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Estimation of first excited singlet-state dipole moments of aminoanthraquinones by solvatochromic method

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ABSTRACT

The ground state (μ_g) and the excited state (μ_e) dipole moments of three substituted anthraquinones, namely 1-aminoanthracene-9,10-dione (AAQ), 1-(methylamino)anthracence-9,10-dione (MAQ) and 1,5-diaminoanthracene-9,10-dione (DAQ) were estimated in various solvents. The dipole moments (μ_g and μ_e) were estimated from Lippert, Bakhshiev, Kawski-Chamma-Viallet, McRae and Suppan equations by using the variation of Stokes shift with the solvent dielectric constant and refractive index. The excited state dipole moments were also calculated by using the variation of Stokes shift with microscopic solvent polarity parameter (E_T^N). It was observed that dipole moment values of excited states (μ_e) were higher than corresponding ground state values (μ_g), indicating a substantial redistribution of the π-electron densities in a more polar excited state for all the molecules investigated.

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1. Introduction

As a continuation of our systematic studies of estimating the ground- and excited-state dipole moments of laser dyes [1,2], we undertook a similar study of some substituted anthraquinones. There are few reports published on the photophysical properties of substituted anthraquinones [3–7]. Anthraquinone is an aromatic organic compound. It is the most important quinone derivative of anthracene as the parent substance of a large class of dyes and pigments. The important property of anthraquinone is that it is chemically fairly stable under normal conditions. Anthraquinones naturally occur in some plants like aloe, cascara, senna, buckthorn, etc. They also serve as a basic skeleton for pigments of fungi, lichens and insects. Natural anthraquinone derivatives tend to have laxative effects. Anthraquinone derivatives are known to be good photosensitizers for photodynamical therapy in cancer treatment [8–10]. Many of them have been used as an analytical tool for the determination of metals, and in electrochemistry [11,12]. Anthraquinone and its derivatives are used in production of dyes, such as alizarin which is the core moiety of adriamycin, an important antitumor drug [13] and it has a remarkable antigenotoxic activity [11]. Alizarin is a component of food, which can act against the action of carcinogens and it is also used as a dye and chemical agent for data recording and storage material [14]. Anthraquinone derivatives are also used as a catalyst to increase pulp production in paper industry. Aminoanthraquinones are good corrosion inhibitors in diesel water mixture [15].

Determination of the ground- and excited-state dipole moments of dye molecules is important, because the values of dipole moments provide information about the change in electronic distribution upon excitation. Knowledge of the excited state dipole moments of electronically excited molecules is quite useful in designing nonlinear materials [16], in elucidation of the nature of the excited states and also it reflects the charge distribution in the molecule and allows one to judge the site of attack by electrophilic and nucleophilic reagents in some photochemical reactions. The excited-state dipole moments of fluorescent molecules such as those studied here also determine the tunability range of the emission energy as a function of the polarity of the medium.

While the ground state dipole moment of a chemical system can be measured using different techniques [17–22], not many techniques are available for the estimation of the dipole moment in short-lived states. Among the different methods available so far for the estimation of dipole moment of short-lived species such as electronically excited state of a molecule are based on the spectral shift caused either externally or internally. Among the different methods like electric polarization of fluorescence [23], electric dichroism [24] and microwave conductivity [25] considered to be very accurate, their use is limited because of equipment intensive and restriction to relatively small molecules. The experimental determination of excited-state dipole moments based on the analysis of the solvatochromism [26] of absorption and fluorescence maxima is quite popular. The solvatochromic method is based on
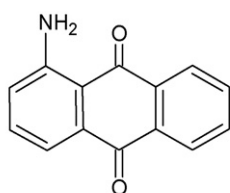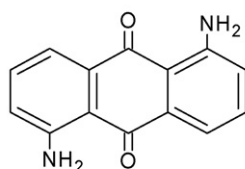
(a) 1-aminoanthracene-9,10-dione (AAQ)
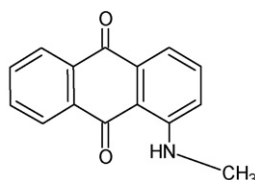
(b) 1-(methylamino)anthracene-9,10-dione (MAQ)

(c) 1,5-diaminoanthracene-9,10-dione (DAQ)

Fig. 1. Molecular structures of (a) AAQ, (b) MAQ and (c) DAQ along with IUPAC names.

a linear correlation between the wave numbers of the absorption and fluorescence maxima and a solvent polarity function which involves both dielectric constant (ε) and refractive index (n) of the medium [27–31].

There are several reports published on experimental and theoretical studies on ground-state (μ_g) and excited-state (μ_e) dipole moments using different techniques in variety of organic fluorescent compounds like coumarins [32,33], purines [34], exalite dyes [35], curcuminoid dyes [36], hemicyanine dyes [37], hydroxycoumarin dyes [38], acridinedione dyes [39], fluorescein [40], flavones [41], PRODAN, BADAN and ACRYLODAN [42], quinazolines [43], acridines and phenazines [44], substituted anthraquinones [45], and some laser dyes [1,2,46], etc.

However, there are no reports available in the literature on the determination of μ_g and μ_e values of the three molecules investigated. This prompted us to carry out the present work. The aim of the present work is to estimate and compare the ground and excited-state dipole moments of AAQ, MAQ and DAQ by various methods. The molecular structures and IUPAC names of AAQ, MAQ and DAQ are shown in Fig. 1.

2. Equations for the estimation of dipole moments

The independent equations used for the estimation of ground and excited state dipole moments are as follows:

Lippert's equation [27]

$$\bar{\nu}_a - \bar{\nu}_f = m_1 F(\varepsilon, n) + \text{constant} \tag{1}$$

Bakhshiev's equation [28]

$$\bar{\nu}_a - \bar{\nu}_f = m_2 F_1(\varepsilon, n) + \text{constant} \tag{2}$$

Kawski-Chamma-Viallet's equation [29]

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -m_3 F_2(\varepsilon, n) + \text{constant} \tag{3}$$

McRae's equation [47]

$$\bar{\nu}_a = -m_4 F_3(\varepsilon) + \text{constant} \tag{4}$$

Suppan's equation [48]

$$\bar{\nu}_a = -m_5 F_4(\varepsilon) + \text{constant} \tag{5}$$

The expressions for [Lippert's polarity function] $F(\varepsilon,n)$, [Bakhshiev's polarity function] $F_1(\varepsilon, n)$ [Kawski-Chamma-Viallet's polarity function] $F_2(\varepsilon, n)$, [McRae's polarity function] $F_3(\varepsilon)$ and [Suppan's polarity function] $F_4(\varepsilon)$ are given as

$$F(\varepsilon, n) = \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right] \tag{6}$$

$$F_1(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \tag{7}$$

$$F_2(\varepsilon, n) = \left[\frac{2n^2 + 1}{2(n^2 + 2)} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + \frac{3(n^4 - 1)}{2(n^2 - 1)^2} \right] \tag{8}$$

$$F_3(\varepsilon) = \left[\frac{2(\varepsilon - 1)}{\varepsilon + 2} \right] \tag{9}$$

$$F_4(\varepsilon) = \left[\frac{2(\varepsilon - 1)}{2\varepsilon + 1} \right] \tag{10}$$

Here $\bar{\nu}_a$ and $\bar{\nu}_f$ are absorption and fluorescence maxima wave numbers in cm^{-1}, respectively. The other symbols ε and n are the dielectric constant and refractive index of the solvents, respectively. From Eqs. (1)–(5) it follows that $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F(\varepsilon,n)$, $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(\varepsilon,n)$, $1/2(\bar{\nu}_a + \bar{\nu}_f)$ versus $F_2(\varepsilon, n)$, $\bar{\nu}_a$ versus $F_3(\varepsilon)$ and $\bar{\nu}_a$ versus $F_4(\varepsilon)$ should give linear graphs with slopes m_1, m_2, m_3, m_4 and m_5, respectively and are given as

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3}, \tag{11}$$

$$m_2 = \frac{2(\mu_e - \mu_g)^2}{hca^3}, \tag{12}$$

$$m_3 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3}, \tag{13}$$

$$m_4 = \frac{\mu_g(\mu_e - \mu_g)}{hca^3} \tag{14}$$

and

$$m_5 = \frac{\mu_g(\mu_e - \mu_g)}{hca^3} \tag{15}$$

where μ_g and μ_e are the ground and excited state dipole moments of the solute molecules. The symbols h and c are Planck's constant and the velocity of light in vacuum, respectively, 'a' is the Onsager radius of the solute molecule, with the values evaluated by using atomic increment method [49]. If the ground state and excited states are parallel, the following expressions are obtained on the basis of Eqs. (12) and (13) [50,51]:

$$\mu_g = \frac{m_3 - m_2}{2} \left[\frac{hca^3}{2m_2} \right]^{1/2} \tag{16}$$

$$\mu_e = \frac{m_2 + m_3}{2} \left[\frac{hca^3}{2m_2} \right]^{1/2} \tag{17}$$

and

$$\mu_e = \left[\frac{m_2 + m_3}{m_3 - m_2}\right]\mu_g \quad \text{for}(m_3 > m_2) \tag{18}$$

The validity of the use of Eqs. (16) and (17) is based on certain assumptions like considering both the dipole moments collinear or almost and also the same 'a' in both the ground and excited states. Lippert, Bakhshiev and Kawski-Chamma-Viallet formulation do not consider the polarizability, hydrogen bonding effect and complex formation and also ignores molecular aspects of solvation. For understanding polarization dependence or hydrogen bonding effect on spectral characteristics, it is better to use the $E_T(30)$ function [52,53]. However, to avoid the dimensionality problems, normalized value of $E_T(30)$, namely E_T^N is employed which includes not only solvent polarity but also the protic hydrogen bond effect [53]. The theoretical basis for the correlation as the spectral shift with E_T^N was proposed by Reichardt [54] and developed by Ravi et al. [55]:

$$\bar{\nu}_a - \bar{\nu}_f = 11307.6\left[\left(\frac{\delta\mu}{\delta\mu_B}\right)^2\left(\frac{a_B}{a}\right)^3\right]E_T^N + \text{constant} \tag{19}$$

where $\delta\mu_B$ and a_B are dipole moment changes on excitation and Onsager cavity radius respectively of a betaine dye, and $\delta\mu$ and a are corresponding quantities for the molecule of interest. The change in dipole moment can be evaluated from the slope of Stokes shift versus E_T^N plot and is given by the equation [33]:

$$\mu_e - \mu_g = \sqrt{\frac{m \times 81}{(6.2/a)^3 11307.6}} \tag{20}$$

where m is the slope between stokes shift versus E_T^N.

3. Results and discussion

Solvent polarity function values $F(\varepsilon, n)$, $F_1(\varepsilon, n)$, $F_2(\varepsilon, n)$, $F_3(\varepsilon)$, $F_4(\varepsilon)$ and microscopic solvent function (E_T^N) for various solvents used in this article are presented in Table 1. The absorption and emission maxima wave numbers, Stokes shift and arithmetic mean of Stokes shift values (in cm^{-1}) for all the three molecules in different solvents are given in Table 2. Absorption and emission maxima wave numbers were calculated from the wavelength maxima values given in Ref. [3]. The large magnitude of Stokes shift indicates that the excited-state geometry could be different from that of the

Table 1
Solvent polarity functions.

Solvents*	F^a	$F_1{}^b$	$F_2{}^c$	$F_3{}^d$	$F_4{}^e$	$(E_T^N)^f$
Hexane	0.0013	0.0025	0.2537	0.4536	0.3697	0.009
Cyclohexane	0.0016	0.0032	0.2875	0.5074	0.4047	0.006
Dioxane	0.0204	0.0414	0.3074	0.5748	0.4464	0.164
Carbon tetrachloride	0.0102	0.0215	0.3221	0.5815	0.4505	0.052
Benzene	0.0026	0.0057	0.3408	0.5981	0.4604	0.111
Toluene	0.0123	0.0270	0.3488	0.6270	0.4773	0.099
Chloroform	0.1480	0.3701	0.4871	1.1176	0.7169	0.259
1-Hexanol	0.2450	0.6917	0.6283	1.6078	0.8913	0.559
1-Butanol	0.2641	0.7532	0.6479	1.6969	0.9180	0.602
Ethanol	0.2884	0.8116	0.6518	1.7718	0.9395	0.654
Methanol	0.3085	0.8544	0.6509	1.8265	0.9546	0.762
Acetonitrile	0.3054	0.8630	0.6658	1.8481	0.9605	0.460
Glycerol	0.2635	0.8350	0.7373	1.8651	0.9651	0.811

*Solvents are listed in the order of increasing dielectric constant.
 [a] Lipperts solvent function.
 [b] Bakhshiev solvent function.
 [c] Kawski-Chamma-Viallet solvent function.
 [d] McRae solvent function.
 [e] Suppan solvent function.
 [f] Microscopic solvent function taken from Ref. [56].

Table 2
Solvatochromic data[a] of AAQ (I), MAQ (II) and DAQ (III).

Solvent	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$\bar{\nu}_a - \bar{\nu}_f$ (cm^{-1})	$(1/2)(\bar{\nu}_a - \bar{\nu}_f)$ (cm^{-1})
Hexane				
I	22,222	18,867	3354	20,545
II	20,576	17,857	2718	19,216
Cyclohexane				
I	22,222	18,867	3354	20,545
II	20,576	17,857	2718	19,216
Dioxane				
I	21,739	17,543	4195	19,641
II	20,242	16,806	3436	18,524
III	21,097	18,018	3079	19,557
Carbon tetrachloride				
I	22,075	18,796	3278	20,436
II	20,325	17,301	3024	18,813
Benzene				
II	20,120	16,949	3171	18,534
Toluene				
I	21,739	17,857	3881	19,798
II	20,120	16,949	3171	18,534
III	21,367	18,348	3018	19,858
Chloroform				
I	21,739	17,699	4040	19,719
II	20,000	16,806	3193	18,403
1-Hexanol				
III	20,408	17,361	3047	18,884
1-Butanol				
III	20,408	17,361	3047	18,884
Ethanol				
I	21,276	16,806	4469	19,041
II	20,000	15,625	4375	17,812
III	20,408	17,361	3047	18,884
Methanol				
I	21,276	16,806	4469	19,041
II	20,000	15,625	4375	17,812
III	20,576	17,123	3452	18,849
Acetonitrile				
I	21,367	16,949	4418	19,158
II	20,000	15,625	4375	17,812
III	21,008	17,241	3767	19,124
Glycerol				
III	20,408	17,361	3047	18,884

 [a] Absorption maxima and fluorescence maxima were calculated from wavelength maxima taken from Ref. [3].

ground state. The general observation is that there is an increase in the Stokes shift values with increasing solvent polarity which shows that there is an increase in the dipole moment on excitation.

The solvatochromic data can be used to identify the spectra, namely $\pi \to \pi^*$, $n \to n^*$, etc. It can be noticed from Table 2 that, with increase in the polarity of the solvent, the fluorescence emission peak undergoes a red shift, confirming a $\pi \to \pi^*$ transition. The shift of the fluorescence wavelengths towards longer wavelengths could be due to the marked difference between the excited state charge distribution in the solute and the ground-state charge distribution, resulting in a stronger interaction with polar solvents in the excited state. It can be noticed in the case of DAQ that on going from methanol to higher alcohols, the emission maxima show a small but noticeable blue shift which can be attributed to a decrease in intermolecular hydrogen bonding in higher alcohols [3,40]. Figs. 2–4 show the graph of $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F(\varepsilon, n)$, $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(\varepsilon, n)$ and $1/2(\bar{\nu}_a + \bar{\nu}_f)$ versus $F_2(\varepsilon, n)$ from which slopes m_1, m_2 and m_3 are obtained, respectively. From the plots of $\bar{\nu}_a$ versus $F_3(\varepsilon)$ and
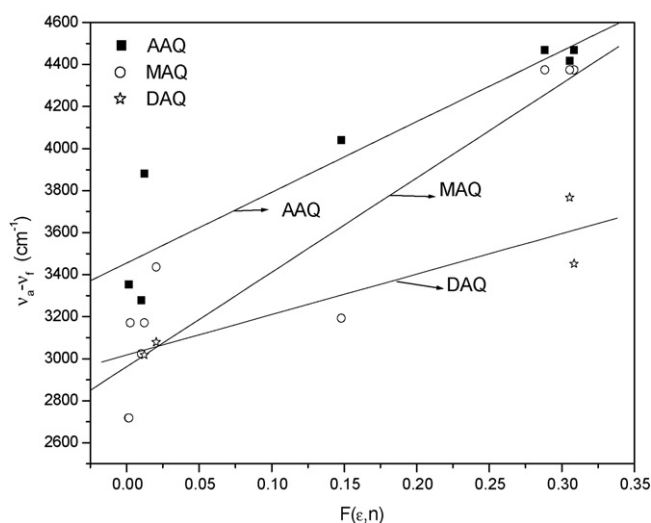
Fig. 2. The variation of Stokes shift with F by using Lippert's equation.
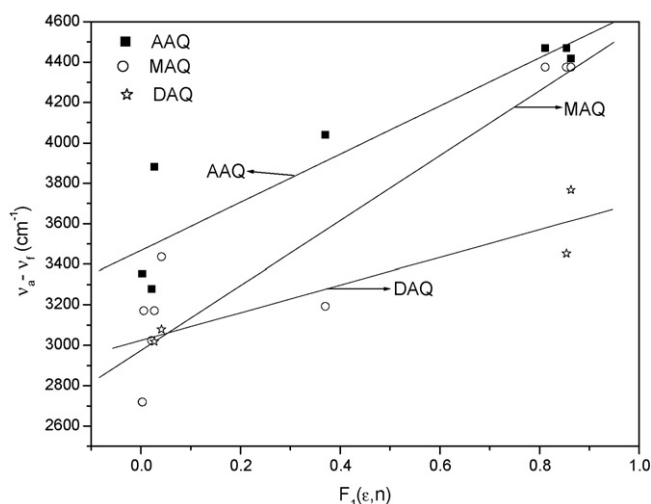

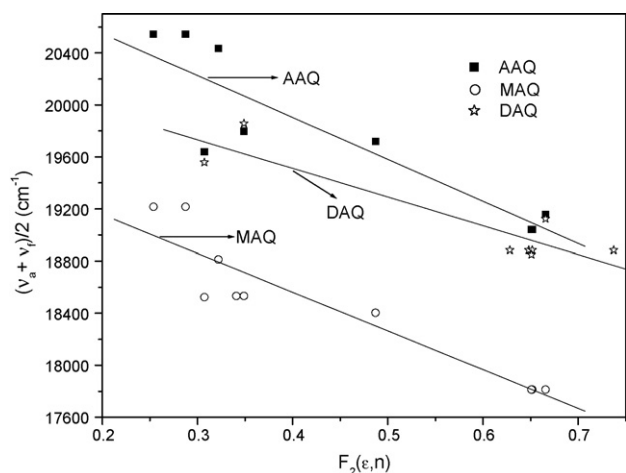**Fig. 3.** The variation of Stokes shift with F_1 by using Bakhshiev's equation.

Fig. 4. The variation of arithmetic mean of Stokes shift with F_2 by using Kawski-Chamma-Viallet's equation.

Table 3
Statistical treatment of the correlations of the spectral shifts of AAQ, MAQ and DAQ.

Compound	Slope	Intercept	Correlation coefficient	No of data
Lippert correlation				
AAQ	3365	3,455	0.93	8
MAQ	4493	2,961	0.93	10
DAQ	1926	3,017	0.92	4
Bakhshiev correlation				
AAQ	1190	3,468	0.93	8
MAQ	1605	2,973	0.93	10
DAQ	682	3,024	0.93	4
Kawski-Chamma-Viallet correlation				
AAQ	−3226	21,194	0.89	9
MAQ	−2977	19,752	0.93	10
DAQ	−2204	20,393	0.91	8
McRae correlation				
AAQ	−559	22,317	0.90	9
MAQ	−284	20,140	0.74	10
DAQ	−660	21,607	0.94	7
Suppan correlation				
AAQ	−1353	22,599	0.91	9
MAQ	−769	20,640	0.77	10
DAQ	−1630	21,970	0.94	7
E_T^N correlations				
AAQ	1598	3,448	0.92	8
MAQ	2310	2,860	0.94	10
DAQ	804	3,030	0.70	4

$F_4(\varepsilon)$ we get m_4 and m_5, respectively. The plot of $(\bar{\nu}_a - \bar{\nu}_f)$ versus E_T^N will give the slope m.

The correlation coefficients, slopes and intercepts of the fitted lines are given in Table 3. Acceptable correlation coefficient is obtained for all cases. In most of the cases the correlation coefficients are larger than 0.92 and indicate a linearity for $m, m_1, m_2, m_3,$ m_4 and m_5 with selected number of Stokes shift data points. In the case of m, m_1 and m_2 for AAQ dioxane exhibited deviation from linearity and was therefore excluded from the correlations. The same was observed for dioxane by Aaron et al. [17]. For MAQ, m_4 and m_5 correlations are around 0.75. This may be due to assumptions made in deriving the equations which do not involve the refractive index of the solvent. For DAQ several solvents (mainly alcohols) exhibited deviations from linearity and were therefore excluded from the correlations. The large deviation from the linearity shown by aqueous solvents may be due to the fact that the hydrogen bond between the solvent and the lone pair of the amino groups in the S_0 ground state is broken upon excitation, and the hydrogen bond is formed between the amino proton and the lone pair of the solvent molecules [51]. The ground-state dipole moments (μ_g) of the three molecules have been estimated by using Eq. (16) and are presented in Table 4. However, no other experimental data on μ_g could be obtained from literature for comparison. The μ_e values obtained from Eq. (17) are given in Table 4. Also the μ_e values obtained from Eq. (11), (14), (15) and (20) and the ratio (μ_e/μ_g) obtained from Eq. (18) are also presented in Table 4. It may be noted that discrepancies occur between the estimated values of μ_e for all the three molecules. These differences between the values of μ_e may be, in part, due to the various assumptions and simplifications made in the use of different solvatochromic methods [17,53]. The μ_e values obtained by Lippert method are large, since it does not consider polarizability. The μ_e values obtained by Suppan method are large compared to all other methods. The μ_e values obtained by McRae method, E_T^N method and Eq. (17), almost agree with one another.

The dipole moments of all the molecules studied here are higher in the first excited state compared to the ground state. This is explained in terms of possible resonance structures as shown in

Table 4
Onsager radius, ground-state and singlet excited-state dipole moments (in Debye*, D) of AAQ, MAQ and DAQ.

Molecule	Radius 'a' (Å)	$\mu_g{}^a$	$\mu_e{}^b$	$\mu_e{}^c$	$\mu_e{}^d$	$\mu_e{}^e$	$\mu_e{}^f$	$(\mu_e/\mu_g)^g$
AAQ	3.628	2.03	4.41	6.03	4.64	8.35	3.55	2.17
MAQ	3.725	1.23	4.10	6.03	3.60	7.66	3.12	3.33
DAQ	3.699	2.06	3.92	5.18	5.28	10.00	3.17	1.89

*1 Debye $= 3.33564 \times 10^{-30}$ cm $= 10^{-18}$ esu cm.

ᵃ Ground state dipole moments calculated from Eq. (16).
ᵇ Excited state dipole moments calculated from Eq. (17).
ᶜ Excited state dipole moments calculated with $\Delta\mu$ from Lippert's equation.
ᵈ Excited state dipole moments calculated with $\Delta\mu$ from McRae's equation.
ᵉ Excited state dipole moments calculated with $\Delta\mu$ from Suppan's equation.
ᶠ Excited state dipole moments calculated with $\Delta\mu$ from microscopic solvent polarity function (E_T^N).
ᵍ The ratio of excited state and ground state dipole moments calculated from Eq. (18).

Fig. 5. The dipole moment of AAQ and MAQ increases almost twice on excitation as compared to DAQ, this change in dipole moment on excitation can be explained in terms of nature of emitting state or intramolecular charge transfer. Further a large change in dipole moment on excitation suggests that excited state is twisted intramolecular charge transfer (TICT) in nature. Thus, presence of a large TICT and increase in planarity on excitation render the molecule more polar (as compared to ground state) giving rise to a large change in the dipole. In literature one may find that large numbers of investigators have used solvatochromic shift method

Fig. 5. Possible resonance structures of (a) AAQ, (b) MAQ and (c) DAQ.

(Eqs. (16) and (17)) to estimate ground- and excited-state dipole moments. In literature there is dearth of data on μ_g and μ_e for the molecules used in the present study. Therefore, we have not made any comparison.

4. Conclusion

We have estimated and compared dipole moments of the three molecules viz., AAQ, MAQ and DAQ in the ground and excited states as a function of the solute–solvent interactions by solvatochromic shift method. It can be seen that the dipole moments of AAQ, MAQ and DAQ are significantly higher in excited singlet state than in ground state. The increase in dipole moments in the excited singlet states range between about 2 and 6.5 D depending on compounds. It may be noted that the measured values of μ_g and μ_e for AAQ, MAQ and DAQ differ from each other. This may be attributed to the structural difference between the molecules. Also, Eq. (18) can be used to estimate the value of excited state dipole moment by pre-knowledge of the value of ground state dipole moment, without the necessity of knowing the Onsager radius of the solute. To our knowledge this is the first report on the dipole moments of these molecules and would be of great help in many fields as mentioned in the introduction.

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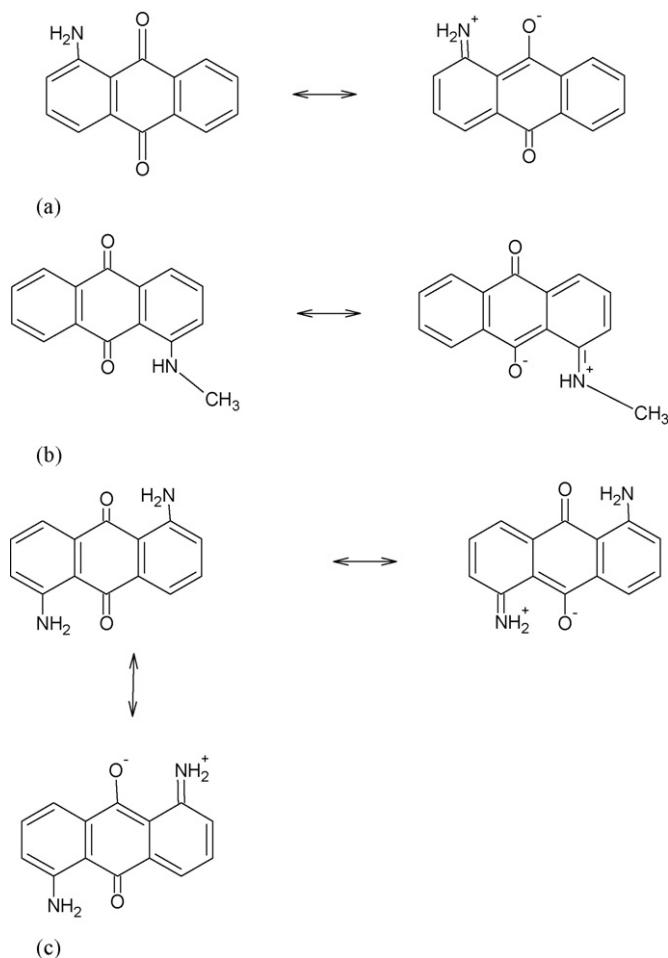[33] V.K. Sharma, P.D. Saharo, N. Sharma, R.C. Rastogi, S.K. Ghoshal, D. Mohan, Spectrochim. Acta A 59 (2003) 1161.

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