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# A study of solvatochromism and proton transfer kinetics of 2,2′-dihydroxybiphenyl

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**Abstract**

Absorption and fluorescence spectra of 2,2′-dihydroxybiphenyl (DHBP) have been studied in different solvents and at various acid concentration. When compared to 2-hydroxybiphenyl a blue shift in absorption and a red shift in fluorescence are observed in all solvents. This reveals that (i) the presence of two –ÖH groups at ortho position makes the molecule more twisted in the ground state (ii) the molecule attains planarity on excitation leading to the formation of intramolecular hydrogen bonding. The stretched sigmoid curves obtained in fluorimetric titration are analysed and the excited state rate constants for proton transfer reaction are determined using lifetime measurements.

*Keywords:* Solvatochromism; Proton transfer rate constants; Excited state kinetics; 2,2′-dihydroxybiphenyl

## 1. Introduction

The title investigation is an off-shoot of our earlier work on solvatochromic and prototropic effects on absorption and fluorescence of hydroxybiphenyls [1–3]. A very interesting results have been obtained for 2- and 3-hydroxybiphenyls. Dual luminescence was observed in 2-hydroxybiphenyl [1] and the fluorimetric titration of 3-hydroxybiphenyl [3] gave stretched sigmoid curves with two inflection points. Similar study of bifunctional molecules having two electron donating groups such as –N̈H$_2$ and –ÖH showed that for most of the molecules the spectral behaviour were different from corresponding monofunctional derivatives [4–9]. For example, in 4,4′-diaminodiphenyl sulphone [5], 2,3-diaminonaphthalene [9] and 4,4′-dihydroxydiphenyl sulphone [10], the fluorescence is blue shifted to the mono functional derivatives, i.e. the net effect of two electron donating groups is less than that of one group. In the case of 4,4′-dihydroxydiphenyl sulphone, it is also reported that the change in dipole moment of dihydroxydiphenyl sulphone on excitation is negligible. In the present work, we have studied the solvatochromic and prototropic effects of 2,2′-dihydroxybiphenyl (DHBP).

## 2. Experimental details

2,2′-Dihydroxybiphenyl (Aldrich) was purified by recrystallisation from water repeatedly. The purity of the compound was checked by noting its sharp melting point and identical fluorescence spectra on excitation at different wavelengths. All the solvents used were of highest grade (spectrograde or AnalaR) commercially available. Triply distilled water was used for aqueous solutions. Analytical grade sulphuric acid and sodium hydroxide were used as such. Solutions in the pH range 1.5–12 were prepared by adding appropriate amounts of NaOH and $H_3PO_4$. A modified Hammett's acidity scale [11] ($H_o$) for solutions below pH 1.5 (using $H_2SO_4$–$H_2O$ mixture) and Yagil's basicity scale [12] ($H_-$) for solutions above pH 13 (using NaOH–$H_2O$ mixture) were employed. Absorption spectra were made using a JASCO UNIDEC-650 spectrophotometer and fluorescence measurements were made using JASCO FP-770 spectrofluorimeter. pH value in the range 1.5–1.2 were measured on a ELICO pH meter model LI 10T. The solutions were prepared just before taking the measurement. The concentrations of the solutions were of the order of $10^{-4}$–$10^{-5}$ M. The isosbestic wavelengths were used as excitation wavelengths for measuring the fluorescence intensities at any analytical wavelength.

## 3. Effects of solvents

The absorption and fluorescence spectra of 2,2′-dihydroxybiphenyl (DHBP) were recorded in different solvents and the relevant data are compiled along with the spectral data for 2-hydroxybiphenyl (HBP) in Table 1. When compared

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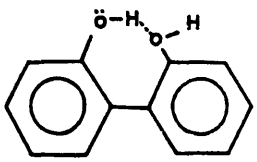
Table 1
Absorption maxima, log ε and fluorescence maxima of 2,2′-dihydroxybiphenyl (DHBP) and 2-hydroxybiphenyl (HBP) in different solvents and at various acid concentrations

| Solvent | DHBP | | | HBP [a] | | |
|---|---|---|---|---|---|---|
| | $\lambda_{abs}$ | log ε | $\lambda_{flu}$ | $\lambda_{abs}$ | log ε | $\lambda_{flu}$ |
| Cyclohexane | 279.2 | 3.85 | 343.5 | 244 | 3.88 | 322 |
| | | | | 283 | 3.54 | |
| Dioxane | 243 | 4.04 | 350 | | | |
| | 282 | 3.93 | | | | |
| Ethyl acetate | 283.8 | 4.02 | 348.5 | | | |
| Chloroform | 245.2 | 4.06 | 353 | | | |
| | 280.6 | 3.92 | | | | |
| Dichloromethane | 244 | 4.08 | 349.5 | | | |
| | 279 | 3.96 | | | | |
| Acetonitrile | 243 | 4.05 | 349 | 245 | 4.08 | 330 |
| | 279 | 3.89 | | 286.8 | 3.71 | 396.6 |
| *t*-Butyl alcohol | 245 | 4.15 | 350 | | | |
| | 285 | 3.96 | | | | |
| Isopropyl alcohol | 244 | 4.16 | 352.5 | | | |
| | 284 | 3.98 | | | | |
| Methanol | 244 | 4.09 | 351 | 245 | 3.99 | 332 |
| | 281.4 | 3.91 | | 286.5 | 3.63 | 398 |
| Glycol | 242 | 4.13 | 348.5 | | | |
| | 283.4 | 4.01 | | | | |
| Water | 278.2 | 3.97 | 358 | 241.8 | 4.04 | 343 |
| | 307.2 | 3.71 | 399 | 281.4 | 3.68 | 415 |
| Monoanion | 307.2 | | 399 | 343.0 | | 415 |
| Dianion | 301.2 | | | | | |

[a] Ref. [1].

with the absorption maxima of HBP, a slight blue shift is observed for DHBP in all the solvents. On the other hand, the fluorescence maximum of DHBP is significantly red shifted compared with that of HBP in all the solvents. Addition of the –ÖH group to HBP at ortho position of the unsubstituted phenyl ring produces a blue shift in absorption and a red shift in fluorescence. Generally the auxochromic –ÖH group produces a bathochromic shift in both absorption and emission. The biphenyl molecule is twisted and non-planar in the ground state but becomes planar in the excited singlet state [13]. The presence of two –ÖH groups at the ortho position makes the molecule more twisted so a blue shift is observed in absorption. But during excitation the molecule attains planarity, leading to the formation of intramolecular hydrogen bonding between two hydroxyl groups.



This results in a significant red shift in fluorescence. The red shift is more marked in a non-polar solvent, e.g. cyclohexane, than in polar solvents, i.e. the red shift decreases from cyclohexane (21.5 nm) to water (15 nm). This reveals that the intramolecular hydrogen bonding in DHBP is affected by intermolecular hydrogen bonding by the polar solvents.

When we compare the spectral shifts of DHBP in various solvents (Table 1), the absorption spectrum is slightly red shifted from cyclohexane to methanol but blue shifted in water relative to other solvents except cyclohexane. The fluorescence spectrum is regularly red shifted as the polarity and hydrogen bonding capacity of the solvent increases. In water two maxima are observed both in absorption (278.2 and 307 nm) and fluorescence (358 and 399 nm). By comparing the maxima in other solvents the shorter wavelength maxima (278.2 nm and 358 nm) are assigned for the absorption and fluorescence of the neutral form. The longer wavelength maxima are due to the monoanion. This is also confirmed by the ground and excited state acidity constants reported later. The maxima for the neutral form in water are taken for the discussion of solvatochromic shifts. The absorption and fluorescence solvatochromic shifts are consistent with the characteristic behaviour of hydroxyl groups [1,2,10], i.e. hydrogen acceptor interaction of solvents produces a red shift while hydrogen donor interaction produces a blue shift. In absorption, the blue shift observed in water relative to other solvents is due to its greater hydrogen donor interaction [2]. The regular red shift in fluorescence can be explained by the fact that the charge migration from hydroxyl group towards the benzene ring increases on excitation, thereby decreasing the charge density on the oxygen atom and increasing the proton donor capacity of the hydroxy group.

Hence the fluorescence solvatochromic shift is due to polar and hydrogen acceptor interaction of solvents. Generally this is confirmed by the comparison of the Stoke's shift with the theoretically derived solvent parameters $E_T(30)$ [14] and BK [15] values. These parameters, as accurate registers of solvent polarity, have been used by several researchers to correlate molecular spectroscopic properties [16–18]. The Stoke's shifts in various solvents together with BK and $E_T(30)$ values are given in Table 2. Although the hydrogen bonding interactions are predominant in the solvatochromic shifts of the compound, the correlation between the Stoke's shifts and the $E_T(30)$ parameter, which incorporates both

Table 2
Stoke's shift ($cm^{-1}$) observed for DHBP in different solvents with $E_T(30)$ and BK values

| Solvent | $\Delta\nu_{ss}$ ($cm^{-1}$) | $E_T(30)$ | BK |
|---|---|---|---|
| Cyclohexane | 6705 | 31.2 | −0.001 |
| Dioxane | 6890 | 36 | 0.043 |
| Ethyl acetate | 6542 | 38.1 | – |
| Chloroform | 7309 | 39.1 | 0.372 |
| Dichloromethane | 7230 | 41.1 | 0.586 |
| Acetonitrile | 7189 | 46 | 0.864 |
| *t*-Butyl alcohol | 6517 | 43.9 | 0.673 |
| Isopropyl alcohol | 6842 | 48.6 | 0.766 |
| Methanol | 7050 | 55.5 | 0.858 |
| Glycol | 6592 | 56.3 | – |
| Water | 8012 | 63.1 | 0.913 |

hydrogen bonding and polarity effects, is very poor ($r=0.464$). This is due to the presence of both intra- and intermolecular hydrogen bonding in polar solvents. So in all hydrogen bonding solvents a large deviation is observed.

## 4. Effects of acid concentration

The spectral characteristics of various prototropic equilibria in the $S_0$ and $S_1$ states of the molecule have been studied in the $H_o$/pH/$H_-$ range of −4 to 16. The relevant data are compiled in Table 1 and the absorption and fluorescence spectra of the prototropic species of DHBP are also shown in Figs. 1 and 2, respectively. The absorption maxima found at 278.2 nm and 307.2 nm are due to neutral and monoanionic species. The ground state p$K_a$ value for equilibrium (I) (neutral–monoanion) is determined spectrophotometrically to be 7.3. In water (pH=7) both the maxima are observed indicating the presence of neutral and monoanionic species.

$$DHBP \rightleftharpoons DHBP^- + H^+ \quad (1)$$

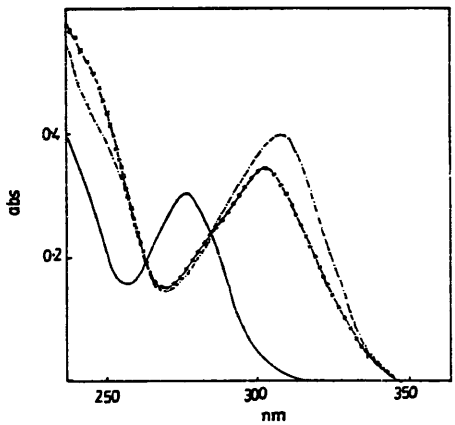



Fig. 1. Absorption spectra of different prototropic species of DHBP at 298 K (concentration, $10^{-5}$ M): ———, neutral (pH 3); – · –, monoanion; – × –, dianion.

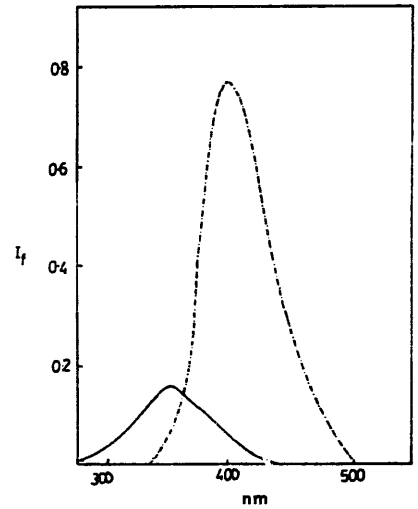
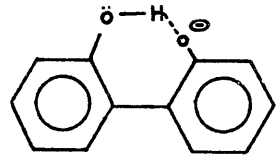



Fig. 2. Fluorescence spectra of different prototropic species of DHBP at 298 K (concentration, $10^{-5}$ M): ———, neutral; – · –, monoanion.

When compared with HBP (p$K_a$=9.3), DHBP is expected to have a higher p$K_a$ value. The lower value of 7.3 for equilibrium (I) reveals that the formed monoanion is more stabilised by intramolecular hydrogen bonding.



When the basicity is increased from pH 10, at around ($H_-$ 15) the absorption maximum is slightly blue shifted. The maximum observed at 301.2 nm is due to the dianion. During the formation of the dianion there is a repulsion between the charges, which are very close together. This repulsive effect results in a blue shifted spectrum. The p$K_a$ value for equilibrium (II) (monoanion–dianion) is not calculated, as there is no clear isosbestic point.

The fluorescence spectra of only two species were observed in the acidity/basicity range mentioned earlier. The fluorescence maximum at 358 nm ($H_o$= −2.3) is attributed to the neutral form and the maximum at 399 nm (pH=10) is due to monoanion. The excited state acidity constants (p$K_a^*$) for equilibrium (I) were calculated from the absorption and fluorescence data of acid–base pair using the Förster cycle method [19]. The values obtained from absorption and fluorescence data are −0.175, 1.27 and 0.72 respectively. These values clearly indicate that the molecule is a stronger acid in the $S_1$ than in the $S_0$ state.

The relative fluorescence intensities for the neutral ($\Phi/\Phi_0$) and monoanionic forms ($\Phi'/\Phi_0'$) for equilibrium (I) were determined from fluorescence measurements. The value of the relative fluorescence intensities ($\Phi/\Phi_0$ and $\Phi'/\Phi_0'$) are plotted as a function of $H_o$/pH in Fig. 3.

Examination of the fluorimetric titration curves indicates that these are stretched sigmoidal curves with two inflection points one of which corresponds to p$K_a$ (7.2) and the other to p$K_a^*$ (0.6). There is a plateau region in the pH range 2.5–5.5. The two curves do not intersect at the middle ($\Phi/$

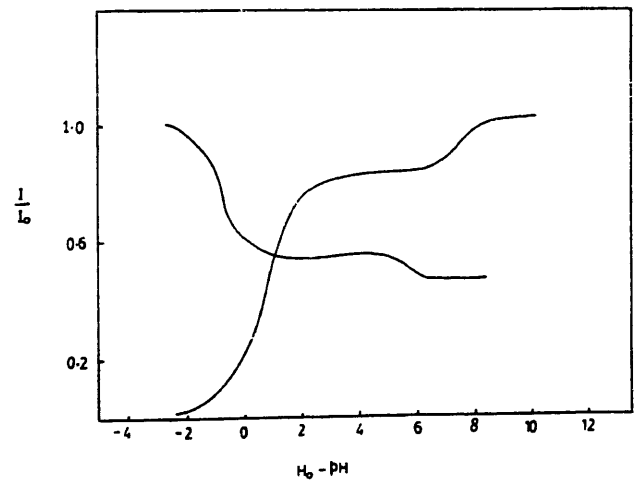



Fig. 3. Plot of the relative fluorescence intensities of DHBP and its monoanion vs. $H_o$/pH.

$\Phi_0' = \Phi'/\Phi_0' = 0.5$). The stretched sigmoidal curves indicate that the rate of proton transfer in $S_1$ state is comparable with the rate of fluorescence. The shapes of the fluorimetric titration curves can be explained on the basis of the kinetics of excited state proton transfer.

The presence of anions at low pH and the lack of dependence of ($\Phi/\Phi_0$) on pH clearly indicate that in the pH range 2.5–5.5, the proton acceptor must be the neutral water molecule and not the hydroxyl ion. The shapes of the curves in this pH range may be understood on the basis of the reaction.

$$DHBP^* + H_2O \rightleftharpoons DHBP^{-*} + H_3O^+ \quad (2)$$

In this pH range the concentration of $OH^-$ is very small and the rate does not depend on $[OH^-]$. In addition, in the plateau region, the rate of back reaction must be very small as no pH dependence of this rate is observed. The behaviour in the latter part of the curves is due to a shift towards (pH > 5.5) the ground state equilibrium reaction. A similar kind of behaviour has been observed for naphthols [20–23]: 9-phenanthrol [24], 3-hydroxybiphenyl [3] and 4-hydroxydiphenyl ether [25].

Scheme 1 explains the above behaviour where $k_1$ is the pseudo-first order rate constant for proton transfer from the excited molecule and $k_f$ and $k_I$ are the rate constants for light emission and radiationless deactivation of DHBP*. The primed values are the analogous terms of $DHBP^{-*}$. If the equations derived by Weller [26–28] using simple steady-state kinetics are applied then the relative quantum yields of DHBP ($\Phi/\Phi_0$) and $DHBP^-$ ($\Phi'/\Phi_0'$) are given by Eqs. (3) and (4) where $\tau_0$ and $\tau_0'$ are the lifetimes of the DHBP and $DHBP^-$ respectively.

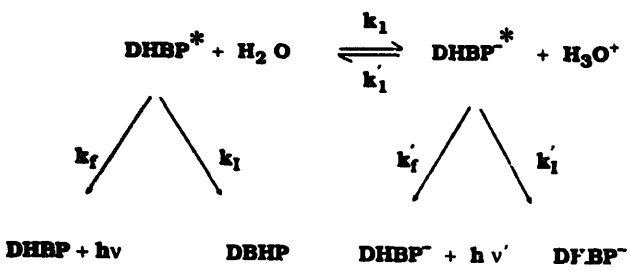
$$\frac{\Phi}{\Phi_0} = \frac{1 + k_1'\tau_0'[H_3O^+]}{1 + k_1\tau_0 + k_1'\tau_0'[H_3O^+]} \quad (3)$$

$$\frac{\Phi'}{\Phi_0'} = \frac{k_1\tau_0}{1 + k_1\tau_0 + k_1'\tau_0'[H_3O^+]} \quad (4)$$

If the rate of the reaction with solvent molecule in Eq. (2) is comparable with or greater than the rate of fluorescence of DHBP and the rate of the second order protonation of $DHBP^-$ is much less than the rate of fluorescence, Eqs. (3) and (4) become

$$\frac{\Phi}{\Phi_0} = \frac{1}{1 + k_1\tau_0} \quad (5)$$

$$\frac{\Phi'}{\Phi_0'} = \frac{k_1\tau_0}{1 + k_1\tau_0} \quad (6)$$




Scheme 1.

Eqs. (5) and (6) indicate that $\Phi/\Phi_0$ and $\Phi'/\Phi_0'$ are independent of $[H^+]$ or $[OH^-]$. Thus plot of $\Phi/\Phi_0$ or $\Phi'/\Phi_0'$ vs. $[H^+]$ or $[OH^-]$ should give a flat horizontal line for each species and this is observed for both the neutral and the monoanionic forms of DHBP in the pH range 2.5–5. At 298 K, the values of $\Phi/\Phi_0$ and $\Phi'/\Phi_0'$ obtained from the flat regions of the curves are, 0.56 and 0.82 respectively. The sum of $\Phi/\Phi_0$ and $\Phi'/\Phi_0'$ is not equal to unity. If $\Phi/\Phi_0 + \Phi'/\Phi_0' = 1$, proton transfer will occur before the deactivation of the excited state. This was observed in the case of 9-phenanthrol [24]. In 3-hydroxybiphenyl [3] the sum of $\Phi/\Phi_0$ and $\Phi'/\Phi_0'$ is less than unity (0.61) and this decrease is reported to be due to the radiationless deactivation of the anion formed. However, like 4-hydroxybiphenyl ether, in DHBP $\Phi/\Phi_0 + \Phi'/\Phi_0' > 1$ ($\approx 1.38$). This high value may be due to the overlap of the fluorescence of DHBP and $DHBP^-$. As the sum is not equal to unity the calculation of $k_1\tau_0$ using Eqs. (5) and (6) will give two different results.

The ratio of relative quantum yields can be obtained from Eqs. (3) and (4)

$$\frac{\Phi/\Phi_0}{\Phi'/\Phi_0'} = \frac{1}{k_1\tau_0} + \frac{k_1'\tau_0'}{k_1\tau_0}[H_3O^+] \quad (7)$$

If we plot the ratio of quantum yields versus $[H_3O^+]$, a straight line should be obtained with a slope of $k_1'\tau_0'/k_1\tau_0$ and intercept of $1/k_1\tau_0$. In the range of 2–3.5 M for $[H^+]$ ($H_0 = -1$ to $-1.5$) $\Phi/\Phi_0 + \Phi'/\Phi_0' \approx 1$. Hence, the $(\Phi/\Phi_0)/(\Phi'/\Phi_0')$ values are plotted against $[H^+]$ (Fig. 4). The plot is linear with a good correlation ($r = 0.998$). The values of $k_1\tau_0$ and $k'_1\tau_0'$ determined from the intercept and slope by the least-squares method are 1.68 and 0.7 respectively. The lifetimes of DHBP and $DHBP^-$ determined using a single-photon counting spectrofluorimeter, are 0.953 and 0.805 ns respectively. The $pK_a^*$ value calculated from the rate constants is $-0.31$. In the fluorimetric titration, the middle point of the inflection of the curves of the lower pH side is around 0.6, which is near to the $pK_a^*$ value $-0.31$ obtained from the rate constants.

When the basicity is further increased, the quenching of fluorescence starts from pH 13 to 15, due to the formation of non-fluorescent dianion. The $pK_a^*$ value for equilibrium between monoanion and dianion, obtained from mid-point of the quenching curve, is found to be 14.4 (Fig. 5).

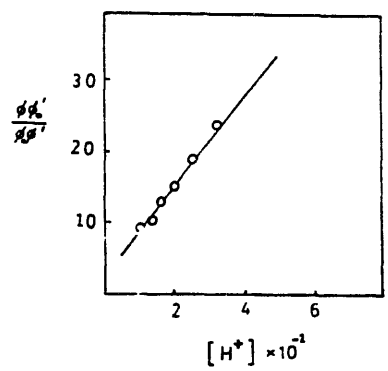



Fig. 4. Plot of $(\Phi\Phi_0')/(\Phi_0\Phi')$ vs. $[H^+]$.

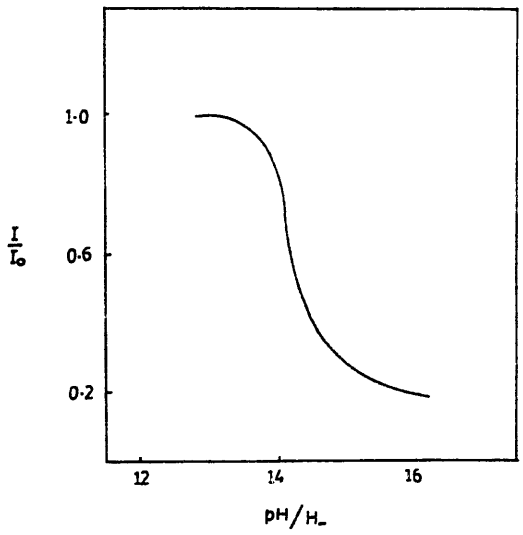



Fig. 5. Plot of $I/I_0$ of $DHBP^-$ vs. pH/H_.

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