

Dual fluorescence of diphenyl carbazide and benzanilide: Effect of solvents and pH on electronic spectra

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Abstract

The absorption and fluorescence spectra of benzanilide (BA) and diphenyl carbazide (DPC) in solvents of different polarities and pH have been analysed. The spectral characteristics of DPC and BA are compared with diphenyl amine molecule. In water and methanol, a dual fluorescence is observed for both DPC and BA molecules. The normal Stokes shifted emission originates from a locally excited π^* electronic state and the large Stokes shifted band is due to emission from a twisted intramolecular charge transfer (TICT) state. pH studies show that both monocations and monoanions are non-fluorescent. The excited state acidity constants determined by fluorimetric titration and Förster cycle methods, have been reported and discussed.

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1. Introduction

Studies on photophysical properties are one of the key-stones in the elucidation of the chemical behaviour and electronic orientation of organic and biomolecules [1]. The spectral shift, shape of the spectral band, Stoke's shift, etc., depend upon the geometry of the molecule in the ground and excited states and the nature and the position of functional groups in the molecule and nature of solvents [2]. In the case of biphenyl [3] S_1 state is relatively more planar than S_0 and large Stoke's shift has been attributed to this change in the geometry on excitation and broad absorption band involving overlapping of two transitions. The presence of groups like SO_2 , O, CH_2 , NH, etc. in between two phenyl rings (diaryl) systems, their behaviour is entirely different [4,5]. Several mono and bichromophoric systems of general structure M–X–M where two identical aromatic moieties (M) are joined to each other by a single bridging group (X = SO_2 , O, NH, CH_2 , CO, etc.) have been reported to have photoinduced charge transfer leading to a twisted intramolecular charge transfer (TICT) [4–6].

Multiple emission is a general phenomenon in non conjugated bichromophoric aromatic systems exhibiting conformational flexibility [7–9]. Bichromophoric systems have been used as references to study multichromophoric interactions in polymers and molecular assemblies [9–11] and have been found particularly efficient as signaling subunits in some photoresponsive when the two chromophores of ions and molecules [12]. When the two chromophores are the same, dual emission can be observed. Early studies of $C_6H_5-CH_2-NH-CH_2-C_6H_5$ and $C_6H_5-O-CH_2-O-C_6H_5$ have shown that three member alkene spacers favour excimer formation [13–15]. Since, diaryls works remarkable in solvents as well as pH, it is worthwhile to investigate diphenyl carbazide (DPC) and benzanilide (BA). In this record, DPC and BA were taken up for the study.

In general, aromatic carbonyls do not fluorescence in aprotic solvents because the lowest energy transition is of $n\pi^*$ type. However, in hydroxylic solvents, $\pi\pi^*$ becomes the lowest energy transition, leading to fluorescence activation [16,17]. The acidity dependence of the absorption and fluorescence spectra of aromatic carbonyls has revealed that carbonyls become more basic upon excitation [18]. In our present study we have selected DPC and BA with the following points in mind (i) whether the spectral charac-

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teristics of diphenyl amine (DPA) will be changed by the presence of carbonyl group (ii) whether the presence of C=O group will under (or decrease) the conjugation (iii) because

the presence of $\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—N—} \end{array}$ centres in the molecules whether $\begin{array}{c} \text{OH} \\ | \\ \text{—C=N—} \end{array}$ will be present as tautomer, and (iv) whether or not the dissociation constants for the different prototropic reactions of the respective basic or acidic centres will be affected by the presence of other basic/acidic centres in both S_0 and S_1 states. Thus, the spectral characteristics of these two molecules have been studied in solvents of different polarity and the pK_a values for the various prototropic reactions have been determined, both in the S_0 and S_1 states and discussed.

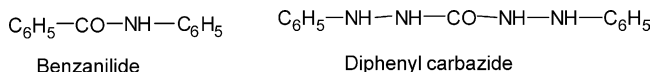
2. Experimental

Benzanilide and diphenyl carbazide (Fluka) was purified by recrystallization from ethanol and its purity was checked by similar fluorescence spectra when excited at different wavelengths. Triply distilled water was used to prepare the aqueous solutions. BDH spectrograde methanol, AR grade sulphuric acid and sodium hydroxide were used as such. Other solvents (AnalaR) were further purified by the methods described in literature [19]. A modified Hammett's acidity scale [20], H_0 solutions below pH ~ 2 (using H_2SO_4 – H_2O mixture) and Yagil's basicity scale [21], H_- for solutions above pH ~ 12 (using $NaOH$ – H_2O mixture) were employed. Absorption spectra were recorded with a HITACHI Model U-2001 spectrophotometer while fluorescence measurements were made using a JASCO FP-550 recording spectrofluorimeter. pH values in the range 2–12 were measured on an ELICO pH meter model LI-10T.

Experimental solutions were prepared by adding an aliquot of the stock solution to appropriate H_0 /pH/ H_- solutions just before taking measurements. The concentration of the resulting solution was about $\sim 10^{-5}$ M. The stock solution was prepared in methanol and the methanol content of the solution was about 2%.

3. Results and discussion

3.1. Effect of solvents



The absorption and fluorescence spectral data of diphenyl carbazide and benzanilide in various solvents are compiled in Table 1 and their fluorescence spectra are displayed in Figs. 1 and 2. The absorption spectrum is structured in cyclohexane and the structure is lost as the polarity and hydrogen bonding ability of the solvent increases. The loss of the structure is due to increased solute–solvent interactions. The ϵ_{max} of the absorption bands are high. These results imply that

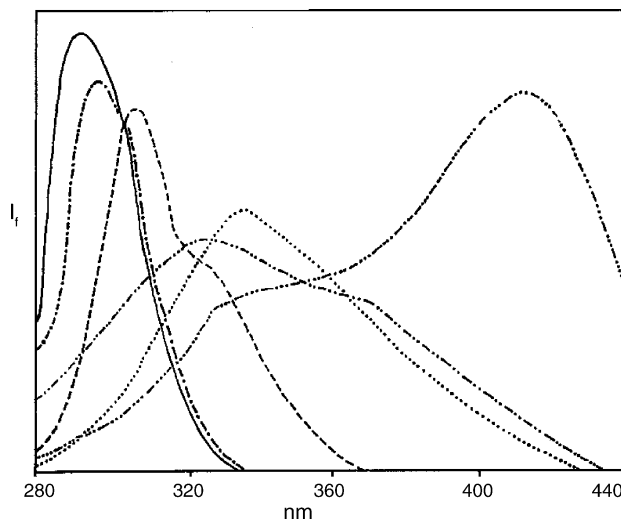


Fig. 1. Fluorescence spectra of DPC in selected solvents at 303 K, concentration $\approx 4 \times 10^{-5}$ mol dm $^{-3}$. 1: (—) cyclohexane, 2: (---) ethyl acetate, 3: (···) acetonitrile, 4: (-·-·-) methanol, 5: (···) *t*-butyl alcohol, 6: (-·-·-) water.

this band is attributed to the (π, π^*) transition of the benzene ring. The spectral shifts observed in the absorption spectrum of both molecules in protic and aprotic solvents are consistent with the characteristic behaviour of groups $>\ddot{\text{N}}\text{H}$ groups [4,5].

Solvents can interact either with carbonyl or $>\ddot{\text{N}}\text{H}$ moiety. The interaction of solvents with the lone pair of the $>\ddot{\text{N}}\text{H}$ moiety will lead to a blue shift and the solvents interaction with hydrogen atom of the $>\ddot{\text{N}}\text{H}$ moiety or lone pair of the carbonyl will lead to a red shift both in absorption and fluorescence. Solvatochromic shifts of DPC and BA reveals that the absorption maximum are red shifted from cyclohexane

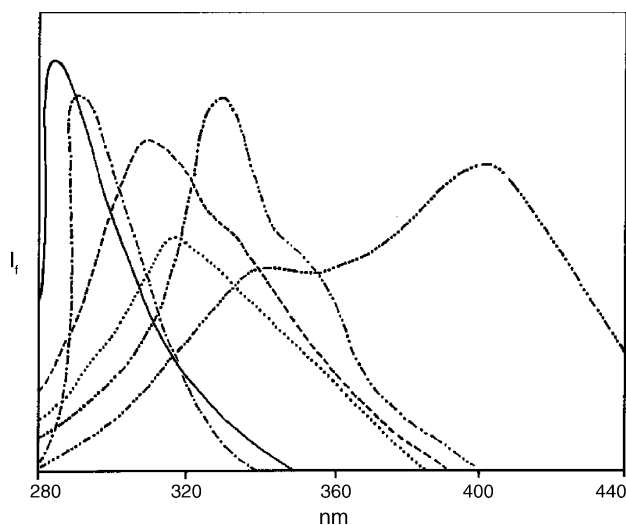


Fig. 2. Fluorescence spectra of BA in selected solvents at 303 K, concentration $\approx 4 \times 10^{-5}$ mol dm $^{-3}$. 1: (—) cyclohexane, 2: (---) ethyl acetate, 3: (···) acetonitrile, 4: (-·-·-) methanol, 5: (···) *t*-butyl alcohol, 6: (-·-·-) water.

Table 1

Absorption and fluorescence spectral data (nm) of diphenyl carbazide (DPC), benzanilide (BA) and diphenyl amine (DPA) in different solvents and pH

No.	Solvents	DPC			BA			DPA [22]		
		λ_{abs}	$\log \varepsilon$	λ_{flu}	λ_{abs}	$\log \varepsilon$	λ_{flu}	λ_{abs}	$\log \varepsilon$	λ_{flu}
1	Cyclohexane	277.0	sat	292	261.6	4.64	284	282	4.30	327
		261.6			254.4	4.63				
		248.8			247.2	4.64				
2	Diethyl ether	281.0	3.70	295	263.6	4.10	294	283	4.40	337
		233.0	4.48							
3	Dioxane	281.0	3.62	295	263.6	4.20	294	285	4.44	340
		232.6	4.46							
4	Ethyl acetate	278.4	3.78	296	265.0	4.19	298			
5	Methyl acetate	278.8	3.80	296	265.2	4.30	298			
6	Dichloro methane	276.6	3.78	296	262.0	4.10	297			
		233.2	4.40							
7	1,2-Dichloro methane	278.4	3.76	296	262.0	4.10	297			
		232.6	4.44							
8	Acetonitrile	281.0	3.76	310	263.2	4.08	310	283	4.31	342
		232.8	4.48	325			340			
9	<i>t</i> -Pentyl alcohol	278.2	3.52	310	263.0	4.30	310			
		231.2	4.48							
10	<i>t</i> -Butyl alcohol	278.4	3.55	320	264.0	4.28	315	285	4.45	347
		231.6	4.46							
11	2-Butanol	277.8	3.56	320	262.0	4.20	315			
		231.8	4.42							
12	2-Propanol	278.6	3.54	325	262.6	4.10	320			
		232.0	4.50							
13	1-Butanol	278.4	3.56	325	262.6	4.00	325			
		232.4	4.50							
14	Ethanol	278.8	3.82	326	263.2	4.20	327			
		232.0	4.40							
15	Methanol	276.4	3.82	326	261.4	4.28	330	283	4.54	348
		232.4	4.48	366			353			
16	Water (neutral)	276.0	3.74	325	256.0	3.78	340	279		363
		228.8	4.30	410			400			
17	Monocation	274.0		–	260		–	255	2.73	315
		225.0								
18	Monoanion	285		–	266.4		–	298		
19	Dianion	–		405	–		420			

to ethanol but blue shifted in water. The red shift observed in the absorption spectra in going from cyclohexane to acetonitrile is due to the dispersive interactions and the most proton accepting nature of acetonitrile. However, methanol and water can act as proton donor solvents and thus produce a blue shift in the absorption spectra. This shows that the interaction of the $\text{>}\ddot{\text{N}}\text{H}$ moiety is large when compared to the carbonyl group. So the above shifts are mainly due to interactions of the solvents with the $\text{>}\ddot{\text{N}}\text{H}$ moiety of DPC and BA. In all solvents the absorption maxima of DPC and BA are blue shifted to diphenyl amine [22] but red shifted to benzophenone (255 nm) [23]. It suggests that the lone pair of electrons on the amido nitrogen atom is shared by both

the conjugated systems and thus the resonance effect of the amido nitrogen lone pair is not contributing completely to the benzene rings. Fluorescence spectra of DPC and BA are regularly red shifted from cyclohexane to water. A continuous red shift observed in the fluorescence spectra of both the molecules with an increase in the polarity of the solvents indicates the increase in the delocalization of the lone pair of electrons of the $\text{>}\ddot{\text{N}}\text{H}$ moiety throughout the aromatic ring in the S_1 state. Hence, the hydrogen acceptor interaction of the solvents is predominant in the excited singlet state.

In order to confirm this we used Reichardt's [24] solvent parameter $E_{\text{T}}(30)$ and $f(D, n)$ [25] solvent parameter and compared with Stoke's shifts. These parameters have been used by

several authors to correlate the molecular spectroscopic properties with solvent polarity [26]. The variation of Stoke's shift with the solvent polarity can be represented by the Lippert [25] equation

$$\Delta\bar{\nu}_{ss} = \frac{2(\mu_e - \mu_g)^2}{hca^3} f(D, n) + c \quad (1)$$

where $\bar{\nu}_{ss}$ is the Stoke's shift ($\bar{\nu}_{ss} = \bar{\nu}_{abs} \max - \bar{\nu}_{ss} \max$), μ_g and μ_e are respectively the ground and excited state dipole moments of the solute molecule, ' a ' is the Onsager cavity radius and $f(D, n)$ is the Onsager polarity function defined by the equation

$$f(D, n) = \frac{D - 1}{2D + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

where ' D ' is the static dielectric constant, ' n ' is the refractive index of the solvent and ' c ' is a constant. The other solvent polarity parameter used as an empirical parameter $E_T(30)$; this is based on the spectral shifts of N-phenolbetaine [24] in different solvents of varying polarity and hydrogen bonding.

In this study, the Stoke's shifts of the DPC and BA molecules determined in solvents of varying polarity have been correlated with the $E_T(30)$ and $f(D, n)$ parameters (Figs. 3 and 4). The Stoke's shift in various solvents along with the $E_T(30)$ and $f(D, n)$ values are given in Table 2. The increase in Stoke's shift from cyclohexane to water are found to be more in accordance with the $E_T(30)$ than with the $f(D, n)$ values. The $E_T(30)$ parameter incorporates both hydrogen bonding and solvent polarity effects whereas the $f(D, n)$,

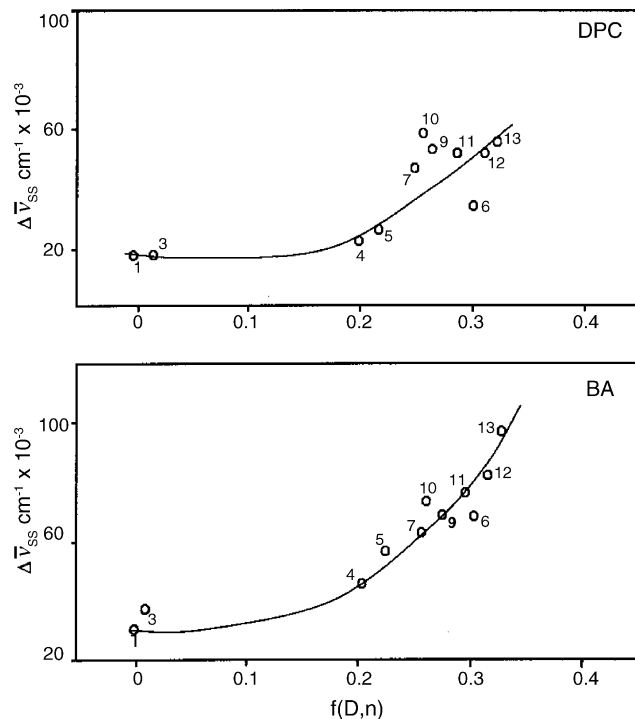


Fig. 4. Plot of Stoke's shifts (cm^{-1}) of DPC and BA vs. $f(D, n)$ solvent parameters (numbers refer to Table 2).

n) parameters represents only solvent polarity effects. Since hydrogen bonding interactions are predominant in the solvatochromic shifts, $E_T(30)$ gives better correlation than $f(D, n)$ values.

3.2. Dual emission

Figs. 1 and 2 shows the fluorescence spectra of DPC and BA in various solvents. In contrast to the weak solvent dependent of absorption maximum, the emission properties of DPC and BA are strongly solvent dependent indicating a possibility of a change in the character of the electronic state. Both molecules gives one emission maximum in non-polar solvent whereas a dual luminescence in methanol and water. Among the two bands one occurs in shorter wavelength region (SW) around 330 nm and the other in longer wavelength region (LW) around 400 nm. The intensity of LW band is more in water. The LW emission more red shifted in water than methanol. It should also be pointed out, the fluorescence intensity of the LW band increases with increase in the $\lambda_{excitation}$ 260 to 300 nm. This may be the extended π -conjugation would induce an excited state resonance contribution of the carbonyl group to the benzene ring resulting in the increased polarity to facilitate the interaction with polar solvents [27].

Several mechanisms have been proposed to account for this anomalous red shifted emission. For example, Lippert et al. [28] have suggested the reversal of S_1 and S_2 states because of the solvent interaction the excimer formation proposed by Khalil et al. [29] a proton transfer in the excited state [30],

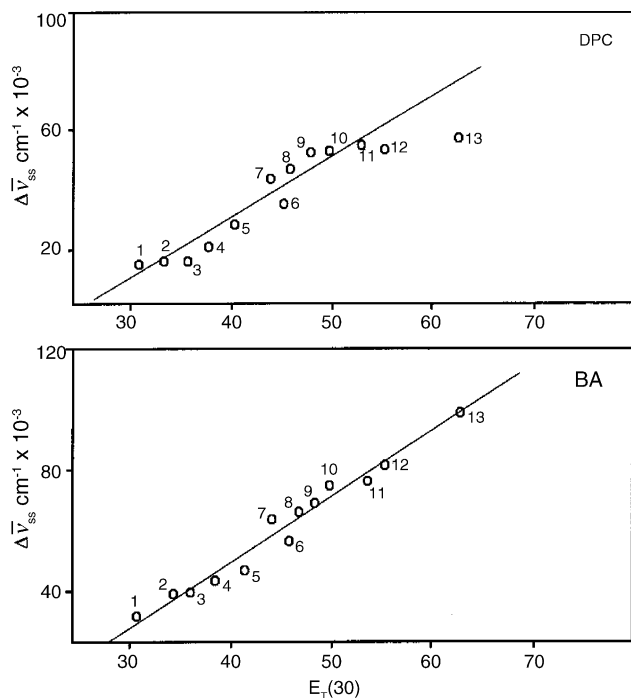


Fig. 3. Plot of Stoke's shifts (cm^{-1}) of DPC and BA vs. $E_T(30)$ solvent parameters (numbers refer to Table 2).

Table 2

Stoke's shifts observed for DPC and BA in different solvents with $E_T(30)$ and $f(D, n)$ values

No.	Solvents	DPC $\Delta\bar{\nu}_{ss}$ (cm ⁻¹)	BA $\Delta\bar{\nu}_{ss}$ (cm ⁻¹)	$E_T(30)$	$f(D, n)$
1	Cyclohexane	1855	3015	31.2	-0.0004
2	Diethyl ether	1689	3923	34.6	—
3	Dioxane	1689	3923	36.0	0.021
4	Ethyl acetate	2136	4179	38.1	0.201
5	Dichloro methane	2359	4497	41.1	0.218
6	Acetonitrile	3329	5736	46.0	0.306
		5006	8582		
7	<i>t</i> -Butyl alcohol	4669	6133	43.9	0.245
8	2-Butanol	4747	6422	47.1	—
9	2-Propanol	5124	6860	48.6	0.274
10	1-Butanol	5150	7312	50.2	0.263
11	Ethanol	5193	7413	53.7	0.289
12	Methanol	5167	7953	55.5	0.309
		8520	9927		
13	Water	5557	9651	63.1	0.320
		11842	14063		
Correlation coefficient					
	$\Delta\bar{\nu}_{ss}$ vs. $E_T(30)$	0.9225	0.9848		
	$\Delta\bar{\nu}_{ss}$ vs. $f(D, n)$	0.6816	0.7990		

complex formation with the solvent [31] and the formation of exciplex with free electron pairs of the solvents [32]. As suggested by Rettig [33] the results obtained in our present work can be explained as follows: (i) hydrogen bond formation between the protic solvents and electron donor group facilitates the formation of the TICT state in the S_1 state [34,35] and (ii) hydrogen bond formation between the protic solvent and the electron withdrawing group will lead the electron withdrawing group to become coplanar with the benzene ring [36]. In other words, this hydrogen bonding seems to make the migration of electron density from benzene ring to the electron withdrawing group more facile. Like Cazeau-Dybroca et al. [35] we have also observed a red shifted fluorescence band at room temperature when the amount of water was increased in the aprotic/non-polar solvents, i.e. the fluorescence spectrum in the cyclohexane solution is changed significantly on addition of water/methanol showing a dual emission (Fig. 5). It is noted that in contrast to other polar solvents, dual emission in water is further red shifted to 400 nm (compared to methanol 360 nm) even though the maximum of the normal emission around 330 nm is nearly independent of the hydrogen bonding ability of solvents. This dual fluorescence behavior was not observed for DPA which shows only normal fluorescence [22]. These observations suggest that the dual emission DPC and BA in water/methanol seems to be influenced by the enhanced intermolecular hydrogen bonding of the carbonyl group in the excited state. Supporting this the fluorescence spectrum in the aqueous solution is changed significantly on addition of dioxane, showing a dual emission and an isoemissive point in dioxane–water mixture (Fig. 6).

It is also noted that the fluorescence spectrum of DPC and BA in water shows a different feature depending on the excitation wavelength (260 and 300 nm) (Fig. 7). In the case of

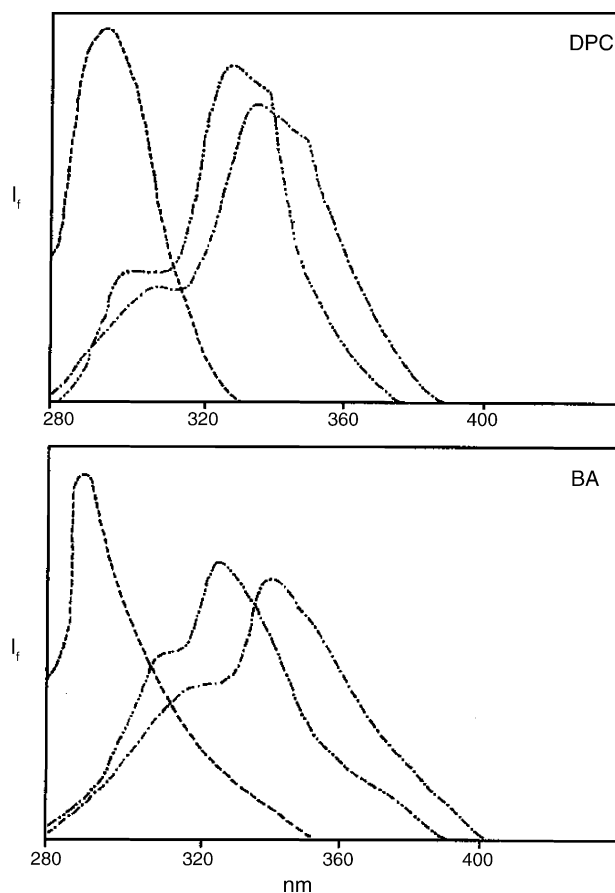


Fig. 5. Fluorescence spectra of DPC and BA in cyclohexane with 1% methanol and 1% water. (—) cyclohexane, (---) cyclohexane with methanol and (-.-) water.

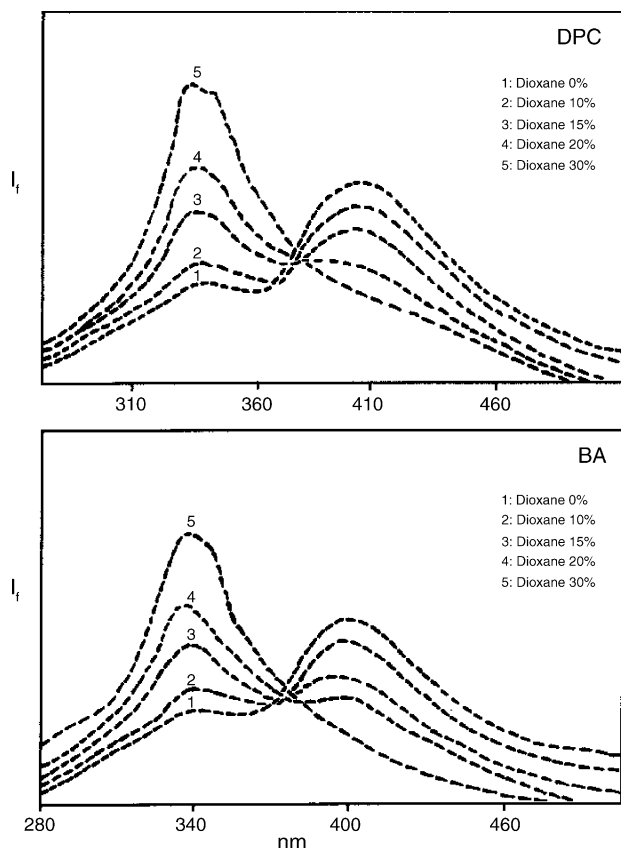


Fig. 6. Fluorescence emission spectra of DPC and BA in water–dioxane mixed solvents. The excitation wavelength DPC = 280 nm; BA = 265 nm.

260 nm excitation, the emission spectrum exhibits the dual emission (330 and 400 nm). However, with an excitation at 280 nm or 300 nm the dual emission at 400 nm is dominant. This excitation wavelength dependence of the dual emission is similar to the typical red edge effect [36] observed in the TICT fluorescence which is usually observed under the restrictive molecular mobility environment like the polymer system [37]. Further, Modiano et al. [6] reported whenever

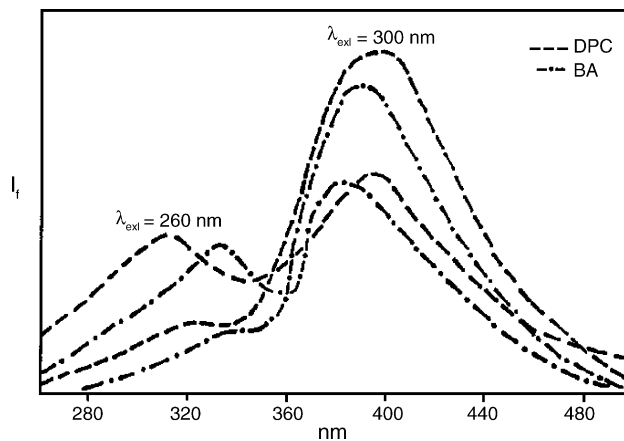


Fig. 7. Fluorescence emission spectra of DPC and BA measured with different excitation wavelengths 260, 300 nm in aqueous solutions.

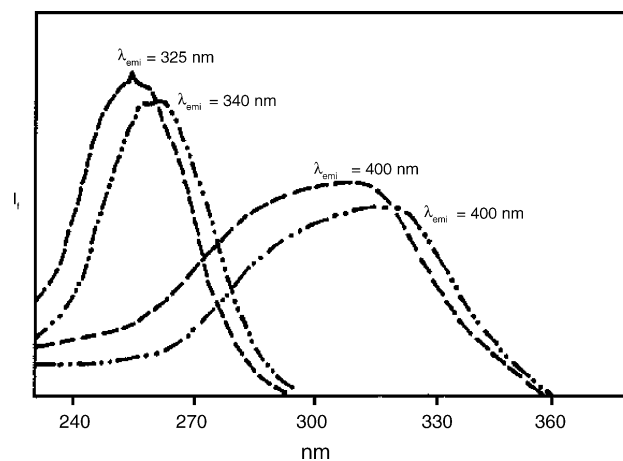


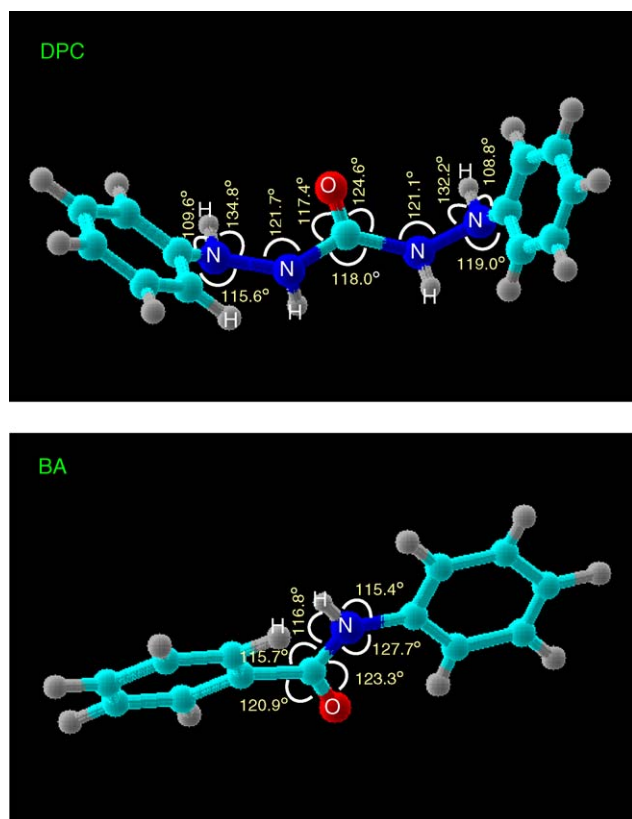
Fig. 8. Fluorescence excitation spectra of DPC and BA in aqueous solutions; DPC: 325, 410 nm; BA: 340, 400 nm emission bands.

two phenyl rings are separated by the groups like SO_2 , CH_2 , CO , NH , etc. they form a TICT state. Thus it can be speculated that the enhanced 400 nm emission should originate from the TICT state. The TICT emission is observed in methanol and water suggesting that the hydrogen bonding plays the major role in the TICT emission [4]. Supporting this implication, the excitation spectra exhibit the monitoring wavelength dependence as shown in Fig. 8. The excitation spectrum for the 400 nm emission is distinctly different from that for the 330 nm emission. Further the AM1 results also suggest that the TICT state may be formed in both molecules (Scheme 1).

3.3. Effect of proton concentration

The absorption and fluorescence spectra of both molecules have been studied in the $\text{H}_0/\text{pH}/\text{H}_-$ range from -5 to 16.0 . The relevant data are compiled in Table 1. Absorption and fluorescence spectra of various prototropic species are shown in Figs. 9 and 10, respectively. When the pH is decreased from 7, the absorption maximum of the long wavelength band is slightly blue shifted in DPC but in BA a red shifted spectrum is observed. This indicates the formation of a monocation obtained in DPC and BA by the protonation of the $>\text{NH}$ moiety. No further change in absorption spectrum is noticed even at $\text{H}_0 - 5$ in both cases.

The absorption spectra of DPC and BA do not change when the basicity is increased until pH 13 then a regular red shift is noticed and it is continued even up to $\text{H}_- 16$ the highest basic conditions used. The red shifted spectra may be due to the formation of a monoanion but the isosbestic points were not constant in both cases. These behaviour is generally observed in aromatic amino compounds [4,5]. When the pH is decreased from 7, the fluorescence intensities of both the emission bands of the neutral species decreased without any change in the $\lambda_{\text{max}}^{\text{flu}}$; (i.e.) the fluorescence maximum (410, 325 nm in DPC and 410, 340 nm in BA) are quenched. The above results indicates that in each case mono-



Scheme 1. The proposed TICT structure of DPC and BA (MOPAC AM1 6.12 Version, PC model).

cations formed by the protonation are non-fluorescent. When the pH is increased from 7, the quenching of fluorescence starts from pH ~ 10 in both cases owing to the formation of monoanion. This is consistent with the earlier results that monoanion formed by deprotonation of group in general are non-fluorescent [4,5]. At very high basicity ($H_- 16$), spectra red shifted in BA and blue shifted in DPC are obtained. This behaviour is also exhibited by many aromatic compounds and this is reported to be due to the formation of dianion [4,5]. The formation of dianion is not complete even at $H_- 16$ at the highest basic conditions used.

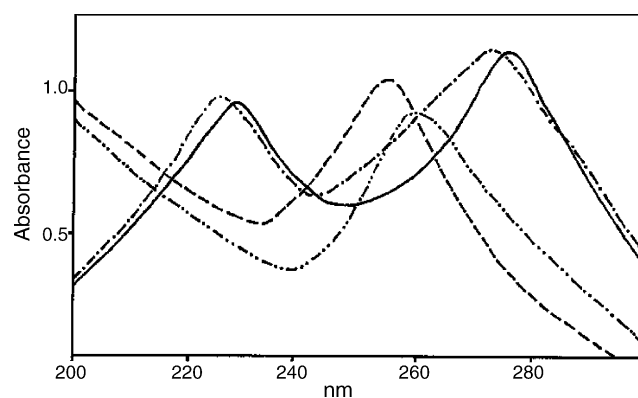


Fig. 9. Absorption spectra of different prototropic species of DPC: (—) neutral, (---) monoanion; BA: (···) neutral, (-·-·) monoanion.

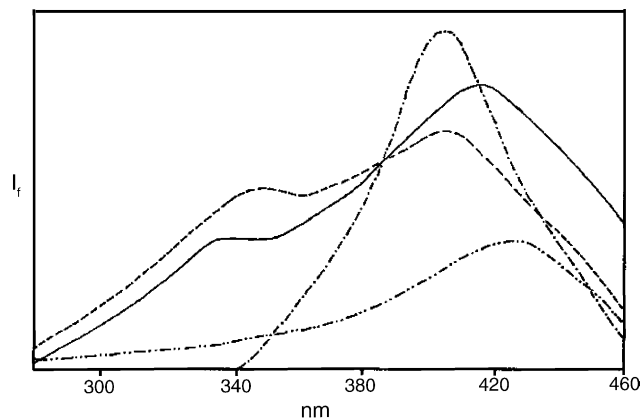


Fig. 10. Fluorescence spectra of different prototropic species of DPC: (—) neutral, (---) dianion; BA: (···) neutral, (-·-·) dianion.

The proton transfer reactions are explained as follows: keto-enol tautomerism is observed whenever a labile hydrogen atom is present in the α or γ position of a carbonyl group [38,39] and the keto form is stabilized in polar solvents [40] whereas the enol form in non-polar solvents. A similar trend is also observed in both cases. The increase in the Stoke's shift of DPC and BA in acetonitrile further indicated that the increase in dipole moment of these molecules upon excitation is large. The increase in the Stoke's shift in polar solvents is quite high. This is due to the presence of keto form in polar solvents. Further more the pK_a (pK_a^*) values for the monocation–neutral and neutral–monoanion equilibria are consistent with DPA molecule [22]. The ground state pK_a value for the deprotonation of imino group is around $H_- 15$ and is decreased or increased further if an electron withdrawing or electron donating group respectively is substituted in the diphenylamine moiety. The pK_a value around 14 observed for above kind of reaction in DPC and BA clearly indicates that monoanion formed in S_0 state is from the deprotonation of the imino group [40].

The ground state pK_a values for various prototropic reactions were calculated spectrophotometrically and are listed in Table 3. The pK_a for the neutral–monoanion equilibria for all these molecules could not be determined because the absorption maxima in each case was continuously red shifted even at the conditions of highest basicity. The excited state pK_a (pK_a^*) values for the different proton transfer reactions of

Table 3
 pK_a values of different prototropic equilibria of DPC and BA

Equilibria	pK_a (abs)	pK_a^* (FT)	Förster cycle method pK_a^* (abs)
DPC			
Monocation \rightleftharpoons neutral	0.26	0.1	−0.37
Neutral \rightleftharpoons monoanion	>14	13.4	—
BA			
Monocation \rightleftharpoons neutral	0.50	0.2	−0.60
Neutral \rightleftharpoons monoanion	>14	13.2	—

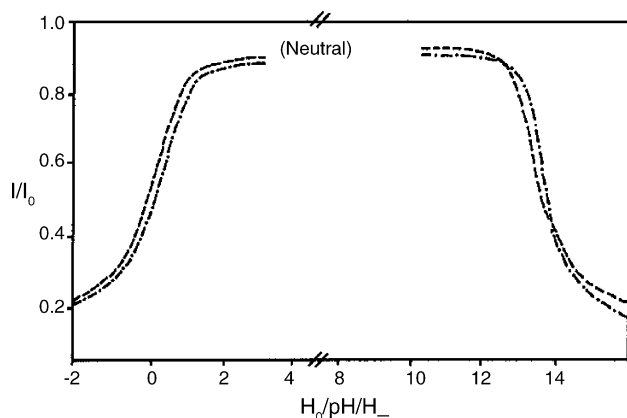


Fig. 11. Plot of I/I_0 vs. $H_0/pH/H_-$ of the various prototropic species of (---) DPC and (- - -) BA.

these molecules were calculated with the help of fluorimetric titration (FT) as well as with the help of Förster cycle methods (Table 3). The excited state pK_a^* values were obtained by FT (Fig. 11) by the quenching curve. Although there is a trend indicating that the imino group becomes less basic on excitation, the difference in the ground and excited singlet state is not that large, as it is normally observed in aromatic amino compounds [39–41]. In reality the pK_a values in the excited singlet state are closer to the ground state values, indicating that the lifetimes of the species are very short and that the prototropic equilibria are not well established in the excited singlet state. The Förster cycle pK_a^* (abs) values reveal that the molecules becomes less basic on excitation. The differences between the values obtained using fluorimetric titration and Förster cycle are very small. This may be due to (i) the difference in solvent relaxation of the species in the ground and excited states. For Förster method, the absorption spectra have been used and (ii) the fact that band maximum is used instead of the 0–0 transitions.

In the case of neutral \rightleftharpoons monoanion equilibrium the excited state pK_a^* values for both molecules could not be determined accurately as the isosbestic points are not constant. Since the monocation and monoanion are non-fluorescent, Förster cycle method using fluorescence maximum is also not applicable thus absorption spectra have been used. But the pK_a^* values from the quenching curves obtained by the formation of non-fluorescent monoanion shows that the $>NH$ group becomes more acidic in the S_1 state. The pK_a^* value for the monoanion \rightleftharpoons dianion equilibrium could not be evaluated by fluorimetric titrations as the changes involved in the formation of this species is not complete even at H^- 16 i.e. the highest basicity used.

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