ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

Computation and Experimental Study on the Dual Fluorescence Phenomenon of 4-(N,N-dimethylamino)-benzonitrile and Related Compounds

GRADUATE PROJECT (Chem.774)

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Computational and Experimental Study on the Dual Fluorescence Phenomenon of 4-(N, N-dimethylamino)-benzonitrile and Related Compounds

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Computational and Experimental Study on the Dual Fluorescence Phenomenon of 4-(N, N-dimethylamino)-benzonitrile and Related Compounds

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Abstract: The behavior of the ground and the first two excited states of the compound 4-(N,N-dimethylamino)-benzonitrile (4DMABN) have been studied using both experimental and theoretical methods. For comparison purpose the ground and the first two excited states of the compounds 3-(N,N-dimethyl amino)-benzonitrile (3DMABN) and 2,3,6,7-tetrahydro-1H,5H-pyridol[3,2,1-ij]quinoline-9-carbonitrile (TMABN) have been studied theoretically. The experimentally achieved absorption spectrum of 4DMABN has shown two distinct bands. And the emission spectrum has also two distinct bands, the behavior of which is dependent on the wavelength of the exciting light. This is attributed to the presence of two stable conformers of the compound in the ground state. Excited state calculations using TDDFT method have shown that the first two excited states of the compound 4DMABN have different properties in the gaseous and the solvated system. This is in agreement with the experimental result that the compound shows two emission bands in the solvent acetonitrile and one band in the gaseous state. The same theoretical calculation has shown higher excitation energy to the S_2 state at the perpendicular conformation of the compound 3DMABN. This agrees with the absence of a CT band in experiment. For the compound TMABN the same calculation has shown for the existence of only one emitting excited electronic state at a considerably twisted conformation. This is in agreement with the experimentally found single CT band.

1. Introduction

There has been an intense study on the photophysical behavior of many organic compounds with donor-acceptor substituent groups. The interesting property of such compounds is the so-called intramolecular charge transfer process. In this process a photo-initiated electron transfer from the donor substituent group to the acceptor group occurs, resulting in an electronic excited state, called charge transfer (CT) state. This property of such compounds gives rise to their possible application in molecular device technology as electro-optical switches, chemical sensors, fluorescent solar collectors, chemical dyes, etc [1]. As a result, studies on such compounds mainly lie on the electron transfer (ET) process and the resulting CT states.

Recently, the dual fluorescence property of donor-acceptor systems has been used in the context of molecular switches [1]. The dual fluorescence phenomenon is a solvent induced appearance of a second red shifted fluorescence emission band. This phenomenon was first discovered by Lippert et.al. [2,3], four decades ago, while studying the photo-physical behavior of 4-(N,N-dimethylamino)-benzonitrile (4DMABN) and derivatives in different solvents. Lippert et.al. [2,3] assigned each of the double fluorescence bands to two different excited states. The second, largely red shifted band, called A band, is from the ^1L_a-type charge transfer state, while the normally expected band called B band is from ^1L_b-type locally excited state.

The appearance of the second (A) band with increasing solvent polarity indicates the ^1L_a-state is a polar charge transfer state, in which there has been an electron transfer from the donor dimethylamino group to the acceptor benzonitrile fragment. The absence of the A band in non polar media and the presence of the B band in both non-polar and polar media (but with decreased quantum yield in the later case), indicates the charge transfer (CT) S_2 state is not directly attainable. Rather, once the molecule is excited to the locally excited (LE) S_1 state, an adiabatic photoreaction, in which the LE state undergoes non-radiative geometric relaxation along with charge transfer occurs to result in the CT state. These emitting states can be in thermal equilibrium with the equilibrium being dependent on the polarity of the medium.

Fig.1 shows the kinetic scheme for the intramolecular charge transfer (ICT) reaction. k_{ba} and k_{ab} are forward and backward reaction rate constants respectively, k_{bf} and k_{af} are radiative decay constants, and k_b^o and k_a^o are non-radiative decay constants.

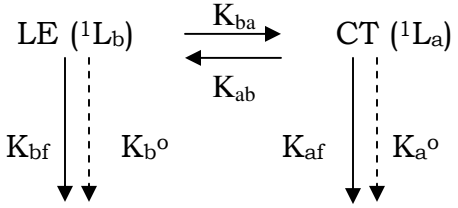


Fig.1. Kinetic scheme for the dual fluorescence of DMABN. Straight arrows represent radiative channel and dotted arrows represent non-radiative channel [1].

A number of models have been proposed to explain the mechanism by which the intramolecular charge transfer excited state is formed out of

the locally excited state, i.e., the geometric relaxation that determines the feasibility of permanent electron transfer, and the final structure of this state.

The first and still widely accepted is the model proposed by Grabowski et. al., [4] called twisted intramolecular charge transfer (TICT) model. According to this model, the planar locally excited (LE) state relaxes to a charge-transfer (CT) state, in which the donor amino group forms a perpendicular conformation with respect to the plane of the benzonitrile acceptor fragment. This conformation results in the decoupling of the lone-pair orbital of the nitrogen atom of the amino group from the delocalized π-molecular orbital of benzene ring, which follows after an electron transfer, facilitating permanent charge transfer.

This model is based on the observation that molecules with a twisted ground state geometry, such as N,N-3,5-tetramethyl-4-aminobenzonitrle (TMABN), show only the second red shifted (A) band, while molecules such as 2,3,6,7-tetrahydro-1H,5H-pyridol[3,2,1-ij]quinoline-9-carbonitrile (TMABN), in which the rotation of the N-atom is restricted, only show the normally expected (B) band [5]. However, this model can not predict the absence of dual fluorescence in systems such as 3-(N,N-dimethyl amino)-benzonitrile (3DMABN) where the rotation of the amino group is still possible [5].

The second alternative model is the planar intramolecular charge-transfer (PICT) model, which was proposed by Zachariasse et. al. [6,7]. This model does not consider the twisting motion of the amino group as

the main relaxation coordinate for the formation of the charge transfer (CT) state. Rather, this model suggests two requirements for the occurrence of dual fluorescence. One is that unlike the TICT model, there should exist two initial interacting states with sufficiently small energy gap between them. The other is that there should exist a promoting mode, such as the nitrogen inversion mode, for the coupling of the states. The two states, with the presence of the promoting mode, vibronically couple to result in a highly dipolar final CT state with a planar structure. This is likely to happen in polar solvents. And as a result of all these one can say the model is based on solvent induced pseudo-Jahn-Teller effect.

The third model, proposed by Gorse and Pesquer [8], considers the pyramidalization of the amino nitrogen as the sole relaxation mode for the formation of the charge transfer (CT) state out of the locally excited (LE) state. The CT state is formed when the amino nitrogen lone pair orbital is decoupled from the benzonitrile π-orbital by means of an amino wagging mode. As a result this model is called waging intramolecular charge transfer (WICT) model.

Rehybridization by intramolecular charge transfer (RICT) model proposed by Domcke and Sobolowski [9,10], is the fourth alternative model. This model considers the in-plane bending of the cyano group as another possible main relaxation coordinate. sp^2 rehybridization of the carbon atom of the cyano-group, causing a relaxation by bending of the cyano angle is presented as the main stabilization factor for the formation of the CT state.

In all the proposed models that try to explain the dual fluorescence phenomenon, there is an agreement that the polar-sensitive anomalous fluorescence is attributed to an electronic charge transfer (CT) state. The

differences in the models lie on the proposed LE → CT reaction mechanisms and the structure of the CT state.

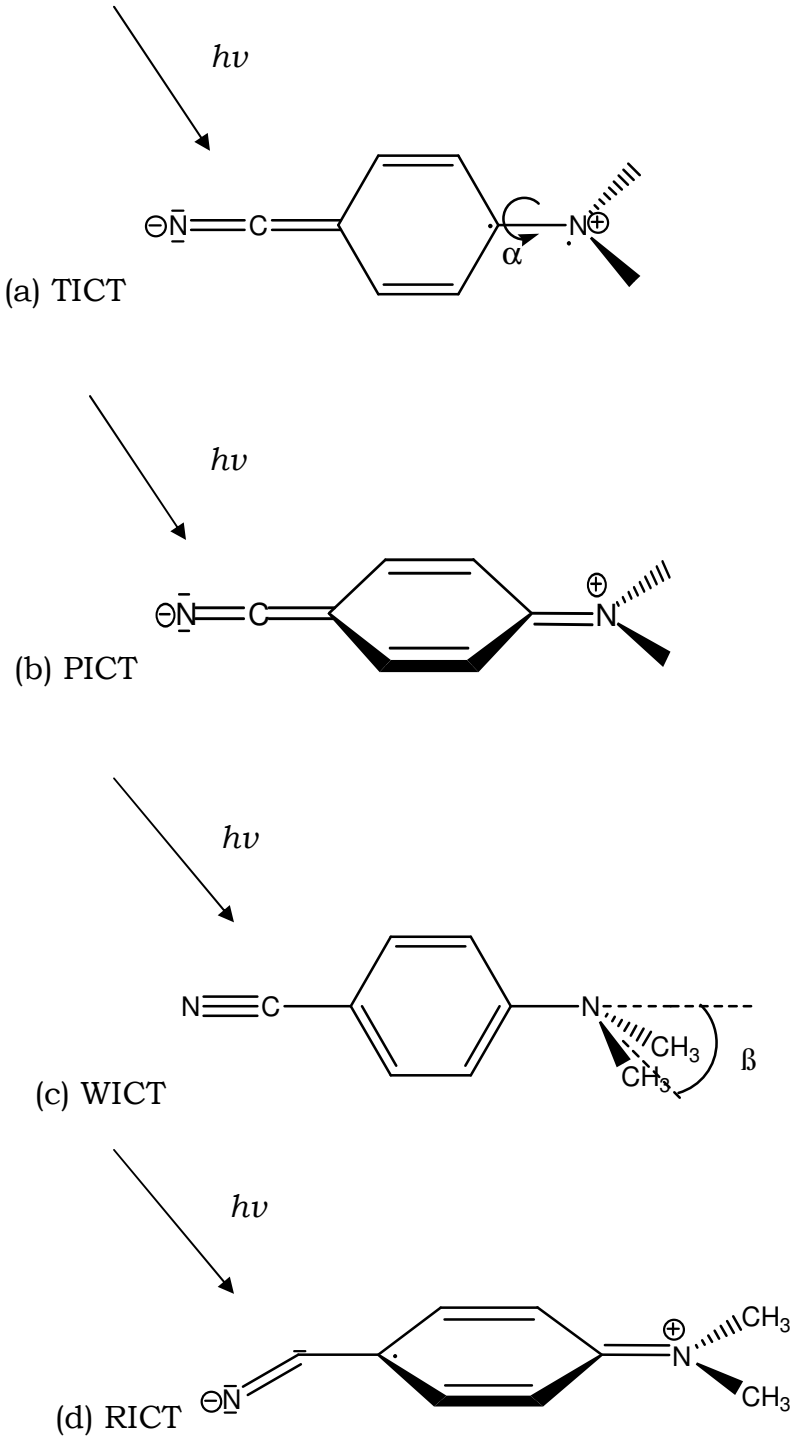


Fig. 2. Illustration of the different models

Even if the dual fluorescence phenomenon has still remained debating, several attempts, using both theoretical and experimental studies, have been made to explain it. Out of the several theoretical studies of dual fluorescence many are in favor of the TICT model. Recently, time-resolved Raman spectra [11] of charge transfer state of DMABN have been reported, also supporting the twisting ICT model. On the other hand, the RICT and WICT models are seen to be frequently rejected, while the Pseudo-Jahn-Teller (PICT) hypothesis is favored by some studies.

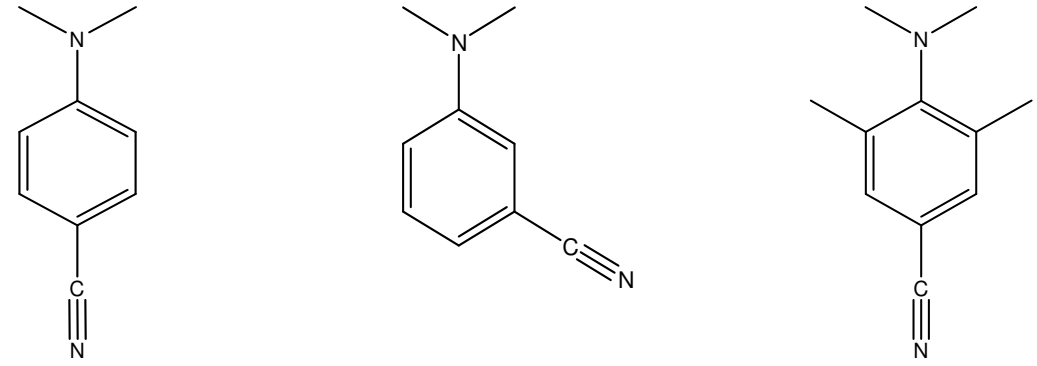
Here, in this particular work, an attempt was made to study the behavior of the ground state and the first two excited states of the compound 4DMABN, both theoretically and using an experimental method, with the main objective of showing that 4DMABN in its ground state exists in the form of two isomers that are in equilibrium. For comparison similar theoretical calculations were done for the two compounds; 3DMABN and TMABN. In all cases a focus was given to testing the TICT model.

As mentioned above, the three compounds have different fluorescence behavior in polar solvents, which is attributed to their different substitution patterns, and 3DMABN and TMABN are non-dual fluorescent with the first showing the normally expected B band only, while the other one showing the “anomalous” A band only. This indicates that in the case of 3DMABN, the CT state is absent or the LE $\rightarrow$ CT reaction is highly unfavored, i.e., the CT state is energetically much higher than the LE state. In the case of TMABN, it can be said that the absence of the B band, in the fluorescence spectra of the compound, is either because of the absence of the LE state or because of the ultra fast formation of the CT state from the LE state. Due to steric repulsion

between the methyl groups of the dimethylamino fragment and that of the benzene ring on the ortho positions, the ground state geometry of TMABN is somewhat twisted. This pretwisted ground state structure of TMABN is expected to contribute to the disfavoring of the LE state and the speedy formation of the CT state.

The experimental investigation [12] focused on trying to check for the existence of two stable ground state structures of 4DMABN, in equilibrium, that are responsible for the dual fluorescence. This was done with a closer study of the absorption spectrum and with the study of the dependence of the fluorescence spectrum on the wavelength of the exciting light.

The TICT mechanism was investigated for the three molecules. Ground state properties were investigated using the density functional theory (DFT) method. The first two singlet electronic excited states were studied using the time dependent self-consistent field (TD-SCF) [13] theory within the DFT framework. Excitation energies to these states were computed and compared with experimental data. Whenever possible calculations were done for solvated systems using the PCM-IEF solvation model.



4DMABN 3DMABN TMABN

Fig. 3. Structures of the molecules investigated

2. Experimental Detail

DMABN was purchased from Aldrich and used without further purification. Samples were prepared in 1 cm quartz cuvettes at concentrations providing optical densities of less than 1 [12].

Absorption measurements were made using a Spectronic, genesis-2 UV-VISIBLE spectrophotometer with a resolution of 1 nm [12].

Emission and excitation spectra were recorded with a Shimadzu 5301 fluorospectrophotometer. Solvent blanks were subtracted from the emission spectra prior to analysis [12].

3. Computational Details

All calculations were performed using the GAUSSIAN 03W program package [13]. For comparison purpose it was tried to follow consistency of the basis set, by using the 6-31G(d) basis set, for all types of calculations. Considering the computation cost [13] and its range of applicability for variety of systems [13], this medium sized basis set is believed to be good enough for computing the desired parameters for the systems in this work.

In the literature, a number of studies [5] showed that the DFT optimized geometries of DMABN are superior to those derived by Hartree-Fock ab initio and AM1 semiempirical methods [13]. So, the ground state optimizations were performed at the DFT level with the exchange correlation functional of Becke, and Lee, Yang, and Parr, in its hybrid form, i.e., with inclusion of non-local corrections and some portion of exact Hartree-Fock exchange (B3LYP) [13] as implemented in the

program package. Also, all other ground state properties are computed with this B3LYP 6-31G(d) DFT method.

All excited state calculations are performed with the TDDFT [13] implementation in Gaussian [13]. For both ground and excited state calculations, where solvent effect is considered, the revised version of the polarizable continuum model (PCM), more commonly indicated as PCM-IEF (PCM within a new integral equation formalism) [14] was used. The extension of PCM-IEF solvation model to analytical gradients at the DFT level has already been proved good to many different systems [5].

4. Results and Discussion

4.1. Experimental Results

The absorption and emission spectra of 4DMABN in acetonitrile are shown in Fig. 4. The absorption spectrum shows two bands at 292 and 345 nm. Gauss fit calculation of the absorption spectrum (Fig. 5) was performed and it was proved that the longer wavelength weak band is a self-standing band (not a shoulder). The emission spectrum shows two distinct bands.

It was found out that the property of the emission spectrum is strongly dependent on the wavelength of the exciting light [12]. This dependency of emission spectrum on the wavelength of the exciting light can only be

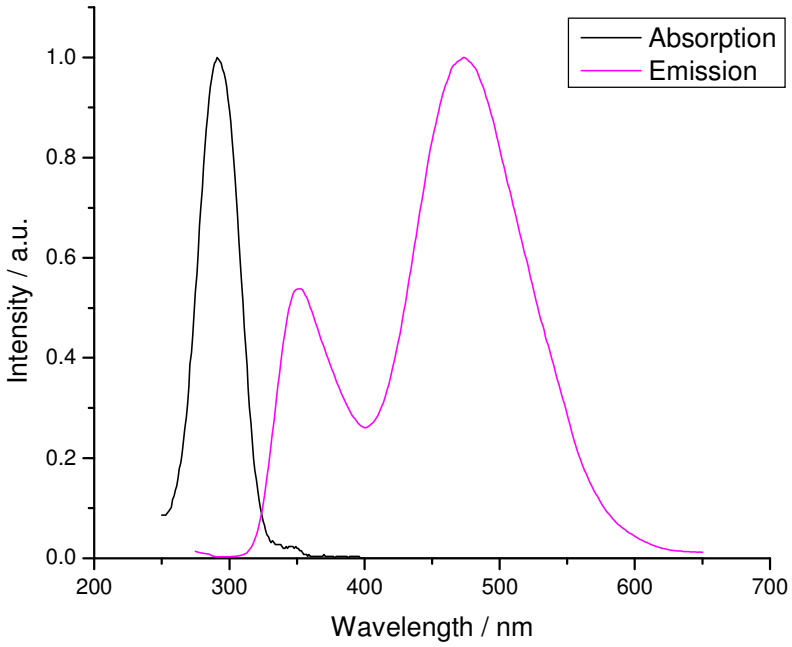


Fig. 4. Normalised Absorption and emission spectra of 4DMABN in acetonitrile Solvent [12].

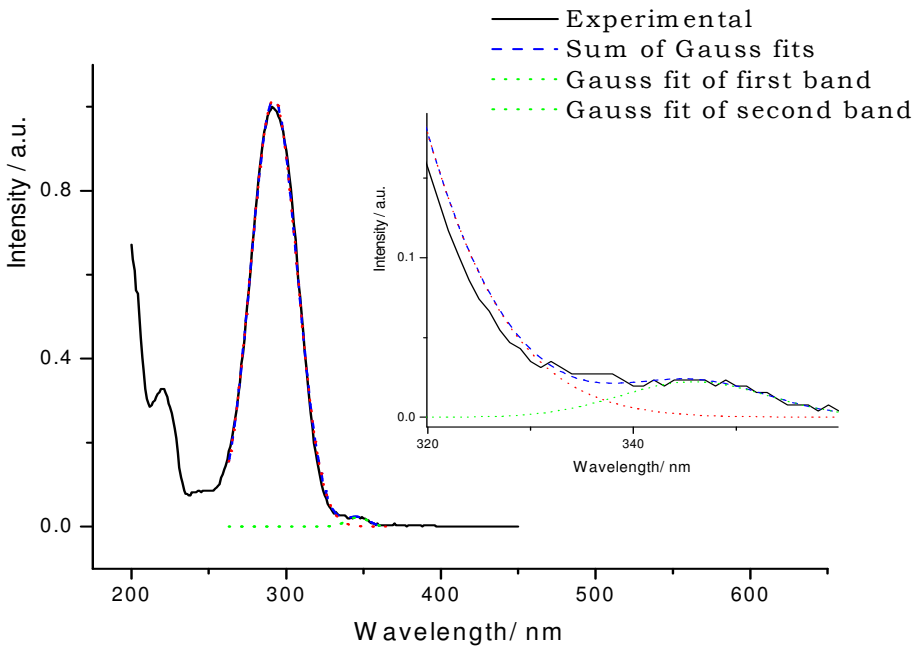


Fig 5. Gauss fit of the absorption spectrum of 4DMABN [12]. The inset shows the absorption region 320-360 nm.

explained by the presence of two relatively stable systems in equilibrium. Therefore, this fact together with the existence of two absorption bands indicate that 4DMABN has two stable conformers in the ground state, which are in equilibrium. Table 1 shows the summarized experimental results. Absorption and emission energies are calculated using spectral results (Wavelength maxima).

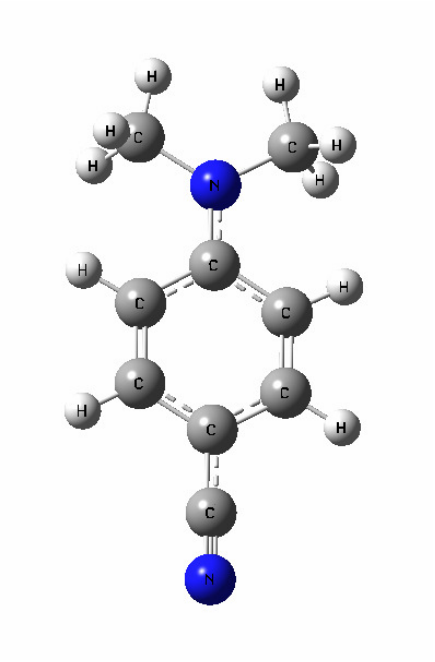
Table 1. The absorption energies (E_{abs}), emission energies (E_{em}), absorption maxima (λ_{abs}) and emission maxima of 4DMABN in acetonitrile.

	λ_{abs}(nm)	E_{abs} (eV)	λ_{em} (nm)	E_{em} (eV)
1st band	292	4.25	352	3.52
2nd band	342	3.59	472	2.63

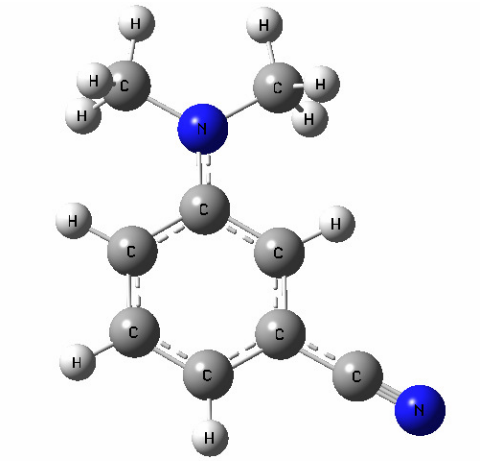
4.2. Computational Results

4.2.1. Ground State Properties

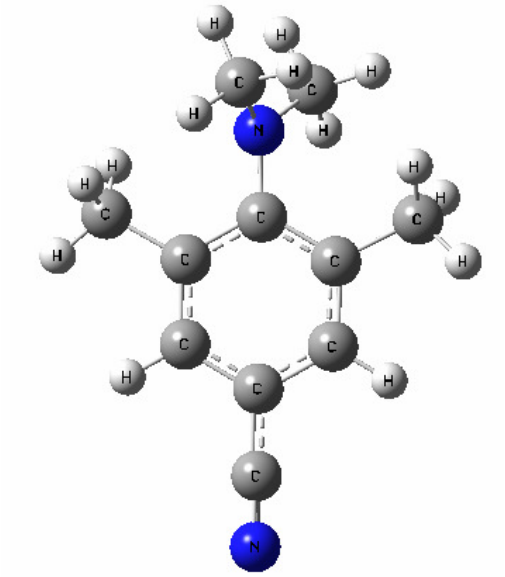
Fig. 6 presents the optimized ground state equilibrium structures of 4DMABN, 3DMABN, and TMABN. These are the results of optimization procedure using the DFT (B3LYP/6-31G(d)) method. For the first two compounds, 4DMABN and 3DMABN, the results show planar geometries. As can be seen in the figure the pyramidalization of the dimethyl amino group for the two compounds is not observable. In the structures, delocalization of the electrons of the lone pair orbital of the nitrogen atom of the dimethylamino group is observed. This indicates sp^2 hybridization, i.e., non-pyramidal structure. Table 2. shows, the calculated ground state properties both in gaseous state and in acetonitrile solution. The wagging



4DMABN



3DMABN



TMABN

Fig.-6. Ground state equilibrium structures calculated by DFT (B3LYP/6-31G(d)).

angles achieved using this computational method for 4DMABN and 3DMABN are practically negligible.In the case of TMABN, the optimized ground state structure possesses somewhat twisted equilibrium geometry. From Table 2, it can be seen that at this level of calculation the torsional angle between the fragments is about 82 degrees. There is also some degree of pyramidalization of the dimethyl amino group with a wagging angle of about 27 degrees. This deviation from planarity of TMABN is caused by the strong sterical interaction that the two methyl groups of the dimethyl amino fragment are experiencing with the two methyl groups at the ortho positions on the benzene ring. Still, the deviation from planarity of this compound is not up to forming a perpendicular conformation of the dimethylamino group with respect to the plane of the benzene ring. This deviation from perpendicular conformation of the amino groups is an indicator of that there is some minimal degree of conjugation that forces, a little bit, the structure towards planarity, i.e., conjugation is acting against steric effect.

In Table 2, the equilibrium structure dipole moments are seen to decrease from 4DMABN down to TMABN. The smaller dipole moment of 3DMABN than that of 4DMABN indicates the absence of an extended charge delocalization between the periphery donor and acceptor groups (dimethylamino and nitrile groups respectively), in the case of 3DMABN, which results from para-substitution of the nitrile group, which is so in the case of 4DMABN. Hence, it can be concluded that the meta substitution of the nitrile group for the case of 3DMABN has resulted in

decreased charge transfer character of the compound. The twisted conformation of the compound TMABN has resulted in an attenuated conjugation, and hence in its smallest dipole moment.

The rotational activation energy barrier to the perpendicular conformation of 4DMABN from its equilibrium planar structure in acetonitrile solution was calculated to be 0.43 eV (see table 2). This energy value is more or less comparable with the energy difference between the two experimental absorption maxima of 4DMABN in acetonitrile (see table 1).

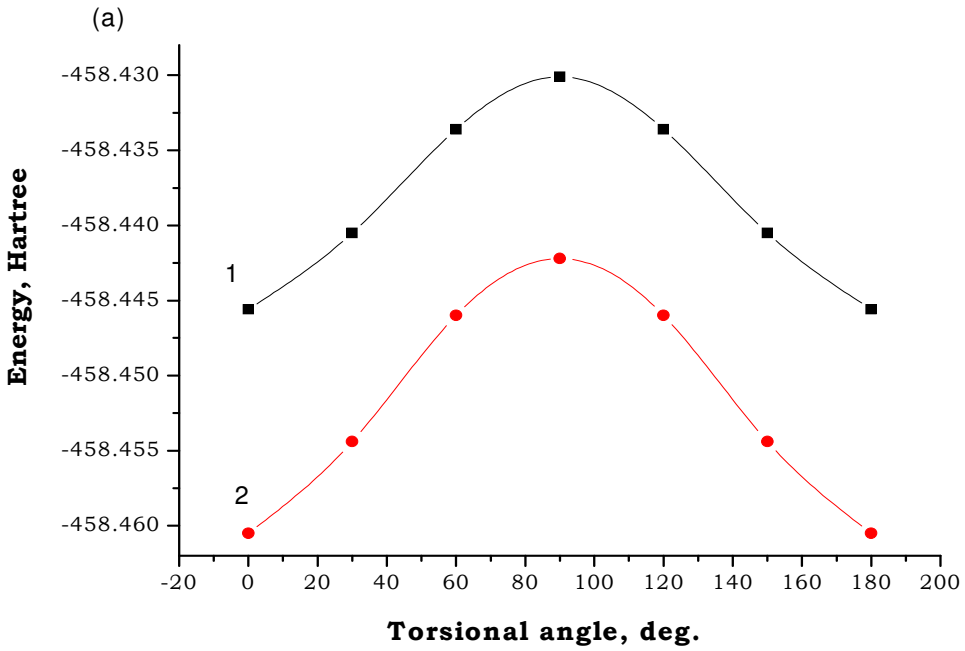
Table 2. Ground state characteristics of the molecules studied in vacuo and in acetonitrile: dipole moment μ_{eq} (D), equilibrium twist angle α_{eq} (deg.), and equilibrium pyramidalization angle β_{eq} (deg), activation barrier of rotation to the planar (ΔH (0^0)) and perpendicular (ΔH (90^0)) geometry (eV), calculated by DFT(B3LYP/6-31G(d))

Compound	μ_{eq}		α_{eq}		β_{eq}		$\Delta H(0^0)$		$\Delta H(90^0)$		$\Delta H(180^0)$	
	vac[a]	acn[b]	vac[a]	acn[b]	vac[a]	acn[b]	vac[a]	acn[b]	vac[a]	acn[b]	vac[a]	acn[b]
4DMABN	7.25	8.75	0.0	0.0	0.95	.95	0.0	0.0	0.42	0.43	0.0	0.0
3DMABN	6.21	7.85	0.0	0.0	.65	.65	0.0	0.0	0.54	.54	0.0	0.0
TMABN	5.93	-	82.23	-	27.19	-	5.4	-	-	-	4.63	-

vac[a] - vacuo, acn[b] -acetonitrile

Fig. 7 shows the ground state potential energy curves of 4DMABN, 3DMABN and TMABN in gaseous state. The reaction coordinate is the torsional angle between the plane of dimethyl amino group and that of the benzene ring. For both 3DMABN and 4DMABN there is a local maximum at a torsional angle of 90^0 (perpendicular conformation) and local minima at 0^0 and 180^0 (planar conformations).

For both compounds the two planar conformers (0^0 and 180^0) are mirror images of each other. This confirms that the equilibrium ground state geometries of both 4DMABN and 3DMABN are planar, and the perpendicular conformers are the transition structures. The planar and



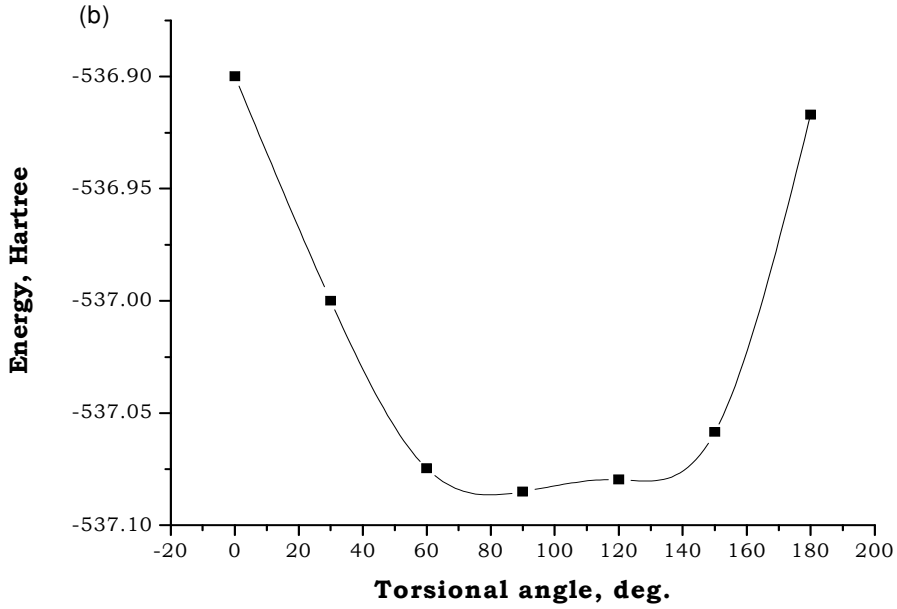


Fig. 7. The ground state potential energy surfaces of 4DMABN (a-1), 3DMABN (a-2) and TMABN (b) calculated by DFT (B3LYP/6-31G(d)) method, in vacuo.

perpendicular geometries of 4DMABN possess C_{2V} symmetry, while these geometries of 3DMABN possess C_s symmetry. Unlike the other two compounds, at 0 degree and 180 degree of torsional angles TMABN has high potential energy and the two conformers are not mirror images of each other. Both the conformers have C_s symmetry and correspond to transition structures. The local minimum of TMABN, at around 82 degree, corresponds to the twisted equilibrium ground state structure.

4.2.2. Excited State Properties

The potential energy curves of the ground and low-lying singlet excited states of 4DMABN, along the twisting coordinate; both in vacuo and acetonitrile solution are presented in Figure 8(a and b). At both the planar and twisted geometries C_{2V} symmetry was maintained. The first exited state (1B) at the non-twisted conformation is dominated by the $\mathrm{HOMO} \rightarrow \mathrm{LUMO}+1$ and $\mathrm{HOMO}-1 \rightarrow \mathrm{LUMO}$ single excitations, while the 2A state is mainly dominated by the singly excited configuration $\mathrm{HOMO} \rightarrow \mathrm{LUMO}$

In vacuo (Fig. 8(a)) the ground state and the first excited state of B symmetry potential curves are seen to increase along the twisting coordinate reaching a maximum at $\alpha = 90^0$ (the definition of α is given in Fig. 2). The twisting barrier of the electronic ground state is calculated to be 0.42 eV. The energy of the A state has its maximum value at the planar ground state optimized geometry ($\alpha = 0^0$) and has its minimum

value at the perpendicular (α = 90^0) geometry. This, therefore, resulted in the crossing of the two excited states.

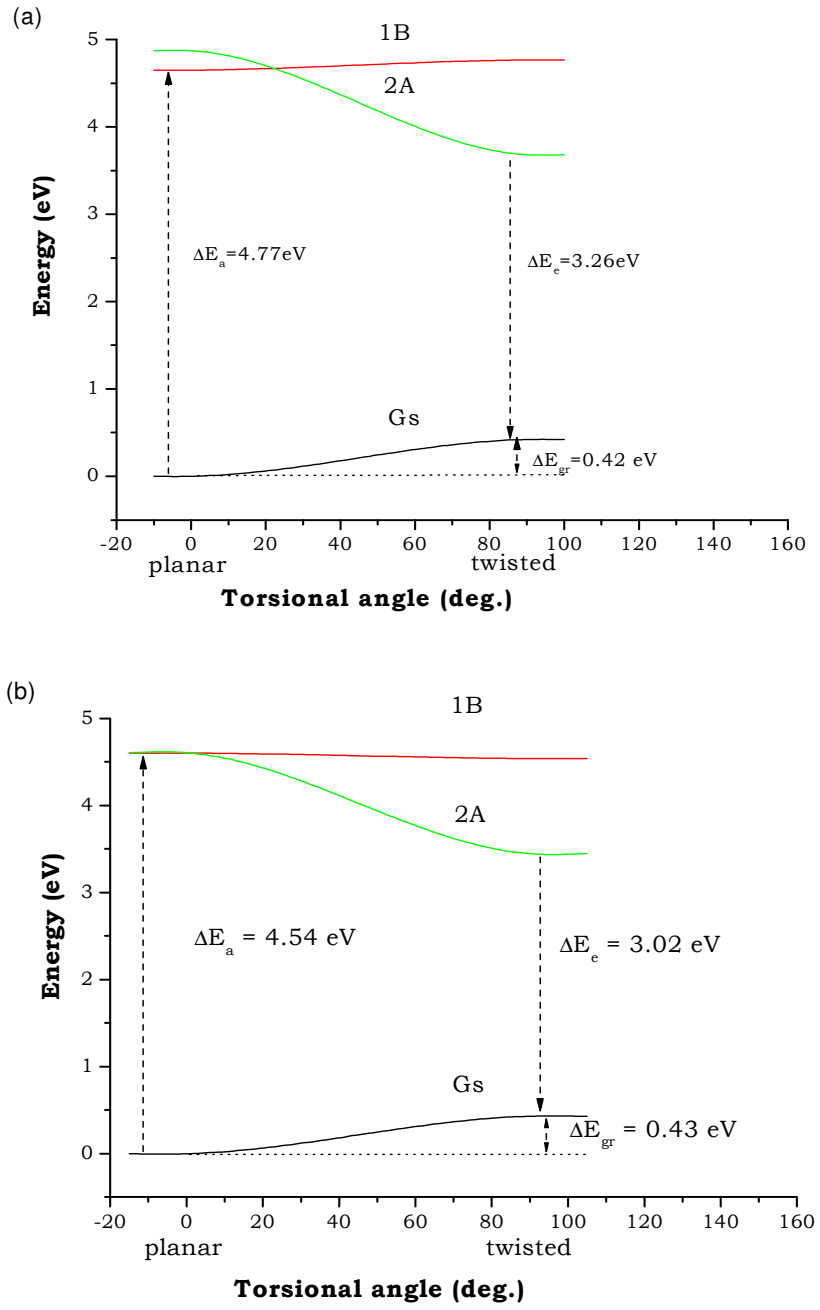


Fig. 8. The ground state and first two excited state potential energy curves of DMABN (a-in Vacuo and b- in acetonitrile). ΔE_a is

absorption energy, ΔE_e emission energy, and ΔE_{gr} is ground state rotational barrier. Energy values are taken relative to the minimum ground state energy.

As can be seen in Fig. 8(b), in the polar solvent acetonitrile, the highly polar A state is stabilized than the less polar B state for all twisting except at the planar conformation, where the two states have almost equal energy. This result is more or less similar to the result achieved by Mennuci et. al. [15] using the configuration interaction with single excitation(CIS) method [13] and the same solvent (acetonitrile).

It is also observed in this figure that the A state at the twisted geometry in acetonitrile is more stable (ΔE_e = 3.02 eV) than it is in Vacuou (ΔE_e = 3.26). This, thermodynamically, means that the increased stabilization, in acetonitrile, of the TICT state is the driving force for more and more molecules in the LE-state to jump the rotational barrier and result in the increased population of the TICT state.

The calculated absorption energy (ΔE_a = 4.54 eV) and emission energy (ΔE_e = 3.02 eV) are comparable with the experimental results of absorption (E (λ_{292}) = 4.25 eV) and emission (E(λ_{352}) = 3.52 eV), which are listed in Table 1.

The potential energy of the ground and low- lying singlet excited states of 3DMBN with respect to the twisting motion in vacuo is shown in Fig. 9. Unlike in the case of 4DMABN, there is no crossing between the curves of the two excited states (S_1 and S_2). Here, since the molecule is with C_s symmetry, the symmetry notations (A and B) for the C_{2v} symmetry, as in the case of 4DMABN, are not used.

The energy of the first excited state remains almost constant up on twisting to the perpendicular conformation. But the second excited state is stabilized along the twisting coordinate. The higher excitation energy to the S_2 state (ΔE = 3.86 eV) at the perpendicular conformation of 3DMABN, relative to 4DMABN (ΔE = 3.2 eV), is an indication for the less probable appearance of the CT (S_2) emission.

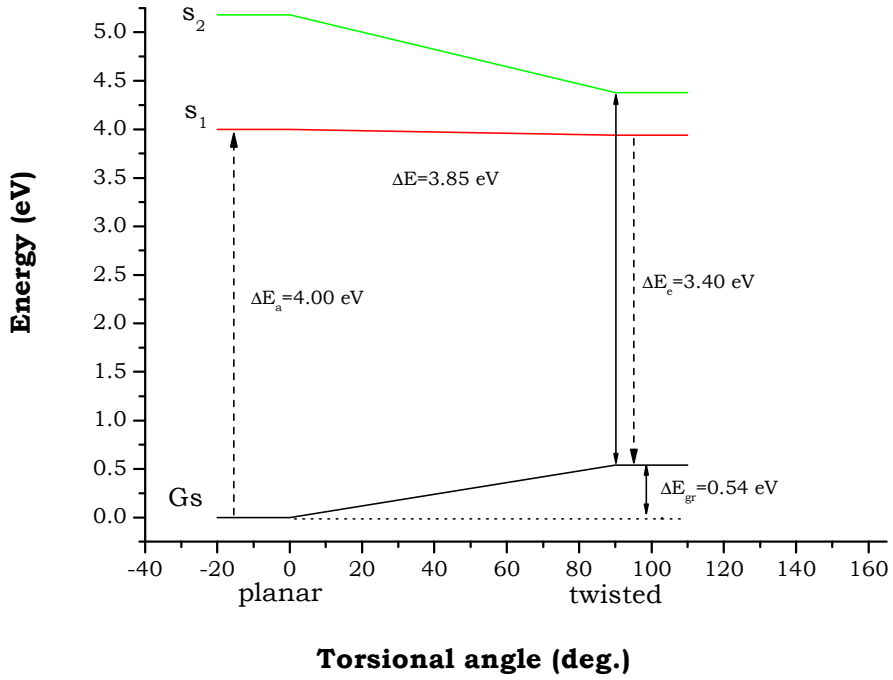


Fig.-9. The potential energy curves of the ground and first two excited states of 3DMABN in vacuo. ΔE_a is absorption energy, ΔE_e emission energy, and ΔE_{gr} is ground state rotational barrier. Energy values are taken relative to the minimum ground state energy.

Fig. 10 shows the energy profile for TMABN in the gaseous state at three different angles. TMABN has a pretwisted ground state equilibrium structure at around 82 degree. In contrast to the first two compounds,

the energies of both the two lowest singlet exited states of TMABN decrease along the twisting coordinate up to the optimized ground state structure ($\alpha = 82.2^0$). However, since at this twisted conformation the S_2 state is higher in energy than the S_1 state, significantly ($\Delta E = 0.88$ eV), there will probably be one emission only out of the S_1 state, which is in agreement with experimental results.

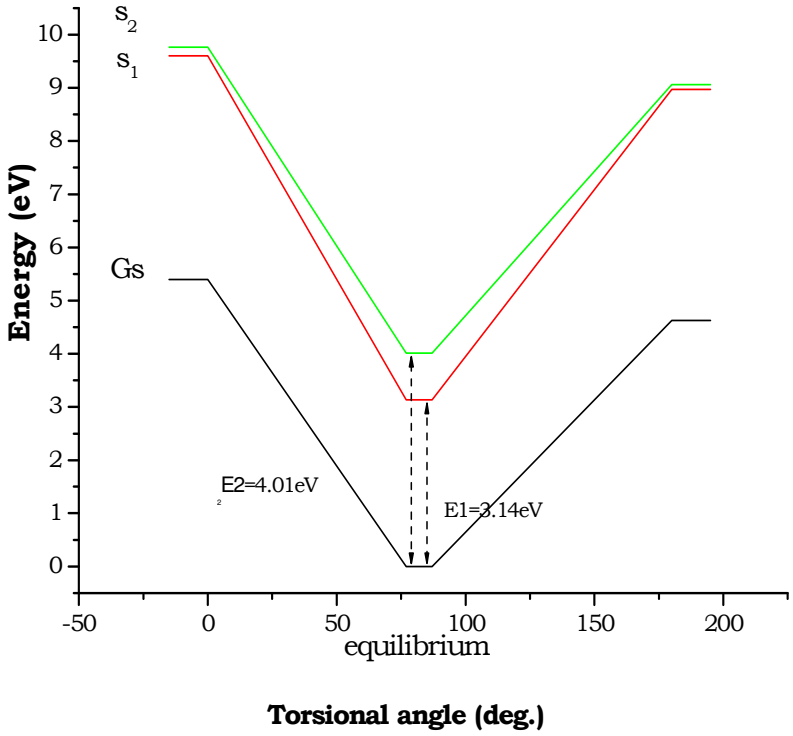


Fig. 10. The ground and the first two excited state potential energy curves of TMABN in vacuo. Energy values are taken relative to the minimum ground state energy

Obviously, this twisted, emitting, singlet electronic state is not the LE state that is known to have a planar structure. Therefore, it can be said that this emitting state is a charge transfer state and the existence of the LE state is very unlikely.

5. Conclusion

A closer examination of the absorption spectrum of 4DMABN showed that the compound is characterized by two independent absorption bands. Also examination of its fluorescence spectrum showed that the spectrum consists two emission bands and the intensities of the bands are proportional to the wavelength of the exciting light. These altogether suggest that the compound, in its ground state, exists in the form of two relatively stable conformers, which are in equilibrium.

Comparison of the calculated absorption and emission energies of 4DMABN in acetonitrile with that of experimental values indicated a reasonable agreement between them. The difference in the behavior of excited states of 4DMABN when computations are performed in vacuo and in acetonitrile solution suggests that solvent effects have to be considered for reliable computational results.

The computational results of the excited state properties (in vacuo) of the three compounds; 4DMABN, 3DMABN and TMABN are very different. The higher excitation energy to the S_2 state at the perpendicular conformation of 3DMABN is an indication for that the CT states is highly unfavored. This agrees with the absence of a CT band in experiment. On the other hand, existence of only one emitting excited electronic state of TMABN at a considerably twisted conformation, for the theoretical result, in vacuo is in agreement with the experimentally found single CT band.

The absence of dual fluorescence, when substitution pattern of 4DMABN is altered, indicates that one of the ground state conformers of the compound is favored depending on the substitution from. From this one can suggest that by finding a particular system, with a special

substitution pattern, in which the stability of the two conformers is comparable, it is possible to find better results to show the co-existence of the conformers.

6. Acknowledgement

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