

Charge Transfer Transition: Investigation of the Effect of Solvents on Electronic Spectra of *N*-Alkyl/*N*-Alkylphenyl Derivatives of *p*-Nitroaniline

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Abstract: The UV absorption spectra of *N*-alkyl and *N*-alkylphenyl derivatives of *p*-nitroaniline were recorded in acetone, acetonitrile, DMSO, toluene, chloroform and dichloromethane. The absorption maxima were calculated (TD-DFT) in the same solvents, using Gaussian 09 software package for windows at B3LYP/6-31G (d, p) level. Both calculated and experimental values of λ_{max} increases with increase in solvent polarity indicating that the absorption involves a charge transfer transition. The interactions of a single molecule of polar and non-polar solvents with the substrate were studied by calculations. The results show that polar solvent (acetone) interacts more strongly than non-polar solvent (toluene) due to H bonding and causes a greater reduction in HOMO-LUMO gap and an increase in λ_{max} .

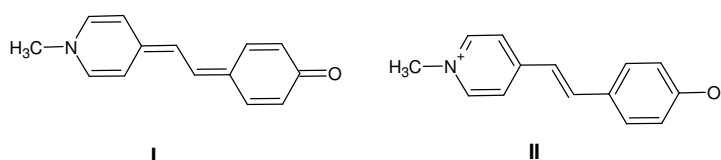
Keywords: Charge transfer transition, Solvatochromism, UV spectroscopy, Single solvent effect, TD-DFT calculation

Introduction

Charge transfer (CT) transitions are important in photosynthesis for the conversion of solar energy into chemical energy¹. CT transitions find applications in different fields as organic semiconductors², photo catalyst³, electronics and solar cells⁴. A typical CT transition occurs between occupied orbital on one part of the molecule and unoccupied orbital at another part of the molecule. If the absorption process is a CT transition process it is characterized by solvent effects *i.e.* the wavelength of absorption (λ_{max}) depends on the solvent polarity⁵. For example the λ_{max} in the UV absorption spectrum of 1-methyl-4-[(oxocyclohexadienylidene) ethylidene]-1, 4 dihydropyridine varies with the polarity of the solvent. In certain molecules the absorption process is not a CT transition but the fluorescence emission is CT.

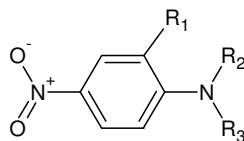
Organic chromophore *p*-nitroaniline belongs to push-pull compounds with an electron donor amino group (NH₂) and electron acceptor nitro group (NO₂)⁶. It has been a subject

of considerable experimental studies because of its non-linear optical properties⁷⁻¹⁴. Also it is a convenient model for theoretical studies of solvent-solute interactions and the solvation of electronic states in different environments¹⁵. The excitation of electron from donor to acceptor group of *p*-nitroaniline is a CT process and is sensitive to solvent environments. An example for a push-pull compound showing solvatochromism is 1-methyl-4-[(oxocyclohexadienylidene) thylidene]-1,4-dihydropyridine. This compound exists in two different resonance forms depending on the solvent. In polar solvents such as water and acetone it exists in zwitter ion form (II), while the neutral form (I) is dominant when dissolved in less polar solvents like chloroform or toluene (Scheme 1). This shows a change in solvent polarity can quickly lead to change in both structure and color. This will in turn cause a change in the relative energy levels of the ground and excited states, allowing for different colorimetric observations¹⁶.



Scheme 1. Resonance form

The extent of solvatochromic effect depends on the structures and acidities of solvents. The UV absorption maxima of *N,N*-diethyl-4-nitroaniline and 4-nitroanisole in aprotic solvents are linearly correlated. In protic solvents, the solvent act as proton donor and nitro oxygen act proton acceptors. This decreases the electron densities on nitro oxygen and bathochromic shift observed. This measures the influence of type-A hydrogen bonding by the protic solvents to the nitro oxygen of *N,N*-diethyl-4-nitroaniline compared with 4-nitroanisole¹⁷. The pH of solvent medium also affects the absorption maxima values due to CT transitions. For example the solvatochromic effect and the effect of pH variation on the absorption maxima of halogen substituted nitro anilines have been investigated¹⁸. The UV absorption maxima of 2,4-dichloro-6-nitroaniline and 4,5-dichloro-2-nitroaniline in benzene, chloroform, ethanol, methanol and water are recorded and shows a blue shift when polarity of solvent increases from benzene to water. This is due to the stabilization of the ground state by hydrogen bonding in ethanol, methanol and water and increase in transition energy which is needed to weaken the hydrogen bonding. The effect of pH on absorption maxima were studied by recording the UV spectra in neutral, acidic and alkaline medium in same solvent. They found that, the absorption maxima shifted to shorter wavelength when pH decreases and shifted to longer wavelength with increase in pH. The effect of single solvent molecule show blue shift in water, methanol and acetonitrile. The shift caused by one molecule of solvent is half of that caused by bulk solvent. Also the shifts are larger in protic solvents due to the hydrogen bond formation to phenolate oxygen¹⁹. By considering above views, the present paper report the solvatochromic effect of some selected *N*-alkyl/*N*-alkyl phenyl derivatives of *p*-nitroaniline, by recording UV-Vis spectra in acetone, acetonitrile, toluene, dichloromethane, DMSO and chloroform.

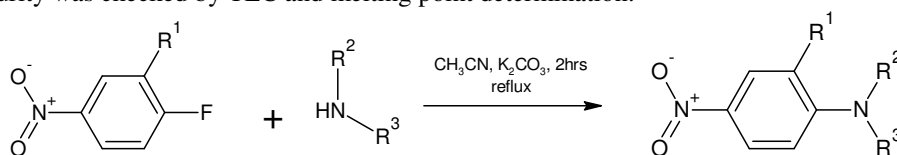


Scheme 2. General structure of *N*-alkyl/*N*-alkyl phenyl derivatives of *p*-nitroaniline

The λ_{\max} values were recorded both by calculation and spectral measurement and observed positive solvatochromism. Calculated absorption spectra obtained by TD-DFT²⁰ method in various solvents using CPCM²¹ solvation model. DFT²² calculations will be performed to understand the interaction of single polar solvent and non-polar solvent molecule with the substrate.

Experimental

Compounds (**1-6**) were prepared by refluxing 1 mL of 1-fluoro-4-nitrobenzene or 1-fluoro-2, 4-dinitrobenzene with one mole of ethanolamine or di ethanol amine or 1 mL of phenyl alkyl amine in acetonitrile for two hours (Scheme 3). The reaction mixture was poured into ice bath and the precipitated yellow colored products were collected by filtration and dried. Purity was checked by TLC and melting point determination.



- | | |
|--|---------------------------------------|
| 1: $R^1=R^2=H$ $R^3=-CH_2CH_2OH$ | 4: $R^1=R^2=H$ $R^3=-CH_2C_6H_5$ |
| 2: $R^1=H$ $R^2=-CH_2CH_2OH$ $R^3=-CH_2CH_2OH$ | 5: $R^1=R^2=H$ $R^3=-(CH_2)_2-C_6H_5$ |
| 3: $R^1=NO_2$ $R^2=H$ $R^3=-CH_2CH_2OH$ | 6: $R^1=R^2=H$ $R^3=-(CH_2)_3-C_6H_5$ |

Scheme 3. Synthesis of compounds **1-6**

UV spectra

Shimadzu UV 1800 double beam spectrophotometer was used to record the absorption spectra of the compound. The UV spectra of the compounds were recorded in acetonitrile, acetone, chloroform, toluene, dichloromethane and DMSO as solvents using 10^{-5} M solutions in the respective solvents.

DFT calculations

The structural optimizations of the compounds were done using B3LYP/6-31G(d,p) method of Gaussian 09 software package for Windows. Frequency calculations were performed on the ground state structures to make sure that there are no negative frequencies. For the calculations in solution phase, both optimization and TDDFT, CPCM model was employed which is part of Gaussian 09. The input files were prepared and the output files visualized using GaussView 05 software.

Results and Discussion

Solvent effects on UV-Visible absorption spectra

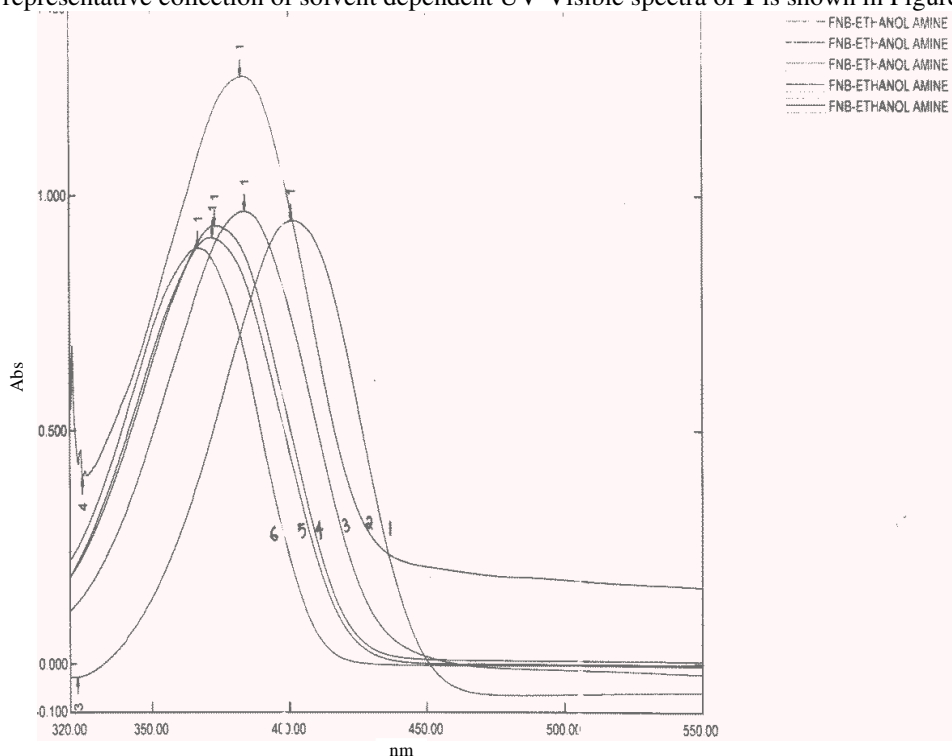
The UV-Visible spectra of **1-6** were measured in various solvents of different polarities. The UV absorption spectra were also recorded by TD-DFT calculation. The λ_{\max} values (in nm) are summarized in Table 1. All compounds show shortest wavelength for absorption maximum in non-polar solvent toluene and largest absorption maximum is observed in polar solvent DMSO. With increasing solvent polarity from toluene to DMSO, the absorption maxima of these compounds show a positive solvatochromic effect. These positive solvatochromic shifts are observed in both calculation and measurement. But in **3**, the λ_{\max} values could not follow the same order as in others due to the presence of an additional nitro group.

Table 1. The measured (Found) and calculated λ_{\max} of compounds **1-6**

	1		2		3		4		5		6	
Solvents used	Found λ_{\max} nm	Calcd. λ_{\max} nm	Found λ_{\max} nm	Calcd. λ_{\max} nm	Found λ_{\max} nm	Calcd. λ_{\max} nm	Found λ_{\max} nm	Calcd. λ_{\max} nm	Found λ_{\max} nm	Calcd. λ_{\max} nm	Found λ_{\max} nm	Calcd. λ_{\max} nm
Toluene	367	357.21	382	390.90	347	381.60	364.5	360.23	359.0	367.0	367.5	358.90
Chloroform	372	371.64	382	405.57	347	369.15	370	374.33	373.0	375.0	374.5	373.11
Dichloro-methane	373	379.66	389.5	414.07	348	393.22	A	382.25	A	381.06	A	381.17
Acetone	382	385.25	393.5	420.03	350	367.17	377.5	387.76	388.6	383.0	384.0	384.35
Acetonitrile	384	387.19	394.5	422.11	350.5	368.42	380	389.67	388.5	384.35	384.5	384.33
DMSO	401	387.82	412	422.79	362	355.87	396	390.29	400	389.21	401	389.37

A - Not measured

The λ_{\max} values of compound **2** shows a bathochromic shifts in all solvents probably due to the presence of additional hydroxyl group. As the spacing between donor (HOMO) and acceptor (LUMO) increases, excitation energy increases and thereby absorption maxima decreases. So that compound **6** shows a hypsochromic shift compared to **4** and **5**. A representative collection of solvent dependent UV-Visible spectra of **1** is shown in Figure 1.

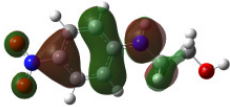
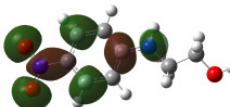
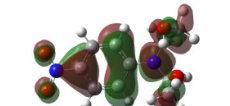
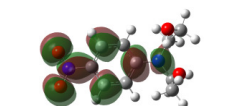
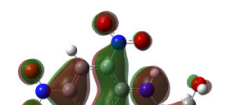
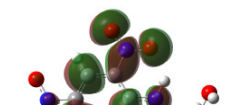
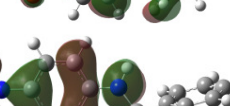
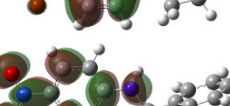
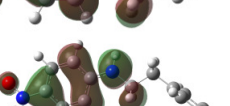
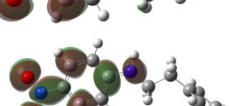
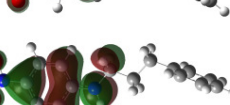
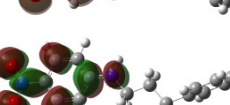
**Figure 1.** The UV-Visible spectra of compound **1** in various solvents

Theoretical calculations

Structures of **1-6** were optimized by DFT calculations at B3LYP/6-31G(d,p) level. DFT calculations were also performed in solvent medium. TD-DFT calculations were performed

to get the calculated absorption maxima values. A comparison of both calculated and measured λ_{max} values are given in Table 1. HOMO-LUMO orbitals and their gaps (HLG) are given in Table 2. Since there are two substituents on the amino group, HLG is lower for **2** compared to **1** consequently the absorption frequency is higher for **2**. In addition the HLG increases in going from compounds **4** to **6** as the number of CH_2 groups between the *N*-atom of the amine and phenyl group increases.

Table 2. HOMO-LUMO orbitals of **1-6** in vacuum

Compound	HOMO	LUMO	HOMO-LUMO gap, eV
1			4.14
2			3.89
3			3.92
4			4.10
5			4.11
6			4.09

The HOMO and LUMO orbitals of the molecule do not cover identical regions of the molecule, hence the transition may be considered as a charge transfer transition. In addition the calculated HOMO-LUMO gaps decrease in going from less polar solvent to more polar solvent (Table 3) indicating that the HOMO-LUMO gaps will depend on the interaction of solvent with the molecules.

Table 3. Calculated HLG (eV) of **1-6** in various solvents

Solvents	1	2	3	4	5	6
Toluene	3.90	3.69	3.80	3.88	3.87	3.86
Chloroform	3.80	3.59	3.73	3.78	3.78	3.76
Dichloromethane	3.75	3.54	3.70	3.72	3.72	3.71
Acetone	3.71	3.51	3.67	3.69	3.69	3.68
Acetonitrile	3.70	3.505	3.66	3.68	3.68	3.67
DMSO	3.69	3.50	3.03	3.67	3.67	3.66

Since the HLG's will depend on the interaction of solvent, the different interactions of compound **1** with a polar (acetone) and non-polar solvent (toluene) were investigated by DFT calculations (Table 4 and Table 5). Three different solvent substrate complex structures, 'a', 'b' and 'c' could be optimized by changing the relative arrangements of acetone and compound **1**. Being a ketone acetone can form a hydrogen bond either with the O-H hydrogen (a) or with the N-H hydrogen (b) atom of compound **1**. The third structure (c) is formed by the attraction of the CH₃ hydrogen of acetone and O-atom of the NO₂ group. The total energies and HLG are different for the solvent-substrate complexes. The lowest energy structure is 'a' in which acetone forms a H-bond with the O-H hydrogen atom of the substrate molecule and the hydrogen bond length is {O-H....O=C} 1.90Å°. The substrate complex attraction energy is highest for this complex and HLG is 3.98 eV which is lower than that of compound **1** (HLG – 4.14 eV). Hence, there are two possible interaction sites for compound **1** that interact with the solvent molecules that lead to a decrease in HLG (i) the N-H group and the OH groups. The preferred site for interaction of acetone is the OH group.

Table 4. Different interactions of **1** with acetone

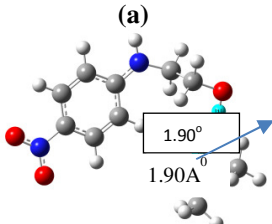
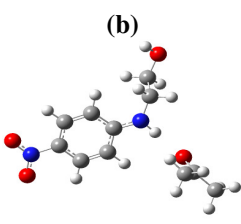
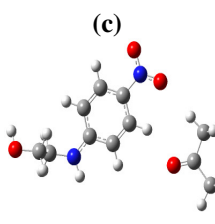
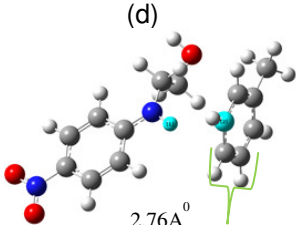
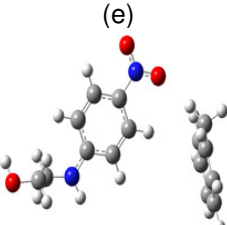
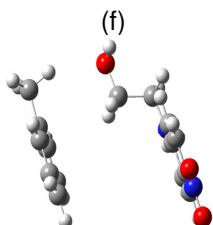
Structures			
Energy (a.u)	-839.13797	-839.13342	-839.1280
HLG (eV)	3.98	3.96	4.01
Interaction energy(eV)	0.383	0.274	0.137

Table 5. Different interactions of **1** with toluene

Structures	(d)	(e)	(f)
			
Energy (a.u)	-917.5424	-917.5390	-917.2073
HLG (eV)	4.01	4.00	4.06
Interaction energy(eV)	0.13	0.043	0.0011

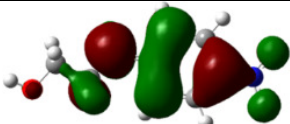
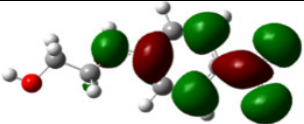
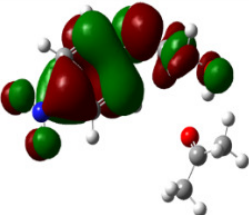
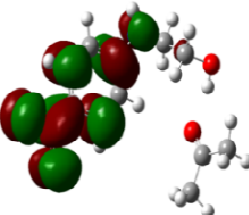
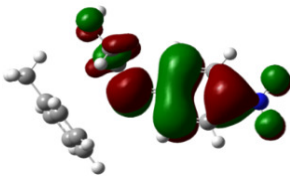
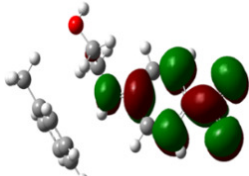
Compound **1** is not going to interact with toluene the same way as acetone. Being the least polar solvent selected for the experiment and a hydrocarbon, it is not expected to form H-bonds. Hence, the possible ways of interactions that lead to a decrease in the total energy were explored by DFT calculations. For toluene-substrate complex three possible structures, 'd', 'e' and 'f', could be identified by changing the relative arrangements of compound **1** and toluene. The interaction of toluene at the NH group yields structure 'd' (NH-C distance

is 2.76\AA^0), interaction at the NO_2 group affords 'e' and the interaction of toluene at the OH group generates 'f'. The lowest energy structure is 'd' in which the interaction is at the NH group and has an HLG of 4.01 eV , comparatively less than the HLG of **1** *in vacuum* (4.14 eV). The decrease in HLG caused by the interaction of toluene at NH group is less than that caused by the interaction of acetone at NH or OH group. The total energy of the substrate-solvent complex is higher for 'd' but this interaction causes significant decrease in the HLG.

Results show that substrate-solvent complexes are formed by interaction (attractive) of the solvent molecule with the NH and OH groups of the substrate. Thus the interactions of the two solvents with the substrate are different.

The HOMO-LUMO gap of substrate-acetone complex is 3.98 eV and for substrate-toluene complex is 4.01 eV which are lower than substrate alone (4.14 eV) indicating that acetone is more strongly attracted to the compound **1** than toluene. The comparison of the HOMO and LUMO orbitals and their energy gaps in the absence of solvent and in the substrate-solvent complex are given in Table 6. Since the interaction of acetone through H-bond is stronger than the interaction of toluene, substrate-acetone complex has lower HLG.

Table 6. HOMO and LUMO orbitals and gaps of compound **1**

Solvent	HOMO	LUMO	HLG (eV)
Vacuum			4.14
Acetone			3.98
Toluene			4.01

Conclusion

The UV-Visible spectra of derivatives of *p*-nitroaniline was recorded and calculated in toluene, chloroform, dichloromethane, acetone, acetonitrile and DMSO. Both calculated and measured λ_{max} values increases with increase in solvent polarity *i.e.* exhibits positive solvatochromism. But in **3**, the λ_{max} values could not follow the same order as in **1** and **2** due to the presence of an additional nitro group. DFT calculations show that substrate-solvent complexes are formed by interaction of the solvent molecule with the NH and OH groups of the substrate. Acetone interacts more strongly with NH and OH of substrate than toluene due to H-bonding. The stronger interaction of acetone causes a greater reduction in HOMO-LUMO gap compare to that for Toluene. The results indicate that attractive interactions of solvent molecules cause decrease in the HOMO-LUMO gaps of substrates.

Acknowledgement

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