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Theoretical investigations on the molecular structure, HOMO–LUMO, Fukui function, NBO analysis and NLO of amino methyl tetrathiafulvalenes compounds by DFT method

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Abstract

The aim of this study is to find out the molecular characteristic and structural parameters that govern the chemical behavior of tetrathiafulvalene derivatives which are amino methyl tetrathiafulvalenes 1-3. The optimized molecular structure, atomic charges, molecular electrostatic potential, NBO, electronic properties, NLO, energy HOMO, LUMO, gap of the title compounds are studied within the best method in this investigation to determine their reactivity. The theoretical calculations were performed by density functional theory (DFT)/B3LYP technique using 6-31G(d,p) basis set.

Keywords: tetrathiafulvalene, density functional theory, computational chemistry, electronic structure

1. Introduction

Tetrathiafulvalene (TTF) and its derivatives are extensively studied as a result of their versatile behaviors, such as reversible oxido-reduction properties and strong electron donating capabilities for preparing charge-transfer (CT) salts [1], D-A systems and alternative fields [2–4]. As a result of their potential applications within the fields of organic functional materials and molecular thin film electronics, conducting films based on TTF derivatives are attracted more and more interest [5, 6]. Tetrathiafulvalene (TTF), a well-known strong organic electron donor molecule with a planar π -conjugated skeleton, and its derivatives are extensively studied as a promising component of functional solids and materials that show (super) conductivity, magnetism, dielectric and optical properties, etc [7]. The reactivity descriptors derived from conceptual density functional theory (DFT) have recently been the foci of organic chemistry researchers as a tool to explain global and/or local reactivity in molecules [8]. The descriptors are defined in terms of general chemical parameters like ionization potential (I), electron affinity (A), electronegativity (χ), hardness (η), chemical potential (μ), electrophilicity index (ω) and local reactivity descriptors such as Fukui function and local hardness [9]. In this paper and in the objective to study the properties of a series of amino methyl tetrathiafulvalenes 1-3 molecules described in literature [10-12] and to predict their applications, we provides a complete description of the molecular geometry, natural bond orbital (NBO) analysis and also the electronic properties such as HOMO-LUMO energy gap, nonlinear optical properties (NLO), chemical hardness, and chemical potential.

2. Material and Methods

All the computational calculations were performed using Gaussian 09 program [13] and the output files were visualized by means of the Gauss view 05 software. The optimized structure of amino methyl tetrathiafulvalenes **1-3** was determined by using B3LYP (Becke's three parameter hybrid model using the Lee-Yang Parr correlation functional) [14, 15]. In the optimized geometry no imaginary frequencies were obtained, therefore there is a true minimum on the potential energy surface.

3. Results and discussion

3.1. Molecular Geometry

The optimized structures of amino methyl tetrathiafulvalenes **1-3** are shown in Fig.1. The most optimized structural parameters, namely Bond length, Bond Angles and dihedral angles calculated with 6-31G(d,p) basis set were listed in tables 1-3.

Generally strong bonds are formed due to large overlap which tends to reduce the bond length. Hence a strong bond will have a short bond length [16]. The Global minimum energy obtained by the DFT structure optimization of amino methyl tetrathiafulvalenes 1-3 varies between -56481.1 eV and -59559.1 eV, which indicate that these compounds were stable.

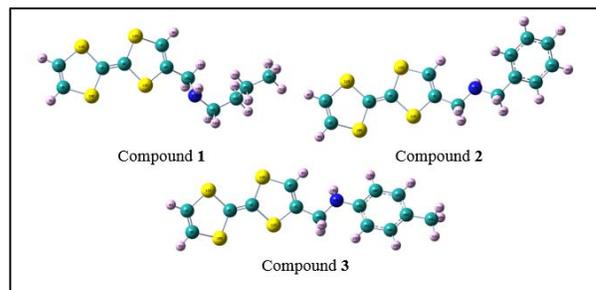


Fig 1: Optimized molecular structure of amino methyl tetrathiafulvalenes 1-3

Table 1: Optimized geometric parameters of compound 1

| Bond Length(Å) | | Bond Angles (°) | | Dihedral Angles (°) | |
|----------------|-------|-----------------|---------|---------------------|---------|
| R(1,3) | 1.337 | A(3,1,4) | 124.874 | D(4,1,3,5) | 0.015 |
| R(1,4) | 1.083 | A(3,1,11) | 117.955 | D(11,1,3,5) | 178.457 |
| R(1,11) | 1.764 | A(4,1,11) | 117.154 | D(3,1,11,2) | 6.332 |
| R(2,6) | 1.350 | A(6,2,10) | 123.118 | D(11,2,6,12) | 178.316 |
| R(2,10) | 1.788 | A(6,2,11) | 123.301 | D(11,2,10,3) | 10.140 |
| R(2,11) | 1.788 | A(10,2,11) | 113.580 | D(6,2,11,1) | 170.180 |
| R(3,5) | 1.083 | A(1,3,5) | 124.813 | D(5,3,10,2) | 175.129 |
| R(3,10) | 1.764 | A(7,8,14) | 126.337 | D(8,14,17,19) | 170.268 |
| R(8,14) | 1.504 | A(8,14,17) | 110.555 | D(15,14,17,18) | 178.451 |
| R(14,15) | 1.099 | A(18,17,19) | 111.004 | D(20,19,22,24) | 176.591 |
| R(14,17) | 1.458 | A(17,19,21) | 107.297 | D(26,25,28,31) | 177.767 |
| R(17,18) | 1.016 | A(17,19,22) | 117.237 | D(18,17,19,21) | 173.499 |
| R(19,20) | 1.097 | A(21,19,22) | 109.207 | D(13,7,8,14) | 178.138 |
| R(19,22) | 1.542 | A(19,22,23) | 107.957 | D(12,8,14,15) | 75.076 |
| R(28,29) | 1.096 | A(29,28,30) | 107.669 | D(9,7,13,6) | 173.679 |

Table 2: Optimized geometric parameters of compound 2

| Bond Length(Å) | | Bond Angles (°) | | Dihedral Angles (°) | |
|----------------|-------|-----------------|---------|---------------------|---------|
| R(1,3) | 1.337 | A(3,1,4) | 124.859 | D(4,1,3,10) | 178.412 |
| R(1,4) | 1.083 | A(3,1,11) | 117.983 | D(4,1,11,2) | 175.007 |
| R(1,11) | 1.764 | A(4,1,11) | 117.141 | D(10,2,6,12) | 0.233 |
| R(2,6) | 1.350 | A(6,2,10) | 123.237 | D(10,2,6,13) | 179.506 |
| R(2,10) | 1.787 | A(6,2,11) | 123.157 | D(6,2,10,3) | 169.741 |
| R(2,11) | 1.787 | A(10,2,11) | 113.606 | D(10,2,11,1) | 10.442 |
| R(3,10) | 1.764 | A(14,17,19) | 113.308 | D(7,14,17,19) | 174.956 |
| R(7,14) | 1.508 | A(12,7,14) | 117.250 | D(14,17,19,22) | 179.246 |
| R(14,16) | 1.099 | A(22,24,28) | 118.957 | D(20,19,22,24) | 173.015 |
| R(14,17) | 1.457 | A(29,27,31) | 120.000 | D(14,7,8,13) | 179.572 |
| R(17,18) | 1.018 | A(19,22,23) | 120.716 | D(15,14,17,18) | 60.514 |
| R(17,19) | 1.465 | A(18,17,19) | 109.250 | D(2,6,13,8) | 168.135 |
| R(19,22) | 1.515 | A(8,7,14) | 126.188 | D(30,25,29,27) | 179.654 |
| R(22,24) | 1.402 | A(15,14,17) | 113.412 | D(8,7,14,16) | 100.131 |
| R(24,28) | 1.086 | A(7,8,9) | 123.325 | D(7,8,13,6) | 7.701 |

Table 3: Optimized geometric parameters of compound 3

| Bond Length(Å) | | Bond Angles (°) | | Dihedral Angles (°) | |
|----------------|-------|-----------------|---------|---------------------|---------|
| R(1,3) | 1.337 | A(3,1,4) | 124.879 | D(4,1,3,5) | 0.005 |
| R(1,4) | 1.083 | A(3,1,11) | 117.975 | D(4,1,3,10) | 178.413 |
| R(1,11) | 1.764 | A(4,1,11) | 117.129 | D(4,1,11,2) | 175.063 |
| R(2,6) | 1.350 | A(6,2,10) | 123.214 | D(10,2,6,12) | 0.232 |
| R(2,10) | 1.787 | A(10,2,11) | 113.631 | D(10,2,6,13) | 179.443 |
| R(3,10) | 1.764 | A(8,7,14) | 126.504 | D(14,7,8,9) | 0.551 |
| R(7,14) | 1.508 | A(12,7,14) | 116.901 | D(7,14,17,19) | 175.601 |
| R(14,17) | 1.451 | A(7,8,9) | 123.753 | D(15,14,17,18) | 76.192 |
| R(17,18) | 1.013 | A(7,14,15) | 109.498 | D(14,17,19,20) | 165.549 |
| R(17,19) | 1.403 | A(7,14,17) | 110.799 | D(14,7,12,6) | 171.441 |
| R(19,20) | 1.408 | A(18,17,19) | 112.992 | D(16,14,17,19) | 56.305 |
| R(20,23) | 1.088 | A(19,20,22) | 120.884 | D(23,20,22,26) | 179.434 |
| R(22,26) | 1.404 | A(26,22,27) | 119.474 | D(25,21,24,26) | 179.069 |
| R(26,29) | 1.510 | A(22,26,29) | 121.092 | D(21,24,26,29) | 179.619 |
| R(29,31) | 1.097 | A(26,29,30) | 111.635 | D(24,26,29,30) | 129.103 |

3.2. Molecular Electrostatic Potential (MEP)

Molecular electrostatic potential (MEP) generally present in the space around the molecule by the charge distribution is very useful in understanding the sites of electrophilic attacks and nucleophilic reaction for the study of biological recognition process [17] and hydrogen bonding interactions [18]. In order to predict the molecular reactive sites, the MEP for the title compound is calculated at B3LYP method as shown in Fig 2. The different values of the electrostatic potential at the surface are represented by different colors. Potential increases in the order red < orange < yellow < green < blue where blue indicates the highest electrostatic potential energy and red indicates the lowest electrostatic potential energy. Intermediary colors represent intermediary electrostatic potentials. The equation used to find the electrostatic potential is [19],

$$V(r) = \sum Z_A / |R_A - r| - \int \rho(r') / |r' - r| d^3r'$$

As seen from the figure that, in all molecules, the regions exhibiting the negative electrostatic potential are localized near the TTF core while the regions presenting the positive potential are localized vicinity of the hydrogen atoms.

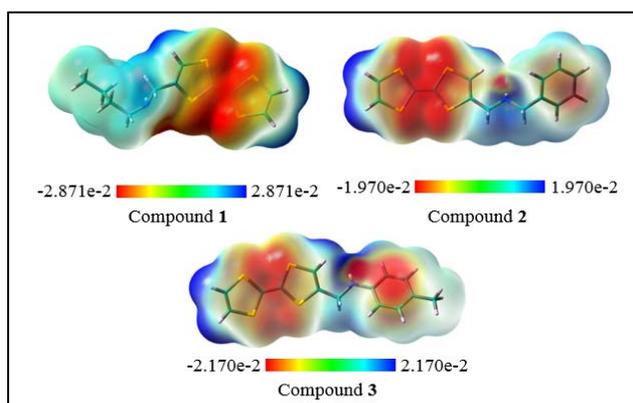


Fig 2: Molecular electrostatic potential surface of amino methyl tetraphiafulvalenes 1-3

3.3. Frontier Molecular Orbitals (FMOs)

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry [20]. We can determine the way the molecule interacts with other species; hence, they are called the frontier orbitals. Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the main orbitals that take part in chemical stability. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor obtains electron. This electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Owing to the interaction between HOMO and LUMO orbitals of a structure, transition of $\pi \rightarrow \pi^*$ type is observed with regards to the molecular orbital theory [21]. Therefore, while the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structures [22]. The HOMO and LUMO energies of compound 2 calculated by the DFT level and B3LYP/6-31G(d,p) method are listed in Table 4. Besides, the pictorial representation of their HOMO-LUMO

distribution and their respective positive and negative regions is shown in Figure 3. The positive and negative phase is represented in green and red color, respectively.

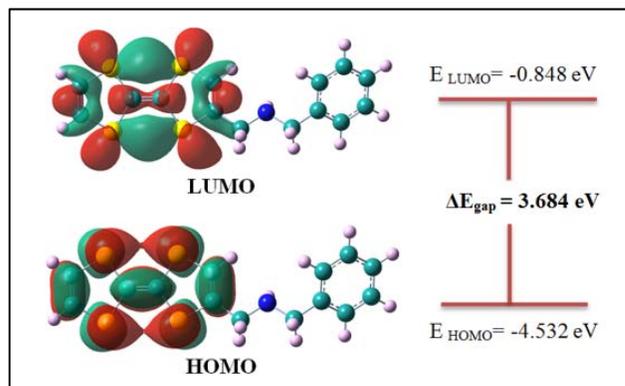


Fig 3: HOMO-LUMO Structure with the energy level diagram of compound 2

3.4. Global Reactivity Descriptors

Based on density functional descriptors, global chemical reactivity descriptors of compounds such as hardness (η), softness (S), chemical potential (μ), electronegativity (χ) and electrophilicity index (ω) as well as local reactivity descriptors as the Fukui function and the philicity have been defined [23-27]. Using Koopman's theorem for closed-shell compounds, η , μ , χ can be defined as:

$$\eta = (I - A) / 2$$

$$\mu = -(I + A) / 2$$

$$\chi = (I + A) / 2$$

$$S = 1 / \eta$$

$$I = -E_{HOMO} \text{ and } A = -E_{LUMO}$$

Where I and A are the ionization potential and electron affinity of the compounds. Electron affinity refers to the capability of a ligand to accept precisely one. Softness is a property of compound that measures the extent of chemical reactivity. It is the reciprocal of hardness. χ is the Mulliken electronegativity, because of the fundamental relationship to the chemical potential, χ is quite different from Pauling's original meaning of electronegativity, which was a property of an atom in a molecule. Now χ is a property of the entire molecule [27]. Recently Parr *et al.* [23] have defined a new descriptor to quantify the global electrophilic power of the compound as electrophilicity index (ω), which defines a quantitative classification of the global electrophilic nature of a compound Parr *et al.* [23] have proposed electrophilicity index (ω) as a measure of energy lowering due to maximal electron flow between donor and acceptor. They defined electrophilicity index (ω) as follows $\omega = \mu^2 / 2\eta$

The electrophilicity is a descriptor of reactivity that allows a quantitative classification of the global electrophilic nature of a molecule within a relative scale. The usefulness of this new reactivity quantity has been recently demonstrated in understanding the toxicity of various pollutants in terms of their reactivity and site selectivity [28, 29]. All the calculated values of HOMO-LUMO, energy gap, ionization potential, Electron affinity, hardness, potential, softness and electrophilicity index are shown in Table 4. As shown in table 4, the compound which have the lowest energetic gap is the compound 2 ($\Delta E_{gap} = 3.684$ eV). This lower gap allows it to

be the softest molecule. The compound that have the highest energy gap is the compound 1 ($\Delta E_{\text{gap}} = 3.730$ eV). The compound that has the highest HOMO energy is the compound 1 ($E_{\text{HOMO}} = -4.439$ eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound 3 ($E_{\text{LUMO}} = -0.958$ 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 allow 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 1 has lowest value of the potential ionization ($I = 4.439$ eV), so that will be the better electron

donor. Compound 3 has the largest value of the affinity ($A = 0.958$ eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound 2 ($\eta = 1.842$ eV, $S = 0.271$ eV) is lesser (greater) among all the molecules. Thus, compound 2 is found to be more reactive than all the compounds. Compound 3 possesses higher electronegativity value ($\chi = 2.801$ eV) than all compounds so; it is the best electron acceptor. The value of ω for compound 3 ($\omega = 2.128$ eV) indicates that it is the stronger electrophiles than all compounds. Compound 2 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.

Table 4: Quantum chemical descriptors of amino methyl tetrathiafulvalenes 1-3

| Parameters | Compound 1 | Compound 2 | Compound 3 |
|------------------------------|------------|------------|------------|
| E_{HOMO} (eV) | -4.439 | -4.532 | -4.644 |
| E_{LUMO} (eV) | -0.710 | -0.848 | -0.958 |
| ΔE_{gap} (eV) | 3.730 | 3.684 | 3.687 |
| IE (eV) | 4.439 | 4.532 | 4.644 |
| EA (eV) | 0.710 | 0.848 | 0.958 |
| μ (eV) | -2.574 | -2.690 | -2.801 |
| χ (eV) | 2.574 | 2.690 | 2.801 |
| η (eV) | 1.865 | 1.842 | 1.843 |
| S (eV) | 0.268 | 0.271 | 0.271 |
| ω (eV) | 1.777 | 1.965 | 2.128 |

3.5. Local Reactivity Descriptors

Density Functional Theory is a powerful tool for the study of reactivity and selectivity in a molecule [30]. Chemical potential, hardness and softness are the global properties related to the chemical reactivity, whereas local reactivity is related to selectivity concept. The most important local reactivity parameter is the Fukui function. The Fukui function for a molecule has been defined as the derivative of electron density with respect to the change of number of electrons, keeping the positions of nuclei unchanged [31, 32]. Fukui function gives us information about a highly electrophilic / nucleophilic center in a molecule. In practice a convenient way of calculating the Fukui functions at atomic resolution is to use the condensed Fukui functions [33]. The condensed Fukui function f_k^+ for nucleophilic attack, f_k^- for electrophilic attack and f_k^0 for free radical attack can be expressed as:

For nucleophilic attack $f_k^+ = [q_k(N+1) - q_k(N)]$

For electrophilic attack $f_k^- = [q_k(N) - q_k(N-1)]$

For radical attack $f_k^0 = [q_k(N+1) - q_k(N-1)]/2$

Where q_k is the electronic population of atom k in the neutral (N), anionic (N+1) or cationic (N-1) chemical species. Morrel *et al.* [34] have proposed a new dual descriptor $\Delta f(r)$ for nucleophilicity and electrophilicity. It is defined as the difference between the nucleophilic and electrophilic Fukui function and is given by the equation:

$$\Delta f(r) = [f_k^+ - f_k^-]$$

If $\Delta f(r) > 0$, then the site is electrophilic, if $\Delta f(r) < 0$, then the site is nucleophilic. In the title compounds, the order of the reactive sites for electrophilic attack, nucleophilic attack and free radical attacks is given in Tables 5 and 6.

Table 5: Order of the reactive sites on compounds 1 and 2

| Compound 1 | | | | | Compound 2 | | | | |
|------------|-------|-------|-------|--------|------------|-------|-------|-------|--------|
| Atom | 6 C | 25 C | 17 N | 7 C | Atom | 6 C | 2 C | 7 C | 22 C |
| f^+ | 0.148 | 0.008 | 0.003 | -0.011 | f^+ | 0.035 | 0.025 | 0.011 | 0.000 |
| Atom | 8 C | 6 C | 17 N | 25 C | Atom | 24 C | 6 C | 2 C | 7 C |
| f^- | 0.014 | 0.007 | 0.007 | 0.005 | f^- | 0.012 | 0.007 | 0.003 | 0.002 |
| Atom | 6 C | 25 C | 17 N | 8 C | Atom | 6 C | 2 C | 7 C | 22 C |
| f^0 | 0.078 | 0.007 | 0.005 | 0.000 | f^0 | 0.021 | 0.014 | 0.007 | -0.002 |

Table 6: Order of the reactive sites on compound 3

| Compound 3 | | | | |
|------------|-------|-------|-------|-------|
| Atom | 6 C | 2 C | 19 C | 7 C |
| f^+ | 0.043 | 0.023 | 0.019 | 0.012 |
| Atom | 19 C | 2 C | 6 C | 7 C |
| f^- | 0.006 | 0.005 | 0.005 | 0.002 |
| Atom | 6 C | 2 C | 19 C | 7 C |
| f^0 | 0.024 | 0.014 | 0.012 | 0.007 |

For compounds 1, 2 and 3, the parameters of local reactivity descriptors show that 6C is the more reactive site for nucleophilic and radical attacks. The more reactive sites for electrophilic attacks are 8C, 24C and 19C for compounds 1, 2 and 3 respectively.

3.6. Natural Bond Orbital Analysis (NBO)

Natural bond analysis gives the accurate possible natural Lewis structure picture of ϕ because all orbital mathematically chosen to include the highest possible percentage of the electron density. Interaction between both filled and virtual orbital spaces information correctly explained by the NBO analysis, it could enhance the analysis of intra- and intermolecular interactions. The second order Fock matrix was carried out to evaluate donor (i) acceptor (j) i.e. donor level bonds to acceptor level bonds interaction in the NBO analysis [35]. The result of interaction is a loss of occupancy from the concentrations of electron NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j). The stabilization energy $E^{(2)}$ associates with the delocalization $i \rightarrow j$ is estimated as,

$$E^{(2)} = -q_i \left(\frac{(F_{ij})^2}{\varepsilon_j - \varepsilon_i} \right)$$

Where q_i is the donor orbital occupancy, ε_j and ε_i are diagonal elements and $F(i,j)$ is the off diagonal NBO Fock matrix element. Natural bond orbital analysis is used for investigating charge transfer or conjugative interaction in the molecular system. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulted from the second-order micro-disturbance theory are reported [36, 37]. The larger $E^{(2)}$ value the more intensive is the interaction between electron donor and acceptor, i.e. the more donation tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system [38]. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydberg) non-Lewis NBO orbitals correspond to a stabilization donor-acceptor interaction. An NBO analysis allowed us to investigate which orbital interactions are mainly involved in the stability of the amino methyl tetrathiafulvalenes **1-3**.

In NBO analysis large $E^{(2)}$ value shows the intensive interaction between electron-donors and electron- acceptors, and greater the extent of conjugation of the whole system, the possible intensive interaction are given in Tables 7-9.

Table 7: 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(2)S10 | 1.78379 | $\pi^*(C1-C3)$ | 0.21587 | 21.96 | 0.26 | 0.067 |
| LP(2)S11 | 1.78504 | $\pi^*(C1-C3)$ | 0.21587 | 21.80 | 0.26 | 0.067 |
| LP(2)S12 | 1.78590 | $\pi^*(C7-C8)$ | 0.22820 | 21.27 | 0.26 | 0.066 |
| LP(2)S13 | 1.78692 | $\pi^*(C7-C8)$ | 0.22820 | 21.02 | 0.26 | 0.066 |
| LP(2)S12 | 1.78590 | $\pi^*(C2-C6)$ | 0.38816 | 15.82 | 0.26 | 0.060 |
| LP(2)S10 | 1.78379 | $\pi^*(C2-C6)$ | 0.38816 | 15.74 | 0.26 | 0.060 |
| LP(2)S13 | 1.78692 | $\pi^*(C2-C6)$ | 0.38816 | 15.56 | 0.26 | 0.060 |
| LP(1)N17 | 1.90468 | $\sigma^*(C19-C22)$ | 0.03112 | 8.98 | 0.66 | 0.070 |
| LP(1)N17 | 1.90468 | $\sigma^*(C14-H16)$ | 0.03301 | 8.81 | 0.71 | 0.072 |
| $\sigma(C7-H9)$ | 1.97407 | $\sigma^*(C8-S12)$ | 0.03876 | 6.16 | 0.75 | 0.061 |
| $\sigma(C3-H5)$ | 1.97556 | $\sigma^*(C1-S11)$ | 0.02124 | 5.42 | 0.76 | 0.057 |
| $\sigma(C1-H4)$ | 1.97565 | $\sigma^*(C3-S10)$ | 0.02144 | 5.40 | 0.76 | 0.057 |
| $\sigma(C14-H16)$ | 1.97997 | $\sigma^*(C8-S12)$ | 0.03876 | 5.34 | 0.71 | 0.055 |
| $\sigma(C6-S12)$ | 1.97164 | $\sigma^*(C2-S11)$ | 0.04202 | 5.20 | 0.81 | 0.058 |
| $\sigma(C6-S13)$ | 1.97285 | $\sigma^*(C2-S10)$ | 0.04192 | 5.18 | 0.81 | 0.058 |
| $\sigma(C2-S10)$ | 1.97288 | $\sigma^*(C6-S13)$ | 0.04226 | 5.10 | 0.82 | 0.058 |
| $\sigma(C2-S11)$ | 1.97338 | $\sigma^*(C6-S12)$ | 0.04352 | 4.97 | 0.83 | 0.058 |
| $\sigma(C7-S13)$ | 1.97867 | $\sigma^*(C8-C14)$ | 0.02693 | 4.93 | 1.06 | 0.065 |
| $\pi(C7-C8)$ | 1.96620 | $\sigma^*(C14-H15)$ | 0.02214 | 2.74 | 0.73 | 0.040 |
| $\pi(C7-C8)$ | 1.96620 | $\sigma^*(C14-N17)$ | 0.02058 | 2.49 | 0.66 | 0.036 |

Table 8: 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(2)S11 | 1.78301 | $\pi^*(C1-C3)$ | 0.21498 | 21.81 | 0.26 | 0.067 |
| LP(2)S10 | 1.78339 | $\pi^*(C1-C3)$ | 0.21498 | 21.74 | 0.26 | 0.067 |
| LP(2)S13 | 1.78638 | $\pi^*(C7-C8)$ | 0.22567 | 21.00 | 0.26 | 0.067 |
| LP(2)S12 | 1.79373 | $\pi^*(C7-C8)$ | 0.22567 | 20.86 | 0.27 | 0.067 |
| $\pi(C24-C27)$ | 1.66861 | $\pi^*(C22-C23)$ | 0.34610 | 20.69 | 0.28 | 0.069 |
| $\pi(C22-C23)$ | 1.66381 | $\pi^*(C25-C29)$ | 0.32852 | 20.56 | 0.28 | 0.068 |
| $\pi(C24-C27)$ | 1.66861 | $\pi^*(C25-C29)$ | 0.32852 | 20.19 | 0.28 | 0.067 |
| $\pi(C25-C29)$ | 1.66867 | $\pi^*(C24-C27)$ | 0.31764 | 20.00 | 0.28 | 0.067 |
| $\pi(C25-C29)$ | 1.66867 | $\pi^*(C22-C23)$ | 0.34610 | 19.86 | 0.28 | 0.067 |
| $\pi(C22-C23)$ | 1.66381 | $\pi^*(C24-C27)$ | 0.31764 | 19.46 | 0.28 | 0.067 |
| LP(2)S10 | 1.78339 | $\pi^*(C2-C6)$ | 0.39163 | 15.92 | 0.26 | 0.060 |

| | | | | | | |
|------------------|---------|----------------------|---------|-------|------|-------|
| LP(2)S11 | 1.78301 | π^* (C2-C6) | 0.39163 | 15.92 | 0.26 | 0.060 |
| LP(2)S13 | 1.78638 | π^* (C2-C6) | 0.39163 | 15.85 | 0.26 | 0.060 |
| LP(2)S12 | 1.79373 | π^* (C2-C6) | 0.39163 | 15.56 | 0.26 | 0.060 |
| LP(1)N17 | 1.91519 | σ^* (C14-H15) | 0.03495 | 7.98 | 0.72 | 0.068 |
| LP(1)N17 | 1.91519 | σ^* (C19-H20) | 0.03004 | 7.54 | 0.73 | 0.067 |
| σ (C8-H9) | 1.97225 | σ^* (C7-S12) | 0.03107 | 6.37 | 0.74 | 0.061 |
| σ (C1-H4) | 1.97553 | σ^* (C3-S10) | 0.02148 | 5.42 | 0.76 | 0.057 |
| σ (C3-H5) | 1.97556 | σ^* (C1-S11) | 0.02133 | 5.41 | 0.76 | 0.057 |
| LP(1)S11 | 1.97389 | σ^* (C2-S10) | 0.04167 | 3.89 | 0.81 | 0.050 |

Table 9: 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)N17 | 1.81851 | π^* (C19-C21) | 0.40137 | 28.44 | 0.32 | 0.090 |
| π (C24-C26) | 1.67377 | π^* (C20-C22) | 0.32743 | 22.00 | 0.28 | 0.070 |
| LP(2)S11 | 1.78142 | π^* (C1-C3) | 0.21435 | 21.74 | 0.26 | 0.067 |
| LP(2)S10 | 1.78176 | π^* (C1-C3) | 0.21435 | 21.68 | 0.26 | 0.067 |
| π (C19-C21) | 1.66070 | π^* (C24-C26) | 0.34787 | 21.63 | 0.29 | 0.071 |
| LP(2)S12 | 1.79186 | π^* (C7-C8) | 0.22980 | 21.16 | 0.26 | 0.067 |
| LP(2)S13 | 1.78605 | π^* (C7-C8) | 0.22980 | 21.14 | 0.26 | 0.067 |
| π (C20-C22) | 1.72528 | π^* (C19-C21) | 0.40137 | 20.48 | 0.28 | 0.070 |
| π (C24-C26) | 1.67377 | π^* (C19-C21) | 0.40137 | 18.23 | 0.27 | 0.064 |
| π (C19-C21) | 1.66070 | π^* (C20-C22) | 0.32743 | 16.98 | 0.29 | 0.062 |
| π (C20-C22) | 1.72528 | π^* (C24-C26) | 0.34787 | 16.94 | 0.29 | 0.064 |
| LP(2)S10 | 1.78176 | π^* (C2-C6) | 0.39093 | 16.13 | 0.26 | 0.061 |
| LP(2)S11 | 1.78142 | π^* (C2-C6) | 0.39093 | 16.13 | 0.26 | 0.061 |
| LP(2)S13 | 1.78605 | π^* (C2-C6) | 0.39093 | 15.53 | 0.26 | 0.059 |
| LP(2)S12 | 1.79186 | π^* (C2-C6) | 0.39093 | 15.25 | 0.26 | 0.059 |
| LP(1)N17 | 1.81851 | σ^* (C14-H15) | 0.03357 | 8.40 | 0.70 | 0.071 |
| σ (C8-H9) | 1.97276 | σ^* (C7-S12) | 0.03072 | 6.27 | 0.74 | 0.061 |
| σ (C1-H4) | 1.97545 | σ^* (C3-S10) | 0.02150 | 5.43 | 0.76 | 0.057 |
| σ (C3-H5) | 1.97549 | σ^* (C1-S11) | 0.02137 | 5.42 | 0.76 | 0.057 |
| LP(1)S10 | 1.97380 | σ^* (C2-S11) | 0.04157 | 3.90 | 0.81 | 0.050 |

The intra molecular interaction for the title compounds is formed by the orbital overlap between: π (C7-C8) and σ^* (C14-H15) for compound 1, π (C24-C27) and π^* (C22-C23) for compound 2, π (C24-C26) and π^* (C20-C22) for compound 3 respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of π (C7-C8) to σ^* (C14-H15) for compound 1, π (C24-C27) to π^* (C22-C23) for compound 2 and π (C24-C26) to π^* (C20-C22) for compound 3 lead to highest stabilization of 2.74, 20.69 and 22 kJ mol⁻¹ respectively. In case of LP(2)S10 orbital to the π^* (C1-C3) for compound 1, LP(2)S11 orbital to π^* (C1-C3) for compound 2, LP(1)N17 orbital to π^* (C19-C21) for compound 3 respectively, show the stabilization energy of 21.96, 21.81 and 28.44 kJ mol⁻¹ respectively.

3.7. Nonlinear Optical Properties (NLO)

The first order hyperpolarizabilities of amino methyl tetrathiafulvalenes molecules is calculated using B3LYP/6-31G(d,p) level of basis set, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to Kleinman symmetry [39]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the $3 \times 3 \times 3$ matrixes is a tetrahedral. The components of β are defined as the

coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes:

$$E = E^0 - \mu_\alpha F_\alpha - 1/2 \alpha_{\alpha\beta} F_\alpha F_\beta - 1/6 \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma$$

Where E^0 is the energy of the unperturbed molecules. F_α is the field at the origin and μ_α ; $\alpha_{\alpha\beta}$; $\beta_{\alpha\beta\gamma}$ is the components of the dipole moment, polarizability and the first order hyperpolarizabilities respectively. The total static dipole moment μ , the mean polarizability α_0 , the anisotropy of polarizability $\Delta\alpha$ and the mean first hyperpolarizability β_0 , using the x, y, z components are defined as

The total static dipole moment is

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

The isotropic polarizability is

$$\alpha_0 = \frac{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})}{3}$$

$$\Delta\alpha = 2^{1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2]^{1/2}$$

and the average hyperpolarizability is

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

Table 10 lists the values of the electric dipole moment (Debye) and dipole moment components. polarizabilities and hyperpolarizabilities of the amino methyl tetrathiafulvalenes 1-3. In addition to the isotropic polarizabilities and polarizabilities anisotropy invariant were also calculated.

Table 10: The dipole moments μ (D), polarizability α , the anisotropy of the polarizability $\Delta\alpha$ (esu), and the first hyperpolarizability β (esu) of amino methyl tetrathiafulvalenes **1-3** calculated by B3LYP/6-31G(d,p) method.

| Parameters | Compound 1 | Compound 2 | Compound 3 |
|--|------------|------------|------------|
| β_{xxx} | 89.3608 | -147.1828 | -148.9244 |
| B_{yyy} | -2.3332 | 1.5827 | -0.4758 |
| B_{zzz} | 0.5027 | 2.4147 | -1.3950 |
| B_{xyy} | -0.5811 | 17.6863 | 3.3468 |
| B_{xxy} | -38.7369 | 6.2484 | -33.1352 |
| B_{xxz} | 3.7906 | -2.5458 | 27.1669 |
| B_{xzz} | -22.4931 | 8.9055 | 6.7711 |
| B_{yzz} | -2.3639 | -3.8876 | 0.9251 |
| B_{yyz} | 3.1657 | 3.5499 | 1.0603 |
| B_{xyz} | -2.5582 | 8.9900 | -16.4806 |
| $B_{tot}(\text{esu}) \times 10^{-33}$ | 783.8292 | 1117.8615 | 1418.3470 |
| μ_x | -1.7750 | 0.6850 | -0.3682 |
| μ_y | 0.1315 | -0.7675 | -0.3768 |
| μ_z | 0.5833 | 0.2499 | 0.0555 |
| $\mu_{tot}(\text{D})$ | 1.8731 | 1.0586 | 0.5298 |
| α_{xx} | -97.3608 | -111.1080 | -114.7304 |
| α_{yy} | -122.9225 | -134.2826 | -134.5315 |
| α_{zz} | -127.6286 | -143.5612 | -143.7162 |
| α_{xy} | -5.8857 | -0.5837 | 5.4723 |
| α_{xz} | 0.1706 | -6.4007 | -5.3997 |
| α_{yz} | 0.5409 | 0.9099 | -3.0989 |
| $\alpha_0(\text{esu}) \times 10^{-24}$ | -17.1868 | -19.2142 | -19.4131 |
| $\Delta\alpha(\text{esu}) \times 10^{-24}$ | 4.4478 | 4.6028 | 4.3573 |

Since the values of the polarizabilities ($\Delta\alpha$) and the hyperpolarizabilities (β_{tot}) 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 1.8731, 1.0586 and 0.5298 D respectively, which are approximately one 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 -17.1868×10^{-24} , -19.2142×10^{-24} and -19.4131×10^{-24} esu respectively; the values of anisotropy of the polarizability are 4.4478, 4.6028 and 4.3573 esu, respectively. The magnitude of the molecular hyperpolarizability (β) is one of important key factors in a NLO system. The DFT/6-31G(d,p) calculated first hyperpolarizability value (β) of amino methyl tetrathiafulvalenes molecules are equal to 783.8292×10^{-33} , $1117.8615 \times 10^{-33}$ and $1418.3470 \times 10^{-33}$ esu. The first hyperpolarizability of title molecules is approximately 2.28, 3.26 and 4.13 times than those of urea (β of urea is 343.272×10^{-33} esu obtained by B3LYP/6-311G (d,p) method). This result indicates the non-linearity of the amino methyl tetrathiafulvalenes **1-3**.

Conclusion

In this work, we have determined the molecular structural parameters like bond length, bond angle and dihedral angles of the optimized geometry, the stability and the reactivity of title molecules within DFT calculations using B3LYP/6-31G(d,p) basis sets. The other molecular properties such as hardness (η), softness (S), chemical potential (μ), electronegativity (χ) and electrophilicity index (ω) were described. NBO result reflects the charge transfer within the molecule and the maximum charge delocalization takes place

during $\pi \rightarrow \pi^*$ transition. The band gap of amino methyl tetrathiafulvalenes **2** molecule was determined about 3.416 eV, which leads the molecule becomes less stability and more reactivity.

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