Original Research Article

Calculation of Electronic Properties of Some 4-Nitroaniline Derivatives: Molecular Structure and Solvent Effects

ABSTRACT

The effects of substituents and solvents on the ground state molecular geometry, dipole moments (μ), polarisabilities (α) and frontier molecular orbital energies (E_{HOMO}, E_{LUMO}) and optical gap (ΔE) of 4-nitroaniline and its *N*-substituted alkyl derivatives were studied by the ab initio restricted HF-DFT self-consistent field method (B3LYP) using the 6-31G* basis set in vacuum, tetrahydrofuran and ethanol. The result revealed that 4-nitroaniline is non-planar but its μ, α and molecular size are enhanced upon successive perturbative substitution with size and number of alkyl group(s) at the amino nitrogen. The μ and α are found to increase as the solvents become more polar. Furthermore, it was found that the enhancement of these properties is associated with decrease in the optical gap of the molecules and/or increase in molecular radius. The findings imply an enhanced reactivity and ground state electro-optic susceptibility of the molecules. *N*,*N*-diethyl-4-nitroaniline exhibits the most reactivity and ground state electro-optic susceptibility.

Keywords: Electronic properties; Molecular structure; Solvent effect; Free electron molecular orbital approximation; Second order perturbation theory; Ab-initio restricted HF-DFT self-consistent field method;4-nitroaniline.

1. INTRODUCTION

Derivatives of aniline and substituted anilines are important starting materials in the manufacture of a variety of pharmaceuticals, pesticides, dyestuffs, non-linear optical (electro-optical) devices and processes, anti-oxidants [1-6] and so on. Some of them are local anaesthetics [5,6], corrosion inhibitors [3], classic-type organic chromophores possessing non-linear optical (NLO) susceptibilities in solution and solid state [7]. Nitroanilines, in particular, are useful as rocket fuels and are important materials for the production of explosive devices [8]. These molecules (nitroanilines) and similar chromophores were among the first organic compounds to be tested as NLO materials [7]. Among these molecules, the amino group due to its lone pair of electrons plays an important role in interacting with the receptor (the aromatic ring or the acceptor group attached to the aromatic ring via the π-conjugation of the ring), thereby giving nitroanilines (and anilines in general) important chemical reactivity [2,4-6,9].

Despite the depth of reports in literature [5,7,8,10, and Refs. in them] on nitroaniline and its derivatives thus far, no report of the variation of the ground state molecular dipole moments, polarisabilities and frontier molecular orbital energies (E_{HOMO} & E_{LUMO}) and their corresponding energy gaps with molecular structure and solvent polarity has been made to date to the best of our knowledge. Nevertheless, it has been established that subtle changes in the molecular structure of organic molecules lead to great variations of their physical,

electronic and optical properties as well as the chemical reactivity of such molecules [1,2,11]. Such changes may result from a large effect of the environment (substituent or solvent shell) of such molecules on their absorption spectrum, leading to the variations in their electric and molecular properties [1,2,12,13].

Herein, we present our investigation of the variation of the ground state electronic properties namely molecular dipole moments, polarisabilities, frontier molecular orbital energies and optical gaps of some 4-nitroaniline derivatives with molecular structure and solvent polarity via ab initio restricted HF-DFT calculations. This is because, DFT has proved to be extremely useful in treating molecular and electronic structure of molecules in the ground state for a good description in recent times [14-16]. This work is therefore, aimed firstly at proffering theoretical explanations to the variation of these properties with molecular structure and solvent polarity so as to augment the understanding of the structure-property relationship of such organic materials/compounds for electro-optic applications (since theory plays a major role to augment the design and guide the synthesis of these organic molecules) and secondly, at checking the workability of modern concepts and computational approaches to structure-property relationship problems. The studied molecules include: 4-nitroaniline (4-NA), *N*-methyl-4-nitroaniline (*N*M-4-NA), *N*-ethyl-4-nitroaniline (*N*E-4-NA), *N,N*-dimethyl-4-nitroaniline (DM-4-NA) and *N,N*-diethyl-4-nitroaniline (DE-4-NA).

2. METHODOLOGY

2.1 Method

The computational method used herein is as described in our earlier article [1] differing only in the molecules of study. Theoretical computations of the ground state molecular geometry parameter(s), dipole moments, polarisabilities, energies and frontier molecular orbital energies of 4-NA, *N*M-4-NA, *N*E-4-NA, DM-4-NA and DE-4-NA were performed at the ab initio restricted HF-DFT self-consistent field (B3LYP) level of theory [6,17,18] in vacuum, tetrahydrofuran (THF; ε = 7.6) and ethanol (EtOH; ε = 24.3) with the SPARTAN'14 software package [19] on a 2.0 GHz PC. The geometry and energy optimisation of these molecules in the different media leading to the determination of their convergence properties [16] and energy minima [18,20] were first performed without any symmetry constraints [17,21] using the B3LYP methods [5,6,16,17,22,23] by means of the 6-31G***** basis set [11,22-28] implemented in the SPARTAN'14 software package [19]. The geometric parameters were then allowed to relax to enable all the calculations converge to the optimised geometries of each of the molecules to correspond to an energy minimum obtained by solving the self-consistent field equation iteratively [24,29,30]. The optimised structures were then used to obtain the ground state molecular geometry parameters, dipole moments, polarisabilities, energies and frontier molecular orbital energies of the studied molecules at the same level of theory (B3LYP/6-31G*****).

2.2 Theoretical Details

2.2.1 Dipole moment (**μ**) [1,12,16,17,31-33]

This property is the most widely used in describing the polarity of a system. It is the measure of the polarity of a polar covalent bond and is defined as;

$$\mu = qR \qquad (2.1)$$

where q is the charge on the atoms involved in the covalent bond and R is the separation between the bonded atoms (molecular radius or size). Nevertheless, for molecular systems, this property is often obtained from;

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{\frac{1}{2}} \quad (2.2)$$

Equation 2.2 is however, the expression for the total static dipole moment of molecular systems and reflects only the global polarity of a molecule. For complete molecules therefore, the total molecular dipole moments may be approximated as the vector sum of the individual bond dipole moments in them. This property is used to study intermolecular interactions involving non-bonded type dipole-dipole interactions; the higher the dipole moments, the stronger the interactions. It is noteworthy that this property has been found to increase with a decrease in the optical or energy gaps of molecular systems.

2.2.2 Polarisability (α) [1,6,15,17,26,31,32]

The polarisability of a molecule is the measure of the distortion of the molecule in an electric field. For a molecule in an electric field of strength, ξ, the induced dipole moment, μ^*, of the molecule varies proportionally with the field thus;

$$\mu^* = \alpha\xi \quad (2.3)$$

where α is the molecular polarisability. When polarisable molecules encounter a varying applied electric field, their polarisabilities are obtained in a simplified form after the application of the second-order perturbation theory as;

$$\alpha = 2 \cdot \left(\frac{(qR)^2}{\Delta E}\right) \quad (2.4)$$

where Δ*E* (ΔE=E_{LUMO}-E_{HOMO}) is the optical gap of such systems. This indicates that molecular polarisability would increase with molecular size and/or a decrease in the energy gap between the frontier molecular orbitals of such systems. This property enables the determination of the strength of molecular interactions (e.g., long-range intermolecular induction, dispersion forces etc.), the cross-sections of different scattering and collision processes and the optical properties of a system. A molecule with a low optical gap is more polarisable and is associated with high chemical reactivity, low kinetic stability, high electro-optical (NLO) activity and is termed a soft molecule.

3. RESULTS AND DISCUSSION

3.1 Results

The result of the B3LYP/6-31G* calculations for the ground state molecular energies, dipole moments, polarisabilities; and wavefunction analysis of the studied molecules in vacuum, tetrahydrofuran and ethanol for the frontier molecular orbital energies and optical gaps at the same level of theory is summarised in **Table 1**. Also, in **Table 1** is the result of the computations of the molecular areas of the molecules in the mentioned media. The quantum chemical computations of some of the dihedral angles (in degrees) of the studied molecules are presented in **Table 2**. The representative B3LYP optimised geometrical structures of the studied molecules are presented in **Figs. 1–5** respectively, **Fig. 6** is the representative dipole vector of the 4-nitroanilines while **Figs. 7** and **8** are the representative plots of the frontier molecular orbitals of the molecules under study.

3.2. Discussion

3.2.1 Molecular structure

The representative optimised molecular structures of 4-nitroaniline (4-NA) and its derivatives considered in our study {*N*-methyl-4-nitroaniline (*N*M-4-NA), *N*-ethyl-4-nitroaniline (*N*E-4-NA), *N*,*N*-dimethyl-4-nitroaniline (DM-4-NA) and *N*,*N*-diethyl-4-nitroaniline (DE-4-NA)} are as presented in **Figs. 1-5** and the calculated dihedral angles summarised in **Table 2**.

Calculations of the dihedral angles on all the molecules give the same outcome and hence, only the dihedral angles of 4-NA and DE-4-NA are presented in **Table 2**. It was found from the computations that the amino group in all the studied molecules is substantially displaced out of the aromatic ring plane of the molecules while the nitro group lies in the same plane as the aromatic ring of the molecules (**Table 2**). This is in line with the assertion that nitroanilines/nitroamines are highly non-planar [7,8]. As such, the planarity of the amino group of the molecules is found to remain unaltered upon either substitution or inclusion of a solvent shell during the computations as earlier observed [1]. This may be attributed to the presence of the nitro group at the 4-position on the aromatic ring of the molecules (the direction of the dipole vector of the molecules – **Fig. 6**) with respect to the amino group which effectively withdraws the electron density around the amino group that would have imposed steric and inductive effects to lead to our earlier observation [1] owning to its high electronegativity. The molecular radius (size) of the molecules is found to increase as a result of substitution at the amino group of the molecules as can be seen by their molecular areas presented in **Table 1**.

Table 1. Results of B3LYP/6-31G* calculations on the optimised geometrical structures of 4-NA, NM-4-NA, NE-4-NA, DM-4-NA and DE-4-NA in vac, THF and EtOH

Molecule/media	Energy/a.u	E_{HOMO}/eV	E_{LUMO}/eV	ΔE/eV	μ/D	α/Å^3	*a*/Å^2
4-NA/vac	-492.091722	-6.96	-2.17	4.79	5.26	50.86	154.49
NM-4-NA/vac	-531.398203	-6.66	-2.17	4.49	5.28	52.56	175.80
NE-4-NA/vac	-570.714979	-6.66	-2.14	4.52	5.41	54.06	196.42
DM-4-NA/vac	-570.701713	-6.46	-2.15	4.31	5.39	54.07	191.62
DE-4-NA/vac	-649.120934	-6.49	-2.12	4.37	5.61	56.61	220.67
4-NA/THF	-492.106044	-6.51	-2.12	4.39	6.37	50.96	154.49
NM-4-NA/THF	-531.411659	-6.29	-2.15	4.14	6.24	52.65	175.80
NE-4-NA/THF	-570.728779	-6.32	-2.14	4.18	6.32	54.14	196.42
DM-4-NA/THF	-570.715018	-6.18	-2.17	4.01	6.23	54.14	191.62
DE-4-NA/THF	-649.135678	-6.16	-2.17	3.99	6.50	56.70	220.67
4-NA/EtOH	-492.106879	-6.58	-2.36	4.22	6.78	51.00	154.49
NM-4-NA/EtOH	-531.412562	-6.34	-2.38	3.96	6.67	52.69	175.80
NE-4-NA/EtOH	-570.729803	-6.36	-2.37	3.99	6.77	54.18	196.42
DM-4-NA/EtOH	-570.715753	-6.21	-2.39	3.82	6.68	54.18	191.62
DE-4-NA/EtOH	-649.136722	-6.17	-2.40	3.77	6.96	56.75	220.67

4-NA = 4-nitroaniline; NM-4-NA = *N*-methyl-4-nitroaniline; NE-4-NA = *N*-ethyl-4-nitroaniline; DM-4-NA = *N,N*-dimethyl-4-nitroaniline and DE-4-NA = *N,N*-diethyl-4-nitroaniline. 'vac' stands for vacuum, 'EtOH' for ethanol and 'THF' for tetrahydrofuran.

Table 2. The dihedral angles/(º) of 4-NA, and DE-4-NA in vacuum, ethanol and tetrahydrofuran

Dihedral Angles	Vacuum	Ethanol	Tetrahydrofuran
4-NA/(H7,N1,C1,C2)	-150.00	-150.00	-150.00
4-NA/(H1,N1,C1,C6)	-90.00	-90.00	-90.00
4-NA/(H7,N1,C1,C6)	30.00	30.00	30.00
4-NA/(H1,N1,C1,C6)	90.00	90.00	90.00
4-NA/(C3,C4,N2,O2)	180.00	180.00	180.00
4-NA/(C5,C4,N2,O1)	180.00	180.00	180.00

4-NA/(C3,C4,N2,O1)	0.00	0.00	0.00
4-NA/(C5,C4,N2,O2)	0.00	0.00	0.00
DE-4-NA/(C7,N1,C1,C2)	-150.00	-150.00	-150.00
DE-4-NA/(C9,N1,C1,C6)	-90.00	-90.00	-90.00
DE-4-NA/(C7,N1,C1,C6)	30.00	30.00	30.00
DE-4-NA/(C9,N1,C1,C2)	90.00	90.00	90.00
DE-4-NA/(C3,C4,N2,O2)	180.00	180.00	180.00
DE-4-NA/(C5,C4,N2,O1)	180.00	180.00	180.00
DE-4-NA/(C3,C4,N2,O1)	0.00	0.00	0.00
DE-4-NA/(C5,C4,N2,O2)	0.00	0.00	0.00

4-NA = 4-nitroaniline and DE-4-NA = *N,N*-diethyl-4-nitroaniline.

3.2.2 Ground state electronic properties

The results of the ab initio SCF calculations on the molecules for ground state molecular dipole moments and polarisabilities are summarised in **Table 1**. It is found from the outcome of the calculations that these properties are increased as the optical gap of the molecules is reduced. This may be due to the increased molecular size of the molecules as perturbative substitution is increased at the amino group of the molecules. In addition, the electronic properties are found to increase as the dielectric constant of the solvents is increased from tetrahydrofuran to ethanol agreeing with Islam *et al*., [12]. The dipole moment of DM-4-NA is noted to be lower than that of NE-4-NA. This may be so because the alkyl groups in DM-4-NA are found to lie in the same plane as the aromatic ring while the *p*-orbital of the free electrons on the nitrogen (N1) is perpendicular to the plane of the ring. As a result, the interaction of the lone pair of electrons on N1 and the π-electrons of the ring is reduced. As such, the inductive effect of the nitrogen atom and electron withdrawal becomes the dominating effects thereby leading to the lowering of the dipole moment of the molecule compared to NE-4-NA which has just an alkyl group at N1. The results in **Table 1** show that DE-4-NA would be the most reactive species of the studied molecules and exhibit the highest EO susceptibility on the basis of its largest molecular size, least optical gap and largest polarisabilities followed by DM-4-NA, NE-4-NA, NM-4-NA and 4-NA in that order.

3.2.3 Molecular orbital energies and related properties

The outcome of the wavefunction analysis of 4-NA, *N*M-4-NA, *N*E-4-NA, DM-4-NA and DE-4-NA for E_{HOMO}, E_{LUMO} and E_{HOMO}–E_{LUMO} gap in vacuum, tetrahydrofuran and ethanol is summed up in **Table 1**. This shows that the HOMO and LUMO are stabilised more upon substitution of the amino hydrogen(s) for alkyl group(s), and even further by the substitution of a hydrogen atom of the alkyl group(s) for another alkyl group to minimise the effect of hyper-conjugation on the amino group and the aromatic ring. It is observed that the solvents stabilise these orbitals even further when a solvent shell is included in the computations. The consequence of this stabilisation is a decrease in the optical gap of the molecules as the size of the molecules is increased and as the polarity of the solvents is increased. As a result, the ground state reactivity and NLO susceptibility of the molecules is enhanced. The HOMO is found to be located over the amino group of the molecules while the LUMO which is of π-nature is delocalised over the nitro group and the entire C-C bonds of the ring (**Figs. 7** and **8**) with the C-C bonds serving as the π-bridge between the donor (D; amino group) and the acceptor (A; nitro group) of the D-π-A system. The HOMO represents the ability of the molecules to donate electron(s) whereas the LUMO represents the ability of the molecules to obtain electron(s) [1,5,6,18]. Consequent upon this, a HOMO→LUMO interaction would imply electron transfer from the amino group to the nitro group via the π-bridge. This is to say that low optical gap would induce efficient charge transfer

[1,6,11,12,17,18,33,34] implying that DE-4-NA has the highest charge transfer character and reactivity in agreement with the submission that the ethyl group has a stronger electron pushing induction effect than the methyl group [35]. This intra-molecular charge transfer from D to A of molecules has been reported to be the most important character of electro-optically active organic molecules [1,12,18].

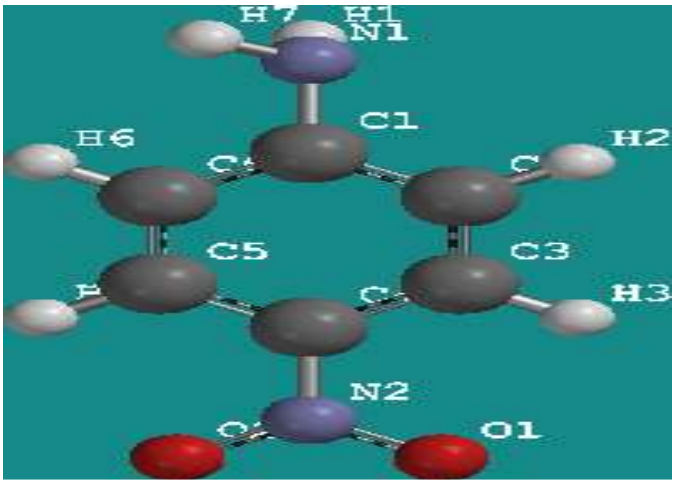

Fig. 1. B3LYP optimised structure of 4-nitroaniline

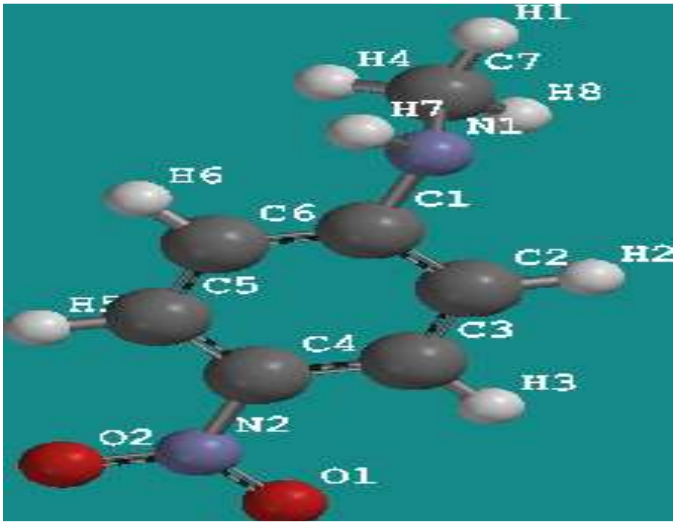

Fig. 2. B3LYP optimised structure of 4-nitro-*N*-methylaniline

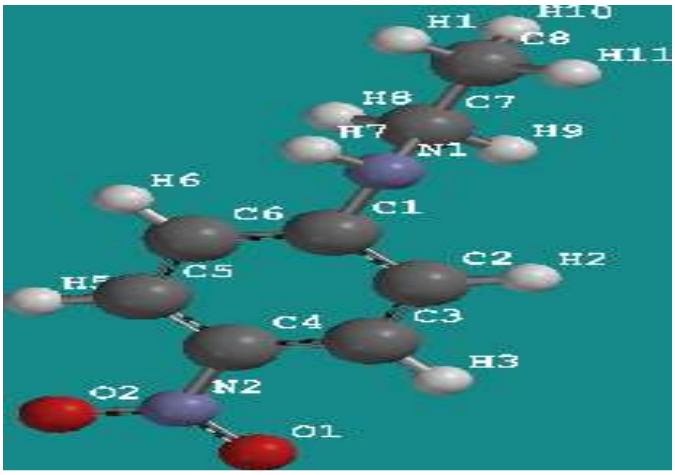

Fig. 3. B3LYP optimised structure of 4-nitro-*N*-ethylaniline

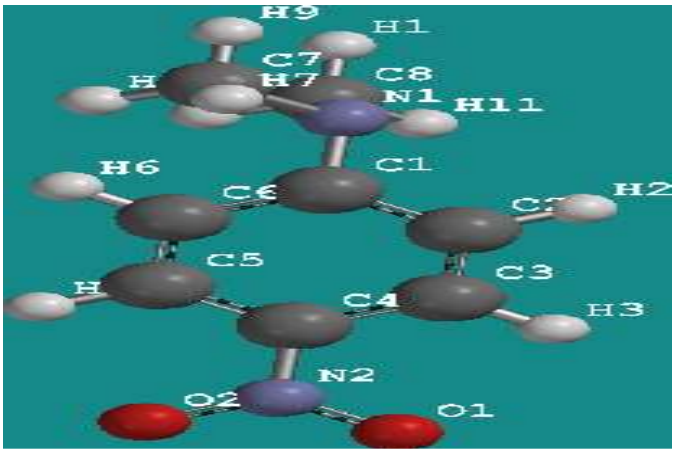

Fig. 4. B3LYP optimised structure of 4-nitro-*N*,*N*-dimethylaniline

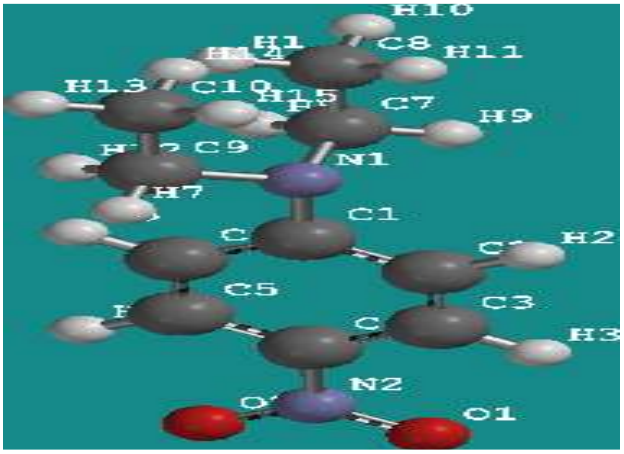

Fig. 5. B3LYP optimised structure of 4-nitro-*N*,*N*-diethylaniline

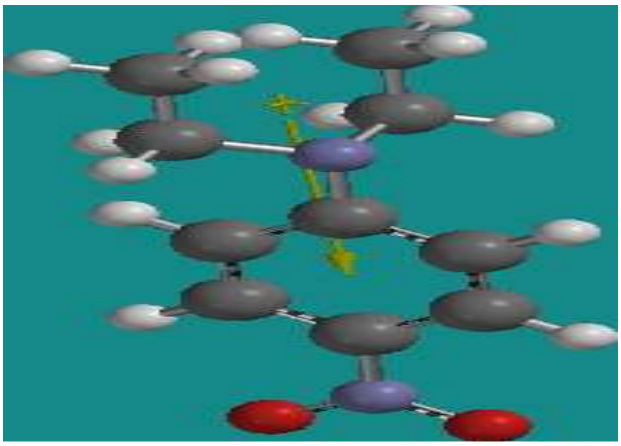

Fig. 6. Representative dipole vector of the 4-nitroanilines

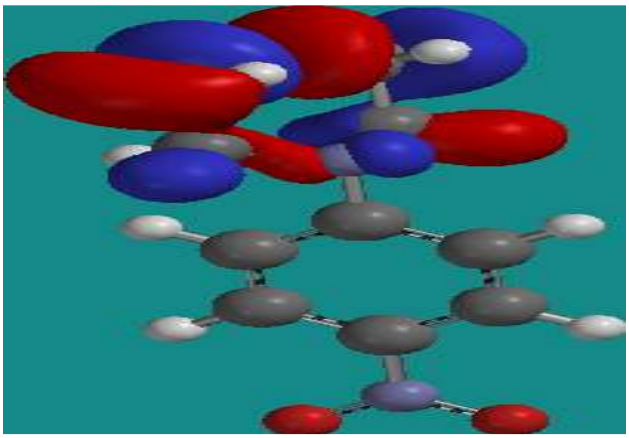

Fig. 7. Representative HOMO plot of the 4-nitroanilines

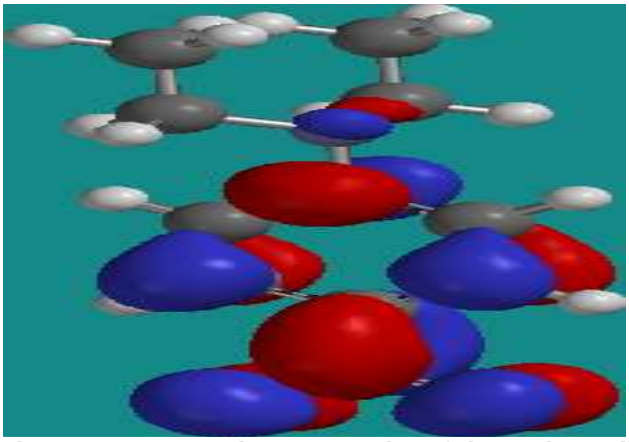

Fig. 8. Representative LUMO plot of the 4-nitroanilines

3.2.4 Substituent effects

It is observed that the ground state molecular geometry, charge transfer, dipole moments and polarisabilities of the studied molecules are enhanced over those of the parent molecule (4-NA) as a result of the insertion of successive size and number of alkyl groups (donors) on the amino nitrogen atom via substitution of the amino hydrogen atoms. DE-4-NA is found to display the most electro-optic susceptibility due to its least optical gap and largest molecular radius (**Table 1**) followed by DM-4-NA, NE-4-NA, NM-4-NA and 4-NA in that order. This finding is in consonance with the free electron molecular orbital approximation (FEMO; $\Delta E \propto \frac{1}{R^2}$; R is the molecular radius of the system and ΔE is the optical gap of same system) [1,32] and the fact that the ethyl group has a stronger electron pushing induction effect than the methyl group [35]. The electron pair forming the C─N sigma bond(s) between the alkyl carbon atoms and the amino nitrogen atom in the molecules is found to be shared unequally because of the difference in electronegativity between the two atoms forming the bond(s). The flow of electrons in the bond is observed to be in the C→N direction. This is observed to be extended to the aromatic ring [1,12,36] and to the $–NO_2$ group as it is the direction of the dipole vector of the molecules (**Fig. 6**). Consequently, the electron density from the donor (amino group) is easily transferred through the π-conjugated aromatic ring (π-bridge) to the acceptor ($–NO_2$ group) due to its strong electron withdrawing ability and the electron pushing induction effect of the alkyl group(s) [1,12,36]. This intra-molecular charge transfer is the most important feature of electro-optically active organic materials from a chemical perspective [1,12,18]. In addition, the planarity of the molecules is noted to remain unchanged upon substitution contrary to our earlier report [1]. This may be accounted for by the effective withdrawal of the electron cloud around the amino group and in the aromatic ring hence, screening the distorting tendency of the steric induction of the cloud on the group by the $–NO_2$ group thereby, maintaining the orientation of the amino group of the molecules during the perturbative substitutions.

3.2.5 Solvent effects

Quantum chemical calculations were performed on the study molecules in vacuum (control), tetrahydrofuran and ethanol to obtain the effects of the solvents on the ground state molecular structure, dipole moments and polarisabilities of the molecules. The results of these calculations are summed up in **Tables 1** and **2**. It is noted from the findings that there is a gradual increase in the calculated electronic properties as the dielectric constant of the solvents increase from tetrahydrofuran to ethanol and the molecular geometries of the molecules remained the same (as in vacuum) in all the solvents. This negates the view that the calculated electronic properties decrease and molecular geometries become altered as solvent polarity increase [1] but agrees strongly with the submission by Islam *et al*., [12] that these properties increase with increased solvent's dielectric constant. This may be attributed to the good linear relationship that exists between the properties and solvent dielectric constants as argued by Islam *et al*., [12] and the presence of the nitro group which screens the effect of the steric induction that was present in the study molecules of [1].

4. CONCLUSION

The effects of substituents and solvents on the ground state molecular geometry and electronic properties of 4-nitroaniline, *N*-methyl-4-nitroaniline, *N*-ethyl-4-nitroaniline, *N,N*-dimethyl-4-nitroaniline and *N,N*-diethyl-4-nitroaniline were studied via quantum chemical calculations on the above molecules in vacuum (control), tetrahydrofuran and ethanol to augment the understanding of the structure-property relationships of organic materials/molecules for electro-optic applications. The results of the calculations revealed that the dipole moments and polarisabilities of the studied molecules are enhanced, both on successive perturbative substitutions with alkyl group(s) at the amino group and as the dielectric constant of the solvents increased from tetrahydrofuran to ethanol. This

enhancement is observed to be associated with a decrease in the optical gap and increased molecular radius of the molecules. As a result of the decreased optical gap of the molecules, it is observed that there is a strong intra-molecular charge transfer from the amino group to the nitro group via the aromatic ring bridge of the D-π-A system. Consequent upon the above observations, DE-4-NA exhibits the most reactivity and ground state electro-optic susceptibility owning to its largest molecular size and relatively smallest optical gap.

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