EFFECT OF SOLVENTS AND pH ON THE SPECTRAL CHARACTERISTICS OF 2-(3′-HYDROXYPHENYL)BENZIMIDAZOLE AND 2-(4′-HYDROXYPHENYL)BENZIMIDAZOLE AND THEIR METHOXY DERIVATIVES

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Summary

The effect of solvents on the spectral characteristics of 2-(3′-hydroxyphenyl)benzimidazole (MHBI) and 2-(4′-hydroxyphenyl)benzimidazole (PHBI) indicate that the former is more polar in the excited singlet state than the latter. The structured absorption and fluorescence spectra in different solvents show that the 4′-hydroxyphenyl ring is conjugated better with the benzimidazole moiety than the 3′-hydroxyphenyl. The fluorescence quantum yield of the monocation of MHBI is much less than that of the monocation of PHBI and their methoxy derivatives. The spectral shifts observed in the absorption and fluorescence spectra for the various prototropic reactions of PHBI and the methoxy derivatives of PHBI and MHBI are consistent with earlier results. The large blue shift observed in the fluorescence spectrum of the dianion of MHBI is due to the electrostatic repulsion between the benzimidazolyl and the phenyl rings which results in the loss of the coplanarity of these two rings. The various prototropic reactions of these compounds are the same in the S_0 and the S_1 states. Their pK_a values in the S_0 and S_1 states are determined and discussed.

1. Introduction

The spectral characteristics (the absorption and fluorescence spectra and their intensities) of an aromatic molecule are dependent on the nature as well as on the position of the substituent in the aromatic ring [1 - 3]. Therefore the fluorescence and absorption spectra of an aromatic molecule may differ significantly from isomer to isomer [1 - 6]. The emission of pyrazine, for example, is quite different from that of pyridazine or pyrimidine [7 - 9].

It is well established that phototautomerism is observed in aromatic molecules if they contain electron-donating or electron-withdrawing groups and either their acidity or their basicity increases upon excitation. The

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phototautomerism can be intramolecular [5, 10 - 13] or intermolecular [14, 15]; the former shows no dependence on the nature of the solvent or the pH of the solution whilst the latter does depend on these factors. For example, salicylic acid [10] shows intramolecular phototautomerism whereas 5-aminoindazole [14] exhibits intermolecular phototautomerism.

The present study on 2-(3′-hydroxyphenyl)benzimidazole (MHBI) and 2-(4′-hydroxyphenyl)benzimidazole (PHBI) was carried out to determine (i) whether the molecules possess phototautomerism, as they contain both electron-withdrawing (tertiary nitrogen atom) and electron-donating (—OH group) groups and (ii) the effect of substituents on the spectral characteristics of benzimidazole in various solvents and at different pHs. The pK_a values of the various prototropic equilibria in the ground and the excited states were determined. The above results were also supplemented by studying the methoxy derivatives.

2. Methods and materials

MHBI, PHBI and the methoxy derivatives were prepared by heating an equimolar mixture of *o*-phenylenediamine and the respective hydroxybenzoic or methoxybenzoic acids at 250 °C in polyphosphoric acid media, as described in the literature [16]. Each compound was crystallized repeatedly from acetone and the purity was checked by noting the melting point and recording the IR and UV spectra, as well as checking that the fluorescence spectra were the same when excited at different wavelengths. BDH spectrograde methanol, analytical grade sulphuric acid, trifluoroacetic acid (TFA; Fluka) and sodium hydroxide were used as received. Analytical grade acetonitrile (E. Merck), cyclohexane (IDPL) and ether (BDH) were purified by methods described in the literature [17]. Triply distilled water was used for the preparation of aqueous solutions. A modified Hammett's acidity scale (H_0) [18] for H_2SO_4–H_2O mixtures and Yagil's basicity scale (H_-) [19] for NaOH–H_2O mixtures were used for solutions below pH 1 and above pH 13 respectively.

Absorption spectra were recorded on a Shimadzu model 190 UV spectrophotometer fitted with a U 135 recorder. Fluorescence measurements were carried out on a recording spectrofluorometer fabricated in our laboratory (the details are available elsewhere [20]). Fluorescence spectra at 77 K were recorded by fitting an Aminco–Bowman low temperature accessory to our spectrofluorometer. The bandwidth of the excitation radiation was 8 nm and both the monochromators were calibrated regularly with a low pressure mercury lamp. pHs in the range 1 - 13 were measured on a Toshniwal model CL-44 A pH meter. The concentrations of the solutions were of the order of 10^{-5} M at 298 K and 10^{-3} M at 77 K. The fluorescence spectra were corrected according to the procedure given in one of our previous papers [20]. Quinine sulphate in 0.1 N H_2SO_4 was employed as the standard for measuring quantum yields [21] and the wavelength used for excitation was

300 nm. The solutions for absorptiometric and fluorometric titrations were prepared just before performing the measurements. In fluorometric titrations, isosbestic wavelengths were used for excitation of different species (see Figs. 4 and 5 below).

3. Results and discussion

3.1. Effect of solvents on absorption and fluorescence spectra

The absorption and fluorescence spectra of MHBI and PHBI were studied in different solvents. The fluorescence spectra of MHBI and PHBI are shown in Figs. 1 and 2 respectively. The λ_{max}(abs), λ_{max}(flu), ϵ_{max} and

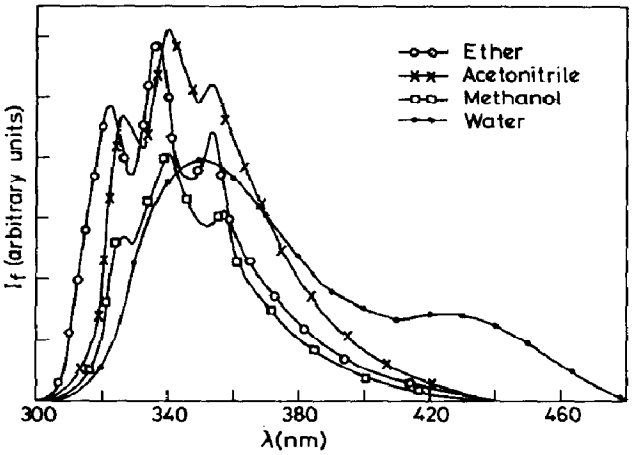


Fig. 1. Fluorescence spectra of MHBI in different solvents at 298 K (concentration, 1.0×10^{-5} M, λ_{exc} = 300 nm).

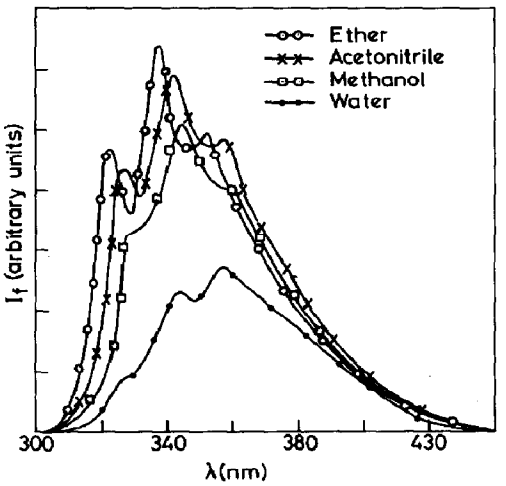


Fig. 2. Fluorescence spectra of PHBI in different solvents at 298 K (concentration, 1.0×10^{-5} M, λ_{exc} = 300 nm).

TABLE 1

Absorption and fluorescence band maxima, molar absorptivities (log ϵ) and quantum yields Φ_f of MHBI in different solvents and at various hydrogen ion concentrations at 298 K

Solvents/species	λ_a (nm) (log ϵ_{max})					λ_f (nm)			Φ_f
Ether	215 (4.72)	242 (4.16)	292 (4.44)	304 (4.48)	319 (4.39)	322	337	354	0.40
Acetonitrile	210 (4.63)	241 (4.15)	291 (4.21)	304 (4.35)	318 (4.22)	326	340	354	0.38
Methanol	212 (4.64)	240 (4.02)	—	300 (4.36)	317 (4.18)	326	341	358	0.20
Water (pH 7)	207 (4.65)	240 (4.04)	—	300 (4.31)	317 (4.16)	330	352	—	0.16
						324, 340, 357, 370			
Monocation (pH 2)	209 (4.50)	244 (4.00)	—	294 (4.32)	325 (3.95)	—	384	—	—
							380[a], 390[b]		
Dication (H_0 −10)	205 (4.45)	243 (4.01)	—	—	300 (4.26)	—	—	—	—
Monoanion (pH 11)	200 (4.73)	246 (4.13)	296 (4.30)	306 (4.22)	325 (3.89)	—	430	—	—
Dianion (H_- 16)	230 (4.62)	250 (4.28)	—	311 (4.37)	333 (4.18)	—	402	—	—

ϵ is in litres per mole per centimetre; the values underlined are at 77 K.
[a]In cyclohexane with 2% TFA.
[b]In methanol with 2% H_2SO_4.

Φ_f are listed in Tables 1 and 2. The absorption band maxima are red shifted as compared with benzimidazole [22] in any given solvent. Both the absorption and the fluorescence spectra of MHBI and PHBI are structured in nearly all the solvents and this is explained by the ground state vibrational frequency of about 1390 cm^{-1} for MHBI and about 1400 cm^{-1} for PHBI. These vibrational frequencies match those observed in 2-phenylbenzimidazole (PBI) [23], 2-(*m*-aminophenyl)benzimidazole (MABI) [5] and 2-(*p*-aminophenyl)benzimidazole (PABI) [6]. The shortest wavelength fluorescence bands at 330 nm and 326 nm in water can be assigned as the 0–0 transition in MHBI and PHBI respectively. The fluorescence quantum yields of MHBI and PHBI are less than that of benzimidazole in any given solvent [24] and decrease with increasing solvent polarity or hydrogen-bonding ability.

Based on the larger values of the extinction coefficients, the greater red shift in the absorption spectra compared with benzimidazole in any given solvent, the higher fluorescence quantum yields and the mirror image symmetry of the absorption and the fluorescence spectra, the following conclusions can be drawn.

(i) The lowest energy transition in these compounds is of $\pi \rightarrow \pi^*$ character.

TABLE 2

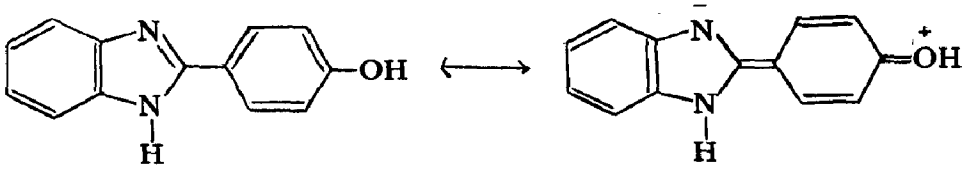
Absorption and fluorescence band maxima, molar absorptivities (log ϵ) and quantum yields Φ_f of PHBI in different solvents and at various hydrogen ion concentrations at 298 K

Solvent/species	λ_a (nm) (log ϵ_{max})				λ_f (nm)			Φ_f
Ether	214	245	299	305	322	338	352	0.5
Acetonitrile	210 (4.03)	245 (3.63)	286 (3.69)	294 (3.71)	328	342	356	0.44
Methanol	209 (4.11)	246 (3.71)	—	292.5 (3.82)	330	345	361	0.42
Water (pH 7)	—	245 (3.97)	—	289 (4.10)	326	344	357	0.19
Monocation (pH 2)	—	255 (3.99)	—	297 (4.17)		366		—
Dication (H_0 −10)	—	242.5 (3.89)	—	288 (4.28)		—		—
Monoanion (pH 11)	202.5 (4.90)	250 (3.96)	—	307.5 (4.23)		386		—
Dianion (H_- 16)	227.5 (4.60)	252 (4.09)	—	312.5 (4.27)		390		—

ϵ is in litres per mole per centimetre.

(ii) The hydroxyphenyl ring in each case is coplanar and conjugated with the benzimidazole moiety, in both the S_0 and the S_1 states. These results are consistent with previous findings [22, 23, 25].

The effect of solvents on the absorption spectra of these compounds is similar to that observed for benzimidazole. The spectral shift on changing the solvent noted for the absorption spectrum of MHBI is small compared with that for the fluorescence spectrum. The behaviour of PHBI is the opposite. This suggests that the change in the dipole moment of MHBI is greater than that of PHBI on excitation. This could be due to the fact that for PHBI two cannonical structures are present, the structure I′ being more favoured in the excited state.



I I′

Thus the charge migration from the carbocyclic ring to the heterocyclic ring will leave some positive charge on the carbocyclic ring, whereas similar

structures are not possible in the case of MHBI. The presence of I′ is also reflected by the fluorescence spectrum being structured even in water. Similar behaviour has been observed for 2-(3′-aminophenyl)benzimidazole [5] and 2-(4′-aminophenyl)benzimidazole [6]. The red shift observed in the fluorescence spectra with increasing solvent polarity or hydrogen-bonding ability is consistent with the behaviour of similar compounds.

With water as the solvent, a long-wavelength fluorescence band (λ_{max} = 440 nm) is observed for MHBI at 298 K together with a fluorescence band at 352 nm. Fluorescence excitation spectra recorded at 352 nm and 440 nm indicated that the ground state species is the same for the two fluorescence bands. I_{440}/I_{354} remains the same over the concentration range 10^{-5} - 10^{-3} M and the pH range 1 - 8, and on lowering the temperature to 77 K. The long wavelength band is absent in the case of its methoxy derivative. These results lead us to reject the idea of the formation of an excimer or exciplex and a zwitterion. The evidence for the identity of this emission is still inconclusive.

3.2. Effect of pH on the absorption and fluorescence spectra: 2-(4′-hydroxyphenyl)benzimidazole and its methoxy derivative

The effect of pH on the absorption and fluorescence spectra of PHBI and its methoxy derivative has been studied in the H_0/pH/H_- range of −10 - 16. The relevant data are listed in Tables 2 and 3. The scheme depicting the various prototropic reactions is given in Fig. 3 and the fluorescence spectra of the various prototropic species of PHBI are given in Fig. 4. From the data of Tables 2 and 3, it is clear that prototropic reactions of PHBI and its methoxy derivatives are the same in S_0. At the highest value of H_-

TABLE 3

Absorption and fluorescence band maxima and molar absorptivities (log ϵ_{max}) of 2-(3′-methoxyphenyl)benzimidazole and 2-(4′-methoxyphenyl)benzimidazole at various hydrogen ion concentrations at 298 K

Species (H_0/pH/H_-)	*2-(3′-Methoxyphenyl)-benzimidazole*				*2-(4′-Methoxyphenyl)-benzimidazole*			
	λ_a (nm) (log ϵ_{max})			λ_f (nm)	λ_a (nm) (log ϵ_{max})			λ_f (nm)
Dication (H_0 −10)	242 (3.94)	294 (4.24)	325 (3.86)	—	248 (3.80)	300 (4.27)	325 (3.90)	—
Monocation (pH 2)	242 (4.03)	294 (4.27)	325 (3.84)	375	248 (3.89)	300 (4.27)	325 (3.94)	362
Neutral (pH 7)	239 (4.03)	294 (4.27)	316 (4.03)	357	246 (3.83)	302 (4.22)	319 (4.00)	350
Monoanion (H_- 16)	250 (4.08)	311 (4.28)	330 (4.05)	382	250 (4.04)	312 (4.31)	325 (4.22)	370

ϵ is in litres per mole per centimetre.

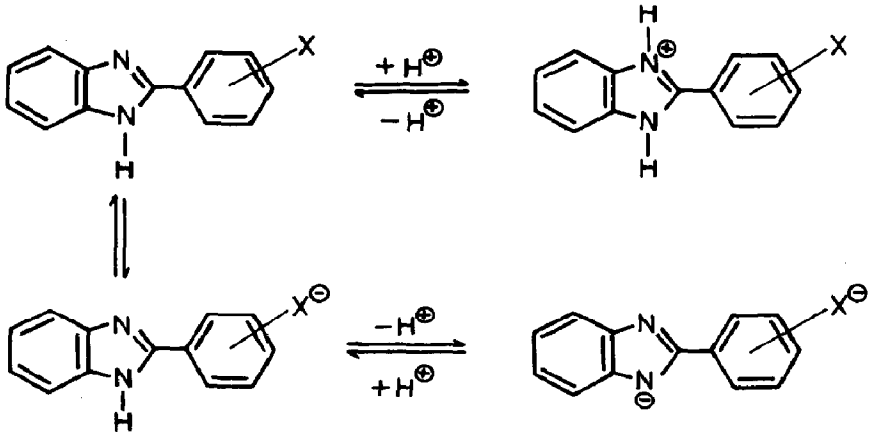


Fig. 3. Scheme representing the prototropic reactions of MHBI and PHBI.

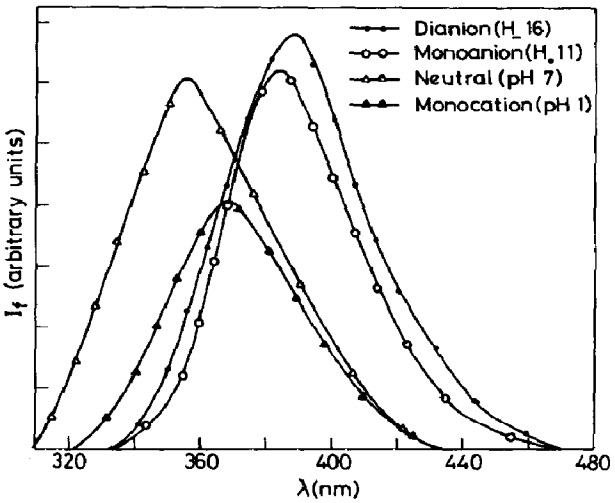


Fig. 4. Fluorescence spectra of various prototropic forms of PHBI at 298 K (concentration, 1.0×10^{-5} M; λ_{exc} = 280 nm for the monocation, 290 nm for the monoanion and 325 nm for the dianion).

16, the formation of the dianion of PHBI (λ_{max} = 312.5 nm) is indicated, this being obtained by the deprotonation of the hydroxyl and the imino groups. With a decrease in pH, a blue shift (to 307.5 nm) is observed in the absorption spectrum and this reflects the formation of the monoanion. The proton can be added to the imino group nitrogen atom or to the phenolate ion. Since the hydroxyl group is more acidic than the imino group, the proton will be added to the imino group at pH > 11. This is further confirmed by the pK_a value of 13.9 for this reaction, calculated spectrophoto-

metrically and in agreement with the value for the deprotonation reaction of the imino group of benzimidazole [6, 26]. A similar pK_a value (12.10) is observed in the case of the methoxy derivative, where there is no dissociable hydroxyl proton. With an increase in hydrogen ion concentration, a further blue shift (to 289 nm) is noted in the absorption spectrum, whereas such a change is not observed in case of the methoxy derivative. The absorption spectrum of the newly formed species matches that of the methoxy derivative as well as that observed in other solvents. This indicates that the species formed by protonating the phenolate ion is a neutral molecule. The pK_a value for the neutral species–anion equilibrium (9.4) falls in the region where the phenolic —OH dissociates [27]. With a further increase in acid strength, a red shift is observed in the absorption spectrum (to 297.5 nm), indicating the formation of the monocation by protonation of the tertiary nitrogen atom. Lastly, at H_0 —10, a small blue shift (to 288 nm) reflects the formation of the dication by protonation of the hydroxyl group of the monocation. This result is similar to that obtained for related compounds [28, 29] as well as with the methoxy derivative. All the above assignments of the various species are consistent with the earlier finding that there is a red shift in the absorption spectrum when protonation takes place at the tertiary nitrogen atom or when deprotonation takes place from the imino and the hydroxy groups [20, 30, 31].

From the data of Tables 2 and 3 it is clear that the prototropic reactions of PHBI and its methoxy derivative are the same in the first excited singlet state and the changes observed in the fluorescence spectra are similar in nature over the complete range of H_0/pH/H_-, *i.e.* for PHBI dianion (λ_{max}(flu) = 390 nm) at H_- 16, monoanion (λ_{max}(flu) = 386 nm) at pH 11, neutral species (λ_{max}(flu) = 356 nm) at pH 7 and monocation (λ_{max}(flu) = 366 nm) at pH 2. The red shift observed in the fluorescence spectrum of PHBI is quite small compared with the shifts observed for the similar species of benzimidazole [25] and their alkyl-substituted derivatives [32], but this small red shift resembles the shift observed for the cations of benzimidazoles when substituted by the phenyl [23] or the 4-thiazolyl groups [25] at the 2-position. On similar grounds, it can be concluded that the emitting state of the cations of PHBI and its methoxy derivative is the same as that observed in the absorption spectrum, *i.e.* ^1L_b. This is because the positive charge of the monocation is delocalized over the complete π system of the phenyl group, instead of being concentrated on the tertiary nitrogen atom. This behaviour is unlike that of the methyl-substituted derivatives of benzimidazole. Thus the charge transfer electronic state is not stabilized to such an extent that the energy is lower than that of the ^1L_b state. In contrast to the absorption spectrum, no further change is observed in the fluorescence spectrum even up to H_0 —10. This indicates that the dication formed in the ground state is unstable in the excited state. This could be due to the distribution of the positive charge of the monocation over the whole molecule, making the OH group more acidic in the S_1 state than in the S_0 state. The methoxy derivative behaves in a similar manner.

3.3. 2-(3'-Hydroxyphenyl)benzimidazole and its methoxy derivative

The absorption and fluorescence spectra of MHBI and its methoxy derivatives have also been studied in the H_0/pH/H_- range −10 - 16. These are shown in Fig. 5 and the relevant data are compiled in Tables 1 and 3. The scheme representing the various prototropic reactions are given in Fig. 3. It is clear from the data of Tables 1 and 3, as well as from Fig. 3, that all the prototropic reactions taking place in MHBI and its methoxy derivative are similar to those of PHBI, in both the ground and the excited singlet states. The changes in the absorption spectra of the two molecules and the changes in the fluorescence spectrum of the methoxy derivative of MHBI follow the same trend as that observed in the corresponding reactions of PHBI. The following changes were observed in the fluorescence spectrum of MHBI and these are quite different from the results for the other molecules in this study.

(i) At the extreme H_- 16, the fluorescence spectrum is assigned to the dianion of MHBI, formed by deprotonation of —OH and >NH groups. Unlike the behaviour of the other molecules mentioned above, there is a large red shift in the fluorescence spectrum (to 430 nm) when the pH is lowered. Under these conditions, the protonation can only take place either at $>N^-$ or at $-O^-$ groups and both these reactions lead to a blue shift in the absorption and fluorescence spectra, as observed in many other similar reactions [20, 27, 30]. This anomalous behaviour can be explained as follows. Unlike the dianion of PHBI or the ground state behaviour of MHBI, the negative charges of $>N^-$ and $-O^-$ groups are only localized on their respective rings because of the meta position of the $-O^-$ in the 2-substituted phenyl ring. Because of this an electrostatic repulsion may develop between the two rings. This will lead to the removal of the coplanarity of the two rings, and thus a blue shift results on the formation of the dianion by deprotonation of the >NH group. Since the methoxy derivative does not possess a dis-

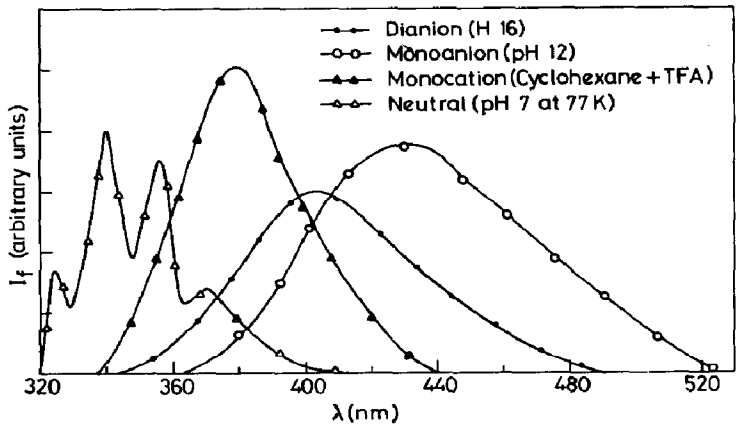


Fig. 5. Fluorescence spectra of various prototropic forms of MHBI at 298 K (concentration, 1.0×10^{-5} M; λ_{exc} = 300 nm for the monocation, 320 nm for the monoanion and 300 nm for the dianion).

sociable proton similar to —OH, this phenomenon is not observed. Thus, based on above results, the 430 nm fluorescence band is assigned to a monoanion formed by protonation of the $>N^-$ group of the dianion.

(ii) The fluorescence intensity of the neutral MHBI is quenched at pH 1 and a new band appears at H_0 —1 with λ_{max} = 384 nm. No further change in λ_{max} is observed even at H_0 —10, once the maximum intensity is attained. Similar behaviour is also obtained in the fluorescence spectrum when methanol is used as the solvent and the hydrogen ion concentration is increased. MHBI in cyclohexane containing 1 - 2 vol.% TFA gave a fluorescence spectrum matching the above (λ_{max} = 380 nm). A fluorescence spectrum was also recorded at 77 K and pH/H_0 2.0 and —2. These are the hydrogen ion concentrations where the monocation of MHBI is present in the S_0 state, but the fluorescence spectrum of the monocation is only observed at H_0 —2 and 298 K. At 77 K, the fluorescence spectra observed at these hydrogen ion concentrations are the same and match that observed at 298 K. The 384 nm fluorescence band is thus assigned to the monocation, this being formed by the protonation of the tertiary nitrogen atom. This assignment is based on the following grounds. (a) Based on the structure of the molecule, no other cationic species can be formed in such acid conditions. A non-fluorescent zwitterion can be formed in the excited singlet state from the neutral molecule with the assumption that the acidity of the —OH group and the basicity of the tertiary nitrogen atom increase upon excitation to match the rate of deprotonation of the —OH group and the rate of protonation of the tertiary nitrogen atom, but this species cannot be formed from the excitation of the monocation, which is present in the S_0 state. (b) Proton-induced fluorescence quenching of monocations of methyl-substituted benzimidazoles have been observed [32] but not of the neutral benzimidazole derivatives. Even if we assume that the fluorescence quenching of the neutral MHBI occurs, the pK_a* value for the monocation–neutral species equilibrium can be calculated only from the formation curve of the fluorometric titration and not from the relative decrease in the fluorescence intensity of neutral MHBI. The pK_a* obtained from the formation curve is 0.5, indicating that the tertiary nitrogen atom becomes less basic upon excitation, whereas it has always been observed that tertiary nitrogen becomes more basic [20, 23, 30]. (c) The fluorescence quantum yield of most of the monocations of benzimidazole derivatives is very small compared with that of the neutral species and this originates either from radiationless processes or from the solvent–solute interaction leading to quenching. Results at low temperature and in non-polar media confirm the above observation, *i.e.* fluorescence from the monocation at 77 K is observed in the regions where it was absent in aqueous media and at 298 K. The monocation of 2-(3′-aminophenyl)-benzimidazole is also found to be non-fluorescent [5]. Thus it can be concluded that the monocation of MHBI is formed at a pH below 3, as the fluorescence intensity of the neutral molecule starts decreasing. That it is only observed at high acid concentration may be due to reasons mentioned above.

As with the compounds described above, no dication is formed even at H_0 −10 and a similar explanation can be given.

3.4. Prototropic equilibria

The ground state values for the various prototropic reactions were calculated spectrophotometrically and are listed in Table 4. The values so obtained are consistent with the literature values for similar reactions and also with the conclusion that an electron-withdrawing group increases the acidity constants and decreases the basicity constants, and vice versa for the electron-donating groups.

The pK_a^* values for the different proton transfer reactions of the compounds were calculated with the help of fluorometric titrations (Fig. 6) and the Förster cycle method [33], using absorption and fluorescence data and the average of the absorption and the fluorescence maxima. The latter method is valid since it was established earlier that the electronic transitions involved in the respective species are the same and that the proton transfer equilibria between the various species are the same in the S_0 and the S_1 states. The exception is the equilibrium between anion–dianion species of MHBI where it was established that in the latter species the phenyl ring is not coplanar with the benzimidazole moiety in the S_1 state. The pK_a^* so obtained are listed in Table 4. The fluorometric titrations gave the ground

TABLE 4

The pK_a values for the various prototropic reactions of MHBI, PHBI and their methoxy derivatives

Equilibrium	pK_a	pK_a^* *(Förster cycle method)*		
		Absorption	*Fluorescence*	*Average*
PHBI				
Monocation ⇌ Neutral	4.40	6.50	5.9	6.2
Neutral ⇌ Anion	9.4	5.00	5.0	5.00
Anion ⇌ Dianion	13.9	12.9	13.4	13.20
Methoxy derivative of PHBI				
Monocation ⇌ Neutral	4.50	5.7	7.3	6.5
Neutral ⇌ Anion	12.1	10.9	8.9	9.9
MHBI				
Monocation ⇌ Neutral	4.5	6.0	9.5	7.8
Neutral ⇌ Anion	9.0	7.5	1.8	—
Anion ⇌ Dianion	13.4	11.9	—	—
Methoxy derivatives of MHBI				
Monocation ⇌ Neutral	4.2	6.0	7.1	6.6
Neutral ⇌ Anion	12.9	10.1	9.1	9.6

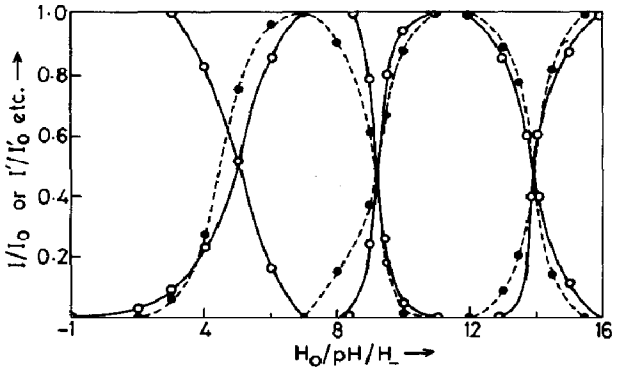


Fig. 6. Plot of I/I_0 *vs.* H_0/pH/H_- for the various prototropic forms of MHBI (—●—) and PHBI (—○—).

state pK_a values, and these indicate that the lifetimes of the respective species are quite short and that the equilibrium is not established in the excited state during their lifetimes. The Förster cycle method has clearly indicated that —OH and >NH groups become more acidic on excitation, whereas the tertiary nitrogen atom becomes more basic. The values of the pK_a* obtained by different methods are not very different from each other. This agrees with the earlier result that, especially for PHBI and its methoxy derivative, the molecules are not very polar in the S_1 state, and thus solvent relaxation for different species is nearly the same in the two states. The small difference can be attributed to the use of band maxima rather than the 0–0 transition, because the neutral species have structured spectra whereas the ionic species have broad bands. The results for the pK_a* of MHBI are the exception. As pointed out earlier, the ions of MHBI are more polar in the excited state than in the ground state.

4. Conclusions

The mirror image relationship between the absorption and the fluorescence spectra of MHBI and PHBI clearly indicates that the geometries of these molecules are not very different in the S_0 and the S_1 states. The effect of the solvent polarity on the spectral characteristics indicates that MHBI is more polar in the S_1 state than PHBI. The proton transfer reactions of MHBI, PHBI and their methoxy derivatives are the same in both the S_0 and the S_1 states. The fluorescence spectrum of the dianion of MHBI, formed by the deprotonation of the >NH and —OH groups, is blue shifted in comparison with that of the monoanion. This is due to the electrostatic repulsion between the benzimidazolyl and the hydroxyphenyl rings, and this reduces the coplanarity of these rings. Lastly, the fluorescence quantum yield of the monocation of MHBI is very low in comparison with those of the monocations of PHBI and their methoxy derivatives.

Acknowledgments

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