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Ground and Excited Singlet (S_1) State Interactions of 2,2′- and 4,4′-Biphenyldiols with Proton Acceptors

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Proton-transfer interactions of 2,2′- and 4,4′-biphenyldiols with urea (U), *N*-methylurea (MU), and triethylamine (TEA) have been investigated in methanol solutions using optical absorption as well as steady-state and time-resolved fluorescence measurements. In the ground state, both 2,2′- and 4,4′-biphenyldiols do not interact with weak proton acceptors, like U and MU. In the excited singlet (S_1) state, only the 2,2′-biphenyldiol is seen to transfer a proton to U and MU, via the formation of intermolecular hydrogen-bonded exciplexes as intermediates. With TEA, a strong proton acceptor, both 2,2′- and 4,4′-biphenyldiols undergo an efficient proton-transfer reaction in their S_1 state. In the ground-state, however, only 2,2′-analogue is seen to transfer a proton to TEA. The differences in the proton-transfer behavior of 2,2′- and 4,4′-biphenyldiols with different proton acceptors have been rationalized in terms of the presence and absence of intramolecular hydrogen bonding in the two diols.

Hydroxy derivatives of aromatic hydrocarbons are stronger acids in their excited states than in the ground states.[1–8] Thus, photoexcitation of these molecules can cause the transfer of a proton from their hydroxy group to a suitable proton acceptor; the latter could be an added solute or a solvent molecule having a reasonable proton-accepting ability.[6–14] Studies on the photoinduced proton-transfer dynamics received momentum in the last two decades, due to the advent of pico and femtosecond spectroscopic techniques.[12–14] The aim of such studies is to obtain insight into the details of the kinetics and the mechanism of the proton-transfer processes and also to understand the role of a solvent environment in the proton-transfer reaction in a condensed phase.[12–14]

Dihydroxy derivatives of aromatic hydrocarbons are simple model compounds for more complex biomolecules, like dityrosine and calmodulin.[15] These molecules display interesting behavior due to the possibilities to form both intra- and intermolecular hydrogen bonding.[16–22] In our earlier studies on the fluorescence properties of 2,2′- and 4,4′-biphenyldiols,[23] it was observed that the presence of intramolecular hydrogen bonding in the 2,2′-analogue causes a drastic change in its photophysical behavior compared to those of the 4,4′-analoge, where intramolecular hydrogen bonding is absent. Our studies on the triplet-state characteristics and the photoionization behavior of the above two diols using a nanosecond laser flash photolysis technique also indicate the role of the intramolecular hydrogen bonding in 2,2′-biphenyldiol to alter its properties in comparison to those of the 4,4-analogue.[24] In the present work, we investigated the proton-transfer interactions of 2,2′- and 4,4′-biphenyldiols, both in their ground and excited singlet (S_1) states, with different proton acceptors, like urea (U), methyl urea (MU) and triethylamine (TEA). The aim of the present work is to understand how the presence and absence of intramolecular hydrogen bonding in the two respective biphenyldiols affect the course of proton-transfer reactions with different acceptors.

Materials and Methods

Both 2,2′- and 4,4′-biphenyldiols were obtained from Aldrich and purified by repeated crystallization from cyclohexane and methanol, respectively. Purest-grade U and MU were obtained from Fluka and used without further purification. TEA from Spectrochem India was purified by distillation just before use. The organic solvents used were of spectroscopic grade from either Spectrochem, India or S. D. Fine Chemicals, India, and were used as received.

Absorption spectra were recorded using a Shimadzu model 160-A UV-vis spectrophotometer. Steady-state (SS) fluorescence spectra were recorded after a correction for the wavelength-dependent instrument responses using a Hitachi model F-4010 spectrofluorimeter. The instrument used for fluorescence lifetime measurements (Edinburgh Instruments model 199, U.K.) have been described elsewhere.[23,25]

Results and Discussion

1. Ground State Interactions of 2,2′- and 4,4′-Biphenyldiols with Different Proton Acceptors. Interactions of 2,2′- and 4,4′-biphenyldiols in their ground states with weak proton acceptors, like U ($pK_b = 13.9$)[26] and MU ($pK_b < 13.9$),[27] have been investigated in methanol (MeOH) solutions using optical-absorption measurements. Since solutions of 2,2′-biphenyldiol in MeOH show a small contribution from the anionic form of the molecule,[23] we intentionally made the solutions slightly acidic by adding a small amount of $HClO_4$ to ensure that the diol completely exists in its neutral form in solution. Unless otherwise stated, all of the present studies with 2,2′-biphenyldiol were carried out with such slightly acidic solutions in MeOH. For 4,4′-biphenyldiol, solutions in MeOH were used without adding any acid.

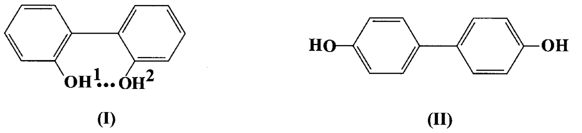
When U or MU was added to solutions of 2,2′- or 4,4′-biphenyldiol in MeOH, even up to the highest concentration of the proton acceptors used (ca. 2.8 mol dm^{-3}) there was no observable change in the absorption spectra of these molecules. These results thus indicate that the ground states of the biphenyldiols do not interact with the U and MU molecules. In our earlier work,[23] it was observed that 2,2′-biphenyldiol undergoes a strong proton-transfer interaction in its ground state with TEA in an acetonitrile solution. Similar results were also obtained with TEA in a MeOH solution in the present study. Since TEA is a strong proton acceptor (pK_b = 3.25),[26] the ground state of 2,2′-biphenyldiol can undergo an efficient proton-transfer reaction (Eq. 1) with TEA, though the diol does not show any interaction with weak proton acceptors, like U and MU.

$$2,2'\text{-Bp(OH)}_2 + \text{TEA} \longrightarrow 2,2'\text{-Bp(OH)O}^- + \text{TEAH}^+. \quad (1)$$

Unlike 2,2′-biphenyldiol, the 4,4′-biphenyldiol in MeOH does not show any appreciable interaction in its ground state, even with a strong proton acceptor, TEA. Thus, the ground states of the two biphenyldiols differ substantially in their interactions with different proton acceptors. We attribute these differences to the presence and absence of intramolecular hydrogen bonding in the two respective diols, as shown below by structures **I** and **II**, respectively (Chart 1). Due to intramolecular hydrogen bonding, the ground state of 2,2′-biphenyldiol is a comparatively stronger acid (pK_a = 7.5)[23] than its 4,4′-analogue (pK_a = 9.4).[23] Thus, the 2,2′-biphenyldiol can easily transfer one of its phenolic protons (marked 2 in structure I) to a suitable proton acceptor, like TEA, though the diol does not interact with weak proton acceptors, like U and MU. Due to its weak acidity, the 4,4′-analogue does not undergo a proton-transfer interaction in its ground state, even with a strong proton acceptor, like TEA.

2. Excited Singlet (S$_1$) State Interactions of 2,2′- and 4,4′-Biphenyldiols with Weak Proton Acceptors like Urea and *N*-Methyl Urea. 2.1. Interactions of the S$_1$ state of 2,2′-Biphenyldiol. The fluorescence spectra of 2,2′-biphenyldiol in MeOH have been seen to undergo substantial changes in the presence of U and MU. Thus, as the concentration of U/MU is increased, the fluorescence intensity at 349 nm due to the neutral form of the diol[23] gradually reduces along with the development of a new emission peak at 398 nm due to fluorescence from the anionic form of the diol.[23] Typical fluorescence spectra for 2,2′-biphenyldiol in the presence of different concentrations of U in MeOH are shown in Fig. 1. The SS fluorescence results thus indicate that the S$_1$ state of the diol {2,2′-Bp(OH)$_2$*} undergoes a proton-transfer interaction with U and MU:

$$2,2'\text{-Bp(OH)}_2{}^* + \text{U/MU} \longrightarrow 2,2'\text{-Bp(OH)O}^{-*} + \text{UH}^+/\text{MUH}^+. \quad (2)$$



(I)
2,2'-biphenyldiol [2,2'-Bp(OH)$_2$]

(II)
4,4'-biphenyldiol [4,4'-Bp(OH)$_2$]

Chart 1.

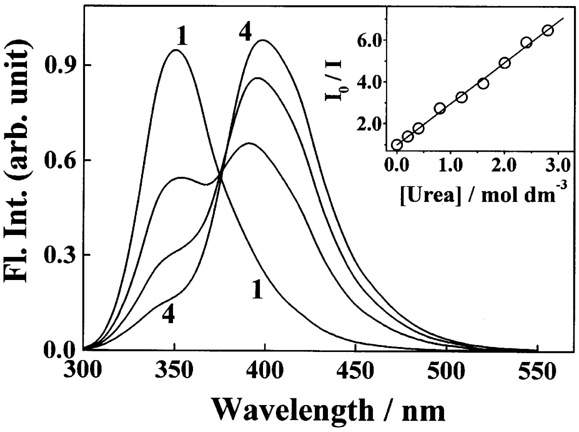


Fig. 1. Changes in the fluorescence spectra of 2,2′-biphenyldiol in methanol with the added urea concentrations of (1) 0.0, (2) 0.4, (3) 1.2, and (4) 2.8 mol dm^{-3}. **Inset**: Stern–Volmer plot for the steady-state fluorescence quenching of 2,2′-biphenyldiol at 349 nm by urea in methanol solution.

The quenching of the fluorescence intensity at 349 nm by U/MU is seen to follow the linear Stern–Volmer (SV) relationship,[28]

$$\frac{I_0}{I} = 1 + K_{\text{SV}}[\text{Q}] = 1 + k_\text{q}\tau_0[\text{Q}], \quad (3)$$

where I_0 and I are the fluorescence intensities in the absence and presence of a quencher (Q = U and MU), K_{SV} is the SV constant, τ_0 is the fluorescence lifetime of 2,2′-biphenyldiol in the absence of a quencher (τ_0 = 1.98 ns in MeOH),[23] and k_q is the bimolecular quenching constant. An SV plot obtained for the 2,2′-biphenyldiol-U system using SS fluorescence measurements in MeOH is shown in the inset of Fig. 1. The k_q values obtained from the slopes of linear SV plots for 2,2′-biphenyldiol-U/MU systems in MeOH solutions are about 1 × 10^9 and 0.8 × 10^9 dm^3 mol^{-1} s^{-1}, respectively. These k_q values are about an order of magnitude lower than the typical bimolecular diffusion-controlled rate constants in MeOH solutions (k_d ca. 1 × 10^{10} dm^3 mol^{-1} s^{-1}),[28] indicating that the proton-transfer interaction is not quite strong for 2,2′-biphenyldiol-U/MU systems.

If the quenching of the fluorescence intensity at 349 nm is due to dynamic interactions between the S$_1$ state of the diol and the U/MU molecules, the fluorescence lifetime (τ) of 2,2′-Bp(OH)$_2$* is expected to be reduced in the presence of quenchers. Hence, the effect of added U/MU on the fluorescence decays of 2,2′-Bp(OH)$_2$* has been investigated in the presence of different concentrations of quenchers. The decays were measured at 330 nm, a reasonably shorter wavelength than the fluorescence peak of 2,2′-Bp(OH)$_2$* (i.e. 349 nm), to minimize the contribution of the emission from the anionic form of the diol {2,2′-Bp(OH)O^{-*}}. It is seen that for the lower concentration range (< 0.5 mol dm^{-3}) of U/MU used, the fluorescence decays fit reasonably well with a mono-exponential function, and that the fluorescence lifetime gradually reduces with the quencher concentration. For a higher concentration range (> 0.5 mol dm^{-3}) of the quenchers, however, the decays are seen to fit better with a bi-exponential function with the short-lifetime component (τ_1) gradually reducing and the long-lifetime component (τ_2) remaining almost constant (ca. 3.3 ns) with U/MU concentrations. The percentage contribution of the long-lifetime component is, however, seen to be quite small, only ca. 5% with the highest concentration of the quenchers used. Further, the value of τ_2 matches well with the fluorescence lifetime of 2,2′-Bp(OH)O^{-*} in MeOH.[23] We thus infer from these results that for all of the U/MU concentrations used, the 2,2′-Bp(OH)$_2$* effectively decays as a single-exponential function, and that the longer-lifetime (τ_2) component at the higher quencher concentrations is due to the small contribution from the overlapping emission of 2,2′-Bp(OH)O^{-*}. Typical fluorescence decay curves for 2,2′-biphenyldiol in a MeOH solution in the absence and in the presence of U are shown in Fig. 2.

It can be seen that the SV plot for the reduction in the fluorescence lifetime of 2,2′-Bp(OH)$_2$* with the U/MU concentrations (Eq. 4)[28] shows a negative deviation from linearity,

$$\frac{\tau_0}{\tau} = 1 + K_{\mathrm{SV}}[\mathrm{Q}] = 1 + k_{\mathrm{q}}\tau_0[\mathrm{Q}], \tag{4}$$

where τ_0 is the lifetime of 2,2′-Bp(OH)$_2$* in the absence of any quencher and τ (= τ_1 for the higher U/MU concentrations) is the lifetime of 2,2′-Bp(OH)$_2$* in presence of the quenchers. A typical τ_0/τ vs. [Q] plot for 2,2′-biphenyldiol-U system in MeOH is shown in Fig. 3A.

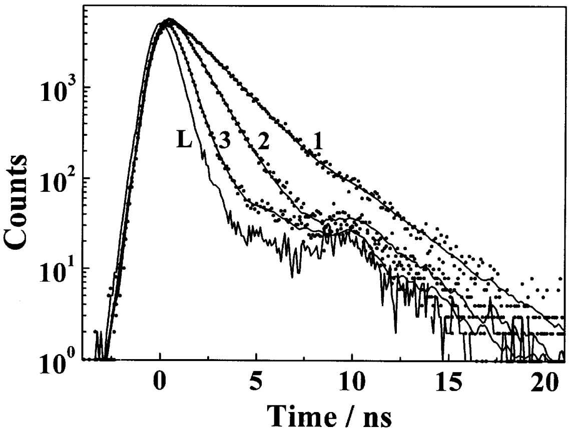


Fig. 2. Fluorescence decay curves of 2,2′-biphenyldiol in methanol measured at 330 nm; (1) in absence of U, (2) in presence of 0.4 mol dm^{-3} of U and (3) in presence of 2.8 mol dm^{-3} of U. Experimental decay curves are shown by dots and the fitted curves are shown by continuous line. The curve L represents the instrument response function. The fitting parameters are: (1) τ = 1.96 ns, χ^2 = 1.15; (2) τ = 1.1 ns, χ^2 = 1.2 and (3) τ_1 = 0.4 ns (95%) and τ_2 = 3.3 ns (5%), χ^2 = 1.0.

The negative deviations in the τ_0/τ vs. [Q] plots obtained from the TR measurements (cf. Fig. 3A) indicate that the proton-transfer from 2,2′-Bp(OH)$_2$* to U/ MU is not a single-step process.[28–30] It is proposed that some nonfluorescent exciplexes (EX) are formed as intermediates during the proton-transfer process, probably via intermolecular hydrogen bonding between 2,2′-Bp(OH)$_2$* and the U/MU molecules. The quenching of 2,2′-Bp(OH)$_2$* by U and MU can thus be represented by Scheme 1,[28–30] where U represents both urea and *N*-methylurea and $h\nu_{\mathrm{n}}$ and $h\nu_{\mathrm{a}}$ represent the fluorescence from the neutral and anionic forms of the diol excited state, respectively.

Following Scheme 1 and assuming the steady-state conditions, one can derive the following expression for the quenching of the fluorescence intensity of 2,2′-biphenyldiol by U and MU:[28–30]

$$\frac{I_0}{I} = 1 + \frac{k_3 k_{\mathrm{p}} \tau_0[\mathrm{Q}]}{k_4 + k_{\mathrm{p}}}. \tag{5}$$

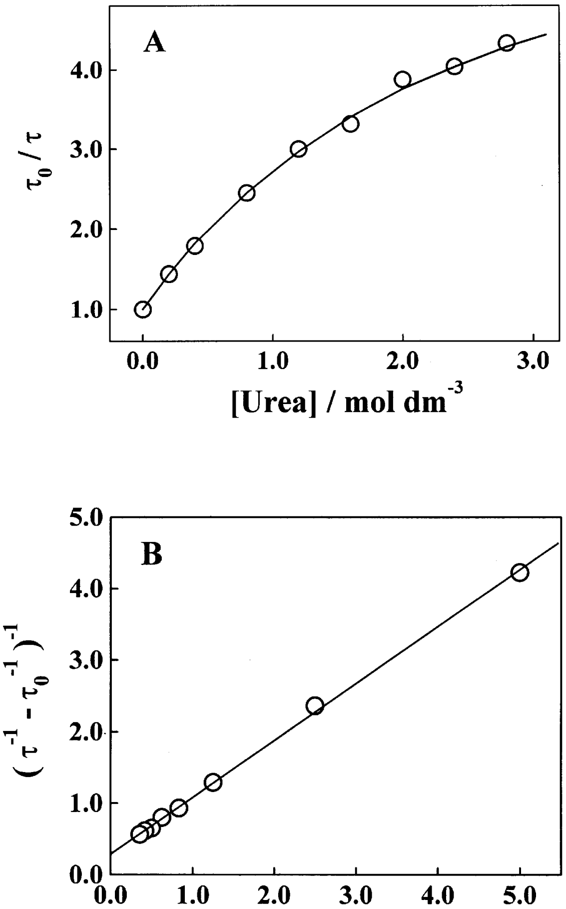
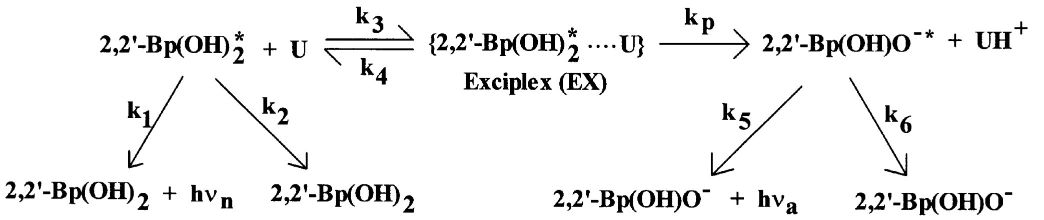


Fig. 3. (A) The τ_0/τ vs. [Q] plot obtained from the TR fluorescence measurements for 2,2′-biphenyldiol-urea system in methanol. The negative deviation from the Stern–Volmer linearity (cf. Eq. 4) is clearly indicated. (B) The $\{\tau^{-1} - \tau_0^{-1}\}^{-1}$ vs. [Q]$^{-1}$ plot for 2,2′-biphenyldiol-urea system in methanol following Eq. 10 in the text.



Scheme 1.

According to Eq. 5, the SS fluorescence quenching should follow a linear SV relationship, as experimentally observed (cf. Inset of Fig. 1). Comparing Eqs. 3 and 5, k_q can be expressed as

$$k_q = \frac{k_3 k_p}{k_4 + k_p}. \tag{6}$$

Thus, k_q for the above-mentioned systems studied does not represent the rate constant of a single step, but rather it is a function of a number of rate constants of different individual steps involved in the exciplex mechanism.

To understand the extent of reduction in the fluorescence lifetime of 2,2′-Bp(OH)$_2$* in the presence of U/MU, one has to consider the dynamic behavior of 2,2′-Bp(OH)$_2$*. Following Scheme 1 and assuming δ-pulse excitation, the dynamic behavior of 2,2′-Bp(OH)$_2$* can be expressed as[28–30]

$$[S_1] = C_1 \exp(-t/\tau_1) + C_2 \exp(-t/\tau_2), \tag{7}$$

where τ_1, τ_2, C_1, and C_2 are the complicated functions of the rate constants of the individual steps in Scheme 1 (i.e. k_1, k_2, k_3, k_4, and k_p) and of the concentration of the quencher.[28–30] Thus, according to Eq. 7, the decay of 2,2′-Bp(OH)$_2$* is expected to follow a bi-exponential behavior under normal circumstances in the presence of quenchers. However, under some limiting conditions, especially when the equilibrium between 2,2′-Bp(OH)$_2$* and EX is established very fast (i.e. when $k_3[Q] >> \{k_1 + k_2\}$ and $k_4 >> k_p$), the fluorescence decay of 2,2′-Bp(OH)$_2$* can effectively show a single-exponential behavior with fluorescence lifetime given by[28–31]

$$\tau = \frac{1 + K[Q]}{\tau_0^{-1} + Kk_p[Q]}, \tag{8}$$

where K (= k_3/k_4) is the equilibrium constant for the EX formation. Rearranging Eq. 8 further in accordance with Eq. 4, one obtains

$$\frac{\tau_0}{\tau} = \frac{1 + Kk_p\tau_0[Q]}{1 + K[Q]}. \tag{9}$$

According to Eq. 9, the τ_0/τ vs. [Q] plots should show a negative deviation from the SV linearity, as experimentally observed for the present systems. To get more insight into the exciplex kinetics, Eq. 9 was further rearranged in a linear form as

$$\{\tau^{-1} - \tau_0^{-1}\}^{-1} = \{K^{-1}(k_p - \tau_0^{-1})^{-1}\}[Q]^{-1} + \{(k_p - \tau_0^{-1})^{-1}\}. \tag{10}$$

Thus, a plot of $\{\tau^{-1} - \tau_0^{-1}\}^{-1}$ vs. $[Q]^{-1}$ should yield a straight line. A typical $\{\tau^{-1} - \tau_0^{-1}\}^{-1}$ vs. $[Q]^{-1}$ plot obtained for the 2,2′-biphenyldiol-U system is shown in Fig. 3B. From the slope and intercept of such plots, the equilibrium constants for exciplex formation ($K = k_3/k_4$) have been estimated to be 0.4 and 1.3 dm^3 mol^{-1} and the exciplex lifetimes ($\tau_{EX} = k_p^{-1}$) have been estimated to be 0.25 and 0.42 ns, respectively, for the 2,2′-biphenyldiol-U/MU systems.

Steady-state fluorescence quenching experiments have also been carried out for the 2,2′-biphenyldiol-U/MU systems in MeOH at different temperatures. Typical temperature dependent SV plots, as obtained from the SS fluorescence quenching of 2,2′-biphenyldiol by U, are shown in Fig. 4. It can be seen that at all temperatures, the SV plots are linear and the quenching becomes more efficient as the temperature of the solution is increased. Similar results have also been obtained for the SS fluorescence quenching of 2,2′-biphenyldiol by MU at different temperatures. The temperature-dependent k_q values obtained from the linear SV plots (cf. Fig. 4) were analyzed using the Arrhenius relation, as Eq. 11,[32]

$$\ln(k_q) = \ln(A) - \frac{\Delta E_{k_q}}{RT}, \tag{11}$$

where A is the preexponential factor, ΔE_{k_q} is the effective activation energy for the quenching process, R is the universal gas constant and T is the absolute temperature. For the limited temperature range studied (25–60 °C), the ln (k_q) vs. $1/T$ plots were linear within the experimental error (cf. Inset of Fig. 4) and the

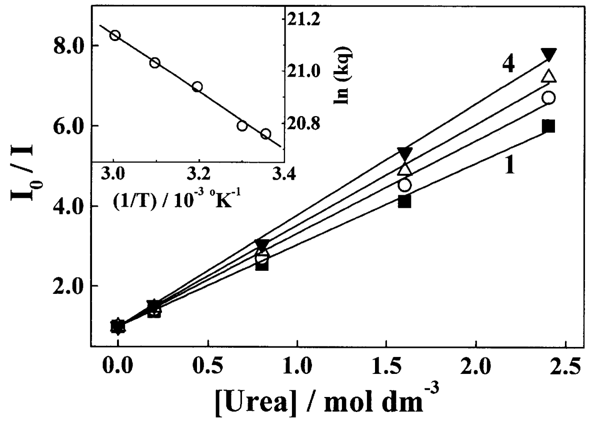


Fig. 4. Stern–Volmer plots from SS fluorescence quenching of 2,2′-biphenyldiol at 349 nm by urea in methanol solution at different temperatures: (1) 30 °C, (2) 40 °C, (3) 50 °C, and (4) 60 °C. **Inset**: The ln(k_q) vs. $1/T$ plot for 2,2′-biphenyldiol-U system in methanol.

ΔE_{k_q} values obtained from the slopes of these plots were 2.1 and 1.8 kcal mol^{-1}, respectively, for the 2,2′-biphenyldiol-U/MU systems. Typical activation energies for the diffusion-controlled processes in MeOH (ΔE_{k_d}) are about 4.8 kcal mol^{-1}.[33] From the fact that the estimated ΔE_{k_q} values are lower than the typical ΔE_{k_d} values, it was expected that in the systems studied the proton-transfer process should have occurred with a diffusion-controlled rate. The estimated k_q values for the systems studied (1.1×10^9 and 0.8×10^9 dm^3 mol^{-1} s^{-1} respectively for 2,2′-biphenyldiol-U/MU systems) are, however, seen to be about an order of magnitude lower than the expected diffusion-controlled rate (k_d ca. 1×10^{10} dm^3 mol^{-1} s^{-1}).[28] Apparently, lower k_q values for the 2,2′-biphenyldiol-U/MU systems in comparison to the typical k_d values may be understood by considering Scheme 1, according to which k_q is a function of various individual rate constants (cf. Eq. 6), and thus can be lower than the k_d value, though, the EX formation step (k_3) may be as fast as the diffusion-controlled rate. Further, the effective ΔE_{k_q} values estimated for the systems studied should also be a function of the activation energies of the individual processes involved in the expression of k_q. Thus, expressing Eq. 6 in accordance with the Arrhenius relation, 11, the expression for ΔE_{k_q} can be obtained as

$$\Delta E_{k_q} = \Delta E_{k_3} + \Delta E_{k_p} - \Delta E_{(k_4+k_p)}, \tag{12}$$

where ΔE_{k_3}, ΔE_{k_p} and $\Delta E_{(k_4+k_p)}$ are the activation energies corresponding to the rate constants of k_3, k_p, and (k_4 + k_p), respectively. Since in taking the logarithm of Eq. 6 one can not separate out the rate constants, k_4 and k_p, in the denominator, one has to express the effective activation energy for the total rate constant of (k_4 + k_p) in Eq. 12 with the assumption that $\Delta E_{(k_4+k_p)}$ is a constant, at least for the limited temperature range used in our experiments. Thus, according to Eq. 12, the effective activation energy for k_q could be very low, or even negative, depending on the relative values of ΔE_{k_3}, ΔE_{k_p} and $\Delta E_{(k_4+k_p)}$.[28–30] The lower ΔE_{k_q} values observed for the present systems in comparison with the typical ΔE_{k_d} values, thus, can not guarantee that the activation energy for the proton-transfer process is lower than that for a typical diffusion-controlled reaction. In fact, due to the involvement of the exciplexes as the intermediates, the effective proton-transfer rate in the systems studied is expected to be lower than the diffusion-controlled rate, as experimentally observed for the 2,2′-biphenyldiol-U/MU systems. Due to the same reason, the observed ΔE_{k_q} values can also be lower than the activation energies of typical diffusion-controlled processes. Thus, the apparently lower ΔE_{k_q} values compared to the typical ΔE_{k_d} values support the exciplex mechanism proposed in Scheme 1.

2.2. Interactions of the S$_1$ state of 4,4′-Biphenyldiol. The fluorescence spectra of 4,4′-biphenyldiol in MeOH solutions show an emission peak at 354 nm due to fluorescence from the neutral form of the diol.[23] The addition of U or MU to these solutions does not cause any change in either the fluorescence spectrum or the intensity, indicating no interaction between the S$_1$ state of the diol {4,4′-Bp(OH)$_2$*} and U/MU molecules. It is known that,[23] due to the absence of intramolecular hydrogen bonding, the 4,4′-biphenyldiol is a much weaker acid, even in its S$_1$ state (pK_a* = 3.27), in comparison to that of its 2,2′-analogue (pK_a* = 0.37), wherein intramolecular hydrogen bonding exists (cf. structures **I** and **II**). Due to the strong acidic nature of 2,2′-Bp(OH)$_2$*, the S$_1$ state of the diol can interact with U and MU, though in its ground state the diol does not have any interaction with these weak proton acceptors. Since the S$_1$ state of 4,4′-biphenyldiol is a much weaker acid, it can not undergo any proton-transfer reaction in both its ground and S$_1$ states with weak proton acceptors, like U and MU. From the present results, it is thus evident that the presence and absence of intramolecular hydrogen bonding largely alters the proton-transfer interactions of the two biphenyldiols with proton acceptors, like U and MU.

3. Comparison of the S$_1$ State Interactions of 2,2′- and 4,4′-Biphenyldiols with Weak and Strong Proton Acceptors. 3.1. 2,2′-Biphenyldiol. As already discussed in section 1, the ground state of 2,2′-biphenyldiol undergoes an efficient proton-transfer interaction with a strong proton acceptor, like TEA. In our earlier studies in acetonitrile solutions,[23] it was observed that not only the ground state, but also the S$_1$ state, of 2,2′-biphenyldiol undergoes a strong proton-transfer interaction with TEA. Similar results have also been obtained in the present study in MeOH solutions using TEA as the proton acceptor. Thus, upon increasing the TEA concentration, the fluorescence intensity at 349 nm for 2,2′-Bp(OH)$_2$* gradually reduces along with a concomitant increase in the fluorescence intensity at 398 nm for 2,2′-Bp(OH)O^{-*}. The k_q value for the 2,2′-biphenyldiol-TEA system, however, could not be estimated accurately from the SS fluorescence quenching results due to the interplay of both ground- and excited-state proton-transfer reactions in this system. From the extent of reductions in the fluorescence intensities at 349 nm with TEA concentrations, it is, however, qualitatively indicated that the k_q value for the 2,2′-biphenyldiol-TEA system must be in the diffusion-controlled limit.

Since TEA is a strong proton acceptor (pK_b = 3.25),[33] it can efficiently abstract the phenolic proton from both ground and excited states of 2,2′-biphenyldiol. Contrary to the results with TEA, the 2,2′-biphenyldiol can undergo a proton-transfer interaction only in its S$_1$ state with weak proton acceptors, like U and MU (cf. sec. 1 and 2.1). Since 2,2′-biphenyldiol is a much stronger acid in its S$_1$ state (pK_a* = 0.37),[23] it can transfer a proton not only to TEA, but also to weak proton acceptors, U and MU, though the ground state of the diol (pK_a = 7.5)[23] does not interact with the latter weak proton acceptors. It is evident from the present results that the proton-transfer interactions of the ground and S$_1$ states of 2,2′-biphenyldiol with U, MU and TEA are in accordance with the acidity of the diol in the two respective electronic states.

The fluorescence decays of 2,2′-biphenyldiol have also been measured in the presence of different concentrations of TEA in MeOH solutions. It is seen that, unlike with U and MU, the fluorescence decays of the diol are always bi-exponential in the presence of TEA. Further, in all of these measurements, it is seen that none of the fluorescence lifetime components (τ_1 and

τ_2) show any systematic reduction along with an increase in the TEA concentration. Since the interaction of TEA with 2,2′-biphenyldiol is very strong, even at a very low concentration of TEA (ca. 4×10^{-3} mol dm^{-3}), there is also a substantial contribution from the ground state anionic form of the diol {2,2′-Bp(OH)O$^-$} in the solution (cf. Eq. 1). Under such conditions, selective excitation of the neutral form of the 2,2′-biphenyldiol was not possible, and thus the observed fluorescence decays were complicated due to an interplay of the ground- and excited-state proton-transfer processes. From our TR measurements, we could thus not estimate the exact proton-transfer rate for the S_1 state of 2,2′-biphenyldiol with TEA. Based on the SS results, we infer that the interaction of the S_1 state of 2,2′-biphenyldiol with TEA is very strong, and that there is no indication of any exciplex formation for the 2,2′-biphenyldiol-TEA system.

3.2. 4,4′-Biphenyldiol. As discussed in section 1, the ground state of 4,4′-biphenyldiol does not show any appreciable interaction with TEA. Since the ground-state acidity constant of 4,4′-biphenyldiol is quite high ($pK_a = 9.4$),[23] these results are quite expected. In our earlier studies we have seen that the S_1 state of 4,4′-biphenyldiol is a much stronger acid ($pK_a^* = 3.24$)[23] than its ground state. It was thus expected that the S_1 state of 4,4′-biphenyldiol might interact with a strong proton acceptor, TEA, though the diol does not interact with weak proton acceptors, like U and MU, even in its excited state. Experimentally, it is seen that the fluorescence intensity of the neutral form of 4,4′-biphenyldiol at 354 nm[23] gradually reduces and, concomitantly, the emission peak for the anionic form of the diol develops at 429 nm[23] as the TEA concentration is increased in the solution. Typical SS fluorescence results for the 4,4′-biphenyldiol-TEA system in MeOH are shown in Fig. 5. It can be seen that the reduction in the fluorescence intensity at 354 nm with TEA concentration follows a linear SV relationship (Eq. 2), as shown in the inset of Fig. 5. The bimolecular quenching constant thus determined for the 4,4′-biphenyldiol–TEA system in MeOH is about 6.0×10^9 dm^3 mol^{-1} s^{-1}, only marginally lower than the diffusion-controlled rate (ca. 1×10^{10} dm^3 mol^{-1} s^{-1}).[28]

Time-resolved fluorescence measurements have also been carried out at 354 nm to estimate the effect of added TEA concentration on the fluorescence lifetime (τ) of 4,4′-biphenyldiol in a MeOH solution. It is seen that the τ of 4,4′-biphenyldiol gradually decreases as the TEA concentration is increased. The reduction in the τ values with the TEA concentration is also seen to follow a linear SV relation (Eq. 3), giving a k_q value of about 6.3×10^9 dm^3 mol^{-1} s^{-1}. Thus, it is seen that for the 4,4′-biphenyldiol-TEA system in MeOH, the k_q values estimated from the SS and TR measurements match well within the experimental error. These results thus indicate that the proton-transfer in the 4,4′-biphenyldiol-TEA system must be a single-step process, and that there is no exciplex formation in the present system.

Comparing the interactions of 2,2′- and 4,4′-biphenyldiols with different proton acceptors, both weak and strong, it is evident that the 2,2′-biphenyldiol interacts much more strongly than 4,4′-biphenyldiol. As already discussed, due to the absence of intramolecular hydrogen bonding, the 4,4′-biphenyldiol is a much weaker acid in both its ground and excited states compared to its 2,2′-analogue. It is thus evident from the present results that the presence and absence of intramolecular hydrogen bonding in 2,2′- and 4,4′-biphenyldiols cause a large difference in the proton-transfer interactions of the two diols with different proton acceptors. Form our results it is further indicated that when the interactions are weak (e.g., 2,2′-Bp(OH)$_2$* – U/MU systems; $k_q << k_d$), the systems undergo proton-transfer interactions via the formation of the intermolecular hydrogen bonded exciplex intermediate. For systems where the interactions are reasonably strong (e.g., 2,2′-Bp(OH)$_2$* – TEA and 4,4′-Bp(OH)$_2$* – TEA systems; $k_q \sim k_d$), the proton-transfer interaction takes place in a single step without the formation of intermediate exciplexes.

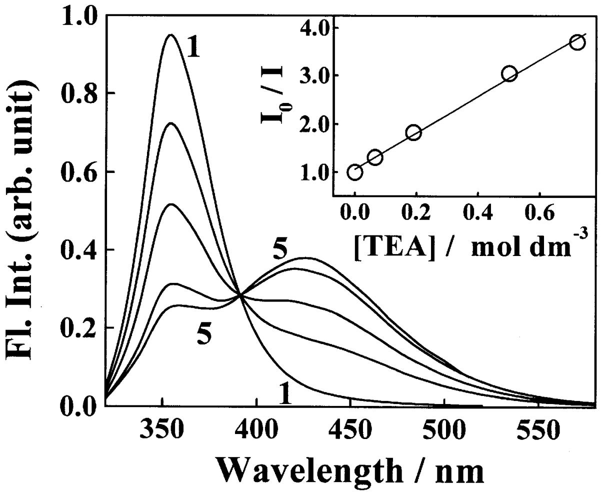


Fig. 5. Changes in fluorescence spectra of 4,4′-biphenyldiol in methanol with added triethylamine (TEA) concentrations: (1) 0.0, (2) 0.065, (3) 0.19, (4) 0.50, and (5) 0.72 mol dm^{-3}. **Inset**: Stern–Volmer plot for the fluorescence intensity quenching of 4,4′-biphenyldiol by TEA in methanol solution.

Conclusions

Ground and excited (S_1) states of 2,2′- and 4,4′-biphenyldiols interact differently with proton acceptors, like U, MU, and TEA. Though the S_1 state of 2,2′-biphenyldiol transfers protons to all of the proton acceptors used, its ground state interacts only with a strong proton acceptor, like TEA. Contrary to 2,2′-biphenyldiol, the ground state of 4,4′-biphenyldiol is seen not to interact with any of the proton acceptors used. The S_1 state of 4,4′-biphenyldiol, however, is seen to undergo an efficient proton-transfer reaction with a strong proton acceptor, TEA; however, with weak proton acceptors, like U and MU, there is no interaction, even in the S_1 state of the diol. From the present results it is seen that when the interaction is weak (e.g., 2,2′-Bp(OH)$_2$* – U/MU systems), proton-transfer takes place via the formation of intermolecular hydrogen-bonded exciplexes as the intermediates. For strongly interacting systems, e.g., 2,2′-Bp(OH)$_2$* – TEA and 4,4′-Bp(OH)$_2$* – TEA, proton-transfer takes place in a single step without forming exciplexes as intermediates. It is seen from the present results that 2,2′-biphenyldiol interacts much more strongly with different proton acceptors than its 4,4′-analogue. The results are interpreted in relation to the presence and absence of intramolecular hydrogen bonding in the two respective molecules.

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