

Prototropism in 2-(*m*-Aminophenyl)benzimidazole in First Excited Singlet State

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The effect of pH on the absorption and fluorescence spectra of 2-(*m*-aminophenyl)benzimidazole indicates that monocation is formed by the protonation of the tertiary nitrogen atom, and the dication by further protonation of the exocyclic amino group, both in S_0 and S_1 states. Monoanion in S_0 state is formed by the deprotonation of the amino group. The fluorescence intensity of monocation is completely quenched by the strong hydrogen bond forming solvents at 298K.

Absorption and fluorescence spectra of benzimidazole have been studied extensively in different solvents and at various pH values¹⁻⁶. The absorption spectrum of the benzimidazole cation is slightly blue-shifted whereas the fluorescence spectrum (360 nm) is largely red-shifted as compared to the neutral molecule (290 nm). Borresen¹ ascribed this large energy shift to the formation of solute-solvent complex in the excited state whereas Kondo and Kuwano³ showed it to be due to the reversal of electronic states on protonation, i.e. in neutral molecule, less polar L_b is the emitting state and in monocation, more polar L_a is the S_1 state. The fluorescence quantum yield (0.67) of neutral molecule is much higher than that (0.06) of monocation².

Similar studies on substituted benzimidazoles are not many. Only recently, Tway and Love⁵ reported that spectral transitions of benzimidazole are insensitive to the nature of the solvents and it was only the substituents which made the molecule sensitive to the environments. We have also carried out such studies on the substituted diazaheterocyclic systems⁷⁻⁹. The present study is an extension of our earlier work¹⁰. The photophysical characteristics of 2-(*m*-aminophenyl)benzimidazole have been studied at different pH values and the equilibrium constants for the various proton transfer reactions have been determined.

Materials and Methods

2-(*m*-Aminophenyl)benzimidazole (MBNH₂) was prepared by refluxing equimolecular quantities of *o*-phenylenediamine and *m*-aminobenzoic acid in polyphosphoric acid at 250°C (ref. 1). The compound was repeatedly crystallised from ethanol and its purity checked by various methods, especially by getting the similar fluorescence spectra when excited with different wavelengths. The MBNH₂.HCl was prepared by passing dry hydrochloric acid gas through the ethereal solution of MBNH₂.

Spectroscopic grade methanol (BDH) and AR grade NaOH, H₂SO₄ (all BDH) and trifluoroacetic acid were used as such. Analytical grade dioxane, ether (both BDH), acetonitrile (E Merck) and ethanol were further purified as suggested in literature¹¹. Triply distilled water was used for the preparation of aqueous solutions. A modified Hammett's acidity scale (H_0)¹² for H₂SO₄-H₂O mixture and Yagil's¹³ basicity scale (H_-) for NaOH-H₂O mixture were used for the solutions below pH 1 and above pH 13 respectively. Hammett's acidity and basicity functions represent the actual (or free) amount of proton or OH⁻ ions available in the desired solution to react with a weak base or weak acid respectively.

Absorption spectra were measured on a Cary 17D spectrophotometer. Fluorescence measurements were made on a scanning spectrofluorimeter fabricated in our laboratory¹⁴. Both the monochromators were standardised from time to time with a low pressure mercury lamp. pHs in the range 1-13 were measured on a Toshniwal pH meter model CL-44A. The band width of the excitation radiation was 8 nm. The solutions (10⁻⁵M to 10⁻⁴M) for absorptiometric and fluorimetric titrations were prepared just before taking measurements. Quinine sulphate in 0.1N H₂SO₄ ($\phi_0 = 0.55$)¹⁵ was taken as the standard for measuring the quantum yield of fluorescence with 300 nm, as the excitation wavelength. In fluorimetric titrations, isosbestic wavelengths 290, 300 and 305 nm were used for excitation of dication-monocation, monocation-neutral and neutral-anion equilibria, respectively.

Results and Discussion

The absorption and fluorescence spectra of various prototropic forms of MBNH₂ have been studied in the H_0 /pH/ H_- range of -9 to 16. The data are recorded in Table 1. Besides the neutral form (pH 8), three new species have been identified in this region from the absorption spectrum. At [H⁺] in the range H_0 -9 to pH 2, the long wavelength absorption maximum is

Table 1—Absorption Band Maxima, Fluorescence Band Maxima and ϕ_f of Various Prototropic Forms of MBNH₂

Solvent	$\lambda_{\max}$ (abs), nm (log E)			$\lambda_{\max}$ (flu), nm	ϕ_f
Water pH 8	220 (4.30)	242 (4.25)	297 (4.34)	420	0.13
0.001M H ₂ SO ₄	227 (4.30)	240 (4.28)	293 (4.35)	—	—
1M H ₂ SO ₄	242 (4.23)	247 (4.20)	297 (4.36)	380	0.22
1M NaOH	—	250 (4.26)	313 (4.34)	— 336, 350, 367, 382*	—

*At 77K and $1 \times 10^{-4}M$ solution.

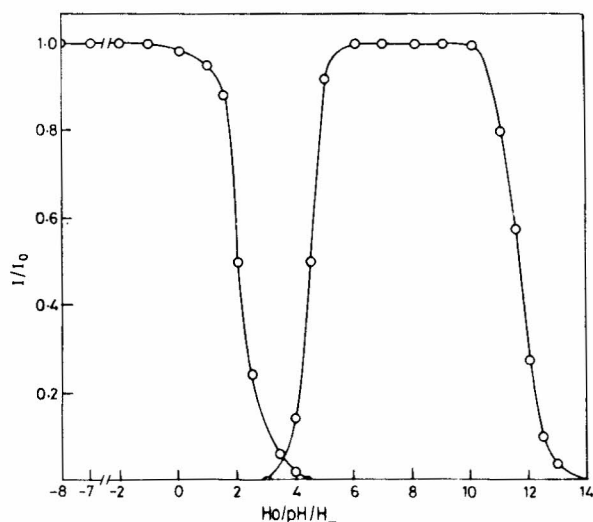
observed at 297 nm, from pH 2 to 4.5 a slightly blue-shifted absorption maximum at 293 nm, from pH 4.5 to 12 at 297 nm and from pH 12 to H⁺ 16 at 313 nm. Whereas for the same [H⁺] ranges, the fluorescence band maximum for the respective species is observed at 360 nm, no fluorescence, at 420 nm and again no fluorescence respectively.

In MBNH₂ protonation can occur at two sites, viz. exocyclic amino group and the tertiary nitrogen atom. Deprotonation can also occur at two sites, viz. exocyclic amino group and the imino group. It is well known that the protonation at the amino group should exhibit the following spectral characteristics: (i) a blue-shifted band for the cation in absorption and fluorescence, (ii) a usual ground state pK_a of ~ 4 (ref. 16), (iii) in general, competing proton-induced fluorescence quenching observed during protonation^{7,17-24} and (iv) a higher acidity of the arylammonium ion in the excited state^{7,17-24}. Protonation at the tertiary site is usually characterised by (i) a red-shift of absorption and fluorescence spectra of cation in comparison to neutral molecule, except in the case of benzimidazole where absorption spectrum of cation gets blue-shifted²⁷ & (ii) an increase in the basicity of the tertiary nitrogen atom in the excited states^{6,25-27} which in benzimidazoles is not manifested in its fluorimetric titrations^{6,8}. Similarly deprotonation of imino and amino group hydrogens exhibits red-shift in the absorption and fluorescence spectra of neutral molecules. Whereas the former anion is generally fluorescent^{6,8,26-29}, the latter anion is non-fluorescent with the exception of 2-naphthylamine³⁰. All these above results are good if $\pi \rightarrow \pi^*$ is the lowest energy transition and benzimidazole exhibits this transition^{1-5,10}.

The long wavelength absorption maximum at 297 nm has been assigned to the neutral form. The absorption band at 293 nm is due to the formation of

monocation and the pK_a value calculated for this reaction from spectroscopic data is found to be 5.0 (5.3 for 2-phenylbenzimidazole⁸). It is also clear from Fig. 1 that the fluorescence intensity of neutral form (420 nm band at pH 8-10) is quenched below pH 5 without the formation of any other fluorescent species on depletion of neutral species. Below pH 3, a new blue-shifted (380 nm) fluorescence band starts appearing, attains maximum intensity at pH 0 and does not change upto H_0-9 . From these results it appears that the formation of monocation occurs by the protonation of the amino group instead of the tertiary nitrogen atom. However, the following facts rule out this possibility: (i) A change in the absorption spectrum (297 nm band) is noticed below pH 2; (ii) pK_a value obtained is more close to the equilibrium constant of the protonation reaction of tertiary nitrogen atom of benzimidazole^{6,8} rather than to that of amino group¹⁶; (iii) for benzimidazoles, it has normally been found that pK_a^* values for protonation or deprotonation reaction, calculated from fluorimetric titrations, resemble the ground state values^{6,8}. In fact pK_a^* obtained from the decay curve of neutral form is found to be 4.8, a value close to that (5.0) calculated above. Thus the 380 nm fluorescence is not due to the monocation formed by protonation of the amino group and it is more reasonable to assume that a non-fluorescent monocation, protonated at tertiary nitrogen atom, exists between pH 2 and pH 4.5. The blue-shift in the absorption spectrum is possibly due to the loss of conjugation by the rotation of the phenyl ring, just as in the case of 2-phenylbenzimidazole⁸, or else it is the normal effect of benzimidazole monocation formation.

It is not easy to offer convincing explanation for the non-fluorescent nature of the monocation but this may be explained on the same lines as has been done earlier for benzimidazole cation^{1,2}. For instance $\phi_f = 0.067$

Fig. 1—Plots of I/I_0 versus $H_0/pH/H_-$ at 298K

for benzimidazole cation. This is roughly ten times less than that (0.7) for the neutral species. In other words non-radiative processes are predominant at 298K. Many collisional or vibrational non-radiative pathways can be eliminated by taking the fluorescence spectrum in frozen state. Therefore, the fluorescence spectrum of MBNH₂ cation was recorded at 77K, in the pH range of 4.5 to 2. This spectrum exhibits a broad band at 450 nm. This is red-shifted in comparison to that of neutral molecule (400 nm) at 77K. That the 450 nm band is due to monocation protonated at the tertiary nitrogen atom, is further supported by the spectral behaviour of MBNH₂.HCl in different solvents at 298K and 77K. The results are given in Table 2. The salt solutions in water and acetonitrile show the absorption spectrum of the cation, whereas the solutions in ether, dioxane and methanol show spectra at 298K typical of neutral species. The fluorescence spectrum of the salt in aqueous solution corresponds to that of neutral species (420 nm), probably due to incomplete protonation of MBNH₂ at this pH (5.1) and/or due to quenching of fluorescence of the cation at 298K. The salt solutions in methanol and dioxane also show fluorescence due to neutral species. Similar results observed for 6-aminoindazole⁹ have been explained by suggesting that the basicity of these solvents are sufficient to quench the MBNH₂ cation fluorescence at very low concentration (10⁻⁵ M).

Concentrated solutions (10⁻³ M) of MBNH₂.HCl in methanol and dioxane showed the presence of two fluorescence bands, one matching with respective neutral fluorescence band in these solvents (~ 380 nm) and another red-shifted band at 430 nm in dioxane and 470 nm in methanol. In acetonitrile solution, even also at 10⁻⁵ M concentration of MBNH₂.HCl, two similar fluorescence bands at 298K were observed. The addition of just 5% water to this acetonitrile solution quenched the 480 nm fluorescence completely. This clearly suggests that strong hydrogen bonding solvents

are efficient fluorescence quenchers of monocation species. The fluorescence spectrum of MBNH₂.HCl at 77K showed the presence of the long wavelength band in all the solvents including water and the results are listed in Table 2. This further confirms the earlier conclusion that the fluorescence of cation is quenched in hydrogen bonding solvents at 298K and the fluorescence band at ~ 450 nm band is due to monocation protonated at tertiary nitrogen atom. The other possibility that this fluorescence is due to an excimer, is ruled out on the following grounds: (i) charged species rarely form excimers, (ii) no new absorption band is observed by increasing the concentration of salt and (iii) since excimer formation occurs only in the excited state and involves diffusion of species, the fluorescence spectrum should not have been observed at 77K because the diffusion process is prevented in the frozen state.

The absorption band at 297 and the fluorescence band at 380 nm in the pH range 2 to H₀ - 9 is assigned to the formation of dication by the protonation of both the tertiary nitrogen atom and exocyclic amino group. It is reasonable to expect that the longer wavelength absorption band of dication of MBNH₂ should match that of the monocation (295 nm) of 2-phenylbenzimidazole because the behaviour of anilinium ion is similar to that of phenyl ring. It is indeed so.

The mid point of the fluorescence quenching curve (i.e. pK_a^*) due to neutral MBNH₂ species occurs at pH 11.9 (Fig. 1), which is also the pK_a for deprotonation. The anion at this temperature is found to be non-fluorescent. The 1M NaOH solution of MBNH₂ is found to be fluorescent at 77K. The spectral data are given in Table 2. Similar behaviour is exhibited by 5-aminoindazole⁷ and 2-aminobenzimidazole⁹. Thus a similar explanation can be offered, i.e. the dissociation occurs from the imino nitrogen atom in S₀ state and from the exocyclic amino group in S₁ state. The imino anions formed by the deprotonation of amino group are generally non-fluorescent, with the exception of 2-naphthylamine³⁰ and the anions formed from the deprotonation of imino nitrogen atom are fluorescent²⁶⁻²⁸. The fluorescence at 77K in basic medium is thus observed from the ions which are present in the ground state configuration, i.e. anion formed by the deprotonation of the imino group. This also confirms that amino group becomes more acidic as compared to the pyrrolic group in S₁ state.

The pK_a^* values calculated from fluorimetric titration curves (Fig. 1) for the equilibrium reactions are found to be close to the ground state values (see Table 3). This may be due to the fact that either there is no change in pK_a values on excitation or the equilibria are not established during the life-times of the species. The latter is generally true if the pK_a^* values fall in the

Table 2—Spectral Data of MBNH₂.HCl in Different Solvents at 298K and 77K

Solvent	298K	298K	77K ^b
	$\lambda_{\max}$ (abs) ^a (nm)	$\lambda_{\max}$ (flu) (nm)	
Dioxane	302	—, 388	420, —
Acetonitrile	317	480 (major), 390 (minor)	440, —
Methanol	324	—, 408 450, 408 ^c	430, 370
Water	330	—, 420	450, 400 450, — ^d

a = 1 × 10⁻⁵ M, b = 1 × 10⁻⁴ M, c = 1 × 10⁻³ M, and d = 1 × 10⁻² M solutions.

Table 3—Equilibrium Constants in S_0 and S_1 States for Various Equilibria

Equilibrium	pK_a	pK_a^* (fluorimetric titration)
Dication $\rightleftharpoons$ Monocation	1.9	2.0
Monocation $\rightleftharpoons$ Neutral	4.5	4.5
Neutral $\rightleftharpoons$ Anion	11.9	11.7

mid pH region^{6,8,25-28}. The Forster cycle method³¹ could not be applied because the monocation and monoanion formed are found to be non-fluorescent at 298K and the absorption spectral shifts observed are too small to get accurate results.

Thus from the results reported in this paper, it can be concluded that: (a) the effect of amino group is localised only on the phenyl ring, affecting the spectral behaviour of benzimidazole indirectly, (b) the pK_a values obtained for the monocation $\rightleftharpoons$ neutral and neutral $\rightleftharpoons$ monoanion equilibria are nearly equal to those of 2-phenylbenzimidazole⁸, (c) the fluorescence of monocation, formed by deprotonation of tertiary nitrogen atom is quenched by strong hydrogen bonding solvents at 298K and (d) the increase in the acidity of amino group proton is more than of imino group upon excitation.

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