Excitation Wavelength Dependence of Dual Fluorescent Molecules

Firew Tarekegn Gemeda[1*], Mesfin Redi Abshiro[2] and Ahmed Mustefa[2]

[1]*Department of Chemistry, Mettu University, Mettu, Ethiopia.*
[2]*Department of Chemistry, College of Natural Sciences, Addis Ababa University, P.O.Box 1176, Ethiopia.*

Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

ABSTRACT

The effect of various polar solvents on the absorption and dual fluorescence of 4-(dimethylamino)benzaldehyde (DMABA) was investigated. It was found that in non- polar solvents DMABA shows only one emission band, however in polar solvents second emission band at longer wavelength was observed. The two emission bands show excitation wavelength dependence. The long wavelength emission band was found to increase in intensity at the expense of the short wavelength emission band. Area normalized intensity versus emission wavelength plot in dichloromethane and ethyl acetate shows isoemissive point. Also excitation spectrum depends on emission wavelength. Therefore in polar solvents two different conformers of the same molecule at equilibrium in ground state are responsible for the dual fluorescence observed. The experimental studies were supported by theoretical calculations. Potential energy surface calculation by Molecular Mechanics results in presence two low energy conformers in polar solvents at ground state and excitation energy calculation for the two conformers by time dependent density functional

_____

Corresponding author: E-mail: firetrkgn@gmail.com;

theory at B3LYP/6-31d level of theory shows agreement with experimental result. Based on solvatochromic shift, excited state dipole moments were calculated and found to be 6.25 D and 10.5 D; this suggests presence of charge transfer for the second conformer.

1. INTRODUCTION

The detailed understanding of the photophysics of dual fluorescent molecules has remained a continuous challenge since the pioneering work of Lippert back 1959 [1]. In the study of dual luminescence phenomena, significant attention was paid to the donor–acceptor substituted aromatics. The best known representative of such compounds is 4-(dimethylamino) benzonitrile (DMABN) [2-4] In addition, however, several other systems were studied, including the DMABA [5-6].

Lippert et al. discovered that dual fluorescence depend strongly on the solvent polarity and on the temperature [7]. In non-polar solutions DMABN and related compounds like DMABA was found to exhibit normal emission related to the benzene derivative around $\lambda_{max} \sim$ 350 nm. However, in a polar environment in addition to the "normal" fluorescence, an "anomalous" red shifted fluorescence band was observed which was solvent dependent, with $\lambda_{max} \sim$ 420 nm- 500 nm [8]. This band was called "anomalous" because it constituted an obvious exception from the well established rule by Kasha stating that the fluorescence spectrum is dominated by a single band arising from emission from the first excited singlet state [9]. These fluorescence bands were assigned to emission from the close-lying ^1L_a and ^1L_b states. In non- polar solvents the ^1L_b state is lower in energy than the ^1L_a sate and hence only the b-band is observed. In polar solvents the ^1L_a state, involving greater charge transfer, is lowered due to the interaction of the dipole moments of the excited state DMABN and solvent molecules, hence a-band fluorescence is observed.

Apart from Lippert mechanism, different hypotheses were formulated [5,10-14] to interpret dual fluorescence, these are emission from, an excimer, Proton transfer and Hydrogen bonding, Exciplexes with the solvent, Twisted Intramolecular charge Transfer (TICT), Wagging of the amino group (WICT), Rehybridization of the acceptor (RICT), planarization of the molecule (PICT). However, when the different hypotheses are compared many of them are being discarded by ample experimental and theoretical evidences [5]. The two main hypotheses are the TICT and PICT. The twisted ICT (TICT) was first put forward by Grabowski et al. and Coworkers [15-16] in the 1970s and later refined as 90° twisted conformation of the Me$_2$N group in the ICT state. This implies that the coordinate of the ICT reaction is the Me$_2$N twist angle [9]. According to this model, in the case of DMABN and DMABA, there exist a reaction path in the excited state leading from the near planar conformation (emitter of the B- band) to an excited photochemical product with an energetic minimum at the perpendicular conformation (emitter of the band A- band). For the perpendicular TICT conformation, donor and acceptor π orbitals are orthogonal (Zero over lap) and thus decoupled leading to maximum for the dipole moment in the excited state. Thus the two bands show mother-daughter relationship [5,17]. On the other hand, the so-called Planar ICT (PICT) model was advocated by Zachariasse and co-workers in series of papers since 1993 [18-19]. The basic assumption of this model is that, in the ICT state the donor and acceptor groups are not decoupled and that the configuration change of the amino nitrogen from the pyramidal toward planar is an important reaction coordinate. In the PICT model, independent of the structure of ICT state, a small energy gap ΔE between the two lowest excited singlet states is considered to be important requirement for the occurrence of dual fluorescence [20,21].

The desire to uncover the reason for the unique photochemical properties of DMABN, DBAMA and like compounds has triggered a large number of experimental and theoretical studies, and many reviews exist. Nevertheless, even for DMABN, the well-studied molecule, the mechanism of the ICT reaction is still a matter of controversial debate [9]. There is also a recent study that shows excitation wavelength dependence of dual fluorescence of DMABN in polar solvents [22].

In this work the effect of polar solvents on excitation and emission spectra of DMABA is studied, also the effect of polar solvents in ground state structure of DMABA and its consequence on dual fluorescent property of the compound is investigated both experimentally and computationally.

2. EXPERIMENTAL DETAILS

DMABA (98%, research Chemicals, Hysham, Lancs) were used for investigation. The solvents used were acetonitrile (HPLC grade reagent, 99.8%), cyclohexane (Analytical Reagent, 99.5%), dioxane (99 %, Scharlau Chemie S.A, European Union), ethyl acetate (99.5%, Megetbrannfarlig), dichloromethane (BDH laboratory Supplies, England), chloroform (Labmerk Chemicals, India), diethyl ether (98%, Haryana, India). For absorption measurement UV-Visible spectrophotometer, SPECTRONIC GENESYS 2PC was used. The concentration of the DMABA in all absorption measurements was prepared in such away that the absorbance is less than 1.5. Quartz cuvettes, 1cm, were used for holding the sample for absorption measurements. For excitation and emission measurements SPECTROFLUOROMAX-4 was used. Absorbance of less than 0.3, were used for excitation and emission measurement. Emission and excitation spectra were measured for DMABA in acetonitrile, dichloromethane, cyclohexane, diethyl ether, dioxane, chloroform,

and ethyl acetate. Blank measurement was made for all the solvents before measurement and subtracted. To see the effect of wavelength excitation spectra at the two emission maxima were recorded for DMABA in all the solvents. Also the emission spectra were taken for different excitation wavelengths in UV and Visible region.

3. COMPUTATIONAL METHOD

Molecular Mechanics was used for potential energy surface calculation of DMABA in polar solvent. MM+ force field calculation was performed using HyperChem 7.5 soft ware. This was done by rotating the dimethyl group between tortional angle of 0° and 180° in periodic box that contains water molecules. In addition to molecular mechanics, TD- DFT/B3LYP/ 6-31Gd level were used to calculate the excitation energies by making use of Gaussian 03 package.

3.1 Excitation Spectra

The absorption and excitation spectra of DMABA were recorded in solvents of different polarities. DMABA shows one absorption band in all solvents. But the two emission bands show excitation wavelength dependences. Fig. 1 show, the two excitation bands of DMABA at λ_{max}, 294 nm and 341 nm in dichloromethane that lead to two distinct emission bands. Similar property was observed in acetonitrile (Fig. 2).
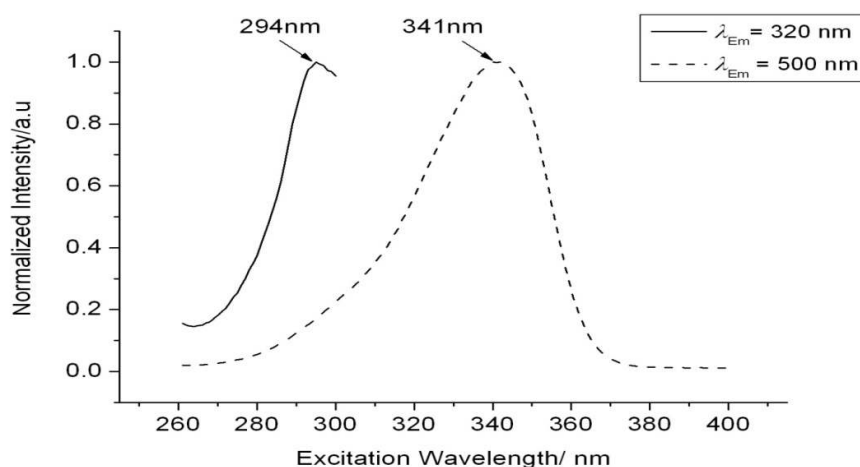
Fig. 1. Normalized excitation band of DMABA in dichloromethane at different emission wavelength
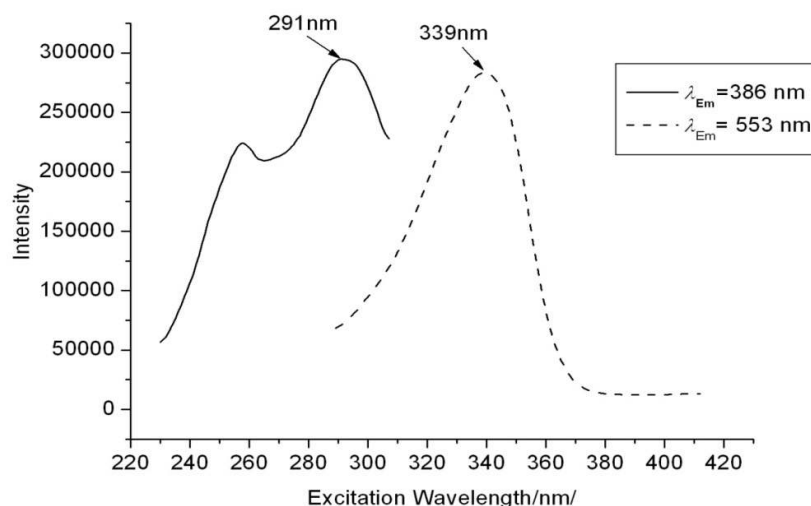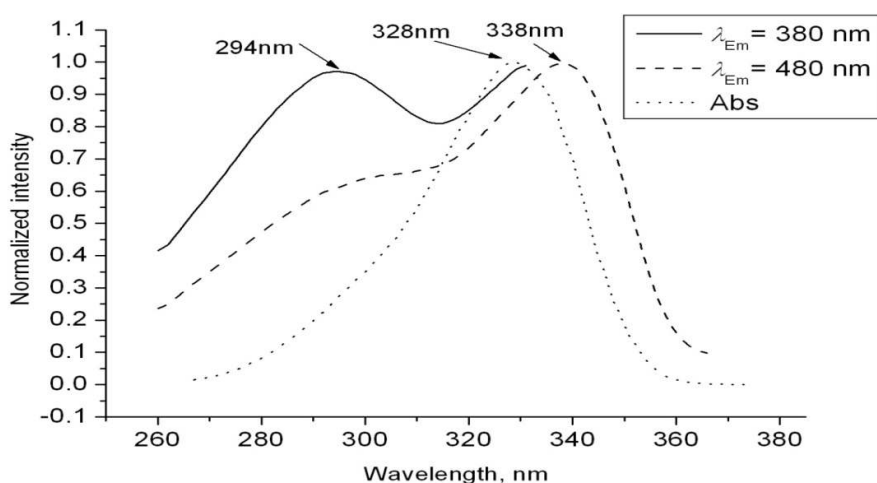
Fig. 2. Excitation spectra of DMABA in acetonitrile

In ethyl acetate similar properties were observed as in other polar solvents. In this case, in moving from short emission wavelength to long, the intensity of the first excitation band decreases. This shows that the quantum efficiency of the first excitation band is decreasing as emission wavelength increases, and this indicates presence different transitions in ground state. The absorption band is also in between the peak of the excitation bands that can also be good evidence to say that the absorption band is an overlap of two excitation bands (Fig. 3).

From the above results, it can be concluded that absorption spectra of DMABA (in polar solvents) is a convolution of two distinct excitation bands, i. e., the short wavelength emission band arises

from the short wavelength excitation spectrum and the long wavelength emission band arises from the long wavelength excitation spectrum. According to Kasha rule, the excitation band of a single transition lead to a single emission band, and thus the emission spectrum of a single transition do not show wavelength dependency. For a single transition the band shape and the position of absorption and excitation wavelength are similar, any significant difference in the position and shape between the bands is an indication of the presence of more than one transition, which may be due to existence of more than one absorbing species in ground states. The observed emission wavelength dependency may signify presence of two conformers of DMABA in ground state absorbing

Fig. 3. Normalized excitation and absorption spectra of DMABA in ethyl acetate

4

and emitting at different positions in polar solvents. In non polar solvents like cyclohexane all excitation spectra leads to a single emission band in agreement with Kasha rule, and testifying the existence of only one transition, and thus only one of the conformer of DMABA.

3.2 Emission Spectra

Emission spectra of DMABA were measured in solvents of different polarities. In non- polar solvents like cyclohexane only one fluorescence band was observed. With increasing excitation wavelength there was no change in the band shape and position of wavelength of maximum emission (Fig. 4). In polar solvents like acetonitrile, dichloromethane and ethyl acetate, however, a long second emission fluorescence

band is observed in addition to the first short emission band. With an increase in excitation wavelength the maximum emission wavelength position remained unchanged, but intensity variation as a function of excitation wavelength in contrast to Pavlov rule [23,24] was observed (Figs. 6-8).

In acetonitrile with an increase in excitation wavelength, proportionally bigger intensity increase in the long wavelength emission band was observed. The plot of ratio of intensity of long wavelength emission band to short wavelength emission band (I_2/I_1) as a function of excitation wavelength showed an increase with an increase in excitation wavelength that the two emission bands are resulted from two separate transition bands (Table 1 and Fig. 5).
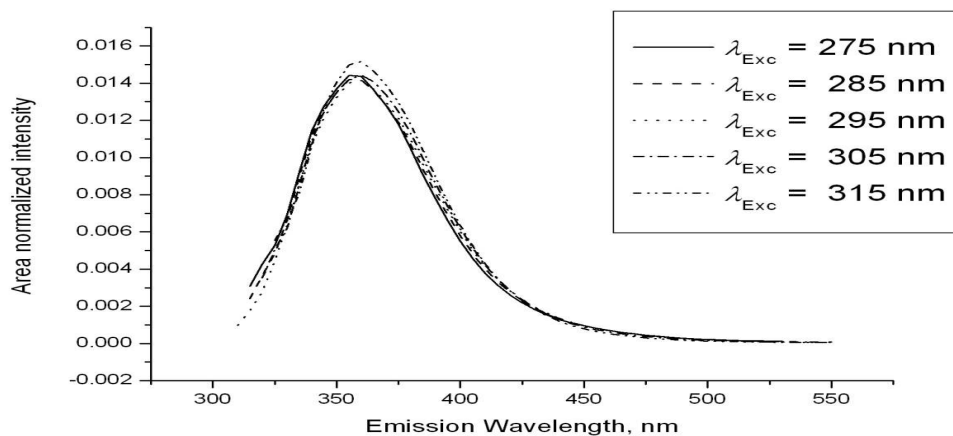

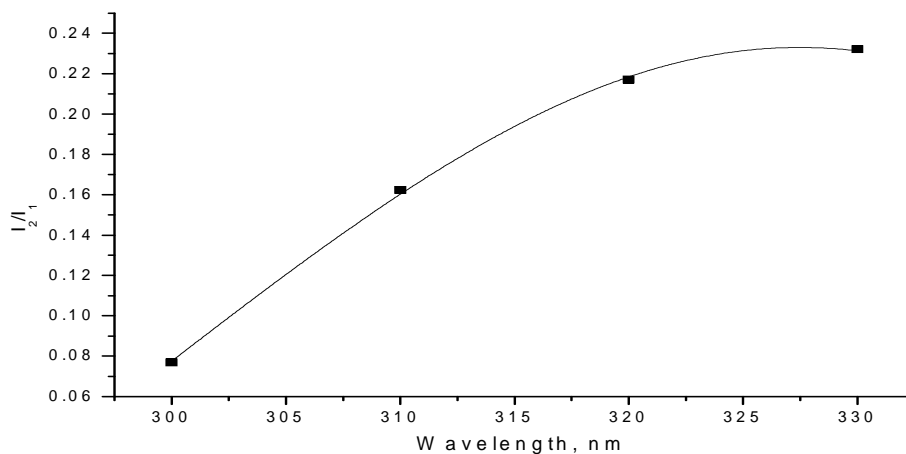**Fig. 4. Area normalized emission Spectra of DMABA in cyclohexane**

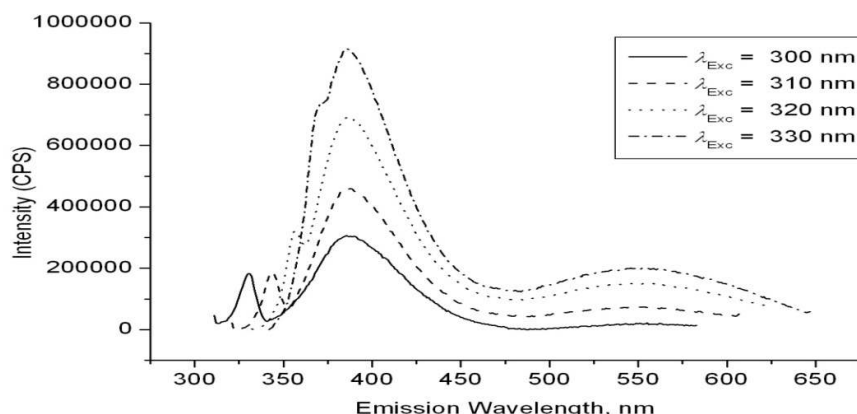**Fig. 5. A Plot of ratio I_2/I_1 as a function of wavelength**

5

Fig. 6. Emission spectra of DMABA in acetonitrile from which I_2/I_1 is taken

Table 1. Table showing variation of intensity of band 1 and 2 as a function Wavelength in acetonitrile

Excitation wavelength	Intensity of band 1 (I_1)	Intensity of band 2 (I_2)	I_2/I_1
300	286	22	0.07692
310	462	75	0.16234
320	691	150	0.21708
330	896	208	0.23214

In dichloromethane a clear separation between the two emission bands is observed (Fig. 7). As the excitation wavelength increases the intensity of the second band increases at the expense of the short wavelength emission band. From this it is clear that there is no mother-daughter relationship between the two emission bands and thus the two emission bands must have originated from two absorbing species, further isoimissive point is observed in area normalized spectra (Fig. 7). The presence of isoimissive point indicates the presence of two states in equilibrium either at ground state or in excited state. In the case of DMABA, the emission bands arise from two excitation spectra. The short emission spectra resulted from short wavelength excitation spectra and the long wavelength emission spectra from the long wavelength excitation spectra. Therefore, the excitation spectrum is dependent on emission wavelength; as a result ground state equilibrium can be considered to be responsible for the dual fluorescence observed in DMABA. This confirms the presence of two conformers in ground state that are responsible for the dual emission observed in DMABA. Computational results also confirm the existence of two low energy ground state structures of DMABA.
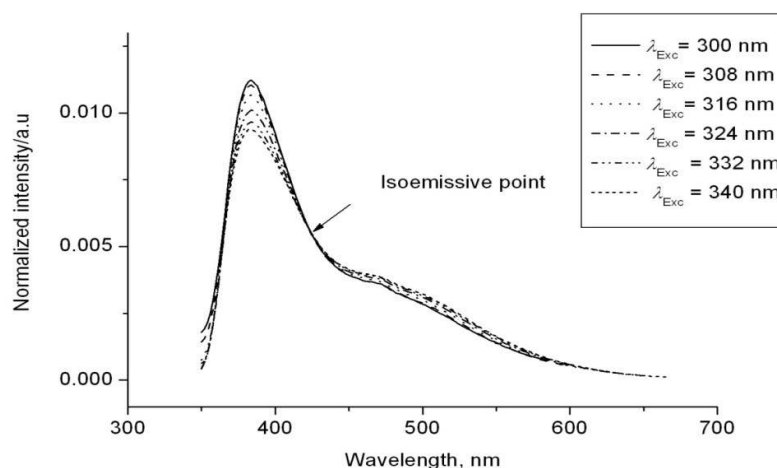

Fig. 7. Area normalized emission Spectra of DMABA in dichloromethane

6

Generally, when the emission band in polar and non- polar solvents is compared, in non- polar solvents only the short emission band is observed. This shows the only stable structure in non- polar solvents is the one excited at short wavelength and the second conformer exists only in polar environment.

3.3 Absorption Spectra and Solvatochromic Shift of DMABA

Absorption and excitation of DMABA was measured in different solvents of different polarities and the effect of solvent on the spectra is given below. The absorption spectra of DMABA shows bathochromic (red) shift with an increase in the solvent polarity.

The solvatochromic shift of the absorption maximum $\tilde{V}_{abs}$ generally follows the functional dependence on the solvents dielectric constant and refractive index given by [24]:

$$hc\tilde{v}_{abs}^{sol} = \tilde{V}_{abs}^{o} - \frac{2\bar{\mu}_g(\bar{\mu}_a - \bar{\mu}_g)}{a_o^3}\left[\frac{\varepsilon-1}{2\varepsilon+1} - \frac{1}{2}\frac{n^2-1}{2n^2+1}\right]$$

The plot of absorption maxima as a function of solvent polarity is given in Fig. 9. Also the plot of absorption maxima as a function of dielectric constant and refractive index are considered separately to observe the effect of the two independently. In general, in case of DMABA the solvatochromic shifts of the absorption maxima plotted against solvent polarity shows strong scattering, this is may be due to the polarization effect, which is refractive index functional, more significant in chloroform and dichloromethane.

Improved linear dependence is obtained when the two functions are treated independently. As can be observed in Fig. 8, the difference between the positions of the maxima in highly dipolar solvent acetonitrile and that in non- polar solvent cyclohexane is almost the same as between that of the highly polarized chloroform or dichloromethane and cyclohexane, indicating that the effect of dielectric interaction is greater.

3.4 Solvatochromic Shift and Excited State Dipole Moment

For a molecule having a permanent dipole moment μ_g in the electronic ground state and a moment μ_a parallel to it in the ground state, the solvent dependence of the wave-number $\tilde{v}_a^{sol}$ of the absorption maximum is given to a good approximation by the following equation [25]

$$\tilde{v}_a^{sol} \cong \tilde{v}_a^{O} - \frac{(\bar{\mu}_a - \bar{\mu}_g)(F_{RM})}{hc} - \frac{2(n^2-1)}{a^3(2n^2+1)}D \quad (1)$$

$\tilde{v}_a^{O}$ is the wave number of the absorption maximum in the free molecule (gas state). The term D describes the solvent dependence of the position of the absorption band due to the dipersion interaction between dissolved molecules and the surrounding solvent molecules. The effective electric field F_{RM} is the mean of the reaction fields of the dissolved molecule in the ground state and in the Franck-Condon excited state. It relates dielectric constant of the solution, refractive index and the polarizability tensor of the molecule.
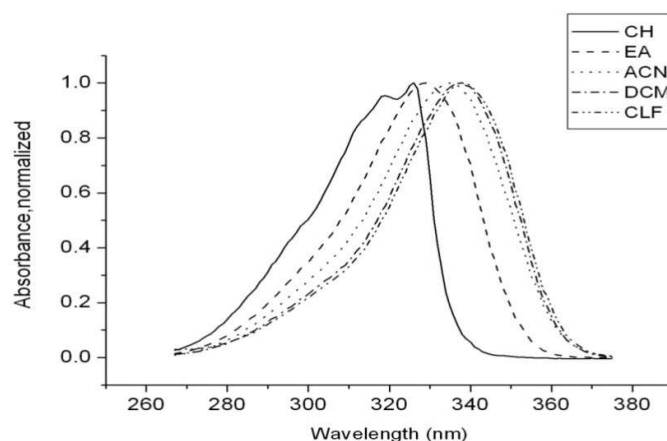

Fig. 8. Normalized absorption Spectra of DMABA in different solvents (CH = cyclohexane, EA= ethyl acetate, ACN = acetonitrile, DCM = dichloromethane, CLF = chloroform)
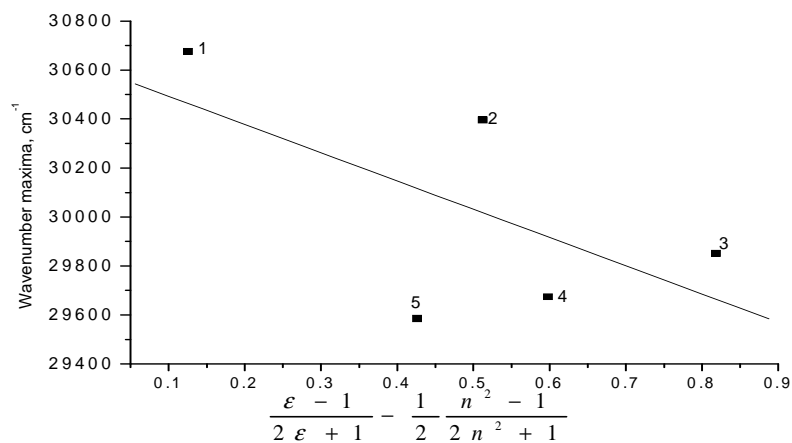
Fig. 9a. Plot of absorption maxima as a function of solvent polarity (1- cyclohexane, 2- ethyl acetate, 3- acetonitrile, 4-dichloromethane, and 5- chloroform)
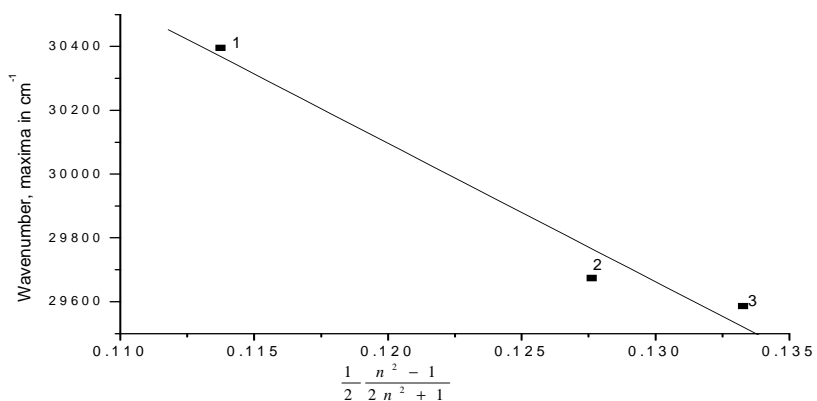

Fig. 9b. Plot of absorption maxima as a function of solvent polarity considering only refractive index (1- ethyl acetate, 2 -dichloromethane, and 3- chloroform)
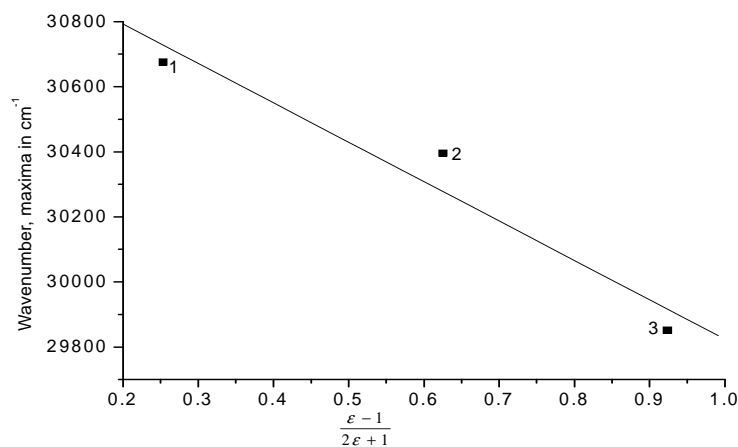

Fig. 9c. Plot of absorption maxima as a function of solvent polarity considering only dielectric constant (1- cyclohexane, 2- ethyl acetate, and 3- acetonitrile)

Assuming a point dipole situated in the center of the spherical cavity and neglecting the mean solute polarizability α in the states involved in the transition ($\alpha = \alpha_a = \alpha_g = 0$), the solvatochromic effects on the spectral position of the absorption maxima can be given by [26,27].

$$hc\tilde{v}^{sol}_{abs} = \tilde{v}^{o}_{abs} - \frac{2\vec{\mu}_g(\vec{\mu}_a - \vec{\mu}_g)}{a_o^3}\left[\frac{\varepsilon-1}{2\varepsilon+1} - \frac{1}{2}\frac{n^2-1}{2n^2+1}\right]$$

(2)

$hc\tilde{v}^{sol}_{abs}$ and $\tilde{v}^{o}_{abs}$ are the energy related to spectral position of charge transfer absorption maxima in solutions and to the value extrapolated to the gas-phase, respectively; $\vec{\mu}_g$ and $\vec{\mu}_a$ are the dipole moments of the solute in the ground and excited state, a_o is the effective radius of Onsager's cavity [28], ε is the dielectric constant, and n is the refractive index of the solvent.

Under the same assumption Lippert and Mataga have obtained the following expression for the fluorescence solvatochromic shit [26, 27].

$$h\tilde{v}^{sol}_{flu} \cong \tilde{v}^{o}_{flu} - \frac{2\vec{\mu}_a(\vec{\mu}_a - \vec{\mu}_g)}{a^3}\left[\frac{\varepsilon-1}{2\varepsilon+1} - \frac{1}{2}\frac{n^2-1}{2n^2+1}\right]$$

(3)

Where, $\tilde{v}^{sol}_{flu}$ and $\tilde{v}^{o}_{flu}$ are the spectral positions of the fluorescence maxima in solution and the value extrapolated to the gas-phase, respectively.

Generally, emission bands result from excitation bands, and excitation bands are similar to absorption bands. However, when there is a difference between absorption and excitation bands, it is appropriate to consider excitation spectrum rather than absorption spectrum. In case of DMABA the absorption spectrum may be considered as an overlap of two excitation spectra. Due to this fact, the two excitation maxima are taken instead of absorption maxima in the equation 2, thus replacing $\tilde{V}_{abs}$ by $\tilde{V}_{exc}$ the equation become:

$$hc\tilde{v}^{sol}_{exc-1} = \tilde{v}^{o}_{exc-1} - \frac{2\vec{\mu}_g^1(\vec{\mu}_a^1 - \vec{\mu}_g^1)}{a_o^3}\left[\frac{\varepsilon-1}{2\varepsilon+1} - \frac{1}{2}\frac{n^2-1}{2n^2+1}\right]$$

(4)

For the first excitation spectrum,

$$hc\tilde{v}^{sol}_{exc-2} = \tilde{v}^{o}_{exc-2} - \frac{2\vec{\mu}_g^2(\vec{\mu}_a^2 - \vec{\mu}_g^2)}{a_o^3}\left[\frac{\varepsilon-1}{2\varepsilon+1} - \frac{1}{2}\frac{n^2-1}{2n^2+1}\right]$$

(5)

For the second excitation spectrum,

where $\tilde{v}^{sol}_{exc-1}$ and $\tilde{v}^{sol}_{exc-2}$ are wave numbers corresponding to maxima of the two excitation bands, $\tilde{v}^{O}_{exc-1}$ and $\tilde{v}^{O}_{exc-2}$ are the corresponding wave numbers in vapour phase. $\vec{\mu}_g^1$ and $\vec{\mu}_a^1$ are ground state and excited state dipole moment of conformer one respectively, $\vec{\mu}_g^2$ and $\vec{\mu}_a^2$ are ground state and excited state dipole moment of conformer two respectively.

Using the plot of excitation maxima and emission maxima verses solvent polarity function the excited state dipole moment of the two conformers can be calculated, by taking the ratio of the slope. Scattering from linearity is observed in case of the plot of excitation versus polarity function, this may be due to the polarization effect, which is refractive index functional, more significant in dichloromethane and dioxane.

The comparative observation of the solvent dependence of the two conformers made possible to estimate the ratio of excited state dipole moment, μ_e, to the ground state, μ_g, for both conformers. From plot of Figs. 10a and 10b, and equation 4 the slopes of the two plots are, respectively:

$$\frac{\vec{\mu}_g^1(\vec{\mu}_a^1 - \vec{\mu}_g^1)}{a_o^3}$$

(6)

$$\frac{\vec{\mu}_g^2(\vec{\mu}_a^2 - \vec{\mu}_g^2)}{a_o^3}$$

(7)

From plot of Figs. 10c and 10d, and equation 5 the slopes of the two plots respectively are

$$\frac{\vec{\mu}_a^1(\vec{\mu}_a^1 - \vec{\mu}_g^1)}{a_o^3}$$

(8)

$$\frac{\vec{\mu}_a^2(\vec{\mu}_a^2 - \vec{\mu}_g^2)}{a_o^3}$$

(9)

From the ratio of equation 8 to 6 and 9 to 7, one can get $\dfrac{\mu^{1}_{a}}{\mu^{1}_{g}} \approx 1.1154$ and $\dfrac{\mu^{2}_{a}}{\mu^{2}_{g}} \approx 1.8724$

Taking the value of ground state dipole moment for DMABA, $\mu_g = 5.6$ D [25,28], and assuming the ground state of the two conformers to be the same for simplicity it follows that $\mu^{1}_{a} \approx 6.25$ D and $\mu^{2}_{a} \approx 10.5$ D. The values A. Kawski and coworkers obtained were 7.6 D and 12 D [29] and the value Labhart and Wagniere obtained was 13.6D for the second one, in their case the first one was for the short emission band and the second large dipole moment was considered to be due to full transfer of electron in TICT state.
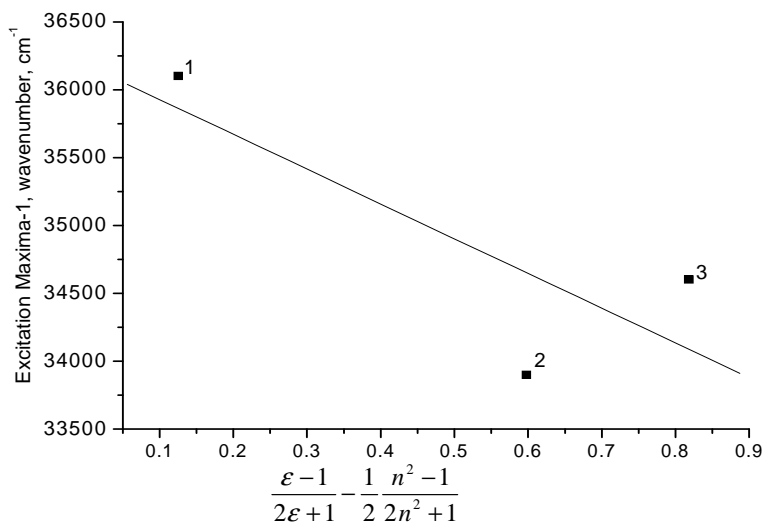

Fig. 10a. Plot of excitation maxima-1 as a function of solvent polarity (1- cyclohexane, 2- dichloromethane, and 3- acetonitrile)
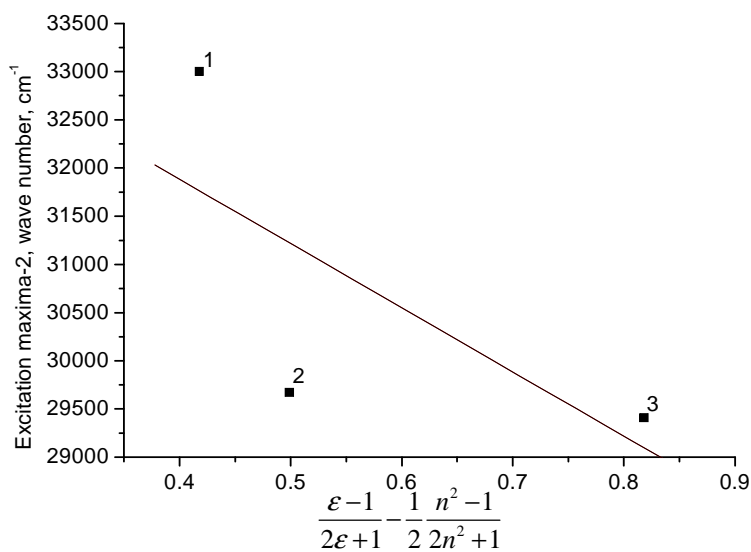

Fig. 10b. Plot of excitation maxima-1 as a function of solvent polarity (1- diethyl ether, 2- dioxane, and 3- acetonitrile)
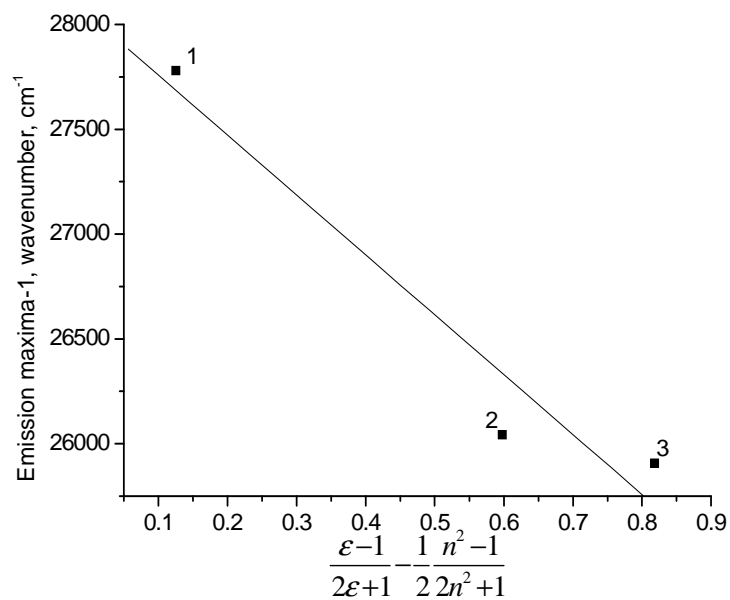
Fig. 10c. Plot of excitation maxima-1 as a function of solvent polarity (1- cyclohexane, 2-dichloromethane, and 3- acetonitrile)
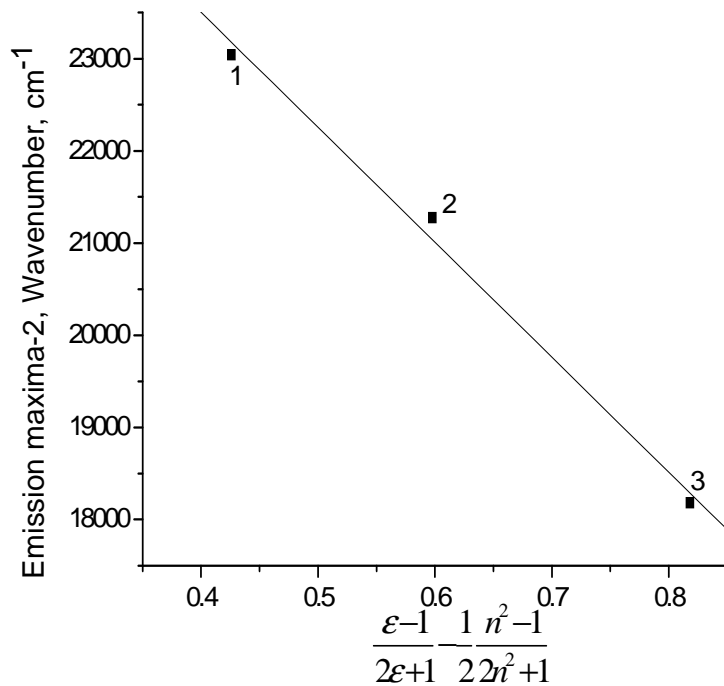

Fig. 10d. Plot of excitation maxima-1 as a function of solvent polarity (1- Chloroform, 2-Dichloromethane, and 3- Acetonitrile)

According to TICT mechanism one of the main arguments is that there is full electron transfer in excited state, as a result decoupling of the orbitals of donor and acceptor group in excited state takes place and thus twisting of the structure will happen which is responsible for the long wavelength emission. By comparing the value of dipole moment obtained by experiment and the value obtained by calculation taking in to consideration the charge separation, one can tell whether charge transfer can exist or not [5]. If the values are equivalent that can indicate full transfer of electron but if there is variation, that again is an indication of absence of full transfer of electron. But somewhat large experimental value can indicate charge transfer. If complete transfer of electron exists, the value of dipole moment can be calculated by taking the charge separation and using definition of dipole moment. From calculation the approximate value obtained is shown in Scheme 1.
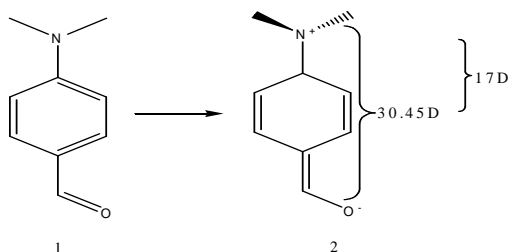
Scheme 1. DMABA (1-normal structure, 2-full transfer of electron)

The value obtained experimentally ($\cong$10.5D) is much less than the value that would have been expected if there is full electron transfer ($\cong$ 30.45D) from the donor group to acceptor group, Scheme 1. Even if only the half upper part of the ring is considered ($\cong$ 17D) still the value obtained from experiment is smaller ($\cong$ 10.5). To say that there is probability of full electron transfer the dipole moment need to be at least nearer to the theoretical value. In this case there is only charge transfer which causes the second dipole moment to increase and there is no full transfer of electron in excited state. And as a result decoupling of the orbital of the donor group and acceptor group does not occur in excited state. Consequently, decoupling of orbital at excited state and thus TICT mechanism, which was believed to be the reason for dual emission of DMABA [28] cannot be responsible for the observed properties. The PICT mechanism,

though shown the absence of decoupling of orbital in excited state, it focuses on excited state plannarization of amino group considering that the two emissions are originated from the same excitation spectrum but the two emission bands show dependence on excitation wavelength, therefore PICT mechanism also can not be the reason for the observed properties of DMABA. However, from experimental results the two values can be taken as the excited state dipole moments of two conformers in ground state. The excited state dipole moment of the second conformer is greater than that of the first, this is because charge transfer is greater in the second conformer. The two conformers can therefore be assigned as conformer A and conformer B.

4. COMPUTATIONAL RESULTS

4.1 Computation of Potential Energy Surfaces using Molecular Mechanics

Since Molecular Mechanics deals very well with calculation of the potential energy surface and is fast method. Computation by this method is selected to access the structural property of the compound. The equilibrium geometry of DMABA at ground state and their relative energies are computed using force field theory/ molecular mechanics/MM$^+$ by making use of HyperChem 7.5 software. Since HyperChem allows solvation of solutes in water the ground state of DMABA was investigated in polar environment by rotating dimethylamino group ($-N(CH_3)_2$). The plot of the potential energy of the structures as a function of tortional angle is given in Fig. 11.

The computation shows presence of two geometries in ground states that have minimum energies, from which one of the structures is the most stable one at minimum energy. The two ground state structures have their minimum energy at, conformer A, tortional angle=14° and potential energy = -141.627KJ/Mol and conformer B, tortional angle = 124° and potential energy = -98.352 KJ/Mol. With conformer A more stable, this two structure are responsible for the dual emission observed in polar solvents.

4.2 Excitation Energy Calculation

TDDFT (B3LYP, 6-31Gd level) were used to calculate excitation energy of the two conformers obtained from potential energy surface calculation by Molecular Mechanics. The excitation wavelength of the two optimized
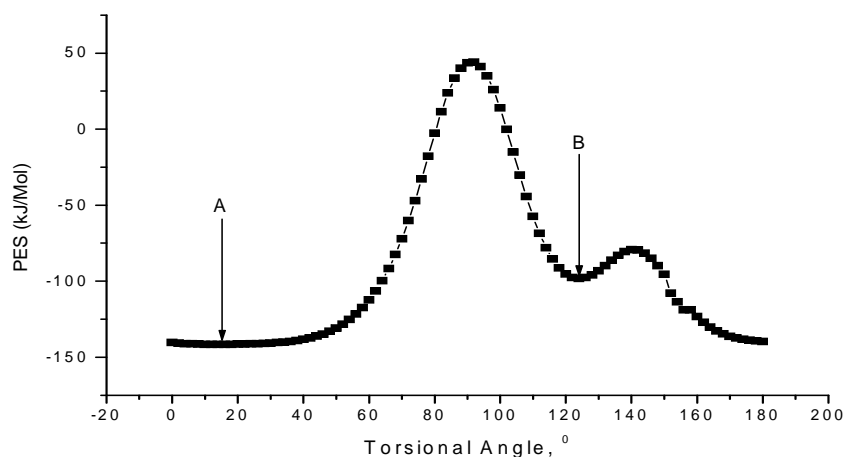
Fig. 11. Potential energy surface of DMABA solvated with water molecules

conformers at the maximum oscillator strength was found to be $\lambda_{max}(1) = 311$nm and $\lambda_{max}(2) = 326$nm. The excitation wavelength at $\lambda_{max} = 311$nm corresponds to the first conformer, A and excitation wavelength at $\lambda_{max} = 326$ nm corresponds to the second conformer, B. The agreement between the theoretical values and experimental results clearly shows that the two emission bands are originated from two structural conformers in ground state that exists in polar solvents.

5. CONCLUSION

Effect of solvents on dual fluorescence in 4-Dimethylamino benzaldehyde was investigated. In non- polar solvents only one fluorescence band is observed, also the band shape and position remain unchanged with increasing excitation wavelength. In polar solvents however, second emission band is observed in addition to the first short emission band. With an increase in excitation wavelength the maximum emission wavelength position remained unchanged, but intensity variation as a function of excitation wavelength was observed. With an increase in excitation wavelength, the intensity of the second band increases largely in proportion to the short emission band. Isoemisive points were also observed. The presence of isoimissive point indicates the presence of two states in equilibrium either at ground state or in excited state. For DMABA excitation band shows dependence on emission wavelength and this suggests presence ground state equilibrium, therefore two transitions from ground state is responsible for the dual emission observed in

polar solvents. Computational results also support the experimental investigation. Potential energy surface calculation using molecular mechanics shows two structures with minimum energy at ground state. Further investigation of excited state energy calculation by time dependent density functional theory for the two structures shows agreement with experimental data. The excited state dipole moment for the two state was also calculated from solvatochromic shift. The result shows greater charge transfer for the long emitting conformer but much less than the value expected if complete electron would transfer. Thus from the investigation made both experimentally and computationally, the ground state equilibrium is suggested to be responsible for the observed dual fluorescence in DMABA in polar solvents.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Demeter A, Berces T, Hinderberger J, Timari G. Dual luminescence properties of differently benzo-fused N-phenylphenanthridinones Photochem. Photobiol. Sci. 2003;2:273.
2. Platt J. Classification of spectra of cata-condensed hydrocarbons. J. Chem. Phys. 1949;17:484.
3. Il'ichev YV, Kuhnle W, Zachariasse KA. Intramolecular charge transfer in dual fluorescent 4 (Dialkylamino)benzonitriles.

Reaction Efficiency Enhancement by Increasing the Size of the Amino and Benzonitrile Subunits by Alkyl Substituents. J. Phys. Chem. A. 1998;102: 5670.

4. Demeter A, Druzhinin S, George M, Hasselbach E, Roulin JL, Zachariasse KA. Dual luminescence properties of differently benzo-fused *N*-phenylphenanthridinones Chem. Phys. Lett. 2000;323:351.

5. Grabowski ZR, Rotkiewicz K, Rettig W. Structural changes accompanying intramolecular electron transfer: Focus on twisted intramolecular charge-transfer states and structures. Chem. Rev. 2003; 103:3899.

6. Volchkov V, Uzhinova L, Uzhinov B. The dynamics of excited state structural relaxation of 4-Dimethylaminobenzonitrile (DMABN) and related compounds international J. Photoenergy. 2006;1.

7. Dobkowiska J, Rettig W, Waluk J. Intramolecular charge-transfer properties of a molecule with a large donor group: The case of 4′-(pyren-1-yl)benzonitrile, phys. Chem. Chem. Phys. 2002;4:4334.

8. Visser RJ, Varma CAGO. Source of anomalous fluorescence from solutions of 4-*N*,*N*-dimethylaminobenzonitrile in polar solvents. J. C. S. Faraday II. 1980;76:453.

9. Rappaport D, Furche F. Time-dependent density functional theory: Past, present, and future. J. Am. Chem. Soc. 2004;126: 1277.

10. Khalil OS, Hofeldt RH, McGlynn SP. Electronic spectroscopy of highly-polar aromatics. Molecular interactions in the ground and excited states of N,N-dimethyl-p-cyanoaniline. Chem. Phys. Lett. 1972;17: 479.

11. Kosower EM, Dodiuk H. Long-range corrected time-dependent density functional study on fluorescence of 4,4′4,4′-dimethylaminobenzonitrile, J. Am. Chem. Soc. 1976;98:924.

12. Chandros EA, Thomas HT. Chem. Phys. Lett. 1971;9:397.

13. Rotkiewicz K, Grellmann KH, Grabowski ZR. Reinterpretation of the anomalous fluorescense of *p*-n,n-dimethylamino-benzonitrile. Chem. Phys. Lett. 1973;19: 315.

14. Leinhos U, Kuhnle W, Zachariase KA. Intramolecular charge transfer and thermal exciplex dissociation with p-aminobenzonitriles in toluene. J. Phys. Chem. 1991;95:2013.

15. Rotkiewicz K, Grellmann KH, Grabowski ZR. Reinterpretation of the anomalous fluorescence of p-(dimethylamino)benzonitrile. Chem. Phys. Lett. 1973;21:212.

16. Kohler G, Rechthaler K, Rotokiewicz K, Rettig W. Chem. Phys. 1996;207: 85.

17. Okamoto H, Kinoshita M. Picosecond infrared spectrum of 4-(Pyrrol-1-yl)benzonitrile: Structure of the excited charge-transfer states of donor-acceptor systems. J. Phys. Chem. A. 2002;106: 3485.

18. Schuddeboom W, Jonker SA, Warman JH, Leinhos U, Kuhnle W, Zachariasse KA. Excited-state dipole moments of dual fluorescent 4-(dialkylamino)benzonitriles: Influence of alkyl chain length and effective solvent polarity. J. Phys. Chem. 1992;96: 10809.

19. Von der Haar T, Hebecker A, Leinhos U, Kuhnle W, Zachariasse KA. Intramolecular charge transfer in aminobenzonitriles: Requirements for dual fluorescence. Pure Appl. Chem. 1993;65:1745.

20. Zachariasse KA. 'Comment on Pseudo-Jahn-Teller and TICT-Models: A photophysical comparison of meta-and para-DMABN derivatives: The PICT model for dual fluorescence of aminobenzonitriles.' Chemical Physics Letters. 2000;320(1-2):8-13.
DOI: 10.1016/S0009-2614(00)00230-X

21. Zachariasse KA, Demeter A, Beres T. Dual luminescence properties of differently benzo-fused *N*-phenylphenanthridinones, J. Phys. Chem. 2000;105:4611.

22. Atsbeha T, Mohammed A, Redi-Abshiro M. Excitation wavelength dependence of dual fluorescence of DMABN in polar solvents. J Fluoresc. 2010;20(6):1241–1248.

23. Lakowicz JR. Principle of Fluorescence Spectroscopy. 2nd edition, Kluwer Academic/Plenum, New York; 1999.

24. Valeur B. Molecular fluorescence: Principles and applications, Wiley-VCH, Verlag GmbH; 2001.

25. Liptay W. Electrochromism and Solvatochromism. Angew, Chem. Internat. Edit. 1969;8:177.

26. Herbich J, Kapturkiewicz A. Electronic structure and molecular conformation in the excited charge transfer singlet states of 9-Acridyl and other Aryl derivatives of

aromatic amines, J. Am. Chem. Soc. 1998; 120:1014.

27. Rechthaler K, Kohler G. Photophysical properties of a highly fluorescent push- pull stilbene. Chem. Phys. Lett. 1996;250:397.

28. Onsager L. Electric moments of molecules in liquids. J. Am. Chem. Soc. 1936;58: 1486.

29. Kawaski A, Kuklinski B, Bojarski P. Chem. Phys. Lett. 2007;448:208.

Peer-review history:
The peer review history for this paper can be accessed here:
http://sciencedomain.org/review-history/18004