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Photophysical Properties of 2,2′- and 4,4′-Biphenyldiols

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The photophysical properties of 2,2′- and 4,4′-biphenyldiols were investigated in aqueous and various organic solvents using optical absorption, steady-state and time-resolved fluorescence measurements. The investigated properties were correlated with the prototropic equilibria between the neutral, monoanionic and dianionic forms of the biphenyldiols. The monoanionic form of 2,2′-biphenyldiol is found to be exceptionally stable and shows interesting solvatochromism in polar protic and aprotic solvents. In solvents having appreciable proton-accepting power, 2,2′-biphenyldiol undergoes deprotonation, causing the coexistence of both the neutral and monoanionic forms in solutions. In presence of a strong proton acceptor, e.g. triethylamine, 2,2′-biphenyldiol undergoes complete deprotonation in a polar solvent like acetonitrile. In a nonpolar solvent, like cyclohexane, however, 2,2′-biphenyldiol forms ground-state intermolecularly hydrogen bonded complex with triethylamine. The photophysical properties of 2,2′-biphenyldiol have been found to be drastically different from those of 4,4′-biphenyldiol. The differences are explained on the basis of the presence and absence of intramolecular hydrogen bonding in the two compounds.

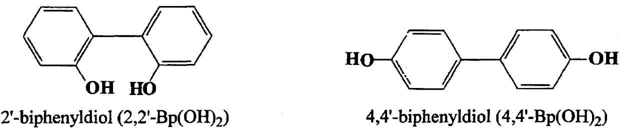
The photophysical properties of molecules having more than one functional group (substituents) attached to the aromatic rings have been of great research interest for many years.[1—15] In a number of cases it has been observed that the solvatochromic as well as other photophysical properties of molecules having two functional groups are often quite different from those observed for similar basic chromophoric structures with one functional group.[6,15] Thus, for 4,4′-biphenyldiamine and 4,4′-oxydianiline, it is seen that the solvatochromic shifts in the fluorescence spectra are much less compared to those observed for the mono amino derivatives.[3,12] Studies on the photophysical characteristics of molecules having more than one substituents are thus very important for understanding the nature of the intramolecular interactions as well as the intermolecular interactions between the solute and the solvent molecules.

Dihydroxy derivatives of aromatic hydrocarbons are simple model compounds for more complex biomolecules, like dityrosine and calmodulin.[16] Such hydroxy derivatives often function as antioxidants in food stuffs, oils and oil additives.[17,18] These compounds exhibit interesting behavior in their properties due to the possibilities of both intra and intermolecular hydrogen bondings.[19—24] Biphenyldiols are simple dihydroxy compounds which display such hydrogen-bonding effects, and consequently their optical absorption and fluorescence characteristics are expected to display a large dependence on the nature of the solvents.[12—15,19] Though some aspects of the solvatochromic and prototropic effects on the optical absorption and fluorescence spectra of the biphenyldiols have been reported in the literature,[13,14,19] a detailed investigation on the photophysical properties is lacking. In the present work we investigated in detail the solvatochromic and photophysical behaviour of 2,2′- and 4,4′-biphenyldiols (Chart 1) in aqueous solutions at different pHs as well as in a number of organic solvents, both protic and aprotic in nature. The results were correlated in terms of the possible intra and intermolecular hydrogen bondings in these molecules. The chemical structures of the biphenyldiols investigated in the present work are given below.

Materials and Methods

Both 2,2′- and 4,4′-biphenyldiols were obtained from Aldrich and were purified by repeated crystallization from cyclohexane. Nanopure water (from Barnstead System, resistivity 18.3 MΩ cm) was used to prepare aqueous solutions of the compounds. All of the organic solvents used were of spectroscopic grade from either Spectrochem, India or S. D. Fine Chemicals, India. Triethylamine was obtained from Glaxo India Ltd. and was purified by distillation just before use.

Absorption spectra were recorded using a Shimadzu model 160-A UV-vis spectrophotometer. Fluorescence spectra were recorded using a Hitachi model 4010 spectrofluorimeter. All fluorescence spectra were recorded using corrections for the wavelength-dependent instrument responses. The fluorescence quantum yields (Φ_f) were determined by comparing the integrated fluorescence spectra of the sample with that of a standard (naphthalene in cyclohexane,[1] $\Phi_f = 0.19$), while keeping the excitation wavelength, slit widths and absorbances at the excitation wavelength equal. Fluorescence lifetime measurements were carried out using a time-correlated single-photon counting spectrometer (Edinburgh Instruments, U. K., model 199). A hydrogen-filled coaxial flash lamp having ca. 1 ns



2,2′-biphenyldiol (2,2′-Bp(OH)$_2$)　　4,4′-biphenyldiol (4,4′-Bp(OH)$_2$)

Chart 1.

pulse width (full width at half maximum) was used as the excitation source in this instrument. The fluorescence-decay curves were analyzed by a reconvolution procedure[25,26] using a proper instrument response function, obtained by substituting the sample cell with a light scatterer. All of the decay curves were fitted as a monoexponential function as

$$I(t) = B\exp(-t/\tau_f), \tag{1}$$

where τ_f is the fluorescence lifetime of the sample and B is the preexponential factor. The quality of the fit was judged from the reduced chi-square (χ_r^2) value and the distribution of the weighted residuals.[25,26] For all fits the χ_r^2 values were within 1 to 1.2.

Results and Discussion

Optical Absorption Studies in Aqueous Solutions. Depending on the pH of the solutions, both 2,2′- and 4,4′-Biphenyldiols ($Bp(OH)_2$) are expected to exhibit two acid-base equilibria (Eqs. 2 and 3) in aqueous solutions.

$$\underset{\text{(I)}}{Bp(OH)_2} \xrightleftharpoons{pK_a(1)} \underset{\text{(II)}}{Bp(OH)O^-} \tag{2}$$

$$\underset{\text{(II)}}{Bp(OH)O^-} \xrightleftharpoons{pK_a(2)} \underset{\text{(III)}}{Bp(O_2)^{2-}} \tag{3}$$

To investigate the above two prototropic equilibria, the ground-state optical absorption characteristics of 2,2′- and 4,4′-biphenyldiols were studied in aqueous solutions at different pHs. Typical absorption spectra thus obtained are shown in Figs. 1A and 1B for 2,2′-$Bp(OH)_2$ and 4,4′-$Bp(OH)_2$ respectively. It can be seen from Fig. 1A that at pH < 6, the spectra of 2,2′-$Bp(OH)_2$ display absorption maxima at ca. 278 nm. Upon increasing the pH of the solutions above 6, the absorbance at 278 nm peak gradually reduced with a concomitant development of a new peak at ca. 307 nm. A clear isosbestic point was also seen at ca. 285 nm in the pH range of 4 to 13. Upon making the solution strongly alkaline (ca. 7 mol dm^{-3} of KOH) the 307 nm peak underwent a small blue shift to appear at about 302 nm. The absorption peaks at 278 (pH < 5), 307 (pH = 9—13) and 302 nm (ca. 7 mol dm^{-3} of KOH) are assigned, respectively, to the neutral (I), monoanionic (II), and the dianionic (III) forms of 2,2′-$Bp(OH)_2$. Similarly for 4,4′-$Bp(OH)_2$ the absorption maxima at 263 (pH < 7), 285 (pH = 11 to 12) and 290 nm (ca. 7 mol dm^{-3} of KOH) (Fig. 1B), have been assigned to its neutral (I), monoanionic (II), and the dianionic (III) forms. The absorption bands with maxima at 278 and 263 nm respectively for 2,2′-$Bp(OH)_2$ and 4,4′-$Bp(OH)_2$ have been assigned to the ^1L_b transition.[27]

The dependence of the optical density (OD) at 310 and 288 nm as a function of the pH/basicity function (H_-) was studied for 2,2′-$Bp(OH)_2$ and 4,4′-$Bp(OH)_2$, and are shown in the insets of Figs. 1A and 1B respectively. These results show two inflection points for each of the molecules, from which the p$K_a(1)$ and p$K_a(2)$ values have been estimated to be 7.5 and 14.7 for 2,2′-$Bp(OH)_2$ and 9.4 and 14.1 for 4,4′-$Bp(OH)_2$ respectively. We used Yagils' basicity scale[28] (i.e. the H_- scale) for highly alkaline solutions (i.e. pH > 13).

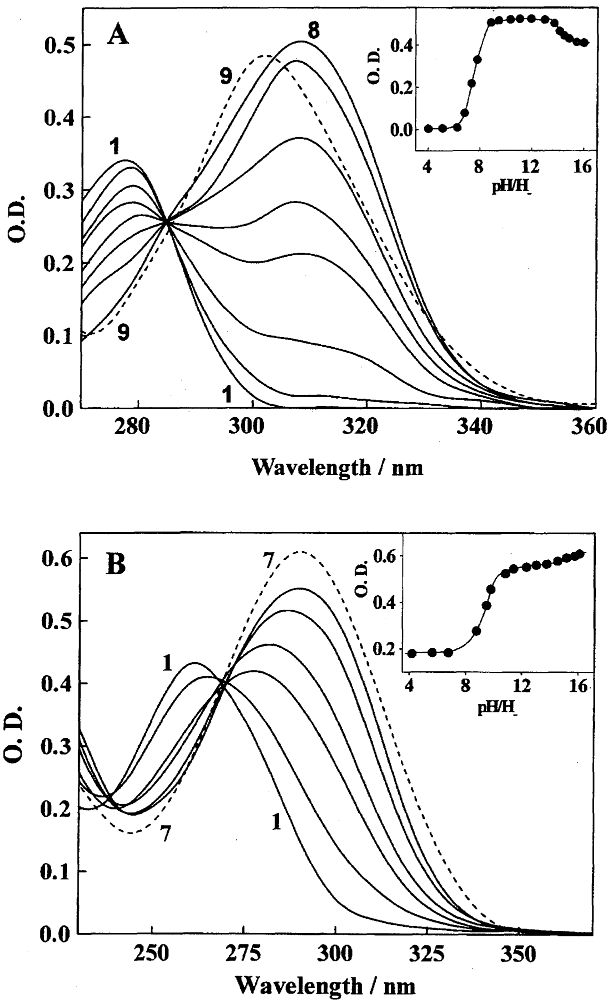
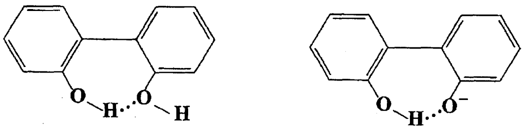


Fig. 1. Absorption spectra of (A) 2,2′-biphenyldiol and (B) 4,4′-biphenyldiol as obtained in aqueous solutions at different pHs. In (A), the pH/H_- are (1) 4.0, (2) 6.1, (3) 6.9, (4) 7.4, (5) 7.65, (6) 7.97, (7) 8.8, (8) 11.59, and (9) 16.0, and in (B) the pH/H_- are (1) 6.0, (2) 8.77, (3) 9.47, (4) 9.78, (5) 10.57, (6) 11.67, and (7) 16.0. Inset: Changes in the optical density (OD) with pH, (A) for 2,2′-biphenyldiol observed at 310 nm and (B) for 4,4′-biphenyldiol observed at 288 nm.

It is interesting to compare the p$K_a(1)$ values of the two biphenyldiols with the pK_a value of phenol[29] (pK_a = 10). It is evident that 2,2′-$Bp(OH)_2$ is a much stronger acid than phenol, while 4,4′-$Bp(OH)_2$ is only a slightly better acid than phenol. The stronger acidity of 2,2′-$Bp(OH)_2$ compared to phenol and 4,4′-$Bp(OH)_2$ can be attributed to the presence of intramolecular hydrogen bonding in the former compound, which is absent in the latter. The intramolecular hydrogen bonding in 2,2′-$Bp(OH)_2$ (Chart 2 structure IV), makes the protic hydrogen of the free OH group more labile for deprotonation in comparison to that of the OH groups of phenol and 4,4′-$Bp(OH)_2$.

The p$K_a(2)$ values of both 2,2′-$Bp(OH)_2$ and 4,4′-$Bp(OH)_2$ indicate that the release of the second proton is difficult and takes place only in highly basic solutions. Further, for the release of the second proton it is seen that the basicity of the



(IV) (V)

Chart 2.

solution required is higher for 2,2′-Bp(OH)$_2$ than for 4,4′-Bp(OH)$_2$. The higher pK_a(2) of 2,2′-Bp(OH)$_2$ in comparison to that of 4,4′-Bp(OH)$_2$ is also due to the presence of strong intramolecular hydrogen bonding in the monoanion (Chart 2 structure V) of 2,2′-Bp(OH)$_2$.

At this point it is interesting to discuss the possibility of the $\mathrm{OH}\cdots\pi$ type of hydrogen bonding (Chart 3 structure VI) for 2,2′-Bp(OH)$_2$, as suggested by many authors based on the infrared[19,30—32] and UV absorption[33] studies. Our results indicate that in water, structure IV dominates over structure VI. This is inferred from the fact that if structure VI predominates in water, the pK_a(1) of 2,2′-Bp(OH)$_2$ should have been higher than the pK_a of phenol and the pK_a(1) of 4,4′-Bp(OH)$_2$, because it will be more difficult to deprotonate this structure VI.

The electronically excited states (S_1) of the biphenyldiols are also expected to display two acid-base equilibria (Eqs. 4 and 5):

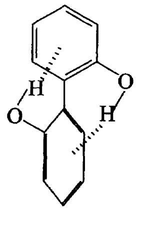
$$\underset{\text{(VII)}}{[\mathrm{Bp(OH)_2}]^*} \xrightleftharpoons{\mathrm{p}K_a^*(1)} \underset{\text{(VIII)}}{[\mathrm{Bp(OH)O^-}]^*} \tag{4}$$

$$\underset{\text{(VIII)}}{[\mathrm{Bp(OH)O^-}]^*} \xrightleftharpoons{\mathrm{p}K_a^*(2)} \underset{\text{(IX)}}{[\mathrm{Bp(O_2)^=}]^*} \tag{5}$$

The excited state (S_1) acidity constants, pK_a^*(1) and pK_a^*(2), can be estimated using the Förster cycle method,[1,29] which correlates the ground- and excited-state acidity constants (i.e. pK_a and pK_a^* respectively) as

$$\mathrm{p}K_a^* = \mathrm{p}K_a + \frac{hc\Delta\overline{\nu}}{2.303RT}, \tag{6}$$

where $\Delta\overline{\nu} = \overline{\nu}_{R^-} - \overline{\nu}_{RH}$, $\overline{\nu}_{R^-}$, and $\overline{\nu}_{RH}$ being the absorption maxima (in cm^{-1}) of the conjugate base (R$^-$) and acid (RH) forms respectively. The pK_a^*(1) and pK_a^*(2) of 2,2′-Bp(OH)$_2$ and 4,4′-Bp(OH)$_2$ have been estimated from the absorption maxima of neutral, mono and dianionic forms of the biphenyldiols using Eq. 6 as 0.37 and 15.8 for 2,2′-Bp(OH)$_2$ and 3.24 and 12.8 for 4,4′-Bp(OH)$_2$ at 298 K.

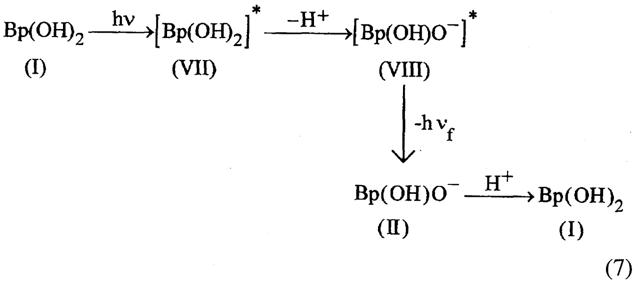


(VI)

Chart 3.

The excited-state pK_a^* value for phenol[29] is ca. 5.7. Compared to this, because the pK_a^*(1) value of 2,2′-Bp(OH)$_2$ is much lower, the compound behaves as a much stronger acid than phenol in the excited S_1 state. On the other hand, pK_a^*(1) of 4,4′-Bp(OH)$_2$ is not that much reduced compared to that of phenol, and thus behaves as a marginally stronger acid in the excited S_1 state. The pK_a^*(2) values of 2,2′-Bp(OH)$_2$ and 4,4′-Bp(OH)$_2$ indicate that the monoanion of the latter behaves as a stronger acid in the excited state than that of the former. Comparatively lower pK_a^*(1) and higher pK_a^*(2) of 2,2′-Bp(OH)$_2$ suggests the presence of strong intramolecular hydrogen bondings in the excited states of neutral and monoanionic forms of 2,2′-Bp(OH)$_2$ (c.f. Chart 2 structures IV and V). The fact that, pK_a^*(1) is much lower and pK_a^*(2) is much higher than the respective ground state pK_a(1) and pK_a(2) values of 2,2′-Bp(OH)$_2$ indicate that the intramolecular hydrogen bonding is much stronger in the excited state than in the ground state for both the neutral and the monoanionic forms of 2,2′-Bp(OH)$_2$.

Fluorescence Studies in Aqueous Solutions. The fluorescence spectra of both 2,2′-Bp(OH)$_2$ and 4,4′-Bp(OH)$_2$ have been studied as a function of the pH in aqueous solutions. Figure 2A shows the normalized fluorescence spectra for aqueous 2,2′-Bp(OH)$_2$ solutions at pH $\approx$ 0.8, 7, and 10, respectively. All three spectra are almost identical with the emission maxima at about 397 nm, and have been assigned to a singlet excited state (VIII) of the monoanionic form of 2,2′-biphenyldiol. Since the pK_a(1) value of 2,2′-Bp(OH)$_2$ is 7.5, in solutions having pH < 7 the neutral form (I) of the biphenyldiol is excited. The fact that for all these solutions the fluorescence arises from VIII clearly indicates that the excited state of the neutral form of 2,2′-Bp(OH)$_2$ quickly undergoes deprotonation in the pH range 1 to 7 (Eq. 7). Such deprotonation in the excited state is expected considering the pK_a^*(1) value (0.37) of 2,2′-Bp(OH)$_2$.



$$\begin{tikzcd}
\underset{\text{(I)}}{\mathrm{Bp(OH)_2}} \arrow[r, "h\nu"] & \underset{\text{(VII)}}{[\mathrm{Bp(OH)_2}]^*} \arrow[r, "-\mathrm{H}^+"] & \underset{\text{(VIII)}}{[\mathrm{Bp(OH)O^-}]^*} \arrow[d, "-h\nu_f"] & \\
 & & \underset{\text{(II)}}{\mathrm{Bp(OH)O^-}} \arrow[r, "\mathrm{H}^+"] & \underset{\text{(I)}}{\mathrm{Bp(OH)_2}}
\end{tikzcd} \tag{7}$$

In the pH range of ca. 8 to 14, 2,2′-Bp(OH)$_2$ exists as monoanion (II), which upon photoexcitation gives fluorescence emission. Since the pK_a^*(2) of 2,2′-Bp(OH)$_2$ is 15.8, the emission from the dianionic form of 2,2′-Bp(OH)$_2$ could be obtained only on making the solution highly alkaline (ca. 7 mol dm^{-3} KOH; $H_- = 16$). The fluorescence spectrum of the dianion, having an emission maximum at 402 nm, is shown in Fig. 2B.

The small hump at the high energy side of the emission spectrum at pH $\approx$ 0.8 is assigned to emission arising from

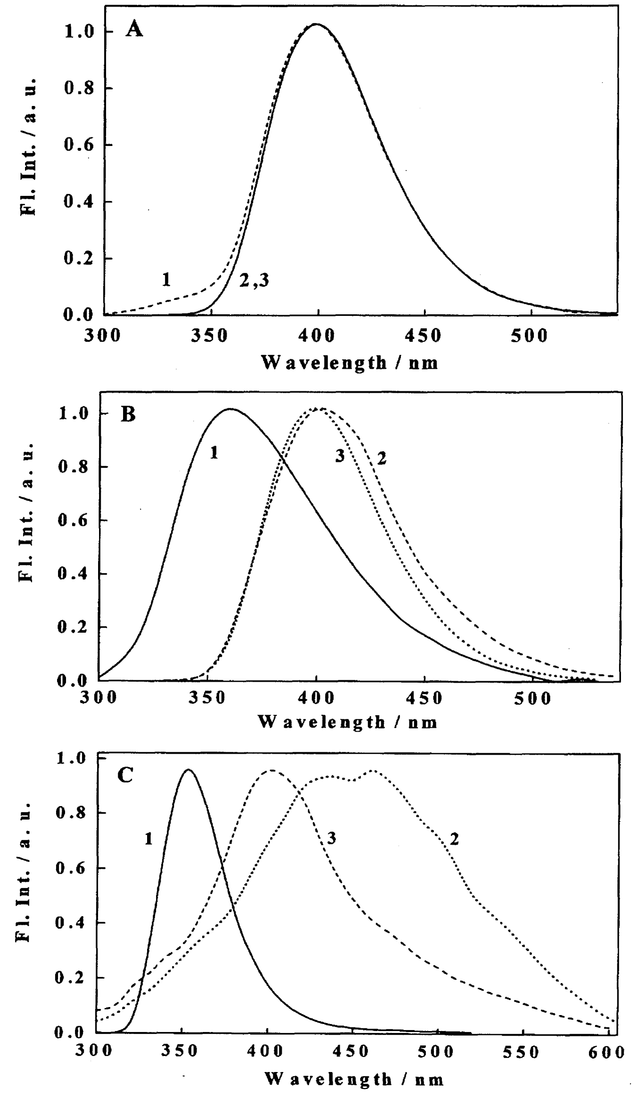


Fig. 2. (A) Normalized fluorescence spectra of 2,2′-biphenyldiol recorded at (1) pH = 0.8, (2) pH = 7 and (3) pH = 10. (B) Normalized fluorescence spectra of 2,2′-biphenyldiol recorded in presence of (1) ca. 2 mol dm^{-3} $HClO_4$, (2) ca. 7 mol dm^{-3} KOH, and (3) at pH = 10. (C) Normalized fluorescence spectra of 4,4′-biphenyldiol at (1) pH = 3, (2) pH = 10, and (3) in presence of ca. 7 mol dm^{-3} KOH.

small quantities of the excited neutral form (VII) of 2,2′-$Bp(OH)_2$, present at this pH. This was confirmed by making a solution of 2,2′-$Bp(OH)_2$ highly acidic (ca. 2 mol dm^{-3} $HClO_4$), when the 356 nm peak fully develops and the 397 nm peak disappears completely, as shown in Fig. 2B.

Figure 2C shows the normalized fluorescence spectra of 4,4′-$Bp(OH)_2$ in aqueous solutions at different pHs. For pH < 2, the fluorescence spectra with peak at ca. 354 nm corresponds to the emission from the neutral form (VII), while the emission peak at ca. 463 nm, obtained in the pH range of 6 to 11, is assigned to the monoanionic form (VIII). In highly alkaline solutions (7 mol dm^{-3} KOH; $H_- = 16$) the emission peak arising at ca. 418 nm is assigned to the excited dianionic form of 4,4′-$Bp(OH)_2$. The above results are consistent with expectations based on the ground and excited state pK_a values of 4,4′-$Bp(OH)_2$. The fact that the fluorescence emission arises from the excited monoanionic form of 4,4′-$Bp(OH)_2$ in the pH range of 6 to 8, where one excites the neutral form of the biphenyldiol, indicates that in this pH range the excited neutral form quickly deprotonates before giving off the emission (cf. Eq. 7).

Absorption and Fluorescence Studies in Organic Solvents. The absorption and fluorescence characteristics of both 2,2′-$Bp(OH)_2$ and 4,4′-$Bp(OH)_2$ have also been investigated in a number of organic solvents. Figure 3 shows the absorption spectra of 2,2′-$Bp(OH)_2$ in some representative solvents, displaying a main absorption peak at ca. 280 nm. In some solvents, e.g. in ethanol, a small shoulder is seen at ca. 310 nm. The 280 nm peak and 310 nm shoulder have been assigned to the neutral (I) and monoanionic (II) form of 2,2′-$Bp(OH)_2$, respectively, as in aqueous solutions. This has been confirmed by the fact that upon making the solutions slightly alkaline the main 280 nm peak disappears along with a concomitant increase in the intensity of the 310 nm peak. The absorption spectra of 2,2′-$Bp(OH)_2$ in organic solvents thus indicate that, depending on the proton-accepting power of the solvents, both the neutral (I) and the monoanionic (II) forms of the biphenyldiol coexist in the solutions (equilibrium reaction 8):

$$Bp(OH)_2 + S \rightleftharpoons Bp(OH)O^- + SH^+, \tag{8}$$

$$K = \frac{[Bp(OH)O^-][SH^+]}{[Bp(OH)_2][S]}, \tag{9}$$

where S is the solvent molecule. Since the donor number (DN) of a solvent is a measure of its proton-accepting power,[34,35] a correlation between the equilibrium constant (K) and the DN of the solvents was attempted, and is shown in the inset of Fig. 3. It can be seen from this figure that K increases with the DN of the solvents. It is evident that the contribution of the monoanionic form of 2,2′-$Bp(OH)_2$ increases as the proton-accepting power of the solvent is increased.

Table 1 lists the absorption and emission maxima for the

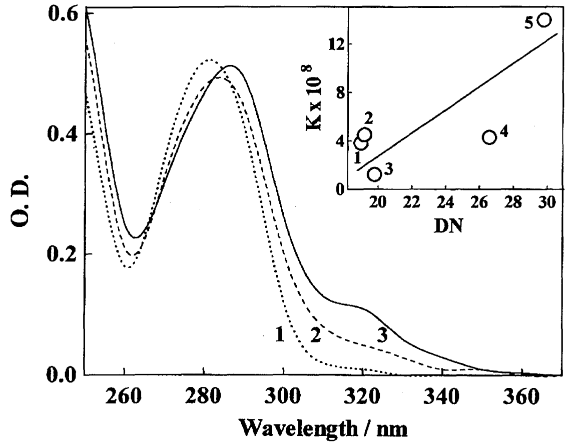


Fig. 3. Normalized absorption spectra of 2,2′-biphenyldiol in (1) acetonitrile, (2) methanol, and (3) ethanol. Inset: Variation of K (cf. Eq. 8) with donor number (DN) of the solvents. Solvents are (1) MeOH, (2) EtOH, (3) 2-PrOH, (4) DMF, and (5) DMSO.

neutral and monoanionic forms of 2,2′-Bp(OH)$_2$ in various solvents. To obtain the absorption and emission spectra only for the neutral or monoanionic forms, the solutions were made more acidic or alkaline, and the changes in the spectra were closely followed after each addition of acid or alkali. When conversion to a desired form was complete, the spectra were almost independent of any small changes in the acidic or alkaline conditions.

The values of the solvent polarity functions,[36,37] Δf, as defined by Eq. 10, are given in Table 1 for the various solvents used in this study.

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}, \qquad (10)$$

where ε and n are the dielectric constant and the refractive index of the solvent, respectively. It can be seen from Table 1 that the absorption and emission maxima of the neutral form (I) of 2,2′-Bp(OH)$_2$ do not show any systematic variation with Δf. An interesting solvatochromic behavior, however, is observed with the absorption and emission maxima of the monoanionic form (II) of 2,2′-Bp(OH)$_2$. Thus, the absorption maxima ($\overline{\nu}_{\rm abs}^{\rm max}$) of 2,2′-Bp(OH)O$^-$ was found to shift to higher energies as the Δf was increased. The most interesting observation with $\overline{\nu}_{\rm abs}^{\rm max}$ of 2,2′-Bp(OH)O$^-$ is that it shows two distinct correlations with Δf: one for the protic solvents and the other for the aprotic solvents, as shown in Fig. 4. It can be seen from this figure that in either series of the solvents (i.e. protic and aprotic), the $\overline{\nu}_{\rm abs}^{\rm max}$ shows a blue shift (ca. 110 cm^{-1}) as the Δf is changed from about 0.22 to about 0.31. In Fig. 4 the linear correlations for the $\overline{\nu}_{\rm abs}^{\rm max}$ vs. Δf variations for the aprotic solvents are given in parallel to the linear correlation obtained for the protic solvents, assuming that the slope for the $\overline{\nu}_{\rm abs}^{\rm max}$ vs. Δf plots could be similar for both series of the solvents. This is done because not many aprotic solvents could be used for the present compound, mostly due to the overlapping solvent absorption with that of the biphenyldiol. From the fact that $\overline{\nu}_{\rm abs}^{\rm max}$ shifts to higher energies upon increasing Δf, one may think that it is n–π* in nature. The large ε (ca. 7000 dm^3 mol^{-1} cm^{-1}) and $k_{\rm R}$ (ca. 7×10^7 s^{-1}) values for 2,2′-Bp(OH)O$^-$, however, indicate that this may not be the case for the monoanion under study. We believe that the transition in 2,2′-Bp(OH)O$^-$ is π–π* in nature and that the blue shift in the absorption maxima with Δf might be related to some extent due to a reduction in the coplanarity of the two phenyl rings of the molecule in its monoanionic form.

Table 1. Absorption and Fluorescence Spectral Characteristics of Neutral and Monoanionic Forms of 2,2′-Bp(OH)$_2$ in Different Solvents

		Neutral form[b)]		Monoanionic form[c)]	
Solvent[a)]	Δf	$\lambda_{\rm abs}^{\rm max}$ (nm)	$\lambda_{\rm em}^{\rm max}$ (nm)	$\lambda_{\rm abs}^{\rm max}$ (nm)	$\lambda_{\rm em}^{\rm max}$ (nm)
OcOH	0.226	287	350	315	399
HepOH	0.236	286	350	315	399
HexOH	0.244	287	350	314	400
PenOH	0.253	286	350	315	401
PrOH	0.275	286	355	312	396
2-PrOH	0.277	285	350	316	401
FM	0.282	283	350	316	405
EtOH	0.29	286	349	313	398
MeOH	0.305	283	349	311	398
H_2O	0.322	278	356	307	397
D_2O	0.322	278	356	307	397
DMSO	0.263	286	343	338	408
DMF	0.275	286	349	333	406
ACN	0.305	283	348	329	404

a) Abbreviations are: OcOH = 1-octanol, HepOH = 1-heptanol, HexOH = 1-hexanol, PenOH = 1-pentanol, PrOH = 1-propanol, 2-PrOh = 2-propanol, FM = formamide, EtOH = ethanol, MeOH = methanol, DMSO = dimethyl sulfoxide, DMF = dimethylformamide, ACN = acetonitrile. b) The solutions were made acidic to measure the absorption and emission peaks of the neutral form (see the text). c) The solutions were made alkaline to measure the absorption and emission peaks of the monoanionic form (see the text).

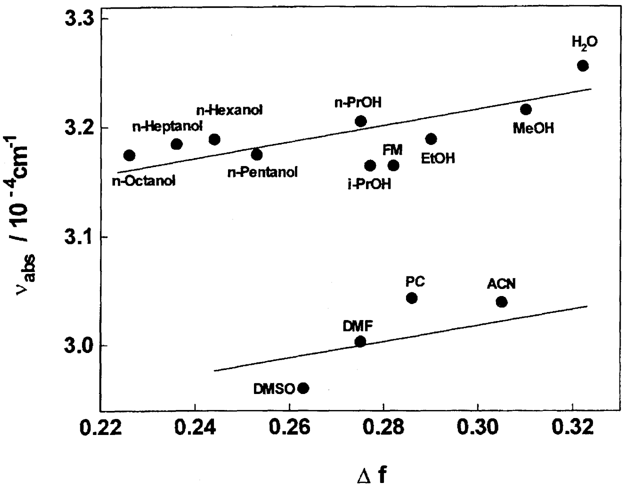
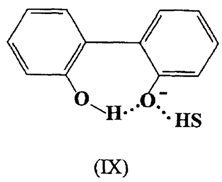


Fig. 4. Changes in the $\overline{\nu}_{\rm abs}^{\rm max}$ with the solvent polarity function Δf for the monoanion of 2,2′-biphenyldiol. Two distinct correlations are seen, one for protic solvents and the other for aprotic solvents. For solvent abbreviations see foot note of Table 1.

It can be seen from Fig. 4 that in protic solvents the $\overline{\nu}_{\rm abs}^{\rm max}$ vs. Δf plot in protic solvents is substantially blue shifted (ca. 300 cm^{-1}) in comparison to that in aprotic solvents. The large shift of the $\overline{\nu}_{\rm abs}^{\rm max}$ vs. Δf plot for the protic solvents in comparison to that in the aprotic solvents can be rationalized by considering that in protic solvents (HS) the 2,2′-Bp(OH)-O$^-$ forms intermolecular hydrogen bonds with the solvent molecules via accepting the protic hydrogen of the latter, as shown in following structure (IX) (Chart 4). Due to such behavior, 2,2′-Bp(OH)O$^-$ might be useful as a good probe for monitoring the hydrogen-bonding interactions of the protic solvents.



(IX)

Chart 4.

Table 2. Fluorescence Characteristics of Neutral and Monoanionic Forms of 2,2′-Bp(OH)$_2$ in Different Solvents

Solvent[a)]	Neutral form[b)]				Monoanionic form[c)]			
	ϕ_f	τ_f	k_R	k_{NR}	ϕ_f	τ_f	k_R	k_{NR}
		ns	10^8 s^{-1}	10^8 s^{-1}		ns	10^7 s^{-1}	10^8 s^{-1}
ACN	0.29	2.01	1.44	3.53	0.25	3.56	7.02	2.11
MeOH	0.25	1.98	1.26	3.79	0.23	3.31	6.95	2.33
EtOH	0.25	1.91	1.31	3.93	0.23	3.32	6.93	2.32
PrOH	0.26	2.06	1.26	3.59	0.22	3.38	6.51	2.31
2-PrOH	0.27	1.88	1.44	3.88	0.22	3.46	6.36	2.25
PenOH	0.27	2.07	1.30	3.53	0.25	3.65	6.85	2.05
HexOH	0.26	2.14	1.22	3.46	0.22	3.63	6.06	2.15
HepOH	0.28	2.15	1.30	3.35	0.19	3.18	5.97	2.55
OcOH	0.28	2.12	1.32	3.40	0.25	3.31	7.55	2.27
H_2O	0.025	0.34	0.74	28.68	0.21	3.68	5.71	2.15
D_2O	0.052	0.65	0.80	14.58	0.20	3.88	5.15	2.06
FM	0.06	0.53	1.13	17.73	0.23	3.74	6.15	2.06
DMF	0.07	0.54	1.30	17.22	0.27	4.23	6.38	1.72
DMSO	0.07	0.57	1.23	16.32	0.22	4.41	4.99	1.77

a) For abbreviations see foot note of Table 1. b) The solutions were made acidic to measure ϕ_f and τ_f values of the neutral form (see the text). c) The solutions were made alkaline to measure ϕ_f and τ_f values of the monoanionic form (see the text).

In contrast to the absorption maxima, the fluorescence emission maxima ($\overline{\nu}_{\text{fl}}^{\text{max}}$) of 2,2′-Bp(OH)O$^-$ is seen to be quite independent of the protic or aprotic nature of the solvents. Thus, unlike the absorption maxima, the position of the emission maxima is seen to be almost the same irrespective of the protic or aprotic nature of the solvents, though a very small red shift in $\lambda_{\text{max}}^{\text{em}}$ with Δf is indicated with fluctuations (cf. Table 1). These results thus indicate that both in protic and aprotic solvents, the emission arises from the same structural form of the excited monoanion of 2,2′-Bp(OH)$_2$. The fluorescence behavior of 2,2′-Bp(OH)O$^-$ in different solvents (protic and aprotic) is thus explained by the following mechanistic Scheme 1, where it is proposed that the intermolecular hydrogen bond in structure IX quickly dissociates following photoexcitation, and thus emission always arises from excited 2,2′-Bp(OH)O$^-$, irrespective of the protic or aprotic nature of the solvents.

The fluorescence quantum yield (ϕ_f) and lifetime (τ_f) for both neutral (I) and the monoanionic (II) forms of 2,2′-Bp(OH)$_2$ were measured in different solvents, and are listed in Table 2. For measuring ϕ_f and τ_f for the neutral form, the solutions were made acidic to the required extent so that the emissions arose from the neutral form only. This was judged by observing the changes in the emission spectra by the progressive addition of an acid. Similarly for the ϕ_f and τ_f estimation for the monoanionic form of 2,2′-Bp(OH)O$^-$, the solutions were made alkaline so as to ensure that emission arises only from the anionic form. The interesting point to be noted from Table 2 is that both ϕ_f and τ_f for the monoanionic form are independent of the protic or aprotic nature of the solvents. These results also support Scheme 1 proposed above, indicating that even in protic solvents the emission arises from the excited free 2,2′-Bp(OH)O$^-$, not from the excited intermolecularly hydrogen bonded structure (X).

In the majority of solvents the ϕ_f and τ_f values for the neutral form (I) are also very similar (Table 2). For solvents like water, formamide (FM), dimethyl formamide (DMF),

In protic solvents (HS):

$$\begin{array}{ccccc} [2,2'\text{-Bp(OH)O}^{-}\cdots\text{HS}] & \xrightarrow{h\nu} & [2,2'\text{-Bp(OH)O}^{-}\cdots\text{HS}]^{*} & \xrightarrow{k_d} & [2,2'\text{-Bp(OH)O}^{-}]^{*} + \text{SH} \\ \text{(IX)} & & \text{(X)} & & \text{(VIII)} \\ & & & & \Big\downarrow h\nu_f \\ & & & & 2,2'\text{-Bp(OH)O}^{-} + \text{SH} \\ & & & & \text{(II)} \end{array}$$

In aprotic solvents:

$$\begin{array}{ccccc} 2,2'\text{-Bp(OH)O}^{-} & \xrightarrow{h\nu} & [2,2'\text{Bp(OH)O}^{-}]^{*} & \xrightarrow{h\nu_f} & 2,2'\text{-Bp(OH)O}^{-} \\ \text{(II)} & & \text{(VIII)} & & \text{(II)} \end{array}$$

Scheme 1.

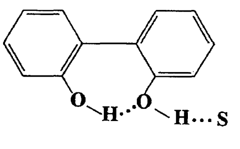
and dimethyl sulphoxide (DMSO), however, both ϕ_f and τ_f are much lower compared to other solvents. Since these solvents are hydrogen-bond accepting in nature, the reduction in the ϕ_f and τ_f values in these solvents can be attributed to the formation of strong intermolecular hydrogen bonds between the neutral form of the biphenyldiol and the solvent molecules involving the protic hydrogen of the solute, as shown in structure XI (Chart 5). It is expected that the excited state of such an intermolecularly hydrogen bonded species (XI) undergoes very fast nonradiative deactivation through the hydrogen bonds,[38—40] thus resulting in a drastic reduction in ϕ_f and τ_f for the neutral form of 2,2′-Bp(OH)$_2$ in water, FM, DMF, and DMSO. To confirm the above ideas, the radiative (k_R) and nonradiative (k_{NR}) decay rates of 2,2′-Bp(OH)$_2$ in different solvents were calculated using relations 11 and 12. The thus-obtained values are listed in Table 2.

$$k_R = \frac{\phi_f}{\tau_f}, \tag{11}$$

$$k_{NR} = \frac{1}{\tau_f} - k_R. \tag{12}$$

It can be seen from Table 2 that while the k_R values are almost in a similar range, the k_{NR} in water, FM, DMF, and DMSO is about 50 to 100-times higher than those in other solvents. It is thus evident that the intermolecular hydrogen bonding in structure XI (Chart 5) opens up a very fast nonradiative deactivation channel for the excited 2,2′-Bp(OH)$_2$. To confirm this point we investigated the photophysical characteristics of 2,2′-Bp(OH)$_2$ in D_2O and compared these results with those obtained in normal water. In D_2O both the protic hydrogens of 2,2′-Bp(OH)$_2$ are substituted by deuterium by the exchange reaction (13):

$$2,2'\text{-Bp(OH)}_2 + D_2O \rightleftarrows 2,2'\text{-Bp(OD)}_2 + H_2O. \tag{13}$$



(XI)

Chart 5.

The photophysical parameters obtained in D_2O for the 2,2′-Bp(OH)$_2$ are given in Table 2. It can be seen that both ϕ_f and τ_f for 2,2′-Bp(OH)$_2$ in D_2O are much higher compared to those in H_2O. For a measurement of ϕ_f and τ_f in D_2O for the neutral form of 2,2′-Bp(OH)$_2$ we had to make the solutions strongly acidic using about 2 mol dm^{-3} $HClO_4$. It may be assumed that the isotope effect on ϕ_f and τ_f could have been much better if we could have used the deuterated perchloric acid instead of normal $HClO_4$. However, even under the experimental conditions used, the isotope effect was quite substantial. The radiative and nonradiative rates estimated in D_2O are also given in Table 2. It is evident from these results in D_2O that the nonradiative rate reduces to about half the value obtained in H_2O, whereas the radiative rate is almost not affected. These results thus clearly indicate that in hydrogen-bond accepting solvents, the intermolecular hydrogen bonding between the solute and solvent molecules causes a very fast nonradiative deactivation of the excited 2,2′-Bp(OH)$_2$. That the intramolecular hydrogen bonding is not responsible for the very fast nonradiative rates in water, FM, DMF, and DMSO is indicated from the fact that the ϕ_f and τ_f for the monoanionic form of 2,2′-Bp(OH)$_2$ are not much affected by substituting solvent water with D_2O.

The absorption and fluorescence characteristics of the dianionic form of 2,2′-Bp(OH)$_2$ in most of the organic solvents could not be obtained due to the fact that to convert 2,2′-Bp(OH)$_2$ completely to the dianion the solutions were to make highly alkaline (cf. $\text{p}K_a(2) = 14.7$). At these strongly alkaline conditions, the solutions become highly turbid and could not be used for any quantitative measurements. Thus, the photophysical parameters for the dianionic form of 2,2′-Bp(OH)$_2$ could not be included in Tables 1 and 2.

The absorption and fluorescence characteristics of 4,4′-Bp(OH)$_2$ were also investigated in a number of organic solvents. The characteristics of the neutral form of 4,4′-Bp(OH)$_2$ in these solvents could be estimated unequivocally, and are given in Table 3. The fluorescence characteristics of the monoanionic form of 4,4′-Bp(OH)$_2$, however, could not be estimated unambiguously in most of the organic solvents, the reason for this being that the pK_a(1) of 4,4′-Bp(OH)$_2$ is quite high (ca. 9.4). Thus, to convert the 4,4′-Bp(OH)$_2$ com-

Table 3. Absorption and Fluorescence Characteristics of Neutral and Dianionic Forms of 4,4′-Bp(OH)$_2$ in Different Solvents

	Neutral form[b)]						Dianionic form[c)]	
Solvent[a)]	λ_{abs}^{max}	λ_{em}^{max}	ϕ_f	τ_f	k_R	k_{NR}	λ_{abs}^{max}	λ_{em}^{max}
	nm	nm		ns	10^7 s^{-1}	10^8 s^{-1}	nm	nm
ACN	263	351	0.08	6.77	1.18	1.36	302	385
MeOH	263	354	0.092	7.22	1.27	1.26	286	418
EtOH	264	354	0.088	7.59	1.16	1.20	289	419
2-PrOH	264	355	0.10	7.84	1.28	1.15	d)	d)
H_2O	263	354	0.095	7.14	1.33	1.27	290	417
D_2O	263	354	0.107	8.53	1.25	1.05	—	—

a) For abbreviations see foot note of Table 1. b) Measurements were done in slightly acidic conditions to ensure all the emissions from the neutral form. c) The measurements were done in strongly alkaline conditions (see the text). d) Solution becomes turbid at high alkalinity (see the text).

pletely to its monoanionic form in a solvent, a reasonably good amount of alkali had to be added. Under such alkaline conditions, in some of the solvents used, the solutions became turbid. Further, it appeared that under reasonably high alkaline conditions both the monoanionic and the dianionic forms gave overlapping emissions (cf. $\mathrm{p}K_a^*(2) = 12.8$), thus making it difficult to resolve the fluorescence characteristics of the two forms. The detailed fluorescence characteristics of the monoanionic and the dianionic forms of 4,4′-Bp$(OH)_2$ could thus not be estimated in this study. In some solvents, however, the fluorescence spectral characteristics of the dianionic form of 4,4′-Bp$(OH)_2$ could be obtained by making the solutions strongly alkaline so that the monoanion contribution in the emission spectra became negligible. The thus-obtained results are given in Table 3.

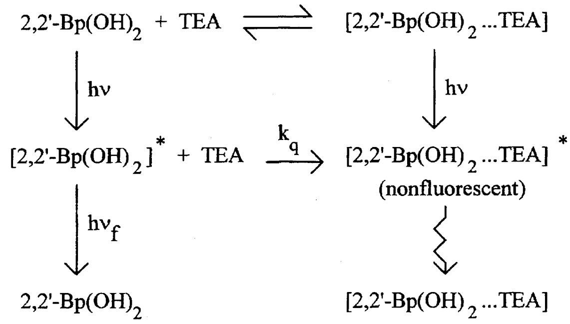
The photophysical characteristics of 4,4′-Bp$(OH)_2$ in D_2O were also investigated so as to understand the possibility of intermolecular hydrogen bondings, as observed for 2,2′-Bp$(OH)_2$ (cf. Chart 4 structure IX). The photophysical parameters obtained for 4,4′-Bp$(OH)_2$ in D_2O are listed in Table 3. Upon comparing the results in D_2O and H_2O, it is evident that in case of 4,4′-Bp$(OH)_2$ the isotope effect is not significant, as observed in the case of 2,2′-Bp$(OH)_2$. It is thus inferred that the intermolecular hydrogen-bonding interaction between 4,4′-Bp$(OH)_2$ and the solvent molecule is weak.

Comparison of the Photophysical Properties of 2,2′- and 4,4′-Biphenyldiols. It is interesting at this stage to compare the photophysical characteristics of 2,2′-Bp$(OH)_2$ with those of 4,4′-Bp$(OH)_2$. It can be seen from Tables 2 and 3 that in most of the organic solvents the ϕ_f for 2,2′-Bp$(OH)_2$ are much higher than those for 4,4′-Bp$(OH)_2$. Let us examine the role of hydrogen bonding in these two molecules. The intramolecular hydrogen bonding in 2,2′-Bp$(OH)_2$ makes the near coplanar 7-membered ring structure (IV) (Chart 2) relatively rigid, causing a better conjugation between the two phenyl rings and, consequently, a higher probability for the radiative process. In 4,4′-Bp$(OH)_2$, since there is no such hydrogen bonding, the conjugation between the two phenyl rings is relatively poor and hence probability for the radiative process is lower. This is further indicated from a comparison of the radiative (k_R) and nonradiative (k_{NR}) rates of 2,2′-Bp$(OH)_2$ and 4,4′-Bp$(OH)_2$ (Tables 2 and 3). It is seen that in the majority of the solvents the radiative rates for 2,2′-Bp$(OH)_2$ are about 10-times higher in comparison to those for 4,4′-Bp$(OH)_2$. It is to be noted that in most of the solvents (excluding water, FM, DMF, and DMSO) the nonradiative rates are also about three-times faster in 2,2′-Bp$(OH)_2$ than in 4,4′-Bp$(OH)_2$. That in 2,2′-Bp$(OH)_2$ conjugation between the two phenyl rings is better than in 4,4′-Bp$(OH)_2$ is also indicated from the fact (cf. Tables 1 and 3) that the absorption maxima for the former in a given solvent is about 20 nm or more red shifted in comparison to those for the latter compound.

The photophysical properties of 2,2′- and 4,4′-Bp$(OH)_2$ in aqueous solutions are also interesting to compare seperately. Both ϕ_f and τ_f for 2,2′-Bp$(OH)_2$ are much lower than those of 4,4′-Bp$(OH)_2$ in aqueous solutions. As already discussed, the formation of intermolecular hydrogen bonding between the neutral form of 2,2′-Bp$(OH)_2$ with water molecules (Chart 5 structure XI) opens up a very fast nonradiative decay channel for the excited molecule, causing a large reduction in the ϕ_f and τ_f values. Such a strong intermolecular hydrogen-bonding effect is not indicated in the ϕ_f, τ_f, k_R, and k_{NR} values of 4,4′-Bp$(OH)_2$ in water. The results can be expected by comparing the $\mathrm{p}K_a(1)$ values of 2,2′-Bp$(OH)_2$ and 4,4′-Bp$(OH)_2$. Due to the presence of strong intramolecular hydrogen bonding in 2,2′-Bp$(OH)_2$ the protic hydrogen of the free OH group is strongly acidic ($\mathrm{p}K_a(1) = 7.5$), and thus it can form strong intermolecular hydrogen bonding with a hydrogen-bond accepting solvent molecule like water. On the contrary, due to the lack of intramolecular hydrogen bondings, the protic hydrogens of the OH groups of 4,4′-Bp$(OH)_2$ are very weakly acidic ($\mathrm{p}K_a(1) = 9.4$) and thus can participate in forming only a very weak intermolecular hydrogen bonds with the solvent molecules, causing not much change in the photophysical characteristics of the molecule. This is, in fact, indicated from the results obtained in D_2O for 4,4′-Bp$(OH)_2$. The observed differences in the photophysical properties of 2,2′-Bp$(OH)_2$ and 4,4′-Bp$(OH)_2$ in water thus seem to be directly related to both the presence and absence of intramolecular hydrogen bondings in the two respective molecules.

Interaction of 2,2′-Biphenyldiol with Triethylamine. As discussed in Section 3.3, in proton-accepting solvents the solutions of 2,2′-Bp$(OH)_2$ show the coexistence of both neutral and the monoanionic forms in different proportions. In this context the interactions of 2,2′-Bp$(OH)_2$ with a strong proton acceptor, namely, triethylamine (TEA), have been investigated both in a polar (acetonitrile, ACN) and a nonpolar (cyclohexane, CH) solvent (Scheme 2). In ACN solution of 2,2′-Bp$(OH)_2$, as TEA is added, the 280 nm absorption peak for the neutral form of 2,2′-Bp$(OH)_2$ gradually decreases and concomitantly the 329 nm peak for the monoanion increases (Fig. 5A). Similarly, Fig. 5B shows that the fluorescence intensity (I_f) at 348 nm (for the neutral form) reduces and the I_f at 404 nm (for the monoanionic form) increases as the TEA is added to the ACN solution of 2,2′-Bp$(OH)_2$. Thus, it is evident that TEA abstracts the phenolic proton from 2,2′-Bp$(OH)_2$ very efficiently and supports the mechanism presented in Eq. 8.

In CH, the 2,2′-Bp$(OH)_2$/TEA system behaves differently



Scheme 2.

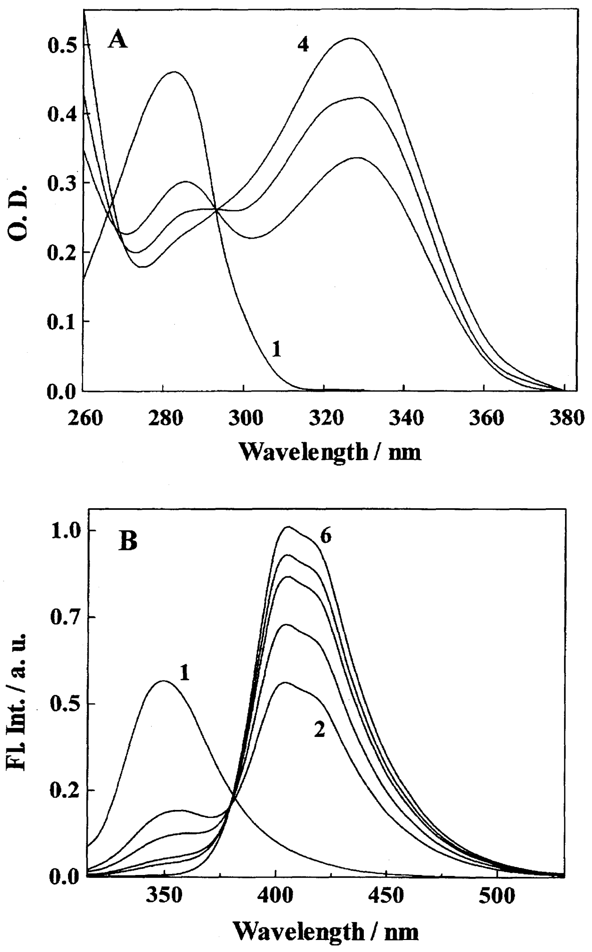


Fig. 5. (A) Changes in the absorption spectra of 2,2′-biphenyldiol in acetonitrile with the added triethylamine (TEA) concentrations of (1) 0 mol dm^{-3}, (2) 1.89×10^{-3} mol dm^{-3}, (3) 4.63×10^{-3} mol dm^{-3}, and (4) 13.04×10^{-3} mol dm^{-3}. (B) Changes in the fluorescence spectra of 2,2′-biphenyldiol in acetonitrile with the added triethylamine concentrations of (1) 0.0 mol dm^{-3}, (2) 1.89×10^{-3} mol dm^{-3}, (3) 4.63×10^{-3} mol dm^{-3}, (4) 13.04×10^{-3} mol dm^{-3}, (5) 35.87×10^{-3} mol dm^{-3}, and (6) 143.5×10^{-3} mol dm^{-3}.

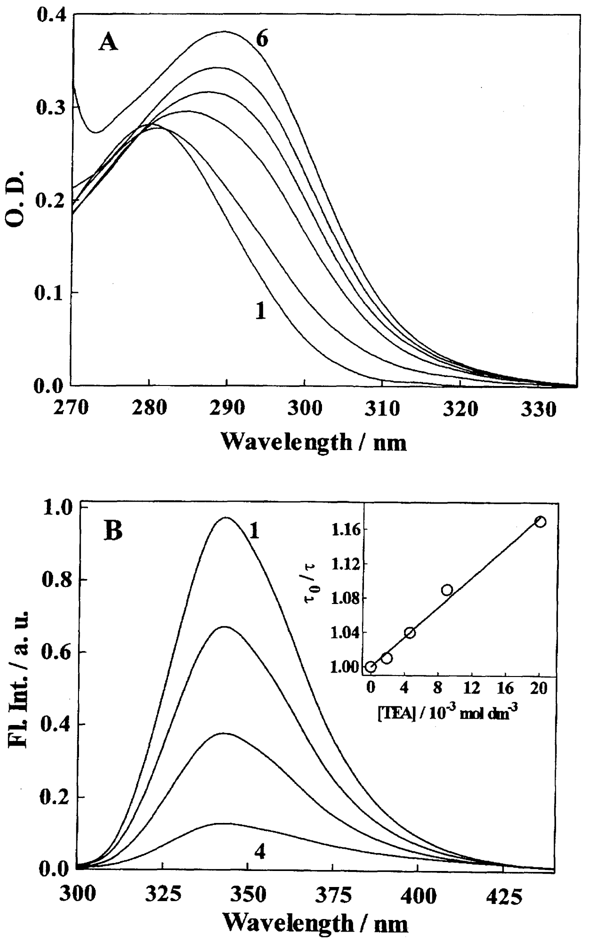


Fig. 6. (A) Changes in the absorption spectra of 2,2′-biphenyldiol in cyclohexane with the added triethylamine (TEA) concentrations of (1) 0.0 mol dm^{-3}, (2) 1.89×10^{-3} mol dm^{-3}, (3) 4.63×10^{-3} mol dm^{-3}, (4) 13.04×10^{-3} mol dm^{-3}, (5) 35.87×10^{-3} mol dm^{-3}, and (6) 143.5×10^{-3} mol dm^{-3}. (B) Changes in the fluorescence spectra of 2,2′-biphenyldiol in cyclohexane with the added TEA concentrations of (1) 0.0 mol dm^{-3}, (2) 1.89×10^{-3} mol dm^{-3}, (3) 4.63×10^{-3} mol dm^{-3}, and (4) 143.5×10^{-3} mol dm^{-3}. Inset: Decrease in fluorescence lifetime (τ) of 2,2′-biphenyldiol with triethylamine concentrations at 350 nm.

in ACN. On increasing the TEA concentration in CH, the 280 nm peak for the 2,2′-Bp(OH)$_2$ gradually shifts towards higher wavelength, as is shown in Fig. 6A. The results indicate the formation of ground-state complexes (2,2′-Bp(OH)$_2$····TEA), probably via the formation of an intermolecular hydrogen bond between TEA and 2,2′-Bp(OH)$_2$. In the fluorescence characteristics of the 2,2′-Bp(OH)$_2$/TEA system in CH it can be seen (Fig. 6B) that the fluorescence intensity of the 350 nm band gradually decreases as the TEA concentration is increased, without giving any new emission band. These results thus indicate that the 2,2′-Bp(OH)$_2$····TEA complexes are nonfluorescent. It is seen that the τ_f measured at 350 nm in CH reduces linearly with the TEA concentration, as shown in the inset of Fig. 6B. It is thus indicated that the excited state of 2,2′-Bp(OH)$_2$ is also quenched by TEA, probably via the same intermolecular hydrogen bonding interaction like in the ground state. The bimolecular quenching rate constant (k_q) of 5.96×10^9 dm^3 mol^{-1} s^{-1} was calculated using Stern–Volmer relation,[26,31]

$$\frac{\tau_f^\circ}{\tau_f} = 1 + k_q\tau_f^\circ[\text{TEA}], \tag{14}$$

where τ_o and τ are the fluorescence lifetimes of 2,2′-Bp(OH)$_2$ in the absence and presence of TEA. Thus, the results for the 2,2′-Bp(OH)$_2$/TEA system in CH can be explained by mechanistic Scheme 2.

Conclusions

The photophysical characteristics of biphenyldiols, 2,2′-Bp(OH)$_2$ and 4,4′-Bp(OH)$_2$, were investigated in water as well as in a number of organic solvents. The different prototropic equilibria of the two biphenyldiols in both ground and excited (S$_1$) states were characterized. The photophysical properties of 2,2′-Bp$(OH)_2$ are seen to be quite different than those of 4,4′-Bp$(OH)_2$, and are attributed to the presence of intramolecular hydrogen bonding in the former compound. The intramolecular hydrogen bonding makes the 2,2′-Bp$(OH)_2$ a much stronger acid in both its ground and excited states in comparison to 4,4′-Bp$(OH)_2$ and phenol. The presence of intramolecular hydrogen bonding in 2,2′-Bp$(OH)_2$ makes the compound structurally rigid, increases the extent of conjugation between the two phenyl rings, and thus increases the radiative rate of the excited 2,2′-Bp$(OH)_2$. The monoanionic form of 2,2′-biphenyldiol shows an interesting solvatochromic behavior with the solvent polarity function (Δf) for protic and aprotic solvents. An enhanced acidity of 2,2′-Bp$(OH)_2$ due to intramolecular hydrogen bonding causes the coexistence of both the neutral and the monoanionic form of the compound in a number of organic solvents having reasonable proton accepting abilities. The interaction of 2,2′-Bp$(OH)_2$ with TEA, a strong proton acceptor, supports this hypothesis. In a polar solvent like ACN, the TEA abstracts the phenolic proton from 2,2′-Bp$(OH)_2$, giving the monoanionic form of the biphenyldiol in the solution. In a nonpolar solvent like CH, TEA forms an intermolecularly hydrogen-bonded complex with 2,2′-Bp$(OH)_2$, which is nonfluorescent in the excited state.

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