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Time resolved spectroscopy of 2-(dimethylamine)fluorene. Solvent effects and photophysical behavior

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ABSTRACT

The effect of different solvents on the fluorescent properties of 2-(dimethylamine)fluorene (DAF) were studied. In aprotic solvents we detected a strongly emissive intramolecular charge transfer (ICT) state that decayed by intersystem crossing to triplet. In proton-accepting solvents DAF exhibits in the excited state an intramolecular proton transfer.

An ionized species is postulated, which simultaneously twists to a rotated conformation in the excited state. Thus, the specific solvent interactions supplement but do not replace the twist mechanism and accompany the charge transfer accepted as the prerequisite for twisted intramolecular charged transfer (TICT) state formation.

1. Introduction

Proton transfer processes in the excited state have become of great interest because of their chemical and biological relevance. Proton transfer effects in the ground and electronic excited states have been extensively investigated [1,2]. The two steps, ionization and dissociation, are influenced in different ways by solvents [3]. The ionization equilibrium is affected by the acidity or basicity of the solvent, dielectric constant, and the ability of the solvent to solvate the species. For uncharged acids a strong influence of the dielectric constant on the ionization equilibrium is expected. On the other hand, the ionization power of a solvent depends on its ability to behave as an electron pair acceptor (EPA) or donor (EPD). Thus, a good ionizing solvent must not only posses a high dielectric constant, but also be a good EPD or EPA solvent. On the other hand, solvents with sufficiently high dielectric constant will be capable of reducing the strong electrostatic attraction between ions with opposite charge and the ion pairs can dissociate into free solvated ions.

Luminescent charge-separated systems provide a powerful tool for the study of systems displaying charge separation, because the internal and environmental influences modify this luminescence in a characteristic way, yielding detailed information on thermodynamic, kinetic, and other photophysical and even photochemical properties of such species. Inter- and intra-molecular charge-transfer phenomena have been the subject of considerable investigations referred to numerous essential problems in chemical, biological and some physical processes. Recently, particular attention has been paid to intramolecular charge transfer (ICT) states with twisted conformation (TICT). The TICT states are energy stabilized by solvation in polar solvents. A specific solvent interaction by overlapping electron clouds, however, should lead to stabilization energies that depend on properties other than the polarity of the interaction partners. This effect is reported for a wide range of molecules such as dialkylamine aromatics, arylamine aromatics [4], amides [5], nitroaromatics [6], diarylindenes [7], sulfones [8], aryldisilanes [9], and biaryls [10–12]. Recent discussions in regarding the TICT stages suggest nonorthogonal geometry of the CT states especially for molecules which do no behavior as the TICT state model [13]. The TICT states are energy stabilized by solvation in polar solvents. A specific solvent interaction by overlapping electron clouds, however, should lead to stabilization energies that depend on properties other than the polarity of the interaction of the interaction partners. This possibility supplements but does not replace the twist mechanism and accompanies the charge transfer accepted as the prerequisite for TICT-state formation.

This present work was designed to study the excitation and emission spectra, the lifetimes and quantum yields of DAF, in solvents of different polarities and basic properties. We hypothesized that DAF might have a strong emissive ICT state that competes with a nonemissive twisted ICT excited state, where the amino group is rotated with regard to the fluorene moiety. We hopped to test this hypothesis by studying the photophysical properties of DAF in aprotic and protic solvents to determine how the polarity and the specific solute–solvent interactions act upon the deactivation of DAF.

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2. Experimental

2.1. Reagents

The 10 mM stock solution of DAF analytical grade (Sigma–Aldrich Química S.A., Spain) was prepared in 1,4-dioxan. All other solvents were reagent grade (Merck).

2.2. Spectra fluorescence and lifetime

Fluorescence and fluorescence-lifetimes were measured with an Aminco SLM 48000S spectrofluorimeter. The instrumentation is described in detail elsewhere [14]. The spectra were obtained by using a 1-nm scanning interval. The excitation monochromator entrance and exit slits, were set to 16 nm and 8 nm, respectively. Entrance and exit slits of the emission monochromator were both 8 nm. Fluorescence-lifetimes were determined by using multifrequency-modulated excitation beams. A scattering-solution of glycogen was the reference. Measurements of the phase and modulation used the "100-average" mode in which each measurement was the average of 100 samplings. The excitation monochromator was set at 307 nm. We used the band pass interference filter to eliminate all wavelengths below 340 nm. This filter was placed in the sample-emission receiving channel. Heterogeneity analysis [15] was performed with SLM software, and used fluorescence-lifetime data recorded at six modulation frequencies.

The procedure used to calculate fluorescence quantum yields (ϕ) is described by Marsh and Lowey [16] and is based on the relationship:

$$\phi_{\mathrm{DAF}} = \frac{(\text{area under emission spectrum of DAF})}{(\text{area under emission spectrum of anthracene})} \times \frac{0.21 A_{307}\text{anthracene}}{A_{307}\text{DAF}} \qquad (1)$$

Radiative rates (k_r) were derived from fluorescence quantum yield and lifetime of ICT emission (ϕ_{ICT} and τ_{ICT}, respectively).

$$k_r = \frac{\phi_{\mathrm{ICT}}}{\tau_{\mathrm{ICT}}} \qquad (2)$$

The rate constant k_{nr} for nonradiative decay was evaluated from ϕ_{ICT} and the rate constant k_r

$$k_{nr} = k_r(\phi_{\mathrm{ICT}}^{-1} - 1) \qquad (3)$$

Chang and Cheung [17] proposes a model to correct the solvent polarity effect on nonradiative decay in which k_{nr} is modified as follows:

$$k_{cor} = l_{nr} \exp\left(-\frac{\beta[E_T(30) - 30]}{RT}\right) \qquad (4)$$

which k_{nr} is given by

$$k_{nr} = k_{nr}^{o} \exp\left(\frac{\beta[E_T(30) - 30]}{RT}\right) \exp\left(-\frac{E_B^{o}}{RT}\right) \qquad (5)$$

$$\ln k_{nr} = B' + \frac{\beta}{RT}[E_T(30)] \qquad (6)$$

If the corrected nonradiative rates (k_{cor}) tend to increase or decrease, several other factors not yet considered might be involved. A good correlation between k_{nr} and $E_T(30)$ will occur if k_{cor} values are randomly distributed within the experimental limits of uncertainty.

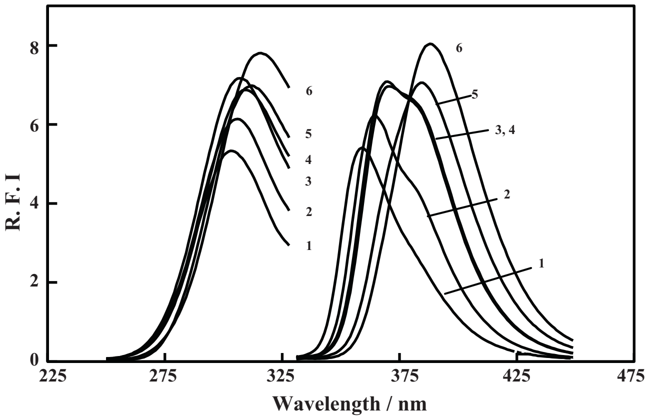

Fig. 1. Excitation and emission spectra of DAF in a serie of aprotic solvents: (**1**) hexane, (**2**) diethyl ether, (**3**) THF, (**4**) ethylacetate, (**5**) N,N-dimethylacetamide, and (**6**) dimethyl sulfoxide.

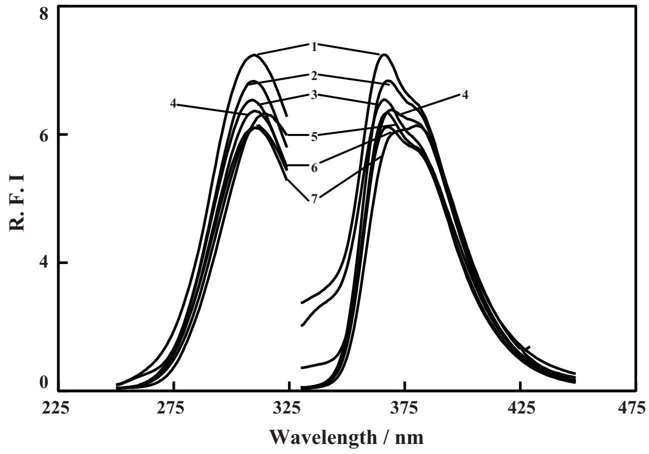

Fig. 2. Excitation and emission spectra of DAF in a serie of protic solvents: (**1**) 1-pentanol, (**2**) cyclohexanol, (**3**) 1-propanol, (**4**) 1-butanol, (**5**) 1-hexanol, (**6**) ethanol, and (**7**) methanol.

3. Results and discussion

3.1. Fluorescence spectra

Fig. 1 shows the fluorescence spectra, a single band was observed for DAF in hexane at 359 nm. Both wavelength and intensity of the emission were sensitive to the solvent. In weak or moderately polar solvents the second fluorescent band is absent or can be hardly detected. The presence of a second weak band in such solvents can be inferred from the increased fluorescence band half-widths. Only solvents with high polarity produce a readily discernible long-wavelength band. In protic solvents, DAF showed easily observable multiple fluorescent bands (Fig. 2) and reduced fluorescence yield. Aqueous media cause the greatest reduction in fluorescence yield (ϕ = 0.43–0.12) and the greatest red shift to 393 nm.

3.2. Polarity solvent effects

Table 1 shows the variation of emission properties of DAF as a function of solvent polarity $E_T(30)$ of a series of aprotic solvents (hexane, diethyl ether, dioxane, tetrahydrofuran, ethylacetate, N,N′-dimethylacetamide and dimethylsulfoxide). With a rise in polarity, the lifetime and radiative constant increased, the nonradiative constant decreased and the emission maximum shifted towards the red. In hexane an anomalous high k_r value was

Table 1
Photophysical properties of DAF in aprotic solvents as a function of the solvent polarity [$E_T(30)$].

Solvent	$E_T(30)$ (kcal mol^{-1})	λ_{exc} (nm)	λ_{em} (nm)	τ (s^{-1}) (ns)	ϕ	10^{-7} k_r (s^{-1})	10^{-8} k_{nr} (s^{-1})
Hexane	31.0	303	359	2.91	0.25	8.59	2.58
Diethyl ether	34.5	305	364	4.02	0.31	7.71	1.72
Dioxane	36.0	310	369	4.68	0.38	8.12	1.32
Tetrahydrofuran	37.4	310	371	4.71	0.39	8.28	1.30
Ethylacetate	38.1	307	370	4.78	0.40	8.37	1.26
N,N′-dimethyl acetamide	43.7	312	385	4.80	0.40	8.33	1.25
Dimethyl sulfoxide	45.1	316	388	4.84	0.42	8.68	1.20

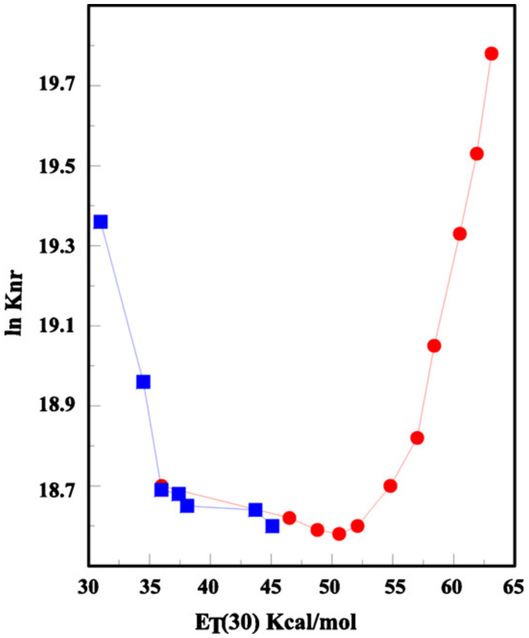

Fig. 3. Effect of solvent polarity on the nonradiative rates of DAF in dioxane:water mixtures (●), and aprotic solvents (■).

obtained. In Fig. 3 the ln k_{nr} against solvent polarity [$E_T(30)$] are plotted. Careful examination of the results indicated two types of solvent effects, one in nonpolar solvents and two in polar solvents, above $E_T(30) = 36$ kcal mol^{-1}. The apolar band is more strongly influenced by polarity than the polar band.

A simple evaluation on solvatochromism is provided by the Lippert–Mataga equation [18,19]. The linearity of the Lippert–Mataga plot can be regarded as evidence for the dominant importance of general solvent effects in the spectral shifts; however, specific solvent effects lead to nonlinear plots. As can be seen in Fig. 4 the experimental results do not allow the linear relationship. The change in slope is observed between aprotic and the more basic protic solvents (water, methanol, ethanol and butanol). The nonlinear behavior could be explained by an specific effect of the more basic solvents. A linear relationship between the Stokes shift and the solvent polarity parameter Δf has been established in the region of aprotic solvents, least-squares analysis of the data (Table 1) fitted to a line (correlation coefficient = 0.8553) with a slope of 2809.

Table 2 shows the emission properties of DAF in a series of protic (hydrogen bonded) solvents (1-pentanol, cyclohexanol, 1-propanol, 1-butanol, 1-hexanol, ethanol, methanol and water). In protic solvents low quantum yields nearly independent of polarity were observed, water was most effective in inhibiting fluorescence. Fig. 4 shows the solvatochromic plot for the more basic protic solvents (water, methanol, ethanol and butanol), the data (Table 2) were fitted to a line (correlation coefficient = 0.8452) with a slope of 36639.

The excitation and emission spectra of DAF were measured for a series of dioxane:water mixtures ranged between 0% and 100% dioxane (Fig. 5). Table 3 shows the variation of photophysical properties of DAF as a function of solvent polarity $E_T(30)$, in these mixtures. It is readily seen that with an increase in polarity, ϕ and τ initially increased to a maximum and then decreased slightly. At $E_T(30)$ above 55 kcal mol^{-1}, a rise in polarity caused a marked decrease of both ϕ and τ. The emission maximum, however, monotonically shifted towards the red when the polarity was increased. Addition of low concentrations of water, which were too small to alter the bulk properties of the solvent, resulted in substantial spectral shifts and increased the intensity of the initial spectrum. The addition of high concentrations of water (from 20% to100%), which can to alter the bulk properties of the solvent, led to a progressive decrease in the fluorescence intensity and a new maximum shifted to the red. The appearance of this new spectral component is a characteristic feature of specific solvent effects.

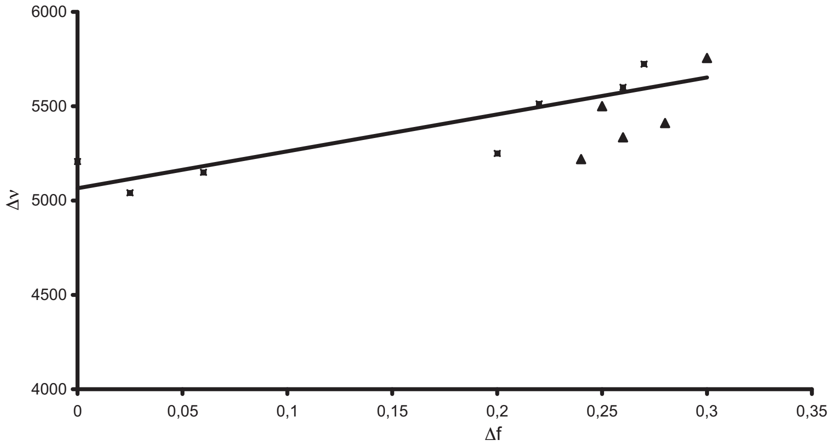

Fig. 4. Solvatochromic plot of DAF in aprotic (▿) and protic (●) solvents.

Table 2
Photophysical properties of DAF in a series of protic solvents as a function of the solvent polarity [$E_T(30)$].

Solvent	$E_T(30)$ (kcal mol^{-1})	λ_{em} (nm)	τ (s^{-1}) (ns)	ϕ	10^{-7} k_r (s^{-1})	10^{-8} k_{nr} (s^{-1})
1-Pentanol	46.5	365[a]–380	3.61	0.19	5.26	2.24
Cyclohexanol	46.9	370[a]–380	4.03	0.22	5.46	1.94
1-Propanol	48.4	367[a]–380	3.95	0.21	5.31	2.00
1-Butanol	48.5	369[a]–381	3.80	0.19	5.00	2.13
Ethanol	51.9	370[a]–380	3.80	0.20	5.27	2.10
1-Hexanol	48.8	367[a]–380	4.37	0.22	5.04	1.79
Methanol	55.4	371[a]–380	3.74	0.20	5.35	2.14
Water	63.1	393	2.26	0.12	5.31	3.89

[a] Wavelength of maxima intensity.

Table 3
Photophysical properties of DAF in dioxane:water mixtures as a function of the solvent polarity [$E_T(30)$].

% Dioxane	$E_T(30)$ (kcal mol^{-1})	λ_{exc} (nm)	λ_{em} (nm)	τ (s^{-1}) (ns)	ϕ	10^{-7} k_r (s^{-1})	10^{-8} k_{nr} (s^{-1})	10^{-6} k_{cor} (s^{-1})
100.0	36.0	310	369	4.68	0.38	8.12	1.32	–
90.5	46.5	310	380	4.75	0.42	8.84	1.22	–
81.1	48.8	310	382	4.83	0.43	8.90	1.18	–
71.8	50.6	310	383	4.84	0.43	8.88	1.18	–
62.4	52.1	310	385	4.85	0.42	8.66	1.20	–
43.6	54.8	310	386	4.62	0.38	8.09	1.32	4.97
31.1	57.0	308	387	4.43	0.34	7.67	1.49	4.20
21.8	58.4	308	389	4.01	0.25	6.23	1.87	4.38
12.4	60.5	301	391	3.30	0.18	5.45	2.48	4.41
6.10	61.9	301	392	2.78	0.16	5.76	3.02	4.45
0.00	63.1	301	393	2.26	0.12	5.31	3.89	4.90

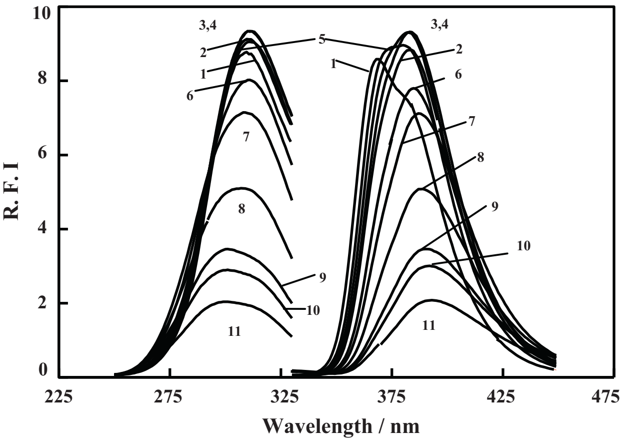

Fig. 5. Excitation and emission spectra of DAF in a series of mixtures of dioxane:water, (**1**) 100%, (**2**) 90.5%, (**3**) 81.1%, (**4**) 71.8%, (**5**) 62.4%, (**6**) 43.6%, (**7**) 31.1%, (**8**) 21.8%, (**9**) 12.4%, (**10**) 6.1% dioxane, and (**11**) water.

In Fig. 3, the logarithms of k_{nr} are plotted as a function of solvent polarity [$E_T(30)$]. Two dependencies with solvent polarity are observed. At polarities above 55 kcal mol^{-1}, $\ln k_{nr}$ and $E_T(30)$ displayed a linear inter-dependence. Least-squares analysis of the data gave $\beta/RT = -0.1322$ mol kcal^{-1} and $\beta = -0.079$. The negative value of β indicates that the energy barrier decreases as the solvent polarity increases. We calculated the polarity-corrected nonradiative rate (k_{cor}) for $\beta = -0.079$ by substituting in Eq. (4). The values are given in Table 3. The mean of the k_{cor} values was 4.55×10^6 s^{-1} and the standard deviation was 0.31×10^6 s^{-1}. These values are essentially the same within experimental error. Thus, the observed 2.95-fold increase in k_{nr} was caused by an increase in solvent polarity.

3.3. *Aprotic solvents*

The photophysics of DAF indicates that this molecule possesses two fluorescent states which differ in response to solvent. Upon electronic excitation a locally excited (LE) or nonpolar state is initially formed. The strong bathochromic shift of the emission maximum of DAF with an increase in polarity of the solvent is consistent with an emissive, lowest energy CT excited state. The change in dipole moment upon excitation to the CT state is estimated to be roughly 4.3 D from the slope of the solvatochromic plot (Fig. 4). This value was calculated from the Lippert–Mataga equation, assuming a value for the Onsager radius a of 4 Å (a value comparable to the radius of typical aromatic fluorophores). The response of the excited state with the solvent change permits its characterization as an intramolecular charge transfer electronic configuration. A charge transfer can occur in the lowest excited state between the dimethylamine electron donor substituent and the fluorene moiety.

An increase in the polarity accelerates formation of the ICT state; it also affects the nonradiative decay rate decreasing it, and the lifetime increasing it. These results discount a TICT mechanism for decay of DAF in aprotic solvents. A wide range of molecules with dimethylamine group deactivate through a TICT state by rotation around the bond joining the donor (amino group) and the acceptor part when the motion is possible [20]. For molecules with dimethylamine substituent, the energy of the TICT state increases when the strength of the acceptor decreases [21–24].

On the other hand, DAF as fluorene and bridged biphenyls display an efficient intersystem crossing to triplet states [25,26], this deactivation to the triplet state explain the nonradiative decay in apolar solvents. DAF shows the higher k_r value in hexane and DMSO, although the nonradiative process is more efficient in hexane than in DMSO. Additionally, the radiative constant is higher than that of the nonradiative and this difference increases with the solvent polarity. These data indicate that DAF exhibits an efficient radiative process at the expenses of the nonradiative one. This fact suggests an enhancement of fluorescence at the expense of intersystem crossing as polarity increases. For the nonpolar (LE) excited state ISC competes with the ICT process. Under conditions where the ICT is very slow (fluid solutions at low polarity) the main nonradiative pathway is ISC. However, at high polarity in fluid solution, where the ICT process is much faster than the ISC process, ISC becomes unimportant. To summarize, the ISC rate depend on the singlet–triplet energy interval, and the ICT rate depends strongly on the polarity of the medium.

3.4. Protic solvents

The anomalies in protic solvents can be attributed to specific solute–solvent interactions. A plot of nonradiative constants vs. the solvent polarity parameter $E_T(30)$ of dioxane–water mixtures (Fig. 3) reveals two slopes. The "low-slope" line appeared at polarities ranged between 36 and 52.1 kcal mol^{-1}, and the "high-slope" at polarities above 55 kcal mol^{-1}. These results indicate that two different excited states can be involved; the variation in the rate constants with solvent polarity was comparable to the change in the position of the fluorescence maximum and the quantum yield of fluorescence of DAF.

The behavior of DAF in protic solvents can be explained by comparing it in dioxane–water mixtures with the behavior of the parent compound, fluorene. Maximum wavelength of fluorene remains unchanged from dioxane to water although fluorescence intensity decreases. It has been reported that the hydrogen methylenic in the fluorene is labile in the excited state ($\mathrm{p}K_a(S_0) = 21$, $\mathrm{p}K_a(S_1) = -8$, and $\mathrm{p}K_a(T_1) = 5$) [27]. The value $\mathrm{p}K_a(S_1) = -8$ suggest that the anion of fluorene in the excited state is likely to be far the most thermodynamically stable excited species at pH 7 (pure water) which decays by emission of light. Usually, substitution of electro donating group reduces the acidity. The dimethyl amino group does not have positive charge in ground state, and in ICT state negative charge will be in fluorine moiety. This also reduces the acidity of methylene proton. This result agrees with a possible production of an intermolecular proton transfer excited state, which would allow the formation of the conjugate base of DAF by an intermolecular proton-transfer from the methylenic group to the hydrogen-bonding solvent. On the other hand, the marked changes observed for DAF in dioxane–water mixtures, in contrast to fluorene, only can be explained by assuming additionally the participation of the methylamino group.

In mixtures of water and dioxane DAF exhibits the typical behavior of a TICT compound. The energy of activation for the TICT process decreases as the polarity of the medium increases because of solvation of the TICT state. According to this model, the fluorescence lifetime of ICT excited state of compounds with possible twisted conformation, as occur in DAF, increase monotonically when the polarity decreases because the TICT process is inhibited. An additional nonradiative conversion of a fluorescent ICT state into a weakly emissive twisted rotamer is postulated. The nonradiative-deactivation constant that governs the TICT state is k_{cor}. The uniformity of our k_{cor} values indicates that they were independent of polarity and consequently they reflect the magnitude of the TICT decay rates.

In addition, a fact favoring the TICT state includes the large dipole moment. For the majority of organic molecules full charge separation is most favorable in a twisted conformation, such a twisting motion would rotate the donor orbital with respect to the acceptor orbital; a necessary condition for complete charge transfer. The resulting state is highly polar ($\mu = 15.2$ D), this dipole moment was estimated from the slope of the solvatochromic plot (Fig. 4) for basic and protic solvents (water, methanol, ethanol and n-butanol which acceptor number (AN) are 54.8, 41.5, 37.9 and 36.8, respectively [3]. Although the absolute values of the excited state dipole moments should be viewed with caution, because the solvatochromic method is rather crude in predicting dipole moment values as there is a certain arbitrariness in the choice of the Onsager radius value, however, the estimated values area good approximation to the true values.

In the charged transfer excited state a greater electronic density is localized in the fluorene moiety, while in that proton transfer excited state the negative charge is localized on the methylene bridged which is stabilized by the positive charge localized in the dimethylamine group:

$$\underset{\text{ICT state}}{\mathrm{Me_2N^{\delta+} - Fl^{\delta-} - H}} \quad \underset{\text{ion pair}}{\mathrm{Me_2N - Fl^{(-)} - H^{(+)}}} \quad \underset{\text{free ions}}{\mathrm{Me_2N^{(+)} - Fl^{(-)} + H^{+}}}$$

A model involving intramolecular twisting of dimethylamino group is proposed to explain the small fluorescence quantum yield of DAF in protic solvents. The geometry and electronic structure of the CT states are still a point of discussion lead to the questioning of a classical TICT model assuming a relaxed state of perpendicular geometry. A realistic model involves broad angular distributions including the perpendicular conformation [28].

4. Conclusions

Upon electronic excitation DAF initially forms a locally excited or nonpolar state with geometry and dipole moments similar to those in the ground state. In polar media, an electron is subsequently transferred from the donor (dimethylamine) to the acceptor (fluorene). At low polarity the intersystem crossing is an important nonradiative pathway. As the polarity of the medium is increased the ICT singlet, TICT singlet and the triplets are solvated to different extents because of their different dipole moments. The differential solvation of those states affects their relative energies. At high polarity the TICT state and the triplet become closer in energy to the ICT singlet but, are still energetically unfavorable compared with that of the lowest excited state ICT of the planar conformation, and the relaxation by twisting and ISC will not take place.

Solvents of high dielectric constant and basic properties cause both ionization and dissociation of DAF. The two steps, ionization and dissociation, are influenced in different ways by solvents. Solvents with high dielectric constant but lacking pronounced EPA-properties, such as N,N′-dimethylacetamide and dimethylsulfoxide are capable of ionizing DAF to a lesser extent than protic solvents of medium to high dielectric constant and pronounced EPA properties. However, in alcohols and water, DAF exhibits an excited state intermolecular proton-transfer reaction which causes the ionization of DAF. This specific solvent interaction, however, leads to stabilization energies; the lower excited state is of high dipole moment (15.2 D) and can be identified as a TICT state of low quantum yield. Thus, the phenomenon of quenching of the fluorescence of DAF in water and other protic solvents can be explained.

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