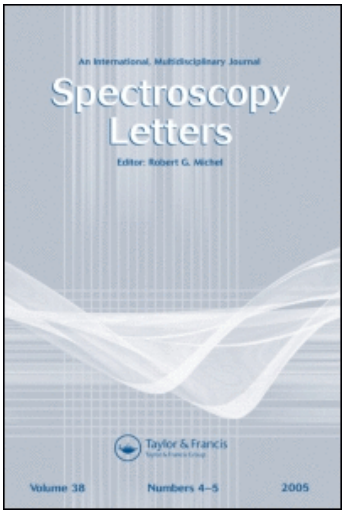

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Tarek A. Fayed[a]; Sameh S. Ali[b]
[a] Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt [b] Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

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Protonation Dependent Photoinduced Intramolecular Charge Transfer in 2-(p-Dimethylaminostyryl)benzazoles

Tarek A. Fayed[1,*] and Sameh S. Ali[2]

[1]Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt
[2]Ain Shams University, Abbassia, Cairo, Egypt

ABSTRACT

The absorption and fluorescence spectra of 2-(p-dimethylaminostyryl)-benzoxazole, DMASBO, and its benzothiazole analogue, DMASBT, have been studied in different solvents and at various acid concentrations. Two types of monocation are formed simultaneously in all solvents at relatively lower acid concentrations. The neutral DMASBO and DMASBT as well as the monocations formed by protonation of the $-N=$ atom exhibit highly solvatochromic intramolecular charge transfer (ICT) emission. This indicated an increase in the dipole moment of the S_1 state (μ_e). The μ_e values, which were calculated from the solvatochromic shifts and the ground state dipole moments, came out to

*Correspondence: Tarek A. Fayed, Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt; E-mail: tfayed@dec1.tanta.edu.eg.

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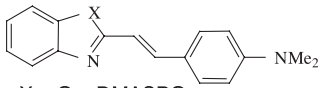
be 14.3 and 12.6 D for DMASBT and DMASBO, respectively. For their azolium cations μ_e are 9.0 and 8.6 D. on the other hand, the monocations formed by protonation of the $-NMe_2$ group as well as the dications formed at relatively higher acid concentration, showed insignificant spectral shift on changing the solvent polarity. Also, the effect of the heteroatom and the protonation site on the ICT process is discussed.

Key Words: Fluorescence spectra; Protonation; Styrylbenzazoles; Dipole moment; Intramolecular charge transfer.

INTRODUCTION

One of the main challenges of applied research is solar energy. The main step to convert solar energy into chemical and electrical potential is photoinduced energy or charge transfer.[1] Therefore, the photophysics and spectroscopy of donor-acceptor molecules, which are capable of photoinduced intramolecular charge transfer (ICT), are the subject of continuing theoretical and experimental interest.[2–5] Such push-pull molecules are dipolar and present relevant hyperpolarizability, a property that is a prerequisite for molecules that are candidate components of non-linear optical materials.[6–9] The dipole moment of their excited state is greater than that of the ground state. Thus, these molecules exhibit molecular fluorescence that is highly sensitive to solvent polarity, pH, local viscosity and electrostatic fields.[10] Owing to these dependencies, such fluorescent probes are valuable in the study of heterogeneous, organized and biological media.[11]

Recently, we have synthesized 2-(p-dimethylaminostyryl)-benzoxazole (DMASBO) which exhibits highly solvatochromic ICT emission.[12] The ICT process takes place from the electron donor $-NMe_2$ group to the electron accepting benzoxazole ring. In addition, DMASBO can serve as a probe for the viscosity of its environment. Thus, the main aims of the present study are to compare the effect of the electron withdrawing benzoxazole and benzothiazole groups as well as their azolium cations on



X = O ; DMASBO
= S ; DMASBT

Scheme 1. Structure of dimethylaminostyryl benzazoles.

the ICT emission of 2-(p-dimethyaminostyryl)benzazoles (Scheme 1), and to determine the dipole moment of the excited molecules.

EXPERIMENTAL

DMASBO was prepared and characterized as reported in a previous work,[12] and the same procedures were utilized for preparation of 2-(p-dimethylaminostyryl)benzothiazole (DMASBT). The yellow solid product was recrystallized from ethanol, and its purity was checked by TLC. All solvents were of spectroscopic grade from Fluka or Aldrich and used without further purification. HCl and trifluoroacetic acid (TFA) were from Merck and used as received.

UV-visible absorption spectra were recorded on a Shimadzu UV-3101PC spectrophotometer while the fluorescence spectra were measured by using a Fluoromax-2 spectrometer. A typical concentration of 2×10^{-5} M was used for measurements. The acidity was controlled by using either HCl (in water, methanol and ethanol) or TFA (in the other solvents).

RESULTS AND DISCUSSION

The fluorescence spectra of DMASBT in some selected solvents are shown in Figure 1, while the relevant data regarding the absorption and

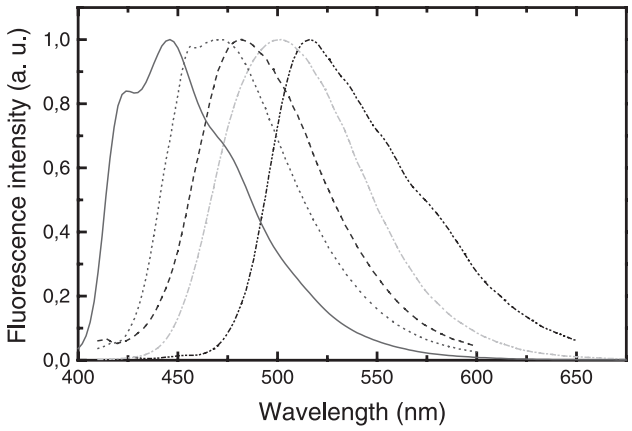


Figure 1. Emission spectra of DMASBT in different solvents: n-hexane, toluene, $CHCl_3$, ethanol and water, on going from left to right.

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Table 1. Absorption and emission maxima (nm) of neutral dimethylaminostyryl benzazoles in different solvents.

	DMASBT		DMASBO			
Solvent	λ_a	λ_f	λ_a	λ_f	$\Delta\lambda_a$	$\Delta\lambda_f$
H_2O	391	516	387	525	4	−9
MeOH	405	512	394	488	11	24
EtOH	402	504	394	482	8	22
CH_3CN	397	508	387	485	10	23
Acetone	397	501	388	478	9	23
CH_2Cl_2	399	489	390	468	9	21
$CHCl_3$	400	481	391	463	9	18
Dioxane	395	471	385	458	10	13
Toluene	398	462	388	460	10	2
c-Hexane	387	449	377	436	10	13
n-Hexane	384	446	375	433	9	13

λ_{ex} is the corresponding absorption maximum.
$\Delta\lambda = \lambda_{max.}$ (DMASBT) $- \lambda_{max}$(DMASBO).

emission spectra of both DMASBT and DMASBO, recorded in different solvents, are compiled in Table 1.

The absorption and emission maxima of BMASBT are at longer wavelengths compared to those of DMASBO. Depending on solvent polarity, the pronounced red shift ranges from (4–11 nm) and (2–24 nm), for the absorption and emission maxima, respectively, Table 1. As can be seen, the absorption maxima of both compounds are less sensitive to the solvent polarity. This implies that the ground state energy distribution is not affected to a great extent, which is possibly due to the less polar nature of the ground state. In contrast, the fluorescence spectra show large bathochromic shifts in polar solvents. This is illustrated by Figure 2 which shows the effect of solvent polarity (expressed as $E_T(30)$[13]) on the emission frequency of DMASBT. These shifts range from 55 to 66 nm on changing the solvent from n-hexane to methanol. In fact, the emission maximum of DMASBT, in water, is ca. 9 nm blue shifted compared to that of DMASBO. This is due to hydrogen bonding interactions between the electron lone pair on the amino group and water molecules, which is affected by the electronegativity difference between the O and S-atom. Also, the fluorescence spectra exhibit vibrational structure in non-polar solvents like n-hexane, while they are broad structureless in polar solvents, Figure 1. In addition, the magnitudes of the Stokes shifts $(\bar{\upsilon}_a - \bar{\upsilon}_f)$ are large, varying from 3570 to 5160 cm^{-1}, and increase with increased

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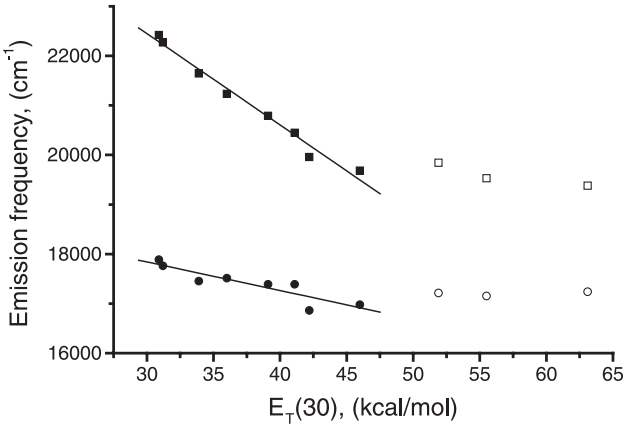

Figure 2. Correlation of the emission frequencies of DMASBT (■) and its azolium cation (●) with the solvent polarity parameter $E_T(30)$. Open and closed symbols represent protic and aprotic solvents, respectively.

solvent polarity, which points to a stronger stabilization of the excited state in polar solvents. All of these features indicate emission from an ICT state.

The excited state dipole moment for ICT molecules can be calculated from the ground state dipole moment, the Stokes shifts and the solvent polarity function Δf (ε, n)[14] using Eq. 1;

$$\Delta\bar{\upsilon}_{st} = \frac{(\mu_e - \mu_g)^2}{hca^3}\Delta f + Const. \quad (1)$$

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

where ε and n represent the dielectric constant and refractive index of the solvent, respectively. μ_g and μ_e are the dipole moments of the ground and excited state, respectively. h is Planck's constant, c is the speed of light and a is the Onsager cavity radius. For an elongated shape molecule, a is usually estimated as 40% of its longest axis.[15] The long axis was obtained from geometrical optimization of both DMASBT and DMASBO molecules using standard software (HyperChem, Version 5.11). The value comes out to be 6.2°A. After optimizing their geometry in the ground state, AM1 semi-empirical mechanical calculations were done to obtain the ground state dipole moments (μ_g). The compiled values are 3.2 and 3.3 D for DMASBT and DMASBO, respectively. Figure 3 depicts plots of $(\bar{\upsilon}_a - \bar{\upsilon}_f)$

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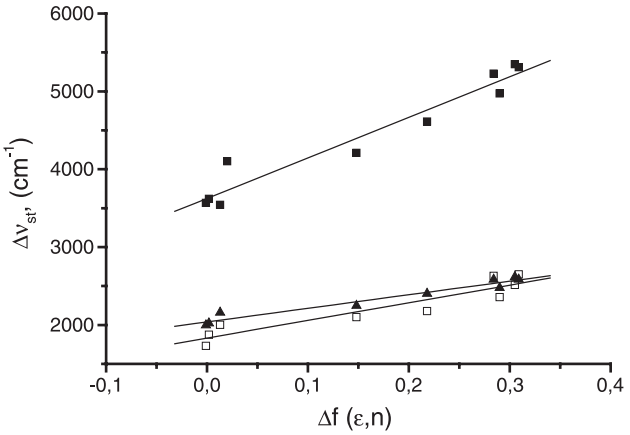
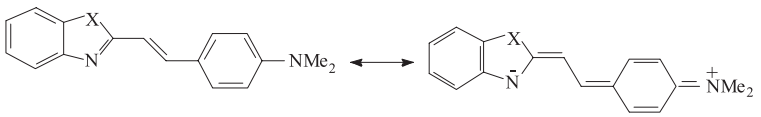


Figure 3. Plots of the Stokes shifts for DMASBT (■), its azolium cation (▲) and the azolium cation of DMASBO (□) versus the polarity function Δf.

vs. f (ε, n) according to Eq. 1. As can be seen, in the absence of water, the plots are quite linear ($r \geq 0.97$). From the slopes of these plots, the excited state dipole moments were calculated as 14.3 D (DMASBT) and 12.6 D (DMASBO). The large increase in the dipole moment upon excitation can be interpreted in terms of a change in the mesomeric resonance structures of the molecules. The ground state is described by the neutral structure (I) while the excited state is mainly described by the zwitterionic structure (II). This change in the charge distribution is also responsible for the observed positive solvatochromism of the fluorescence band.



(I) (II)

In structure II, positive and negative charges become localized on the dimethylamino and benzazole residues, respectively. These groups are located on opposite sides of the molecule, and therefore, a large increase in the dipole moment occurs as a result of charge separation. The previous results indicate a sizeable electronic interaction of the dimethylamino group as an electron donor with the benzazole ring as an acceptor mediated by the intervening double bond. This conclusion was supported by the finding that the absorption maximum of these compounds, in water, is blue-shifted

compared to that in alcohols. This is due to specific hydrogen bonding interactions between water molecules and the nitrogen atom of the $-NMe_2$ group which restrict the ICT process.

In slightly acidic media ($[H^+]$ depends on the nature of the solvent and whether the heteroatom X = S or O (Table 3). Both compounds show quite different behaviour. Figure 4 shows the influence of changing acidity on the absorption and emission spectra of DMASBT in ethanol, as an example. In

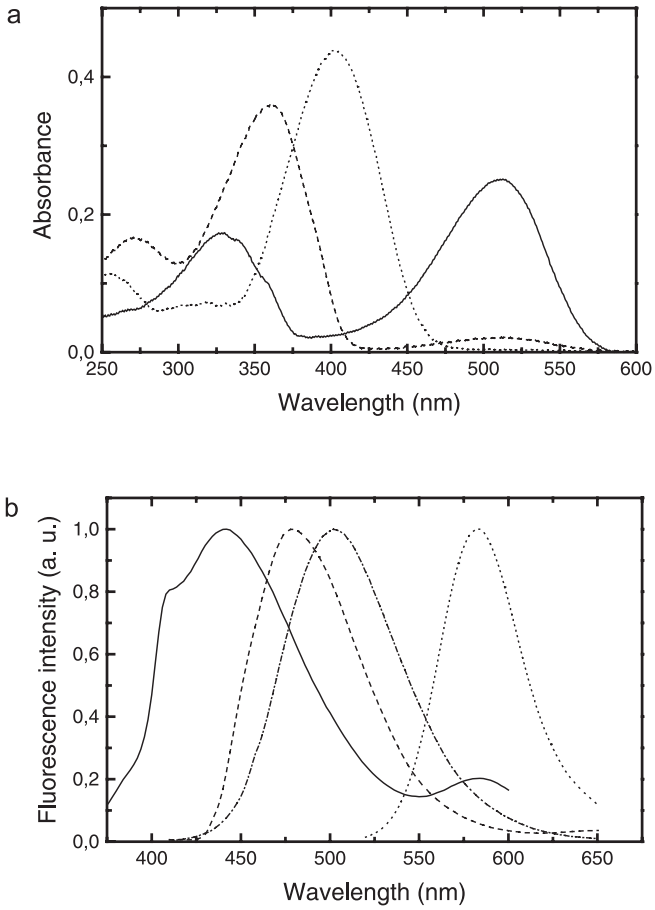


Figure 4. (a) Absorption and (b) emission spectra of DMASBT in ethanol at different acid concentrations: 0.0 M HCl, λ_{ex} = 405 nm (-.-.-); 0.01 M HCl, λ_{ex} = 325 nm (—); 0.2 M HCl, λ_{ex} = 361 nm (-----) and 0.01 M HCl, λ_{ex} = 511 nm (. . .. . .). The acid concentrations and labels are the same for both absorption and emission spectra.

Table 2. Absorption and emission maxima (nm) of protonated dimethylaminostyryl benzazoles (monocation I) in different solvents.

	DMASBT		DMASBO			
Solvent	λ_a	λ_f	λ_a	λ_f	$\Delta\lambda_a$	$\Delta\lambda_f$
H_2O	485	580	470	542	15	38
MeOH	505	583	480	548	25	35
EtOH	511	581	481	546	30	35
CH_3CN	513	589	480	549	33	40
Acetone	513	593	480	548	33	45
CH_2Cl_2	511	575	478	540	33	35
$CHCl_3$	513	575	476	533	37	42
Dioxane	493	571	475	539	18	32
Toluene	514	573	478	533	36	40
c-Hexane	513	563	476	526	37	37
n-Hexane	506	559	473	523	33	36

$\Delta\lambda = \lambda_{max.}$ (DMASBT) $- \lambda_{max}$ (DMASBO).

Table 3. Absorption and emission maxima (nm) for different prototropic forms of dimethylaminostyryl benzazoles.

		DMASBT			DMASBO	
Solvent	$[H^+]$, M	λ_a	λ_f	$[H^+]$, M	λ_a	λ_f
H_2O	0.0	391	516	0.0	387	525
	10^{-2}	335; 485	420; 580	0.05	324; 470	403; 542
	0.2	353	433	1.0	343	428
EtOH	0.0	402	504	0.0	394	482
	10^{-2}	328; 511	409; 583	0.05	322; 484	338,404; 546
	0.2	361	442	1.0	338	408
CH_3CN	0.0	397	508	0.0	387	485
	10^{-4}	332; 502	410; 589	0.001	321; 480	390; 549
	10^{-2}	358	432	0.05	338	401
c-Hexane	0.0	387	449	0.0	377	436; 465
	10^{-4}	332; 513	404; 563	0.005	325; 483	367,386, 408; 526
	10^{-3}	360	436	0.15	339	410,434

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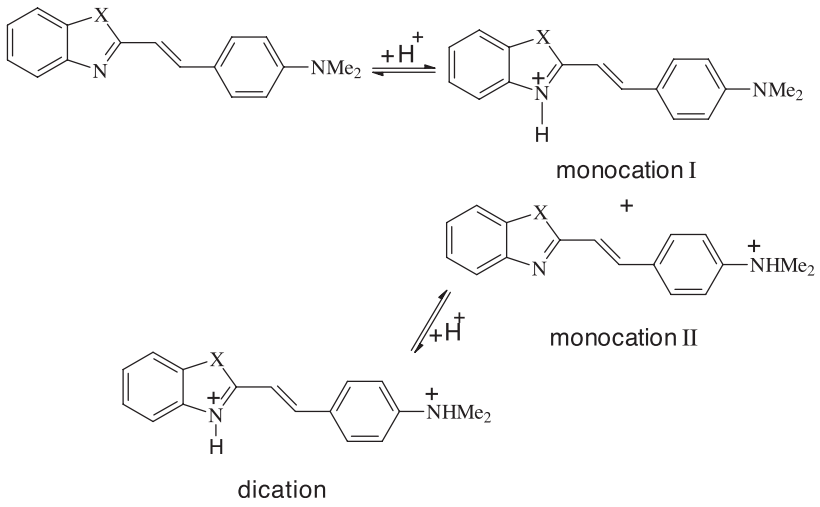
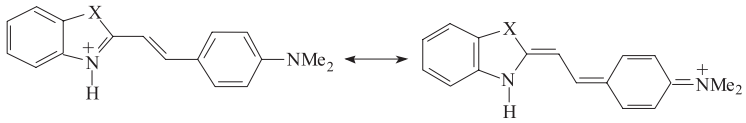
ethanolic solution at $[H^+] = 0.01$ M the absorption band at 402 nm is replaced by a large red-shifted band ($\lambda_{max} = 511$ nm) and a blue-shifted one ($\lambda_{max} = 328$ nm). Similarly, the fluorescence band at 504 nm is replaced by two bands with λ_{max} at 583 and 409 nm when excited at 511 and 325 nm, respectively. Such changes were observed for both compounds in the other solvents, see Tables 2 and 3. These changes can be discussed as follows; there are two basic sites in the compounds under investigation, the benzazole nitrogen atom and the $-NMe_2$ group, Scheme 2. Addition of a proton to the heterocyclic nitrogen atom (monocation I) will shift the absorption and emission maxima to the red due to increasing of the electron pulling ability, which enhances charge transfer from the amino group to the azolium cation. In contrast, protonation of the $-NMe_2$ group (monocation II) leads to quenching of the ICT effect, thus shifting the spectra to the blue compared to those of neutral molecules. These assignments are consistent with the results obtained from fluorescence excitation (Fig. not shown) and emission spectral measurements, Figure 4b. The 505 nm band in the fluorescence excitation spectrum ($\lambda_{em} = 580$ nm) and the 583 nm in the fluorescence spectra can be assigned to monocation I, whereas the 339 nm band in the fluorescence excitation spectrum ($\lambda_{em} = 410$ nm) and 409 nm in the emission spectra can be attributed to monocation II.

The spectral data of charge transfer band, due to protonation of the benzazole $-N=$ atom, are listed in Table 2. As mentioned previously,



Scheme 2. Prototropic equilibria of dimethylaminostyryl benzazoles.

the absorption and emission spectra of azolium cations display large red-shifts relative to those of their neutral counterparts. The large red-shift in the spectra of azolium cations was explained by the resonance interaction of the $-NMe_2$ group with the heterocyclic ring which stabilizes the species.



The shift in absorption maxima is large compared to that in the emission maxima, and decreases with increasing the solvent polarity or substituting the benzothaizolium cation by benzoxazolium one. The red-shift in the spectral maxima on going from benzoxazolium to benzo-thiazolium derivative is large compared to that observed in the case of their neutral derivatives. These shifts range from 15 to 43 nm and from 32 to 45 nm for the absorption and emission spectra, respectively, see Table 2. Although the ICT absorption and emission spectra of azolium cations are highly sensitive to the nature of the benzazole heteroatom, they are less sensitive to the solvent polarity, Figure 2. On going from n-hexane to methanol, the spectra suffer red shifts, ca. 7 and 25 nm for the absorption and emission maxima, respectively. However, in water the absorption maximum is blue-shifted relative to alcohols due to decrease in the ICT process due to hydrogen bonding interactions as mentioned previously.

The change in the dipole moments upon excitation of azolium cations ($\mu_e - \mu_g$) was calculated using Eq. 1. From these values and the calculated ground state dipole moments ($\mu_g = 2.29$ and 1.84 D, for DMASBO and DMASBT, respectively) as well as the radius of cations ($a = 6.2$ A), the excited state dipole moments obtained are 8.58 and 9.01 D for DMASBO and DMASBT, respectively.

Our results, therefore, reveal that the dipole moment of the excited styrylbenzazoles is much greater than that of their azolium cations. This is due to charge creation and separation in the former compounds upon excitation while excitation of the later ones leads to a charge shift and localization of the positive charge on the dimethylamino group.

Further increase in $[H^+]$ leads to dramatic changes in the absorption and emission spectra of both DMASBT and DMASBO. The charge transfer absorption and emission bands of monocation I (Scheme 2) disappear with a slight red shift in the absorption and emission bands of monocation II, see Figure 4 and Table 3. This indicates that protonation at the $-NMe_2$ group is

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taking place thus forming the dication, which does not suffer any charge transfer interactions.

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