

# Solvent polarity and intramolecular hydrogen bonding effects on the photophysical properties of 1-amino-9,10-anthraquinone dye

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## Abstract

Photophysical properties of 1-amino-9,10-anthraquinone (1AAQ) dye have been investigated in different solvents using steady-state and time-resolved fluorescence measurements. The behavior of the dye is different in nonpolar solvents than in other solvents of moderate to higher polarities. In nonpolar solvents, the absorption and fluorescence maxima ( $\bar{\nu}_{\text{abs}}$  and  $\bar{\nu}_{\text{fl}}$ , respectively) are largely blue-shifted and fluorescence quantum yields ( $\Phi_f$ ) and fluorescence lifetimes ( $\tau_f$ ) are unusually higher in comparison to those in other solvents. Further, in nonpolar solvents, the fluorescence decay kinetics is strongly temperature-dependent, while decay kinetics is temperature-independent in all other solvents of moderate to higher polarities. The differences in the behavior of 1AAQ dye in nonpolar and other solvents are suggestive of a structural change in the dye in the two sets of solvents. It is inferred that this structural change arises through the 1-NH<sub>2</sub> group of the dye. Deuterium isotope effect on the fluorescence decays of the dye in nonpolar and polar solvents also supports the above structural changes. To obtain further supportive evidences for the above structural changes, ab initio quantum chemical studies have been carried out on the ground and excited state structures of the dye under different environmental conditions. Correlating different experimental and theoretical results we infer that in nonpolar solvents 1AAQ dye adopts a nonplanar conformation where as in all other solvents the dye adopts a planar conformation with strong intramolecular charge transfer (ICT) character. Present results also indicate a strong role of intramolecular hydrogen bonding on the deexcitation mechanism of the excited state of the dye both in its nonplanar and planar ICT structures.

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**Keywords:** Photophysical properties; Quinone dyes; Intramolecular hydrogen bonding; Solvent polarity; Intramolecular charge transfer; Nonplanar structure

## 1. Introduction

Amino- and hydroxy-substituted quinones are important class of molecules of having immense importance in dye industry, biology, and pharmaceutical chemistry [1–9]. Many of these molecules are reasonably fluorescent and their fluorescence characteristics have often been used to investigate the excited state properties of these molecules [10–14]. The effects of intra- and intermolecular hydrogen bonding on the photophysical properties of amino- and hydroxy-quinones have been investigated quite extensively [10–14]. Excited state proton transfer reaction has been shown to play a significant role in the deexcitation

mechanism for some of these excited molecules [10–14]. Due to the presence of the quinonoid moiety, these molecules act as good electron acceptors and extensive studies have been carried out to investigate the reduced radical characteristics of these molecules using both pulse radiolysis and laser flash photolysis techniques [15–22]. Due to good electron accepting properties, a variety of quinones and substituted quinones have also been used in exploring the dynamics and mechanism of electron transfer processes under both intramolecular and intermolecular conditions [23–27].

Though photochemistry of different quinone derivatives have been the subject of intense research for many years [1–5,9–14], the effect of solvent polarity on their photophysical properties are not that systematically studied. In the literature, photophysical properties of amino- and hydroxy-substituted quinones are mostly discussed in relation to the effect of intramolecu-

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lar hydrogen bonding on the deexcitation mechanism of the  $S_1$  state [9–14], and also on the  $S_1$  to  $T_1$  intersystem crossing (ISC) process [9–14,19–22]. It is reported that the  $S_1$  state of amino- and hydroxy-substituted quinones are mostly of intramolecular charge transfer (ICT) character [9–14,19–22]. In our recent studies with aminocoumarin dyes, e.g. coumarin-120 (C120; 7-NH<sub>2</sub>-4-CH<sub>3</sub>-1,2-benzopyrone) and coumarin-151 (C151; 7-NH<sub>2</sub>-4-CF<sub>3</sub>-1,2-benzopyrone), the molecules that are also known to have ICT character both in the ground and excited electronic states, it has been observed that depending on solvent polarity these dyes can adopt either a nonplanar or a planar intramolecular charge transfer (ICT) conformation and accordingly display drastically different photophysical properties in nonpolar and polar solvents [28,29]. Further, in their nonplanar conformation, the  $S_1$  state of these dyes shows an additional nonradiative deexcitation channel, which is absent in their planar ICT structure. Assuming the possibility of similar conformational changes for the amino-substituted quinones, we have recently investigated photophysical properties of 2-amino-9,10-anthraquinone (2AAQ) dye in solvents of varying polarities [30]. Interestingly it has been observed that 2AAQ displays substantially different photophysical properties in lower polarity solvents than in other solvents of medium to higher polarities. From the experimental results supported by Quantum chemical calculations, it has been understood that in nonpolar solvents 2AAQ dye exists in a nonplanar structure, with its 2-NH<sub>2</sub> plane away from that of the 9,10-anthraquinone moiety whereas in other solvents the dye exists in a polar ICT structure, where the amino lone pair of the 2-NH<sub>2</sub> group is in strong resonance with the anthraquinone  $\pi$ -cloud. These structural changes for 2AAQ dye in nonpolar and other solvents are exactly similar to those reported earlier by us for the coumarin dyes, C120 and C151. In the present work, photophysical properties of 1-amino-9-10-anthraquinone (1AAQ) dye have been investigated in different solvents and solvent mixtures of varying polarities to understand if structural changes similar to those in 2AAQ, C120 and C151 are also possible for 1AAQ dye. Unlike 2AAQ, C120 and C151 dyes, there is a possibility of strong intramolecular hydrogen bonding in 1AAQ, involving one of the hydrogen atoms of the 1-NH<sub>2</sub> group and the adjacent quinonoid oxygen. It is thus also interesting to know if such hydrogen bonding does have any effect on the possible structural changes of the dye in nonpolar and other solvents. Chemical structures of 1AAQ, 2AAQ, C120 and C151 dyes are shown in Chart 1 for an easy comparison.

## 2. Materials and methods

1AAQ was obtained from TCI (Tokyo, Japan) and purified by repeated crystallization from cyclohexane–ethyl acetate solvent mixture. All the solvents used were of spectroscopic grade, obtained either from Spectrochem (Mumbai, India), S.D. Fine Chemical (Mumbai, India), SISCO Research Laboratories (Mumbai, India), E. Merck (Mumbai, India) or Fluka (Buchs, Switzerland).

Absorption spectra were recorded using a JASCO (Tokyo, Japan) spectrophotometer model V530. Fluorescence spectra were recorded with corrections for the wavelength-dependent instrument responses using a Hitachi (Tokyo, Japan) spectrofluorimeter model F-4010. The  $\Phi_f$  values were measured by a comparative method [31,32], using  $\Phi_f$  of 1AAQ in benzene as the reference ( $\Phi_f^R = 0.058$ ; [13]). For all fluorescence measurements, the optical density (O.D.) of the solutions was kept quite low ( $\sim 0.2$ ) at the excitation wavelength.

Fluorescence lifetimes of 1AAQ in different solvents were measured using time-correlated-single-photon-counting (TCSPC) spectrometers, either from Edinburgh Instrument, Edinburgh, U.K. (model 199) or from IBH, Glasgow, U.K. (model IBH Data Station Hub). The TCSPC setup from Edinburgh Instrument uses a hydrogen flash lamp (25 kHz) for sample excitation and the instrument response function for this setup is  $\sim 1.2$  ns at FWHM. The details of this spectrometer are described elsewhere [33]. In the TCSPC setup from IBH, a 455 nm nano-LED was used for sample excitation and the instrument response function for this setup is  $\sim 1.2$  ns at FWHM. Observed fluorescence decays were analyzed following a re-convolution procedure [34], using a proper instrument response function, obtained by replacing the sample cell with a light scatterer (suspended TiO<sub>2</sub> particles in water). For all the cases, the decays were seen to fit well with a single-exponential function, as judged from the reduced  $\chi^2$  values and the distribution of the weighted residuals among the data channels [34]. For all the accepted fits, the  $\chi^2$  values were within 1.00–1.20, and the distribution of the weighted residuals were quite random among the data channels used [34].

To study deuterium isotope effect on the fluorescence decay characteristics of 1AAQ dye, following procedure was adopted to exchange the amino hydrogens of the dye with deuterium atoms [10,13]. About 1 ml of D<sub>2</sub>O was added to about 5 ml solution of 1AAQ in hexane. The mixture was thoroughly shaken for about 5 min. The mixture was then allowed for

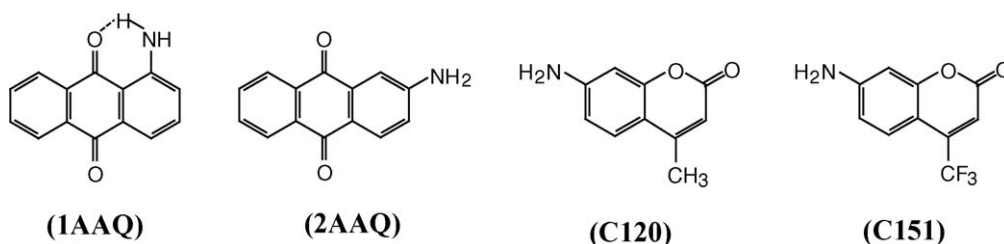


Chart 1.

sometime to separate out the organic and the aqueous layers. The organic layer containing the dissolved dye was collected. The procedure was repeated for six times for almost quantitative exchange of the amino hydrogens by deuterium atoms. The hexane solution thus obtained was shaken with activated molecular sieves (from Acros Organics; 4 Å, 8–12 meshes) to remove dissolved/dispersed D<sub>2</sub>O in the solution. The mixture was then allowed to settle down and the supernatant solution of the deuterated dye in hexane was collected to carry out the fluorescence decay measurements. For experiment with deuterated IAAQ dye in polar acetonitrile solution, the above hexane solution was mixed with dehydrated acetonitrile solvent (dehydrated using activated molecular sieves). The mixture was shaken thoroughly, allowed the two solvent layers to separate out, and the heavier acetonitrile layer containing dissolved deuterated dye was collected to carry out the fluorescence decay measurements.

### 3. Results and discussion

#### 3.1. Absorption and fluorescence spectral characteristics

Absorption and fluorescence spectra of IAAQ were recorded in different solvents and solvents mixtures. Table 1 lists the longer wavelength absorption ( $\lambda_{\text{abs}}^{\text{max}}$  in nm) and the fluorescence ( $\lambda_{\text{fl}}^{\text{max}}$  in nm) maxima of the dye in different solvents along with the Lippert–Mataga solvent polarity parameter  $\Delta f$ , as estimated

using Eq. (1) [31,32,35,36].

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

where,  $\varepsilon$  is the static dielectric constant and  $n$  is the refractive index of the solvent. The  $\varepsilon$  and  $n$  values of pure solvents were obtained from literature [37], and those of the mixed solvents ( $\varepsilon_{\text{MS}}$  and  $n_{\text{MS}}$ , respectively) were estimated from the volume fractions ( $f$ ) of the co-solvents using Eqs. (2) and (3), respectively [28–30,38–43].

$$\varepsilon_{\text{MS}} = f_A \varepsilon_A + f_B \varepsilon_B \quad (2)$$

$$n_{\text{MS}}^2 = f_A n_A^2 + f_B n_B^2 \quad (3)$$

where, subscripts A and B represent the respective co-solvents. It has been seen earlier that the  $\Delta f$  values for different mixed solvent systems calculated based on the  $\varepsilon_{\text{MS}}$  and  $n_{\text{MS}}$  values estimated using Eqs. (2) and (3) correlate different physico-chemical properties of many probe molecules quite satisfactorily [28–30,41–43].

The changes in the longer wavelength absorption and fluorescence maxima ( $\bar{\nu}_{\text{abs}}$  and  $\bar{\nu}_{\text{fl}}$ , respectively, in  $\text{cm}^{-1}$ ) of IAAQ dye with the  $\Delta f$  values of the solvents have been plotted in Fig. 1A and B, respectively. It is seen that the  $\bar{\nu}_{\text{abs}}$  and  $\bar{\nu}_{\text{fl}}$  values follow a reasonably linear correlations with  $\Delta f$  for almost all the solvents of moderate to higher polarities but excluding the nonpolar solvents ( $\Delta f \approx 0$ ), where in the latter cases the  $\bar{\nu}_{\text{abs}}$  and  $\bar{\nu}_{\text{fl}}$  values are substantially deviated towards higher energies. Normally,

Table 1  
Absorption maxima ( $\lambda_{\text{abs}}^{\text{max}}$ ), fluorescence maxima ( $\lambda_{\text{fl}}^{\text{max}}$ ), Stokes' shift ( $\Delta\bar{\nu}$ ), fluorescence quantum yields ( $\Phi_f$ ), fluorescence lifetimes ( $\tau_f$ ), radiative rate constants ( $k_f$ ) and nonradiative rate constants ( $k_{\text{nr}}$ ) for IAAQ in different solvents

Solvent <sup>a</sup>	$\Delta f$	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{fl}}^{\text{max}}$ (nm)	$\Delta\bar{\nu}$ ( $\text{cm}^{-1}$ )	$\Phi_f$	$\tau_f$ (ns)	$k_f$ ( $10^7 \text{ s}^{-1}$ )	$k_{\text{nr}}$ ( $10^8 \text{ s}^{-1}$ )
CHX	0	452	543	3708	0.066	1.75	3.80	5.32
HX	0	451	542	3736	0.068	1.73	3.93	5.38
MCHX	0	452	543	3708	0.069	1.77	3.90	5.25
3MP	0	450	542	3738	0.066	1.74	3.79	5.37
DL	0.002	454	544	3644	0.064	1.70	3.77	5.51
CHX <sub>95</sub> EA <sub>5</sub>	0.025	460	562	3935	0.054	1.52	3.53	6.23
CHX <sub>90</sub> EA <sub>10</sub>	0.046	463	567	3947	0.050	1.45	3.41	6.54
CHX <sub>80</sub> EA <sub>20</sub>	0.081	464	567	3911	0.044	1.36	3.21	7.04
CHX <sub>70</sub> EA <sub>30</sub>	0.108	466	572	3995	0.042	1.31	3.20	7.28
CHX <sub>60</sub> EA <sub>40</sub>	0.128	466	574	4046	0.040	1.26	3.13	7.60
CHX <sub>40</sub> EA <sub>60</sub>	0.160	467	576	4057	0.036	1.20	2.99	8.03
CHX <sub>20</sub> EA <sub>80</sub>	0.183	466	580	4197	0.035	1.16	3.01	8.34
EA	0.201	467	579	4148	0.032	1.14	2.82	8.53
EA <sub>90</sub> ACN <sub>10</sub>	0.240	467	582	4231	0.029	1.04	2.74	9.30
EA <sub>80</sub> ACN <sub>20</sub>	0.259	468	585	4288	0.028	1.02	2.73	9.51
EA <sub>70</sub> ACN <sub>30</sub>	0.272	468	587	4360	0.026	1.00	2.63	9.76
EA <sub>60</sub> ACN <sub>40</sub>	0.280	467	587	4362	0.025	0.98	2.52	9.99
EA <sub>50</sub> ACN <sub>50</sub>	0.287	467	588	4381	0.025	0.96	2.62	10.14
EA <sub>40</sub> ACN <sub>60</sub>	0.292	468	588	4371	0.024	0.95	2.52	10.33
EA <sub>30</sub> ACN <sub>70</sub>	0.296	468	590	4435	0.024	0.96	2.55	10.21
EA <sub>20</sub> ACN <sub>80</sub>	0.300	468	591	4492	0.023	0.95	2.40	10.31
EA <sub>10</sub> ACN <sub>90</sub>	0.303	467	590	4450	0.023	0.93	2.51	10.49
ACN	0.305	467	590	4469	0.022	0.94	2.39	10.40

The solvent polarity function ( $\Delta f$ ) is also listed for the solvents used.

<sup>a</sup> Abbreviations for the solvents and solvent mixtures are used as follows: ACN: acetonitrile; CHX: cyclohexane; DL: decalin; EA: ethyl acetate; HX: *n*-hexane; MCHX: methylcyclohexane; 3MP: 3-methylpentane; CHX<sub>x</sub>EA<sub>y</sub>: *x*% CHX & *y*% EA (v/v); EA<sub>x</sub>ACN<sub>y</sub>: *x*% EA & *y*% ACN (v/v).

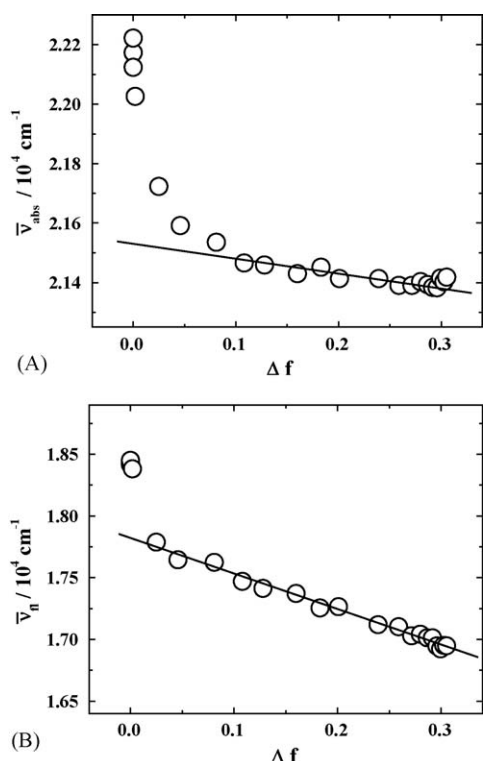
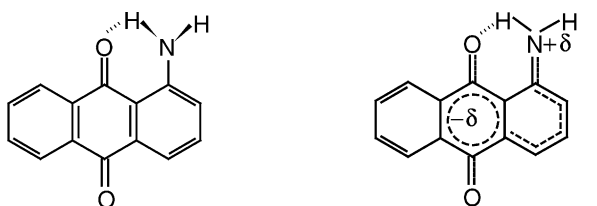


Fig. 1. Plot of absorption maxima ( $\bar{\nu}_{\text{abs}}$ ) and fluorescence maxima ( $\bar{\nu}_{\text{fl}}$ ) of 1AAQ against the solvent polarity function  $\Delta f$ . In nonpolar solvents  $\bar{\nu}_{\text{abs}}$  and  $\bar{\nu}_{\text{fl}}$  values deviate in comparison to the linear correlations observed for moderate to higher polarity solvents.

the longer wavelength absorption and the fluorescence bands of a molecule in different solvents are due to the electronic transitions involving the same two ground ( $S_0$ ) and excited ( $S_1$ ) states. For such cases,  $\bar{\nu}_{\text{abs}}$  and  $\bar{\nu}_{\text{fl}}$  values are expected to follow a linear correlation with solvent polarity [31,32,35,36]. Thus, from present results, it is indicated that the natures of the  $S_0$  and  $S_1$  states of 1AAQ dye remain unchanged for the moderate to higher polarity solvents but they undergo a change in nonpolar solvents. We infer that these changes are due to the existence of the dye in different structural forms in nonpolar and other solvents, as we predicted earlier for some other dyes like C120, C151 and 2AAQ [28–30]. Thus, just like the latter three dyes, 1AAQ is also predicted to adopt a nonplanar structure (pyramidal) with respect to its 1-NH<sub>2</sub> group in nonpolar solvents and a planar ICT structure in solvents of moderate to higher polarities, as can be schematically shown in Chart 2. In the nonplanar structure, as the amino lone pair will have a largely reduced resonance with the



(nonplanar structure)  
(in nonpolar solvents)

(planar ICT structure)  
(in polar solvents)

Chart 2.

9,10-antraquinone  $\pi$ -cloud, the  $\bar{\nu}_{\text{abs}}$  and  $\bar{\nu}_{\text{fl}}$  values of the dye in nonpolar solvents will be unusually blue shifted in comparison to those in moderate to higher polarity solvents [28–30].

Since in moderate to higher polarity solvents the natures of  $S_0$  and  $S_1$  states of 1AAQ are indicated to remain unchanged (cf. Fig. 1), the Stokes' shifts ( $\Delta\bar{\nu}$ ) between absorption and fluorescence maxima of the dye in these solvents are expected to follow a linear correlation with  $\Delta f$ , as predicted from Lippert and Mataga relationship given by Eq. (4) [31,32,35,36].

$$\Delta\bar{\nu} = \Delta\bar{\nu}_0 + \frac{2(\mu_e - \mu_g)^2}{hcr^3} \Delta f \quad (4)$$

where  $\mu_e$  and  $\mu_g$  are the excited and ground state dipole moments of the dye, respectively,  $h$  the Planck's constant,  $c$  the velocity of light and  $r$  is the Onsager radius of the dipole–solvent interaction sphere. Table 1 lists the  $\Delta\bar{\nu}$  values for 1AAQ dye in different solvents and solvent mixtures. Fig. 2 shows the  $\Delta\bar{\nu}$  versus  $\Delta f$  plot for the dye in moderate to higher polarity solvents. The plot is in fact linear as expected. From the slope of this plot, the  $\mu_e$  value of the dye is estimated to be  $\sim 7.6$  D, considering  $\mu_g \sim 2.6$  D (cf. Section 3.5) and  $r \sim 4.65$  Å (based on ab initio quantum chemical calculation; cf. Section 3.5). Such a high  $\mu_e$  value suggests quite a polar nature of the  $S_1$  state of the dye. It is inferred from the present observation in conjunction with the literature reports [9–14,19–22] that in moderate to higher polarity solvents the  $S_1$  state of the dye is of polar ICT character. Though a  $\mu_g$  value of  $\sim 2.6$  D is not that large, yet a planar ICT structure for the  $S_0$  state of the dye in moderate to higher polarity solvents is indicated from a comparison of the results of 1AAQ with those of C120, C151 and 2AAQ dyes [28–30]. This is further supported by the results of ab initio quantum chemical calculations as are presented in Section 3.5.

### 3.2. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields ( $\Phi_f$ ) of 1AAQ dye in different solvents were estimated at room temperature and are listed in Table 1. Fig. 3A shows the  $\Phi_f$  versus  $\Delta f$  plot for the dye. It is seen from this figure that for moderate to higher polarity solvents

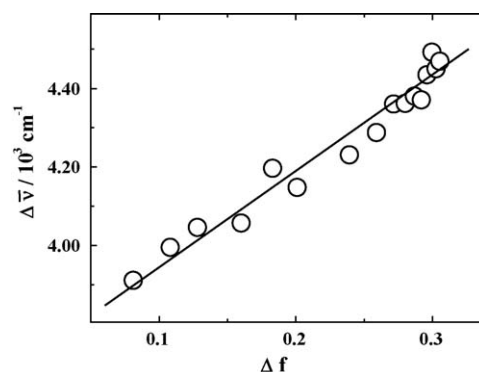


Fig. 2. Plot of the Stokes' shifts ( $\Delta\bar{\nu}$ ) for 1AAQ against the solvent polarity function  $\Delta f$  for moderate to higher polarity solvents. The plot is linear within experimental error. The slope of this plot was used to estimate the change in the dipole moment for the dye using Eq. (4).

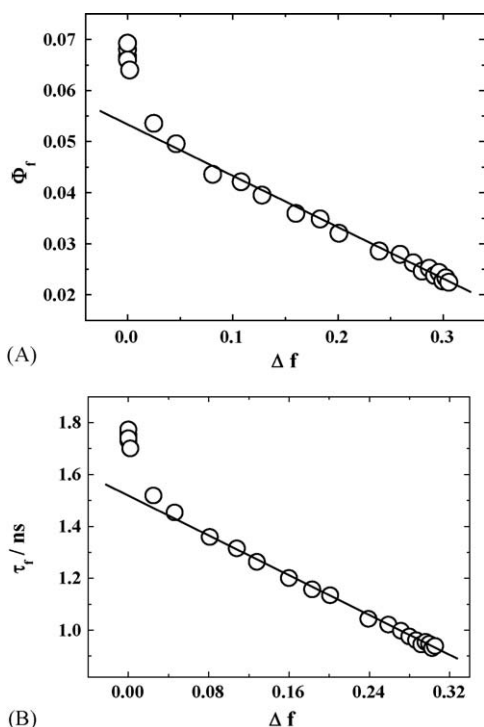


Fig. 3. Variations in (A)  $\Phi_f$  and (B)  $\tau_f$  values of 1AAQ dye with the solvent polarity function  $\Delta f$ . In nonpolar solvents  $\Phi_f$  and  $\tau_f$  values deviate largely in comparison to the linear correlations observed for moderate to higher polarity solvents.

the plot is reasonably linear. For the nonpolar solvents ( $\Delta f \approx 0$ ), however, the  $\Phi_f$  values are largely deviated towards higher side in comparison to the linear  $\Phi_f$  versus  $\Delta f$  correlation observed for the other solvents.

Fluorescence decays of 1AAQ dye in different solvents were recorded at room temperature, keeping measuring wavelengths at the emission maxima of the dye in different solvents. In all the solvents, fluorescence decays were found to be single-exponential in nature. The  $\tau_f$  values estimated in different solvents are listed in Table 1. Fig. 3B shows the  $\tau_f$  versus  $\Delta f$  plot for the dye. Just like the  $\Phi_f$  values, the  $\tau_f$  values are also seen to follow a reasonably linear correlation with  $\Delta f$  for the moderate to higher polarity solvents. The  $\tau_f$  values in nonpolar solvents are, however, seen to deviate largely towards higher side in comparison to the linear correlation observed for the other solvents.

Though there is no simple theoretical basis available to correlate  $\Phi_f$  and  $\tau_f$  values of the dye with  $\Delta f$ , yet the reasonably linear  $\Phi_f$  versus  $\Delta f$  and  $\tau_f$  versus  $\Delta f$  plots for moderate to higher polarity solvents indicate that the nature of the  $S_0$  and  $S_1$  states of 1AAQ dye remain same in all these solvents [28–30]. The deviations in the  $\Phi_f$  and  $\tau_f$  values in nonpolar solvents indicate that in these solvents the natures of the  $S_0$  and  $S_1$  states must have changed in comparison to those in other solvents. These results are thus in accordance to our presumption that the dye adopt a nonplanar structure in nonpolar solvents but a planar ICT structure in other solvents of moderate to higher polarities (cf. Chart 2). To understand the characteristic of 1AAQ dye in different solvents further, radiative ( $k_f$ ) and nonradiative ( $k_{nr}$ ) rate constants for the  $S_1$  state of the dye in different solvents

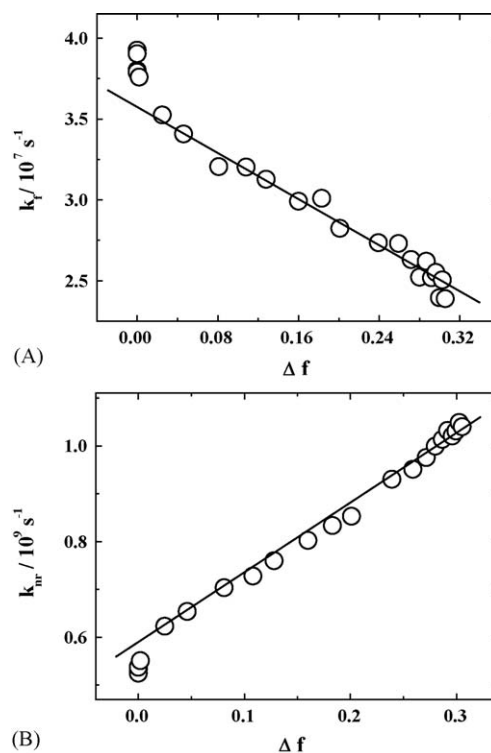


Fig. 4. Plot of (A) radiative ( $k_f$ ) and (B) nonradiative ( $k_{nr}$ ) decay rate constants for 1AAQ against the solvent polarity function  $\Delta f$ . In nonpolar solvents the  $k_f$  values are apparently higher and the  $k_{nr}$  values are apparently lower in comparison to the linear correlations observed for moderate to higher polarity solvents.

were estimated using Eqs. (5) and (6) [31,32] and are listed in Table 1.

$$k_f = \frac{\Phi_f}{\tau_f} \quad (5)$$

$$k_{nr} = \left( \frac{1}{\tau_f} \right) - k_f \quad (6)$$

Fig. 4A and B show the  $k_f$  versus  $\Delta f$  and  $k_{nr}$  versus  $\Delta f$  plots for the dye, respectively. It is seen from this figure that the  $k_f$  values are somewhat higher and the  $k_{nr}$  values are somewhat lower in nonpolar solvents in comparison to the linear  $k_f$  versus  $\Delta f$  and  $k_{nr}$  versus  $\Delta f$  plots observed for rest of the solvents of moderate to higher polarities. These results with  $k_f$  and  $k_{nr}$  values are thus also in accordance with our expectations, indicating a behavioral difference for the dye in nonpolar solvents than in other solvents. To be mentioned here that like 1AAQ dye, almost similar deviations in the  $\Phi_f$ ,  $\tau_f$ ,  $k_f$  and  $k_{nr}$  values in nonpolar solvents were also observed earlier by us for some other fluorescent dyes like, 2AAQ, C120 and C151 [28–30]. For these latter dyes, the behavioral differences in nonpolar solvents in comparison to those in other solvents were attributed and established to be due to the structural changes at the amino substituent of the dyes, similar to that predicted in Chart 2 for the present dye. We thus infer that all these dyes having an electron donating  $\text{NH}_2$  group in conjugation with an electron-accepting moiety can undergo a structural change at their  $\text{NH}_2$  group on changing the solvents from nonpolar to other solvents. One important point, however, to be considered in the present case that unlike 2AAQ, C120

and C151 dyes, in 1AAQ there is a possibility of intramolecular hydrogen bonding involving one of the amino hydrogen atoms and the adjacent quinonoid oxygen (cf. Chart 1). It is thus important to look into the effect of this intermolecular hydrogen bonding on the photophysical properties of 1AAQ dye, and in particular to see if this hydrogen bonding have some consequences on the structural changes of the 1-NH<sub>2</sub> group of the dye on changing the solvents from nonpolar to other solvents. This aspect is discussed latter in Sections 3.3 and 3.4.

### 3.3. Temperature effect on fluorescence decays

Temperature effect on the fluorescence decay characteristics of a dye can give many useful information regarding the deexcitation mechanisms of the excited molecules. In the present work, temperature effect on the fluorescence decays of 1AAQ dye have been investigated in different solvents of varying polarities. It is seen that in nonpolar solvents the decays are strongly temperature dependent, and becomes faster as the temperature is increased. Excluding nonpolar solvents, in all the other solvents, however, the fluorescence decays are found to be effectively temperature independent. Fig. 5A and B shows two typical ( $1/\tau_f$ ) versus ( $1/T$ ) plots for 1AAQ dye in a nonpolar solvent 3-methylpentane and a polar solvent acetonitrile, respectively. Since the radiative process ( $k_f$ ) for a fluorescent state is usually temperature independent [31,32], present results suggest that in nonpolar solvents, there is an additional activation-controlled nonradiative deexcitation channel for the S<sub>1</sub> state of the dye, which is absent in moderate to higher polarity solvents. To be mentioned that in our earlier studies, exactly similar activation-controlled additional nonradiative deexcitation channel for the excited states was also observed for C120 and C151 dyes in nonpolar solvents, which was absent in all other solvents of moderate to higher polarities [28,29]. For these latter dyes, this additional deexcitation channel was established to be due to the flip–flop motion of the 7-NH<sub>2</sub> group of the dye in its nonplanar S<sub>1</sub> state structure in nonpolar solvents [28,29]. Drawing an analogy, temperature effect on the fluorescence decays of 1AAQ dye in nonpolar solvents is also attributed to the similar flip–flop motion of the 1-NH<sub>2</sub> group of the dye in its nonplanar S<sub>1</sub> state structure. In moderate to higher polarity solvents, we presume that the S<sub>1</sub> state of the dye exists in its planar ICT structure where the flip–flop motion of the 1-NH<sub>2</sub> group is highly restricted and thus cannot introduce any additional deexcitation channel as it happens in nonpolar solvents. To be mentioned here that for a better understanding of the temperature effects on the fluorescence decays, it would have been more useful if one could obtain the individual  $k_f$  and  $k_{nr}$  values for all the temperatures studied. As in our steady-state fluorescence measurements, due to some inadequate arrangements in the spectrofluorimeter, we could not measure the fluorescence below  $\sim 10^\circ\text{C}$ , it was not possible to obtain  $\Phi_f$  values of the dye for any reasonable range of temperature changes. Accordingly, individual  $k_f$  and  $k_{nr}$  values also could not be obtained for all the temperatures studied in investigating the temperature effect on the  $\tau_f$  values of the dye. Thus, for the present dye, we were not able to analyze the temperature effect on the individual radiative ( $k_f$ ) and nonradiative

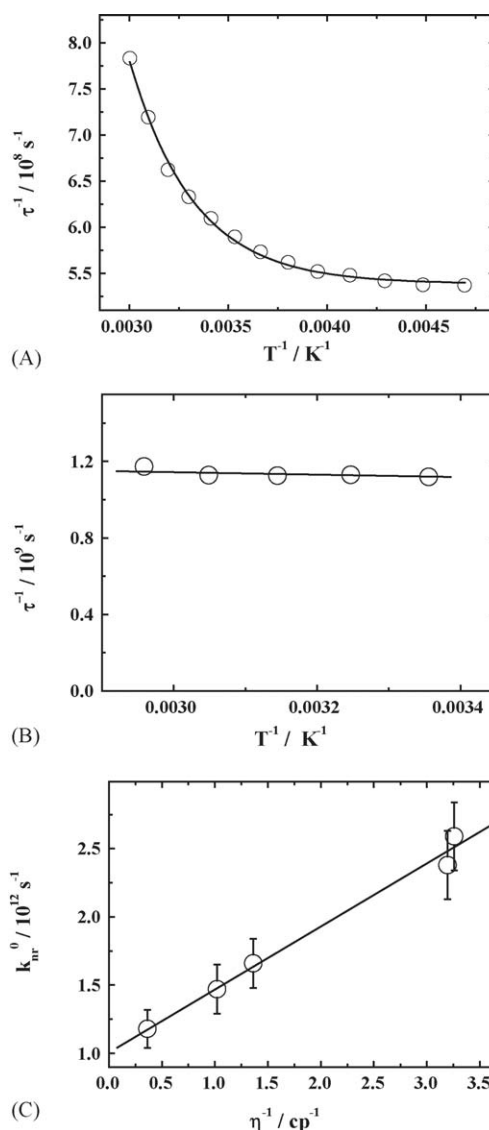


Fig. 5. (A) Temperature effect on the  $\tau_f$  values of 1AAQ in nonpolar 3-methylpentane solvent. The  $\tau_f$  drastically reduces on increasing the temperature. Circles represent the experimental points and continuous curve represents the fitted curve following Eq. (7). (B) Temperature effect on the  $\tau_f$  values of 1AAQ in polar acetonitrile solvent. The  $\tau_f$  is effectively independent of temperature. (C) Variations in the  $k_{nr}^0$  values with the inverse of the viscosity ( $\eta$ ) of the nonpolar solvents used. The plot is linear within experimental error.

( $k_{nr}$ ) rates. However, considering the fact that radiative process for a fluorescent molecule is usually temperature independent [31,32], we can easily infer that the temperature effect on the  $\tau_f$  values of 1AAQ dye in nonpolar solvents arises due to the participation of an additional activation-controlled nonradiative deexcitation channel for the dye. In a molecule, since total  $k_{nr}$  is a sum of all the nonradiative decay rate constants of which some are temperature independent [31,32], the observed temperature effect on the  $\tau_f$  values of 1AAQ in nonpolar solvents can be conveniently analyzed using the following modified Arrhenius equation [28,29,44].

$$\tau_f^{-1} = \tau_0^{-1} + k_{nr}^0 \exp\left(-\frac{\Delta E_a}{RT}\right) \quad (7)$$

Table 2

Arrhenius parameters, namely the  $\tau_0^{-1}$ ,  $\Delta E_a$  and  $k_{nr}^0$  values, as obtained for 1AAQ in different nonpolar solvents

Solvents <sup>a</sup>	$\eta$ (20 °C)/cP	$\tau_0^{-1}$ ( $10^8$ s <sup>-1</sup> )	$\Delta E_a$ (kcal mol <sup>-1</sup> )	$k_{nr}^0$ ( $10^{12}$ s <sup>-1</sup> )
3MP	0.307	5.39	6.2	2.59
HX	0.313	4.82	5.9	2.38
MCHX	0.734	5.57	5.9	1.66
CHX	0.98	4.87	5.7	1.47
DL	2.75	4.99	5.9	1.18

The solvent viscosities ( $\eta$ ) are also listed in the table.

<sup>a</sup> Abbreviations for the solvents are as used in the footnote of Table 1.

where,  $\Delta E_a$  is the activation energy,  $k_{nr}^0$  the pre-exponential factor,  $R$  the universal gas constant,  $T$  the absolute temperature and  $\tau_0^{-1}$  is the sum of the rate constants for all the temperature-independent deexcitation channels including the radiative rate constant  $k_f$  [31,32]. The  $\tau_0^{-1}$ ,  $k_{nr}^0$  and  $\Delta E_a$  values thus estimated for the dye in different nonpolar solvents are listed in Table 2. It is seen from this table that  $\tau_0^{-1}$  and  $\Delta E_a$  values are almost in the similar range for all the nonpolar solvents studied. The  $k_{nr}^0$  values, however, show a decreasing trend with an increase in viscosity ( $\eta$ ) of the solvents used (cf. Table 2). In fact, a plot of the  $k_{nr}^0$  values against  $\eta^{-1}$ , as shown in Fig. 5C, indicates an apparently linear correlation within the experimental error. These results thus indicate that the efficiency of the activation-controlled nonradiative deexcitation channel for 1AAQ dye in nonpolar solvents, as introduced by the flip–flop motion of the 1-NH<sub>2</sub> group in its nonplanar structure, is mainly determined by the collisions of the dye with the surrounding solvent molecules. Similar observations were also made earlier by us on investigating the temperature effect on the fluorescence decays of C120 and C151 dyes [28,29]. The interesting point to be noted here is that the  $k_{nr}^0$  values obtained for 1AAQ dye in different nonpolar solvents are much lower (of the order of  $10^{12}$  s<sup>-1</sup>) than those obtained for C120 and C151 dyes (of the order of  $10^{14}$  s<sup>-1</sup>). The unusually lower  $k_{nr}^0$  values for 1AAQ dye is possibly related to the presence of intramolecular hydrogen bonding in this dye (cf. Chart 1), which will cause the flip–flop motion of 1-NH<sub>2</sub> group quite retarded in comparison to that of the free 7-NH<sub>2</sub> groups in C120 and C151 dyes.

### 3.4. Deuterium isotope effect on fluorescence decays

To understand the effect of intramolecular hydrogen bonding on the excited state behavior, fluorescence decays were measured with deuterated 1AAQ dye in a nonpolar solvent hexane and a polar solvent acetonitrile and the results were compared with those obtained with nondeuterated dye. Both in hexane and acetonitrile solutions, the fluorescence decays of the deuterated dye were much slower than those observed with nondeuterated dye. Like the nondeuterated dye, the fluorescence decays of the deuterated dye also follow the single exponential behavior. Fig. 6A and B compare the fluorescence decays for the deuterated and nondeuterated 1AAQ dye in hexane and acetonitrile solutions, respectively. The  $\tau_f$  values obtained for the deuterated dye in hexane and acetonitrile solutions are 5.70 and 4.75 ns, respectively. Comparing these  $\tau_f$  values of the deuterated dye

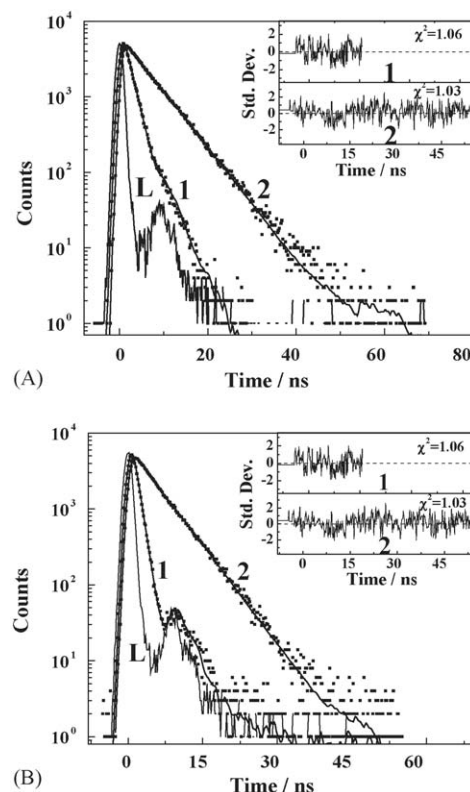


Fig. 6. Fluorescence decay curves of nondeuterated (1) and deuterated (2) 1AAQ dye in (A) hexane and (B) acetonitrile solutions. The dots represent the experimental decays and the continuous curves represent the fitted decays. The curves marked L represent the instrument response functions. Insets of the figures show the distribution of the weighted residuals among the data channels and also the  $\chi^2$  values.

with those of the nondeuterated dye (cf. Table 1) it is seen that the deuteration of the dye causes its fluorescence lifetime to increase by a factor of about 3 in hexane solution and by a factor of about 5 in acetonitrile solution.

As reported in the literature, for amino- and hydroxy-substituted quinones, where intramolecular hydrogen bonding is present, the nonradiative internal conversion (IC) process in the excited state is strongly coupled with the vibrational modes associated with the hydrogen bonds [10,13]. As the frequency of these vibrational modes are reduced largely due to deuteration, it causes a large reduction in the IC rates and consequently increases the  $\tau_f$  values for the deuterated dyes [10,13]. Further, the literature report indicates that in solution phase the amino- and hydroxy-substituted quinones mostly exist in their planar ICT structures, which is also supported by the present results on the photophysical properties of 1AAQ dye in moderate to higher polarity solvents. It is expected that the intramolecular hydrogen bond present in 1AAQ dye will be very strong in its planar ICT structure that exists in moderate to higher polarity solvents in comparison to the nonplanar structure of the dye that exists in nonpolar solvents. Thus, deuterium isotope effect on the fluorescence lifetime of 1AAQ dye was expected to be much stronger in a polar acetonitrile solvent than in nonpolar hexane solvent, as observed experimentally. Deuterium isotope effect for 1AAQ dye in hexane and acetonitrile solutions are thus in support of our

inferences that in nonpolar solvents the dye exists in a nonplanar structure but in other solvents of moderate to higher polarities the dye exists in a planar ICT structure.

Considering the observed isotope effect for 1AAQ dye in nonpolar solvent hexane, where the dye exists in its nonplanar structure, the effect is expected to be due to the combination of two factors. In our earlier studies with C120 dye, it was observed that in nonpolar solvent, due to the existence of the nonplanar structure of the dye and the coupling of the associated flip–flop motion of its amino group to the nonradiative decay mechanism, the  $\tau_f$  value of the dye increased by a factor of about 2 on deuteration. A similar isotope effect arising via the flip–flop motion of the amino group is also expected for the present 1AAQ dye in nonpolar solvent hexane. In 1AAQ dye, however, the effect of the flip–flop motion of the amino group in the deexcitation mechanism is not indicated to be that strong as in the case of C120 dye (e.g.  $k_{nr}^0$  values are only of the order  $10^{12} \text{ s}^{-1}$  for 1AAQ dye in comparison to the order of  $10^{14} \text{ s}^{-1}$  observed for C120 dye; cf. Section 3.3). Accordingly, deuterium isotope effect arising via the flip–flop motion of the amino group in 1AAQ is expected to be much less than that in C120 dye. The fact that the isotope effect for 1AAQ dye in hexane ( $\tau_f$  increases by about three times) is substantially higher than that of C120 dye ( $\tau_f$  increases by about two times) is thus expected to be due to the additional effect of intramolecular hydrogen bonding present in 1AAQ molecule. In 1AAQ dye, even in its nonplanar structure, weak intramolecular hydrogen bond formation between the amino hydrogen and the adjacent quinonoid oxygen is quite possible. Thus, isotope effect is also expected to arise via this hydrogen bond, even though the effect in this case might be much lower than that in the planar ICT structure of the dye in polar acetonitrile solvent. Accordingly, a higher isotope effect for 1AAQ dye in hexane solution in comparison to that observed for C120 dye is supposed to be due to the combination of the effect of flip–flop motion of the amino group of the dye and that of the intramolecular hydrogen bonding present in 1AAQ molecule. To be mentioned, however, from the present results it is not possible to separate out the contributions of the flip–flop motion and the intramolecular hydrogen bonding on the observed isotope effect for the 1AAQ dye in nonpolar hexane solution.

### 3.5. Quantum chemical calculations on the structures of 1AAQ

As discussed in Sections 3.1–3.3, results on the photophysical properties of 1AAQ dye in different solutions suggest that the dye exists in a planar ICT structure in moderate to higher polarity solvents but in a nonplanar structure in nonpolar solvents. To obtain a support for this hypothesis, theoretical studies were also carried out to predict the structures of the dye under (i) isolated gas phase condition and (ii) in the presence of polar solvent. Full geometry optimization in the ground state of 1AAQ dye was performed following Hartree–Fock (HF) as well as second order Moller–Plesset (MP2) perturbation method adopting a  $6-31+G(d,p)$  set of basis function (368 Cartesian basis functions). Excited state calculation was carried out following

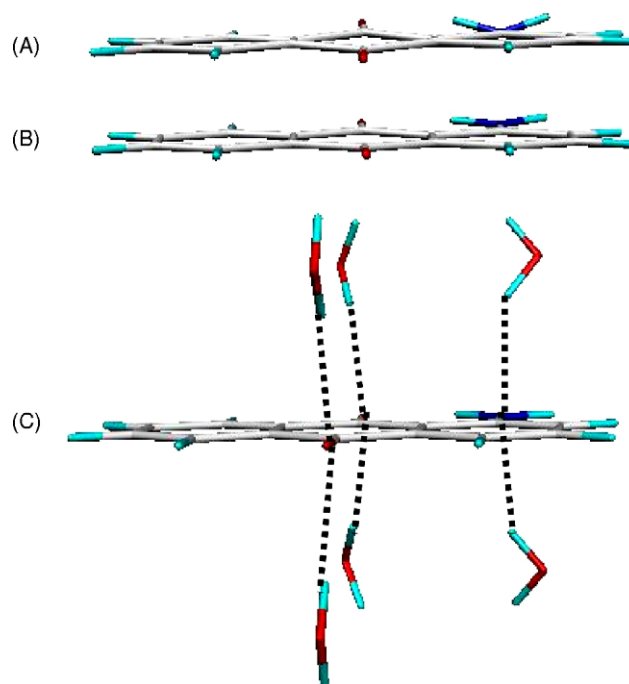


Fig. 7. The most relaxed structures of 1AAQ dye; (A) in the ground state under isolated gas phase condition, (B) in the excited state under isolated gas phase condition and (C) in the ground state in the presence of polar solvent.

Configuration Interaction with Single-electron-excitation (CIS) with the same set of basis function. All these calculations were performed adopting GAMESS suite of program on a PC-based LINUX cluster [45]. The most relaxed ground state structure of the dye obtained under isolated gas phase condition based on MP2 method is shown in Fig. 7A. In this structure, the three rings of the molecule are on the same plane. However, the two amino hydrogen atoms are out of the above molecular plane and the calculated dihedral angles for the two amino hydrogen atoms are found to be  $19.4^\circ$  and  $21.5^\circ$ . To be mentioned that a calculation performed at the HF level with  $6-311++G(d,p)$  set of basis function (454 Cartesian basis functions) resulted the dihedral angles for the two amino hydrogen atoms as  $12.1^\circ$  and  $15.5^\circ$ , respectively. Due to the large size of the molecule, MP2 calculation could not be performed with  $6-311++G(d,p)$  set of basis function. In nonpolar solvents, since dielectric interaction of the solvent with the dye molecule is negligible, the structure of the dye in these solvents must be similar to that in the isolated gas phase condition. Thus, present results from quantum chemical calculations support our hypothesis that in nonpolar solvents the dye adopts a nonplanar structure with respect to its  $1\text{-NH}_2$  group in its ground state. Geometry optimization for the excited state ( $S_1$ ) of 1AAQ based on CIS method with  $6-31+G(d,p)$  set of basis function yields a structure with the dihedral angles for the two amino hydrogen atoms as  $1.5^\circ$  and  $4.5^\circ$ , as shown in Fig. 7B. Based on this structure it is difficult to conclude if the dye can adopt a nonplanar structure in nonpolar solvents even though the two amino hydrogen atoms in the calculated structure are not exactly on the anthraquinone plane as otherwise would be expected for a planar ICT structure. From experimental results, especially from the fluorescence properties of the dye,



it is clearly indicated that the dye in the excited state behaves differently in nonpolar solvents than in other solvents. Thus, the calculated close to a planar structure in the gas phase excited state may be due to the overestimation of the effect of intramolecular hydrogen bonding that involves one of the amino hydrogen atoms and the adjacent quinonoid oxygen. Possibly, calculation at a higher level (than CIS) could have resulted a nonplanar excited state structure for the dye, as inferred from the experimental results. However, such a higher level of calculation in the excited state is beyond our scope at present. The observation from CIS method that the amino hydrogen atoms are not perfectly on the same plane of the anthraquinone moiety probably indicates towards a possible nonplanar excited state structure of the dye. To check this point further, we also calculated the structures of an analogue of the 1AAQ dye, namely 2AAQ, where intramolecular hydrogen bonding is not possible due to non-proximity of the amino group and the quinonoid oxygen. For 2AAQ, in the isolated gas phase condition the dihedral angles for the two amino hydrogen atoms are predicted to be  $25.7^\circ$  and  $27.3^\circ$  in the ground state  $\{\text{MP2/6-31} + G(d, p)\}$  and  $18.6^\circ$  and  $20.4^\circ$  in the excited state  $\{\text{CIS/6-31} + G(d, p)\}$ . Thus, the nonplanar structures for both ground ( $S_0$ ) and excited ( $S_1$ ) states of 2AAQ are clearly indicated for the gas phase condition and correlate well with its photophysical properties in nonpolar solvents in comparison to those in other solvents [30]. Drawing analogy with 2AAQ dye, we presume that similar nonplanar structure also exists for the excited 1AAQ dye in nonpolar solvents. That the intramolecular hydrogen bonding causes an effect on the calculated structure is also indicated by the fact that the dihedral angles for the two amino hydrogen atoms are always found to be much higher for 2AAQ than 1AAQ.

To understand the effect of solvent polarity on the structure of 1AAQ dye, the gas phase molecular geometry was re-optimized fully in presence of six discrete polar solvent molecules surrounding the dye, three on the top and three below the molecular plane. To simplify this calculation, water molecules were considered to incorporate the polar solvent effect rather than using acetonitrile molecules. The 1AAQ dye itself is quite large for ab initio quantum chemical calculation and adding eight acetonitrile molecules would make it more difficult. Thus, for the purpose of a qualitative description of the solvent polarity effect, water was considered as a representative of the polar solvent. Water molecules were added orienting the H atoms toward either N or O atoms of 1AAQ, keeping at a distance of  $2.5 \text{ \AA}$  in the starting geometry for optimization at MP2 level. After full geometry optimization at MP2 level, it is found that the distance becomes  $\sim 2.25 \text{ \AA}$  for  $\text{H} \cdots \text{O}$  and  $\sim 2.36 \text{ \AA}$  for  $\text{H} \cdots \text{N}$ . It is seen that due to inclusion of the solvent effect, the two amino hydrogen atoms are now placed almost on the plane of the anthraquinone moiety, as shown in Fig. 7C. The calculated dihedral angles for both the amino hydrogen atoms in the present case are estimated to be close to zero ( $0.2^\circ$ ). The inclusion of solvent effect enhances the calculated ground state dipole moment of the molecule, and it is now estimated to be  $\sim 2.6 \text{ D}$  in comparison to the value of  $1.5 \text{ D}$  for gas phase structure. It is worth mentioning that this dipole moment was calculated based on the solvent modified optimized dye structure only (excluding added water molecules). Present

results based on ab initio quantum chemical calculations thus support our inference based on experimental results that the dye 1AAQ undergoes a structural change at its 1-NH<sub>2</sub> group on changing the solvents from nonpolar to other solvents of moderate to higher polarities.

#### 4. Conclusions

Photophysical properties of 1AAQ show unusually different behavior in nonpolar solvents than in other solvents of moderate to higher polarities. Unusually blue shifted  $\bar{\nu}_{\text{abs}}$  and  $\bar{\nu}_{\text{fl}}$  values and substantially higher  $\Phi_{\text{f}}$  and  $\tau_{\text{f}}$  values in nonpolar solvents in comparison to those in other solvents indicate that the dye exists in different structural forms in the two sets of solvents. It is inferred that in moderate to higher polarity solvents the dye exists in a planar ICT structure where as in nonpolar solvents the dye exists in nonplanar structure. It is predicted that in nonpolar solvents the nonplanar structure of the dye is due to a kind of pyramidal conformation at the 1-NH<sub>2</sub> group of the dye. It is understood that the observed temperature effect on the  $\tau_{\text{f}}$  values of the dye in nonpolar solvents is associated with the possible flip-flop motion of the 1-NH<sub>2</sub> group of the dye in its nonplanar structure. Since a similar motion is not possible for the planar ICT structure of the dye in moderate to higher polarity solvents, in these solvents the  $\tau_{\text{f}}$  values of the dye are temperature independent. That the dye adopts a nonplanar structure in nonpolar solvents is also supported by the observed differences in the deuterium isotope effect on the  $\tau_{\text{f}}$  values in a nonpolar and in a polar solvents, though in both the sets of solvents the presence of intramolecular hydrogen bonding plays a significant role in determining the extent of the observed isotope effect. A support for the predicted structural change for the dye 1AAQ in nonpolar and polar solvents is also obtained from the quantum chemical calculations on the structures of the dye under isolated gas phase condition and also in the presence of discrete polar solvent molecules.

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