

Solvent Effects on Nonlinear Optical Properties of Novel Para-nitroaniline Derivatives: A Density Functional Approach

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Abstract: *The ground state geometrical energy, dipole moment, polarizability and first static hyperpolarizability of para-nitroaniline (PNA), 2-methyl-4-nitroaniline (MNA), N-methyl-4-nitroaniline (HMNA), N-methyl-2-methyl-4-nitroaniline (HMMNA), 4-nitrodimethylaniline (NDMA) and N-(4-nitrophenyl)-N-methylaminoacetonitrile (NPAN) has been investigated by density functional theory (DFT) using B3LYP/6-311G* basis set. The calculation results revealed that hyperpolarizability and its related properties were enhanced in various degrees upon successive substitution of alkyl groups at amino group of the PNA molecule. In order to study the effects of solvents, quantum chemical calculations on the studied molecules were carried out in different dielectric constants media, in vacuum, chloroform, ethanol and DMSO. The solvent induced effects on the non-linear optical properties were studied and found to be enhanced NLO properties of the molecules as dielectric constants of the solvents increases. The frontier molecular orbital of the compounds also computed and it was found that for all of the studied molecules the enhanced NLO properties are associated with the decrease in the $E_{\text{HOMO}}-E_{\text{LUMO}}$ gap.*

Keywords: DFT, HOMO-LUMO, Hyperpolarizability, Reactivity, DMSO

1. Introduction

In recent years, a large number of research have been performed to investigate different types of nonlinear optical (NLO) materials [1-7] in order to design excellent NLO materials which show potential application in modern communication technology, data storage and optical signal processing [8-11]. In particular, organic nonlinear optical materials have shown great promise in the area of photonics due to their useful physical and optical properties. The microscopic structure-property relationship for such molecules may lead to discovery of improved NLO characteristics material, thus, facilitating the design of new molecules for potential NLO applications. This could be done through study of response electric properties, namely, polarizability, hyperpolarizability of the molecules using computational methods. Theoretical study has been played a crucial role in designing and development of novel materials for nonlinear optics. By modeling a novel compound's electronic, optical and NLO properties it is possible to eliminate the high cost associated with the synthetic exploration which are time consuming and expensive. During the past few decades, after the development of quantum procedures the science of designing nonlinear optical material has taken a different route especially due to the birth of quantum chemistry packages.

It is well known that if the molecule has many delocalization π electrons, bigger change of dipole moment from ground state to excited state, large transition moment and noncentrosymmetry structure, the molecule will have strong second order NLO response [12-18]. Para-nitro aniline (PNA) is such a material which known for its nonlinear optical properties. In PNA, the presence of a desirable resonance structure, in addition to the intermolecular charge transfer, leads to high value of polarizability (α) and hyperpolarizability (β). However, the crystalline form of PNA has a centrosymmetric structure that does not show any

macroscopic second-order NLO response. We have, therefore considered the some of the derivatives of PNA, which eliminates center of symmetry in the molecule thus leading to noncentrosymmetric crystal structure. On the other hand, a theoretical and experimental investigation [19-22] shows that the NLO response of materials can be improved by optimizing the donor/acceptor strength and/or by extending the conjugated bridge [23-26]. With this view in mind we herein wish to report NLO properties of some of the para-nitroaniline derivatives and understanding their calculated non-linear optical properties in solvents of varying dielectric constants. Our objective is to design a range of novel molecular system, which shows efficient NLO activity. Our work is to find the NLO parameters and an attempt to proper theoretical explanations to the variation of the molecular dipole moment, polarizabilities, hyperpolarizabilities of the selected compounds. In our present study the electronic dipole moment, molecular polarizability, anisotropy of polarizability, molecular first hyperpolarizability and frontier orbital energies of paranitrobenzene derivatives were investigated.

2. Computational Methods

All calculations in this work were carried out using the Gaussian 09W program package [27]. The geometries of all complexes were optimized with no symmetry constraint using Becke's 3-parameter hybrid exchange functional combined with Lee-Yang-Parr's gradient-corrected correlation functional (B3LYP) [28, 29] by means of the standard polarized basis set 6-311G*. The optimum geometry is determined by minimizing the energy with respect to all possible geometrical parameters without imposing molecular symmetry constraints. The optimized geometry were then used to obtain the second-order polarizability or first hyperpolarizability β dipole moment μ and polarizability α , energies and frontier orbital energies

(E_{HOMO} and E_{LUMO}) of the investigated molecules at the same level of theory (B3LYP/6-311G*).

In order to gain insight into the non-linear optical (NLO) property of the molecules, the first static hyperpolarizability (β) were calculated with double numerical differentiation of energies that is by the finite field perturbation method in vacuum as well as incorporating the solvent factors with increasing polarity. Hyperpolarizability is given by the coefficients in the Taylor's series expansion [27–30] of the energy in the external electric field. If the external electric field is weak and homogenous, the expansion becomes:

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma + \dots \quad (1)$$

Where E^0 is the energy of the unperturbed molecules, F_α is the field of origin, μ_α , $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first

$$\Delta\alpha = \frac{1}{\sqrt{2}} \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2 \right]^{1/2} \quad (4)$$

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (5)$$

The polarizability and hyperpolarizability are reported in atomic units (a.u.), the calculated values have been

hyperpolarizability, respectively. The mean first hyperpolarizability β is defined as

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (2)$$

Where β_x , β_y and β_z are defined as

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz} \quad (3)$$

The β_x , β_y and β_z refer the components of hyperpolarizability along x, y and z components of molecular dipole moment.

The anisotropy of polarizability ($\Delta\alpha$) and dipole moments (μ) can be calculated using the following equations:

converted in to electrostatic units (esu) (for α : 1 a.u. = 0.1482×10^{-24} esu, for β : 1 a.u. = 8.6393×10^{-33} esu).

Table 1: Calculated energies (a.u.), dipole moment (Debye), static polarizability ($\times 10^{-24}$ esu), first hyperpolarizability ($\times 10^{33}$ esu) and optical gap (a.u.) of the selected molecules in different solvent medium.

	Energy	β	α	μ (D)	E_{HOMO}	E_{LUMO}	ΔE
PNA/vacuum	-489.11	8652.41	2893.98	3.1872	-0.3274	0.0485	0.3759
MNA/vacuum	-528.14	8706.14	1465.41	3.2492	-0.3215	0.0503	0.3718
HMNA/vacuum	-528.12	10797.60	1591.77	3.3585	-0.3187	0.0499	0.3687
HMMNA/vacuum	-567.14	11600.60	1811.13	3.425	-0.3109	0.0506	0.3615
NDMA/vacuum	-658.83	10445.01	1349.91	3.294	-0.3347	0.0396	0.3743
NPAN/vacuum	-567.13	12348.31	4208.77	3.4621	-0.3121	0.0503	0.3624
PNA/Cloroform	-489.13	29147.27	4944.86	4.0893	-0.3162	0.0384	0.3545
MNA/Cloroform	-528.15	28982.34	2990.19	4.1142	-0.3129	0.0384	0.3513
HMNA/Cloroform	-528.14	34191.15	3258.53	4.2358	-0.3101	0.0381	0.3482
HMMNA/Cloroform	-567.15	33586.42	3376.73	4.1026	-0.3042	0.0404	0.3445
NDMA/cloroform	-566.45	35431.89	3032.65	4.0936	-0.3067	0.0369	0.3436
NPAN/cloroform	-567.15	36528.98	3370.28	4.2694	-0.0929	0.2408	0.3337
PNA/ethanol	-489.13	45311.52	3738.38	4.4725	-0.3127	0.0341	0.3468
MNA/ethanol	-528.16	36402.61	3900.85	4.4832	-0.3102	0.0337	0.3439
HMNA/ethanol	-528.15	51708.18	4270.42	4.6098	-0.3078	0.0338	0.3408
HMMNA/ethanol	-567.15	47782.75	4114.68	4.3344	-0.3024	0.0371	0.3391
NDMA/ethanol	-568.45	53742.34	4211.34	4.2373	-0.3110	0.0357	0.3347
NPAN/ethanol	-567.15	61992.66	4251.63	4.5754	-0.3053	0.0321	0.3374
PNA/DMSO	-489.13	47965.59	6171.83	4.5291	-0.3124	0.0334	0.3458
MNA/DMSO	-528.16	47293.87	4035.88	4.5328	-0.3099	0.033	0.3429
HMNA/DMSO	-528.15	53486.62	4421.19	4.6613	-0.3071	0.0328	0.3398
HMMNA/DMSO	-567.16	49912.29	4214.53	4.364	-0.3017	0.0366	0.3383
NDMA/DMSO	-568.13	54482.87	4.4532	4.5456	-0.3245	0.0373	0.3618
NPAN/DMSO	-567.15	56626.88	6355.92	4.6177	-0.3051	0.0315	0.3366

3. Results and Discussion

The result of the B3LYP/6-31G* calculations for the ground state molecular energies, dipole moments, static polarizabilities, first hyperpolarizabilities are presented in the Table1. The frontier molecular orbitals and optical gaps of the studied molecules in vacuum, chloroform, ethanol and DMSO at the same level of theory is also summarized in the Table 1.

3.1 Substituent Effects

It is observed that the insertion of successive size and number of alkyl groups (donors) on the amino group of the PNA molecule, enhances the molecular properties (in compared to the un-substituted PNA molecule) namely; dipole moments, polarizabilities, hyperpolarizabilities of the molecules. The result of the B3LYP/6-311G* calculations revealed that these properties of the studied molecules

increases upon successive substitution. This may be attributed to the increase in size and planarity of the molecules as the substitution is increased leading to enhance the polarizabilities. The molecular geometry of the studied molecules becomes more planar due to introduction of successive substituents and as a result of increased steric and inductive effects as well as electronic properties (smaller optical gap, intra-molecular charge transfer, dipole moments and polarizabilities). The α and β values of methyl substituted PNA derivatives i.e. MNA is greater than PNA is due to the elimination of center of symmetry in the molecule which leads to noncentro symmetric crystal structure. Thus significant increase the α and β values in molecule MNA, HMNA, HMMNA and NDMA is due to substitution of methyl group in amino nitrogen atom and to the benzene ring which leads asymmetry to a high degree in the electronic distribution. The maximum value of α and β were observed in NPAN molecule where we have introduced one extra double bond by inserting (-CN) group which will enhance the conjugation.

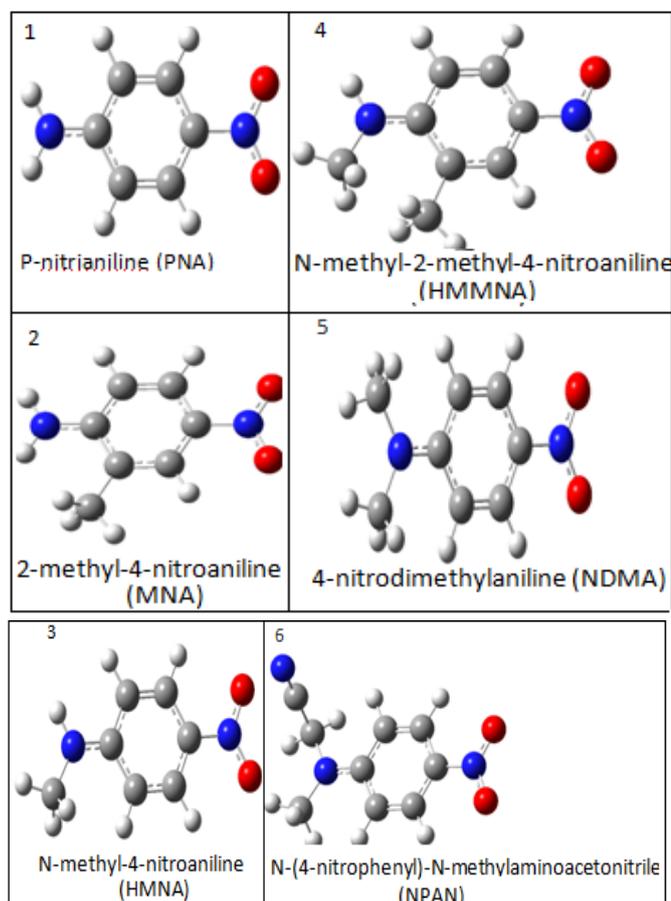


Figure 1: optimized geometrical structure of studied molecules

3.2 Dipole Moment and Frontier Molecular Orbitals

The dipole moment in a molecule is an important electronic property which results from non-uniform distribution of charges on the various atoms in the molecule. Based on predicted dipole moment values, we can say that in going from solvent phase from the gas phase, the dipole moment values increases. In order to understand the variation of dipole moment and polarizabilities in the context of frontier molecular orbitals we examined the the molecular HOMOs and molecular LUMOs generated in the output files. The highest occupied molecular orbitals (HOMOs) and the lowest -lying unoccupied molecular orbitals (LUMOs) are named as frontier molecular orbitals (FMOs). The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The energy gap between HOMO and LUMO determines the kinetic stability, chemical reactivity, optical polarizability and chemical hardness-softness of a molecule. In order to evaluate energetic behavior of the studied molecules, we carried out calculations in DMSO, ethanol, chloroform and vacuum. The Table 1 indicates that the HOMO and LUMO are stabilized more when the hydrogen atoms of the amino group of the molecules are successively replaced with methyl groups and even further by CN group. Furthermore, the solvents are also seen to stabilize these molecular orbitals. These results a decrease in HOMO-LUMO gap of the molecules as the size of the molecules and dielectric constants of the solvents increased. As a result chemical reactivity, optical polarizabilities of these molecules are enhanced. The increased size and planarity of the molecules induces a decrease in orbital gap of the molecules, which in turn leads to increased charge transfer that is responsible for the increased nonlinear optical properties. The 3D plots of HOMO-1, HOMO, LUMO and LUMO+1 orbitals computed at the B3LYP/6-311G* level in vacuum for MNA molecule are illustrated in the Fig. 2. It is clear from the figure that, while HOMO is localized on ring and the nitro group, LUMO is delocalized on the methyl and around the amino group. Consequently, a HOMO→LUMO interaction would imply the movement of electrons (or an electron) within the molecule.

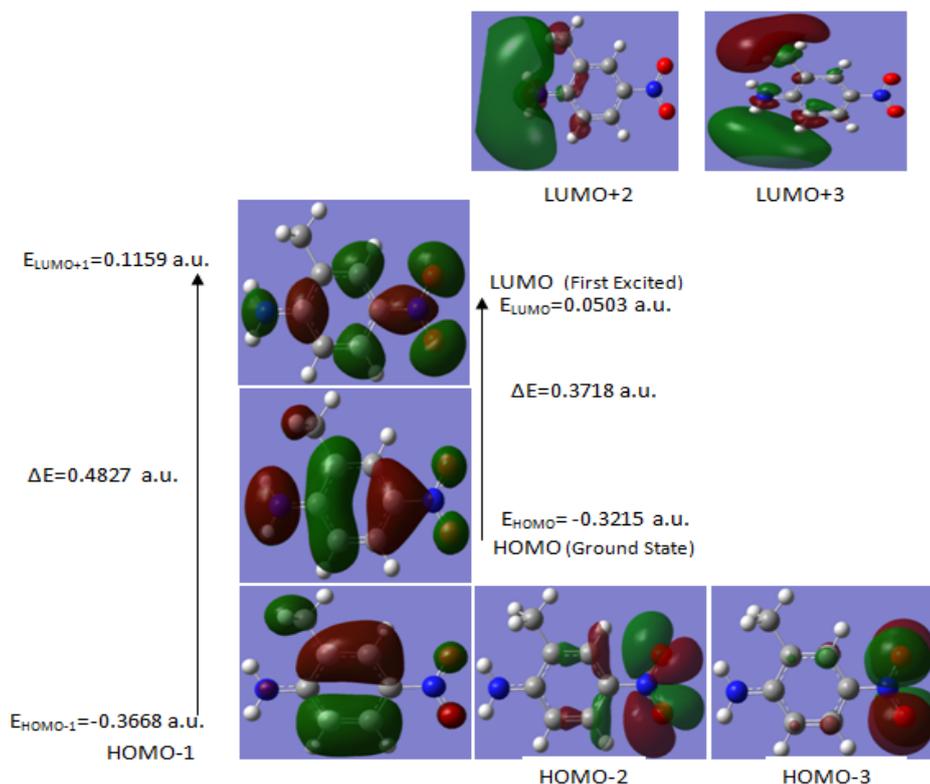


Figure 2: Frontier molecular orbital's of 4-nitrodimethylaniline (MNA)

3.3 Nonlinear Optical Properties

It is well known that the higher values of polarizability and hyperpolarizability are important for more active NLO properties. The second order polarizability or first hyperpolarizability β and static polarizability α is calculated using B3LYP/6-311G* basis set on the basis of the finite field approach. The polarizabilities and hyperpolarizabilities are reported in atomic units (a.u.), the calculated values have been converted into electrostatic units (esu). The enhanced nonlinear optical properties were found to be associated with HOMO-LUMO gap and dielectric constants of the solvents.

It was found that both polarizability and hyperpolarizability were follow inverse relationships with the orbital gaps and these properties were enhanced, upon successive substitution and as the dielectric constant of the solvent increased. For a small optical gap, the charge transfer occurs easily, which in turn, giving higher values of polarizability and hyperpolarizability. It is noted from the Table 1 that there is gradual increase in calculated polarizability and hyperpolarizabilities with an increase in the dielectric constants of the solvents which may be explained due to the different stabilization mechanisms of the frontier orbital's of different solvents [30-32]. On the overall, the results show that NPAN is found to be most reactive, as well as exhibit the highest order nonlinear optical responses on the basis of its larger dipole moment, polarizabilities and least optical gap.

4. Conclusions

The quantum chemical studies of the effects of substituent's and solvents on the linear and nonlinear optical properties of para-nitroaniline (PNA), 4-nitrodimethylaniline (MNA),

N-methyl-4-nitroaniline (HMNA), N-methyl-2-methyl-4-nitroaniline (HMMNA), 2-methyl-4-nitroaniline (NDMA) and N-(4-nitrophenyl)-N-methylaminoacetonitrile (NPAN) were investigated. It was found that the dipole moments, polarizabilities, hyperpolarizabilities were enhanced upon successive substitution with alkyl groups and further -CN group. The effects of solvent study revealed that there is a gradual increase in the calculated properties with increase in dielectric constant of the solvents. In all the studied molecules, the enhanced nonlinear optical properties were found to be associated with a decreased HOMO-LUMO gap. Of the studied molecules NPAN is found to exhibit the most reactivity and intermolecular charge transfer and higher order nonlinear optical properties. The present quantum chemical study may play an important role in understanding more properties of the molecules and further study of the dynamics of the molecules.

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