



ISSN: 2350-0328

International Journal of Advanced Research in Science,
Engineering and Technology

Vol. 6, Issue 1, January 2019

Molecular geometry and charge transfer contributions to nonlinear optical property of 2,4,5-trisubstituted-(1,3,4)-thiadiazole benzene sulfonamides

T. Abbaz*, A. Bendjeddou, D. Villemin

Senior lecturer, University of Mohamed-Cherif Messaadia, Souk Ahras, 41000, Algeria
Professor, University of Mohamed-Cherif Messaadia, Souk Ahras, 41000, Algeria
Professor, University of Caen, Caen 14050, France

ABSTRACT: A theoretical quantum chemical study was carried out on 2,4,5-trisubstituted-(1,3,4)-thiadiazole benzene sulfonamides **1-4** using the DFT/B3LYP methods with 6-31G (d,p) basis set. The optimized geometrical parameters of these compounds were calculated by the same method. Additionally, the molecular electrostatic potential was simulated to describe the reactive sites of electrophilic or nucleophilic attacks. The determined HOMO-LUMO energy gap revealed that charge transfer occurs within the molecule. Chemical reactivity has been measured by reactivity descriptors and the results illustrate that Compound **1** has the smaller frontier orbital gap so; it is the more reactive compound. Mulliken analysis of atomic charges is also calculated. Natural bond orbital (NBO) analysis is carried out to investigate the various intra and intermolecular interactions in 2,4,5-trisubstituted-(1,3,4)-thiadiazole benzene sulfonamides molecules and their corresponding second order stabilization energy $E(2)$. The calculated first hyperpolarizability of the title compounds show that β of compound **1** is 1.22 time that of the standard NLO material urea and hence is an attractive object for future studies of nonlinear optical properties.

KEYWORDS: sulfamide; density functional theory; computational chemistry; quantum chemical calculations.

I. INTRODUCTION

Among the numerous categories of antibiotics, sulfonamides are the most frequent used substance around the world, both in developed and developing countries. In the last decade, the sulfonamides have been used as precursor to develop biologically active compounds [1]. The sulfonamide derivatives are known for their numerous pharmacological activities, antibacterial, antitumor, insulin-release stimulation and antithyroid properties [2]. Many important physicochemical properties of biological and chemical systems, investigation of structural properties and theoretical modeling of drug functional material can be predicted by various computational techniques [3,4]. DFT offers a better compromise between computational cost and accuracy for medium size molecules, and hence it has been successfully applied in many previous studies [5-7].

The purpose of the present work is to describe and characterize the molecular structures parameters, NBO and NLO analysis, the total energy, molecular frontier orbital energies (HOMO and LUMO), electronegativity (χ), hardness (η), softness (S), Mulliken charges, molecular electrostatic potential surface (MEP) of the 2,4,5-trisubstituted-(1,3,4)-thiadiazole benzene sulfonamides **1-4** described in the literature [8] using density functional theory (DFT) and B3LYP method with 6-31G (d,p) basis set.

II. MATERIALS AND METHODS

The entire calculations of the title compounds were carried out with Gaussian09 software [9] program using B3LYP/6-31G (d,p) basis set to predict the molecular structures and electronic behaviors. The Calculations were carried out with Becke's three parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method.

III. RESULTS AND DISCUSSION

A. Molecular Geometry: The numbering system adopted in the molecular structures of 2,4,5-trisubstituted-(1,3,4)-thiadiazole benzene sulfonamides **1-4** is shown in Fig 1. The optimized structure parameters of title compounds were calculated by DFT/B3LYP methods with 6-31G (d,p) basis set and are listed in Tables 1-4.

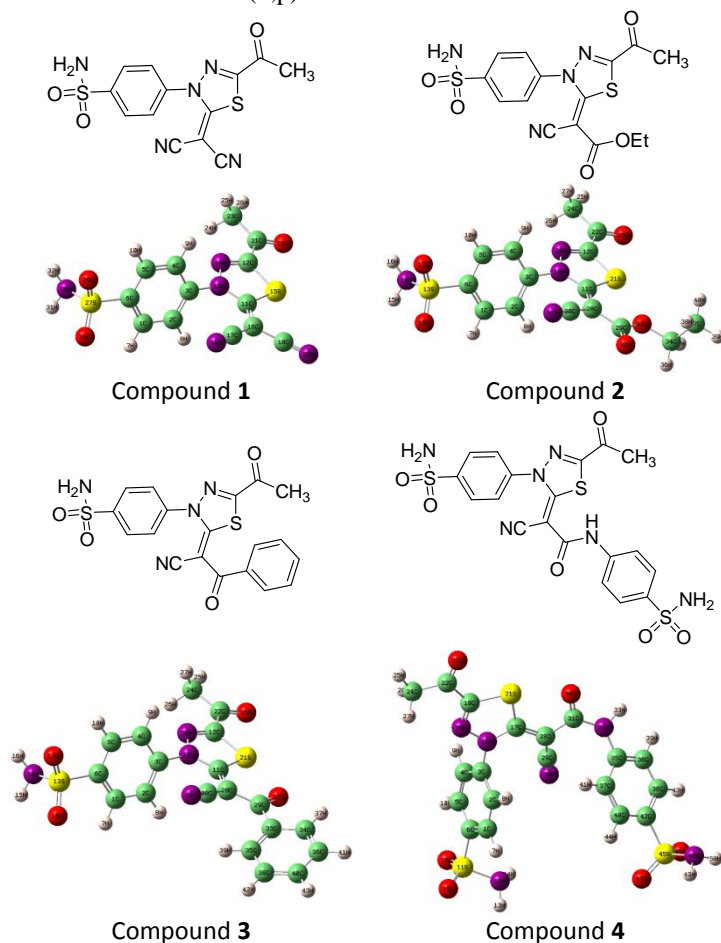

 Fig 1. Optimized molecular structure of 2,4,5-trisubstituted-(1,3,4)-thiadiazole benzene sulfonamides **1-4**

 Table 1. Optimized geometric parameters of compound **1**

| Bond Length (Å) | | Bond Angles (°) | | Dihedral Angles (°) | |
|-----------------|-------|-----------------|---------|---------------------|---------|
| R(1,2) | 1.393 | A(2,1,6) | 119.208 | D(2,1,6,27) | 178.911 |
| R(2,3) | 1.395 | A(2,1,7) | 120.758 | D(7,1,6,5) | 178.138 |
| R(2,8) | 1.084 | A(4,5,10) | 120.836 | D(2,3,4,9) | 179.594 |
| R(3,13) | 1.439 | A(1,6,27) | 119.239 | D(13,3,4,5) | 177.042 |
| R(11,13) | 1.385 | A(13,11,16) | 128.787 | D(2,3,13,14) | 115.899 |
| R(11,15) | 1.762 | A(14,12,21) | 124.593 | D(4,3,13,11) | 122.547 |
| R(11,16) | 1.387 | A(3,13,11) | 127.312 | D(3,4,5,10) | 178.698 |
| R(13,14) | 1.364 | A(3,13,14) | 116.192 | D(1,6,27,29) | 155.818 |
| R(16,17) | 1.422 | A(11,16,17) | 124.878 | D(15,11,13,3) | 172.640 |
| R(17,19) | 1.165 | A(11,16,18) | 117.785 | D(16,11,13,14) | 174.356 |
| R(21,22) | 1.218 | A(12,21,22) | 117.993 | D(13,11,16,18) | 178.475 |
| R(23,24) | 1.094 | A(24,23,25) | 106.920 | D(15,11,16,17) | 172.834 |
| R(27,28) | 1.464 | A(6,27,28) | 107.352 | D(21,12,14,13) | 178.767 |

| | | | | | |
|----------|-------|-------------|---------|----------------|---------|
| R(27,30) | 1.694 | A(6,27,30) | 102.962 | D(21,12,15,11) | 179.585 |
| R(30,31) | 1.017 | A(27,30,31) | 109.454 | D(22,21,23,24) | 122.859 |

Table 2. Optimized geometric parameters of compound 2

| Bond Length (Å) | | Bond Angles (°) | | Dihedral Angles (°) | |
|-----------------|-------|-----------------|---------|---------------------|---------|
| R(5,6) | 1.395 | A(1,6,5) | 121.558 | D(2,1,6,13) | 178.921 |
| R(5,10) | 1.084 | A(20,12,22) | 123.936 | D(2,3,4,9) | 179.614 |
| R(6,13) | 1.797 | A(6,13,14) | 103.093 | D(19,3,4,5) | 176.412 |
| R(12,20) | 1.292 | A(6,13,17) | 107.477 | D(2,3,19,20) | 116.988 |
| R(12,21) | 1.761 | A(17,13,18) | 122.919 | D(3,4,5,10) | 178.549 |
| R(13,14) | 1.696 | A(13,14,15) | 109.209 | D(1,6,13,17) | 155.820 |
| R(13,17) | 1.465 | A(11,19,20) | 116.926 | D(21,11,19,3) | 167.645 |
| R(14,15) | 1.017 | A(11,21,12) | 88.254 | D(21,11,28,30) | 167.959 |
| R(19,20) | 1.363 | A(23,22,24) | 123.940 | D(22,12,21,11) | 179.473 |
| R(22,23) | 1.219 | A(22,24,25) | 108.900 | D(6,13,14,15) | 118.403 |
| R(22,24) | 1.509 | A(11,28,29) | 124.023 | D(18,13,14,16) | 127.040 |
| R(28,29) | 1.478 | A(29,28,30) | 113.867 | D(23,22,24,26) | 123.718 |
| R(29,32) | 1.214 | A(32,29,33) | 123.722 | D(11,28,29,32) | 179.007 |
| R(29,33) | 1.358 | A(29,33,34) | 116.605 | D(28,29,33,34) | 179.213 |
| R(30,31) | 1.165 | A(33,34,36) | 108.184 | D(29,33,34,35) | 155.825 |

Table 3. Optimized geometric parameters of compound 3

| Bond Length (Å) | | Bond Angles (°) | | Dihedral Angles (°) | |
|-----------------|-------|-----------------|---------|---------------------|---------|
| R(11,19) | 1.381 | A(6,1,7) | 119.981 | D(2,1,6,13) | 179.075 |
| R(11,21) | 1.762 | A(2,3,19) | 119.766 | D(7,1,6,5) | 178.385 |
| R(11,28) | 1.397 | A(4,3,19) | 118.732 | D(8,2,3,4) | 179.966 |
| R(13,14) | 1.695 | A(19,11,21) | 108.981 | D(19,3,4,5) | 176.696 |
| R(13,18) | 1.465 | A(21,11,28) | 123.477 | D(2,3,19,20) | 116.133 |
| R(14,15) | 1.017 | A(6,13,18) | 107.455 | D(3,4,5,10) | 178.506 |
| R(19,20) | 1.367 | A(13,14,15) | 109.303 | D(1,6,13,17) | 156.280 |
| R(22,23) | 1.219 | A(12,20,19) | 110.333 | D(5,6,13,14) | 89.357 |
| R(22,24) | 1.510 | A(12,22,23) | 118.504 | D(28,11,19,20) | 174.079 |
| R(28,29) | 1.472 | A(22,24,25) | 108.899 | D(21,11,28,30) | 164.656 |
| R(29,32) | 1.240 | A(11,28,29) | 116.953 | D(22,12,21,11) | 179.877 |
| R(29,33) | 1.495 | A(28,29,32) | 118.655 | D(6,13,14,15) | 118.385 |
| R(30,31) | 1.166 | A(32,29,33) | 118.981 | D(23,22,24,26) | 123.475 |
| R(33,35) | 1.403 | A(29,33,34) | 116.853 | D(29,33,35,38) | 177.085 |
| R(35,39) | 1.083 | A(33,35,39) | 120.679 | D(41,36,40,38) | 179.436 |

Table 4. Optimized geometric parameters of compound 4

| Bond Length (Å) | | Bond Angles (°) | | Dihedral Angles (°) | |
|-----------------|-------|-----------------|---------|---------------------|---------|
| R(1,6) | 1.396 | A(2,1,6) | 119.080 | D(7,1,2,3) | 179.430 |
| R(3,19) | 1.441 | A(2,3,19) | 119.066 | D(1,2,3,19) | 179.471 |
| R(6,11) | 1.798 | A(12,11,15) | 105.161 | D(2,3,4,9) | 179.487 |
| R(11,16) | 1.466 | A(11,12,14) | 111.709 | D(9,4,5,6) | 179.197 |
| R(17,21) | 1.761 | A(19,17,21) | 108.822 | D(4,5,6,11) | 179.085 |
| R(18,21) | 1.766 | A(21,17,28) | 124.245 | D(5,6,11,12) | 122.646 |
| R(19,20) | 1.365 | A(20,18,22) | 123.339 | D(6,11,12,13) | 146.553 |
| R(28,29) | 1.421 | A(3,19,20) | 116.055 | D(15,11,12,14) | 156.877 |
| R(29,30) | 1.166 | A(18,20,19) | 110.302 | D(20,18,22,23) | 178.107 |
| R(31,32) | 1.385 | A(23,22,24) | 123.885 | D(3,19,20,18) | 172.316 |

| | | | | | |
|----------|-------|-------------|---------|----------------|---------|
| R(31,34) | 1.237 | A(22,24,25) | 108.908 | D(18,22,24,25) | 178.534 |
| R(32,33) | 1.013 | A(17,28,29) | 121.392 | D(29,28,31,34) | 159.852 |
| R(32,35) | 1.413 | A(28,31,34) | 120.768 | D(28,31,32,33) | 166.078 |
| R(37,41) | 1.084 | A(31,32,33) | 110.395 | D(31,32,35,36) | 156.328 |
| R(45,46) | 1.466 | A(31,32,35) | 131.371 | D(37,35,36,39) | 178.886 |

B. Molecular Electrostatic Potential (MEP): The molecular electrostatic potential is related to the electronic density and is a very useful descriptor for determining the sites for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions [10]. To predict reactive sites of electrophilic or nucleophilic attack for the investigated molecules, the MEP at the DFT/B3LYP method and 6-31G (d,p) basis set was calculated. The negative (red and yellow) regions of the MEP are related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity, as shown in Fig 2.

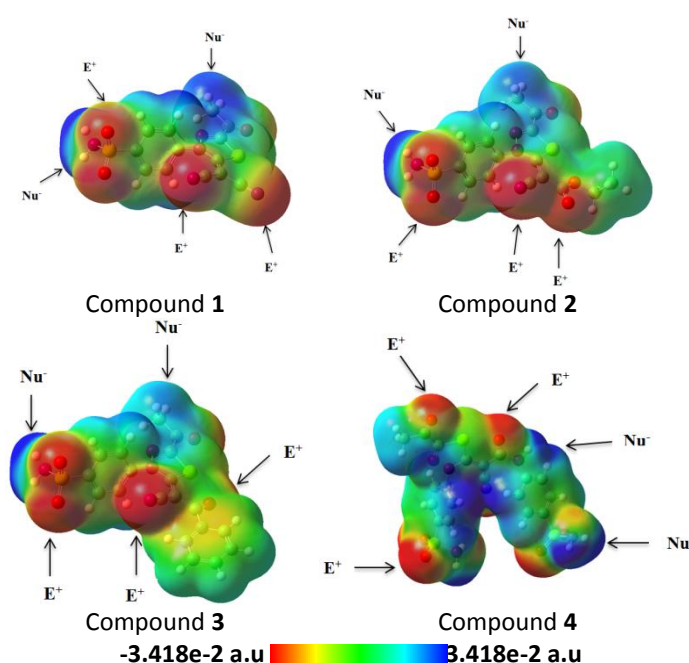


Fig 2. Molecular electrostatic potential surface of 2,4,5-trisubstituted-(1,3,4)-thiadiazole benzene sulfonamides 1-4

In all molecules, the regions exhibiting the negative electrostatic potential are localized on sulfamide, ketone and the amide function; while the regions presenting the positive potential are localized vicinity of the hydrogen atoms.

C. Basin Analysis: The concept of basin was first introduced by Bader in his atom in molecular (AIM) theory, after that, this concept was transplanted to the analysis of ELF by Savin and Silvi. In fact, basin can be defined for any real space function, such as molecular orbital, electron density difference, electrostatic potential and even Fukui function. A real space function in general has one or more maxima, which are referred to as attractors or (3,-3) critical points. Each basin is a subspace of the whole space, and uniquely contains an attractor. The basins are separated with each other by interbasin surfaces (IBS), which are essentially the zero-flux surface of the real space functions; mathematically, such surfaces consist of all of the points \mathbf{r} satisfying $\nabla f(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0$, where $\mathbf{n}(\mathbf{r})$ stands for the unit normal vector of the surface at position \mathbf{r} . Interbasin surfaces (IBS) dissect the whole molecular space into individual basins, each IBS actually is a bunch of gradient paths derived from a (3,-1) critical points (CP). The interbasin surfaces of compounds 1-4 generated by (3,-1) critical points are illustrated below.

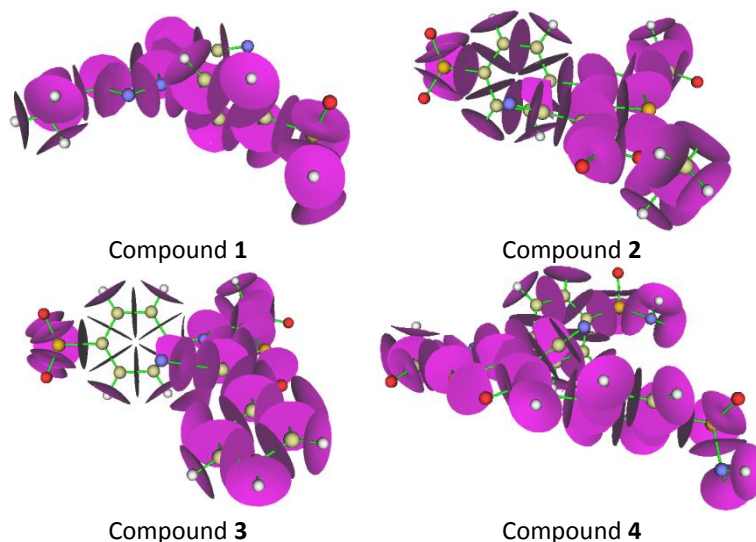


Fig 3. Plots of the interbasin surfaces of compounds 1-4

The number of interbasin surfaces is 34, 43, 48 and 55 for compounds 1-4 respectively.

D. Frontier Molecular Orbitals (FMOS): The frontier orbitals, HOMO and LUMO determine the way how the molecule interacts with other species and helps to characterize the chemical reactivity and kinetic stability of the molecule. They play an important role in the electric and optical properties, as well as in the chemical reactions. HOMO energy determines the ability to donate an electron and LUMO energy determines the capacity to accept an electron. The energy gap between the HOMO and LUMO is very important in determining the chemical reactivity of the molecule. A small HOMO-LUMO energy gap implies low kinetic stability, because it is energetically favorable to add electrons to a low-lying LUMO and to receive electrons from a high-lying HOMO. The distributions and energy levels of the HOMO-1, HOMO, LUMO and LUMO+1 orbitals are computed at the B3LYP/6-31G (d,p) level for compound 1 with a small energy gap comparing with the rest compounds and shown in Fig 4.

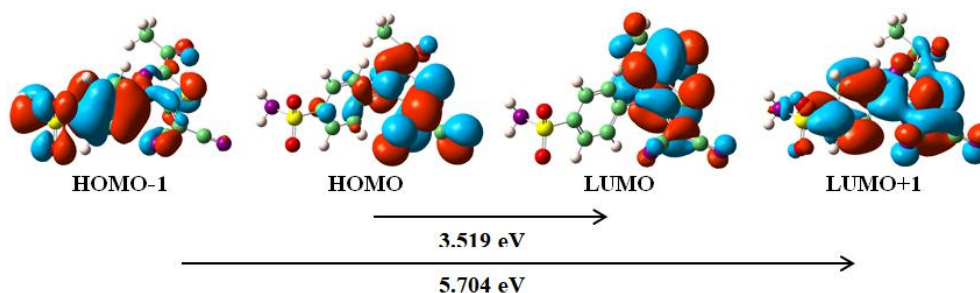


Fig 4. HOMO-LUMO Structure with the energy level diagram of compound 1

HOMO-1 and LUMO+1 are confined over the whole molecule, while HOMO and LUMO are on (1,3,4)-thiadiazole ring for compound 1 which gives charge transfer process in the molecular system.

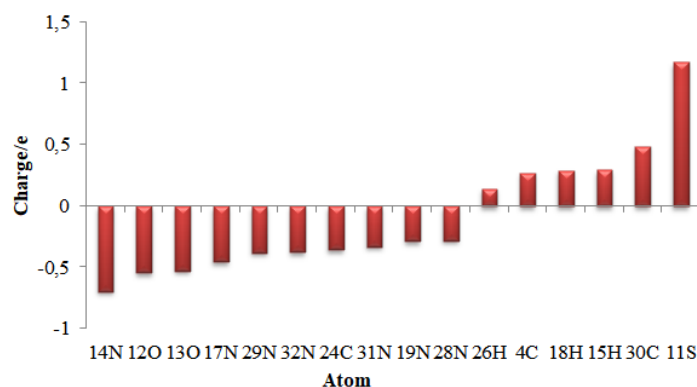
E. Global Reactivity Descriptors: The chemical reactivity and site selectivity of the molecular systems have been determined by the conceptual density functional theory [11]. Electronegativity (χ), chemical potential (μ), global hardness (η), global softness (S) and electrophilicity index (ω) are global reactivity descriptors, highly successful in predicting global reactivity trends. On the basis of Koopman's theorem [12], global reactivity descriptors are calculated using the energies of frontier molecular orbital's HOMO and LUMO. The calculated values of the global reactivity descriptors for the title molecules are collected in Table 5.

Table 5. Quantum chemical descriptors of 2,4,5-trisubstituted-(1,3,4)-thiadiazole benzene sulfonamides **1-4**

| Parameters | Compound 1 | Compound 2 | Compound 3 | Compound 4 |
|------------------------------|------------|------------|------------|------------|
| E_{HOMO} (eV) | -6.550 | -6.295 | -6.321 | -6.361 |
| E_{LUMO} (eV) | -3.030 | -2.727 | -2.605 | -2.663 |
| ΔE_{gap} (eV) | 3.519 | 3.568 | 3.716 | 3.698 |
| I (eV) | 6.550 | 6.295 | 6.321 | 6.361 |
| A (eV) | 3.030 | 2.727 | 2.605 | 2.663 |
| μ (eV) | -4.790 | -4.511 | -4.463 | -4.512 |
| χ (eV) | 4.790 | 4.511 | 4.463 | 4.512 |
| η (eV) | 1.760 | 1.784 | 1.858 | 1.849 |
| S (eV) | 0.284 | 0.280 | 0.269 | 0.270 |
| ω (eV) | 6.519 | 5.703 | 5.359 | 5.506 |

The compound which has the lowest energy gap is the compound **1** ($\Delta E_{\text{gap}} = 3.519$ eV). This lower gap allows it to be the softest molecule. The compound that has the highest energy gap is the compound **3** ($\Delta E_{\text{gap}} = 3.716$ eV). The compound that has the highest HOMO energy is the compound **2** ($E_{\text{HOMO}} = -6.295$ eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound **1** ($E_{\text{LUMO}} = -3.030$ eV) which signifies that it can be the best electron acceptor. The two properties like I (potential ionization) and A (affinity) are so important, the determination of these two properties allows us to calculate the absolute electronegativity (χ) and the absolute hardness (η). These two parameters are related to the one-electron orbital energies of the HOMO and LUMO respectively. Compound **2** has the lowest value of the potential ionization ($I = 6.295$ eV), so that will be the better electron donor. Compound **1** has the largest value of the affinity ($A = 3.030$ eV), so it is the better electron acceptor. The chemical reactivity varies with the structure of molecules. Chemical hardness (softness) value of compound **1** ($\eta = 1.760$ eV, $S = 0.284$ eV) is lesser (greater) among all the molecules. Thus, compound **1** is found to be more reactive than all the compounds. Compound **1** possesses higher electronegativity value ($\chi = 4.790$ eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **1** ($\omega = 6.519$ eV) indicates that it is the stronger electrophiles than all compounds. Compound **1** has the smaller frontier orbital gap so, it is more polarizable and is associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule.

F. Mulliken Analysis: It is evident that the atomic charges are very much dependent on how the atoms are defined. Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation of the molecular system. The natural population analysis of 2,4,5-trisubstituted-(1,3,4)-thiadiazole benzene sulfonamides **1-4** obtained by Mulliken [13] population analysis using B3LYP/6-31G (d,p) basis set. The total atomic charges of Compound **1** (the more reactive compound) obtained by Mulliken population analysis with DFT/B3LYP method and 6-31G (d,p) basis set and presented in Fig 5.


 Fig. 5. Mulliken's plot of compound **1**

The atom 30N shows more negative (-0.73574e) charge and 27S more positive (1.197607e) charge, which suggests extensive charge delocalization in the entire molecule. The charge noticed on the 19N, 20N, 13N and 14N is smaller in this molecule and equal to -0.482902e, -0.469509e, -0.407857e and -0.244264e respectively. This can be explained by the high degree of conjugation, with a strong push-pull effect between the sulfamide function, benzene ring, (1,3,4)-thiadiazole ring and ketone function. Negatively charged oxygen (29O, 28O and 22O) atoms shows that charge is transferred from sulfur to oxygen. Carbon atoms 23C and 6C are more negatively charged which indicate that the charge transfers from sulfamide function to ketone function. The maximum atomic charge of carbons is obtained for 17C and 21C. This is due to the attachment of negatively charged atoms 19N and 22O respectively. The positive charges are localized on the hydrogen atoms. Very similar values of positive charges are observed for the hydrogen atoms (24H, 32H and 31H (0.15~0.28e)) bonded to the negative atoms (23C and 30N) respectively.

G. Natural Bond Orbital Analysis (NBO): The NBO studies a basic for exploring charge transfer or conjugative interaction in molecular systems and is an efficient method to know about intra- and intermolecular bonding and interaction among bonds. In order to investigate the intramolecular interactions, the stabilization energies of the title compounds were performed by using second-order perturbation theory. The larger E (2) values were listed in Tables 6-9.

Table 6. Second order perturbation theory analysis of Fock matrix on NBO of compound 1

| Donor(i) | ED/e | Acceptor(j) | ED/e | E(2) Kcal/mol | E(j)-E(i) a.u | F(i,j) a.u |
|-----------------|---------|---------------------|---------|------------------|------------------|---------------|
| LP (1) N13 | 1.58649 | $\pi^*(C11-C16)$ | 0.45783 | 49.42 | 0.28 | 0.106 |
| LP (1) N13 | 1.58649 | $\pi^*(C12-N14)$ | 0.30378 | 32.20 | 0.27 | 0.085 |
| LP (2) S15 | 1.66504 | $\pi^*(C12-N14)$ | 0.30378 | 27.47 | 0.24 | 0.073 |
| LP (2) S15 | 1.66504 | $\pi^*(C11-C16)$ | 0.45783 | 27.05 | 0.25 | 0.076 |
| π (C4-C5) | 1.63958 | $\pi^*(C2-C3)$ | 0.36936 | 22.08 | 0.27 | 0.069 |
| LP (3) O29 | 1.77906 | $\sigma^*(S27-O28)$ | 0.15678 | 21.54 | 0.57 | 0.100 |
| LP (3) O28 | 1.77713 | $\sigma^*(S27-O29)$ | 0.15585 | 21.49 | 0.57 | 0.100 |
| LP (2) O22 | 1.88228 | $\sigma^*(C12-C21)$ | 0.07422 | 21.33 | 0.68 | 0.108 |
| π (C1-C6) | 1.66295 | $\pi^*(C4-C5)$ | 0.29174 | 20.50 | 0.29 | 0.070 |
| π (C2-C3) | 1.66661 | $\pi^*(C1-C6)$ | 0.35594 | 20.42 | 0.29 | 0.069 |
| π (C4-C5) | 1.63958 | $\pi^*(C1-C6)$ | 0.35594 | 19.58 | 0.28 | 0.066 |
| LP (2) O22 | 1.88228 | $\sigma^*(C21-C23)$ | 0.05059 | 19.53 | 0.66 | 0.103 |
| π (C1-C6) | 1.66295 | $\pi^*(C2-C3)$ | 0.36936 | 19.32 | 0.28 | 0.066 |
| π (C2-C3) | 1.66661 | $\pi^*(C4-C5)$ | 0.29174 | 18.94 | 0.30 | 0.068 |
| LP (2) O28 | 1.81408 | $\sigma^*(C6-S27)$ | 0.20840 | 16.83 | 0.44 | 0.077 |
| LP (2) O29 | 1.81469 | $\sigma^*(C6-S27)$ | 0.20840 | 16.65 | 0.44 | 0.077 |
| LP (1) N14 | 1.91187 | $\sigma^*(C12-S15)$ | 0.06463 | 13.74 | 0.60 | 0.082 |
| LP (2) O29 | 1.81469 | $\sigma^*(S27-N30)$ | 0.24201 | 13.63 | 0.41 | 0.068 |
| LP (2) O28 | 1.81408 | $\sigma^*(S27-N30)$ | 0.24201 | 13.53 | 0.41 | 0.068 |
| π (C12-N14) | 1.90947 | $\pi^*(C21-O22)$ | 0.12712 | 12.04 | 0.37 | 0.060 |

Table 7. Second order perturbation theory analysis of Fock matrix on NBO of compound 2

| Donor(i) | ED/e | Acceptor(j) | ED/e | E(2) Kcal/mol | E(j)-E(i) a.u | F(i,j) a.u |
|-----------------|---------|---------------------|---------|------------------|------------------|---------------|
| LP (1) N19 | 1.58772 | $\pi^*(C11-C28)$ | 0.43129 | 45.50 | 0.29 | 0.102 |
| LP (2) O33 | 1.80858 | $\pi^*(C29-O32)$ | 0.29506 | 44.84 | 0.34 | 0.113 |
| LP (2) O32 | 1.83377 | $\sigma^*(C29-O33)$ | 0.10906 | 34.18 | 0.61 | 0.131 |
| LP (1) N19 | 1.58772 | $\pi^*(C12-N20)$ | 0.30570 | 31.91 | 0.27 | 0.085 |
| LP (2) S21 | 1.66334 | $\pi^*(C12-N20)$ | 0.30570 | 27.82 | 0.24 | 0.073 |
| LP (2) S21 | 1.66334 | $\pi^*(C11-C28)$ | 0.43129 | 25.75 | 0.26 | 0.074 |
| π (C4-C5) | 1.64132 | $\pi^*(C2-C3)$ | 0.36800 | 22.17 | 0.27 | 0.070 |
| π (C11-C28) | 1.81523 | $\pi^*(C29-O32)$ | 0.29506 | 21.47 | 0.31 | 0.075 |

| | | | | | | |
|---------------|---------|---------------------|---------|-------|------|-------|
| LP (3) O17 | 1.77898 | $\sigma^*(S13-O18)$ | 0.15627 | 21.46 | 0.57 | 0.100 |
| LP (3) O18 | 1.77806 | $\sigma^*(S13-O17)$ | 0.15625 | 21.44 | 0.57 | 0.100 |
| π (C2-C3) | 1.66058 | $\pi^*(C1-C6)$ | 0.36224 | 21.05 | 0.29 | 0.070 |
| LP (2) O23 | 1.88479 | $\sigma^*(C12-C22)$ | 0.07286 | 21.02 | 0.68 | 0.108 |
| π (C1-C6) | 1.66629 | $\pi^*(C4-C5)$ | 0.29281 | 20.56 | 0.29 | 0.070 |
| LP (2) O32 | 1.83377 | $\sigma^*(C28-C29)$ | 0.07108 | 20.39 | 0.68 | 0.108 |
| LP (2) O23 | 1.88479 | $\sigma^*(C22-C24)$ | 0.05113 | 19.56 | 0.66 | 0.103 |
| π (C4-C5) | 1.64132 | $\pi^*(C1-C6)$ | 0.36224 | 19.55 | 0.27 | 0.065 |
| π (C1-C6) | 1.66629 | $\pi^*(C2-C3)$ | 0.36800 | 18.89 | 0.28 | 0.066 |
| π (C2-C3) | 1.66058 | $\pi^*(C4-C5)$ | 0.29281 | 18.79 | 0.30 | 0.067 |
| LP (2) O18 | 1.81516 | $\sigma^*(C6-S13)$ | 0.20606 | 16.68 | 0.44 | 0.077 |
| LP (2) O17 | 1.81555 | $\sigma^*(S13-N14)$ | 0.24310 | 13.57 | 0.41 | 0.068 |

Table 8. Second order perturbation theory analysis of Fock matrix on NBO of compound 3

| Donor(i) | ED/e | Acceptor(j) | ED/e | E(2) Kcal/mol | E(j)-E(i) a.u | F(i,j) a.u |
|-----------------|---------|---------------------|---------|------------------|------------------|---------------|
| LP (1) N19 | 1.57416 | $\pi^*(C11-C28)$ | 0.47063 | 49.25 | 0.28 | 0.106 |
| LP (1) N19 | 1.57416 | $\pi^*(C12-N20)$ | 0.30229 | 29.87 | 0.27 | 0.083 |
| LP (2) S21 | 1.61789 | $\pi^*(C11-C28)$ | 0.47063 | 28.55 | 0.24 | 0.076 |
| LP (2) S21 | 1.61789 | $\pi^*(C12-N20)$ | 0.30229 | 27.68 | 0.23 | 0.073 |
| π (C11-C28) | 1.76376 | $\pi^*(C29-O32)$ | 0.27606 | 24.42 | 0.30 | 0.078 |
| π (C4-C5) | 1.63882 | $\pi^*(C2-C3)$ | 0.36746 | 22.33 | 0.27 | 0.070 |
| π (C38-C40) | 1.64802 | $\pi^*(C33-C35)$ | 0.36747 | 22.11 | 0.28 | 0.071 |
| LP (3) O17 | 1.77894 | $\sigma^*(S13-O18)$ | 0.15645 | 21.48 | 0.57 | 0.100 |
| LP (3) O18 | 1.77839 | $\sigma^*(S13-O17)$ | 0.15611 | 21.44 | 0.57 | 0.100 |
| π (C34-C36) | 1.65651 | $\pi^*(C38-C40)$ | 0.31922 | 21.27 | 0.28 | 0.069 |
| LP (2) O23 | 1.88550 | $\sigma^*(C12-C22)$ | 0.24253 | 21.17 | 0.68 | 0.108 |
| π (C2-C3) | 1.66080 | $\pi^*(C1-C6)$ | 0.36349 | 21.13 | 0.28 | 0.070 |
| π (C1-C6) | 1.66677 | $\pi^*(C4-C5)$ | 0.29221 | 20.48 | 0.29 | 0.070 |
| π (C33-C35) | 1.64047 | $\pi^*(C34-C36)$ | 0.29431 | 19.94 | 0.29 | 0.069 |
| π (C4-C5) | 1.63882 | $\pi^*(C1-C6)$ | 0.36349 | 19.72 | 0.27 | 0.066 |
| LP (2) O23 | 1.88550 | $\sigma^*(C22-C24)$ | 0.05171 | 19.63 | 0.66 | 0.103 |
| π (C33-C35) | 1.64047 | $\pi^*(C29-O32)$ | 0.27606 | 19.17 | 0.25 | 0.063 |
| π (C1-C6) | 1.66677 | $\pi^*(C2-C3)$ | 0.36746 | 18.85 | 0.28 | 0.066 |
| π (C34-C36) | 1.65651 | $\pi^*(C33-C35)$ | 0.36747 | 18.84 | 0.28 | 0.065 |
| π (C2-C3) | 1.66080 | $\pi^*(C4-C5)$ | 0.29221 | 18.75 | 0.30 | 0.067 |

Table 9. Second order perturbation theory analysis of Fock matrix on NBO of compound 4

| Donor(i) | ED/e | Acceptor(j) | ED/e | E(2) Kcal/mol | E(j)-E(i) a.u | F(i,j) a.u |
|------------------|---------|-------------------|---------|------------------|------------------|---------------|
| π (C3-C4) | 1.50195 | $\pi^*(C5-C6)$ | 0.35356 | 65.89 | 0.10 | 0.075 |
| σ (C2-C3) | 1.82807 | $\pi^*(C3-C4)$ | 0.32266 | 48.72 | 0.77 | 0.180 |
| π (C3-N19) | 1.59901 | $\pi^*(C17-C28)$ | 0.47447 | 48.42 | 0.28 | 0.106 |
| LP (1) N32 | 1.70483 | $\pi^*(C31-O34)$ | 0.35000 | 46.50 | 0.28 | 0.103 |
| σ (C3-C4) | 1.84845 | $\pi^*(C3-C4)$ | 0.32266 | 38.31 | 0.80 | 0.163 |
| π (C3-N19) | 1.59901 | $\pi^*(C18-N20)$ | 0.30246 | 30.44 | 0.28 | 0.084 |
| LP (2) S21 | 1.62609 | $\pi^*(C17-C28)$ | 0.47447 | 29.43 | 0.24 | 0.077 |
| LP (2) S21 | 1.62609 | $\pi^*(C18-N20)$ | 0.30246 | 27.64 | 0.23 | 0.073 |
| π (C3-C4) | 1.50195 | $\sigma^*(C2-C3)$ | 0.02350 | 27.62 | 0.74 | 0.146 |
| π (C3-C4) | 1.50195 | $\pi^*(C1-C2)$ | 0.28625 | 27.46 | 0.11 | 0.052 |
| π (C35-C37) | 1.63381 | $\pi^*(C40-C42)$ | 0.38657 | 24.62 | 0.28 | 0.074 |
| π (C3-C4) | 1.50195 | $\sigma^*(C3-C4)$ | 0.02254 | 24.15 | 0.74 | 0.137 |

| | | | | | | |
|-----------------|---------|----------------------|---------|-------|------|-------|
| π (C17-C28) | 1.78493 | π^* (C31-O34) | 0.35000 | 23.76 | 0.31 | 0.079 |
| LP (2) O34 | 1.83898 | σ^* (C31-N32) | 0.06768 | 23.69 | 0.71 | 0.118 |
| LP (3) O15 | 1.79101 | σ^* (S11-O16) | 0.16604 | 22.74 | 0.56 | 0.102 |
| π (C36-C38) | 1.67225 | π^* (C35-C37) | 0.37724 | 22.29 | 0.28 | 0.071 |
| π (C40-C42) | 1.68116 | π^* (C36 -C38) | 0.30147 | 21.98 | 0.29 | 0.072 |
| LP (1) N32 | 1.70483 | π^* (C35-C37) | 0.37724 | 21.92 | 0.29 | 0.073 |
| LP (3) O46 | 1.78062 | σ^* (S45-O47) | 0.15787 | 21.59 | 0.57 | 0.100 |
| LP (3) O47 | 1.77999 | σ^* (S45-O46) | 0.15512 | 21.24 | 0.57 | 0.100 |

The intra molecular interaction for the title compounds is formed by the orbital overlap between: π (C4-C5) and π^* (C2-C3) for compound **1** and **2**, π (C11-C28) and π^* (C29-O32) for compound **3** and π (C3-C4) and π^* (C5-C6) for compound **4** respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of π (C4-C5) to π^* (C2-C3) for compound **1**, π (C4-C5) to π^* (C2-C3) for compound **2**, π (C11-C28) to π^* (C29-O32) for compound **3** and π (C3-C4) to π^* (C5-C6) for compound **4** lead to highest stabilization of 22.08, 22.17, 24.42 and 65.89 kJ mol⁻¹ respectively. In case of LP (1) N13 orbital to the π^* (C11-C16) for compound **1**, LP (1) N19 orbital to π^* (C11-C28) for compound **2** and **3**, LP (1) N32 orbital to π^* (C31-O34) for compound **4** respectively, show the stabilization energy of 49.42, 45.50, 49.25 and 46.50 kJ mol⁻¹ respectively.

H. Nonlinear Optical Properties (NLO): The development of materials with large nonlinear optical (NLO) properties has been of great interest in past few decades. These materials find numerous device applications, from lasers to optical switches and electronics [14]. So far, the organic π -conjugated molecules have been considered mostly for this purpose because of their easy functionalization to fine tune the desired properties and the ease of fabrication and integration into devices [15-17]. The dipole moment, polarizability, anisotropy of polarizability and first hyperpolarizability of title compounds were calculated using B3LYP/6-31G (d,p) basis set and determined in Table 10.

 Table 10. Nonlinear optical properties of 2,4,5-trisubstituted-(1,3,4)-thiadiazole benzene sulfonamides **1-4**

| Parameters | Compound 1 | Compound 2 | Compound 3 | Compound 4 |
|---|------------|------------|------------|------------|
| β_{xxx} | 178.7492 | -5.1626 | -163.5570 | 15.8680 |
| β_{yyy} | -172.7725 | 114.9212 | 10.6731 | -76.1196 |
| β_{zzz} | -9.3614 | -13.1907 | -12.4334 | -24.6251 |
| β_{xyy} | 64.4826 | -5.3237 | 23.0556 | 230.9353 |
| β_{xxy} | -164.4687 | 33.0239 | -24.7461 | -23.7967 |
| β_{xxz} | -41.3275 | -72.9868 | -37.7823 | -84.0402 |
| β_{xzz} | 8.2776 | -1.6630 | -30.8845 | 23.7143 |
| β_{yzz} | -15.9413 | 7.8951 | 25.2627 | -16.9202 |
| β_{yyz} | -1.3740 | -3.2005 | -2.3366 | 50.6058 |
| β_{xyz} | 7.7205 | 9.2675 | -15.8825 | 0.3381 |
| $\beta_{\theta}(\text{esu})\times 10^{-33}$ | 417.3543 | 177.7073 | 179.6109 | 300.3356 |
| μ_x | 1.0333 | 1.4907 | -2.6324 | -0.1755 |
| μ_y | -9.5994 | 7.6647 | 3.3859 | -3.1673 |
| μ_z | -1.5576 | -2.3512 | -1.9293 | -1.7998 |
| $\mu(\text{D})$ | 9.7797 | 8.1546 | 4.7028 | 3.6472 |
| α_{xx} | -170.6494 | -154.3970 | -166.8609 | -196.1134 |
| α_{yy} | -157.8797 | -176.4355 | -183.2053 | -245.4121 |
| α_{zz} | -138.0251 | -156.7327 | -175.6467 | -208.9829 |
| α_{xy} | -3.1128 | -27.5381 | -35.2191 | -17.9174 |
| α_{xz} | -11.5250 | 9.5589 | 12.8195 | -13.7524 |
| α_{yz} | -3.2651 | 9.1357 | 11.8904 | -1.3760 |
| $\alpha(\text{esu})\times 10^{-24}$ | 35.6418 | 56.9141 | 69.5633 | 58.5093 |
| $\Delta\alpha(\text{esu})\times 10^{-24}$ | 5.2821 | 8.4347 | 10.3093 | 8.6711 |



ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 6, Issue 1, January 2019

Since the values of the polarizabilities ($\Delta\alpha$) and the hyperpolarizabilities (β_0) of the GAUSSIAN 09 output are obtained in atomic units (a.u.), the calculated values have been converted into electrostatic units (e.s.u.) (for α ; 1 a.u. = 0.1482×10^{-24} e.s.u., for β ; 1 a.u. = 8.6393×10^{-33} e.s.u.). The calculated values of dipole moment (μ) for the title compounds were found to be 9.7797, 8.1546, 4.7028 and 3.6472 D respectively, which are approximately between three and nine times than to the value for urea ($\mu = 1.3732$ D). Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore, it has been used frequently as a threshold value for comparative purposes. The calculated values of polarizability are 35.6418×10^{-24} , 56.9141×10^{-24} , 69.5633×10^{-24} and 58.5093×10^{-24} esu respectively; the values of anisotropy of the polarizability are 5.2821, 8.4347, 10.3093 and 8.6711 esu, respectively. The magnitude of the molecular hyperpolarizability (β_0) is one of the important key factors in a NLO system. The DFT/6-31G (d,p) calculated first hyperpolarizability value (β_0) of 2,4,5-trisubstituted-(1,3,4)-thiadiazole benzene sulfonamides molecules are equal to 417.3543×10^{-33} , 177.7073×10^{-33} , 179.6109×10^{-33} and 300.3356×10^{-33} esu. The first hyperpolarizability of title molecules is approximately 1.22, 0.51, 0.52 and 0.87 times than those of urea (β of urea is 343.272×10^{-33} esu obtained by B3LYP/6-311G (d,p) method). The above results show that only compound **1** might has the NLO applications.

IV. CONCLUSION

In this study, we carried out the theoretical analysis of 2,4,5-trisubstituted-(1,3,4)-thiadiazole benzene sulfonamides **1-4** using the DFT/B3LYP methods with 6-31G (d,p) basis set. The optimized geometric parameters (bond lengths, bond angles and dihedral angles) are computed by the same method cited above. Molecular electrostatic potential of the title compounds shows that the negative potential sites are on the sulfamide, ketone and the amide function, while the positive potential sites are around the hydrogen atoms. The frontier molecular orbitals have been visualized and the HOMO-LUMO energy gap has been calculated and results confirm that the charge transfer occurs within the molecule. The chemical reactivity is understood from chemical potential, electrophilicity and global hardness and results show that compound **1** is the more reactive. Mulliken atomic charges are obtained to understand the atomic theory in detail. The NBO analysis have been made with which the stability and intra molecular interactions have been interpreted and the transactions give stabilization to the structure have been identified by second order perturbation energy calculations. The dipole moment, polarizability and hyperpolarizability data indicate that the compound **1** possesses NLO behavior.

V. ACKNOWLEDGMENTS

This work was generously supported by the (General Directorate for Scientific Research and Technological Development, DGRS-DT) and Algerian Ministry of Scientific Research.

REFERENCES

- [1] J. Y. Winum, A. Scozzafava, J. L. Montero, C. T. Supuran. Therapeutic potential of sulfamides as enzyme inhibitors. *Med. Res. Rev.*, vol. 26, 2006, pp 767-792.
- [2] T. H. Maren. Relations between structure and biological activity of sulfonamides. *Ann. Rev. Pharmacol. Toxicol.*, 1976; vol. 16: pp 309-327.
- [3] W. M. F. Fabian, G. Kollenz, Y. Akcamur, T. R. Kok, M. Tezcan, M. Akkurt, W. Hiller. Reaktionen cyclischer Oxalylverbindungen, 34. Mitt.: Synthese von Dibenzoylacet-N-carboxyalkylamiden und semiempirische Rechnungen zur Keto-Enol Tautomerie. *Monatsh. Chem.*, vol. 123, 1992, pp 265-275.
- [4] H. Tanak, A. A. Ađar, O. Bykgngr. Experimental (XRD, FT-IR and UV-Vis) and theoretical modeling studies of Schiff base (E)-N'-((5-nitrothiophen-2-yl)methylene)-2-phenoxyaniline. *Spectrochim. Acta Part A*, vol. 118, 2014, pp 672-682.
- [5] A. K. Srivastava, A. K. Pandey, S. Jain, N. Misra. FT-IR spectroscopy, intra-molecular C-H...O interactions, HOMO, LUMO, MESP analysis and biological activity of two natural products, triclisine and rufescine: DFT and QTAIM approaches. *Spectrochim. Acta A*, vol. 136, 2015, pp 682-689.
- [6] A. K. Srivastava, N. Misra. A comparative theoretical study on the biological activity, chemical reactivity, and coordination ability of dichloro-substituted (1,3-thiazol-2-yl)acetamides. *Can.J.Chem.*, vol. 92, 2014, pp 234-239.
- [7] A. K. Srivastava, V. Baboo, B. Narayana, B. K. Sarojini, N. Misra. Comparative DFT study on reactivity, acidity and vibrational spectra of halogen substituted phenylacetic acids. *Indian J. Pure Appl. Phys.*, vol. 52, 2014, pp 507-519.
- [8] A. M. Alafeefy, H. A. Abdel-Aziz, D. Vullo, A.M. S. Al-Tamimi, N. A. Al-Jaber, C. Capasso, C. T. Supuran. Inhibition of carbonic anhydrases from the extremophilic bacteria *Sulfurihydrogenibium yellostonense* (SspCA) and *S. azorensis* (SazCA) with a new series of sulfonamides incorporating aroylhydrazone-, [1,2,4]triazolo[3,4-b][1,3,4]thiadiazinyl- or 2-(cyanophenylmethyl-ene)-1,3,4-thiadiazol-3(2H)-yl moieties. *Bioorg. Med. Chem.*, vol. 22, 2014, pp 141-147.



ISSN: 2350-0328

**International Journal of Advanced Research in Science,
Engineering and Technology**

Vol. 6, Issue 1, January 2019

- [9] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, et al. Gaussian 09, Revision C.01; Gaussian Inc.: Wallingford, CT, USA, 2010.
- [10] V. Karunakaran, V. Balachandran. FT-IR, FT-Raman spectra, NBO, HOMO-LUMO and thermodynamic functions of 4-chloro-3-nitrobenzaldehyde based on ab initio HF and DFT calculations. Spectrochim. Acta A, vol. 98, 2012, pp 229-239.
- [11] J. Padmanabhan, R. Parthasarathi, V. Subramaniaan, P. K. Chattaraj. Electrophilicity-Based Charge Transfer Descriptor. J. Phys.Chem. A, vol. 111, 2007, pp 1358-1361.
- [12] R. G. Parr, W. Yang. Density Functional Theory of Atoms and Molecules, Oxford University Press, Oxford, New York, 1989.
- [13] R. S. Mulliken. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. I. J. Chem. Phys, vol. 23, 1955, pp 1833-1840.
- [14] P. N. Prasad, D. J. Williams. Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley, New York, 1991.
- [15] G. A. Lindsay, K. D. Singer. Polymers for Second-order Nonlinear Optics, ACS Symposium Series, No. 601, ACS, Washington, DC, 1995.
- [16] D. Burland. Optical Nonlinearities In Chemistry: Introduction. Chem. Rev, vol. 94, 1994, pp 1-2.
- [17] E. Hanamura. Very large optical nonlinearity of semiconductor microcrystallites. Phys. Rev, vol. B37, 1988, pp 1245-1261.