# Electronic absorption and fluorescence spectra of 2-phenyl-substituted benzothiazoles: study of excited-state proton transfer reactions

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The absorption and fluorescence spectral properties of 2-(3′-hydroxyphenyl)-, 2-(4′-hydroxyphenyl)-, and 2-(3′,4′-dihydroxyphenyl)-, and 2-(4′-hydroxy-3′-methoxyphenyl), 2-(3′-hydroxy-4′-methoxyphenyl)-, and 2-(3′-methoxyphenyl)benzothiazoles have been studied in a number of solvents of varying polarity. The ionization constants ($pK_a$) for various prototropic reactions of these molecules in both $S_0$ and $S_1$ states are determined. The effect of substitution on the spectral properties and on the $pK_a$ values are discussed. The molecules have been found to undergo biprotonic phototautomerism in dilute acid solutions. On the basis of the fluorimetric titration behaviour of the molecules (except 2-(3′-methoxyphenyl)benzothiazole), the existence of monocation–zwitterion equilibrium in the $S_1$ state is proposed. PPP-SCF-MO-CI method has been used to calculate charge densities on the heteroatoms.

*Key words*: spectra, proton transfer.

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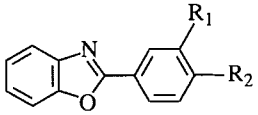
On a étudié, dans un certain nombre de solvants de polarité différente, les propriétés spectrales d'absorption et de fluo rescence des composés suivants : 2-(hydroxy-3′-phényl), 2-(hydroxy-4′-phényl), 2-(3′,4′-dihydroxyphényl)-, 2-(4′-hydroxy-3′-méthoxyphényl), 2-(3′-hydroxy-4′-méthoxyphényl)-, et 2-(3′-méthoxyphényl)benzothiazole. On a déterminé les constantes d'ionisation ($pK_a$) de plusieurs réactions prototropiques de ces molécules dans les états $S_0$ et $S_1$. On discute de l'effet des substitutions sur les propriétés spectrales et sur les valeurs du $pK_a$. On a trouvé que les molécules subissent un phototautomérisme biprotonique en solution diluée acide. On propose l'existence d'un équilibre monocation-zwittérion dans l'état $S_1$ en se basant sur le comportement du titrage fluorométrique des molécules (à l'exception du 2-(3′-méthoxyphényl)-benzothiazole). On a utilisé la méthode PPP-SCF-MO-CI pour calculer la densité de charge des hétéroatomes.

*Mots clés* : spectres, transfert de proton.

[Traduit par la rédaction]

## 1. Introduction

The excited state proton-transfer (ESPT) reactions in organic molecules capable of emitting fluorescence has been a subject of great interest among researchers. It has been observed that the basicity or acidity of aromatic amines and alcohols changes by several orders of magnitude upon electronic excitation. The proton dissociation constants ($pK_a^*$) in the lowest excited singlet state ($S_1$) of a large number of organic acids and bases have been reported (1–5). The ESPT reactions of naphthols (6, 7) in aqueous and micellar media are well studied. Recently, the excited-state intramolecular proton-transfer reaction of 2-(2′-hydroxyphenyl)benzothiazole (8) and similar molecules (9, 10), because of their uses as potential proton-transfer lasers (11), have been studied extensively. However, no attention has been paid for such studies to 2-(3′-hydroxyphenyl)- and 2-(4′-hydroxyphenyl)benzothiazoles. In a continuation of our studies on the proton-transfer reactions of 2-[phenyl-substituted]benzazoles (benzimidazoles (10, 12), benzoxazoles (9*a*, 13), and benzothiazoles (14)) we have undertaken this investigation to study the absorption and fluorescence spectral properties of **I** and **II** in organic solvents of different polarity and in aqueous solutions of various acid/base concentrations. To study the effect of substituent on the spectral properties and proton-transfer reactions of **I** and **II** we have also included **III**, **IV**, **V**, and **IM**.




**I**: $R_1 = OH$, $R_2 = H$ — **IV**: $R_1 = OCH_3$, $R_2 = OH$
**II**: $R_1 = H$, $R_2 = OH$ — **V**: $R_1 = OH$, $R_2 = OCH_3$
**III**: $R_1$, $R_2 = OH$ — **IM**: $R_1 = OCH_3$, $R_2 = H$

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To support our experimental results semiempirical PPP-SCF-MO-CI calculations have been performed to calculate charge densities on the basic centers of **I**, **II**, and **III**.

## 2. Experimental

*Materials*

All compounds were prepared as described in the literature (15) and purified by repeated recrystallization from aqueous ethanol. The purity of the compounds was established by TLC, melting points, and fluorescence excitation spectra in methanol. $H_2SO_4$ (98%), KOH (B.D.H.), and ortho-$H_3PO_4$ (B.D.H.) were all reagent grade. Analytical grade cyclohexane (SRL), 1,4-dioxane (E. Merck), acetonitrile (E. Merck), and methanol (B.D.H.) were purified by usual methods (16). Spectrograde ethylacetate (B.D.H.) and analytical grade ethanediol and glycerol (SRL) were used directly. Triply distilled water was used for studies in aqueous solution. The solvents thus obtained showed no detectable fluorescence in the region 250 to 500 nm. pH values of the solutions made by mixing appropriate amount of dilute KOH and $H_3PO_4$ solutions were measured in a Toshniwal digital 46 CL pH-meter fitted with a combined glass electrode. Aqueous solutions of higher acidity/basicity were prepared following the Hammett's acidity ($H_0$) (17*a*) and Yagil's basicity ($H_-$) (17*b*) scales. The fluorescence quantum yields were measured in solutions having absorbances less than 0.1, by comparison with a quinine bisulfate (0.1 N $H_2SO_4$) solution ($\phi_f = 0.55$) (18). The fluorophore concentration of the solutions (containing not more than 1% (v/v) methanol) was $\sim 5 \times 10^{-5}$ M. All solutions were prepared just before measurements. No attempt was made to remove oxygen from the solutions for fluorescence measurements. All experiments were carried out at ~298 K.

*Absorption and fluorescence spectra*

The absorption spectra were measured on Shimadzu UV-190 spectrophotometer. All fluorescence measurements were performed in the spectrofluorimeter fabricated in our laboratory which has been described earlier (19). Fluorescence spectra reported here are all corrected.

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TABLE 1. Absorption maxima ($\lambda_a$ nm) and molar extinction coefficient (log $\epsilon$) of molecules **I** to **V** in different solvents

| | I | | II | | III | | IV | | V | |
|---|---|---|---|---|---|---|---|---|---|---|
| Solvent | $\lambda_a$ | log $\epsilon$ | $\lambda_a$ | log $\epsilon$ | $\lambda_a$ | log $\epsilon$ | $\lambda_a$ | log $\epsilon$ | $\lambda_a$ | log $\epsilon$ |
| Cyclohexane | 301 | | 316 | (sh) | | | 332 | (sh) | 332 | (sh) |
| | 255 | | 303 | | | | 323 | — | 320 | — |
| | 247 | | 257 | | | | 310 | (sh) | 310 | (sh) |
| | | | 249 | | | | 297 | (sh) | 295 | (sh) |
| Dioxane | 303 | 4.32 | 318 | 4.41 | 335 | (sh) | 335 | (sh) | 332 | (sh) |
| | 256 | 3.92 | 307 | 4.41 | 326 | 4.43 | 326 | 4.47 | 324 | 4.45 |
| | | | 258 | 3.85 | 313 | (sh) | 313 | (sh) | 313 | (sh) |
| | | | 250 | 3.87 | 300 | (sh) | 297 | (sh) | 300 | (sh) |
| Acetonitrile | 300 | 4.30 | 316 | 4.42 | 335 | (sh) | 332 | (sh) | 332 | (sh) |
| | 255 | 3.91 | 306 | 4.42 | 323 | 4.41 | 324 | 4.45 | 322 | 4.43 |
| | | | 257 | 3.85 | 310 | (sh) | 313 | (sh) | 300 | (sh) |
| | | | 249 | 3.86 | 300 | (sh) | 300 | (sh) | | |
| Ethylacetate | 294 | 4.29 | 317 | 4.47 | 333 | (sh) | 332 | (sh) | 330 | (sh) |
| | | | 307 | 4.47 | 324 | 4.43 | 324 | 4.47 | 322 | 4.41 |
| | | | | | 313 | (sh) | 313 | (sh) | 313 | (sh) |
| | | | | | 300 | (sh) | 300 | (sh) | 300 | (sh) |
| Methanol | 298 | 4.28 | 318 | 4.42 | 328 | 4.42 | 335 | (sh) | 324 | 4.40 |
| | | | | | 313 | (sh) | 327 | 4.46 | 300 | (sh) |
| | | | | | 300 | (sh) | 300 | (sh) | | |
| Dichloromethane | 308 | (sh) | 316 | (sh) | 330 | (sh) | 332 | (sh) | 332 | (sh) |
| | 300 | 4.22 | 306.5 | 4.33 | 321 | 4.48 | 324 | 4.43 | 322.5 | 4.33 |
| | | | | | 313 | (sh) | 313 | (sh) | 312 | (sh) |
| | | | | | 300 | (sh) | 300 | (sh) | 295 | (sh) |
| Water (pH 6.7) | 302 | 4.24 | 316 | 4.34 | 323 | 4.38 | 324 | 4.38 | 321 | 4.33 |

*Method of calculation*

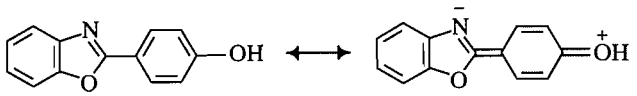
The molecular orbital calculations have been performed by using the semi-empirical PPP-SCF-MO method combined with a singly excited CI calculation (20–22). The one center repulsion integrals ($\gamma_{\mu\mu}$) were calculated from the corresponding valence-state ionization potentials ($I_\mu$) and electron affinities ($A_\mu$) by using the Pariser–Parr approximation. The two-centre repulsion integrals ($\gamma_{\mu\nu}$) were determined by using the Nishimoto–Mataga (22*b*) approximation. The two-centre core resonance integrals ($\beta_{\mu\nu}$) were calculated by the Nishimato–Forster (22*c*) approximation. The empirical parameters used for the calculations were the same as given in ref. 13. The C—C and C—O bond lengths were assumed to be 1.395 and 1.35 Å, respectively. The bond angles were taken to be equal to those of regular hexagon (120°) and pentagon (108°).

The calculations have been carried out on our institute's Dec-1090 computer. The program (23) for the calculations was obtained from QCPE, Indiana University, Bloomington, USA.

## 3. Results and discussion

### 3.1. Solvent dependence of absorption and fluorescence spectra

The absorption and fluorescence spectral data of the molecules studied in different solvents are compiled in Tables 1 and 2, respectively. The absorption spectra of the molecules in methanol agree with those reported in the literature (24). The long wavelength absorption band of **II** is red-shifted relative to that of **I** and can be explained by the resonance effect of the —OH group. This increases the magnitude of transition moment vector, which is reflected by the high intensity (log $\epsilon$, Table 1) of the lowest energy absorption band and by the higher fluorescence quantum yield. The absorption spectrum




**II** **II'**

of **I** closely resembles that of 2-phenylbenzothiazole (PBT) (24) and is consistent with the fact that the charge migration from the —OH group at 3′ position will be localized on the phenyl ring rather than delocalized over the whole molecule and therefore, it has very little effect on the absorption spectrum of (PBT).

The absorption spectra of **III**, **IV**, and **V** are structured and are not very different from each other. The longest wavelength absorption bands of these molecules are red-shifted compared to that of **II**. This can be explained by the resonance effect as described earlier for **II**. The structured absorption spectra may be caused by the formation of hydrogen bond between the hydroxyl proton and the oxygen atom of adjacent —OH or —$OCH_3$ group. This intramolecular hydrogen bond (IHB), which makes the molecule more rigid, may also be one of the reasons for the red shift of the longest wavelength absorption band of the molecules.

The absorption spectra of the molecules almost remain unaffected by the solvents employed, except for the loss of the vibrational structure and a small blue shift in water. This is consistent with the fact that the resonance effect of hydroxyl group is smaller than that of amino group and thereby the absorption spectra will not be affected much by the solvents. Water, being a very strong hydrogen-bonding solvent, will

TABLE 2. Fluorescence maxima ($\lambda_f$ nm) and quantum yields ($\phi_f$) of molecules **I** to **V** in different solvents

| | I | | II | | III | | IV | | V | |
|---|---|---|---|---|---|---|---|---|---|---|
| Solvent | $\lambda_f$ | $\phi_f$ | $\lambda_f$ | $\phi_f$ | $\lambda_f$ | $\phi_f$ | $\lambda_f$ | $\phi_f$ | $\lambda_f$ | $\phi_f$ |
| Cyclohexane | 370 | 0.03 | 370 | 0.05 | | | 380<br>360<br>350 | 0.11 | 377<br>360<br>350 | 0.09 |
| Dioxane | 365 | 0.04 | 380 | 0.11 | 375 | 0.32 | 374 | 0.25 | 375 | 0.23 |
| Acetonitrile | 370 | 0.06 | 370 | 0.13 | 380 | 0.38 | 380 | 0.35 | 380 | 0.35 |
| Ethylacetate | 365 | 0.06 | 370 | 0.17 | 380 | 0.35 | 380 | 0.27 | 380 | 0.25 |
| Methanol | 380 | 0.05 | 380 | 0.28 | 400 | 0.60 | 390 | 0.73 | 395 | 0.41 |
| Dichloromethane | 360 | 0.03 | 370 | 0.09 | 373 | 0.17 | 373<br>360 | 0.19 | 370 | 0.17 |
| Water (pH 6.7) | 390 | <0.001 | 380 | 0.36 | 410 | 0.02 | 400 | 0.02 | 400 | <0.001 |

break the IHB in **III**, **IV**, and **V**, resulting in a blue-shifted broad absorption band. Like absorption spectra, the fluorescence spectra of **III**, **IV**, and **V** in cyclohexane are also structured and the emission maxima are red-shifted relative to that of **I** or **II**. This can be explained on the same lines as described above for the absorption spectra. In contrast to the absorption spectra, the fluorescence spectra of the molecules are red-shifted in hydrogen-bonding solvents. It is well known that —OH group becomes more acidic in the $S_1$ state. As a result the hydrogen bond between the positively polarized hydrogen of the —OH group and the acceptor atom of the proton acceptor solvent becomes stronger in $S_1$ state and thus the fluorescence maximum shifts to longer wavelength.

The results in Table 2 indicate that the fluorescence quantum yields of the molecules increase with the increase of polarity and hydrogen-bonding capacity of solvents. The higher quantum yield of **II** in polar solvents can be attributed to the stabilization of the rigid structure **II′**. The same is also true for **III**, **IV**, and **V**. Moreover, it is now firmly established that the presence of IHB enhances the rates of radiationless transitions in a molecule (25). This explains the low fluorescence quantum yields for **III**, **IV**, and **V** in cyclohexane. In polar and protic solvents, IHB is partially broken in competition with the intermolecular hydrogen bond resulting in an increase of quantum yield. The very low fluorescence quantum yield of all the neutral molecules in dichloromethane is due to fluorescence quenching by the solvent molecules, as it is well established (26) that dichloromethane quenches the fluorescence of the fluorophores although not too efficiently. Similar behaviour in water is explained below.

**I** exhibits a dual fluorescence ($\lambda_f$ = 390 nm, 510 nm) in methanol and water. The longest wavelength emission band is relatively weak and is only observed at higher solute concentration ($\sim 10^{-4}$ M). When water is added to methanol the intensity of 510 nm band increases and reaches a maximum in solution containing 35% (v/v) water, whereas the intensity of 390 nm band decreases and reaches a minimum at this composition of methanol–water. With further increase in the percentage of water, intensity of the long wavelength band decreases. Similar behaviour has also been observed in acetonitrile–water and dioxane–water mixtures, indicating that the dual fluorescence in methanol, acetonitrile, and dioxane is due to the presence of a trace amount of water. We attribute the appearance of the 510 nm band to the formation of anion, a result of deprotonation from the —OH group. The very low $\phi_f$ value of the neutral molecule in water is thus due to monoanion formation, whereas similar behaviour is not observed in **II** and thus its fluorescence quantum yield increases as compared to other solvents. This assignment is based on the following facts.

(*i*) The fluorescence excitation spectra (pH ~ 7) recorded for both emission bands are similar and resemble the absorption spectra of neutral species. This indicates that both species have the same ground state precursor, *i.e.* neutral molecule.

(*ii*) The addition of KOH to the solution in 35% water – methanol mixture increases the intenstiy of the 510 nm band and decreases that of the other fluorescence band (390 nm). Furthermore, on acidification (3 < pH < 7) the opposite behaviour is observed. This proves that the species in the $S_1$ state are in reversible equilibrium.

(*iii*) Under similar conditions the methoxy derivative (**IM**) of the molecule **I** exhibits only the normal Stokes-shifted band characteristic of the neutral molecule. Therefore, the excited state process in **I** must involve deprotonation from the —OH group.

(*iv*) The fluorescence excitation spectrum (in the basified water–methanol mixture) recorded at the 510 nm emission band is similar to the absorption spectrum of anion in the same solution.

Assignment of 510 nm fluorescence band to the formation of excimer or exciplex is neglected on the ground that the ratio of fluorescence intensities at the band maxima ($I_{510}/I_{390}$) does not change with the increase of solute concentration.

Thus water molecules in methanol, acetonitrile, or dioxane act as proton acceptors leading to the following reaction.

$$[1] \quad ROH^* + H_2O \rightleftharpoons RO^- + H_3O^+$$

The decrease of fluorescence intensities of neutral and monoanion species with the increase of percentage of water (>35%) may be due to quenching by water molecules.

*Effect of acid concentrations*

The absorption and fluorescence spectra of all the molecules have been studied in the $H_-$/pH/$H_0$ range of 16 to −10.4. The spectral properties of the prototropic species of all molecules, compiled in Table 3, are discussed under the following headings.

*2-(3′-Methoxyphenyl)benzothiazole (**IM**)*

**IM** is present as a neutral in the $H_-$/pH range of 16 to 3.0. In solutions of pH less than 3.0 both absorption and fluorescence spectra shift to longer wavelengths. Based on earlier results (14) (*i.e.* protonation at tertiary nitrogen atom leads to

TABLE 3. Absorption ($\lambda_a$ nm) and fluorescence maxima ($\lambda_f$ nm), molar extinction coefficient (log $\epsilon$), and fluorescence quantum yields of different prototropic species of molecules **I** to **V** and **IM** in aqueous solution

| | Prototropic species | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Neutral | | Monocation | | Dication | | Monoanion | | Dianion | |
| Molecule | $\lambda_a$ (log $\epsilon$) | $\lambda_f$ ($\phi_f$) | $\lambda_a$ (log $\epsilon$) | $\lambda_f$ ($\phi_f$) | $\lambda_a$ (log $\epsilon$) | $\lambda_f$ ($\phi_f$) | $\lambda_a$ (log $\epsilon$) | $\lambda_f$ ($\phi_f$) | $\lambda_a$ (log $\epsilon$) | $\lambda_f$ ($\phi_f$) |
| **I** | 302 (4.24) | 390 (<0.001) | 320 (4.31) | 440 (0.05) | | | 345 298 (4.26) | 510 (<0.001) | | |
| **II** | 316 (4.34) | 380 (0.36) | 349 (4.5) | 410 (0.68) | 343 (4.42) | | 348 (4.55) | 420 (0.11) | | |
| **III** | 323 (4.38) | 410 (0.02) | 363 (4.43) 248 (3.97) | 440 (0.12) | 348 (4.38) 240 (3.63) | 415 | 358 (4.42) | 443 (0.02) | 394 (4.34) 322 (4.01) 277 (4.17) | |
| **IV** | 324 (4.38) | 400 (0.02) | 364 (4.46) 248 (4.02) | 440 (0.16) | 360 (4.40) 246 (3.95) | 420 | 362 (4.54) | 443 (0.04) | | |
| **V** | 321 (4.33) | 400 (<0.001) | 361 (4.38) 249 (3.9) | 440 (0.22) | 356 (4.41) 248 | 420 | 353 (4.1) 313 (4.12) 268 (4.16) | 510 (<0.001) | | |
| **IM** | 301 (4.3) | 380 (0.1) | 319 256 | 445 (0.11) | — | — | — | — | — | — |

a red shift in the absorption and fluorescence spectra if $\pi \rightarrow \pi$ is the lowest energy transition) the red-shifted absorption and fluorescence bands can be assigned to the monocation formed by protonation of the ring nitrogen atom. The value of the acidity constant for the monocation–neutral equilibrium (Table 4) as well as the similarity of the spectral characteristics of monocation of **IM** with those of PBT (27) ($\lambda_f$ = 390 nm) also confirm this assignment. The fluorescence intensity of the neutral band ($\lambda_a$ = 380 nm) decreases with the concomitant rise of the monocation band ($\lambda_f$ = 445 nm) as the pH is lowered. No further change in the spectral properties is observed when acid concentration is increased below $H_0$ = 0.0. The spectral characteristics of neutral and monocation forms of **IM** are depicted in Fig. 1 and the relative intensity change of the monocation and neutral molecule are plotted as a function of pH/$H_0$ in Fig. 2.

*Compounds II, III, IV, and V*

The absorption of fluorescence spectra of these molecules are red-shifted in solutions of pH > 7.0. This can be ascribed to the formation of the monoanion. The absorption spectra of **III** exhibit a further red shift in solutions of pH > 10.0. Since **III** has two dissociable —OH groups, the latter shift is due to the dianion formation. The red shifts in the absorption and fluorescence maxima of the monoanions relative to those of the corresponding neutral molecules (**II**, **III**, and **IV**) are almost similar, indicating thereby that monoanions are formed by the deprotonation of the 4′-OH groups. Consequently the dianion of **III** is formed from dissociation of 3′-OH group. This is further manifested by the fact that p$K_a$ for neutral–monoanion equilibrium is nearly similar for **II**, **III**, and **IV** (Table 4). The fluorescence spectrum ($\lambda_f$ = 510 nm) of the monoanion of **V** is very significantly red-shifted, as compared to those of **II**, **III**, and **IV**, although there is not much difference in the absorption band maxima of this species in these molecules. This is due to the large solvent relaxation in the excited state as observed in **I** as discussed below. In all cases, as the pH is raised, the fluorescence intensity of the monoanion increases simultaneously with the decrease of the neutral band. Since **III** decomposes at higher pH, it was not possible to record fluorescence spectra in solutions of pH above 11.0.

In the pH region of 7 to 3, the molecules are neutral in both the $S_0$ and $S_1$ states. Like **IM**, the absorption and fluorescence spectra shift to longer wavelengths (except for **II**) at $H_0 < 0$ and red-shifted bands can be assigned to monocation formed by protonating tertiary nitrogen atom. The fluorescence intensity of the monocation species of the compounds, especially for **III** and **IV**, increases slowly up to $H_0$ −3 and then sharply with further increase of acidity. Although nice isosbestic points are observed in the absorption spectra of these conjugate acid–base pair in the pH/$H_0$ range of 3 to −1.0, no correspondence is noticed between the decrease in the fluorescence intensity of the neutral species and increase in the fluorescence intensity of monocation (see Fig. 3). This indicates that either the fluorescence intensity of the neutral molecule is quenched by the protons (because the fluorescence intensity of neutral species is not quenched by the equivalent amount of $SO_4^{2-}$ ions, obtained by the addition of $K_2SO_4$) or

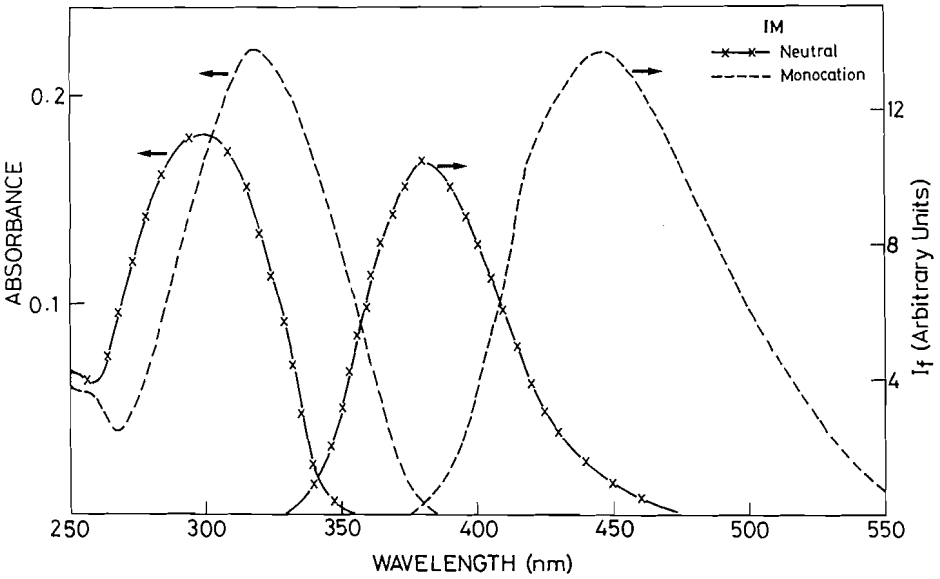



FIG. 1. Absorption (left) and fluorescence (right) spectra of the prototropic species of 2-(3′-methoxyphenyl)benzothiazole (**IM**).

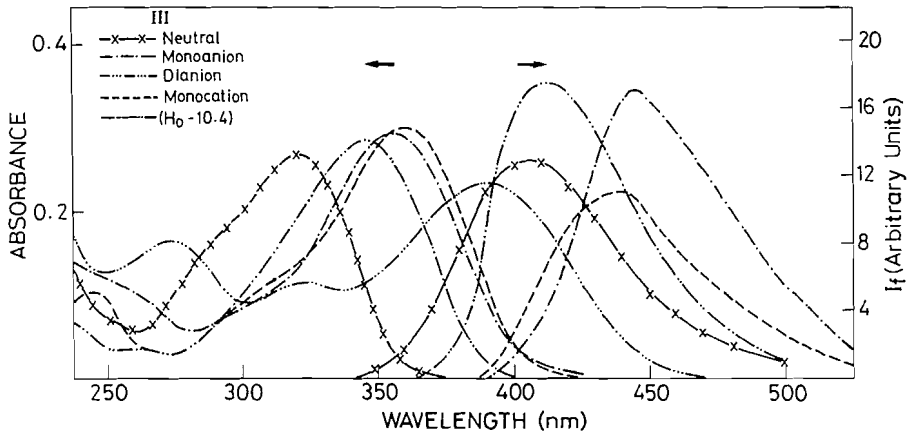



FIG. 2. Absorption (left) and fluorescence (right) spectra of the prototropic species of 2-(3′,4′-dihydroxyphenyl)benzothiazole (**III**).

there exists a non-fluorescent species in between neutral and monocation. The existence as well as nature of this species will be established in the subsequent section. In concentrated $H_2SO_4$ acid ($H_0$ −10.4), the absorption and fluorescence spectra of the monocations of all these molecules shift to shorter wavelengths which can be ascribed to the protonation on the —OH or —$OCH_3$ group at the 4′ position (since the protonation of —OH or —$OCH_3$ group at the 3′ position in **I** or **IM** does not bring about any spectral change) forming dications. The spectral profiles of the various prototropic species of **III** are depicted in Fig. 3.

*2-(3′-Hydroxyphenyl)benzothiazole (I)*

The absorption properties of I in aqueous solutions of pH/$H_0$ ranging from 13 to −10.4 are similar to those of the **II**, **III**, **IV**, and **V**. Thus the red-shifted absorption spectra of **I** (Fig. 4) at pH 13.0 and $H_0$ −1.0 can be assigned to the monoanion and monocation, respectively. The fluorescence characteristics of I in solutions pH/$H_0$ <2 are also similar to those observed for molecules discussed in the last section.

The fluorescence spectral characteristics in the pH range 0.0 to 13 are different from the ground state reactions and also different from those of the other molecules. The molecule exhibits dual fluorescence ($\lambda_f$ = 390, 510 nm) in this pH region. As already mentioned the short and long wavelength bands are due to the neutral molecule and monoanion, respectively. The intensities of the bands remain unchanged in the pH range 3.0 to 8.0. When the pH increases to above 8.0 the intensity of the 510 nm band increases and that of 390 nm band decreases. On the other hand, when the pH is decreased to below 3.0, the intensities of both bands decrease. The relative intensity change of the 510 nm band as a function of pH/$H_0$ is shown in Fig. 3. The plot thus obtained is a stretched sigmoid curve with two inflection points, one corresponds to the ground state p$K_a$ value (9.8) and the other to the excited state p$K_a$ value (1.8). The intensity change of the 390 nm band could not be plotted because of its very low intensity in aqueous solutions. Similar features have also been observed in 1-, 2-naphthols (6) and 9-phenanthrol (28). This indicates that the rate of proton transfer in the $S_1$ state of **I** is comparable to the rate of its fluorescence decay.

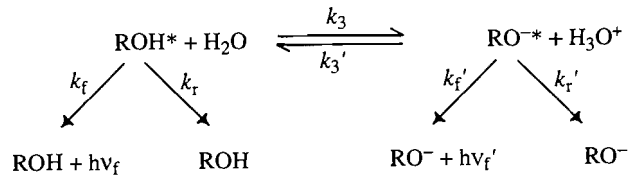
The appearance of the monoanion fluorescence band in the region of pH 3 to 8 must be due to the excited state prototropic reaction because anionic species is completely absent in solu-

TABLE 4. $pK_a$ and $pK_a^*$ values of the prototropic equilibria of molecules **I**, **II**, **III**, **IV**, **V**, and **IM**

| Molecules/equilibrium 1 | | | $pK_a$ 2 | $pK_a^*$ FT 3 | $pK_a^*$ FC[a] 4 | $pK_a^*$ FC[f] 5 |
|---|---|---|---|---|---|---|
| **I** | Dication | ⇌ monocation | <−10.4 | — | — | — |
| | Monocation | ⇌ zwitterion | | −6.6 | — | — |
| | Neutral | ⇌ zwitterion | | | — | — |
| | Monocation | ⇌ neutral | 0.7 | — | 4.6 | — |
| | Neutral | ⇌ monoanion | 9.5 | 1.5 | 0.8 | −3.1 |
| **II** | Dication | ⇌ monocation | <−10.4 | — | — | — |
| | Monocation | ⇌ zwitterion | | −2.7 | — | — |
| | Neutral | ⇌ zwitterion | | 1.6 | — | — |
| | Monocation | ⇌ neutral | 1.5 | — | 7.8 | — |
| | Neutral | ⇌ monoanion | 8.8 | 9.0 | 2.5 | 3.5 |
| **III** | Dication | ⇌ monocation | <−10.4 | — | — | — |
| | Monocation | ⇌ zwitterion | | −7.0 | — | — |
| | Neutral | ⇌ zwitterion | | 1.5 | — | — |
| | Monocation | ⇌ neutral | 1.5 | — | 8.7 | — |
| | Neutral | ⇌ monoanion | 8.5 | 8.3 | 2.1 | 4.7 |
| | Monoanion | ⇌ dianion | 12.5 | — | 7.1 | — |
| **IV** | Dication | ⇌ monocation | <−10.4 | — | — | — |
| | Monocation | ⇌ zwitterion | | −6.3 | — | — |
| | Neutral | ⇌ zwitterion | | 1.4 | — | — |
| | Monocation | ⇌ neutral | 1.4 | — | 8.5 | — |
| | Neutral | ⇌ monoanion | 9.1 | 9.2 | 2.3 | 4.0 |
| **V** | Dication | ⇌ monocation | <−10.4 | — | — | — |
| | Monocation | ⇌ zwitterion | | −7.0 | — | — |
| | Neutral | ⇌ zwitterion | | 1.4 | — | — |
| | Monocation | ⇌ neutral | 1.4 | — | 8.6 | — |
| | Neutral | ⇌ monoanion | 9.3 | 9.6 | 3.4 | −2.0 |
| **IM** | Monocation | ⇌ neutral | 0.7 | 1.2 | 4.6 | 8.8 |

[a,f]Calculated using absorption and fluorescence maxima of the species, respectively.

tions of pH < 7 in the ground state. Therefore, the fluorescence properties in the region corresponding to the complete titration curve can be explained by the kinetics of the excited state reaction. The pathways of decay available to the excited-state prototropic species can be represented by the scheme




SCHEME 1

where $k_3$ and $k_3'$ are the pseudo first order rate constants for the deprotonation and second order protonation reactions, $k_f$ and $k_r$ are the radiative and non-radiative decay constants for ROH* and $k_f'$ and $k_r'$ are the corresponding quantities for $RO^{-}$*. If the equations derived by Weller (2), using the steady-state principle, are applied, then the relative fluorescence intensities of the neutral and monoanion species can be given by the equations

$$[5] \quad I/I_0 = \frac{1 + k_3'\tau_0'[H_3O^+]}{1 + k_3\tau_0 + k_3'\tau_0'[H_3O^+]}$$

$$[6] \quad I'/I_0' = \frac{k_3\tau_0}{1 + k_3\tau_0 + k_3'\tau_0'[H_3O^+]}$$

where $I_0$ or $I_0'$ is the fluorescence intensity of only one species, and $I$ or $I'$ is the same for the species at any pH in which both the conjugate acid and base are present; $\tau_0$ and $\tau_0'$ are the radiative life times of the neutral and monoanion species, respectively. Since in the pH region 8.0 to 3.0, the concentration of $H_3O^+$ is very small, the rate ($k_3'$) of the backward reaction will be very small compared to the radiative decay rate ($1/\tau_0'$) of the monoanion. Under such condition the eqs. [5] and [6] reduce to equations

$$[7] \quad I/I_0 = \frac{1}{1 + k_3\tau_0}$$

and

$$[8] \quad I'/I_0' = \frac{k_3\tau_0}{1 + k_3\tau_0}$$

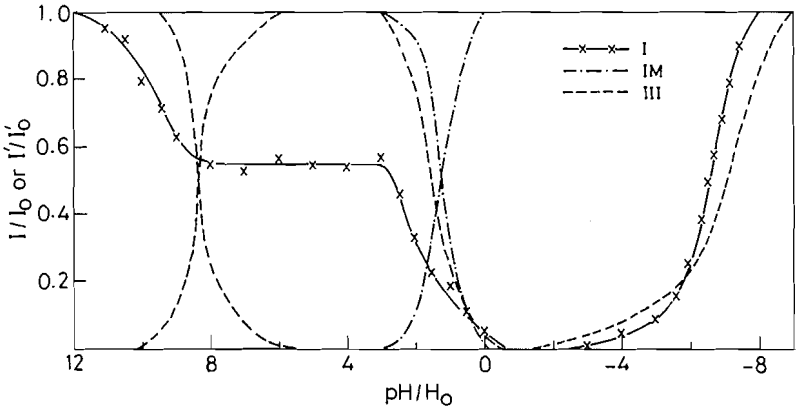



FIG. 3. Fluorimetric titration curves for compounds **I**, **IM**, and **III**.

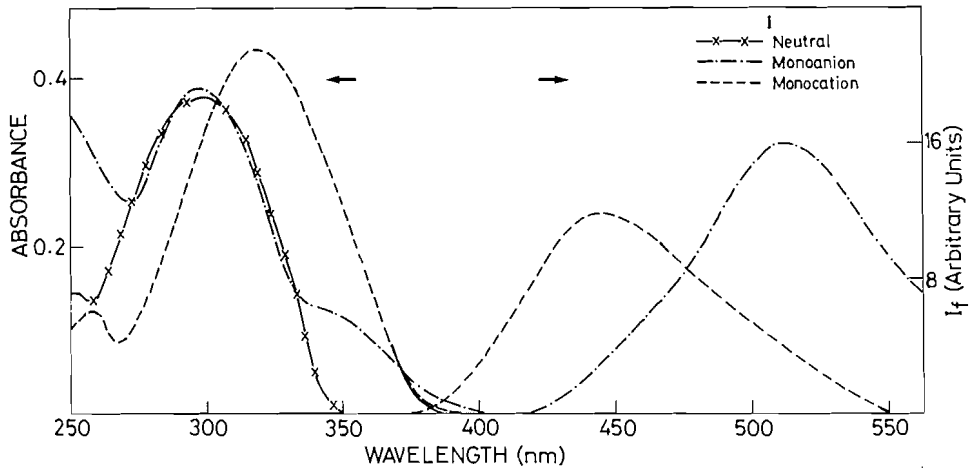



FIG. 4. Absorption (left) and fluorescence (right) spectra of the prototropic species of 2-(3′-hydroxyphenyl)benzothiazole (**I**).

respectively, which clearly show that the relative intensities of the neutral and anion forms are independent of $[H_3O^+]$ in the above pH region. Substituting the value of $I'/I_0' = 0.55$ in eq. [8] we get $k_3\tau_0 = 1.22$. Thus knowing $\tau_0$ one can calculate $k_3$.

*Acidity constants*

The acidity constants of the various prototropic reactions, as mentioned below, in the $S_0$ state are determined using absorption spectral data and the p$K_a$ values so obtained are tabulated in Table 4.

[1] Dication $\rightleftharpoons$ monocation + $H^+$

[2] Monocation $\rightleftharpoons$ neutral + $H^+$

[3] Neutral $\rightleftharpoons$ monoanion + $H^+$

[4] Monoanion $\rightleftharpoons$ dianion + $H^+$

Equilibrium [4] is possible only for **III**. The p$K_a$ value for equilibrium [1] could not be determined as the formation of dication was not complete even at $H_0$ −10.4. From the data of Table 4, it is clear that for **II**, the p$K_a$[3] value of reaction [3] is much smaller and that of reaction [2] is higher than that for **I**. This is consistent with the fact, as discussed earlier, that **II** is resonance-stabilized, as a result of which the hydroxyl proton becomes more acidic and the pyridinic nitrogen atom becomes more basic. MO calculations show that the π-electron density (Table 5) at the oxygen atom of —OH group in **II** is smaller than that in **I**. This is more pronounced in the $S_1$ state thus providing that —OH group becomes more acidic upon excitation. On the other hand, charge density at the tertiary nitrogen atom of **II** is more than that in **I** and thus making it more basic. Based on this discussion, p$K_a$[3] value for **III** indicates that the first deprotonation will occur from the hydroxyl group at position 4′, followed by from position 3′. Little higher values of p$K_a$[3] for **IV** and **V** could be because of the presence of electron donating methoxy group at the ortho-position to the hydroxyl group. Similarity of p$K_a$[2] values for compounds **I** and **IM** and higher value for **II** can be explained on the same lines as has been done before for p$K_a$[3].

The p$K_a$* values for the various prototropic reactions have been determined using fluorimetric titrations and Forster cycle method employing absorption and fluorescence data wherever applicable and are compiled in Table 4. The Forster cycle method cannot be used to calculate (*a*) p$K_a$*[1], because ground state p$K_a$ value is not known, (*b*) p$K_a$*[2], because the prototropic reaction involved in the ground state is different from that occurring in the $S_1$ state (see below), (*c*) p$K_a$*[4] cannot be determined using fluorescence data as the dianion of **III** is non-fluorescent. As expected, p$K_a$*[3] values indicate that hydroxyl group become stronger acid on excitation. On the other hand, ground state p$K_a$[3] values have been obtained

TABLE 5. $\pi$-Electron densities on the hetero atoms of 3′-HPBT, 4′-HPBT, and 3′,4′-DHPBT

| Molecule | Atom | $\pi$-Electron density $S_0$ | $\pi$-Electron density $S_1$ |
|---|---|---|---|
| 3′-HPBT | S | 1.422 | 1.457 |
| | N | 1.382 | 1.443 |
| | O | 1.917 | 1.915 |
| 4′-HPBT | S | 1.427 | 1.438 |
| | N | 1.385 | 1.457 |
| | O | 1.907 | 1.887 |
| 3′,4′-DHPBT | S | 1.426 | 1.471 |
| | N | 1.385 | 1.436 |
| | $O^a$ | 1.933 | 1.901 |
| | $O^b$ | 1.936 | 1.932 |

[a,b]Oxygen atom of the —OH group at 4′ and 3′ position, respectively.

from the fluorimetric titrations curves (Fig. 3) for **II**, **III**, **IV**, and **V**, indicating that prototropic equilibrium [3] is not established in the $S_1$ state during the lifetimes of these molecules. Stretched sigmoid fluorimetric titration curves have been noticed for **I** in the pH range to 11, giving two p$K_a$[3] values, one agreeing with the ground state p$K_a$[3] value and the other the excited state p$K_a$[3] value. This indicates that the lifetimes of the respective conjugate acid–base pair of **I** are comparable with the reciprocal rate constants of these prototropic reactions.

As mentioned earlier, no correspondence is observed between the decrease in the fluorescence intensity of neutral species and the increase in the fluorescence intensity of monocation. On the basis of the following discussion, we conclude that the decrease in the fluorescence intensity of neutral species is due to the formation of non-fluorescent zwitterion rather than due to proton-induced fluorescence quenching. (*i*) Prototropic equilibrium for the monocation–neutral reaction of **IM** has clearly established that formation of non-fluorescent species is because of the presence of —OH group, which is absent in **IM**. Further the structures of **I** and **IM** are not very different from each other. If **I** undergoes proton-induced fluorescence quenching it should also be observed for **IM**. On the other hand, the proton-induced fluorescence quenching has been observed for both 2-naphthol and 2-methoxy naphthalene (29). (*ii*) p$K_a$* values are generally determined from the formation curve of that species. The p$K_a$*[2] values thus obtained for the monocations of these molecules indicate that the tertiary nitrogen atom become weaker base upon excitation, which is contrary to the established results. (*iii*) Our PPP calculations have also indicated that charge density increases at the basic nitrogen atom, suggesting that the tertiary nitrogen atom becomes a stronger base in the $S_1$ state. (*iv*) Since the formation of zwitterion in the $S_1$ state involves biprotonic mechanism, its formation will depend on the environments. That is why it is only formed in the pH/$H_0$ range 3 to −2. (*v*) When similar titration is performed in cyclohexane with trifluoroacetic acid the formation of monocation is complete at much lower acid concentration and the increase in the intensity of monocation is comparable with the decrease of the neutral species. This is because the formation of zwitterion will be less favourable in non-polar than in polar media.

It has also been noticed that the shape of the fluorimetric titration (Fig. 3) curves for the formation of monocation do not conform to the trend observed in the titration curves for neutral molecules, *i.e.* it rises very slowly in the beginning and then sharply, as if there are two breaks. Since no changes have been noticed in the absorption spectra at $H_0 < -2$, we attribute this to an excited state phenomenon. In our opinion, the first break is due to the formation of monocation from non-fluorescent zwitterion and the increase of intensity in the second step is due to the decrease in the rates of radiationless processes in monocation. This could be due either to an increase in viscosity of the medium or a decrease in the number of free water molecules to solvate the monocations with the increase of acid concentration. Because of this, only the approximate values of p$K_a$* for the monocation–zwitterion equilibria are reported.

## Conclusions

The higher values of molar extinction coefficient of the lowest energy transition and fluorescent quantum yield and low value of p$K_a$[3] of **II** compared to the corresponding values of **I** indicate the resonance effect of the —OH group leading to structure **II′**. The structured absorption and fluorescence spectra exhibited by **III**, **IV**, and **V** are indicative of the presence of intramolecular hydrogen bond between the —OH proton and the oxygen atom of the adjacent —OH or —$OCH_3$ group. The rate of deprotonation reaction in molecules **II**, **III**, **IV**, and **V** is slower than the rates of radiative decays whereas in **I** the proton-transfer rate is comparable to the rate of radiative decay. The prototropic reactions of the molecules, except for **IM**, in the acidity region of $H_0 = 0.0$ to $H_0 = -9.0$ in the $S_1$ state are different from those in the $S_0$ state. The fluorimetric titration curves in this region of acidity have led to a prediction of the monocation–zwitterion equilibrium. The zwitterions are formed from neutral molecules as a result of biprotonic photoautomerism.

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