, p. 180.
18 C. A. Matuszak and A. J. Matuszak, *J. Chem. Educ.*, 1976, **53**, 281.
19 C. M. Harris and B. K. Sellinger, *J. Phys. Chem.*, 1980, **84**, 891 and references mentioned.
20 M. Swaminathan and S. K. Dogra, unpublished results.

Received 29th *November* 1982; *Paper* 2/2004