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Molecular orbital studies (hardness, chemical potential, electro negativity and electrophilicity) of TTFs conjugated between 1, 3-dithiole

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ABSTRACT: The aim of this study is to find out the molecular characteristics and structural parameters that govern the chemical behavior of TTFs conjugated between 1, 3-dithiole. The electric dipole moment (μ) and first hyper polarizability (β) values of the investigated molecules were computed using density functional theory calculations within B3LYP/6-31G(d,p) basis set. Stability of the molecules arising from hyper conjugative interactions leading to its chemical reactivity, charge delocalization have been analyzed using natural bond orbital (NBO) analysis. The calculated HOMO–LUMO energies shows that charge transfer occur within the molecules.

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

I. INTRODUCTION

Since the discovery of the properties of tetrathiafulvalene (TTF) [1], much effort has been devoted to achieve the synthesis of sophisticated derivatives of this π -donor in order to improve the electro conducting properties of the corresponding charge-transfer complexes or cation radical salts [2]. It has been widely recognized that the conductive properties depend on their crystal structures and electronic states. Recently, TTFs have been employed as building blocks for molecular devices such as switches [3], sensors [4], nonlinear optical devices [5], organic field-effect transistors [6], rectifiers [7], and organic photovoltaic cells [8]. This results from their good electron-donating ability and reversible one-electron oxidation at accessible potentials, and these properties can be finely tuned by peripheral substitution or chemical modification of the TTF framework [9].

Density functional theory (DFT) [10,11] is an effective tool in quantum chemistry for evaluation of the molecular structures, spectral analysis, intra-/intermolecular interactions and nature of chemical reactions. DFT is a computational method that derives properties based on a determination of the electron density.

In this investigation, we have presented a detailed study of various aspects of TTFs conjugated between 1, 3-dithiole described in literature [12] using density functional theory (DFT). Also the nature of chemical reactivity and site selectivity of these molecules has been determined on the basis of Global and Local reactivity descriptors. The first hyperpolarizability (β_0) has been computed to indicate suitability for non-linear optical response. All these calculations have been obtained using the DFT/B3LYP method with 6-31G(d,p) basis set.

II. MATERIALS AND METHODS

The entire set of calculations was performed at the density functional theory (DFT) level on a personal computer by energy optimization [13], using the GAUSSIAN 09W [14] program package. The optimized structural parameters for the TTFs conjugated molecules were calculated using the B3LYP functional and 6-31G(d, p) basis set. The potential

energy surface was studied at the 6-31G(d, p) level. All the parameters were allowed to relax and the calculations converged to an optimized geometry which corresponds to a true minimum, as seen from the figure 1.

III. RESULTS AND DISCUSSION

MOLECULAR GEOMETRY: The optimized molecular structure for TTFs conjugated **1-4** in the ground state is computed by the B3LYP calculations computed by the 6-31G(d,p) basis set. The values of the total energy for title compounds from the B3LYP calculation by employing the 6-31G(d,p) basis set is found to be between -1901.1566 and -2854.8098 a.u. The optimized structural parameters are listed in Tables 1-4, in accordance with the atom numbering scheme given in Fig 1.

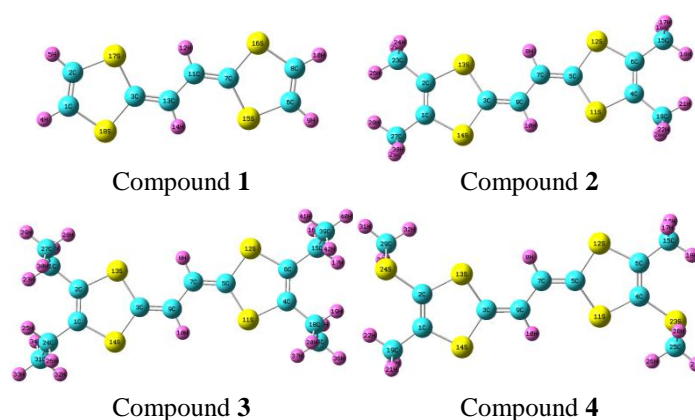


Fig.1 .Optimized molecular structure of TTFs conjugated 1-4

Table 1.Optimized geometric parameters of compound 1

BondLength(Å)		BondAngles(°)		DihedralAngles(°)	
R(1,2)	1.337	A(2,1,4)	124.909	D(4,1,2,17)	180.001
R(1,4)	1.083	A(2,1,18)	117.785	D(18,1,2,5)	179.999
R(1,18)	1.759	A(4,1,18)	117.304	D(2,1,18,3)	120.002
R(2,17)	1.762	A(13,3,17)	124.415	D(4,1,18,3)	179.998
R(3,13)	1.357	A(13,3,18)	122.462	D(1,2,17,3)	150.003
R(3,17)	1.787	A(17,3,18)	113.122	D(17,3,11,13)	130.001
R(3,18)	1.786	A(11,7,15)	125.415	D(13,3,17,2)	179.996
R(6,8)	1.337	A(11,7,16)	122.462	D(17,3,18,1)	135.004
R(6,15)	1.762	A(7,11,12)	116.821	D(9,6,8,16)	179.999
R(7,11)	1.357	A(7,11,13)	125.411	D(15,6,8,10)	180.001
R(8,10)	1.083	A(12,11,13)	117.766	D(9,6,15,7)	179.997
R(8,16)	1.759	A(3,11,11)	125.411	D(15,7,11,12)	179.999
R(11,12)	0.087	A(3,13,14)	116.821	D(16,7,11,13)	179.997
R(11,13)	0.438	A(6,15,7)	95.518	D(16,7,15,6)	152.004
R(11,14)	1.087	A(7,16,7)	95.675	D(11,7,16,8)	179.996

Table 2.Optimized geometric parameters of compound 2

BondLength(Å)		BondAngles(°)		DihedralAngles(°)	
R(1,2)	1.345	A(2,1,14)	116.909	D(27,1,2,23)	110.010
R(1,14)	1.778	A(2,1,27)	127.900	D(27,1,14,3)	179.994
R(1,27)	1.502	A(14,1,27)	115.190	D(2,1,27,29)	120.232
R(3,9)	1.356	A(1,2,13)	117.025	D(14,1,27,28)	179.929
R(3,13)	1.779	A(1,2,23)	127.945	D(14,1,27,30)	59.622
R(3,14)	1.777	A(13,2,23)	115.028	D(1,2,13,3)	125.005
R(7,8)	1.088	A(9,3,13)	124.650	D(1,2,23,24)	120.288
R(7,9)	1.438	A(9,3,14)	122.736	D(13,2,23,25)	59.663
R(15,16)	1.096	A(13,3,14)	112.602	D(13,2,23,26)	179.977
R(15,18)	1.091	A(5,7,8)	116.874	D(13,3,9,10)	179.995
R(2,13)	1.780	A(5,7,9)	125.399	D(14,3,9,7)	179.997
R(4,6)	1.345	A(1,14,3)	96.812	D(9,3,13,2)	179.997
R(5,7)	1.356	A(6,15,16)	111.049	D(9,3,14,1)	60.004
R(6,15)	1.502	A(16,15,17)	107.357	D(6,4,19,22)	120.289
R(27,30)	1.096	A(11,5,12)	112.612	D(11,4,19,20)	59.664

Table 3.Optimized geometric parameters of compound 3

BondLength(Å)		BondAngles(°)		DihedralAngles(°)	
R(1,2)	1.346	A(2,1,14)	116.861	D(24,1,14,3)	178.995
R(1,14)	1.779	A(2,1,24)	127.419	D(2,1,24,31)	105.023
R(1,24)	1.509	A(14,1,24)	115.714	D(14,1,24,25)	163.261
R(3,9)	1.357	A(9,3,13)	124.642	D(14,1,24,26)	48.207
R(4,6)	1.346	A(9,3,13)	122.723	D(21,2,13,3)	179.626
R(4,11)	1.782	A(13,3,14)	112.634	D(1,2,21,27)	105.966
R(4,18)	1.509	A(5,7,9)	125.419	D(13,2,21,23)	164.080
R(5,11)	1.357	A(4,11,5)	96.680	D(11,4,6,15)	179.171
R(6,12)	1.779	A(6,15,16)	108.889	D(6,4,18,19)	16.763
R(7,8)	1.088	A(6,15,39)	113.812	D(6,4,18,20)	131.825
R(7,9)	1.438	A(16,15,17)	105.891	D(11,4,18,35)	73.351
R(15,16)	1.097	A(16,15,39)	109.630	D(4,6,15,17)	17.437
R(18,35)	1.539	A(21,27,28)	111.353	D(6,15,39,42)	60.561
R(24,25)	1.093	A(24,31,33)	110.511	D(22,21,27,29)	57.353
R(24,31)	1.539	A(37,35,38)	107.716	D(20,18,35,37)	62.680

Table 4.Optimized geometric parameters of compound 4

BondLength(Å)		BondAngles(°)		DihedralAngles(°)	
R(1,2)	1.350	A(2,1,14)	116.358	D(19,1,2,13)	178.693
R(1,4)	1.772	A(2,1,19)	127.411	D(19,1,2,24)	53.101
R(1,19)	1.500	A(14,1,19)	116.224	D(2,1,19,22)	42.567
R(3,9)	1.956	A(1,2,13)	117.401	D(14,1,19,21)	61.675
R(3,14)	1.781	A(1,2,24)	125.087	D(1,2,13,3)	56.023
R(4,6)	1.350	A(9,3,14)	122.342	D(13,2,24,29)	74.343
R(4,11)	1.778	A(13,3,14)	112.480	D(13,3,9,7)	40.200
R(6,12)	1.772	A(5,7,9)	125.297	D(13,3,9,10)	179.651
R(6,15)	1.500	A(4,,11,5)	96.975	D(14,3,9,10)	141.210
R(7,8)	1.088	A(6,15,16)	110.907	D(9,3,13,2)	172.199
R(7,9)	1.433	A(16,15,17)	107.449	D(13,3,14,1)	89.146
R(15,16)	1.096	A(16,15,18)	108.438	D(7,5,12,6)	172.234
R(19,21)	1.096	A(2,24,29)	101.549	D(4,5,15,16)	117.450
R(32,25)	1.838	A(23,25,27)	106.053	D(4,23,25,26)	58.326
R(29,31)	1.092	A(26,25,27)	109.288	D(2,24,29,30)	64.351

MOLECULAR ELECTROSTATIC POTENTIAL: The molecular electrostatic potential (MEP) is widely used to grasp molecular interactions and as a reactivity map splaying most probable regions for the electrophilic attack of charged point-like reagents in organic molecules and in studies of biological recognition and hydrogen bonding interactions [15,16]. It is a very useful tool in molecular modeling studies. MEP and contour provides a simple way to predict how different geometries could interact. In the present study, the electrostatic potential (ESP), total electron density (ED) and molecular electrostatic potential (MEP) of the title compounds is illustrated in Fig 2. The ED plots for title molecules show a uniform distribution. However, it can be seen from the ESP figure that while the negative ESP is localized more over the molecules and is reflected as a yellowish blue. This result is expected, because ESP correlates with electro negativity and partial charges.

The different values of the electrostatic potential are represented by different colors. Potential increases in the order red < orange < yellow < green < blue. The importance of MEP lies in the fact that it mutinously displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of color grading. MEP is also very useful in research of molecular structure with its physiochemical property relationship [17–22].

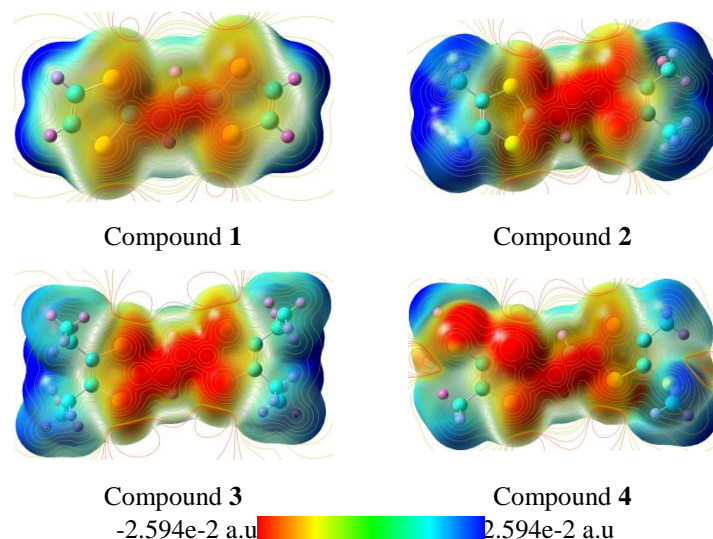


Fig. 2. Molecular electrostatic potential surface of TTFs conjugated 1-4

As seen from the figure 2 that, in all molecules, the regions exhibiting the negative electrostatic potential are localized near the TTF core and in groupings that contains the sulfur atoms for the compound 4 while the regions presenting the positive potential are localized vicinity of the hydrogen atoms and alkyl groups.

FRONTIER MOLECULAR ORBITALS (FMOs): The highest occupied molecular orbitals (HOMOs) and the lowest-lying unoccupied molecular orbitals (LUMOs) are named as frontier molecular orbitals (FMOs). The FMOs play an important role in the optical and electric properties, as well as in quantum chemistry [23]. HOMO–LUMO orbitals are also called frontier orbitals as they lie at the outermost boundaries of the electrons of the molecules. The frontier orbital gap helps characterize the chemical reactivity and the kinetic stability of the molecule. A molecule with a small frontier orbital gap is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule [23]. The 3D plots of the frontier orbitals HOMO and LUMO figures for the TTFs conjugated 1-4 are shown in Fig 3, while the HOMO and LUMO energies, electro negativity, chemical hardness and total energy for title compounds have been tabulated in Table 5.

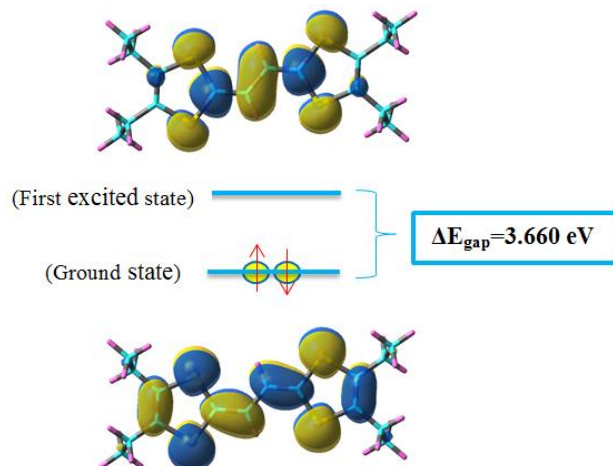


Fig. 3. HOMO-LUMO Structure with the energy level diagram of compound 3

GLOBAL REACTIVITY DESCRIPTORS: The energy gap between HOMO and LUMO is a critical parameter to determine molecular electrical transport properties. By using HOMO and LUMO energy values for a molecule, the global chemical reactivity descriptors of molecules such as hardness (η), chemical potential (μ), softness (S), electronegativity (χ) and electrophilicity index (ω) have been defined [24,25]. On the basis of E_{HOMO} and E_{LUMO} , these are calculated using the below equations. Using Koopman's theorem [26] for closed-shell molecules, the hardness of the molecule is $\eta = (I - A)/2$

The chemical potential of the molecule is $\mu = -(I + A)/2$

The softness of the molecule is $S = 1/2\eta$

The electro negativity of the molecule is $\chi = (I + A)/2$

The electrophilicity index of the molecule is $\omega = \mu^2 / 2\eta$

Where A is the ionization potential and I is the electron affinity of the molecule. I and A can be expressed through HOMO and LUMO orbital energies as $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$. All the calculated values of ionization potential, electron affinity, hardness, potential, softness and electrophilicity index are shown in Table 5.

Table 5. Quantum chemical descriptors of TTFs conjugated 1-4

Parameters	compound 1	compound 2	compound 3	compound 4
E_{HOMO} (eV)	-4.413	-4.195	-4.139	-4.462
E_{LUMO} (eV)	-0.730	-0.510	-0.479	-0.801
ΔE_{gap} (eV)	3.683	3.686	3.660	3.661
IE (eV)	4.413	4.195	4.139	4.462
A (eV)	0.730	0.510	0.479	0.801
μ (eV)	-2.572	-2.353	-2.309	-2.632
χ (eV)	2.572	2.353	2.309	2.632
η (eV)	1.841	1.843	1.830	1.830
S (eV)	0.272	0.271	0.273	0.273
ω (eV)	1.796	1.502	1.457	1.892

As presented in table 5, the compound which have the lowest energetic gap is the compound 3 ($\Delta E_{\text{gap}} = 3.660$ eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound 2 ($\Delta E_{\text{gap}} = 3.686$ eV). The compound that has the highest HOMO energy is the compound 3 ($E_{\text{HOMO}} = -4.139$ eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound 4 ($E_{\text{LUMO}} = -0.801$ 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 electro negativity (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 ($I = 4.139$ eV), so that will be the better electron donor. Compound **4** has the largest value of the affinity ($A = 0.801$ eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound **3** ($\eta = 1.830$ eV, $S = 0.273$ eV) is lesser (greater) among all the molecules. Thus, compound **3** is found to be more reactive than all the compounds. Compound **4** possesses higher electro negativity value ($\chi = 2.632$ eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **4** ($\omega = 1.892$ eV) indicates that it is the stronger electrophiles than all compounds. Compound **3** 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: Fukui function is one of the widely used local density functional descriptors to model chemical reactivity and site selectivity. The atom with the highest Fukui function is highly reactive compared to the other atoms in the molecule. Fukui functions have been calculated for large number of organic molecules, and are found to be always positive. Numeric and algebraic considerations allowed the identification of several boundary conditions for negative values for Fukui functions. Negative Fukui functions are found to be unlikely, except when very short inter atomic distances are present. Fukui function predicts favorable interactions between molecules that are far apart. The Fukui function [27] denoted by $f(r)$ is defined as the differential change in electron density due to an infinitesimal change in the number of electrons

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{V(r)}$$

Where $\rho(r)$ is the electron density, $N = \int \rho(r) dr$ is the total number of electron in the system and $V(r)$ is the external potential acting on an electron. A molecule is susceptible to nucleophilic attack at sites where $f^+(r)$ is large. Similarly, a molecule is susceptible to electrophilic attack at sites where $f^-(r)$ is large, because these are the regions where electron removal leads to least destabilization. In density functional theory, the Fukui functions are the selectivity indicators for electron-transfer controlled reactions. The electron density based local reactivity descriptors namely local hardness η , local softness S , and the Fukui function (f) are proposed to explain the chemical selectivity or reactivity at a particular site of a chemical system. It has also been shown that local hardness is a reliable intermolecular reactivity descriptor [28] and local softness and Fukui function are more reliable intramolecular site selectivity descriptors [29]. Yang and Mortier [30] have given a simple procedure to calculate the atomic condensed Fukui function indices based on Mulliken population analysis are

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

Where N , $N-1$ and $N+1$ are total electrons present in neutral, cation and anion state of molecule respectively. f^-_k , f^+_k describe the ability of an atom to accommodate an extra electron or to cope with the loss of an electron and f^0_k is considered as an indicator for radical reactivity. q_k is the atomic charge at the k^{th} site. Fukui functions for selected atomic sites in TTFs conjugated **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	13C	11C	2C	6C	Atom	6C	1C	2C	4C
f^+	-0.027	-0.027	-0.050	-0.050	f^+	0.016	0.016	0.015	0.015
Atom	3C	7C	1C	8C	Atom	6C	1C	2C	4C
f	-0.001	-0.001	-0.059	-0.059	f	0.008	0.008	0.004	0.004
Atom	3C	7C	13C	11C	Atom	6C	1C	2C	4C
f^0	-0.027	-0.027	-0.044	-0.044	f^0	0.012	0.012	0.010	0.010

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

Compound 3					Compound 4				
Atom	4C	2C	1C	6C	Atom	4C	2C	1C	6C
f^+	0.012	0.012	0.009	0.008	f^+	0.024	0.024	0.005	0.005
Atom	6C	1C	2C	4C	Atom	6C	1C	2C	4C
f	0.005	0.005	0.001	0.001	f	0.014	0.014	0.002	0.002
Atom	6C	1C	4C	2C	Atom	2C	4C	6C	1C
f^0	0.007	0.007	0.006	0.006	f^0	0.013	0.013	0.009	0.009

From the tables 6-7, the parameters of local reactivity descriptors show that 4C is the more reactive site in compounds **3** and **4** and 13C, 6C are the more reactive sites in compounds **1** and **2** respectively for nucleophilic attacks. The more reactive sites in radical attacks are 3C, 2C, for compounds **1**, **4** respectively and 6C for the both compounds **2** and **3**. The more reactive sites for electrophilic attacks are 6C for compounds **2**, **3** and **4** and 3C for compound **1**.

NATURAL BOND ORBITAL ANALYSIS (NBO): NBO analysis provides the most accurate possible natural Lewis structure of wave function, because all orbital details are mathematically chosen to include the highest possible percentage of the electron density. The larger $E(2)$ value implies the more intensive 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 [31]. The energy of these interactions can be estimated by second order perturbation theory by the equation:

$$E(2) = \Delta E_{ij} = q_i \frac{(F_{ij})^2}{E_j - E_i}$$

q_i is the donor orbital occupancy, E_i , E_j is the diagonal elements, F_{ij} is the off diagonal NBO Fock matrix element. The second-order perturbation theory analysis of Fock matrix in NBO basis of TTFs conjugated **1-4** is given in Tables 8-11.

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) S16	1.76391	$\pi^*(C6-C8)$	0.21868	22.59	0.25	0.068
LP(2) S18	1.76391	$\pi^*(C1-C2)$	0.21868	22.59	0.25	0.068
LP(2) S15	1.76804	$\pi^*(C6-C8)$	0.21868	22.29	0.25	0.067
LP(2) S17	1.76804	$\pi^*(C1-C2)$	0.21868	22.29	0.25	0.067
LP(2) S15	1.76804	$\pi^*(C7-C11)$	0.32787	19.24	0.27	0.066
LP(2) S17	1.76804	$\pi^*(C3-C13)$	0.32787	19.24	0.27	0.066
LP(2) S16	1.76391	$\pi^*(C7-C11)$	0.32787	17.88	0.27	0.063
LP(2) S18	1.76391	$\pi^*(C3-C13)$	0.32787	17.88	0.27	0.063
$\pi(C3-C13)$	1.91276	$\pi^*(C7-C11)$	0.32787	14.48	0.30	0.063
$\pi(C7-C11)$	1.91276	$\pi^*(C3-C13)$	0.32787	14.48	0.30	0.063
$\sigma(C11-H12)$	1.96459	$\sigma^*(C7-S15)$	0.04570	7.86	0.68	0.066
$\sigma(C13-H14)$	1.96459	$\sigma^*(C3-S17)$	0.04570	7.86	0.68	0.066
$\sigma(C1-H4)$	1.97586	$\sigma^*(C2-S17)$	0.01859	5.37	0.76	0.057
$\sigma(C8-H10)$	1.97586	$\sigma^*(C6-S15)$	0.01859	5.37	0.76	0.057
$\sigma(C2-H5)$	1.97604	$\sigma^*(C1-S18)$	0.01727	5.31	0.76	0.057
$\sigma(C6-H9)$	1.97604	$\sigma^*(C8-S16)$	0.01727	5.31	0.76	0.057
$\sigma(C11-C13)$	1.96858	$\sigma^*(C3-S18)$	0.03701	4.09	0.84	0.052
$\sigma(C11-C13)$	1.96858	$\sigma^*(C7-S16)$	0.03701	4.09	0.84	0.052
$\sigma(C3-S18)$	1.97787	$\sigma^*(C11-C13)$	0.01977	4.06	1.18	0.062
$\sigma(C7-S16)$	1.97787	$\sigma^*(C11-C13)$	0.01977	4.06	1.18	0.062

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) S12	1.77891	$\pi^*(C4-C6)$	0.23688	20.42	0.27	0.066
LP(2) S14	1.77891	$\pi^*(C1-C2)$	0.02990	20.42	0.27	0.066
LP(2) S11	1.78244	$\pi^*(C4-C6)$	0.23688	20.09	0.27	0.066
LP(2) S13	1.78244	$\pi^*(C1-C2)$	0.02990	20.09	0.27	0.066
LP(2) S11	1.78244	$\pi^*(C5-C7)$	0.32684	19.64	0.27	0.067
LP(2) S13	1.78244	$\pi^*(C3-C9)$	0.32684	19.64	0.27	0.067
LP(2) S12	1.77891	$\pi^*(C5-C7)$	0.32684	18.28	0.27	0.064
LP(2) S14	1.77891	$\pi^*(C3-C9)$	0.32684	18.28	0.27	0.064
$\pi(C3-C9)$	1.91216	$\pi^*(C5-C7)$	0.32684	14.48	0.30	0.063
$\pi(C5-C7)$	1.91216	$\pi^*(C3-C9)$	0.32684	14.48	0.30	0.063
$\sigma(C7-H8)$	1.96497	$\sigma^*(C5-S11)$	0.04255	7.86	0.69	0.066
$\sigma(C9-H10)$	1.96497	$\sigma^*(C3-S13)$	0.04255	7.86	0.69	0.066
$\sigma(C1-S14)$	1.97322	$\sigma^*(C2-C23)$	0.01860	5.23	1.04	0.066
$\sigma(C6-S12)$	1.97322	$\sigma^*(C4-C19)$	0.01860	5.23	1.04	0.066
$\sigma(C2-S13)$	1.97290	$\sigma^*(C1-C27)$	0.01853	5.22	1.04	0.066
$\sigma(C4-S11)$	1.97290	$\sigma^*(C6-C15)$	0.01853	5.22	1.04	0.066
$\sigma(C1-C27)$	1.97897	$\sigma^*(C1-C2)$	0.02990	5.15	1.29	0.073
$\sigma(C6-C15)$	1.97897	$\sigma^*(C4-C6)$	0.02990	5.15	1.29	0.073
$\sigma(C2-C23)$	1.97912	$\sigma^*(C1-C2)$	0.02990	5.14	1.29	0.073
$\sigma(C4-C19)$	1.97912	$\sigma^*(C4-C6)$	0.02990	5.14	1.29	0.073

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) S14	1.77637	$\pi^*(C1-C2)$	0.23200	20.20	0.27	0.066
LP(2) S12	1.77639	$\pi^*(C4-C6)$	0.23198	20.19	0.27	0.066
LP(2) S11	1.78010	$\pi^*(C4-C6)$	0.23198	19.86	0.27	0.066
LP(2) S13	1.78011	$\pi^*(C1-C2)$	0.23200	19.86	0.27	0.066
LP(2) S11	1.78010	$\pi^*(C5-C7)$	0.32984	19.70	0.27	0.067
LP(2) S13	1.78011	$\pi^*(C3-C9)$	0.32985	19.70	0.27	0.067
LP(2) S12	1.77639	$\pi^*(C5-C7)$	0.32984	18.34	0.27	0.064
LP(2) S14	1.77637	$\pi^*(C3-C9)$	0.32985	18.34	0.27	0.064
$\pi(C3-C9)$	1.91185	$\pi^*(C5-C7)$	0.32984	14.49	0.30	0.063
$\pi(C5-C7)$	1.91185	$\pi^*(C3-C9)$	0.32985	14.49	0.30	0.063
$\sigma(C7-H8)$	1.96496	$\sigma^*(C5-S11)$	0.04256	7.88	0.69	0.066
$\sigma(C9-H10)$	1.96496	$\sigma^*(C3-S13)$	0.04256	7.88	0.69	0.066
$\sigma(C1-C24)$	1.97367	$\sigma^*(C1-C2)$	0.02941	5.32	1.28	0.074
$\sigma(C6-C15)$	1.97367	$\sigma^*(C4-C6)$	0.02941	5.32	1.28	0.074
$\sigma(C2-C21)$	1.97384	$\sigma^*(C1-C2)$	0.02941	5.31	1.28	0.074
$\sigma(C4-C18)$	1.97384	$\sigma^*(C4-C6)$	0.02941	5.31	1.28	0.074
$\sigma(C1-S14)$	1.97348	$\sigma^*(C2-C21)$	0.02605	5.13	1.04	0.065
$\sigma(C2-S13)$	1.97317	$\sigma^*(C1-C24)$	0.02599	5.13	1.04	0.065
$\sigma(C4-S11)$	1.97317	$\sigma^*(C6-C15)$	0.02599	5.13	1.04	0.065
$\sigma(C6-S12)$	1.97348	$\sigma^*(C4-C18)$	0.02605	5.13	1.04	0.065

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) S12	1.76469	$\pi^*(C4-C6)$	0.26730	23.38	0.25	0.069
LP(2) S14	1.76469	$\pi^*(C1-C2)$	0.26730	23.38	0.25	0.069
LP(2) S11	1.77998	$\pi^*(C5-C7)$	0.32131	19.54	0.27	0.066
LP(2) S13	1.77998	$\pi^*(C3-C9)$	0.32131	19.54	0.27	0.066
LP(2) S11	1.77998	$\pi^*(C4-C6)$	0.26730	18.54	0.25	0.062
LP(2) S13	1.77998	$\pi^*(C1-C2)$	0.26730	18.54	0.25	0.062
LP(2) S12	1.76469	$\pi^*(C5-C7)$	0.32131	17.64	0.27	0.063
LP(2) S14	1.76469	$\pi^*(C3-C9)$	0.32131	17.64	0.27	0.063
$\pi(C3-C9)$	1.91062	$\pi^*(C5-C7)$	0.32131	14.51	0.30	0.063
$\pi(C5-C7)$	1.91062	$\pi^*(C3-C9)$	0.32131	14.51	0.30	0.063
$\sigma(C7-H8)$	1.96505	$\sigma^*(C5-S11)$	0.04686	7.85	0.69	0.066
$\sigma(C9-H10)$	1.96505	$\sigma^*(C3-S13)$	0.04686	7.85	0.69	0.066
$\sigma(C1-S14)$	1.97053	$\sigma^*(C2-S24)$	0.03312	5.64	0.84	0.061
$\sigma(C6-S12)$	1.97053	$\sigma^*(C4-S23)$	0.03312	5.64	0.84	0.061
$\sigma(C15-H18)$	1.98338	$\sigma^*(C6-S12)$	0.03190	5.20	0.70	0.054
$\sigma(C19-H22)$	1.98338	$\sigma^*(C1-S14)$	0.03190	5.20	0.70	0.054
$\sigma(C1-C19)$	1.97920	$\sigma^*(C1-C2)$	0.03833	4.99	1.26	0.071
$\sigma(C6-C15)$	1.97920	$\sigma^*(C4-C6)$	0.03833	4.99	1.26	0.071
$\sigma(C2-S13)$	1.97701	$\sigma^*(C1-C19)$	0.01810	4.92	1.05	0.064
$\sigma(C4-S11)$	1.97701	$\sigma^*(C6-C15)$	0.01810	4.92	1.05	0.064

The intra molecular interaction for the title compounds is formed by the orbital overlap between: $\pi(C3-C13)$ and $\pi^*(C7-C11)$ for compound **1**, $\pi(C3-C9)$ and $\pi^*(C5-C7)$ for compound **2**, $\pi(C3-C9)$ and $\pi^*(C5-C7)$ for compound **3** and $\pi(C3-C9)$ and $\pi^*(C5-C7)$ for compound **4** respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of $\pi(C3-C13)$ to $\pi^*(C7-C11)$ for compound **1**, $\pi(C3-C9)$ to $\pi^*(C5-C7)$ for compound **2**, $\pi(C3-C9)$ to $\pi^*(C5-C7)$ for compound **3** and $\pi(C3-C9)$ to $\pi^*(C5-C7)$ for compound **4** lead to highest stabilization of 14.48, 14.48, 14.49 and 14.51 kJ mol⁻¹ respectively. In case of LP(2) S16 orbital to the $\pi^*(C6-C8)$ for compound **1** LP(2) S12 orbital to $\pi^*(C4-C6)$ for compound **2**, LP(2) S14 orbital to $\pi^*(C1-C2)$ for compound **3**, LP(2) S12 orbital to $\pi^*(C4-C6)$ for compound **4** respectively, show the stabilization energy of 22.59, 20.42, 20.20 and 23.38 kJ mol⁻¹ respectively.

NONLINEAR OPTICAL PROPERTIES (NLO): Non-linear 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 fields [32]. For an isolated molecule, the nonlinear optical response in an electric field $E_i(\omega)$ can be presented as a Taylor series expansion of the total dipole moment, μ_{tot} , induced by the field:

$$\mu_{tot} = \mu_0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \dots$$

Where α_{ij} is the linear polarizability, μ_0 the permanent dipole moment and β_{ijk} are the first hyperpolarizability tensor components. The isotropic (or average) linear polarizability is defined as [33]:

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

First hyperpolarizability is a third rank tensor that can be described by $3 \times 3 \times 3$ matrix. The 27 components of 3D matrix can be reduced to 10 components due to the Kleinman symmetry [34].

The output from Gaussian 09 provides 10 components of this matrix as β_{xxx} , β_{xxy} , β_{xyy} , β_{yyy} , β_{xxz} , β_{xyz} , β_{yyz} , β_{xzz} , β_{yzz} , β_{zzz} , respectively. The components of the first hyperpolarizability can be calculated using the following equation [33]:

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji})$$

Using the x, y and z components of β , the magnitude of the first hyperpolarizability tensor can be calculated by:

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

The complete equation for calculating the magnitude of β from Gaussian 09 output is given as follows:

$$\beta_{tot} = \sqrt{(\beta_{xxx} + \beta_{xyy} + \beta_{zzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2}$$

DFT has been extensively used as an effective method to investigate the organic NLO materials [35]. The electronic dipole moment μ_i ($i = x, y, z$), polarizability α_{ij} and the first hyperpolarizability β_{ijk} of the title compound were calculated at the B3LYP/6-31G(d,p) level and listed in Table 12.

Table 12. The dipole moments μ (D), polarizability α , the average polarizability α (esu), the anisotropy of the polarizability $\Delta\alpha$ (esu), and the first hyperpolarizability β (esu) of TTFs conjugated 1-4 calculated by B3LYP/6-31G(d,p) method

Parameters	compound 1	compound 2	compound 3	compound 4
β_{xxx}	0.0000	0.0000	-0.0161	0.0021
β_{yyy}	0.0000	0.0000	0.0012	0.0010
β_{zzz}	0.0000	0.0019	0.0087	0.0000
β_{xyy}	0.0000	0.0000	0.0069	-0.0011
β_{xxy}	0.0000	0.0000	-0.0044	0.0016
β_{xxz}	0.0000	-0.0031	0.0298	0.0007
β_{xzz}	0.0000	0.0000	-0.0120	0.0010
β_{yzz}	0.0000	0.0000	0.0011	-0.0002
β_{yyz}	0.0000	-0.0034	0.0011	0.0001
β_{xyz}	0.0000	-0.0077	-0.0228	-0.0009
$\beta_{tot}(\text{esu}) \times 10^{-33}$	0.0000	0.0089	0.0547	0.0033
μ_x	0.0000	0.0000	-0.0002	0.0000
μ_y	0.0000	0.0000	-0.0002	0.0001
μ_z	0.0000	0.0001	0.0023	0.0000
$\mu_{tot}(\text{D})$	0.0000	0.0001	0.0023	0.0001
α_{xx}	-67.1153	-80.6408	-106.0503	-123.8799
α_{yy}	-94.8320	-120.3215	-146.2333	-140.2277
α_{zz}	-104.4091	-129.2090	-154.8702	-153.5063
α_{xy}	-3.8358	3.5805	2.9274	1.7958
α_{xz}	0.0011	0.0006	0.7573	17.2543
α_{yz}	-0.0001	0.0003	2.0099	-4.2183
$\alpha(\text{esu}) \times 10^{-24}$	34.1982	45.2180	45.5617	40.2099
$\Delta\alpha(\text{esu}) \times 10^{-24}$	5.0681	6.7013	6.7522	5.9591

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 0.0000, 0.0001, 0.0023 and 0.0001D respectively, which are approximately zero 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 34.1982×10^{-24} , 45.2180×10^{-24} , 45.5617×10^{-24} and 40.2099×10^{-24} esu respectively; the values of anisotropy of the polarizability are 5.0681, 6.7013, 6.7522 and 5.9591 esu, respectively. The



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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 TTFs conjugated molecules are equal to 0.0000×10^{-33} , 0.0089×10^{-33} , 0.0547×10^{-33} and 0.0033×10^{-33} esu. The above results show that TTFs conjugated **1-4** might have not the NLO applications.

IV. CONCLUSION

In the present study, the structural geometrical parameters and nonlinear optical properties of TTFs conjugated **1-4** have been studied using the DFT method and DFT/B3LYP 6-31G(d,p) basis set. The first order hyperpolarizability value implies that the title molecules may be not useful as a non-linear optical material. Stability of the molecules arising from hyper-conjugative interaction and charge delocalization has been analyzed using NBO analysis. MEP, HOMO and LUMO analysis are also reported. The HOMO and LUMO analysis are used to determine the charge transfer within the molecule and the HOMO–LUMO energy gap shows the chemical activity of the molecules. The HOMO of π nature is delocalized over the C=C bonds and sulfur atoms of TTF in all the molecule and in LUMO, only between 1, 3-dithiole of TTF.

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