PROTON TRANSFER OF 2-(2′-HYDROXYPHENYL)BENZOXAZOLE IN THE EXCITED SINGLET STATE

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(Received March 26, 1985)

Summary

The solvent and pH dependence of the absorption and fluorescence of 2-(2′-hydroxyphenyl)benzoxazole was studied. Four different species were observed in both ground and excited states: the anion, the neutral molecule with intramolecular hydrogen bonding, the monocation and the dication. The pK_a and pK_a^* were calculated by absorptiometric and fluorometric titrations respectively.

1. Introduction

Proton transfer plays an important role in many chemical and biochemical phenomena. Having two heteroatoms and one hydroxy group, 2-(2′-hydroxyphenyl)benzoxazole (HPBX) is a compound of chemical importance which acts as a multisite proton acceptor as well as a proton donor, in addition to forming a strong intramolecular hydrogen bond [1]. Betin *et al.* [2] reported on the excited state spectra of HPBX. The occurrence of an excited state proton transfer from the hydroxyl group to the heteroatom of HPBX is also confirmed in further studies [2 - 5]. However, no attempt has been made so far to study the acid–base properties of HPBX. In continuation of our recent studies on proton transfer reactions in the excited state of multifunctional compounds [6 - 9], we now report the solvent and pH dependence of the absorption and fluorescence spectra of HPBX and the acidity constants of the different prototropic equilibria of HPBX in aqueous solution.

2. Experimental details

HPBX was obtained from Aldrich and purified by repeated recrystallization from methanol. Its purity was established by the presence of the same fluorescence maxima when excited at different wavelengths. Solvents were purified and solutions of known H_0, pH and H_- were prepared as we have reported previously [9].

0047-2670/86/$3.50

Concentrations of 5×10^{-5} M were used for the absorption spectra in different solvents and the spectra were recorded using a Shimadzu UV-190 spectrophotometer, with a model U-135 recorder attached. The fluorescence spectra were recorded using a scanning spectrofluorometer fabricated in our laboratory [10], by exciting the solutions (concentrations of about 10^{-6} M) at 334 nm. The quantum yields in the various solvents were calculated using quinine sulphate as a standard.

Owing to the low solubility of HPBX in water, a 5×10^{-3} M stock solution in 80vol.%methanol–20vol.%water was prepared for the pH study. 0.2 ml of the solution was diluted each time to 10 ml using different H_0/pH/H_- solutions for absorptiometric titrations. For fluorometric titrations, the relative fluorescence intensities at the analytical wavelength as a function of pH were calculated by exciting the respective species at their isosbestic wavelength.

3. Results and discussion

3.1. Effect of solvents on absorption spectra

The wavelengths λ_{max}^{ab} of maximum absorbance and the molar absorptivities ϵ in different solvents are compiled in Table 1. The results indicate that increasing the solvent polarity causes a blue shift of the 320 nm absorp-

TABLE 1

Absorption maxima λ_{max}^{ab} and molar absorptivity ϵ of HPBX in various solvents

Solvent or species	λ_{max}^{ab} (log ϵ)									
Cyclohexane	334 (4.13)	320.2 (4.18)	292.8 (4.19)	285 (4.14)	280 (4.14)	273.4 (4.09)	261 (4.01)	238 (3.80)	227.6 (4.02)	216.4 (4.16)
Ether	331.6 (4.27)	391 (4.32)	291.6 (4.37)	283 (4.27)	278.4 (4.26)	272.2 (4.21)	260.6 (4.16)	237.6 (3.93)	227.4 (4.13)	
Acetonitrile	330 (4.00)	318.2 (4.05)	291.8 (4.07)	283 (3.97)	279 (3.97)	273.2 (3.92)	260.6 (3.86)	238 (3.65)	227.6 (3.82)	212.2 (4.12)
Methanol	330 (4.10)	318 (4.15)	291.4 (4.17)	282.6 (4.10)	278.4 (4.10)	273 (4.06)	260.6 (4.00)	238 (3.74)	227.6 (3.95)	214.4 (4.11)
Ethanol	330 (4.14)	318 (4.18)	291.6 (4.19)	282.8 (4.15)	278.6 (4.15)	273.2 (4.11)	260.4 (4.06)	238 (3.89)		218.6 (4.16)
Neutral (pH 2)	327.6 (3.22)	314.2 (3.79)	291.4 (3.36)			273 (3.41)	262 (3.43)			204 (3.86)
Anion (pH 13)	351 (4.12)		294.6 (3.98)	284 (4.10)						220 (4.39)
Cation (H_0 −6)	352 (4.23)	338 (4.27)	309 (4.29)	294.6 (4.28)			248.2 (3.95)	242.4 (3.83)	223.6 (3.90)	204.6 (4.34)

λ_{max}^{ab} is in nanometres; ϵ is in decimetres cubed per mole per centimetre.

tion band and a loss in the vibronic structure of HPBX. This loss is most predominant in the highly polar solvent water. The results on the absorption spectra from the present study are in good agreement with those reported in the literature [2 - 5, 11, 12]. The 375 nm absorption band appears in protic solvents as reported by Cohen and Flavian [12] as well as in ethanol and water. This band may be due to the open structure of HPBX, which can be stabilized by protic solvents such as alcohols, and this behaviour is suggested by its non-existence in aprotic solvents such as hexane and acetonitrile.

3.2. Effect of solvents on fluorescence spectra

The fluorescence maxima and the quantum yields for HPBX in different solvents are given in Table 2. The emission spectra with a long wavelength fluorescence band are slightly red shifted in going from the non-polar solvent cyclohexane to the polar solvent water. This band arises from the excited state phototautomer of HPBX [13]. The second emission band with short wavelength fluorescence maxima is attributed to a different hydrogen-bonded conformer of HPBX which does not give rise to proton transfer, as reported by Woolfe *et al.* [5] and Itoh and Fujimaza [13], and is blue shifted in going from non-polar to polar solvents. Furthermore, its stabilization is suggested by the relatively high quantum yields in protic solvents. In water, however, the hydrogen-bonded structure of HPBX is found to be more widely established than the open-structured HPBX.

TABLE 2

Fluorescence maxima λ_{max}^{fl} and quantum yields ϕ_f of HPBX in various solvents

Solvent or species	λ_{max}^{fl} (ϕ_f)	
Cyclohexane	502 (0.016)	365 (0.0017)
Ether	502 (0.010)	365 (0.0066)
Acetonitrile	504 (0.007)	364 (0.0021)
Methanol	504 (0.007)	363 (0.0116)
Ethanol	504 (0.009)	363 (0.0106)
Neutral (pH 2)	504 (0.065)	361 (0.0028)
Anion (pH 13)		440 (0.0441)
Cation ($H_0 - 6$)		398 (0.0402)

λ is in nanometres.

3.3. Effect of pH *on the absorption spectra*

The absorption spectra of HPBX and its different forms in aqueous solution as a function of pH are shown in Fig. 1. The spectra in neutral aqueous solution resemble those in moderately polar solvents and thus it was concluded that the spectra between pH 0 and pH 10 correspond to the neutral HPBX. Although both the heteroatoms are potential hydrogen-bond acceptors in HPBX, the involvement of the nitrogen atom in the intramolecular hydrogen bond is generally accepted [1, 5].

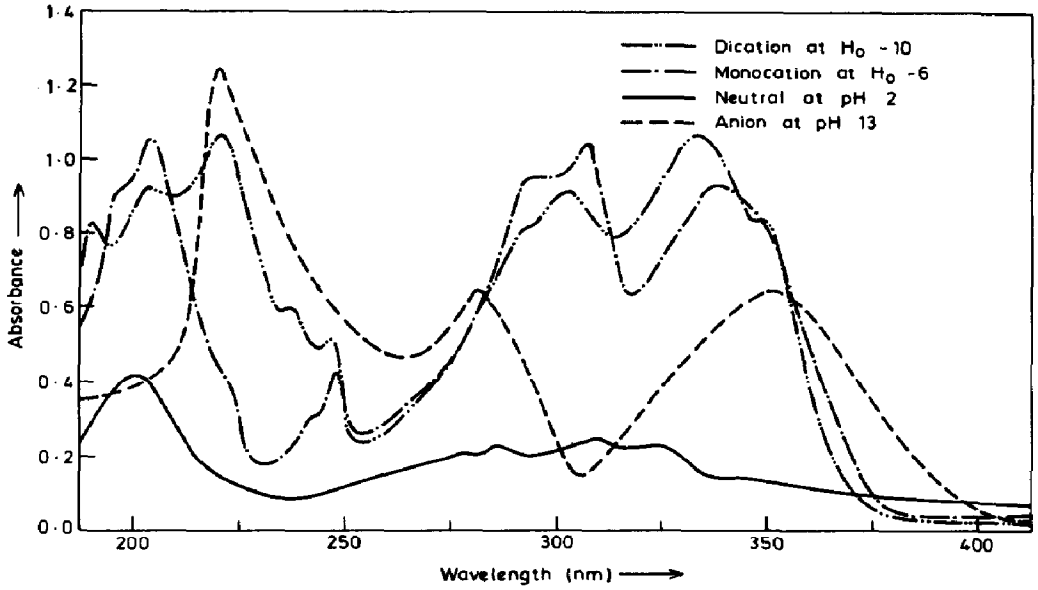

Fig. 1. Absorption spectra of different species of HPBX at 298 K.

The appearance of the 351 nm band at a pH above 10 is associated with a large red shift and is attributed to the dissociation of the hydroxy group leading to the formation of $HPBX^-$. The pK_a for this dissociation is found to be 10.4.

The pK_a for such a dissociation in phenol is 10 [14] and decreases with the introduction of electron withdrawing groups or the extension of the ring system, *e.g.* giving a pK_a of 9.1 for 9-phenanthrol [15]. $HPBX^-$ is expected to be highly basic, even if we assume that phenol is the basic unit in HPBX, owing to the involvement of the hydroxy group in intramolecular hydrogen bonding.

In dilute acid solutions the positions of the absorption maxima are observed to transform slowly to 338 nm. This change is believed to be due to protonation of the nitrogen atom and the pK_a is found to be -0.3. This value of pK_a for the protonation of the tertiary nitrogen atom is quite small compared with that of benzimidazole (5.53 [16]) and indazole (1.22 [16]). This could be due to the presence of the more electronegative oxygen atom in the ring and the intramolecular hydrogen bonding.

Very little change is noticed in the absorption spectrum between $H_0 - 1$ and $H_0 - 8$. At $H_0 - 10$, however, a different absorption spectrum having absorption maxima at 334, 305, 247, 241, 233 and 205 nm, is observed. This might be due to dication formation, with a second protonation either on the phenolic oxygen or on the ring oxygen. Protonation at the oxygen atom of the ring can be neglected on the grounds that protonation at this site would lead to a red shift as a result of the increase in the electron density on excitation, if the transition is $\pi \rightarrow \pi^*$. A second protonation on the same ring may be a little more difficult. The pK_a for the protonation at

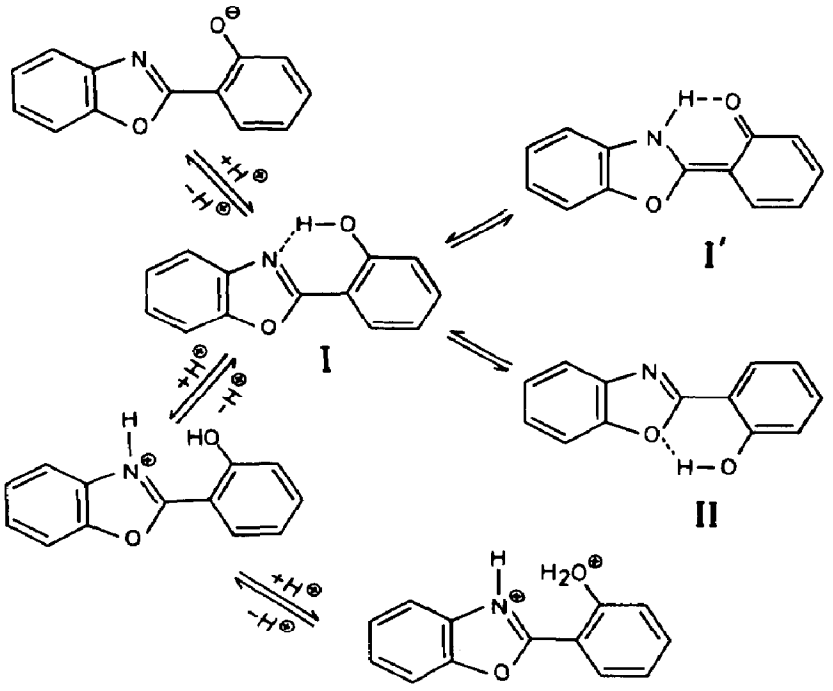

Fig. 2. Acid–base equilibria scheme for HPBX.

the carbon centre of benzene is reported to be −10.2 [14], but is associated with a red shift in the spectrum. Thus the observed blue shift in the present system confirms that the dication is as indicated in Fig. 2, with the protonation on the phenolic oxygen. Similar behaviour has also been observed in the case of 2-hydroxybenzimidazole [17] and 2-hydroxycarbazole [18].

3.4. Effect of pH *on fluorescence spectra*

From the fluorescence spectra of HPBX in aqueous solution (Fig. 3), it can also be inferred that four species are present: the monoanion in the region H_- 16 to pH 11, the neutral open structure in the pH range 10 - 1, a monocation in the range pH 0 to H_0 −8 and a dication (fluorescence maxima at 360 nm and 377 nm) at H_0 −10. The assignment of the respective species according to their fluorescence maxima (Table 2) is also consistent, because deprotonation of the hydroxyl group and protonation at the tertiary nitrogen atom leads to a red shift, while protonation at the hydroxyl group leads to a blue shift, if $\pi \rightarrow \pi^*$ is the lowest energy transition [17, 18].

The fluorescence spectrum of the monocation, formed at pH 0, slowly shifts from 420 nm to 398 nm at H_0 −8, whereas a similar slow fluorescence shift is not observed for 2-(2′-methoxyphenyl)benzoxazole (MPBX). In the case of MPBX the monocation is formed at pH 1 and the fluorescence maximum at 403 nm is observed to be constant up to H_0 −7. The slow shift in the fluorescence maxima of $HPBX^+$ may be due to the presence of strong intramolecular hydrogen bonding which is absent in $MPBX^+$.

The pK_a^* for the respective equilibria have been calculated using the Förster cycle method [19], with both absorption and fluorescence data. These results together with those from the fluorometric titrations (Fig. 4) are listed in Table 3. The pK_a and pK_a^* for the formation of the dication cannot be calculated as the species appears only in the highest acid concentration used and the change is not complete. However, the ΔpK_a^* obtained using the Förster cycle method does indicate that $-OH_2^+$ is a stronger acid than $-NH_3^+$. Furthermore, the data of Table 3 show that the tertiary nitrogen atom is more basic and the hydroxy group is more acidic in the S_1 state than in the S_0 state. These observations are consistent with the behaviour of similar groups in other compounds [18, 20]. The difference between

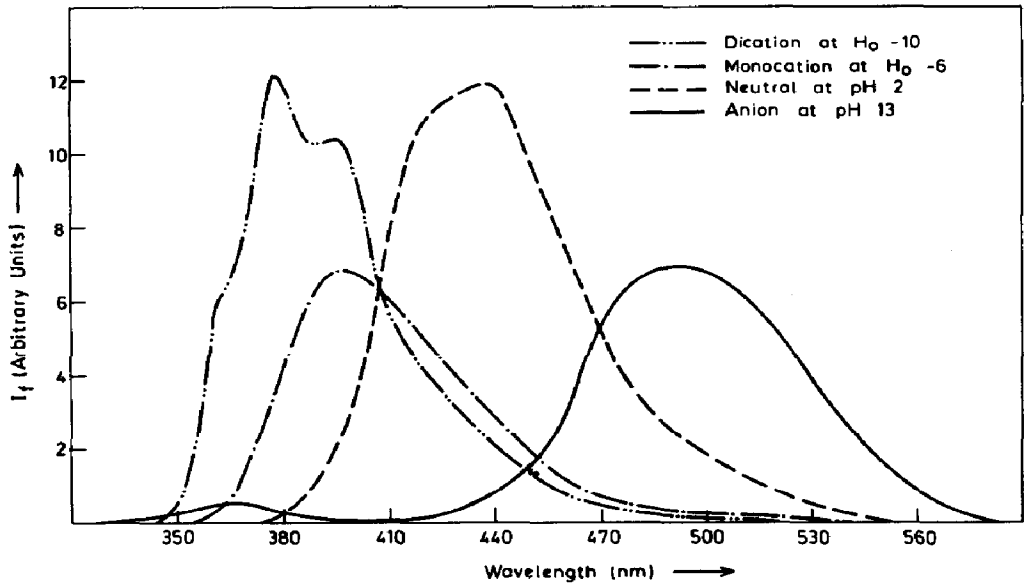

Fig. 3. Fluorescence spectra of different species of HPBX at 298 K.

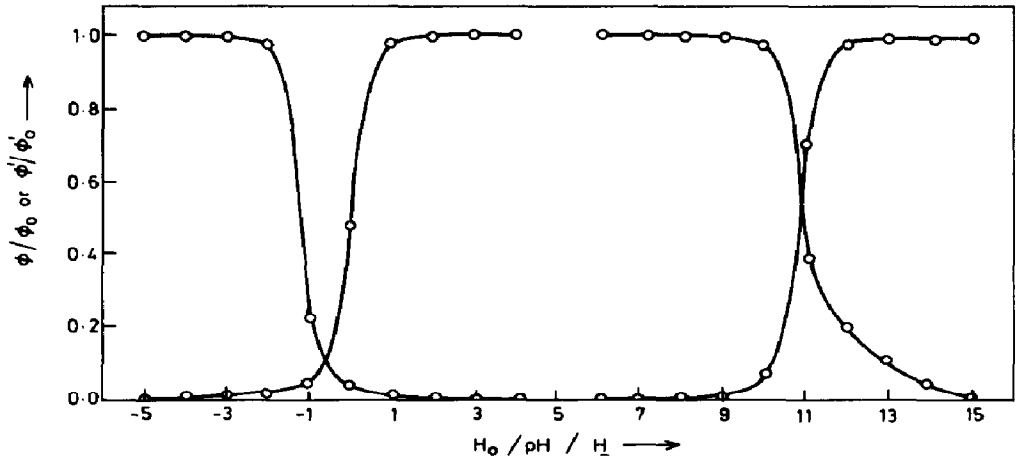

Fig. 4. Plot of the relative fluorescence intensities of HPBX *vs.* H_0/pH/H_-.

TABLE 3

pK_a and pK_a^* values

Equilibrium	pK_a [a]	*Förster cycle method*		pK_a^* [b]
		pK_a(ab)	pK_a^*(fl)	
Dication–cation	—	−3.21[c]	−2.94[c]	—
Cation–neutral	−0.3	5.24	1.67	0.05
Neutral–anion	10.4	−0.04	6.13	10.9

[a] Absorptiometric titration.
[b] Fluorometric titration.
[c] Only $\Delta pK_a^* = pK_a^* - pK_a$ are indicated.

the pK_a^* obtained from absorption and fluorescence data could be due to the difference in the structure and solvent relaxation in the two states and to using the band maxima instead of the 0–0 band. The non-correspondence in the fluorometric titration curves of monocation–neutral species (Fig. 4) does suggest that this equilibrium is not a pure two-component (acid–base) reaction and this can be attributed to the presence of an intramolecular hydrogen-bonded structure, as discussed above. The pK_a^* for this equilibrium is calculated from the decay curve of the neutral species.

Acknowledgment

We are grateful to the Department of Science and Technology, New Delhi, for their financial assistance to the project entitled "Proton Transfer Reactions in the Excited State".

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