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Research Article

**THEORETICAL INVESTIGATIONS ON MOLECULAR
STRUCTURE, HOMO, LUMO, NBO ANALYSIS AND
HYPERPOLARIZABILITY CALCULATIONS OF MONO AND
EXTENDED-TETRATHIAFULVALENES (MONO/EX-TTFS)**Tahar Abbaz^{1*}, Amel Bendjeddou¹ and Didier Villemin²¹ Laboratory of Aquatic and Terrestrial Ecosystems, Org. and Bioorg. Chem. Group, University of Mohamed-Cherif Messaadia, Souk Ahras, 41000, Algeria² Laboratory of Molecular and Thio-Organic Chemistry, UMR CNRS 6507, INC3M, FR 3038, Labex EMC3, ensicaen & University of Caen, Caen 14050, France**Abstract:**

The optimized molecular structure of (Mono/ex-TTFS) 1-4 has been investigated theoretically using Gaussian 09 software package. This theoretical calculation was carried out by density functional theory (DFT) using B3LYP with 6-31G (d,p) basis set. The stability of the molecule arising from hyper-conjugative interaction and load delocalization has been analyzed using NBO analysis. The HOMO and LUMO energies were also evaluated for these molecules to demonstrate the chemical stability. First and second hyperpolarizability are calculated in order of their role in non-linear optics. Molecular electrostatic potential and all other calculations were performed by the same method cited above.

Keywords: tetrathiafulvalenes; density functional theory; computational chemistry; electronic structure; quantum chemical calculations.

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1. INTRODUCTION:

Tetrathiafulvalene TTF is rare among organic compounds in that it is characterized by a relatively simple structure yet is associated with a broad range of applications [1–5]. This π -electron donor, synthesized nearly forty years ago [6,7], has received a tremendous attention over the years.

The TTF system has received a renewed interest in recent years. This has been due in part to advances in synthetic methods that have resulted in a myriad of new TTF derivatives becoming available for use as “molecular building blocks”. This, in turn, has opened the door to an incredible variety of new functions and applications [8].

The syntheses of two dithiole rings separated by a conjugated spacer have received great attention as a consequence of their potential interest in the preparation of compounds with nonlinear optical properties or useful as semiconductors. The synthesis of derivatives and analogues of dithiafulvalene and tetrathiafulvalene is of considerable interest [9].

For decades, considerable efforts have been made to design and synthesize novel π -extended analogues of TTF (ex-TTFs) in order to exploit the application in electronic and optoelectronic devices.

The present work aims to investigate the molecular structure, electronic and non-linear optical properties of (Mono/ex-TTFs) **1-4** described in literature [10]. We give a global study of the molecular geometry, natural bond orbital (NBO) analysis, nonlinear

optical (NLO) properties, energies HOMO, LUMO and gap, global and local reactivity descriptors to predict their applications.

2. MATERIALS AND METHODS

Calculations of the title compounds were carried out with Gaussian 09 software [11] using DFT/B3LYP with 6-31G(d,p) basis set to predict the molecular structure. This basis set was chosen particularly because of its advantage of doing faster calculations with relatively better accuracy and structures and it contains both soft and polarization functions and it has proven to yield reliable descriptions of the molecular structure [12,13]. The assignments of the calculated geometries are aided by the animation option of GAUSSVIEW program [14]. The theoretically optimized geometrical parameters are given in Tables 1-4.

3. RESULTS AND DISCUSSION

3.1. Molecular Geometry

(Mono/ex-TTFs) **1-4** are subjected to geometry optimization in the ground state. The optimized structure belongs to C₁ point group symmetry. The molecular structure along with numbering of atoms of (Mono/ex-TTFs) molecules is obtained from Gaussian 09 and GAUSSVIEW programs and is shown in Fig 1. The most optimized structural parameters (bond length, bond angle and dihedral angles) calculated by DFT/B3LYP with 6-31G(d,p) basis set are presented in Tables 1-4.

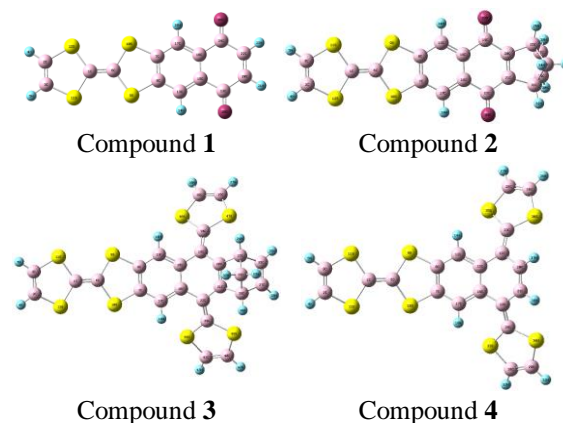


Fig. 1. Optimized molecular structure of (Mono/ex-TTFs) 1-4

Table 1: Optimized geometric parameters of compound 1

| Bond Length(Å) | Bond Angles (°) | | Dihedral Angles (°) | | |
|----------------|-----------------|-------------|---------------------|----------------|---------|
| R(1.6) | 1.349 | A(6.1.11) | 123.095 | D(12.1.6.9) | 179.999 |
| R(1.11) | 1.787 | A(11.1.12) | 113.810 | D(6.1.12.2) | 179.998 |
| R(1.12) | 1.787 | A(3.2.4) | 124.925 | D(12.2.3.5) | 180.000 |
| R(2.3) | 1.336 | A(3.2.12) | 118.074 | D(5.3.11.1) | 179.999 |
| R(2.4) | 1.083 | A(4.2.12) | 117.002 | D(1.6.9.8) | 179.993 |
| R(3.11) | 1.762 | A(1.6.9) | 122.737 | D(17.7.10.6) | 179.996 |
| R(7.8) | 1.410 | A(8.7.10) | 116.827 | D(10.7.17.16) | 179.999 |
| R(7.17) | 1.393 | A(8.7.17) | 120.250 | D(8.13.15.19) | 180.000 |
| R(8.13) | 1.393 | A(10.7.17) | 122.923 | D(14.13.15.16) | 180.000 |
| R(13.15) | 1.397 | A(6.9.8) | 95.910 | D(19.15.16.17) | 180.000 |
| R(16.24) | 1.490 | A(8.13.15) | 119.571 | D(16.15.19.25) | 179.999 |
| R(19.25) | 1.226 | A(15.19.20) | 117.152 | D(17.16.24.22) | 179.999 |
| R(20.22) | 1.343 | A(20.19.25) | 120.628 | D(15.19.20.21) | 179.999 |
| R(22.24) | 1.485 | A(19.20.21) | 115.405 | D(19.20.22.23) | 180.000 |
| R(24.26) | 1.226 | A(21.20.22) | 122.379 | D(20.22.24.26) | 179.999 |

Table 2: Optimized geometric parameters of compound 2

| Bond Length(Å) | Bond Angles (°) | | Dihedral Angles (°) | | |
|----------------|-----------------|-------------|---------------------|----------------|---------|
| R(1.6) | 1.349 | A(6.1.11) | 123.097 | D(12.1.6.9) | 180.001 |
| R(1.11) | 1.788 | A(11.1.12) | 113.805 | D(6.1.12.2) | 179.848 |
| R(2.3) | 1.337 | A(3.2.12) | 118.085 | D(5.3.11.1) | 179.930 |
| R(3.5) | 1.083 | A(5.3.11) | 117.007 | D(9.8.13.15) | 179.995 |
| R(6.10) | 1.785 | A(8.7.17) | 120.193 | D(13.15.19.20) | 179.111 |
| R(7.8) | 1.408 | A(9.8.13) | 122.949 | D(15.19.20.25) | 178.736 |
| R(7.17) | 1.394 | A(8.13.15) | 119.785 | D(19.20.25.33) | 145.882 |
| R(15.16) | 1.413 | A(16.15.19) | 121.334 | D(20.21.22.24) | 179.260 |
| R(17.18) | 1.085 | A(16.22.21) | 115.217 | D(20.21.31.32) | 163.494 |
| R(20.21) | 1.353 | A(21.22.24) | 122.517 | D(22.21.31.29) | 112.951 |
| R(20.25) | 1.531 | A(26.25.27) | 116.738 | D(20.25.27.28) | 111.501 |
| R(22.24) | 1.228 | A(25.27.29) | 107.492 | D(20.25.33.35) | 170.884 |
| R(25.27) | 1.545 | A(21.31.33) | 97.891 | D(25.27.29.30) | 176.543 |
| R(27.29) | 1.336 | A(25.33.31) | 92.702 | D(30.29.31.33) | 147.655 |
| R(31.33) | 1.565 | A(34.33.35) | 110.414 | D(29.31.33.34) | 170.579 |

Table 3: Optimized geometric parameters of compound 3

| Bond Length(Å) | Bond Angles (°) | | Dihedral Angles (°) | | |
|----------------|-----------------|-------------|---------------------|----------------|---------|
| R(1,6) | 1.330 | A(6,1,11) | 124.135 | D(12,1,6,9) | 179.944 |
| R(1,11) | 1.760 | A(11,1,12) | 111.730 | D(6,1,12,2) | 179.960 |
| R(2,3) | 1.332 | A(3,2,12) | 116.784 | D(5,3,11,1) | 179.980 |
| R(2,4) | 1.086 | A(2,3,5) | 126.914 | D(10,7,8,13) | 178.977 |
| R(7,8) | 1.396 | A(1,6,10) | 123.401 | D(10,7,17,16) | 179.014 |
| R(7,17) | 1.392 | A(8,7,17) | 121.029 | D(14,13,15,16) | 175.662 |
| R(13,14) | 1.093 | A(8,13,15) | 118.930 | D(16,15,19,34) | 143.926 |
| R(15,19) | 1.486 | A(16,15,19) | 119.046 | D(22,16,17,7) | 178.236 |
| R(20,21) | 1.368 | A(16,17,18) | 121.097 | D(20,19,34,46) | 172.485 |
| R(25,27) | 1.346 | A(22,21,29) | 131.473 | D(19,20,23,31) | 143.614 |
| R(29,31) | 1.581 | A(23,25,27) | 107.781 | D(20,21,29,30) | 162.133 |
| R(35,36) | 1.331 | A(23,31,32) | 114.047 | D(20,23,31,33) | 171.403 |
| R(39,44) | 1.754 | A(32,31,33) | 108.078 | D(28,27,29,31) | 145.169 |
| R(40,41) | 1.331 | A(35,36,46) | 116.692 | D(27,29,31,32) | 170.824 |
| R(41,44) | 1.758 | A(41,40,42) | 127.015 | D(22,39,44,41) | 178.508 |

Table 4: Optimized geometric parameters of compound 4

| Bond Length(Å) | Bond Angles (°) | Dihedral Angles (°) |
|----------------|-----------------|---------------------|
| R(1,6) | 1.350 | A(6,1,11) 123.207 |
| R(1,12) | 1.787 | A(11,1,12) 113.585 |
| R(2,3) | 1.337 | A(3,2,4) 124.909 |
| R(2,4) | 1.083 | A(2,3,11) 117.959 |
| R(6,10) | 1.783 | A(8,7,10) 116.566 |
| R(7,17) | 1.389 | A(8,7,17) 119.756 |
| R(13,15) | 1.407 | A(6,9,8) 94.792 |
| R(15,19) | 1.477 | A(8,13,14) 118.351 |
| R(19,23) | 1.375 | A(13,15,19) 121.567 |
| R(21,22) | 1.455 | A(15,19,20) 114.783 |
| R(22,28) | 1.375 | A(15,19,23) 126.094 |
| R(23,35) | 1.784 | A(20,21,22) 122.033 |
| R(24,36) | 1.754 | A(19,23,36) 121.126 |
| R(28,34) | 1.792 | A(30,29,31) 125.127 |
| R(30,33) | 1.757 | A(28,33,30) 96.344 |

3.2. Molecular Electrostatic Potential

Molecular electrostatic used extensively for interpreting potentials have been and predicting the reactive behavior of a wide variety of chemical system in both electrophilic and nucleophilic reactions, the study of biological recognition processes and hydrogen bonding interactions [15]. $V(r)$, at a given point $r(x, y, z)$ in the vicinity of a molecule, is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and positive test charge (a proton) located at r . Unlike many of the other quantities used at present and earlier as indices of reactivity, $V(r)$ is a real physical property that can be determined experimentally by diffraction or by computational methods. For the systems studied the MEP values were calculated as described previously, using the equation [16]:

$$v(r) = \sum \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')}{|r' - r|} dr'$$

Where the summation runs over all the nuclei A in the molecule and polarization and reorganization effects are neglected. Z_A is the charge of the nucleus A, located at R_A and $\rho(r')$ is the electron density function of the molecule. To predict reactive sites for electrophilic and nucleophilic attack for the investigated molecule, molecular electrostatic potential (MEP) was calculated at B3LYP/6-31G(d) optimized geometries. 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. In the present study, 3D plots of molecular electrostatic potential (MEP) of (Mono/ex-TTFs) **1-4** has been draw in Fig 2.

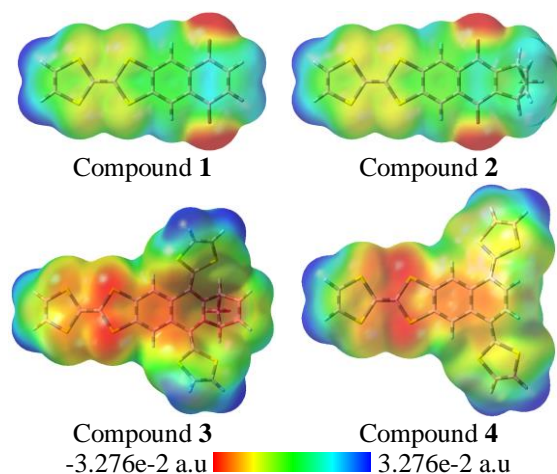


Fig. 2: Molecular electrostatic potential surface of (Mono/ex-TTFs) 1-4

As seen from the figure 2 that, in the compounds 1 and 2, the regions exhibiting the negative electrostatic potential are localized near the oxygen atoms for the carbonyl groups and for the compounds 3 and 4 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 of alkyl and cycled groups in the all molecules.

3.3. Frontier Molecular Orbitals (FMOs)

The highest occupied molecular orbital's (HOMO) and the lowest-lying unoccupied molecular orbital's (LUMO) are named as frontier molecular orbital's (FMO). The FMO plays an important role in the optical and electric properties, as well as in quantum chemistry [17]. 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 [18,19]. The hard molecules are not more polarizable than the soft ones because they need big energy to excitation. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the compound 1 with a small energy gap are given in Fig 3.

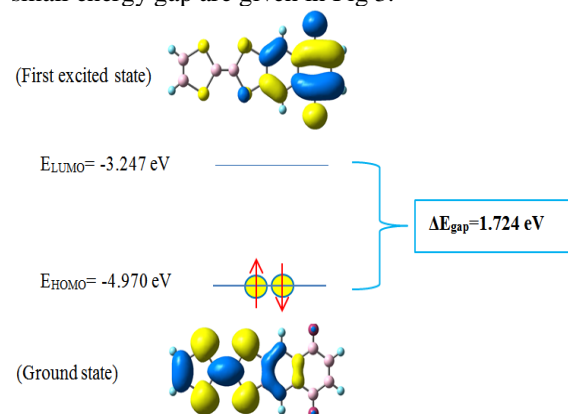


Fig. 3: HOMO-LUMO Structure with the energy level diagram of compound 1

According to Figure 3, the positive phase is shown as blue color region whereas the negative one is provided as yellow color region.

3.4. Global Reactivity Descriptors

In the light of density functional theory, it can be possible to define universal concepts of molecular structural stability and reactivity through the global reactivity parameters. These global reactivity parameters are the electronic chemical potential (μ) and hardness (η) which may be defined by the following equations [20,21],

$$\mu = - \left(\frac{\partial E}{\partial N} \right)_{v(\vec{r})}$$

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\vec{r})} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(\vec{r})}$$

Where E, N and $v(\vec{r})$ respectively are the total energy of the system, the number of electrons in the system and the external potential of the system. For the sake of simplicity and computational time, we have taken recourse to calculate the chemical hardness (η) and chemical potential (μ) in the spirit of Koopmans' theorem employing the following equations [20]:

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2}$$

$$\mu = \frac{E_{LUMO} + E_{HOMO}}{2}$$

The global electrophilicity index (ω) as defined by Parr et al. has been described as [22]:

$$\omega = \frac{\mu^2}{2\eta}$$

The global electrophilicity index is a useful parameter that permits to have an insight into the reactivity of a molecule in its ground state. It can be reckoned that the hardness is directly connected with the stability and reactivity of a chemical system in its ground state. Again, the hardness is the measure of the resistance imparted during the change in the electronic distribution in a molecule [20,21,23]. Conclusively, larger the value of η for a complex, the higher is its stability and lesser is its reactivity. The chemical potential, μ describes the change in electronic energy with respect to the number of electrons and is usually associated with the charge transfer ability of the system in its ground state. Alternatively, this μ is the index of escaping tendency of electrons from an equilibrium system. Energies of frontier molecular orbitals (E_{HOMO} , E_{LUMO}), have been used to calculate global reactivity descriptors such as, electronegativity (χ), chemical potential (μ), Global hardness (η), global softness (S), and electrophilicity index (ω) of (Mono/ex-TTFs) 1-4 have been listed in Table 5.

Table 5: Quantum chemical descriptors of (Mono/ex-TTFs) 1-4

| Parameters | Compound 1 | Compound 2 | Compound 3 | Compound 4 |
|------------------------------|------------|------------|------------|------------|
| E_{HOMO} (eV) | -4.970 | -4.871 | -4.257 | -4.342 |
| E_{LUMO} (eV) | -3.247 | -3.124 | -1.515 | -1.546 |
| ΔE_{gap} (eV) | 1.724 | 1.747 | 2.742 | 2.796 |
| I (eV) | 4.970 | 4.871 | 4.257 | 4.342 |
| A (eV) | 3.247 | 3.124 | 1.515 | 1.546 |
| μ (eV) | -4.108 | -3.998 | -2.886 | -2.944 |
| χ (eV) | 4.108 | 3.998 | 2.886 | 2.944 |
| η (eV) | 0.862 | 0.873 | 1.371 | 1.398 |
| S (eV) | 0.580 | 0.572 | 0.365 | 0.358 |
| ω (eV) | 9.793 | 9.149 | 3.038 | 3.099 |

As presented in table 5, the compound which have the lowest energetic gap is the compound **1** ($\Delta E_{\text{gap}} = 1.724$ eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound **4** ($\Delta E_{\text{gap}} = 2.796$ eV). The compound that has the highest HOMO energy is the compound **3** ($E_{\text{HOMO}} -4.257$ eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound **1** ($E_{\text{LUMO}} = -3.247$ 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 **3** has lowest value of the potential ionization ($I = 4.257$ eV), so that will be the better electron donor. Compound **1** has the largest value of the affinity ($A = 3.247$ eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound **1** ($\eta = 0.862$ eV, $S = 0.580$ 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 ($\chi = 4.108$ eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **1** ($\omega = 9.793$ 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.

3.5. Local Reactivity Descriptors

The frontier-electron theory of chemical reactivity by Fukui recognizes the key role of the valence electrons in forming molecules and considers therefore the distribution of the highest energy orbital electron density as being most important for electrophilic attack and the lowest energy vacant orbitals in nucleophilic substitution reactions. In reactions with radicals both orbitals become important. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are in this way considered as the principal factors governing the easiness of chemical reactions and the stereo selective path. Parr and Yang [24] have demonstrated that most of the frontier-electron density theory of chemical reactivity can be rationalized from the DFT. Parr and Yang defined a Fukui function (f_k) to describe electrophilic attack (f_k^-), nucleophilic attack (f_k^+) and neutral (radical) attack (f_k^0). Yang and Mortier proposed a finite difference approach to calculate Fukui function indices [25]. In a finite difference approximation, the condensed Fukui function values are given Yang et al. as

$$f^+ = [q(N+1) - q(N)], \text{ for nucleophilic attack,}$$

$$f^- = [q(N) - q(N-1)], \text{ for electrophilic attack,}$$

$$f^0 = [q(N+1) - q(N-1)]/2, \text{ for radical attack.}$$

Where q_k is the gross charge of the k^{th} atom in the neutral (N), anionic (N+1) and cationic (N-1) molecule, respectively, all with the ground state geometry of the N electron molecule. Gross charges may be determined by Mulliken, Hirshfeld and Natural charge analysis. In a molecular system, the atomic site, which possesses the highest condensed Fukui function, favors the higher reactivity. Fukui functions for selected atomic sites in (Mono/ex-TTFs) **1-4** are shown in Tables 6-7.

Table 6: Order of the reactive sites on compounds 1 and 2

| Compound 1 | | | | | Compound 2 | | | | |
|------------|-------|--------|--------|--------|------------|-------|--------|--------|--------|
| Atom | 6 C | 15 C | 16 C | 1 C | Atom | 23 O | 24 O | 19 C | 22 C |
| f^+ | 0.026 | -0.002 | -0.002 | -0.014 | f^+ | 0.116 | 0.116 | 0.072 | 0.072 |
| Atom | 7 C | 8 C | 1 C | 19 C | Atom | 6 C | 7 C | 8 C | 1 C |
| f^- | 0.016 | 0.016 | 0.001 | -0.007 | f^- | 0.010 | -0.002 | -0.002 | -0.015 |
| Atom | 6 C | 7 C | 8 C | C1 | Atom | 7 C | 8 C | 19 C | 22 C |
| f^0 | 0.004 | -0.001 | -0.001 | -0.007 | f^0 | 0.008 | 0.008 | 0.000 | 0.000 |

Table 7: Order of the reactive sites on compounds 3 and 4

| Compound 3 | | | | | Compound 4 | | | | |
|------------|-------|-------|-------|-------|------------|-------|-------|-------|--------|
| Atom | 1 C | 22 C | 46 S | 3 C | Atom | 23 C | 28 C | 20 C | 21 C |
| f^+ | 0.059 | 0.02 | 0.014 | 0.004 | f^+ | 0.090 | 0.090 | 0.079 | 0.079 |
| Atom | 3 C | 34 C | 40 C | 7 C | Atom | 6 C | 19 C | 22 C | 1 C |
| f^- | 0.027 | 0.008 | 0.008 | 0.008 | f^- | 0.028 | 0.003 | 0.003 | -0.019 |
| Atom | 1 C | 3 C | 46 S | 22 C | Atom | 23 C | 28 C | 28 C | 13 C |
| f^0 | 0.026 | 0.016 | 0.009 | 0.008 | f^0 | 0.014 | 0.014 | 0.004 | 0.002 |

From the tables 6-7, the parameters of local reactivity descriptors show that 6C, 23O, 1C, 3C are the more reactive sites in compounds **1**, **2**, **3** and **4** respectively for nucleophilic attacks. The more reactive sites in radical attacks are 6C, 7C, 1C and 23C for compounds **1**, **2**, **3** and **4** respectively. The more reactive sites for electrophilic attacks are 6C for compounds **2**, **4** and 7C, 3C for compounds **1** and **3** respectively.

3.6. Natural Bond Orbital Analysis (NBO)

The NBO analysis offers a handy basis for exploring charge transfer or conjugative interaction in molecular systems and is an efficient method for studying the intra and intermolecular bonding and

interaction among bonds. NBO analysis has been performed on the molecule at the B3LYP/6-31G(d,p) and a summary of electron donor orbitals, acceptor orbitals and the interaction stabilization energy that resulted from the second-order perturbation theory is reported in Tables 8-11. The larger the E(2) value, the stronger is the interaction between electron donors and electron acceptors reflects a more donating tendency from electron donors to electron acceptors and a greater degree of conjugation of the whole system. Delocalization of the electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond and Rydberg) non-Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction.

Table 8: 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) S11 | 1.77814 | $\pi^*(C2-C3)$ | 0.21562 | 22.26 | 0.26 | 0.067 |
| LP(2) S12 | 1.77814 | $\pi^*(C2-C3)$ | 0.21562 | 22.26 | 0.26 | 0.067 |
| $\pi(C15-C16)$ | 1.61795 | $\pi^*(C7-C17)$ | 0.36616 | 21.49 | 0.27 | 0.068 |
| LP(2) S11 | 1.77814 | $\pi^*(C1-C6)$ | 0.41531 | 20.67 | 0.24 | 0.066 |
| LP(2) S12 | 1.77814 | $\pi^*(C1-C6)$ | 0.41531 | 20.67 | 0.24 | 0.066 |
| LP(2) O25 | 1.89225 | $\sigma^*(C15-C19)$ | 0.06602 | 20.01 | 0.70 | 0.107 |
| LP(2) S9 | 1.77402 | $\pi^*(C1-C6)$ | 0.41531 | 19.64 | 0.24 | 0.064 |
| LP(2) S10 | 1.77402 | $\pi^*(C1-C6)$ | 0.41531 | 19.64 | 0.24 | 0.064 |
| LP(2) O25 | 1.89225 | $\sigma^*(C19-C20)$ | 0.05633 | 19.40 | 0.70 | 0.105 |
| LP(2) S9 | 1.77402 | $\pi^*(C8-C13)$ | 0.36616 | 19.26 | 0.26 | 0.066 |
| LP(2) S10 | 1.77402 | $\pi^*(C7-C17)$ | 0.36616 | 19.26 | 0.26 | 0.066 |
| $\pi(C15-C16)$ | 1.61795 | $\pi^*(C19-O25)$ | 0.17634 | 18.51 | 0.27 | 0.066 |
| $\pi(C7-C17)$ | 1.65504 | $\pi^*(C8-C13)$ | 0.36616 | 18.34 | 0.28 | 0.065 |
| $\pi(C20-C22)$ | 1.83878 | $\pi^*(C19-O25)$ | 0.17634 | 18.31 | 0.30 | 0.066 |
| $\pi(C7-C17)$ | 1.65504 | $\pi^*(C15-C16)$ | 0.43308 | 18.03 | 0.30 | 0.067 |
| $\pi(C19-O25)$ | 1.94639 | $\pi^*(C20-C22)$ | 0.05459 | 6.77 | 0.40 | 0.047 |
| $\sigma(C2-H 4)$ | 1.97503 | $\sigma^*(C3-S11)$ | 0.01932 | 5.45 | 0.76 | 0.058 |
| $\pi(C19-O25)$ | 1.94639 | $\pi^*(C15-C16)$ | 0.43308 | 5.32 | 0.40 | 0.046 |
| $\sigma(C1-S11)$ | 1.97294 | $\sigma^*(C6-S10)$ | 0.03762 | 5.17 | 0.82 | 0.058 |
| $\sigma(C6-S 9)$ | 1.97252 | $\sigma^*(C1-S12)$ | 0.04008 | 5.08 | 0.82 | 0.058 |

Table 9: 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 | 1.77926 | $\pi^*(C2-C3)$ | 0.21615 | 22.30 | 0.26 | 0.067 |
| LP(2) S12 | 1.77926 | $\pi^*(C2-C3)$ | 0.21615 | 22.30 | 0.26 | 0.067 |
| $\pi(C20-C21)$ | 1.78304 | $\pi^*(C19-O23)$ | 0.19149 | 21.27 | 0.29 | 0.070 |
| $\pi(C20-C21)$ | 1.78304 | $\pi^*(C22-O24)$ | 0.19149 | 21.27 | 0.29 | 0.070 |
| $\pi(C13-C15)$ | 1.63838 | $\pi^*(C7-C8)$ | 0.47921 | 21.26 | 0.25 | 0.067 |
| LP(2) S11 | 1.77926 | $\pi^*(C1-C6)$ | 0.41503 | 20.49 | 0.24 | 0.065 |
| LP(2) O23 | 1.89062 | $\sigma^*(C15-C19)$ | 0.06668 | 20.25 | 0.69 | 0.107 |
| LP(2) O24 | 1.89062 | $\sigma^*(C16-C22)$ | 0.06668 | 20.25 | 0.69 | 0.107 |
| LP(2) S9 | 1.77645 | $\pi^*(C7-C8)$ | 0.47921 | 20.07 | 0.24 | 0.066 |
| $\pi(C13-C15)$ | 1.63838 | $\pi^*(C16-C17)$ | 0.35110 | 19.98 | 0.28 | 0.067 |
| $\pi(C16-C17)$ | 1.63838 | $\pi^*(C13-C15)$ | 0.35110 | 19.98 | 0.28 | 0.067 |
| LP(2) S9 | 1.77645 | $\pi^*(C1-6C)$ | 0.41503 | 19.72 | 0.24 | 0.064 |
| LP(2) O23 | 1.89062 | $\sigma^*(C19-C20)$ | 0.06266 | 19.11 | 0.73 | 0.107 |
| $\pi(C13-C15)$ | 1.63838 | $\pi^*(C19-O23)$ | 0.19149 | 18.68 | 0.27 | 0.066 |
| $\pi(C7-C8)$ | 1.64299 | $\pi^*(C13-C15)$ | 0.35110 | 18.56 | 0.31 | 0.068 |
| $\pi(C19-O23)$ | 1.94632 | $\pi^*(C20-C21)$ | 0.11770 | 6.95 | 0.41 | 0.049 |
| $\sigma(C20-C25)$ | 1.96084 | $\sigma^*(C21-C22)$ | 0.06266 | 5.61 | 1.07 | 0.069 |
| $\sigma(C2-H4)$ | 1.97509 | $\sigma^*(C3-S11)$ | 0.01934 | 5.45 | 0.76 | 0.058 |
| $\sigma(C1-S11)$ | 1.97295 | $\sigma^*(C6-S10)$ | 0.03755 | 5.15 | 0.82 | 0.058 |
| $\sigma(C6-S9)$ | 1.97252 | $\sigma^*(C1-S12)$ | 0.04017 | 5.10 | 0.82 | 0.058 |

Table 10: 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(2) S45 | 1.75533 | $\pi^*(C40-C41)$ | 0.21938 | 22.77 | 0.26 | 0.068 |
| LP(2) S44 | 1.75111 | $\pi^*(C40-C41)$ | 0.21938 | 22.57 | 0.25 | 0.068 |
| LP(2) S11 | 1.78186 | $\pi^*(C2-C3)$ | 0.21871 | 22.46 | 0.26 | 0.068 |
| $\pi(C13-C15)$ | 1.65811 | $\pi^*(C7-C8)$ | 0.48896 | 21.57 | 0.25 | 0.068 |
| LP(2) S11 | 1.78186 | $\pi^*(C1-C6)$ | 0.40312 | 18.41 | 0.25 | 0.064 |
| LP(2) S9 | 1.79305 | $\pi^*(C7-C8)$ | 0.48896 | 18.27 | 0.25 | 0.065 |
| $\pi(C13-C15)$ | 1.65811 | $\pi^*(C16-C17)$ | 0.37740 | 18.13 | 0.28 | 0.064 |
| LP(2) S9 | 1.79305 | $\pi^*(C1-C6)$ | 0.40312 | 17.93 | 0.25 | 0.063 |
| $\pi(C7-C8)$ | 1.66939 | $\pi^*(C13-C15)$ | 0.37740 | 17.77 | 0.31 | 0.067 |
| LP(2) S44 | 1.75111 | $\pi^*(C22-C39)$ | 0.36317 | 17.66 | 0.28 | 0.065 |
| LP(2) S45 | 1.75533 | $\pi^*(C22-C39)$ | 0.36317 | 17.19 | 0.28 | 0.064 |
| $\pi(C20-C21)$ | 1.83069 | $\pi^*(C19-C34)$ | 0.36317 | 15.15 | 0.28 | 0.061 |
| $\pi(C13-C15)$ | 1.65811 | $\pi^*(C19-C34)$ | 0.36317 | 13.46 | 0.27 | 0.055 |
| $\pi(C19-C34)$ | 1.86760 | $\pi^*(C20-C21)$ | 0.19921 | 10.95 | 0.36 | 0.057 |
| $\pi(C19-C34)$ | 1.86760 | $\pi^*(C13-C15)$ | 0.37740 | 8.11 | 0.32 | 0.049 |
| $\sigma(C20-C23)$ | 1.95641 | $\sigma^*(C21-C22)$ | 0.03338 | 5.52 | 1.09 | 0.07 |
| $\sigma(C2-H4)$ | 1.97535 | $\sigma^*(C3-S11)$ | 0.01973 | 5.42 | 0.76 | 0.057 |
| $\sigma(C7-C17)$ | 1.97183 | $\sigma^*(C7-C8)$ | 0.03589 | 5.30 | 1.26 | 0.073 |
| $\sigma(C36-H38)$ | 1.97554 | $\sigma^*(C35-S47)$ | 0.01997 | 5.24 | 0.77 | 0.057 |
| $\sigma(C35-H37)$ | 1.97567 | $\sigma^*(C36-S46)$ | 0.02423 | 5.22 | 0.77 | 0.057 |

Table 11: 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 |
|-------------------|---------|---------------------|---------|------------------|------------------|---------------|
| LP(2) S34 | 1.75099 | $\pi^*(C29-C30)$ | 0.21885 | 22.80 | 0.25 | 0.068 |
| $\pi(C15-C16)$ | 1.59022 | $\pi^*(C7-C17)$ | 0.40196 | 22.74 | 0.26 | 0.068 |
| LP(2) S33 | 1.74398 | $\pi^*(C29-C30)$ | 0.21885 | 22.29 | 0.25 | 0.068 |
| LP(2) S11 | 1.77905 | $\pi^*(C2-C3)$ | 0.21521 | 21.77 | 0.26 | 0.067 |
| LP(2) S33 | 1.74398 | $\pi^*(C22-C28)$ | 0.37485 | 18.47 | 0.28 | 0.066 |
| $\pi(C7-C17)$ | 1.69624 | $\pi^*(C8-C13)$ | 0.40196 | 18.22 | 0.28 | 0.066 |
| LP(2) S9 | 1.79560 | $\pi^*(C8-C13)$ | 0.40196 | 17.57 | 0.27 | 0.064 |
| LP(2) S34 | 1.75099 | $\pi^*(C22-C28)$ | 0.37485 | 17.40 | 0.28 | 0.064 |
| $\pi(C7-C17)$ | 1.69624 | $\pi^*(C15-C16)$ | 0.43837 | 16.81 | 0.3 | 0.065 |
| LP (2) S11 | 1.77905 | $\pi^*(C1-C6)$ | 0.38525 | 16.81 | 0.26 | 0.061 |
| $\pi(C15-C16)$ | 1.59022 | $\pi^*(C19-C23)$ | 0.37485 | 16.57 | 0.26 | 0.059 |
| LP(2) S9 | 1.79560 | $\pi^*(C1-C6)$ | 0.38525 | 14.99 | 0.25 | 0.058 |
| $\pi(C20-C21)$ | 1.86666 | $\pi^*(C19-C23)$ | 0.37485 | 14.09 | 0.28 | 0.060 |
| $\pi(C19-C23)$ | 1.85615 | $\pi^*(C20-C21)$ | 0.17184 | 12.59 | 0.34 | 0.059 |
| $\pi(C19-C23)$ | 1.85615 | $\pi^*(C15-C16)$ | 0.43837 | 9.27 | 0.32 | 0.053 |
| $\sigma(C2-H4)$ | 1.97549 | $\sigma^*(C3-S11)$ | 0.02175 | 5.41 | 0.76 | 0.057 |
| $\sigma(C19-C20)$ | 1.96296 | $\sigma^*(C23-S35)$ | 0.03642 | 5.40 | 0.81 | 0.059 |
| $\sigma(C7-C17)$ | 1.97225 | $\sigma^*(C7-C8)$ | 0.03642 | 5.26 | 1.26 | 0.073 |
| $\sigma(C25-H27)$ | 1.97577 | $\sigma^*(C24-S36)$ | 0.02006 | 5.22 | 0.77 | 0.057 |
| $\sigma(C6-S9)$ | 1.97206 | $\sigma^*(C1-S12)$ | 0.04210 | 5.16 | 0.82 | 0.058 |

The intra molecular interaction for the title compounds is formed by the orbital overlap between: $\pi(C15-C16)$ and $\pi^*(C7-C17)$ for compound **1**, $\pi(C20-C21)$ and $\pi^*(C19-O23)$ for compound **2**, $\pi(C13-C15)$ and $\pi^*(C7-C8)$ for compound **3** and $\pi(C15-C16)$ and $\pi^*(C7-C17)$ for compound **4** respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of $\pi(C15-C16)$ to $\pi^*(C7-C17)$ for compound **1**, $\pi(C20-C21)$ to $\pi^*(C19-O23)$ for compound **2**, $\pi(C13-C15)$ to $\pi^*(C7-C8)$ for compound **3** and $\pi(C15-C16)$ to $\pi^*(C7-C17)$ for compound **4** lead to highest stabilization of 21.49, 21.27, 21.57 and 22.74 kJ mol⁻¹ respectively. In case of LP(2)S11 orbital to the $\pi^*(C2-C3)$ for compound **1**, LP(2)S11 orbital to $\pi^*(C2-C3)$ for compound **2**, LP(2) S45orbital to $\pi^*(C40-C41)$ for compound **3**, LP(2)S34 orbital $\pi^*(C29-C30)$ for compound **4** respectively, show the stabilization energy of 22.26, 22.30, 22.77 and 22.80 kJ mol⁻¹ respectively.

3.7. Nonlinear Optical Properties (NLO)

In order to investigate the relationship between molecular structure and NLO response, first hyperpolarizability (β_0) of (Mono/ex-TTFs) **1-4**, and related properties ($|\alpha_0|$ and $\Delta\alpha$) are calculated using B3LYP/6-31G(d,p), based on the finite-field approach and their calculated values are given in Table 12. 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 the Kleinman symmetry [26]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the $3 \times 3 \times 3$ matrix is a tetrahedral. The components of μ , α , 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 of the energy in the external electric field is weak and homogeneous, this expansion becomes

$$E = E^0 - \mu_i F_i - 1/2\alpha_{ij} F_i F_j - 1/6\beta_{ijk} F_i F_j F_k + \dots$$

Where E^0 is the energy of the unperturbed molecules, F_i is the field at the origin, μ_i is component of the dipole moment and α_{ij} , β_{ijk} are the polarizability, first hyperpolarizability and second hyperpolarizability tensors, respectively. Total static dipole moment (μ_0), mean polarizability ($|\alpha_0|$), anisotropy of polarizability ($\Delta\alpha$) and first hyperpolarizability (β_0), using x, y, z components are defined as [26].

$$\mu_0 = [\mu_x^2 + \mu_y^2 + \mu_z^2]^{1/2}$$

$$|\alpha_0| = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

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

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

Where

$$\beta_x = \beta_{xxx} + \beta_{xyx} + \beta_{xzx}$$

$$\beta_y = \beta_{yyy} + \beta_{xyy} + \beta_{yyz}$$

$$\beta_z = \beta_{zzz} + \beta_{xzz} + \beta_{yyz}$$

Table 12: The dipole moments μ_0 (D), polarizability α , the average polarizability α_0 (esu), the anisotropy of the polarizability $\Delta\alpha$ (esu), and the first hyperpolarizability β_0 (esu) of (Mono/ex-TTFs) 1-4 calculated by B3LYP/6-31G (d,p) method

| Parameters | Compound 1 | Compound 2 | Compound 3 | Compound 4 |
|---|------------|------------|------------|------------|
| β_{xxx} | 0.0021 | -0.2923 | 311.9026 | -11.2838 |
| B_{yyy} | 118.9969 | 172.9513 | 0.0040 | 257.0843 |
| B_{zzz} | 0.0000 | 0.0000 | -10.4585 | 0.0000 |
| B_{xyy} | -0.1029 | -9.5302 | -112.6137 | -26.5587 |
| B_{xxy} | -19.1293 | -36.5011 | -0.0003 | -26.7342 |
| B_{xxz} | 0.0000 | 0.0000 | -4.1749 | 0.0000 |
| B_{xzz} | -0.0082 | -4.9230 | -31.2334 | -85.6791 |
| B_{yzz} | 68.6048 | 40.1129 | -0.0029 | -137.4527 |
| B_{yyz} | 0.0000 | 0.0000 | -102.4158 | 0.0000 |
| B_{xyz} | 0.0000 | 0.0000 | 0.0004 | 0.0000 |
| $B_0(\text{esu})\times 10^{-33}$ | 168.4724 | 176.6401 | 304.0985 | 134.2822 |
| μ_x | -0.0021 | -0.1575 | -1.3557 | -1.4563 |
| μ_y | 2.6678 | 0.8816 | 0.0000 | -1.1339 |
| μ_z | 0.0000 | 0.0000 | -1.0682 | 0.0000 |
| $\mu_0(\text{D})$ | 2.6678 | 0.8956 | 1.7260 | 1.8457 |
| α_{xx} | -144.0328 | -170.5226 | -206.4471 | -218.2788 |
| α_{yy} | -107.8281 | -119.9426 | -209.4767 | -177.4242 |
| α_{zz} | -151.5311 | -178.6350 | -244.3465 | -181.5064 |
| α_{xy} | -0.0008 | -0.0295 | 0.0000 | 0.8042 |
| α_{xz} | 0.0000 | 0.0000 | 2.6139 | 0.0000 |
| α_{yz} | 0.0000 | 0.0000 | 0.0001 | 0.0000 |
| $\alpha_0(\text{esu})\times 10^{-24}$ | 40.4781 | 55.0860 | 36.7589 | 38.9990 |
| $\Delta\alpha(\text{esu})\times 10^{-24}$ | 5.9988 | 8.1637 | 5.4476 | 5.7796 |

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 x 10⁻²⁴ e.s.u., for β ; 1 a.u. = 8.6393 x 10⁻³³ e.s.u.). The calculated values of dipole moment (μ_0) for the title compounds were found to be 2.6678, 0.8956, 1.7260 and 1.8457 D respectively, which are approximately two times than to the value for urea (μ = 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 40.4781 x 10⁻²⁴, 55.0860 x 10⁻²⁴, 36.7589 x 10⁻²⁴ and 38.9990 x 10⁻²⁴ esu respectively; the values of anisotropy of the polarizability are 5.9988, 8.1637, 5.4476 and 5.7796 esu, respectively. The magnitude of the molecular hyperpolarizability (β_0) is one of important key factors in a NLO system. The DFT/6-31G(d,p) calculated first hyperpolarizability value (β_0) of (Mono/ex-TTFs) molecules are equal to 168.4724x 10⁻³³, 176.6401 x 10⁻³³, 304.0985 x 10⁻³³ and 134.2822 x 10⁻³³ esu. The first hyperpolarizability of title molecules is approximately 0.49, 0.51, 0.88, and 0.39 times than those of urea (β of urea is 343.272 x 10⁻³³ esu obtained by B3LYP/6-311G (d,p) method).

This result indicates that (Mono/ex-TTFs) **1-4** are not nonlinear.

4. CONCLUSION:

In the present work, All theoretical calculations is performed with DFT/B3LYP/6-31G(d,p). The optimized geometric parameters (bond lengths, bond angle and dihedral angles) of the structure of the minimum energy were determined. NBO result reflects the charge transfer within the molecule and the maximum charge delocalization takes place during π - π^* transition. The band gap of compound **1** was determined about 1.724 eV, which leads the molecule becomes less stability and more reactivity. The HOMO is mainly located on the TTF core, whereas the electron density on the LUMO is mainly localized on the quinone ring.

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