Electronic absorption and fluorescence spectral characteristics and prototropic reactions of some hydroxy- and methoxy-substituted derivatives of 2-(2′-hydroxyphenyl)benzothiazoles

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Abstract

The absorption and fluorescence spectral characteristics of 2-(2′,3′-, 2′,4′- and 2′,5′-dihydroxyphenyl)benzothiazoles (2′,3′-DHPBT, 2′,4′-DHPBT, 2′,5′-DHPBT), 2-(2′-hydroxy-3′-methoxyphenyl)benzothiazole (2′-H-3′-MPBT) and 2-(2′-hydroxy-4′-methoxyphenyl)-benzothiazole) (2′-H-4′-MPBT) were studied in various solvents. The dual fluorescence indicates the presence of two species; the normal Stokes-shifted fluorescence band is assigned to the enol form and the large Stokes-shifted band to the keto form, a tautomer produced on excitation. The fluorescence excitation spectrum indicates that these two species have the same precursor. Ground state prototropic reactions indicate the presence of the dication, monocation, neutral molecule and monoanion, whereas in the excited singlet state the species observed are the dication, monocation, zwitterion (non-fluorescent), neutral (enol and keto) form and anion. The pK_a values were calculated for different prototropic reactions in the S_0 state. In the S_1 state, these values were difficult to determine because of the complexity of the prototropic reactions. Molecular orbital calculations using the Pariser–Parr–Pople (PPP) method were performed to calculate the spectral properties and electron densities at the acidic and basic centres of the molecules.

1. Introduction

The fluorescence emission properties of crystalline 2-(2′-hydroxyphenyl)-benzothiazole (2′-HPBT) and some substituted derivatives [1–3] have been studied in detail. Similarly, the dynamic properties of the excited state intramolecular proton transfer (ESIPT) reaction in solution have been investigated [1–14]. The ESIPT process in 2′-HPBT has been studied as a function of solvent polarity [3], viscosity [3] and temperature [6]. From these studies, it has been concluded that the rate of ESIPT is very fast (approximately 10^{12} s^{-1}) and the activation barrier (approximately 120 cm^{-1}) is very small. These studies also indicate that the fluorescence decay is temperature dependent and can be represented by two exponential decay functions. Itoh and Fujiwara [9] have proposed that tautomer fluorescence is due to two isomers: the cis and twisted conformers. The tautomerization process of 2′-HPBT in the ground state has also received considerable attention and it has been established that two conformers

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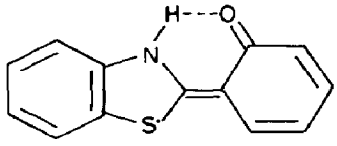
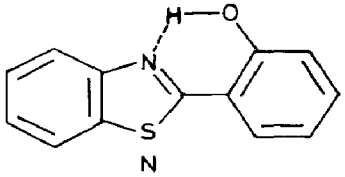
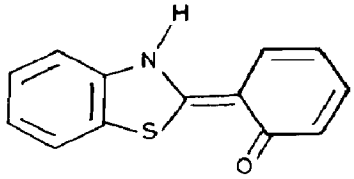
are present in the ground state. The cis form (**I**) is responsible for the strongly Stokes-shifted fluorescence band (approximately 520 nm) and undergoes rapid reverse proton transfer in the S_0 state. The other form is a long-lived phototautomer, ascribed as the twisted (**II**) or trans (**III**) conformer. The structures of the various forms are given below.



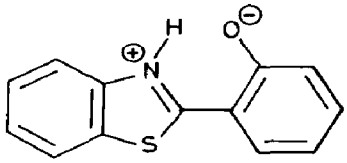
I cis form



Normal

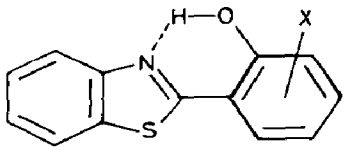


III trans form



II Twisted form

Recently [15], attention has been drawn to the prototropic species formed when 2′-HPBT is subjected to varying concentrations of acid and base; however, the results are not very conclusive. Labedeva *et al.* [16] have also reported the effect of halogen, amino and nitro substituents on the dissociation constants of 2′-HPBT. The aims of the present work are as follows: (i) to study the effect of varying concentrations of acid and base on the spectral characteristics of hydroxy- and methoxy-substituted derivatives of 2′-HPBT and to identify the various prototropic species formed, and (ii) to observe the effect of a second hydroxyl group present at the 3′, 4′ or 5′ position of the phenyl group. It has been shown that the presence of only one hydroxyl group at the 3′ position of the phenyl group of the benzoxazole moiety (3′-HPBO) [17] leads to different kinetics of proton transfer than for compounds with the hydroxyl group at the 2′ or 4′ position. Therefore we also aim to determine how the presence of a second hydroxyl group at the 3′ position affects the prototropic behaviour of 2′-HPBT. The following molecules were chosen for this study: 2-(2′,3′-dihydroxyphenyl)benzothiazole (2′,3′-DHPBT; **1**; X=3′-OH); 2-(2′,4′-dihydroxyphenyl)benzothiazole (2′,4′-DHPBT; **2**; X=4′-OH); 2-(2′,5′-dihydroxyphenyl)benzothiazole (2′,5′-DHPBT; **3**; X=5′-OH); 2-(2′-hydroxy-3′-methoxyphenyl)benzothiazole (2′-H-3′-MPBT; **4**; X=3′-OMe); 2-(2′-hydroxy-4′-methoxyphenyl)benzothiazole (2′-H-4′-MPBT; **5**; X=4′-OMe).



To substantiate the spectral characteristics obtained and the formation of the prototropic species, attempts have been made to carry out theoretical calculations of spectral transitions and charge densities at the various basic centres.

2. Experimental details

The compounds were synthesized by heating *o*-aminothiophenol and the corresponding salicylaldehydes in glacial acetic acid and were purified by repeated recrystallization from acetic acid and aqueous ethanol as described in the literature [18]. The purity was checked by thin layer chromatography (TLC), melting point determination and fluorescence excitation spectroscopy. Analytical grade cyclohexane, methanol (S. D. fine) dioxane, acetonitrile and dichloromethane (E. Merck) were further purified by the general methods described elsewhere [19]. Spectro grade ethylacetate (S. D. fine) was used directly from the bottle. All the solvents were checked for spurious fluorescence in the wavelength region in which the fluorescence spectra were recorded. NaOH, H_2SO_4 and H_3PO_4 (ortho) were of analytical grade. Aqueous solutions of pH 3–10 were prepared by mixing appropriate amounts of 10^{-3} M NaOH and H_3PO_4 solutions. Hammett's acidity scale [20] and Yagil's basicity scale [21] were followed in the preparation of solutions of $pH < 1.0$ and $pH > 14$ respectively. Due to the poor solubility of the compounds, the aqueous solutions were prepared in a methanol–water mixture, containing not more than 20% (v/v) methanol in the final solution; solutions of $H_0 < -5$ contain only 0.5% methanol (v/v). All spectral measurements were made at a solute concentration of 2×10^{-5} M. Fluorescence quantum yields were calculated for solutions having an absorbance of less than 0.1 at the excitation wavelength relative to quinine sulphate in 0.1 N H_2SO_4 ($\theta_f = 0.55$) [22]. For fluorometric titrations the solutions were excited at the isosbestic wavelength of the absorption spectra.

Absorption spectra were measured using a Shimadzu UV-190 spectrophotometer equipped with a 135U chart recorder. Steady state fluorescence spectra were recorded in a scanning spectrofluorometer fabricated in our laboratory as described elsewhere [23]. The pH measurements were performed in a Toshniwal digital pH meter (model CL 46), fitted with a combined single-probe glass electrode.

Molecular orbital calculations were performed using the Pariser–Parr–Pople (PPP) method [24–26]. The excited states were generated by configuration interaction of the states obtained by transitions between the three highest occupied and three lowest unoccupied molecular orbitals. The empirical parameters used for the calculations were taken from Dorr *et al.* [27]. The molecules were assumed to be planar with ring C–C, C–N and C–S bond distances equal to 1.395 Å. For other bond lengths, standard values were used. As suggested by Woolfe *et al.* [28], the intramolecular hydrogen bonding in the molecules was taken into account by lowering the value of the core integral U_{kk} of the hydrogen-bond acceptor by 3 eV. The calculations were performed using the Institutes' Dec-1090 computer. The program [29] was obtained from QCPE, Indiana University, USA.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra data of the molecules are given in Table 1, and Fig. 1 shows the absorption spectra profiles of the molecules in cyclohexane. The spectrum

TABLE 1

Absorption maxima (λ_a (nm)), log ϵ, fluorescence maxima (λ_f (nm)) and fluorescence quantum yields (ϕ_f) of 2′,3′-, 2′,4′- and 2′,5′-DHPBT, 2′-H-3′-MPBT and 2′-H-4′-MPBT in various solvents

Solvent	2′,3′-DHPBT		2′-H-3′-MPBT		2′, 4′-DHPBT		2′-H-4′-MPBT		2′,5′-DHPBT	
	λ_a (log ϵ)	λ_f (ϕ_f)	λ_a (log ϵ)	λ_f (ϕ_f)	λ_a (log ϵ)	λ_f (ϕ_f)	λ_a (log ϵ)	λ_f (ϕ_f)	λ_a (log ϵ)	λ_f (ϕ_f)
Cyclohexane	–	–	–	–		390	261 (3.46)	500	251	400
	–		260 (3.78)		287	(<0.001)	287 (3.76)	(<0.001)	261	(<0.001)
	–		295 (4.22)		336	500	291(sh)		282	545
	307 (4.24)		306 (4.23)		348(sh)	(<0.001)	299(sh)		293	
	310 (4.25)		319 (4.21)				338 (4.13)		305	
	338(sh)		344 (4.0)				350(sh)		364	
Dioxane	310 (4.24)	385	–	375	289 (4.2)	–	262 (3.55)	500	284(sh)	405
		(<0.001)	259 (3.74)	(0.02)	337 (4.55)		290 (3.88)	(<0.001)	294 (4.23)	(0.01)
	320 (4.24)		299(sh)		348(sh)		337 (4.26)		364 (4.12)	
	338(sh)		307 (4.2)				350(sh)			
			319(sh)							
			337(sh)							
Acetonitrile	307 (4.24)	400	–	390	288 (4.12)	–	260 (3.47)	–	283(sh)	410
	318 (4.23)	505	258 (3.7)	(0.01)	334 (4.45)		290 (3.86)		293 (4.21)	(0.005)
	338(sh)		297 (4.17)		346(sh)		334 (4.22)		362 (4.11)	
			305 (4.18)				350 (sh)			
			317(sh)							
			337(sh)							
Ethylacetate	308 (4.25)	395	–	385	288 (4.13)	–	260	500	283 (4.2)	405
	319 (4.23)	(<0.001)	259 (3.74)	(0.01)	336 (4.47)		289	(<0.001)	294 (4.24)	(0.005)
	338(sh)		297 (4.21)		346(sh)		336	380	367 (4.13)	
			306 (4.22)				346(sh)	(<0.001)		
			318 (4.19)							
			334(sh)							

Dichloromethane	307 (4.24) 319 (4.25) 338(sh)	–	260 (3.76) 298 (4.23) 306 (4.23) 318 (4.21) 340(sh)	385 (0.001)	289 (4.12) 335 (4.44) 347(sh)	–	262 292 337 348(sh)	500 (<0.001)	284(sh) 294 (4.16) 360 (4.09)	–
Methanol	308 (4.24) 320(sh) 338(sh)	420 (<0.005) 500(sh)	– 258 (3.71) 299(sh) 307 (4.21) 317(sh) 334(sh)	410 (0.04)	289 (4.11) 336 (4.46) 345(sh)	390 (0.036)	260 (3.66) 290 (4.0) 334.5 (4.34) 350(sh)	380 (0.03)	251 294 361	430 (0.06)
Water (pH 6.3)	314 330(sh)	–	314 330(sh)	520 (0.005)	290 (3.9) 331 (4.31)	400 440 500	292 332	400 440 500	250 257(sh) 293 350	440 500

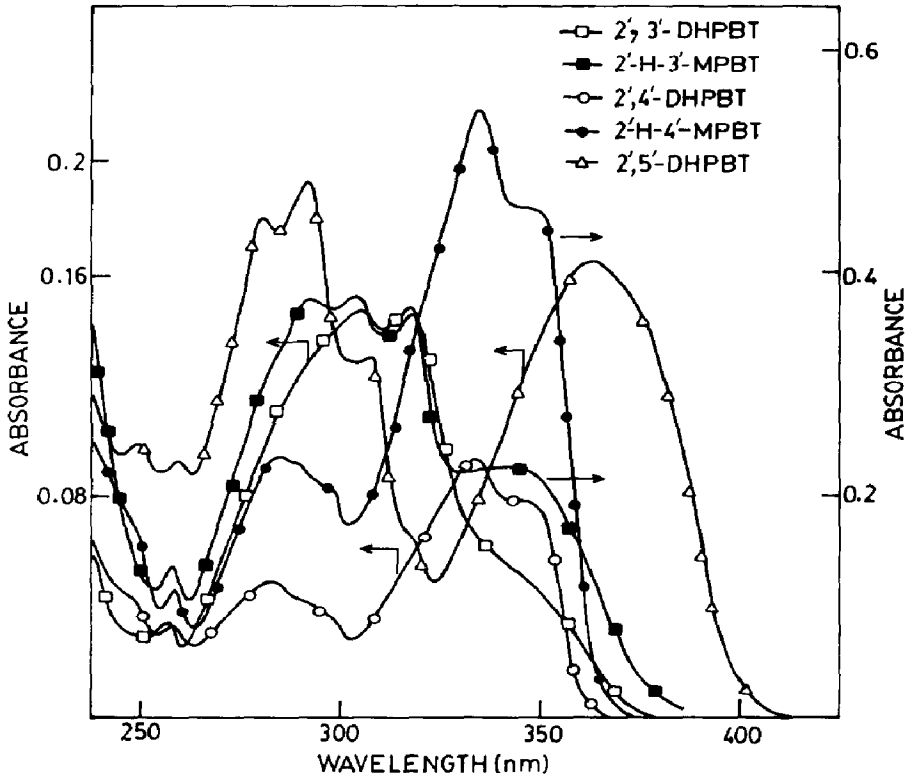


Fig. 1. Absorption spectra of 2',3'-DHPBT, 2'-H-3'-MPBT, 2',4'-DHPBT, 2'-H-4'-MPBT and 2',5'-DHPBT in cyclohexane.

of each molecule consists of four absorption bands, centred at around 340, 300, 250 and 220 nm. The spectra are similar, but red shifted, relative to that of 2'-HPBT. The longest wavelength band of 2',5'-DHPBT is more red shifted relative to that of 2'-HPBT than those of the other molecules. The two long-wavelength bands of 2',4'-DHPBT, 2',5'-DHPBT and 2'-H-4'-MPBT are well separated, whereas in 2',3'-DHPBT and 2'-H-3'-MPBT the longest wavelength band appears as a shoulder on the second absorption band. The second absorption band of the molecules is structured in non-polar or weakly polar solvents. The structure is lost with an increase in polarity or hydrogen-bonding tendency of the solvent. The intensity of the lowest energy band is lower than that of the second absorption band in 2',5'-DHPBT, 2',3'-DHPBT and 2'-H-3'-MPBT, whereas it is higher in 2',4'-DHPBT and 2'-H-4'-MPBT. The positions of the absorption maxima hardly change with increasing solvent polarity. However, in hydroxylic solvents, the longest wavelength band of the molecules shifts to lower wavelength.

The longest wavelength band is due to the presence of intramolecular hydrogen bonding (IHB) as observed in 2'-HPBT. This has been substantiated by the pK_a value [30, 31], nuclear magnetic resonance (NMR) and IR spectroscopy and X-ray crystallography [32]. Furthermore, the corresponding band system is absent in 2-(3'-hydroxyphenyl)- and 2-(4'-hydroxyphenyl)benzothiazole (3'-HPBT and 4'-HPBT), where there is no IHB [33].

The effect of the second hydroxyl group on the spectral characteristics of 2'-HPBT is similar to that observed when the second amino group is added to either

aniline [34, 35] or naphthylamine [36, 37]. From these studies [34–37], it has been concluded that the two hydroxyl groups in the 2′,3′ derivative are twisted and remove the lone pair of the oxygen atom from the plane of the π cloud of the aromatic moiety; in the 2′,4′ derivative the two hydroxyl groups are in plane, whereas in the 2′,5′ derivative the two groups are out of the plane of the aromatic ring. The result is that the hydroxyl groups have a maximum effect on the spectrum of the parent hydrocarbon when they are in the para position and a minimum effect when they are in the ortho position. The long-wavelength absorption band maximum of the ortho derivative (2′,3′) of HPBT is lower than that of the 2′,4′ form which is, in turn, lower than that of the 2′,5′ derivative. Furthermore, this explains why the two long-wavelength bands of 2′,3′-DHPBT and 2′-H-3′-MPBT are not separated, whereas they are separated in the other molecules.

The effect of the solvent on the absorption spectra of hydroxy-substituted derivatives of aromatic hydrocarbons is much weaker than that observed for amino-substituted derivatives. This is because the resonance effect of the lone pair of the amino group is more pronounced than that of the hydroxyl group. Our results are consistent with this interpretation, except for the effect of water on the longest wavelength band. This is because water is a strong hydrogen-bonding solvent and thus there is competition between intramolecular and intermolecular hydrogen bonding. Due to the breaking of IHB, the spectrum shifts towards the blue when water is used as solvent.

3.2. Fluorescence spectra

The fluorescence spectra of the molecules in cyclohexane and water are shown in Fig. 2. The fluorescence spectral data given in Table 1 show that all the molecules, except for 2′,3′-DHPBT and 2′-H-3′-MPBT, exhibit dual fluorescence in all the solvents. The intensities of the bands are very low. The fluorescence intensity of the normal Stokes-shifted band increases in protic solvents (methanol and water). The short-wavelength band of 2′,5′-DHPBT is more red shifted in methanol compared with other aprotic polar solvents. Both 2′,4′-DHPBT and 2′-H-4′-MPBT give three fluorescence bands ($\lambda_f \approx 390$, 440 and 500 nm) in water, whereas 2′,5′-DHPBT shows only two bands centred around 440 and 500 nm. 2′,3′-DHPBT is non-fluorescent in water and 2′-H-3′-MPBT gives only the large Stokes-shifted band at 520 nm.

Earlier studies [1–14] have clearly established that the large Stokes-shifted fluorescence band in 2′-HPBT is due to the keto tautomer or the zwitterion and the normal Stokes-shifted band is due to the normal molecule. The very low fluorescence quantum yields of both bands are consistent with the observation that the ESIPT rate is very fast; in addition, the rate of internal conversion in the ESIPT process is high if the energy gap between the tautomer levels is not large. Our results can be explained in a similar manner. The increase in the fluorescence quantum yield of the normal Stokes-shifted band in protic solvents, as mentioned earlier, is due to the breaking of IHB and the formation of intermolecular hydrogen bonding. Depending on the nature of the molecule, the intermolecular hydrogen bonding with water can be sufficiently strong in the excited singlet state so that dissociation of the OH group can take place, leading to the formation of the monoanion in near–neutral aqueous solution. For example, the 440 nm band of 2′,4′-DHPBT and 2′-H-4′-MPBT, as well as the 500 nm band of 2′,5′-DHPBT, can be assigned to the formation of the monoanion. This is based on the observation that the addition of water to methanol gives rise to the appearance of these fluorescence bands at the expense of normal or strongly Stokes-shifted bands. Further support for the formation of the monoanion is given in the next section:

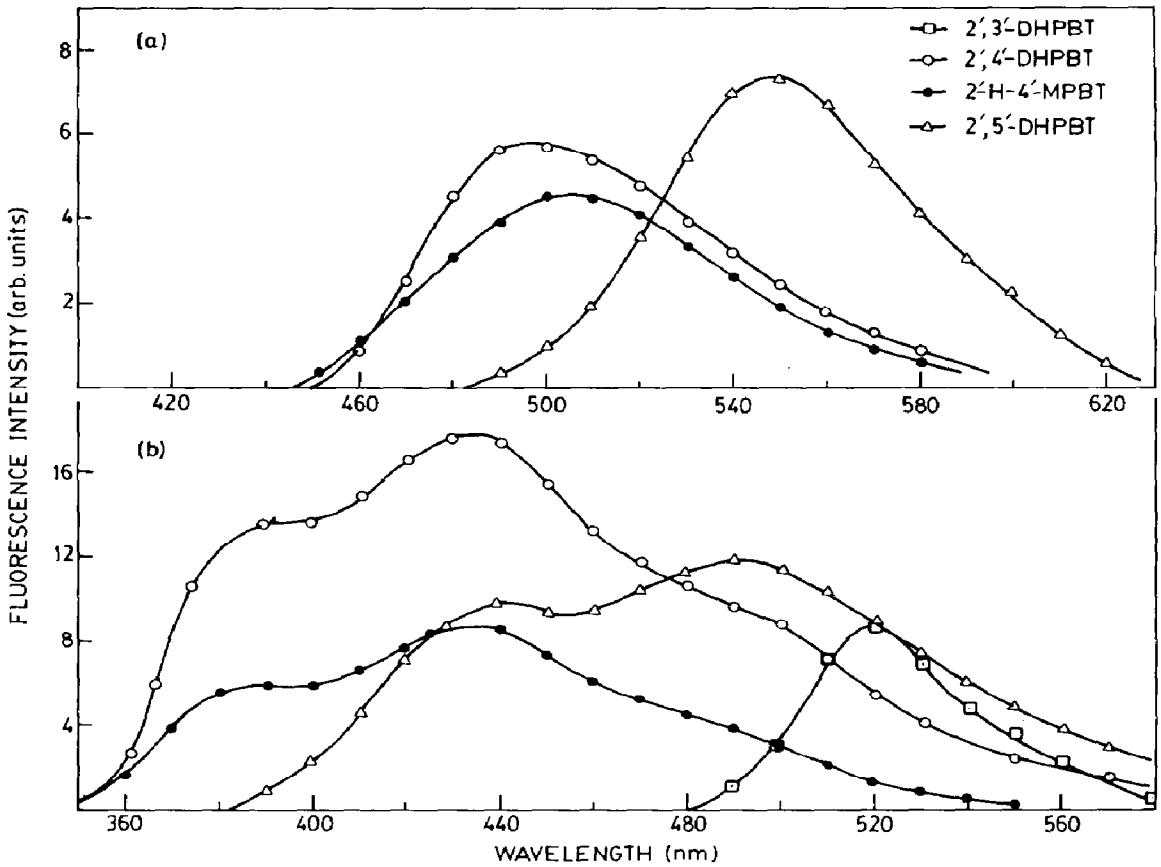


Fig. 2. Fluorescence spectra of 2',3'-DHPBT, 2',4'-DHPBT, 2'-H-4'-MPBT and 2',5'-DHPBT in (a) cyclohexane and (b) water.

obviously, the fluorescence intensity of the monoanion should increase with an increase in base concentration and decrease with an increase in acid concentration.

A larger red shift is observed in the normal Stokes-shifted fluorescence band of 2',5'-DHPBT in comparison with the other molecules. This is consistent with our earlier studies on 1,4-diaminobenzene [35] and 1,4-diaminonaphthalene [37], in the sense that the two groups try to become coplanar with the parent hydrocarbon in the S_1 state. The strongly red-shifted fluorescence band maximum of the monoanion of 2',5'-DHPBT can be explained in this way and thus large solvent relaxation is observed.

3.3. Effect of acid–base concentration

The absorption and fluorescence spectra of the molecules were studied in the acidity–basicity range of $-H_0$ 10.4 to H_- 16. Because of poor solubility, the spectra of 2',3'-DHPBT, 2'-H-3'-MPBT and 2'-H-4'-MPBT were recorded in 20% (v/v) aqueous ethanolic solutions. The solutions were prepared following the acidity scale of Dolman and Stewart [38]. Since 2',5'-DHPBT decomposes, it could not be studied in solutions of pH > 9.5.

3.3.1. Absorption spectra

The absorption spectral data of the molecules as a function of pH/H_0 are given in Table 2. The molecules are neutral in the pH range 3–7, as the spectral characteristics

TABLE 2

Absorption maxima (λ_a (nm)), log ϵ, fluorescence maxima (λ_f (nm)) and fluorescence quantum yields (ϕ_f) of the prototropic species of 2′,3′-, 2′,4′- and 2′,5′-DHPBT, 2′-H-3′-MPBT and 2′-H-4′-MPBT

Species	2′,3′-DHPBT		2′-H-3′-MPBT		2′,4′-DHPBT		2′-H-4′-MPBT		2′,5′-DHPBT	
	λ_a (log ϵ)	λ_f (ϕ_f)	λ_a (log ϵ)	λ_f (ϕ_f)	λ_a (log ϵ)	λ_f (ϕ_f)	λ_a (log ϵ)	λ_f (ϕ_f)	λ_a (log ϵ)	λ_f (ϕ_f)
Neutral (pH 6.0)	314[d] 330(sh)	–	314[e] 330(sh)	– 520	290 (3.9) 331 (4.31)	400 500	292[e] 332	390 500	250 257(sh) 293 350	– 440
Monoanion	304 315 372	500[c]	303 314 382[c]	500[c] (0.04)	254(sh) 293 300 362 (4.35)[b]	440[b] (0.08)	257 293 300 370[c]	440[c] (0.3)	–	500
Dianion	325 400[c]	–			272 (3.9) 318 (3.9) 380 (4.46)[c]	440	–	–	–	
Keto tautomer	–		–	520	–	500	–	500[d]	–	
Monocation	265 334 362(sh)[a]	490	265 334 362(sh)[a]	490[f]	268 (3.58) 325(sh) 368 (4.48)[a]	410[f] (0.39)	246 270 319 371	410[f] (0.33)	256 317 390[a]	510[g]
$-H_0$ 10.4	261 312(sh) 349	430	247 251 334	435	250 307 354	400	252 262 308 355	405	261 316 357	430

[a]Measured in $-H_0$ 2.0 solution. [b]Measured at pH 9.6. [c]Measured at pH 12.0. [d]Measured at pH 1.0. [e]Measured in 20% ethanol–water mixture. [f]Measured at $-H_0$ 9.0. [g]Measured at $-H_0$ 5.0.

resemble those observed in non-aqueous solvents. In slightly basic solutions ($7 < pH < 10$), the molecules form the monoanion as the spectral band maxima are red shifted. Since the absorption spectra of the monoanions and the dissociation constants (see Table 3, Section 3.4) of all the compounds are similar, the first deprotonation occurs from the OH group at position 2'. Similar deprotonation in various solvents has also been reported for 2'-HPBT [4, 12, 13].

Only the 2',3'-, 2',4'- and 2',5'-DHPBT molecules have a second hydroxyl group that can be dissociated and thus undergo further red shifts in the absorption spectra of the monoanions with an increase in OH^- concentration. The dianions are formed by deprotonation of the OH groups at position 3' or 4'. A red shift in the absorption band maxima of neutral molecules with an increase in acid concentration indicates the formation of monocations, obtained by the protonation of the tertiary nitrogen atom. This is consistent with literature results [17]. The spectra of the monocations of these molecules, with the exception of 2',5'-DHPBT, do not exhibit any change in the acidity range H_0 −2 to −9. At the highest concentration of acid used (H_0 −10), a blue shift is observed in the absorption spectra, indicating protonation of the OH group, as observed in the corresponding hydroxy-substituted derivatives of aromatic molecules [39, 40]. In the case of 2',5'-DHPBT, the longest wavelength band of the monocation spectrum shifts gradually to the blue (Fig. 3) as the concentration of acid is increased. We assign this behaviour to a medium effect rather than to the formation of the dication because of the following observations: (i) there is no clear isosbestic point in this H_0 range; (ii) the pK_a value calculated by Henderson's equation, on the assumption that this acid range represents dication–monocation equilibrium, gives a slope of only 0.37, *i.e.* much less than unity (the possibility that Hammett's acidity scale may not be obeyed by this molecule is rejected on the grounds that the other four similar molecules follow Hammett's scale very well); (iii) in general, protonation of either the hydroxyl or methoxyl group occurs only at $H_0 < -9$, resulting in a blue shift of the absorption spectrum, and this is observed at H_0 −10.4. Similar medium effects have been observed in the protonation reaction of amides [41] and carbonyls [42].

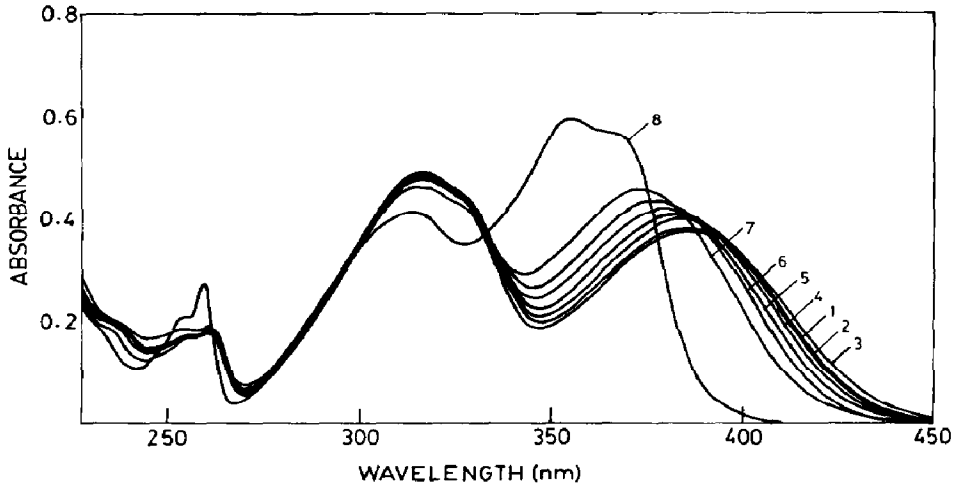


Fig. 3. Absorption spectra of 2',5'-DHPBT as a function of H_0: 1, −3; 2, −4; 3, −5; 4, −6; 5, −7; 6, −8; 7, −9; 8, −10.

3.3.2. Fluorescence spectra

3.3.2.1. 2',4'-DHPBT and 2'-H-4'-MPBT. The spectral characteristics of these two molecules are similar, except at pH > 10, as observed from the data in Table 2. Both molecules give three overlapping fluorescence bands (390, 440 and approximately 500 nm) in the pH range 2.0–8.5 and the intensity of the bands remains unchanged over the pH range 3.0–7.5. In the case of 2'-H-4'-MPBT, the 500 nm band exhibits higher intensity than the other bands, whereas the 440 nm band of 2',4'-DHPBT is more intense. The fluorescence excitation spectra recorded at each emission maximum are similar and also closely resemble the absorption spectra. This suggests that all the bands result from the same ground state species (neutral molecule). This also agrees with the observation that, in this pH region, the pK_a values (Table 3, Section 3.4) render the presence of other species (*i.e.* monocation or monoanion) highly improbable. Thus the short-wavelength fluorescence band (390 nm), which resembles the spectrum in methanol or non-polar solvents, is assigned to the intramolecular-hydrogen-bonded free neutral molecule (N), whereas the 500 nm band is assigned either to the phototautomer (I) or the zwitterion (II), most probably the former in this region of pH (see below).

With an increase in pH, the intensity of the 440 nm band increases at the expense of the neutral and keto forms and reaches a maximum at pH 10.5, where the only ground state species is the monoanion. The fluorescence excitation spectrum recorded at 440 nm and pH 10.5 closely resembles the absorption spectrum of the monoanion and thus the 440 nm band can be assigned to the monoanion. The intensity of the monoanion fluorescence of 2'-H-4'-MPBT does not change, but that of 2',4'-DHPBT decreases with increasing OH^- ion concentration. It does not go to zero even at H_- 16 and no other fluorescence band is observed. After pH 14, the intensity of the 440 nm band remains constant. In addition, the positions of the band maximum and the bandwidth at half-maximum (BWHM) remain constant with increasing OH^- concentration. The fluorescence excitation spectrum recorded at H_- 16 is different from the absorption spectrum of the monoanion and similar to that of the dianion. This indicates that the fluorescence spectrum of the dianion may be similar to that of the monoanion. This assignment is based on the following observations: (i) the formation of the dianion is complete at H_- 14 in the ground state and (ii) the presence of another negative charge at a meta position relative to the first may not change the energy of the emitting state of the monoanion. Unfortunately, other molecules, in which the two hydroxyl groups are either ortho or para to each other, decompose in such a highly basic medium.

An increase in H^+ concentration (pH < 3.0) leads to a decrease in the intensity of each band in neutral or near-neutral solution, without the appearance of any other band. These results are different from those obtained by Potter and Brown [15], as well as from our own results on the molecule 2'-HPBT, in the sense that a correlation was observed between the decrease in the fluorescence intensity of the 2'-HPBT neutral and zwitterion forms and the increase in the fluorescence intensity of the monocation. It is only at $H_0 < 0$ that a band at 440 nm starts to appear in both cases and its intensity continues to increase with increasing acid concentration up to $H_0 - 9$. Similar behaviour, *i.e.* no correlation between the decrease in the fluorescence intensity of the neutral species and the increase in the fluorescence intensity of the monocation and an increase in the fluorescence intensity of the monocation with increasing acid concentration, is also observed in 3'-HPBT and 4'-HPBT [17]. The decrease in the fluorescence intensity of the neutral species at pH < 3 is due to the formation of a

non-fluorescent zwitterion, and the increase in the fluorescence intensity at $H_0 < -3$ is due to the decrease in the solvent relaxation rate of the monocation. The behaviour of the 500 nm fluorescence band of the keto form in the pH range 1–9 can be explained in the same manner as discussed for the neutral species (see below). The blue shift observed at H_0 −10 is due to the formation of a dication by protonation of the hydroxyl or methoxyl group in agreement with earlier results [39, 40].

3.3.2.2. 2',3'-DHPBT and 2'-H-3'-MPBT. The compound 2',3'-DHPBT is non-fluorescent in neutral and acidic solutions; in contrast, in slightly alkaline or acidic medium 2'-H-3'-MPBT exhibits a weak and strongly Stokes-shifted band at approximately 520 nm, which can be assigned to the keto form, as explained earlier. Because 2',3'-DHPBT decomposes at pH > 10.5, its emission characteristics could not be studied beyond this pH value. However, both molecules give a very strongly red-shifted fluorescence band at 500 nm at pH 10 and a 490 nm band at H_0 −9; these can be assigned to the monoanion and monocation respectively. The appearance of the monocation emission band at H_0 −3 for 2'-H-3'-MPBT and at H_0 −6 for 2',3'-DHPBT can be explained in a similar manner as discussed for 2',4'-DHPBT. The large Stokes shifts of the fluorescence spectra of the monoanion and monocation are due to greater solvent relaxation in the S_1 state. Similar results are also observed for 3'-HPBT [17], 2-(3'-hydroxyphenyl)benzoxazole [43] and 2-(3'-hydroxyphenyl)-benzimidazole [39]. Like the absorption spectra, the fluorescence spectra are blue shifted in H_0 −10.4 solution indicating protonation of the OH or OCH_3 group.

3.3.2.3. 2',5'-DHPBT. The fluorescence characteristics of this molecule in the pH range 3–10 are different from those of 2',4'-DHPBT, in that only two fluorescence bands are observed in near-neutral solution. The 500 nm band is assigned to the monoanion and the 440 nm band to the neutral, non-intramolecular-hydrogen-bonded structure (as stated earlier). The former assignment is based on the observation that the fluorescence intensity of this band increases at the expense of the 440 nm band with increasing pH and the fluorescence excitation spectrum recorded at 500 nm at pH 10 resembles the absorption spectrum of the monoanion. The spectral behaviour of 2',5'-DHPBT below pH 3 is similar to that of the other molecules and can be explained in a similar manner.

3.4. Acidity constants

The pK_a and pK_a^* values of the various prototropic reactions of the molecules are given in Table 3. The pK_a values of the neutral–monoanion equilibria of all five molecules are almost the same. This supports our earlier conclusion that the first deprotonation occurs from the OH group at the 2' position. This value is lower than that observed for 2'-HPBT (10.3). This is because 2'-HPBT was studied in 50% dioxane–water (v/v) solution. Since the dielectric constant of pure water or 20% methanol–water is greater than that of 50% dioxane–water, the formation of the monoanion will be stabilized in the more polar solutions. This will lead to a higher dissociation constant or a lower pK_a value. Our results are consistent with this fact. The pK_a value for the monoanion–dianion equilibrium of 2',4'-DHPBT is, as expected, nearly equal to that of normal phenols. This is because the negative charge, due to the first deprotonation, is meta to the hydroxyl group at the 4' position and will not significantly affect the charge density on the hydroxyl oxygen at the 4' position. The dissociation constants ($pK_a \approx 1.3$) for the monocation–neutral equilibria of all the molecules, except 2',4'-DHPBT and 2'-H-4'-MPBT (1.8), are equal. This indicates

TABLE 3

pK_a and pK_a^* values of different prototropic reactions of 2′,3′-, 2′,4′- and 2′,5′-DHPBT, 2′-H-3′-MPBT and 2′-H-4′-MPBT

Compound/equilibrium	pK_a	pK_a^*	
		FC[a]	FC[b]
2′,3′-DHPBT			
Monocation ⇌ neutral	1.2	6.8	–
Neutral ⇌ monoanion	8.6	1.4	0.6
Monoanion ⇌ dianion			
2′-H-3′-MPBT			
Monocation ⇌ neutral	1.3	5.3	–
Neutral ⇌ monoanion	8.7	0.04	−0.5
2′,4′-DHPBT			
Monoanion ⇌ neutral	1.85	8.2	–
Neutral ⇌ monoanion	8.4	3.0	3.6
Monoanion ⇌ dianion	10.5	7.8	–
2′-H-4′-MPBT			
Monocation ⇌ neutral	1.8	8.5	–
Neutral ⇌ monoanion	8.6	2.1	2.3
2′,5′-DHPBT			
Monocation ⇌ neutral	1.3	7.5	–
Neutral ⇌ monoanion	9.0		5.5

[a]Calculated from absorption maxima.
[b]Calculated from fluorescence maxima.

that the OH or OCH_3 groups at the 3′ or 5′ positions have no effect on the basicity of the tertiary nitrogen atom and will not affect the charge density at this basic centre. In contrast, the OH or OCH_3 groups have greater conjugation with the benzothiazole moiety in 2′,4′-DHPBT or 2′-H-4′-MPBT which increases the charge density on the nitrogen atom.

The prototropic reactions of these molecules in the S_1 state are more complex than those in the ground state and thus their analysis poses more problems as observed in the case of 2′-HPBT [15]. For example, as mentioned earlier, the monoanion is present at pH ≈ 10 in all the molecules, but as the pH is lowered, two more species start to appear (one neutral and one keto form) and the presence of all three species continues until they all disappear at pH ≈ 0. Because of the simultaneous presence of all three species, it is difficult to draw fluorometric titration curves. In the case of 2′,5′-DHPBT, where there are only two species (neutral and monoanion) in the pH range 0–10, we attempted to plot the fluorometric titration curves. However, it was not possible because of the overlap of the fluorescence spectra of the monoanion and neutral species (the fluorescence intensity of the neutral species is variable over the entire pH range). The relative intensity of the monoanion *vs.* the pH is plotted in Fig. 4. The plot is a stretched sigmoidal curve, giving ground state (8.5) and excited state (1.6) pK_a values. Further kinetic analysis could not be carried out because of the inaccuracy of these curves. However, it is certain that the lifetimes of these species are comparable with the reciprocal rates of protonation and deprotonation.

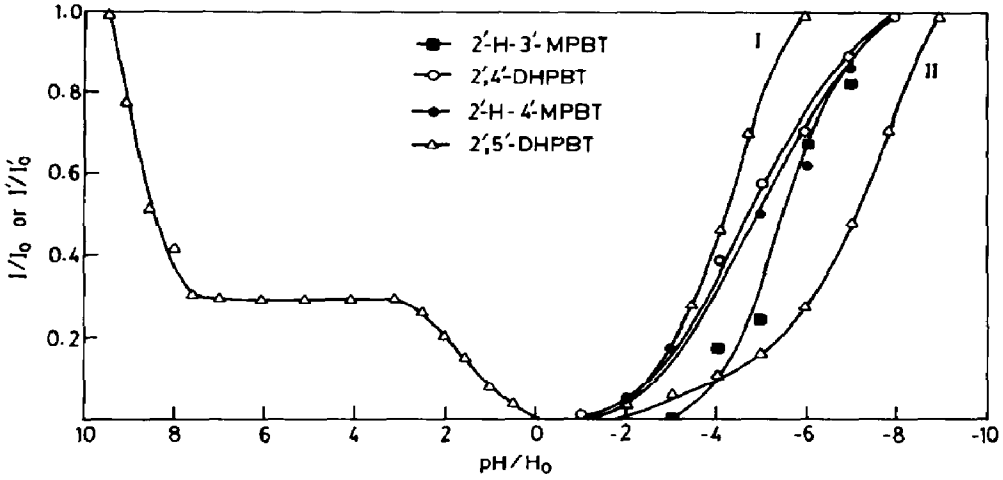
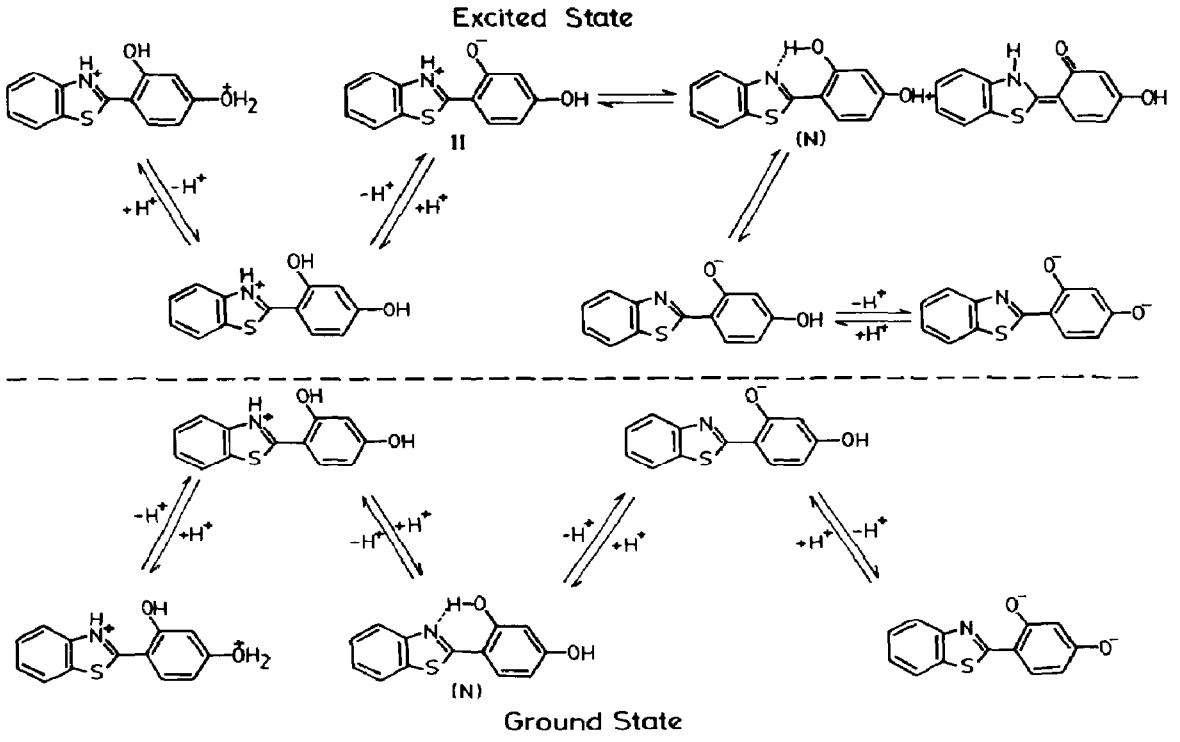


Fig. 4. Plot of I_0/I *vs.* pH/H_0.

The assignment of the long-wavelength band (approximately 500 nm) of 2',3' and 2',4'-DHPBT and 2'-H-3'- and 2'-H-4'-MPBT to the keto form is based on the following observations. As stated earlier, no correlation is observed between the decrease in the fluorescence intensity of the neutral or keto form and the increase in the fluorescence intensity of the monocation. This may either be due to proton-induced fluorescence quenching of the neutral species or to the formation of a non-fluorescent species at the expense of the neutral form. The latter is preferred because the results of Potter and Brown [15] on 2-(2'-methoxyphenyl)benzothiazole (2'-MBT) have established that the depletion of the neutral species and the formation of the monocation are simultaneous processes. Furthermore, proton-induced fluorescence quenching should have been observed for both hydroxy-substituted and methoxy-substituted derivatives, as demonstrated by Shizuka and Tobita [44] for the case of naphthols and methoxynaphthalenes. Lastly, if we assume that proton-induced fluorescence quenching of the neutral species is observed, the pK_a* values calculated from the formation curves of the monocations (Fig. 4) would indicate that the tertiary nitrogen atom becomes less basic in the S_1 state, which is not possible. Similar results have been observed for 2'-HPBT, with the difference that both the keto and zwitterion forms are fluorescent. Thus it is concluded that a non-fluorescent zwitterion is formed as an intermediate between the neutral species and the monocation. The fluorometric titration curves (Fig. 4) for the monocations are relatively poor due to solvent interaction and thus pose a problem for the calculation of I_0. This is illustrated by the fluorometric titration curve of the monocation of 2',5'-DHPBT (II). After correction for solvent interaction in the S_0 state, a satisfactory fluorometric titration curve is obtained (I) (Fig. 4). The pK_a* values for the monocation–zwitterion equilibria, obtained in this way from fluorometric titration curves, are expected to be accurate to within +1 pK_a unit.

Prototropic reactions occurring in the S_0 and S_1 states are given in Scheme 1. The Förster cycle method, using absorption and fluorescence data to calculate pK_a*, can only be applied to neutral–monoanion equilibria. The values are given in Table 3, indicating that the OH group becomes more acidic in the S_1 state, as expected. Other pK_a* values cannot be determined as the acid–base equilibria in the S_0 and S_1 states are different.



Scheme 1.

TABLE 4

Calculated transition wavelengths (λ (nm)), oscillator strengths (f), transition polarizations (α^0) and π-electron densities at the basic centre of 2′,3′-, 2′,4′-and 2′,5′-DHPBT

Molecule	λ (nm)	f	α^0	Atom	π-Electron density	
					S_0	S_1
2′,3′-DHPBT	345	0.8474	190	S1	1.4834	1.507
	310	0.2561	136	N3	1.6909	1.730
	297	0.2323	261	O16	1.916	1.879
	245	0.4756	162	O17	1.9343	1.931
	236	0.083	113			
2′,4′-DHPBT	349	0.9911	186	S1	1.489	1.500
	294	0.2026	260	N3	1.683	1.729
	290	0.069	131	O16	1.911	1.881
	245	0.4894	294	O17	1.926	1.920
	240	0.1288	342			
2′,5′-DHPBT	356	0.8999	191	S1	1.4849	1.514
	304	0.1934	137	N3	1.680	1.727
	298	0.1893	255	O16	1.9141	1.864
	246	0.6048	313	O17	1.9357	1.907
	240	0.0374	354			

3.5. Molecular orbital (MO) calculations

The results of the MO calculations for the enol form (with IHB) of 2′,3′-, 2′,4′- and 2′,5′-DHPBT are given in Table 4. The calculated wavelengths of the band maxima are in good agreement with the corresponding experimental values in cyclohexane. The data clearly indicate that the two long-wavelength transitions are polarized along the long axis of the molecules. Due to the mixing of the bands with each other, it is very difficult to calculate experimentally the oscillator strengths of the transitions; therefore the calculated values do not compare well with experiment. However, the values agree qualitatively with the intensity (log ϵ) of the absorption bands . The charge density data indicate that the π-electron density on the oxygen atom (O16) of the 2′-OH group is lower than that on the oxygen atom (O17) of the other hydroxyl group present in the molecules. This suggests that the hydrogen atom of the 2′-OH group is more acidic than that of the other OH group. Similar results have been observed experimentally (*i.e.* the first deprotonation in all the five molecules takes place from the 2′-OH group). It should also be noted that the π-electron density on the tertiary nitrogen atom (N3) and O16 atom increases and decreases respectively on excitation to the S_1 state, a situation which favours the formation of strong IHB between the nitrogen atom and the hydroxylic proton in the S_1 state and thus facilitates proton transfer to yield the keto form.

4. Conclusions

The following conclusions can be drawn from this study.

(i) The long-wavelength fluorescence band in all the molecules, except 2′,5′-DHPBT, is due to the keto form and the normal Stokes-shifted band to the enol form. The intensity of the former band decreases in polar/protic solvents.

(ii) The first deprotonation always occurs from the 2′-OH group and the second from either the 3′ or 4′ position. 2′,5′-DHPBT is unstable at pH > 10.5.

(iii) The pK_a value of the neutral–monoanion equilibrium is not affected by the presence of the second hydroxyl group.

(iv) The presence of the OH group at the 4′ position shifts the monocation–neutral equilibrium to a higher value.

(v) Accurate fluorometric titration curves could not be drawn either because more than two species were present simultaneously or the corrections could not be applied because of overlap of the fluorescence spectra.

(vi) The zwitterion produced in the pH/H_0 range of 2 to −2 is non-fluorescent.

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