

Research Article



Structural, HOMO-LUMO, NBO, NLO Analysis and Reactivity Descriptors of a Series of Bis-fused Tetrathiafulvalene

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ABSTRACT

In the present work, All theoretical calculations is performed with DFT/B3LYP/6-31G(d,p). The electron density based local reactivity descriptor such as Fukui functions were calculated to explain the chemical reactivity and the reactive sites in the molecules. The optimized molecular structure, atomic charges, molecular electrostatic potential, NBO, electronic properties, NLO, energy HOMO, LUMO, gap of 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) and its derivatives 1-4 are studied within the best method in this investigation get a better insight of the molecular properties.

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

INTRODUCTION

The applications of heterocyclic compounds in our life are undeniable. So there's an increasing demand for synthesizing new heterocyclic compounds and this has stimulated research activities within the field of heterocyclic compound chemistry. Heterocyclic compounds containing sulfur have maintained the interest of organic researchers on decades of historical development of chemistry. 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) and its derivatives have attracted attention for several years as a result of their electron donor ability and also the electrical conductivity of their charge transfer salts. Among the wide variety of chemical modifications performed on the TTF skeleton, the introduction of aromatic rings into the TTF skeleton are known to be an attractive electron-donor molecule which may give an extremely conductive charge transfer complex owing to its highly extended π -conjugate part¹⁻³. The synthesis of highly extended and sulfur rich systems has recently received particular attention⁴⁻⁶, TTFs derivatives currently play an important role as redox sites in totally different areas of supramolecular chemistry. Some applications in materials chemistry⁷ such their use as molecular switches rotaxanes and catenanes⁸, conductive materials⁹ and superconductors¹⁰, complex with the C₆₀¹¹, conductive polymers¹², materials for nonlinear optics¹³, sponges cations¹⁴, ferromagnetic organic magnets¹⁵, liquid crystals¹⁶, and dendrimers¹⁷.

On the other hand computational ways of quantum chemistry have found an increasing number of applications to chemical problems over the previous few decades. Thus, quantum chemistry has been very successful as a predictive tool within the study of little or

medium size organic molecules and properties like the ground state molecular geometries, conformational preferences, transition state geometries and energies, Born-Oppenheimer potential energy surfaces, reaction pathways and also the rates of organic reactions may well be predicted^{18,19}. At constant time, quantum chemistry has additionally been applied within the field of transition metal compounds and organometallics^{20,21}. However, despite the greatly improved computational facilities and also the accessibility of sophisticated quantum chemical calculations, the quantum chemistry of molecular systems containing heavy atoms appears to be less advanced^{22,23}. This is often largely as a result of difficulties was arising within the treatment of heavy atoms and molecules containing such atoms, associated with the quasi-degeneracy of their lowest atomic states, correlation and relativistic effects.

In this paper and in the aim to study the properties of a series of bis-fused tetrathiafulvalènes described in literature²⁴ and to predict their applications, we give a complete description of the molecular geometry, natural bond orbital (NBO) analysis, nonlinear optical (NLO) properties, and chemical reactivity as HOMO-LUMO energy gap, chemical hardness, and chemical potential.

MATERIALS AND METHODS

The optimum geometry was determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints. The structural and spectroscopic characterization was carried out using Gaussian 09 program package on the personal computer. DFT computations were performed by using the closed-shell Becke-Lee-Yang-Parr hybrid exchange-correlation three-parameter functional (B3LYP) in



combination with 6-31G (d,p) basis set to derive the complete geometry optimizations and normal-mode analysis on isolated entities. All optimized structures were confirmed to be minimum energy conformations.

RESULTS AND DISCUSSION

Molecular Geometry

The optimized DFT geometries by B3LYP/6-31G (d,p) of the bis-fused TTF ligands with atom numbering are shown in Figure 1. The internal coordinates describe the position

of the atoms in terms of distances, angles and dihedral angles with respect to an origin atom. The symmetry coordinates are constructed using the set of internal coordinates. In this study, the standard internal coordinates for compounds **1-4** are presented in Tables 1-4. By allowing the relaxation of all parameters, the calculations converge to optimized geometries, which correspond to true energy minima, as revealed by the lack of imaginary frequencies in the vibrational mode calculation.

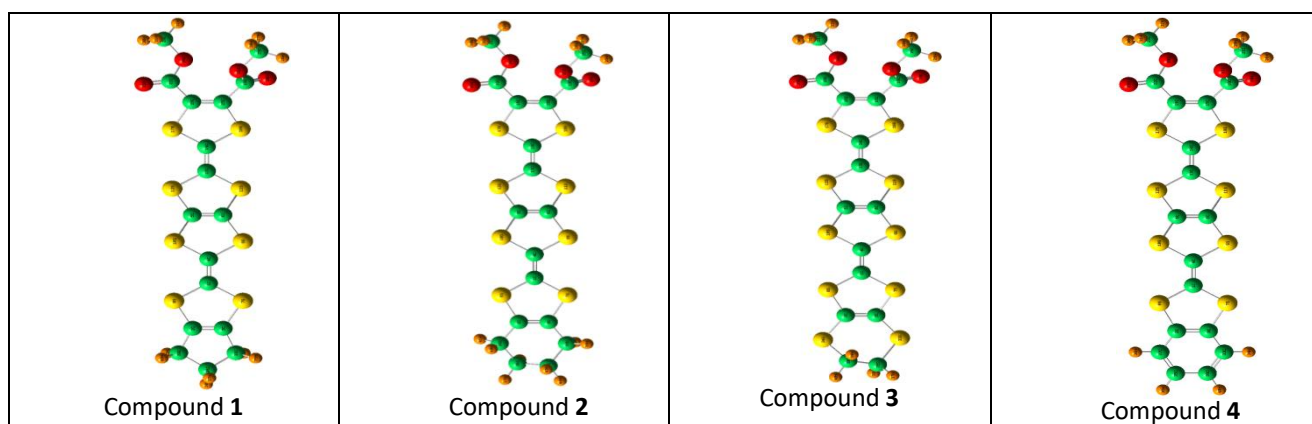


Figure 1: Optimized molecular structure of bis-fused tetrathiafulvalènes **1-4**

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

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,4)	1.350	A(4,1,7)	122.849	D(8,1,4,9)	178.321
R(1,7)	1.791	A(7,1,8)	114.350	D(4,1,8,2)	172.193
R(2,3)	1.339	A(3,2,8)	118.337	D(39,2,3,7)	177.937
R(2,8)	1.761	A(3,2,39)	112.755	D(3,2,39,40)	132.914
R(2,39)	1.506	A(8,2,39)	128.870	D(1,4,9,6)	160.187
R(3,33)	1.506	A(2,3,7)	118.330	D(9,4,10,5)	21.681
R(5,6)	1.343	A(6,5,12)	117.911	D(10,5,6,11)	179.981
R(11,13)	1.789	A(17,14,18)	113.819	D(12,5,10,4)	166.632
R(14,17)	1.782	A(16,15,19)	129.224	D(10,5,12,13)	167.204
R(16,22)	1.487	A(15,19,20)	122.708	D(6,11,13,14)	160.793
R(22,23)	1.215	A(20,19,21)	124.870	D(5,12,13,11)	21.126
R(24,29)	1.440	A(23,22,24)	124.277	D(11,13,14,17)	178.637
R(29,30)	1.092	A(21,25,27)	110.389	D(13,14,17,16)	166.111
R(36,37)	1.094	A(33,36,37)	109.050	D(19,15,18,14)	169.966
R(36,39)	1.559	A(37,36,38)	107.440	D(16,22,24,29)	179.618

Table 2: Optimized geometric parameters of compound 2

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,8)	1.780	A(4,1,8)	123.245	D(8,1,4,9)	178.701
R(3,7)	1.777	A(7,1,8)	113.489	D(4,1,8,2)	169.937
R(5,6)	1.343	A(3,2,8)	117.335	D(8,2,3,33)	178.224
R(5,10)	1.769	A(3,2,39)	124.055	D(3,2,39,40)	106.884
R(6,11)	1.769	A(8,2,39)	118.580	D(8,2,39,36)	167.257
R(13,14)	1.350	A(2,3,33)	124.100	D(33,3,7,1)	174.925
R(15,16)	1.353	A(7,3,33)	118.469	D(2,3,33,34)	106.345
R(16,17)	1.773	A(1,4,10)	123.178	D(7,3,33,35)	41.345
R(16,22)	1.487	A(9,4,10)	113.620	D(7,3,33,42)	163.368
R(19,20)	1.213	A(6,5,12)	117.912	D(1,4,9,6)	159.498
R(19,21)	1.340	A(10,5,12)	124.208	D(10,5,6,11)	179.932
R(21,25)	1.441	A(1,8,2)	95.252	D(12,5,10,4)	166.302
R(25,26)	1.092	A(20,19,21)	124.864	D(10,5,12,13)	167.394
R(33,35)	1.097	A(21,25,26)	110.422	D(16,22,24,29)	179.669
R(36,39)	1.539	A(26,25,28)	110.785	D(34,33,42,43)	162.882

Table 3: Optimized geometric parameters of compound 3

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,7)	1.781	A(4,1,8)	123.713	D(8,1,4,9)	177.525
R(4,10)	1.790	A(7,1,8)	112.890	D(4,1,8,2)	158.979
R(5,6)	1.343	A(3,2,8)	117.150	D(8,2,3,33)	177.607
R(5,12)	1.769	A(3,2,34)	123.720	D(33,3,7,1)	168.015
R(11,13)	1.790	A(9,6,11)	124.104	D(7,3,33,35)	149.553
R(13,14)	1.350	A(5,12,13)	92.702	D(1,4,9,6)	162.929
R(15,18)	1.767	A(13,14,17)	123.160	D(10,5,6,11)	179.745
R(15,19)	1.496	A(15,16,22)	129.379	D(12,5,10,4)	167.561
R(21,25)	1.441	A(14,18,15)	94.460	D(10,5,12,13)	167.304
R(22,23)	1.215	A(15,19,20)	122.665	D(6,11,13,14)	160.458
R(22,24)	1.343	A(15,19,21)	112.298	D(5,12,13,11)	21.330
R(24,29)	1.440	A(26,25,28)	110.788	D(11,13,14,17)	178.862
R(29,30)	1.092	A(3,33,35)	103.768	D(19,15,18,14)	170.100
R(33,35)	1.863	A(34,38,35)	113.103	D(16,22,24,29)	179.675
R(35,36)	1.092	A(39,38,40)	108.590	D(3,33,35,36)	117.892

Molecular Electrostatic Potential (MEP)

Molecular electrostatic potential (MEP) is related to the electronic density and is a very useful descriptor in understanding sites for electrophilic attack and nucleophilic reactions as well as hydrogen bonding interactions^{25,26}. Being a real physical property $V(r)$ can be determined experimentally by diffraction or by computational methods²⁷. To investigate the reactive sites of the title compound the molecular electrostatic potential was evaluated using B3LYP/6-31G(d,p) method.

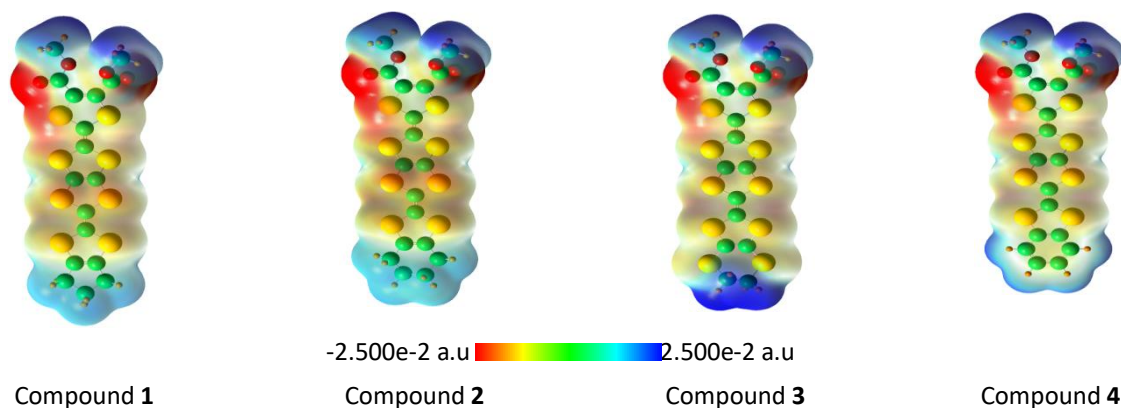
Molecular electrostatic potential, $V(r)$, at a given point $r(x,y,z)$ in the vicinity of a molecule, is defined in terms of the interaction energy between the electrical charge generated from the molecule's electrons and nuclei and a positive test charge (a proton) located at r . For the system studied the $V(r)$ values were calculated as described previously using the equation²⁸.

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

Table 4: Optimized geometric parameters of compound 4

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,7)	1.780	A(4,1,8)	122.949	D(8,1,4,9)	177.675
R(2,3)	1.403	A(7,1,8)	114.099	D(4,1,8,2)	165.460
R(2,37)	1.396	A(3,2,8)	116.498	D(8,2,3,33)	178.397
R(4,10)	1.791	A(3,2,37)	120.264	D(33,3,7,1)	171.709
R(5,6)	1.343	A(8,2,37)	123.217	D(2,3,33,34)	179.523
R(6,11)	1.769	A(5,6,11)	117.908	D(7,3,33,39)	178.030
R(11,13)	1.790	A(13,14,18)	123.011	D(1,4,9,6)	161.147
R(14,18)	1.779	A(17,14,18)	113.842	D(10,5,6,11)	179.723
R(15,18)	1.767	A(14,18,15)	94.471	D(12,5,10,4)	166.768
R(16,17)	1.773	A(15,19,21)	112.288	D(10,5,12,13)	167.468
R(19,20)	1.213	A(20,19,21)	124.888	D(6,11,13,14)	160.791
R(22,23)	1.215	A(19,21,25)	115.003	D(11,13,14,17)	178.650
R(22,24)	1.343	A(21,25,27)	110.382	D(13,14,17,16)	166.434
R(24,29)	1.440	A(3,33,34)	120.228	D(19,15,18,14)	170.114
R(25,26)	1.092	A(33,39,35)	120.417	D(17,16,22,23)	20.335

The color scheme for the MEP surface is red, electron rich, partially negative charge; blue, electron deficient, partially positive charge; light blue, slightly electron deficient region; yellow, slightly electron rich region; green, neutral; respectively.

**Figure 2.** Molecular electrostatic potential surface of bis-fused tétrathiafulvalènes 1-4

As seen from the figure that, in all molecules, the regions exhibiting the negative electrostatic potential are localized near the carbonyl group of the ester function while the regions presenting the positive potential are localized vicinity of the hydrogen atoms of alkyl groups.

Frontier Molecular Orbitals (FMOs)

The analysis of frontier molecular orbitals describes one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The energy of HOMO is directly related to the ionization potential and the energy of LUMO is related to the electron affinity. The HOMO and LUMO energy gap explains the eventual charge transfer interaction taking within the molecules. A molecule with a

small frontier orbitals gap is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecules^{29,30}. A hard molecule has a large HOMO-LUMO gap and a soft molecule has a small HOMO-LUMO gap. In quantum theory, changes in the electron density of a chemical system result from the mixing of suitable excited-state wave function with the ground and excited state. The value of energy separation between the HOMO and LUMO of bis-fused TTF ligands explains the eventual charge transfer interactions within the molecules, which influences on chemical reactivity of the molecules. The frontier molecular orbitals HOMO and LUMO of bis-fused tétrathiafulvalènes 1-4, with B3LYP/6-31G (d,p) method is plotted in Fig. 3 and given in Table 5.

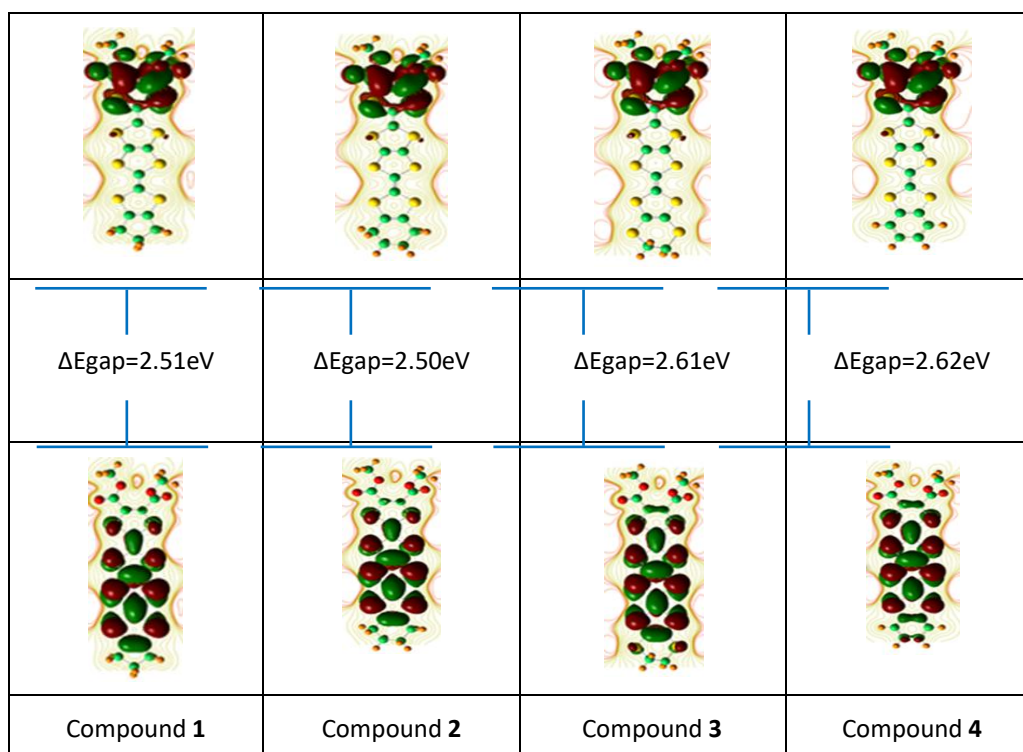


Figure 3: Highest occupied molecular orbitals and lowest unoccupied molecular orbitals of compounds 1-4

Global Reactivity Descriptors

The energies of frontier molecular orbitals (E_{HOMO} , E_{LUMO}), energy band gap ($E_{HOMO} - E_{LUMO}$), electronegativity (χ), chemical potential (μ), global hardness (η), global softness (S) and global electrophilicity index (ω)³¹⁻³⁵ of bis-fused TTF ligands have been listed in Table 5. On the basis of E_{HOMO} and E_{LUMO} , these are calculated using the below equations.

$$\chi = (E_{HOMO} - E_{LUMO}) / 2$$

$$\mu = -(IE + EA) / 2 = (E_{N+1} - E_{N-1}) / 2 = -\chi$$

$$\eta = (IE - EA) / 2 = (E_{N-1} - E_{N+1} - 2E_N) / 2$$

$$S = 1 / 2\eta$$

$$\omega = \mu^2 / 2\eta$$

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 selectivity³⁶⁻³⁸.

Table 5: Quantum chemical descriptors of bis-fused tétrathiafulvalènes 1-4

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
E_{HOMO} (eV)	-4.702	-4.680	-4.843	-4.856
E_{LUMO} (eV)	-2.196	-2.177	-2.229	-2.230
ΔE_{gap} (eV)	2.507	2.503	2.613	2.626
IE (eV)	4.702	4.680	4.843	4.856
EA (eV)	2.196	2.177	2.229	2.230
μ (eV)	-3.449	-3.428	-3.536	-3.543
χ (eV)	3.449	3.428	3.536	3.543
η (eV)	1.253	1.252	1.307	1.313
S (eV)	0.399	0.399	0.383	0.381
ω (eV)	4.746	4.695	4.785	4.782

As presented in table 5, the compound which have the lowest energetic gap is the compound 2 ($\Delta E_{gap} = 2.503$ eV). This lower gap allows it to be the softest molecule.

The compound that have the highest energy gap is the compound 4 ($\Delta E_{gap} = 2.626$ eV). The compound that has the highest HOMO energy is the compound 2 ($E_{HOMO} = -$

4.680 eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound **4** ($E_{\text{LUMO}} = -2.230$ 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 **2** has lowest value of the potential ionization ($I = 4.680$ eV), so that will be the better electron donor. Compound **4** has the largest value of the affinity ($A = 2.230$ eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound **2** ($\eta = 1.252$ eV, $S = 0.399$ eV) is lesser (greater) among all the molecules. Thus, compound **2** is found to be more reactive than all the compounds. Compound **4** possesses higher electronegativity value ($\chi = 3.543$ eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **3** ($\omega = 4.785$ 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.

Local Reactivity Descriptors

Using Hirschfeld atomic charges of neutral, cation, and anion states, Fukui functions are calculated using the following equations^{39,40}.

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

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

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

In these equations, q is the atomic charge (evaluated from Mulliken population analysis, electrostatic derived charge, etc.) at the k_{th} atomic site is the neutral (N), anionic ($N+1$) or cationic ($N-1$) chemical species. In order to solve the negative Fukui function problem, different attempts have been made by various groups⁴¹⁻⁴³. Kolandaivel et al.⁴⁴ introduced the atomic descriptor to determine the local reactive sites of the molecular system. In the present study, the optimized molecular geometry was utilized in single-point energy calculations, which have been performed at the DFT for the anions and cations of the title compound using the ground state with doublet multiplicity. The individual atomic charges calculated by Mulliken population analysis (MPA) have been used to calculate the Fukui function. In order to confirm that the atomic descriptor would produce the reactive sites without disturbing the trend; we have performed the calculation for the reactive sites of the stable structures of bis-fused TTF ligands. The parameters of local reactivity descriptors show that 14C is the more reactive site in compounds **1**, **2**, **3** and **4** respectively for

nucleophilic attacks. The more reactive site in radical attacks is 4C for compounds **1**, **2**, **3** and **4** respectively. The more reactive sites for electrophilic attacks are 13C for compounds **1**, **2** and 16C for compounds **3** and **4** respectively.

Natural Bond Orbital Analysis (NBO)

Natural bond orbital analysis has been carried out to explain the charge transfer or delocalization of charge due to the intramolecular interaction among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulting from the second-order micro-disturbance theory is reported^{45,46}. The larger the stabilization energy value, the more intensive is the interaction between electron donors and electron acceptors, i.e. the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (anti-bond or Rydberg) non-Lewis NBO orbitals corresponds to a stabilizing donor-accepter interaction.

NBO analysis has been performed on the molecule at the B3LYP/6-311G (d,p) level in order to elucidate the intramolecular, re-hybridization and delocalization of electron density within the molecule. The intra molecular interaction for the title compounds is formed by the orbital overlap between: $\pi(\text{C15-C16})$ and $\pi^*(\text{C22-O23})$ for compound **1**, $\pi(\text{C15-C16})$ and $\pi^*(\text{C22-O23})$ for compound **2**, $\pi(\text{C15-C16})$ and $\pi^*(\text{C22-O23})$ for compound **3** and $\pi(\text{C35-C39})$ and $\pi^*(\text{C2-C37})$ for compound **4** respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of $\pi(\text{C15-C16})$ to $\pi^*(\text{C22-O23})$ for compound **1**, $\pi(\text{C15-C16})$ to $\pi^*(\text{C22-O23})$ for compound **2**, $\pi(\text{C15-C16})$ to $\pi^*(\text{C22-O23})$ for compound **3** and $\pi(\text{C35-C39})$ to $\pi^*(\text{C2-C37})$ for compound **4** lead to highest stabilization of 14.09, 14.13, 14.08 and 21.90 kJ mol⁻¹ respectively. In case of LP(2) O24 orbital to the $\pi^*(\text{C22-O23})$ for compound **1**, LP(2) O20 orbital to $\sigma^*(\text{C19-O21})$ for compound **2**, LP(2) O24 orbital to $\pi^*(\text{C22-O23})$ for compound **3**, LP(2) O24 orbital to $\pi^*(\text{C22-O23})$ for compound **4** respectively, show the stabilization energy of 50.17, 32.31, 50.24 and 50.23 kJ mol⁻¹ respectively.

Nonlinear Optical Properties (NLO)

Nonlinear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields⁴⁷. The first hyperpolarizability (β_0) of this novel molecular system and related properties (β , α_0 and $\Delta\alpha$) of bis-fused TTF ligands molecules are calculated using B3LYP/6-31G(d,p) method based on the finite-fields approach. In the presence of applied electric fields, the energy of a

system is a function of the electric fields. First order hyperpolarizability is a third rank tensor that can be described $3 \times 3 \times 3$ matrices. The 27 components of the 3D matrix can be reduced to 10 components due to the Klein-man symmetry⁴⁸. It can be given in the lower tetrahedral format. It is obvious that the lower part of the $3 \times 3 \times 3$ matrices is a tetrahedral. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric fields. When the external electric field is weak and homogenous 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 is the fields at the origin and μ_α , $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first order hyperpolarizabilities, respectively. The total static dipole moment μ , the mean polarizability α_0 , the anisotropy of the polarizability $\Delta\alpha$ and the mean first order hyperpolarizability β_0 , using the x, y, z components are defined as,

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

$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

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

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

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

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

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

Since the values of the polarizabilities (α) and hyperpolarizability (β) of the Gaussian 09W output are reported in atomic units (a.u.), the calculated values have been converted into electrostatic units (e.s.u.) (α : 1 a.u. = 0.1482×10^{-24} e.s.u.; β : 1 a.u. = 8.639×10^{-33} e.s.u.).

The first order hyperpolarizability is 15 times greater than that of urea (β of urea 0.3728×10^{-30} esu) obtained by B3LYP/6-31G (d,p) method. This result indicates the non-linearity of the bis-fused TTF ligands molecules. 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 1.1628, 1.2668, 2.3516 and 1.2611 D respectively, which are approximately six 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 107.4237×10^{-24} , 112.6782×10^{-24} , 123.2464×10^{-24} and 100.5385×10^{-24} esu respectively; the values of anisotropy of the polarizability are 15.9202, 16.6989, 18.2651 and 14.8998 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 bis-fused tétrathiafulvalènes **1-4** molecules are equal to 241.5724×10^{-33} , 249.3951×10^{-33} , 266.9326×10^{-33} and 313.5916×10^{-33} esu. The first hyperpolarizability of title molecules is approximately 0.70, 0.73, 0.77 and 0.91 times than those of urea (β of urea is 343.272×10^{-33} esu obtained by B3LYP/6-31G (d,p) method). This result indicates that bis-fused tétrathiafulvalènes **1-4** are not nonlinear.

CONCLUSION

In summary, we have successfully demonstrated that the sites of interaction of the title compounds **1-4** can be predicted by using DFT-based reactivity descriptors such as the hardness, softness, and electrophilicity, as well as Fukui-function calculations. The chemical reactivity and the Fukui function are found to be the most efficient descriptors to characterize the regio-selectivity that might be driving to different reactions. NLO behavior of the title molecule has been investigated by dipole moment, polarizability and first hyperpolarizability. The lowest singlet excited state of the molecule is mainly derived from the HOMO→LUMO ($\pi \rightarrow \pi^*$) electron transition, NBO analysis reveals that some important intramolecular charge transfer can induce large nonlinearity to the title molecule and the intramolecular conjugative interaction around the tetrathiafulvalene core can induce the large conductivity in the compound. Finally we hope that these consequences will be of assistance in the quest of the experimental and theoretical evidence for the title compounds in molecular bindings.

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