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Photophysical properties of 1-*N*-methylamino- and 1-*N*,*N*-dimethylamino-9,10-anthraquinone dyes: A comparison with 1-amino-9,10-anthraquinone dye

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Abstract

Photophysical properties of 1-*N*-methylamino-9,10-anthraquinone (1-MAAQ) and 1-*N*,*N*-dimethylamino-9,10-anthraquinone (1-DMAAQ) dyes have been investigated in different solvents and solvent mixtures and the results are compared with those of the lower analogue 1-amino-9,10-anthraquinone (1-AAQ) dye [P. Dahiya, M. Kumbhakar, D.K. Maity, T. Mukherjee, A.B.R. Tripathi, N. Chattopadhyay, H. Pal, J. Photochem. Photobiol. A: Chem. 181 (2006) 338]. Qualitatively, 1-MAAQ behaves similar to 1-AAQ dye, displaying unusual deviations in photophysical properties in nonpolar solvents in comparison to the linear solvent polarity dependent changes in the properties for solvents of moderate to higher polarities. Moreover, the fluorescence decays of the dye show strong temperature-dependence in nonpolar solvents though the decays are temperature independent in solvents of moderate to higher polarities. It is inferred from the present results that 1-MAAQ dye adopts two different structures, one nonplanar structure in nonpolar solvents and the other planar intramolecular charge transfer structure in other solvents of moderate to higher polarities. A support for the above has been obtained from ab initio quantum chemical calculations. It is observed that in absolute term the nonradiative deexcitation channel is more dominating in 1-MAAQ than in 1-AAQ dye and this is attributed to the stronger intramolecular hydrogen bond present in the former dye than the latter. This is also supported by the deuterium isotope effect on the fluorescence decays of 1-MAAQ dye. Unlike 1-AAQ and 1-MAAQ dyes, their higher analogue 1-DMAAQ dye is found to be unusually weak in its fluorescence. This is attributed to the possible distortion in the anthraquinone moiety from planarity due to the steric effect of the bulky 1-N$(CH_3)_2$ group, which is also supported by the results from ab initio quantum chemical calculations.

Keywords: Photophysical properties; Aminoanthraquinone dyes; Solvent polarity effect; Conformational changes

1. Introduction

Quinones and quinone-derivatives are important class of molecules, having immense importance in areas like dye industry, biology, pharmaceutical chemistry, etc. [1–9]. Among different quinones, the ones having amino and hydroxy substituents have been investigated quite extensively for many years, to understand their both photochemical and radiation chemical activities [10–22]. Many of the amino- and hydroxy-substituted quinones show reasonably good fluorescence quantum yields. Thus, the steady-state and time-resolved fluorescence studies of the amino- and hydroxy-quinones have been used quite extensively to obtain the insight of the excited state behavior of the quinonoid molecules, especially in the understanding of the effect of intra- and inter-molecular hydrogen bonding on the de-excitation rates of the excited molecules involving internal conversion and intersystem crossing processes [10–14]. Due to the presence of the quinonoid moiety, these molecules act as good electron acceptors, and have been investigated quite extensively using both pulse radiolysis and laser flash photolysis techniques to understand the reduced radical characteristics of these molecules [15–22]. In large number of studies on the mechanism and dynamics of electron transfer processes, quinones and quinone-derivatives have also been used as efficient electron

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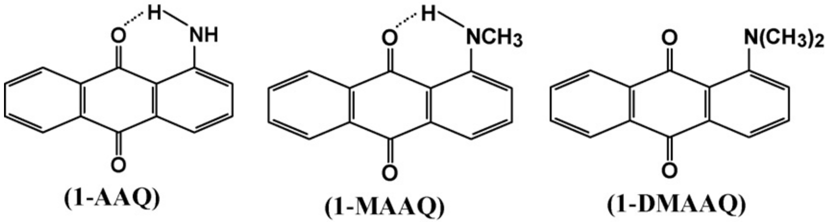


Fig. 1.

acceptors [23–27]. Though photophysical properties of different quinonoid molecules have been investigated quite extensively, the effect of solvent polarity on the photophysical properties of these dyes are not that systematically investigated. In our recent study dealing with the effect of solvent polarity on the photophysical properties of 1-amino-9,10-anthraquinone (1-AAQ) dye it has been observed that the dye shows unusually different behavior in nonpolar solvents in comparison to those in other solvents of medium to higher polarities [28]. The observed results of 1-AAQ dye in nonpolar and other solvents have been rationalized assuming that the dye adopts different conformational structures in the two sets of solvents. From experimental results and from ab initio quantum chemical calculations it has been inferred that in nonpolar solvents the dye 1-AAQ adopts a nonplanar structure where its 1-NH_2 substituent is out of the plane of the 9,10-anthraquinone moiety. In moderate to higher polarity solvents, however, the dye adopts a planar intramolecular charge transfer (ICT) structure where its 1-NH_2 substituent is on the same plane of the 9,10-anthraquinone moiety and accordingly the amino lone pair is in full resonance with the anthraquinone π-cloud. In the present work, photophysical properties of 1-*N*-methylamino-9,10-anthraquinone (1-MAAQ) and 1-*N*,*N*-dimethylamino-9,10-anthraquinone (1-DMAAQ) dyes have been investigated in different solvents and solvent mixtures and the results have been compared with those of the 1-AAQ dye. The aim of the present study is to understand the effect of *N*-alkyl or *N*,*N*-dialkyl substitutions on the solvent polarity dependent conformational changes in the aminoanthraquinone dyes. Chemical structures of 1-AAQ, 1-MAAQ and 1-DMAAQ dyes are shown in Fig. 1 for a quick comparison.

2. Materials and methods

1-MAAQ was prepared from 1-AAQ dye, by treatment with formaldehyde in sulphuric acid [29]. 1-DMAAQ was prepared by the condensation of 1-chloro-9,10-anthraquinone and dimethylamine in ethanol [30]. Both 1-MAAQ and 1-DMAAQ samples prepared in the present work were purified by column chromatography on silica gel. The purity of the samples was checked by NMR and IR data. All the solvents used in the present work were of spectroscopic grade, either from Spectrochem (Mumbai, India), S.D. Fine Chemical (Mumbai, India), SISCO Research Laboratories (Mumbai, India), E. Merck (Mumbai, India) or Fluka (Buchs, Switzerland). Dielectric constants (ε) and refractive indices (n) of the pure solvents were obtained from the literature [31] and those of the mixed solvents (ε_{MS}, n_{MS}, respectively) were estimated using Eqs. (1) and (2), respectively [28,32–36]:

$$\varepsilon_{MS} = f_A\varepsilon_A + f_B\varepsilon_B \tag{1}$$

$$n_{MS}^2 = f_A n_A^2 + f_B n_B^2 \tag{2}$$

where the subscripts A and B represent the two co-solvents used and f_A and f_B represent their respective volume fractions. Following Lippert and Mataga [37–40], the polarity parameter (Δf) for different solvents and solvent mixtures used were calculated using the following relation:

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{3}$$

Absorption and fluorescence spectra were recorded using a JASCO (model V530) spectrophotometer and a Hitachi (model F-4010) spectrofluorimeter, respectively. The Φ_f values were estimated by a comparative method [37,38] using 1-MAAQ in benzene as the reference ($\Phi_f^R = 0.0076$ [13]), Fluorescence lifetimes in different solvents were measured using a time-resolved fluorescence spectrometer from IBH (model IBH Data Station Hub), UK. This instrument works on the principle of time-correlated-single-photon-counting [41]. For the present measurements, a 455 nm LED (frequency 1 MHz) was used as the excitation source and a TBX4 detection module coupled with a special Hamamatsu PMT was used for the detection of the fluorescence photons. The instrument response function for the present setup is ∼1.2 ns at FWHM. For all the solvents used, the observed decays were analyzed as a single exponential function as:

$$I(t) = B\exp\left(\frac{-t}{\tau_f}\right) \tag{4}$$

where τ_f is the fluorescence lifetime of the dye and B is the pre-exponential factor. For all the accepted fits, the reduced chi-square (χ^2) values were within 1.00–1.20 and the weighted residuals were distributed quite randomly among the data channels [41].

For experiments with deuterated 1-MAAQ dye, the amino hydrogen of the 1-$NHCH_3$ group of the dye was first exchanged with deuterium using the following procedure [10,13,28]. In about 5 ml solution of 1-MAAQ dye in hexane about 1 ml of D_2O was added and the mixture was shaken thoroughly for about 5 min. After allowing the mixture to separate out into the organic and the aqueous layers, the organic layer containing the dissolved dye was collected. This procedure was repeated for six times and the hexane solution finally obtained was shaken with activated molecular shieves (from Acros Organics; 4 Å, 8–12 Meshes) to remove the dissolved/dispersed D_2O if any. The supernatant hexane solution containing the deuterated 1-MAAQ dye was then collected to carryout the fluorescence decay measurement. To carry out experiment with deuterated 1-AAQ dye in polar acetonitrile solution, about 4 ml of dehydrated acetonitrile solvent (dehydrated using activated molecular shieves) was added to the above hexane solution. The mixture was shaken thoroughly for about 5 min and then allowed to separate out the two solvent layers. The heavier acetonitrile layer containing the dissolved deuterated dye was collected for the fluorescence decay measurement.

3. Results and discussion

3.1. Fluorescence quantum yields and fluorescence lifetimes

Fluorescence quantum yields (Φ_f) and lifetimes (τ_f) of 1-MAAQ dye were measured in different solvents and solvent mixtures at room temperature and are listed in Table 1. Fig. 2A and B shows the Φ_f versus Δf and τ_f versus Δf plots, respectively, for the dye. It is seen that the plots are reasonably linear if we exclude the nonpolar solvents ($\Delta f \sim 0$) and consider the rest of the solvents of moderate to higher polarities as a separate group. In nonpolar solvents, the Φ_f and τ_f values are evidently deviated towards unusually higher values in comparison to the

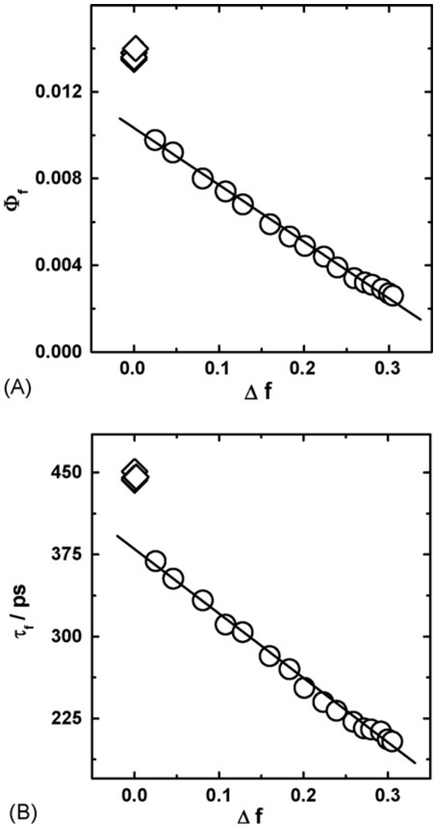


Fig. 2. (A) The Φ_f vs. Δf plot and (B) the τ_f vs. Δf plot for 1-MAAQ dye. In nonpolar solvents the data points (◇) are clearly deviated towards higher values with respect to the linear correlations observed for the data in moderate to higher polarity solvents (○).

Table 1

Fluorescence quantum yields (Φ_f), fluorescence lifetimes (τ_f), radiative rate constants (k_f), nonradiative rate constants (k_{nr}), absorption maxima (λ_{abs}^{max}), fluorescence maxima (λ_{fl}^{max}) and Stokes' shift ($\Delta\bar{\nu}$) for 1-MAAQ in different solvents

Solvent[a]	Δf	Φ_f	τ_f (ps)	k_f ($\times 10^7$ s^{-1})	k_{nr} ($\times 10^9$ s^{-1})	λ_{abs}^{max} (nm)	λ_{fl}^{max} (nm)	$\Delta\bar{\nu}$ (cm^{-1})
CHX	0	0.0135	443	3.05	2.23	488	563	2730
HX	0	0.0136	451	3.01	2.19	487	560	2677
MCHX	0	0.0138	445	3.09	2.22	489	565	2751
3MP	0	0.0136	444	3.07	2.22	487	562	2740
DL	0.002	0.0140	446	3.13	2.21	488	565	2793
$CHX_{95}EA_5$	0.025	0.0098	369	2.65	2.68	491	572	2884
$CHX_{90}EA_{10}$	0.046	0.0092	353	2.61	2.81	492	576	2964
$CHX_{80}EA_{20}$	0.081	0.008	333	2.40	2.98	493	582	3102
$CHX_{70}EA_{30}$	0.108	0.0074	311	2.38	3.19	494	586	3178
$CHX_{60}EA_{40}$	0.128	0.0068	304	2.24	3.27	495	589	3224
$CHX_{40}EA_{60}$	0.160	0.0059	282	2.09	3.52	496	594	3326
$CHX_{20}EA_{80}$	0.183	0.0051	270	1.97	3.68	497	597	3370
EA	0.201	0.0048	253	1.93	3.93	497.5	600	3434
$EA_{95}ACN_5$	0.223	0.0044	240	1.83	4.15	498	604	3524
$EA_{90}ACN_{10}$	0.240	0.0039	232	1.68	4.29	499	606	3538
$EA_{80}ACN_{20}$	0.259	0.0034	222	1.53	4.49	500	608	3553
$EA_{70}ACN_{30}$	0.272	0.0032	216	1.48	4.61	500	610	3607
$EA_{60}ACN_{40}$	0.280	0.0031	215	1.44	4.64	500	613	3687
$EA_{40}ACN_{60}$	0.292	0.0029	213	1.36	4.68	501	614	3673
$EA_{20}ACN_{80}$	0.300	0.0027	206	1.31	4.84	501	616	3726
ACN	0.305	0.0026	204	1.27	4.89	501	617	3753

The Δf values of the solvents are also listed.

[a] 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_xEA_y: *x*% CHX and *y*% EA (v/v); EA_xAN_y: *x*% EA and *y*% AN (v/v).

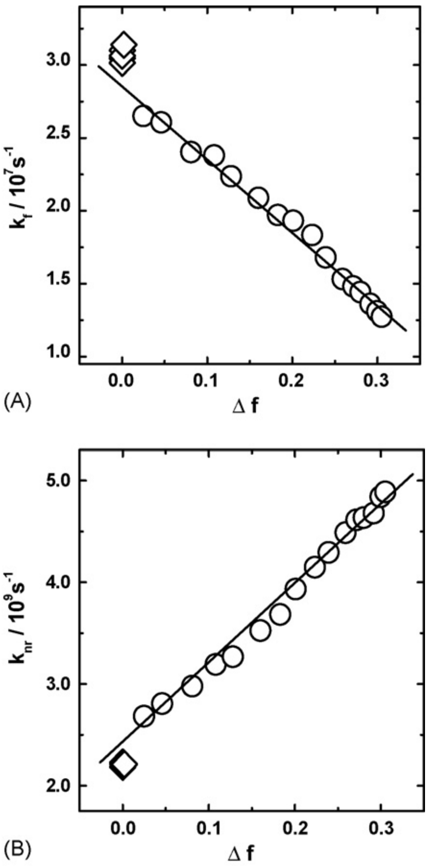


Fig. 3. (A) The k_f vs. Δf plot and (B) the k_{nr} vs. Δf plot for 1-MAAQ dye. The data points in nonpolar solvents are indicated by symbol (◊) and those in other solvents are indicated by symbol (○). In nonpolar solvents the k_f values are distinctly higher and the k_{nr} values are distinctly lower in comparison to the linear correlations observed in solvents of moderate to higher polarities.

linear Φ_f versus Δf and τ_f versus Δf correlations observed for the moderate to higher polarity solvents. These results clearly indicate that the fluorescence characteristics of 1-MAAQ dye in nonpolar solvents are distinctly different than in other solvents of moderate to higher polarities. It is thus expected from the present results that the fluorescent state of the dye might undergo a structural change in nonpolar solvents in comparison to that in other solvents of moderate to higher polarities.

Following the solvent polarity dependent changes in the Φ_f and τ_f values, it is expected that the changes in the radiative (k_f) and nonradiative (k_{nr}) decay rate constants of the dye with Δf should also reflect their characteristic deviations in nonpolar solvents in comparison to their trends in rest of the solvents. Thus, the k_f and k_{nr} values of the dye in different solvents were estimated using Eqs. (5) and (6) [37,38] and the values are listed in Table 1:

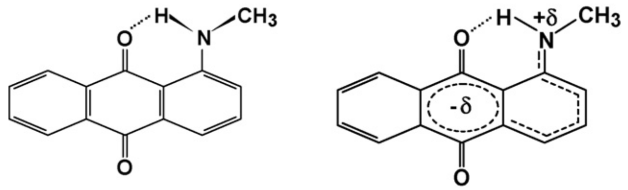
$$k_f = \frac{\Phi_f}{\tau_f} \tag{5}$$

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

Fig. 3A shows the k_f versus Δf plot of the dye. It is seen that the plot is reasonably linear considering the solvents of moderate to higher polarities as a set but excluding the nonpolar solvents. The k_f values in nonpolar solvents are distinctly deviated towards higher values in comparison to the linear correlation observed for rest of the solvents. These results thus support the expected structural change in the fluorescent state of the dye in nonpolar solvents in comparison to that in other solvents of moderate to higher polarities. Fig. 3B shows the k_{nr} versus Δf plot of the dye. In this case also, the plot is reasonably linear for moderate to higher polarity solvents but the data points for nonpolar solvents are distinctly deviated towards lower values in comparison to the linear correlation observed for the other solvents. Though the deviations in the k_f and k_{nr} values in nonpolar solvents are not as large as in the Φ_f and τ_f values, yet the effect is quite evident as the data points in nonpolar solvents cannot be brought under the same linear correlation along with the other solvents of moderate to higher polarities. Thus, the results in the Φ_f, τ_f, k_f and k_{nr} values together suggest that there must be a structural change in fluorescent state of the dye in nonpolar solvents in comparison to that in other solvents of moderate to higher polarities.

At this point it is interesting to compare the results of 1-MAAQ dye with those of 1-AAQ dye reported earlier [28]. Though the ranges of the absolute Φ_f, τ_f, k_f and k_{nr} values for 1-MAAQ dye are quite different than those of 1-AAQ dye [28], which we suppose to be related to the effect of 1-*N*-methyl substitution in 1-MAAQ dye as discussed in the latter part of this section, the overall trends in the changes of the above photophysical parameters with solvent polarity function Δf qualitatively show very similar behavior for both the dyes. Thus, in both the cases, the above photophysical parameters show unusual deviations in nonpolar solvents in comparison to the effective linear correlations observed for rest of the solvents of moderate to higher polarities. For 1-AAQ dye, these deviations in the photophysical properties in nonpolar solvents were attributed to a structural change of the dye, proposing that the dye adopts a nonplanar structure with respect to its 1-NH_2 substituent in nonpolar solvents but a planar ICT structure in all other solvents of moderate to higher polarities. Drawing an analogy with 1-AAQ dye, we propose that in nonpolar solvents the 1-MAAQ dye also adopts a nonplanar and relatively nonpolar structure, where its 1-$NHCH_3$ group is out of plane of the 9,10-anthraquinone moiety and accordingly the amino lone pair is not in full resonance with the anthraquinone π-cloud. On the contrary, in moderate to higher polarity solvents, the dye adopts a planar ICT structure, where the 1-$NHCH_3$ substituent is on the same plane of the 9,10-anthraquinone moiety and the amino lone pair is in full resonance with the anthraquinone π-cloud. Obviously, the ICT structure of the dye in moderate to higher polarity solvents is much polar in nature than the nonplanar structure of the dye in nonpolar solvents. These structural changes of 1-MAAQ dye on the basis of the solvent polarity used can schematically be presented as in Fig. 4.

From the results presented so far it is indicated that the 1-NCH_3 substitution in 1-MAAQ dye does not alter the trends of the solvent polarity dependent changes in the photophysical properties with respect to those of the 1-AAQ dye. With respect to the absolute values of different photophysical parameters, however, it is clearly indicated from the present results that the



(non-planar structure)
(in nonpolar solvents)

(planar ICT structure)
(in polar solvents)

Fig. 4.

1-NCH$_3$ substitution in 1-MAAQ dye in fact causes a significant change in the magnitudes of the parameters in comparison to those of 1-AAQ dye. Thus, it is seen that the Φ_f values of 1-MAAQ dye in different solvents (range of Φ_f is ~0.0025–0.014 in different solvents) are much lower (~5–8 times) than those of 1-AAQ dye (range of Φ_f is ~0.023–0.07 in different solvents [28]). Similarly, the τ_f values of 1-MAAQ dye in different solvents (range of τ_f is ~220–450 ps in different solvents) are also about 3–5 times lower than those of 1-AAQ dye (range of τ_f is ~1.0–1.8 ns in different solvents [28]). Interestingly, however, the k_f values of 1-MAAQ (range of k_f is $\sim 1.3 \times 10^7$ to $3.0 \times 10^7\,\mathrm{s}^{-1}$ in different solvents) and 1-AAQ (range of k_f is $\sim 1.3 \times 10^7$ to $3.0 \times 10^7\,\mathrm{s}^{-1}$ in different solvents) dyes are found to be almost in the similar range though the k_{nr} values for 1-MAAQ dye (k_{nr} is in the range of $\sim 2 \times 10^9$ to $4 \times 10^9\,\mathrm{s}^{-1}$ in different solvents) are much higher (~4–5 times) than those of 1-AAQ dye (k_{nr} is in the range of $\sim 5 \times 10^8$ to $1 \times 10^9\,\mathrm{s}^{-1}$ in different solvents [28]). Since 1-NHCH$_3$ group is better electron-donating in nature than 1-NH$_2$ group and since an electron donating substituent normally enhances the fluorescence properties of the anthraquinone dyes due to enhanced ICT character, the drastic reduction in the Φ_f and τ_f values for 1-MAAQ dye in comparison to those of the 1-AAQ dye is apparently an unexpected observation. It is evident from the comparison of the Φ_f, τ_f, k_f and k_{nr} values of 1-MAAQ and 1-AAQ dyes that the 1-NCH$_3$ substitution in 1-MAAQ dye causes a large enhancement in the nonradiative decay channel for the excited 1-MAAQ dye. We feel that this enhancement in k_{nr} is directly related to the relative strengths of the intramolecular hydrogen bonds present in 1-MAAQ and 1-AAQ dyes. In aminoanthraquinone dyes, it is reported that the nonradiative internal conversion (IC) processes is strongly coupled to the vibrational modes associated to the intramolecular hydrogen bonds present [10,13,14]. Since the positive inductive effect of the 1-NCH$_3$ group is expected to increase the intramolecular hydrogen bond strength in 1-MAAQ in comparison to 1-AAQ dye, it can effectively cause an enhancement in the nonradiative IC process in the former dye, resulting a large reduction in the Φ_f and τ_f values for the dye in comparison to those of 1-AAQ dye.

At this juncture we would like to consider the photophysical properties of 1-DMAAQ dye, the higher analogue of the 1-aminoanthraquinone dyes considered. It is interestingly seen that the 1-DMAAQ dye behaves quite differently than 1-AAQ and 1-MAAQ dyes discussed earlier. Thus, with 1-DMAAQ dye it is found that the dye is unusually weak in its fluorescence in comparison to those of 1-AAQ and 1-MAAQ dyes. That 1-DMAAQ dye is unusually weak in its fluorescence behavior is also reported in the literature, indicating the Φ_f value of the dye as low as about 10^{-5} [13]. In fact, in the present study, the fluorescence intensity for 1-DMAAQ dye in the solvents studied was so weak that we were not able to accurately estimate the Φ_f values of the dye. Similarly, due to very weak fluorescence, we were also not able to measure the fluorescence decays of 1-DMAAQ dye in any of the solvents studied. Thus, unlike 1-AAQ and 1-MAAQ dyes, the Φ_f versus Δf and τ_f versus Δf plots could not be obtained and compared for 1-DMAAQ dye. Since like 1-AAQ and 1-MAAQ dyes, there is no intramolecular hydrogen bond present in 1-DMAAQ dye, the unusually low fluorescence quantum yield for 1-DMAAQ dye could not be justified on the basis of the better electron donating nature or stronger positive inductive effect of the 1-N(CH$_3$)$_2$ substituent in the present dye. Thus, from the present results, we feel that due to large steric effect of the bulky 1-N(CH$_3$)$_2$ group, the chromophoric anthraquinone moiety of the 1-DMAAQ dye might undergo a large distortion from planarity and thus causing the dye to be very inefficient in its fluorescence properties in comparison to those of 1-AAQ and 1-MAAQ dyes. We will discuss this aspect further in the following sections with respect to the other results obtained either from experimental studies or from ab initio quantum chemical calculations.

3.2. Absorption and fluorescence spectral characteristics

Following the discussion presented in the previous section, if the dye 1-MAAQ adopts a structural form in nonpolar solvents different than that in other solvents, the absorption and fluorescence spectral characteristics of the dye in nonpolar and other solvents should also show some characteristic differences. Thus, absorption and fluorescence spectra of 1-MAAQ dye were recorded in different solvents and solvents mixtures. Table 1 lists the longer wavelength absorption maxima (λ_{abs}^{max} in nm) and fluorescence maxima (λ_{fl}^{max} in nm) of the dye in different solvents. Fig. 5A and B shows the changes in the absorption and fluorescence maxima ($\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$, respectively, in cm^{-1}) of 1-MAAQ dye with Δf values of the solvents used. It is seen that in the solvents of moderate to higher polarities, both $\bar{\nu}_{abs}$ versus Δf and $\bar{\nu}_{fl}$ versus Δf plots are effectively linear. For the nonpolar solvents, however, both $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values deviate largely towards higher side relative to the linear correlations observed for rest of the solvents. These results corroborate the results obtained with Φ_f and τ_f variations with Δf, suggesting a different structural form of 1-MAAQ dye in nonpolar solvents than that in other solvents of moderate to higher polarities.

For a molecule, if the chromophoric structure does not change with solvent polarity, the Stokes' shift ($\Delta\bar{\nu}$) between $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ is expected to follow a linear correlation with the solvent polarity function Δf, as given by the following Lippert and Mataga relation [37–40]:

$$\Delta\bar{\nu} = \Delta\bar{\nu}_0 + \frac{2(\mu_e - \mu_g)^2}{hcr^3}\Delta f \qquad (7)$$

where μ_e and μ_g are the excited and ground state dipole moments, respectively, h the Planck's constant, c the velocity

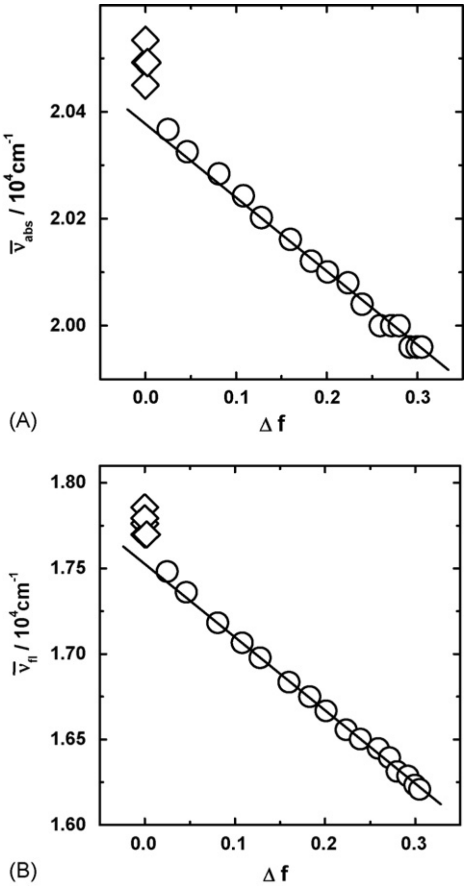


Fig. 5. (A) The $\bar{\nu}_{abs}$ vs. Δf plot and (B) the $\bar{\nu}_{fl}$ vs. Δf plot of 1-MAAQ dye. The $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values in nonpolar solvents (◇) deviate largely towards higher side relative to the linear correlations observed for the data (◯) in rest of the solvents.

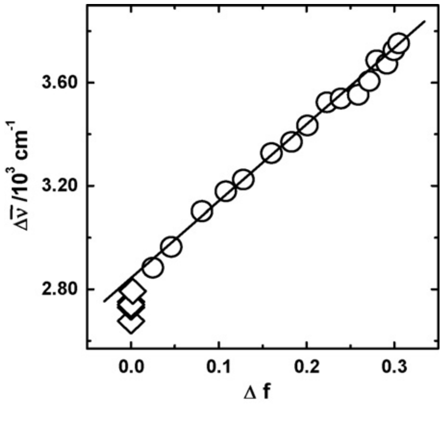


Fig. 6. Plot of the Stokes' shifts ($\Delta\bar{\nu}$) for 1-MAAQ dye against the solvent polarity function Δf. The data in nonpolar solvents are indicated by symbol (◇) and those in other solvents are indicated by symbol (◯). The plot is linear within experimental error for moderate to higher polarity solvents but deviates toward lower values in nonpolar solvents.

Table 2
Absorption maxima (λ_{abs}^{max}), fluorescence maxima (λ_{fl}^{max}) and Stokes' shifts ($\Delta\bar{\nu}$) for 1-DMAAQ dye in different solvents

Solvent[a]	Δf	λ_{abs}^{max} (nm)	λ_{fl}^{max} (nm)	$\Delta\bar{\nu}$ (cm^{-1})
CHX	0	487	566	2866
HX	0	487.5	566.2	2851
MCHX	0	487.5	566.5	2861
3MP	0	487	566	2866
$CHX_{90}EA_{10}$	0.046	491	572	2884
$CHX_{80}EA_{20}$	0.081	492	574	2904
$CHX_{70}EA_{30}$	0.108	494	577	2912
$CHX_{60}EA_{40}$	0.128	494.5	579	2951
$CHX_{40}EA_{60}$	0.160	496.5	582	2959
$CHX_{20}EA_{80}$	0.183	497.5	584	2977
EA	0.201	498	585	2986
$EA_{90}ACN_{10}$	0.239	500	588	2993
$EA_{80}ACN_{20}$	0.259	500	589	3022
$EA_{60}ACN_{40}$	0.280	500	589	3022
$EA_{20}ACN_{80}$	0.300	501.5	592	3048
ACN	0.305	502	593	3057

The Δf values of the solvents are also listed.

[a] Abbreviations for the solvents and solvent mixtures are as given in the foonote of Table 1.

of light and r is the Onsager radius. Table 1 lists the $\Delta\bar{\nu}$ values of 1-MAAQ dye in different solvents. Fig. 6 shows the $\Delta\bar{\nu}$ versus Δf plot for the dye. It is indicated that the plot is reasonably linear for the moderate to higher polarity solvents. The data points in nonpolar solvents, however, deviate quite substantially towards lower side relative to the linear correlation observed for rest of the solvents. For the linear part of the $\Delta\bar{\nu}$ versus Δf plot, the value of the slope is determined to be ∼2896 cm^{-1}, which is a reasonably high value for a molecule [37,38], suggesting that in these solvent polarity region the dye 1-MAAQ exists in a polar ICT structure. In nonpolar solvents, the positive deviations in the $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values in combination with the negative deviations in the $\Delta\bar{\nu}$ values suggest that in nonpolar solvent the dye 1-MAAQ adopts a relatively nonpolar structure than its ICT structure [28], which actually corroborates with the two structures given for the dye in Fig. 6 for nonpolar and polar solvents. To be mentioned here that the absorption and fluorescence spectral characteristics of 1-MAAQ dye as observed in the present work are qualitatively very similar to those reported earlier for its lower analogue, viz. 1-AAQ dye [28]. It is thus indicated that even in the presence of 1-NCH_3 substituent, the 1-MAAQ dye displays the similar solvent polarity dependent conformational changes as are also reported for 1-AAQ dye [28].

Absorption and fluorescence spectra of 1-DMAAQ dye were recorded in different solvents and solvents mixtures. As already mentioned in Section 3.1, unlike 1-AAQ and 1-MAAQ dyes, the fluorescence from 1-DMAAQ was unusually weak. Thus, to record the fluorescence spectra of 1-DMAAQ dye in different solvents we had to use very large excitation and emission bandpass (20 nm) and also high PMT gain. Table 2 lists the λ_{abs}^{max} and λ_{fl}^{max} values of 1-DMAAQ dye in different solvents. Fig. 7A and B shows the $\bar{\nu}_{abs}$ versus Δf and $\bar{\nu}_{fl}$ versus Δf plots for the dye. It is seen from Fig. 7 that similar to 1-AAQ and 1-MAAQ dyes, the two plots for 1-DMAAQ dye are also effectively linear for the solvents of moderate to higher polarities. The $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values in nonpolar solvents, however, show small deviations towards higher sides relative to the linear correlations observed for rest of the solvents, though for the present dye these deviations are much less compared to those observed for 1-AAQ and

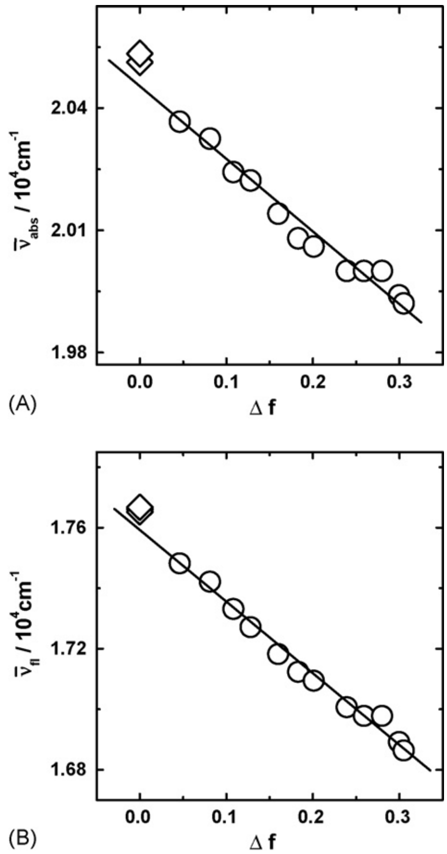


Fig. 7. (A) The $\bar{\nu}_{abs}$ vs. Δf plot and (B) the $\bar{\nu}_{fl}$ vs. Δf plot of 1-DMAAQ dye. The $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values apparently deviate in nonpolar solvents (◊) in comparison to the linear correlations observed for the data in rest of the solvents of moderate to higher polarities (○). The deviations, however, are much less than those observed for 1-MAAQ dye (*cf.* Fig. 6).

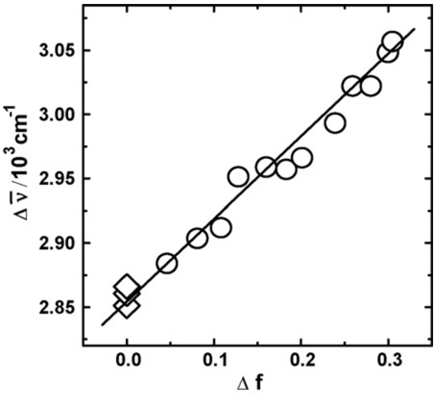
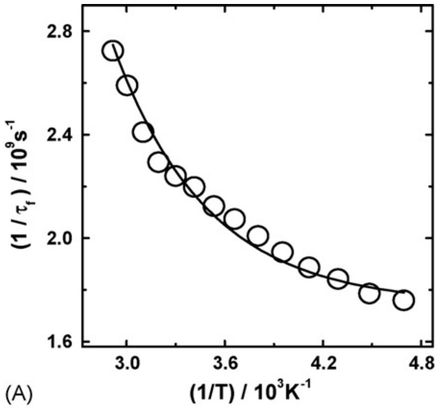


Fig. 8. Plot of the Stokes' shifts ($\Delta\bar{\nu}$) for 1-DMAAQ dye against the solvent polarity function Δf. The data in nonpolar solvents are indicated by symbol (◊) and those in other solvents are indicated by symbol (○). The plot is apparently linear including all the solvents of varying polarities under the same correlation.

1-MAAQ dyes. The linear correlations in Fig. 7 suggest that the structure of 1-DMAAQ dye remains the same in all these solvents of moderate to higher polarities. In nonpolar solvents, the small deviations in the $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values could be related to some structural changes similar to those of 1-MAAQ and 1-AAQ dyes. This, however, cannot be substantiated by other photophysical properties of 1-DMAAQ dye, as the solvent polarity dependent changes in the Φ_f and τ_f values of the dye could not be investigated in the present work (*cf.* Section 3.1). In the present context, however, correlation of the Stokes' shifts with solvent polarity provides us some interesting information. Table 2 lists the $\Delta\bar{\nu}$ values for 1-DMAAQ dye in different solvents and solvent mixtures. Fig. 8 shows the $\Delta\bar{\nu}$ versus Δf plot for 1-DMAAQ dye. As expected, the plot is linear for the moderate to higher polarity solvents. Interestingly, however, the $\Delta\bar{\nu}$ values of the dye in nonpolar solvents are also seen to apparently come under the same linear correlation as observed for rest of the solvents. Thus, on the basis of the solvent polarity dependent Stokes' shifts it is difficult to infer if the dye 1-DMAAQ also undergoes a structural change similar to those of 1-AAQ and 1-MAAQ dyes in nonpolar solvents. Another interesting point to note form the $\Delta\bar{\nu}$ versus Δf plot for 1-DMAAQ dye is that the slope of the plot is unusually low in comparison to slopes of the similar plots for 1-AAQ and 1-MAAQ dyes. Thus, for 1-DMAAQ dye the slope is estimated to be only ~636 cm^{-1} in comparison to the slopes of ~2363 and ~2896 cm^{-1} estimated for 1-AAQ and 1-MAAQ dyes, respectively. The unusually lower slope for the $\Delta\bar{\nu}$ versus Δf plot of 1-DMAAQ dye in fact suggests that this dye possibly cannot adopt a planar ICT structure even in the solvents of moderate to higher polarities. Since the 1-N(CH$_3$)$_2$ substituent is quite bulky, it is expected that the substituent will have a steric hindrance in adopting a planar ICT structure. It is also possible that the presence of bulky 1-N(CH$_3$)$_2$ substituent might cause the 9,10-anthraquinone chromophore to undergo some kind of distortion from planarity to accommodate the substituent. If such a distortion occurs in the chromophoric moiety, it will cause a large reduction in the resonance among the π-electrons as well as the lone pair of the amino nitrogen. Accordingly, the ICT character for 1-DMAAQ dye will be very weak in comparison to that of 1-AAQ and 1-MAAQ dyes, resulting a large reduction in the fluorescence quantum yield of the former dye. A support of the above distortion in the chromophoric structure of 1-DMAAQ dye is in fact obtained from ab initio quantum chemical calculations as are discussed in Section 3.5.

3.3. Temperature effect on the fluorescence decay kinetics

The effect of temperature on the fluorescence decays of 1-MAAQ dye was investigated in different solvents of varying polarities. It is observed that in nonpolar solvents the fluorescence decays of 1-MAAQ dye are strongly dependent on temperature. Thus, the decays are seen to gradually become faster as the temperature of the solution is increased. Excluding the nonpolar solvents, in all other solvents of moderate to higher polarities, however, the fluorescence decays of 1-MAAQ dye are found to be temperature independent. Fig. 9A and B shows two typical results on the temperature dependent changes in the fluorescence lifetimes (τ_f) of 1-MAAQ dye, one in a nonpolar solvent methylcyclohexane and the other in a polar solvent acetonitrile. Present results indicate that an additional activation-controlled nonradiative de-excitation channel operates for the



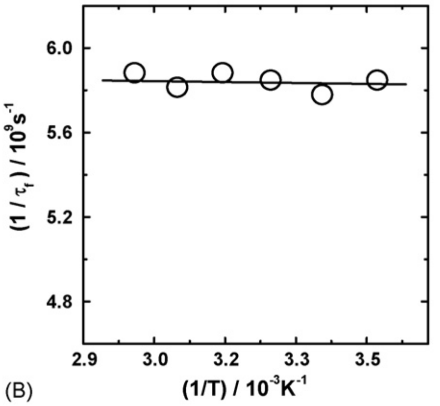


Fig. 9. (A) Temperature effect on the fluorescence lifetime (τ_f) of 1-MAAQ dye in a nonpolar solvent methylcyclohexane. The τ_f drastically reduces on increasing the temperature of the solution. The circles represent the experimental data points and the continuous curve represents the fitted curve following Eq. (8). (B) Temperature effect on the fluorescence lifetime (τ_f) of 1-MAAQ dye in a polar solvent acetonitrile. The τ_f is effectively independent of temperature.

fluorescent state of the dye in nonpolar solvents, which is apparently absent in all other solvents of moderate to higher polarities. To be mentioned that similar results were also obtained earlier while investigating the temperature effect on the fluorescence decays of 1-AAQ dye in different solvents [28]. That the τ_f for 1-AAQ dye was strongly temperature dependent in nonpolar solvents but temperature independent in all other solvents was justified by considering that in nonpolar solvent the 1-NH_2 group of the dye in its nonplanar structure can undergo a fast flip-flop motion and this motion is in fact responsible for the additional activation-controlled nonradiative deexcitation channel for the dye excited state in nonpolar solvents [28]. Drawing an analogy with the 1-AAQ dye, we propose that in the present case of 1-MAAQ dye also the additional nonradiative de-excitation channel in nonpolar solvents is due to the flip-flop motion of the 1-$NHCH_3$ group of the dye in its nonplanar structure. In other solvents of moderate to higher polarities, since the dye 1-MAAQ exists in its planar ICT structure, the flip-flop motion of the 1-NHMe group is highly restricted and accordingly the fluorescence decays of the dye in these solvents are effectively temperature independent.

Under normal circumstances, the k_f values of the fluorophores are temperature independent and the temperature effect on the τ_f values is mainly due to the temperature-dependent changes in k_{nr} values of the dyes [37,38]. Thus, the temperature effect on the τ_f values can logically be expressed by the following modified Arrhenius equation [28,42]:

Table 3
The τ_0^{-1}, ΔE_a and k_{nr}^0 values for 1-MAAQ dye as obtained by analysis of the temperature dependent changes in the τ_f values of the dye in different nonpolar solvents following Eq. (8)

Solvents[a]	η (cP) (20 °C)	τ_0^{-1} ($\times 10^9$ s^{-1})	ΔE_a (kcal mol^{-1})	k_{nr}^0 ($\times 10^{11}$ s^{-1})
3MP	0.307	1.82	3.22	1.83
HX	0.313	1.87	3.17	1.74
MCHX	0.734	1.74	3.45	1.56
CHX	0.98	1.81	3.23	1.45
DL	2.75	1.83	3.28	1.33

The table also lists the viscosity (η) of the solvents used.
[a] Abbreviations for the solvents and solvent are as given in the footnote of Table 1.

$$\tau_f^{-1} = \tau_0^{-1} + k_{nr}^0 \exp\left(\frac{-\Delta E_a}{RT}\right) \quad (8)$$

where ΔE_a is the activation energy, k_{nr}^0 the pre-exponential factor, R the universal gas constant, T the absolute temperature and τ_0^{-1} is the overall rate constant for the temperature-independent deexcitation processes. Temperature-dependent τ_f values of 1-MAAQ in different nonpolar solvents were analyzed following Eq. (8) and the τ_0^{-1}, k_{nr}^0 and ΔE_a values thus estimated are listed in Table 3. It is seen that for all the nonpolar solvents studied, the τ_0^{-1} and ΔE_a values are almost in similar range. The k_{nr}^0 values are, however, seen to undergo a gradual change as the viscosity (η) of the solvent is changed. In fact, a plot of k_{nr}^0 against the inverse of η appears to follow effectively a linear correlation within the experimental error, as shown in Fig. 10. The results in Fig. 10 indicate that the collisional interaction of the excited dye with the surrounding solvent molecules play an important role in the activation-controlled nonradiative de-excitation channel of the present dye in nonpolar solvents. To be mentioned here that exactly similar k_{nr}^0 versus η^{-1} plot was also obtained earlier by us with 1-AAQ dye in nonpolar solvents [28]. It is interesting

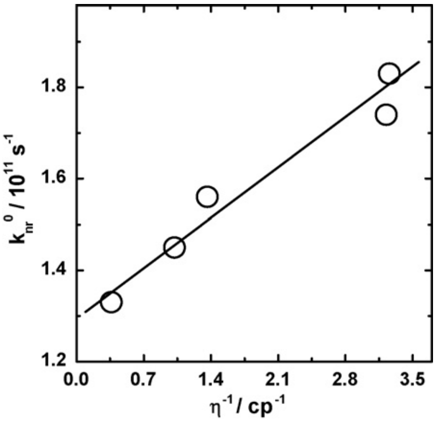


Fig. 10. Variations in the k_{nr}^0 values for 1-MAAQ dye with the inverse of viscosity (η) of the nonpolar solvents used. The plot is linear within experimental error.

to note here that the k_{nr}^{0} values obtained for 1-MAAQ dye in different nonpolar solvents are always much lower (of the order of 10^{11} s^{-1}) than those obtained earlier for 1-AAQ dye (of the order of 10^{12} s^{-1} [28]). The lower k_{nr}^{0} values for 1-MAAQ dye in comparison to those of 1-AAQ dye is possibly due to the heavier 1-NHMe substituent of the dye in comparison to the 1-NH_2 group in 1-AAQ dye. Accordingly, it is expected that the flip-flop motion of the 1-NHMe group in 1-MAAQ dye will be much slower than that of the 1-NH_2 group in 1-AAQ dye, resulting a lower k_{nr}^{0} value for the former dye. As mentioned earlier, due to very low fluorescence quantum yields of 1-DMAAQ dye, it is not possible to measure the fluorescence lifetimes of this dye. Obviously, the temperature effect on the fluorescence decay kinetics of 1-DMAAQ could also not be studied in the present work.

3.4. *Deuterium isotope effect on the fluorescence decay kinetics*

In 1-MAAQ dye, the hydrogen atom of the 1-$NHCH_3$ group can form intramolecular hydrogen bond with the adjacent quinonoid oxygen (*cf.* Fig. 4). Since the positive inductive effect of the 1-NCH_3 group is expected to increase the intramolecular hydrogen bond strength in 1-MAAQ dye, an enhancement in the nonradiative IC process is expected for the dye compared to that in its lower analogue 1-AAQ dye. This is in fact indicated by the fact that the k_{nr} values for 1-MAAQ dye (k_{nr} in the range of $\sim 2 \times 10^9$ to 5×10^9 s^{-1}) are almost 4–5 times higher than those of 1-AAQ dye (k_{nr} in the range of $\sim 0.5 \times 10^9$ to 1×10^9 s^{-1}). To understand further on the role of intramolecular hydrogen bonding on the nonradiative de-excitation process of 1-MAAQ dye, we carried out the fluorescence decay measurements using deuterated 1-MAAQ dye, where the amino hydrogen of the 1-$NHCH_3$ group is replaced by deuterium. The deuterated 1-MAAQ dye was prepared using the procedure given in Section 2. The fluorescence decays of deuterated 1-MAAQ dye were measured in a nonpolar solvent hexane and in a polar solvent acetonitrile and the estimated lifetimes were compared with those obtained for the nondeuterated dye in the respective solvents. It is seen that on deuteration the τ_f value of the dye increases from 0.45 to 2.6 ns in hexane solution and from 0.20 to 1.2 ns in acetonitrile solution. Thus, the relative increase in the τ_f values on deuteration of the dye is about 5.8 times in hexane solution and about six times in acetonitrile solution. To be mentioned here that with 1-AAQ dye also we observed similar isotope effect on the τ_f values in hexane and acetonitrile solution, showing a relative increase in the τ_f values of about three times in hexane solution and about five times in acetonitrile solution [28]. It is thus indicated that the deuterium isotope effect on the τ_f values is more prominent in the case of 1-MAAQ dye, especially in the case of nonpolar hexane solution. This increased isotope effect for 1-MAAQ dye in comparison to that in 1-AAQ dye is supposed to be related to the stronger intramolecular hydrogen bond in the former dye as compared to that in the latter. In polar acetonitrile solution, the dye 1-MAAQ exists in its planar ICT structure where the flip-flop motion of the 1-$NHCH_3$ group cannot participate. Thus in acetonitrile solution the observed isotope effect is related only to the vibrational modes associated with the intramolecular hydrogen bond. In hexane solution, since the dye exists in its nonplanar structure, not only the vibrational modes associated with intramolecular hydrogen bond but also the flip-flop motion of the 1-$NHCH_3$ group can get affected on deuteration. Accordingly, deuterium isotope effect on the τ_f values is seen to be relatively higher in hexane solution than in acetonitrile solution.

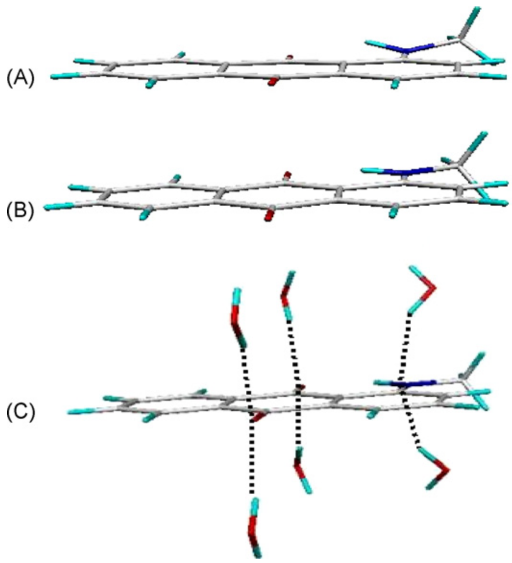


Fig. 11. The most relaxed structures of 1-MAAQ dye: (A) in the ground state under isolated gas phase condition, (B) in the excited state under isolated gas phase condition and (C) in the ground state in the presence of polar solvent.

3.5. *Quantum chemical calculations on the structures of the dye*

To obtain a theoretical support for the proposed structural changes in the dyes as inferred from the observed experimental results, we carried out ab initio quantum chemical calculations under both in the isolated gas phase condition and also in the presence of polar solvent. Full geometry optimization in the ground state of 1-MAAQ dye was performed following 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 configuration interaction with single-electron-excitation (CIS) with the same set of basis function as in MP2 method. All these calculations were performed adopting GAMESS suite of program on a PC-based LINUX cluster [43]. The most relaxed ground state structure of 1-MAAQ dye obtained under isolated gas phase condition is shown in Fig. 11A. In this structure, the three rings of anthraquinone moiety are found to be on the same plane. The hydrogen atom and the CH_3 unit of the 1-$NHCH_3$ group are, however, found to be moved away from the above molecular plane, making dihedral angles as $\delta(\Phi\text{–N–H}) = 10.5^\circ$ and $\delta(\Phi\text{–N–CH}_3) = 8.8^\circ$. Geometry optimization in the excited state (S_1) of 1-MAAQ dye based on CIS method with 6-31 + G(d, p) set of basis function yields a structure with the dihedral angles $\delta(\Phi\text{–N–H}) = 1.2^\circ$ and $\delta(\Phi\text{–N–CH}_3) = 1.5^\circ$, as shown in Fig. 11B. Based on these structures, especially that in the excited state, it is difficult to conclude if the dye adopts a nonplanar structure in the isolated gas phase condition and consequently in a nonpolar solvent where solute–solvent dielectric interaction is quite negligible. The experimental results, however, strongly indicated that the dye behaves differently in nonpolar solvents than in other solvents and this can be rationalized by considering a nonplanar structure for the dye in nonpolar solvent in comparison to the planar ICT structure of the dye in other solvents of moderate to higher polarities. That in the quantum chemical calculations the dihedral angles $\delta(\Phi\text{–N–H})$ and $\delta(\Phi\text{–N–CH}_3)$ are not found to be significantly large is possibly due to the overestimation of the intramolecular hydrogen bonding effect on the calculated structures under isolated gas phase condition. To check this point, we also performed similar calculations on the structures of the analogous dye 2-NHCH$_3$-9,10-anthraquinone (2-MAAQ), where intramolecular hydrogen bonding is not possible due to non-proximity of the amino hydrogen and the quinonoid oxygen. For 2-MAAQ dye, in the isolated gas phase condition the dihedral angles $\delta(\Phi\text{–N–H})$ and $\delta(\Phi\text{–N–CH}_3)$ are thus obtained as about 12.4° and 28° in the ground state {MP2/6-31 + G(d, p)} and 8.2° and 24.3° in the excited state {CIS/6-31 + G(d, p)}. Thus, nonplanar structures for both ground (S_0) and excited (S_1) states of 2-MAAQ dye are clearly indicated in the isolated gas phase condition, and similar nonplanar structures are also expected in nonpolar solvents. Drawing an analogy with the calculated structures of 2-MAAQ dye, we presume that similar nonplanar structures are also possible for the ground and excited states of 1-MAAQ dye in nonpolar solvents. That the calculated structures of 1-MAAQ dye do not show very clear nonplanar character for the 1-NHCH$_3$ group is certainly due to the overestimation of the effect of intramolecular hydrogen bonding on the calculated structures of the dye.

To study the effect of solvent polarity on the structure of 1-MAAQ dye, the gas phase molecular geometry was reoptimized fully in the presence of six discrete polar solvent (water) molecules surrounding the dye, three on the top and three below the molecular plane. To simplify the calculation, water molecules were considered to incorporate the polar solvent effect rather than using acetonitrile molecules. The 1-MAAQ 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 the representative of the polar solvent. It is seen that due to polar solvent effect, the amino hydrogen atom and the amino methyl group are now placed effectively on the same plane of the 9,10-anthraquinone moiety, as shown in Fig. 11C. The calculated dihedral angles $\delta(\Phi\text{–N–H})$ and $\delta(\Phi\text{–N–CH}_3)$ in the present case are estimated to be very close to zero (~0.2°). Similar planar structure is also obtained for 2-MAAQ dye based on similar quantum chemical calculations in the presence of polar solvent. These results thus suggest that in polar solvents both 1-MAAQ and 2-MAAQ dyes preferably exist in their planar ICT structures. In brief, the results from ab initio quantum chemical calculations grossly support our hypothesis that the dye 1-MAAQ (and also 2-MAAQ) exists in a nonplanar structure with respect to its 1-NHCH$_3$ group in nonpolar solvents but in a planar ICT structure in other solvents of moderate to higher polarity. These structural changes of 1-MAAQ dye depending on the polarity of the solvent used can easily explain the observed differences in the photophysical properties of the dye in nonpolar and other solvents.

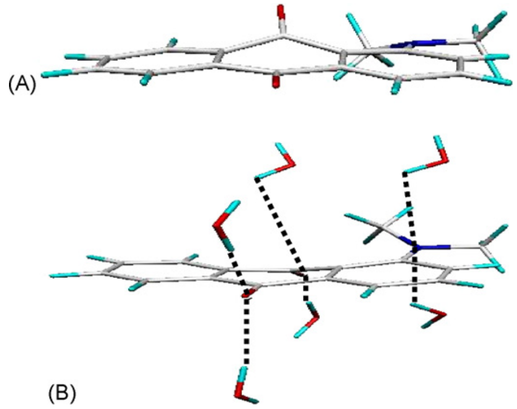


Fig. 12. The most relaxed structures of 1-DMAAQ dye: (A) in the ground state under isolated gas phase condition and (B) in the ground state in the presence of polar solvent.

For 1-DMAAQ dye also we also carried out similar quantum chemical calculations on the structures of the dye under both isolated gas phase condition and in the presence of polar solvents. The most relaxed ground state structure of 1-DMAAQ dye under isolated gas phase condition is shown in Fig. 12A. It is clearly seen that in this structure the main chromophore, viz. the 9,10-anthraquinone moiety has undergone a substantial distortion from planarity ($\delta = 18.4^\circ$), and it happens due to the large steric effect of the bulky 1-NH(CH$_3$)$_2$ group. Moreover, the 1-NH(CH$_3$)$_2$ group is also seen to be out of plane of the adjacent π-ring as indicated in Fig. 12A. The most relaxed structure of the dye in the presence of polar solvent is shown in Fig. 12B. In this structure also the 9,10-anthraquinone moiety has undergone a significant distortion from planarity. Thus, from the calculated structures of 1-DMAAQ dye it is expected that the dye will show unusually weak fluorescence behavior as we actually observe from experimental measurements.

4. Conclusion

Photophysical properties of 1-MAAQ and 1-DMAAQ dyes have been investigated in different solvents and solvent mixtures and the results are compared with those of their lower analogue 1-AAQ dye. All the photophysical properties like Φ_f, τ_f, k_f, k_{nr}, $\bar{\nu}_{abs}$, $\bar{\nu}_{fl}$ and $\Delta\bar{\nu}$ indicate that the 1-MAAQ dye behaves quite differently in nonpolar solvents than in other solvents of moderate to higher polarities showing unusual deviations in the properties in the former solvents in comparison to the trend observed for the latter solvents. It is also found that the fluorescence decay of 1-MAAQ dye is strongly temperature-dependent in nonpolar solvents though the decays are temperature-independent in the other solvents of moderate to higher polarities. These results are qualitatively very similar to those of the 1-AAQ dye, and are rationalized assuming that both 1-AAQ and 1-MAAQ dyes adopt nonplanar structure in nonpolar solvents but a planar intramolecular charge transfer structure in rest of the solvents. The proposed structural changes with reference to the nonpolar and other solvents has been supported by the results of the ab initio quantum chemical calculations carried out on the structures of 1-MAAQ dye under both isolated gas phase condition and in the presence of polar solvent. It is seen that the absolute magnitudes for different photophysical parameters of 1-MAAQ dye are quite different than those of 1-AAQ dyes. These are rationalized on the basis of the relative strengths of the intramolecular hydrogen bonds present in 1-MAAQ and 1-AAQ dyes, which is also substantiated by the observed deuterium isotope effect on the fluorescence decay of 1-MAAQ dye. Unlike 1-AAQ and 1-MAAQ dyes, the 1-DMAAQ dye is seen to be unusually weak in its fluorescence and accordingly the details of the photophysical properties of 1-DMAAQ dye could not be investigated in any of the solvent studied. The extremely weak fluorescence of 1-DMAAQ dye is attributed to a possible distortion of the anthraquinone moiety from planarity due to the steric effect of the bulky 1-$N(CH_3)_2$ group. The results of the ab initio quantum chemical calculations on the structure of 1-DMAAQ dye also support the above distortion in the chromophoric moiety of the present dye.

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