

Fluorescence studies of photoactivated acidity of 2,2'-Dihydroxy-1,1'-Binaphthalene

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ABSTRACT. Linear and multilinear relationships between some solvent polarity parameters and solvatochromic shifts of absorption and fluorescence of 2,2'-dihydroxy-1,1'-binaphthalene (DHBN) revealed strong charge transfer excitations (formation of $S_{1,CT}$ with higher dipole moment) in this dipolar system. This dihydroxy molecule with $pK_a(S_0)$ of 10.9 becomes a weak acid with $pK_a(S_1)$ of 6.8 in its first excited singlet state. We studied the excited state proton-transfer process from DHBN to the base water in acetonitrile solution by means of fluorescence spectroscopy. We found that the process occurs via a 1 : 1 very weak (with equilibrium constant $K = 9 \times 10^{-3} M^{-1}$) hydrogen-bonded adduct between the photoacid DHBN and the base. Moreover, the rate constant of fluorescence quenching of DHBN by some Lewis acids; Ag^{+1} , Cu^{+2} , Fe^{+2} or Fe^{+3} metal ions in methanol solution as well as the binding constant of the formed complexes are correlated with the size and charge of the metal ion. Furthermore, photostability studies of DHBN in aqueous solutions at different pHs point to photolability of DHBN with formation of different photo-oxidation products similar to simple naphthols.

1. INTRODUCTION

The spectroscopic and dynamics of bichromophoric molecules have been the subject of a great deal of research over several decades [1]. Biaryl species, where the chromophores are single and fused aromatic rings, have been extensively studied [1] because of their promising technological applications. Both enantiomers of 2,2'-Dihydroxy-1,1'-binaphthalene (DHBN) which serve as ligands for a variety of stereoselective carbon-carbon bond forming reaction have received considerable interest [2, 3]. Some disubstituted binaphthol derivatives show second-order nonlinear optical phenomena. Due to high molecular hyperpolarizabilities such organic molecular materials display a number of significant nonlinear optical properties and hence are emerging as possible materials for future technologies of next generation telecommunication technologies, optical information processing, and storage.

In this study we intend to investigate the photophysical properties of 2,2'-dihydroxy-1,1'-binaphthalene in neat solvent as well as in water-acetonitrile mixed solvents. Moreover, the acidity constants of both ground (S_0) and excited state (S_1) will be determined. The fluorescence quenching of DHBN in methanol by Ag^{+1} , Cu^{+2} , Fe^{+2} and Fe^{+3} metal ions will be also studied and the formation constants for the complexes formed and bimolecular quenching rate constants will be calculated. Finally the photostability of DHBN in aqueous solutions of different pHs will be discussed.

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2. MATERIAL AND METHODS

2,2'-dihydroxy-1,1'-binaphthalene (Fluka) is used as received. The solvents used were of the purest grade available.

Absorption spectra were recorded with an UNICAM (Helios- α) spectrophotometer.

Corrected fluorescence spectra for dilute solutions (Absorbance < 0.05) were taken with a Shimadzu 5301PC spectrofluorometer.

Fluorescence lifetime was measured using computer controlled Time Correlated Single Photon Counting Spectrometer FL900 from Edinburgh Instruments with hydrogen filled nF900 flash lamp. Using a $5 \times 10^{-5} M$ concentration of degassed cyclohexane solution of anthracene sample of single decay time of 5.15 ns (± 0.05 ns) tested instrument performance. All solutions of DHBN were purged by dry Argon for few minutes before lifetime measurements.

The photochemical reactor (ACE GLASS INC.) is a cylindrical double walled quartz, 50 mm diameter, with inlet and outlet for cooling by water to maintain the temperature constant.

During irradiation DHBN solutions were stirred with THERMOLYNE magnetic stirrer. The light source was 75 Watt xenon arc lamp (PTI) powered with a PTI model LPS-250 arc lamp power supply. The light intensity was measured using INTERNATIONAL LIGHT research radiometer model IL1700 equipped with appropriate solar-blind vacuum photodiodes head. The light intensity was found to be $13.2 W/cm^2 \cdot min$.

3. RESULTS AND DISCUSSION

3.1. Solvatochromic behavior. The absorption and fluorescence spectra of 2,2'-Dihydroxy-1,1'-binaphthalene show positive solvatochromic behavior, as shown in Figure 1. Figure 1 shows the results of correlating the data in Table 1 with various solvent polarity parameters according to the well-known following multiparameter equation of Taft-Kamlet [4]:

$$\lambda = \lambda_0 + a\alpha + b\beta + c\pi^* \quad (1)$$

where a , b and c are measures of the susceptibility of the absorption or emission spectra of a probe molecule to solvent hydrogen bond donor (HBD) acidity, to

hydrogen bond acceptor (HBA) basicity and to solvent polarisability, respectively. α , β and π^* refers to scales used to characterize solvents with respect to these properties. Figure 1 displays the plot of the calculated maxima of absorption and fluorescence as a function of the corresponding experimental values (cf. Table 1) for various solvents [5]. The calculated maxima are obtained from the multiparameter fit, using eqs. (2) and (3):

$$\lambda_a = 331.94(\pm 1.55) - 5.99(\pm 3.20)\alpha + 5.65(\pm 4.47)\beta + 0.49(\pm 1.58)\pi^* \quad (r = 0.715) \quad (2)$$

$$\lambda_f = 365.67(\pm 1.14) + 7.03(\pm 1.99)\alpha - 11.54(\pm 2.92)\beta - 4.37(\pm 1.55)\pi^* \quad (r = 0.948) \quad (3)$$

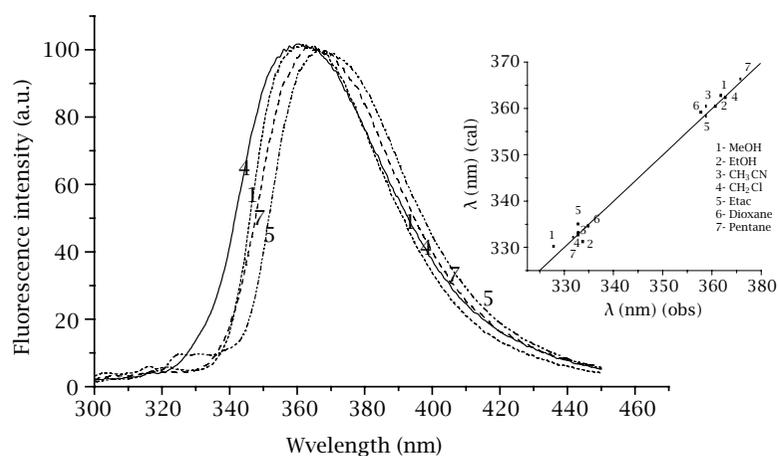


Figure 1. Normalized (at 336 nm) fluorescence spectra of 1×10^{-5} M DHBN in different solvents ($\lambda_{exc} = 290$ nm). The inset shows the plot of the calculated maxima of absorption and emission as a function of the corresponding experimental maxima for various solvents.

Table 1. Absorption (λ_{abs}) and fluorescence emission (λ_{em}) Wavelengths, fluorescence quantum yields (Φ_f), radiative (k_r) and radiationless rate constants (k_{nr}) of DHBN in different solvents.

Solvent	λ_{abs} (log ϵ^a) (nm)	λ_{flu} (nm)	Φ_f^b	τ_0^c (ns)	τ_r^d (ns)	$k_r^e \times 10^9$ s $^{-1}$	$k_{nr}^f \times 10^9$ s $^{-1}$
1-MeOH	328.00(4.04)	362.00	0.14 ± 0.01	9.10	1.27	0.79	4.85
2-EtOH	334.00(4.03)	361.00	0.18 ± 0.02	9.40	1.69	0.60	2.69
3-Isopropanol	334.00(4.09)	365.00	0.17 ± 0.02	8.16	1.39	0.72	3.52
4-Acetonitril	332.61(4.00)	359.00	0.14 ± 0.01	7.90	1.11	0.90	5.54
5-DMSO	341.80(3.48)	368.00	0.47 ± 0.05	26.67	12.50	0.08	0.09
6-CH ₂ Cl ₂	333.00(4.14)	363.00	0.05 ± 0.01	7.27	0.36	2.75	52.25
7-CHCl ₃	332.00(3.92)	365.00	0.10 ± 0.01	11.94	1.19	0.84	7.54
8-Ethylacetate	333.40(3.60)	359.00	0.20 ± 0.02	25.00	5.00	0.20	0.80
9-Dioxane	335.65(3.90)	358.00	0.13 ± 0.01	11.67	1.52	0.66	4.40
10-Pentane	332.00(4.44)	366.00	0.14 ± 0.01	3.64	0.51	1.96	12.06
11-Cyclohexane	331.00(4.21)	360.00	0.24 ± 0.02	6.10	1.47	0.68	2.16

^a ϵ is the molar absorptivity,

^b $\Phi_f = \Phi_r \cdot F_f/F_r \cdot A_r/A_f \cdot n^2_f/n^2_r$ where r and f stand for reference and unknown, respectively, A is the absorbance of the exciting wavelength, F is the area under the emission spectrum, n is the solvent refractive index and Φ_r is the reference quantum yield ($\Phi_r = 0.546$ for quinine sulfate in 1 M H₂SO₄),

^c τ_0 (Calculated using approximate formula) = $1 \times 10^{-4}/\epsilon$,

^d $\tau_f = \tau_0 \times \Phi_f$,

^e $k_r = 1/\tau_f$ and

^f $k_{nr} = k_r((1/\Phi) - 1)$.

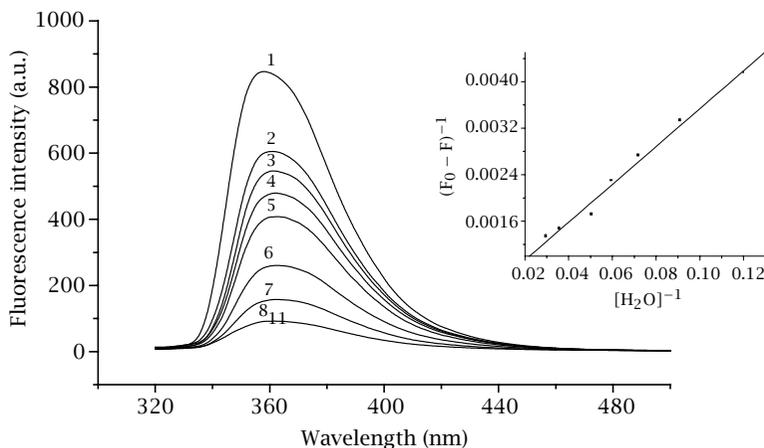


Figure 2. Fluorescence quenching of 2×10^{-5} M DHBN in CH_3CN in the presence of increasing amounts of H_2O ($[\text{H}_2\text{O}] = 1-0.00, 2-8.31, 3-10.94, 4-13.85, 5-16.68, 6-19.64, 7-27.79, 8-33.33$ M) ($\lambda_{\text{exc}} = 310$ nm). The inset shows the plot of $[\text{H}_2\text{O}]^{-1}$ vs. $(F_0 - F)^{-1}$.

The values of the coefficients in eqs. (2) and (3) reflect the relative contribution of H-bond-donating and -accepting properties of solvent to stabilize the excited state [5]. The line in Figure 1 represents a perfect fit of which calculated and experimental values would be equal and each square represents the fitted value of λ for a given solvent. The solvatochromism is thus more pronounced on the fluorescence side, as shown by the much higher weights of the solvent parameter, $a(\alpha)$, $b(\beta)$ and $s(\pi^*)$, as compared to the corresponding values on the absorption side.

Specific solvent effects (α and β) are more important than general effects of dipole solvation (π^*). In the S_0 state the OH groups of DHBN can form two types of hydrogen bonds [6] with solvent denoted as HS. The first $\text{ArOH} \cdots \text{SH}$, in which the solvent acts as proton acceptor, and $\text{ArHO} \cdots \text{HS}$, where the solvent donates a proton to DHBN (= ArOH, which is used for simplification). Moreover, the ratios $\alpha/\beta = 1.060$ and 0.609 for S_0 and S_1 , respectively, suggesting a slight enhancement in the H-donor ability over the acceptor ability of DHBN in the S_0 state. However, no good correlations between the spectroscopic or the photophysical parameters such as the rate constant of nonradiative transitions (k_{nr} , see Tables 1 and 2) were obtained using the multiparameter eq. (4) of Kamlet-Taft or the conventional E_{T}^{N} solvent parameter (See Tables 1 and 2). The positive solvatochromism that we observe, namely a bathochromic shift, to longer wavelengths, upon increasing the solvent's polarity, shows that the excited state is more dipolar than the ground state.

Upon excitation it is expected that these dyes exhibit a dipole moment increase in the $S_{1,\text{CT}}$ state relative to the S_0 state. An important support for this prediction could be obtained by estimating the relative values of the static dipole moment μ_{g} and μ_{e} , in the S_0 and

$S_{1,\text{CT}}$, respectively. The spectral shift method is used (using the fluorescence and absorption maxima [6]) to give a rough estimate of relative dipole moment change. The bulk dielectric constant (D) and refractive index (n) functions employed are represented according to the following equations [7]:

$$F_2(D, n) = \frac{D-1}{D+2} - \left(\frac{n^2-1}{n^2+2} \right) \left(\frac{2n^2+1}{n^2+2} \right) \quad (4)$$

$$F_7(D, n) = 0.5 F_2(D, n) + 1.5 \left[\frac{n^4-1}{(n^2+2)^2} \right] \quad (5)$$

Excluding amphiprotic and chlorinated solvents, to minimize specific interaction and complex formation [6], the usual linear least squares treatment gives the following equations:

$$\nu_a - \nu_f = 452.64(\pm 144.86)F_2(D, n) + 1865.61(\pm 68.99) \quad (r = 0.911) \quad (6)$$

$$\frac{\nu_a + \nu_f}{2} = -1731.65(\pm 583.08)F_7(D, n) + 29300.75(\pm 218.48) \quad (r = -0.903) \quad (7)$$

Slope ratio can be readily converted to $\mu_{\text{g}}/\mu_{\text{e}}$ relative values [= $(1 + \text{slope ratio})/(1 - \text{slope ratio})$], where the slope ratio = $(\mu_{\text{e}} - \mu_{\text{g}})^2/(\mu_{\text{g}} - \mu_{\text{e}})$, giving $\mu_{\text{e}} = 1.71\mu_{\text{g}}$. The results lead to the conclusion that the optical excitation populates a CT S_1 state with a higher dipole moment value relative to that in the S_0 state.

3.2. Effect of mixed solvents. Addition of different concentration of water to DHBN acetonitrile solution results in a slight red shift (Figure 2) with simultaneous fluorescence quenching. The observed quenching (Figure 2) is attributed to hydrogen bonding complex formation with water molecules. The formation constant of the formed complex was calculated by

Table 2. Solvent parameters^a used to establish correlations (See the text).

Solvent	E_T^N	α	β	π^*	$F_2(D, n)$	$F_7(D, n)$
1- MeOH	0.765	0.93	0.62	0.60	0.6692	0.5583
2- EtOH	0.654	0.83	0.77	0.54	0.6165	0.5542
3- Isopropanol	0.552	0.76	0.95	0.48	0.5801	0.5466
4- Acetonitrile	0.472	0.19	0.31	0.75	0.6749	0.5653
5- DMSO	0.441	0.00	0.76	1.00	0.5742	0.6111
6- CH ₂ Cl ₂	0.321	0.00	0.00	0.82	0.4052	0.4904
7- CHCl ₃	0.259	0.00	0.00	0.58	0.2219	0.4130
8- Ethylacetate	0.228	0.00	0.45	0.55	0.3467	0.4267
9- Dioxane	0.164	0.00	0.37	0.55	-0.0249	0.2742
10- Pentane	0.127	0.00	0.00	-0.08	-0.0487	0.2190
11- Cyclohexane	0.077	0.00	0.00	0.00	-0.0683	0.2550

^a M. J. Kamlet, J. L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.* **48** (1983), 2877; Y. Marcus, *Chem. Soc. Rev.* **22** (1993), 409.

Table 3. Stern-Volmer constant, (K_{sv}), bimolecular rate constant, (k_q), formation constant, (K), critical concentration, (C_0), and critical radii, (R_0) for quenching of DHBN by Ag^{+1} , Cu^{+2} , Fe^{+2} and Fe^{+3} metal ions in methanol and by H_2O in acetonitrile.

Quencher	Ionic radius of the Cation (Å ⁰)	K_{sv} (M ⁻¹)	k_q (M ⁻¹ s ⁻¹)	K (M ⁻¹)	C_0^a (M)	R_0^b (Å ⁰)
Ag ⁺	1.26	35 ± 3	6.11 × 10 ⁹	44	2.9 × 10 ⁻²	24
Cu ²⁺	0.72	1507 ± 202	2.66 × 10 ¹¹	711	6.4 × 10 ⁻³	40
Fe ²⁺	0.74	48030 ± 3145	10.27 × 10 ¹²	26606	2.1 × 10 ⁻⁵	267
Fe ³⁺	0.64	20616 ± 536	3.65 × 10 ¹²	5523	4.9 × 10 ⁻⁵	201
H ₂ O	-	0.061 ± 0.041	1.08 × 10 ⁷	0.009	16.39	2.9

^a An apparent critical concentration [C_0] for fluorescence quenching can be experimentally determined. This parameter is defined as the acceptor concentration at which the fluorescence quantum yield of the donor is reduced to 0.5 Φ_0 [12]:

$$C_{01/2} = 1/K_{sv}.$$

^b The corresponding apparent critical radius can also be calculated from the equation $R_0 = 7.34(C_0)^{-1/3}$ (see reference [12]). Error in C_0 or R_0 values is within 15-20%.

means of the following equation [8]

$$\frac{1}{F_0 - F} = \frac{1}{F_0 - F_c} + \frac{1}{K[Q](F_0 - F_c)} \quad (8)$$

where F_0 represents the fluorescence intensity in absence of quencher, F is the fluorescence intensity in presence of certain concentration of quencher, F_c is the fluorescence intensity of the complex, K is the formation constant of the formed complex and $[Q]$ is the concentration of quencher. Linear plot of $1/(F_0 - F)$ versus $1/[H_2O]$ was obtained suggesting that only a 1 : 1 complex formed between DHBN and H_2O molecules in the concentration range measured (inset of Figure 2).

Linear Stern-Volmer [9] plot (eq. (9)) is obtained only at water concentration < 1.5 M indicating presence of dynamic quenching. At concentration > 1.5 M Stern-Volmer plots showed upward curvature indicating a further quenching process. The combined quenching can be expressed by the modified Stern-Volmer equation [9] (equation (10) below):

$$\frac{F_0}{F} - 1 = K_{sv}[Q] \quad (9)$$

$$\frac{F_0}{F} = (1 + K_{sv}[Q])(1 + K_{eq}[Q]) \quad (10)$$

where F_0 and F are the fluorescence intensity of DHBN in absence and presence of quencher, K_{sv} is the Stern-Volmer constant and equals to $K_q \tau$ and $[Q]$ is the quencher concentration, K_{eq} is the equilibrium constant of

the fluorophores-quencher complex, K_q is the bimolecular rate constant and τ is the lifetime of DHBN in absence of quencher. The plot of $((F_0/F) - 1)/[H_2O]$ versus $[H_2O]$ gives an excellent linear least square correlation; from the slope and the intercept K_{sv} could be calculated (Table 3).

Water as a moderate proton acceptor (Taft parameter β [4]) and one of the strongest proton donors (α [4]) is therefore the best for solvating both proton form and anion. It, thus, plays a crucial role in the thermodynamics by stabilizing the anion by non-fluorescent H-bond complex formation ($(ArO^- \cdots HS)$ [5]).

3.3. Excited state proton transfer. Acidity constant of DHBN (pK_a) for ground state (S_0) was obtained by means of the known methods [10] using the experimental curves of titration (Figure 3). Acidity constant of DHBN (pK_a^*) for the first excited state (S_1) was calculated via simple Förster thermodynamic equation (11):

$$pK_a = pK_a^* + 2.1 \times 10^{-3} \Delta\nu \quad (11)$$

where pK_a is the value of acidity for S_0 , pK_a^* is the value of the acidity constant for S_1 and $\Delta\nu$ is the difference in cm^{-1} between the maxima of absorption of acid and base forms.

The value of pK_a of DHBN decreases from 10.9 in the S_0 state to 6.8 in the S_1 state indicating that DHBN is a weak photoacid.

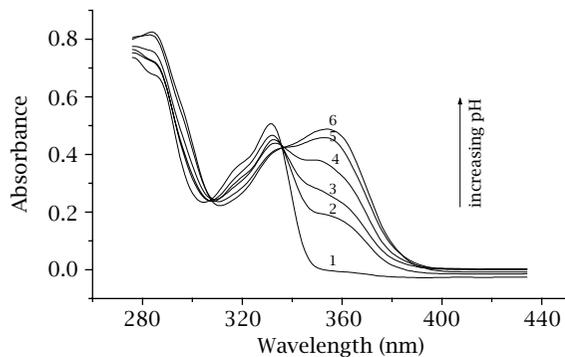


Figure 3. Absorption spectra of DHBN at different pHs.

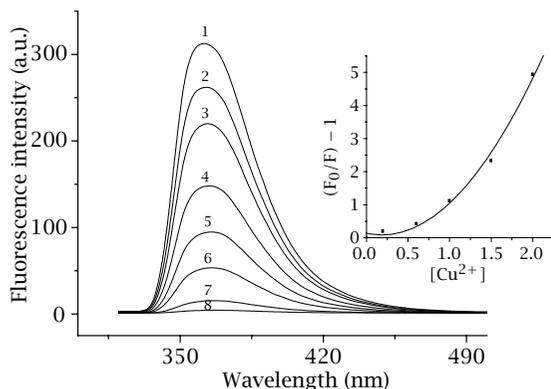


Figure 4. Fluorescence quenching of 2×10^{-5} M DHBN in MeOH in the presence of increasing concentration of Cu^{2+} ($\lambda_{\text{exc}} 310$ nm). The inset shows Stern-Volmer plot for the quenching of DHBN luminescence by Cu^{2+} .

3.4. Quenching by metal ions. The fluorescence spectra of DHBN in the presence of different concentrations of Cu^{2+} ions in methanol solution are shown in Figure 4. Similar results are obtained in the case of other ions Ag^+ , Fe^{2+} and Fe^{3+} . It has been found that increasing metal ions concentration led to progressive decrease in the emission intensity with a slight bathochromic shift of the maximum fluorescence wavelength. Quenching data for Ag^+ , Cu^{2+} , Fe^{2+} and Fe^{3+} metal ions in methanol solution were analyzed by Stern-Volmer (eq. (9)) and modified Stern-Volmer equation (eq. (10)). The results show that Stern-Volmer plot for Ag^+ metal ion and DHBN agrees nicely to the linear portion of the plot of $(F_0/F) - 1$ versus $[Q]$, indicating that fluorescence quenching is dynamic in nature in the linear part (same results are obtained for the other metals). In dynamic quenching sometimes an additional static quenching can be observed in case of higher quencher concentration. The combined quenching recognized by the upward curvature of Stern-Volmer plot (see inset of Figure 4). Linear plots of $(F_0/F - 1)/[Q]$ versus $[Q]$ are obtained from which the Stern-Volmer constants K_{sv} could be calculated. A second solution was obtained corresponding to the complex formation using eq. (8) above. The obtained linear fit of $(F_0 - F)^{-1}$

versus $[\text{metal ions concentration}]^{-1}$ according to equation (8) indicates that the stoichiometry ratio between metal ions and DHBN is 1 : 1, and from the intercept and the slope the formation constants are calculated (Table 3).

The results show significant fluorescence quenching of the methanolic solution of DHBN in presence of the four metal ions via formation of excited state complexes. Recent studies on the electronic spectroscopy of 2,2'-binaphthyl in solution, cryogenic matrix and supersonic jet showed that the molecule is planar in the excited state and $\sim 32^\circ$ out-of-plane in the ground state [1]. This geometry finding (planarity of the DHBN) favors the excited state formations of complexes with the Lewis acids studied.

Data from Table 3 indicate that the quenching mechanism of DHBN by the metal ions in methanol could be by energy transfer. Solutions of metal ions (Ag^+ , Cu^{2+} , Fe^{2+} or Fe^{3+}) containing DHBN in 1 : 1 stoichiometry have absorption transitions in the visible which overlap the fluorescence of DHBN, suggesting the possibility of energy transfer. The estimated value of critical radii are $> 10 \text{ \AA}^0$; however Förster-type dipole-dipole energy transfer is expected [11].

It is seen from Table 3 that k_q values are quite high. It has been shown that in case of strong quencher, the quenching effect is large and distinct positive deviation from Stern-Volmer plots are observed. In such cases the k_q values obtained are about two orders of magnitude higher than those obtained in the case of weak dynamic quenching [13-15]. In the present case, therefore, it may be argued therefore, that the k_q values and observed positive deviations are the results of efficient quenching due to strong and rapid interaction between the colliding species [15].

A good number of earlier works on quenching reaction have shown that polarity of the solvent medium plays an important role in the mechanism of fluorescence quenching reaction [16, 17]. It is proposed that the solvent effect is partly due to solvophobic interaction or due to stabilization of charge transfer interaction, which is associated with the occurrence of polar structures along the reaction coordinates [18-20]. Hence, the relatively high values for k_q compared to that of diffusion controlled reaction rate, is mainly due to the nature of the solvents used. In fact, in the case of strong quenching, a very rapid process may occur which not only involve the stationary diffusion process but also may have contributions from long range interactions. If the long-range interactions are present, the charge transfer process can also be assumed to be induced by the hydrogen bonding interactions. Similar conclusion has been reported in a previous study. It has been shown that aromatic hydrocarbon/ Ag^+ exciplex systems have been postulated to occur in various solvents [21]. The quenching process is due

to non-fluorescent complex followed by rapid intersystem crossing. The main contribution to the stabilization of the exciplex formed in the excited state between suitable organic electron donor and acceptor molecules such as N,N-diethyl-aniline (D) and perylene (A) is assumed to result mainly from Coulomb attraction between completely or partially separated charges in the ($A^{\cdot-}D^+$) exciplex.

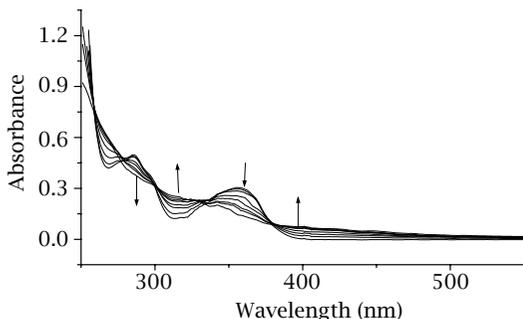


Figure 5. Effect of light irradiation on the absorption spectrum of 1,1'-2,2'-binaphthol at pH 11.4.

3.5. Photostability of DHBN. Figure 5 shows the effect of the time of illumination by polychromatic light on the absorption spectrum of alkaline (pH 11.4) aqueous solution of DHBN. It has been noticed that after 10 minutes of irradiation the absorption intensities of anionic form around 355 nm and 287 nm decrease and it concomitant with increase in the absorption of the 310 nm and 260 nm bands. This is due to oxidative transformation of DHBN resulting in the formation of secondary products similar to previous results reported in the literature in the case of simple naphthol (i.e. naphthol: hydroxy-naphthoquinone) [22]. This process is pH dependant since faster photo-oxidative transformation of DHBN is occurred in alkaline aqueous solution relative to the case of neutral aqueous solution or in acidic solution at pH 3.3. Further detailed studies are in progress.

4. CONCLUSIONS

It has been found that DHBN behaves as a weak photoacid. It shows proton transfer to water molecules upon light absorption leading to the formation of 1 : 1 water DHBN adduct. The results also show significant fluorescence quenching of the methanolic solution of DHBN in presence of the four metal ions (Ag^{1+} , Cu^{2+} , Fe^{2+} or Fe^{3+}) via formation of excited state complexes. Photosensitivity of DHBN is revealed by its fast pH-dependant photo-oxidative transformation of DHBN to secondary products.

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