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# Quantum Investigation of Structure Electronic and Non-Linear Optical Properties of TTF Separated by Thiophene

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## Authors' contributions

*This work was carried out in collaboration between all authors. Author TA designed the study, carried out literature searches and wrote the first draft of the manuscript. Authors AB and DV guided in the analyses of the study and interpretation of the results. All authors read and approved the final manuscript.*

## Article Information

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## ABSTRACT

We investigate in this study, the quantum chemical computations of a series of tetrathiafulvalene (TTF) separated by thiophene 1-4 using the DFT/B3LYP method with 6-31G (d,p) basis set. The optimized structures and geometrical parameters were determined by the same method cited above. In addition, a molecular electrostatic potential map (MEP) has been analyzed for predicting the reactive sites. The calculated HOMO and LUMO energies showed that charge transfer occurs within the molecule. The chemical reactivity parameters (chemical hardness and softness, electro negativity, chemical potential and electro philicity index) were discussed clearly. To find out more reactive sites of the title molecules, condensed Fukui functions have been also calculated. Stability of the compounds arising from hyper-conjugative interaction and charge delocalization has been analyzed using Natural bond orbital (NBO) analysis. NLO properties related to polarizability and hyperpolarizability are also discussed to predict the applications of title compounds.

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

## 1. INTRODUCTION

Among sulfur-rich  $\pi$ -conjugated molecules, thiophene and tetrathiafulvalene (TTF) which are two extraordinary candidates, which show remarkable electronic properties and ample application potentials. Thiophene is the essential repeat unit for a class of well-known conducting polymers (CPs), poly/oligo-thiophenes [1-3], while TTF and its derivatives are excellent organic electron donors widely applicable in various fields ranging from charge-transfer complexes, nonlinear optical materials, organic transistors, to molecular switches and sensors [4-7]. Tetrathiafulvalene and its derivatives have been extensively investigated as an electron-donating unit in molecular conductors due to strong intermolecular  $\pi$ - $\pi$  stacking [8,9].

Density functional theory (DFT) is a quantum mechanical method used in chemistry and physics to calculate the electronic structure of atoms, molecules and solids and it has been very popular in computational chemistry since the late 1980s and 1990s. Within this context density, functional theory (DFT) is a source whose importance is increasing in terms of computational techniques [10].

Taking into account the above, in this Letter we describe a global computational study on a series of TTF separated by thiophene 1-4 illustrate in the literature [11] by using a DFT/B3LYP method with 6-31G (d,p) basis set. The optimized molecular structures and geometrical parameters of all molecules have been performed using the same method. The chemical activity and reactivity have been studied by calculating molecular electrostatic potential surfaces (MEPS). Natural bond analysis (NBO) has been used to explore the stability of the molecules arising from hyperconjugative and charge transfer interaction. The first hyperpolarizability ( $\beta_0$ ) has been computed to indicate suitability for a non-linear optical response.

## 2. MATERIALS AND METHODS

All computational calculations have been performed on a personal computer. The geometries of all compounds investigated were completely optimized. The imaginary frequencies are absent which confirms that the structures are

true minima on the potential energy surface. In this work all the calculations were performed in the Gaussian 09W package [12] program. Vibrational frequency assignments were made with a high degree of accuracy by combining the results of the Gauss view 05 software program with symmetry considerations. The Becke's three-parameter hybrid functional using the LYP correlation functional (B3LYP), one of the most robust functional of the hybrid family, was herein used for all the calculations, with 6.31G (d,p) basis set.

## 3. RESULTS AND DISCUSSION

### 3.1 Molecular Geometry

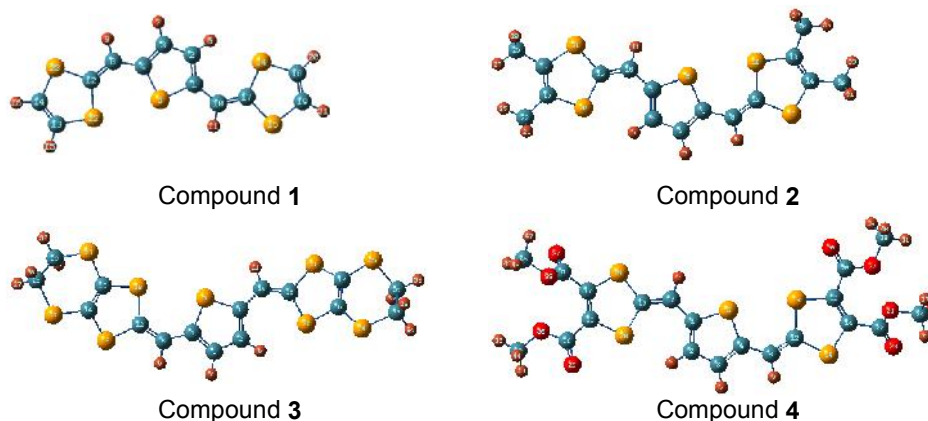
The optimized molecular structures of TTF separated by thiophene 1-4 with atom numbering scheme adopted in this study is shown in Fig. 1. Geometry optimization has been achieved by energy minimization, using DFT at the B3LYP level, employing the basis set 6-31G (d,p). The following Fig. 1 and Tables 1-4 represent the schemes of the optimized molecules, their bond lengths and their angle measurement.

### 3.2 Molecular Electrostatic Potential (MEP)

Molecular electrostatic potentials have been used extensively for interpreting and predicting the reactive behavior of a wide variety of chemical systems in both electrophilic and nucleophilic reactions [13].  $V(r)$ , 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 [14]:

$$V(r) = \sum \frac{Z_A}{R_{A-r}} - \int \frac{\rho(r')}{|r-r'|} dr'$$

Where the summation runs over all the nuclei A in the molecule and polarization and reorganization effects is neglected.  $Z_A$  is the



**Fig. 1. Optimized molecular structure of TTF separated by thiophene 1-4**

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

Bond length (Å)		Bond angles (°)		Dihedral angles (°)	
R(1,2)	1.387	A(2,1,5)	109.610	D(5,1,2,3)	56.001
R(1,5)	1.763	A(2,1,10)	132.790	D(10,1,2,3)	179.999
R(1,10)	1.440	A(5,1,10)	117.600	D(2,1,10,17)	47.002
R(2,3)	1.411	A(1,2,3)	113.782	D(6,2,3,4)	179.997
R(2,6)	1.082	A(1,2,6)	123.664	D(7,3,4,5)	180.000
R(4,5)	1.757	A(5,4,8)	125.711	D(8,4,5,1)	179.999
R(8,12)	1.358	A(1,5,4)	92.695	D(3,4,8,9)	86.014
R(10,11)	1.088	A(4,8,12)	130.859	D(5,4,8,12)	78.018
R(10,17)	1.358	A(1,10,11)	115.474	D(1,10,17,25)	179.997
R(12,22)	1.783	A(11,10,17)	115.652	D(8,12,22,13)	179.994
R(13,14)	1.338	A(22,12,23)	112.979	D(22,13,14,16)	179.999
R(13,15)	1.083	A(14,13,15)	125.019	D(16,14,23,12)	179.997
R(17,24)	1.781	A(14,13,22)	117.896	D(10,17,24,18)	180.002
R(18,20)	1.083	A(18,19,25)	117.725	D(25,17,24,18)	55.004
R(18,24)	1.761	A(21,19,25)	117.385	D(21,19,25,17)	180.002

**Table 2. Optimized geometric parameters of compound 2**

Bond length (Å)		Bond angles (°)		Dihedral angles (°)	
R(2,3)	1.411	A(2,1,5)	109.599	D(10,1,5,4)	180.000
R(2,6)	1.082	A(2,1,10)	132.753	D(6,2,3,4)	179.993
R(3,4)	1.387	A(5,1,10)	117.648	D(7,3,4,5)	179.999
R(3,7)	1.085	A(1,2,3)	113.785	D(8,4,5,1)	180.000
R(4,5)	1.758	A(1,2,6)	123.598	D(3,4,8,12)	179.999
R(4,8)	1.438	A(3,2,6)	122.618	D(5,4,8,9)	179.999
R(8,9)	1.089	A(2,3,4)	114.601	D(8,12,18,13)	179.992
R(8,12)	1.358	A(2,3,7)	123.461	D(14,13,34,36)	120.294
R(10,11)	1.088	A(4,3,7)	121.938	D(18,13,34,35)	180.000
R(10,15)	1.358	A(3,4,5)	109.307	D(18,13,34,37)	59.705
R(12,18)	1.774	A(3,4,8)	124.985	D(30,14,19,12)	179.994
R(12,19)	1.780	A(5,4,8)	125.709	D(13,14,30,31)	120.264
R(13,14)	1.346	A(1,5,4)	92.709	D(19,14,30,32)	59.695
R(13,18)	1.780	A(4,8,9)	113.194	D(19,14,30,33)	179.979
R(13,34)	1.503	A(4,8,12)	130.816	D(10,15,20,16)	179.986

**Table 3. Optimized geometric parameters of compound 3**

Bond length (Å)		Bond angles (°)		Dihedral angles (°)	
R(1,10)	1.440	A(2,1,5)	109.842	D(5,1,2,6)	176.969
R(2,6)	1.083	A(2,1,10)	131.829	D(10,1,2,3)	178.908
R(3,4)	1.387	A(5,1,10)	118.324	D(2,1,10,11)	163.802
R(3,7)	1.085	A(1,2,3)	113.707	D(5,1,10,15)	162.758
R(4,5)	1.756	A(1,2,6)	123.415	D(1,2,3,7)	179.230
R(4,8)	1.438	A(3,2,6)	122.814	D(2,3,4,8)	179.926
R(8,9)	1.089	A(2,3,4)	114.391	D(8,4,5,1)	179.957
R(8,12)	1.357	A(2,3,7)	123.582	D(3,4,8,12)	179.050
R(10,11)	1.088	A(4,3,7)	122.019	D(5,4,8,9)	178.780
R(10,15)	1.357	A(3,4,5)	109.585	D(4,8,12,19)	176.395
R(12,18)	1.778	A(3,4,8)	124.761	D(9,8,12,18)	179.704
R(12,19)	1.784	A(5,4,8)	125.654	D(1,10,15,21)	174.384
R(13,14)	1.350	A(4,8,9)	113.287	D(11,10,15,20)	176.650
R(13,18)	1.780	A(4,8,12)	130.757	D(19,12,18,13)	18.3890
R(14,22)	1.766	A(9,8,12)	115.956	D(8,12,19,14)	164.026

**Table 4. Optimized geometric parameters of compound 4**

Bond length (Å)		Bond angles (°)		Dihedral angles (°)	
R(4,8)	1.438	A(3,2,6)	122.658	D(10,1,5,4)	179.560
R(8,9)	1.089	A(2,3,4)	114.429	D(6,2,3,4)	177.663
R(8,12)	1.357	A(2,3,7)	123.512	D(7,3,4,5)	179.518
R(10,11)	1.088	A(4,3,7)	122.056	D(8,4,5,1)	179.963
R(10,15)	1.357	A(3,4,5)	109.523	D(8,12,18,13)	177.895
R(12,18)	1.780	A(3,4,8)	124.880	D(25,13,18,12)	177.172
R(12,19)	1.784	A(5,4,8)	125.597	D(22,14,19,12)	175.300
R(13,14)	1.354	A(4,8,9)	113.226	D(10,15,20,16)	173.348
R(13,18)	1.769	A(4,8,12)	130.703	D(28,16,20,15)	178.902
R(13,25)	1.488	A(9,8,12)	116.071	D(31,17,21,15)	173.854
R(14,19)	1.757	A(1,10,11)	115.847	D(22,24,34,36)	62.336
R(14,22)	1.496	A(1,10,15)	128.132	D(25,27,38,40)	61.652
R(17,21)	1.757	A(11,10,15)	116.019	D(16,28,30,42)	179.919
R(17,31)	1.498	A(8,12,18)	126.266	D(28,30,42,44)	61.352
R(22,23)	1.213	A(8,12,19)	120.372	D(31,33,46,48)	62.571

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 molecules, molecular electrostatic potential (MEP) was calculated at B3LYP/6-31G (d,p). Red and blue areas in the MEP map refer to the regions of negative and positive potentials and correspond to the electron-rich and electron-poor regions, respectively, whereas the green colour signifies the neutral electrostatic potential. The MEP surface provides necessary information about the reactive sites. The electron total density has been mapped as shown in Fig. 2.

As seen in Fig. 2 the regions exhibiting the negative electrostatic potential are localized near the thiophene in all molecules, except compound 4 where it is localized in carbonyl of the ester function while the regions presenting the positive

potential are localized vicinity of the hydrogen atoms.

### 3.3 Frontier Molecular Orbitals (FMOs)

The most important frontier molecular orbitals (FMOs) such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) play a crucial part in the chemical stability of the molecule [15]. The HOMO represents the ability to donate an electron and LUMO represents the ability to accept an electron. The energy gap between HOMO and LUMO also determines the chemical reactivity, optical polarizability and chemical hardness-softness of a molecule [16]. The energy gap is calculated at B3LYP/6-31G (d,p) level and it's given in Table 5. The energies HOMO, LUMO, LUMO+1 and HOMO-1 and the  $\Delta E_{\text{gap}}$  of compound 4 are shown in Fig. 3.

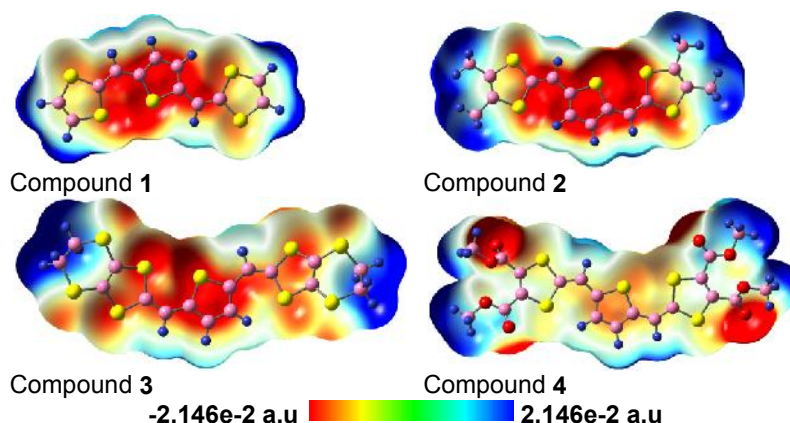


Fig. 2. Molecular electrostatic potential surface of TTF separated by thiophene 1-4

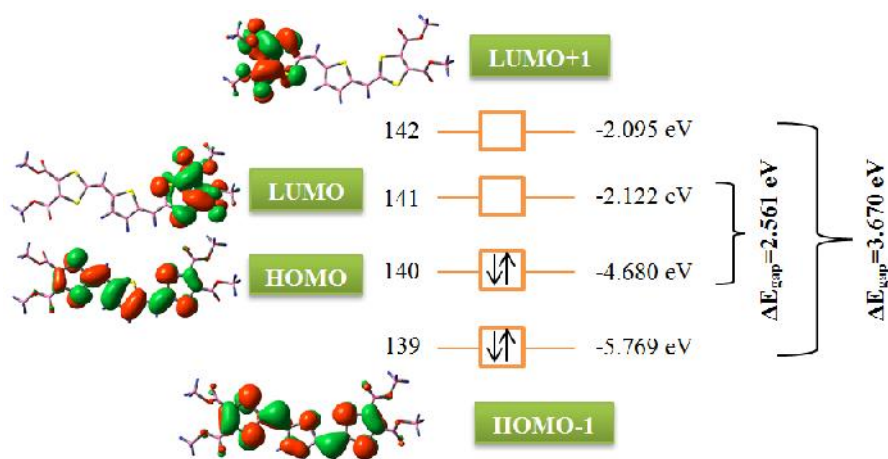


Fig 3. HOMO-LUMO Structure with the energy level diagram of compound 4

### 3.4 Global Reactivity Descriptors

The chemical reactivity and site selectivity of the molecular systems have been determined by the conceptual density functional theory [17]. Electronegativity ( $\chi$ ), the chemical potential ( $\mu$ ), global hardness ( $\eta$ ), global softness ( $S$ ) and electrophilicity index ( $\omega$ ) are global reactivity descriptors highly successful in predicting global reactivity trends. On the basis of Koopman's theorem [17], global reactivity descriptors are calculated using the energies of frontier molecular orbitals  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  and given by the equations below [18-22].

$$\chi = -1/2(E_{\text{LUMO}} + E_{\text{HOMO}})$$

$$\mu = -\chi = 1/2(E_{\text{LUMO}} + E_{\text{HOMO}})$$

$$\eta = 1/2(E_{\text{LUMO}} - E_{\text{HOMO}})$$

$$S = 1/\eta$$

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

According to Parr et al., electrophilicity index ( $\omega$ ) [21] is a global reactivity index similar to the chemical hardness and chemical potential.  $I$  and  $A$  can be expressed through HOMO and LUMO orbital energies as  $I = -E_{\text{HOMO}}$  and  $A = -E_{\text{LUMO}}$ . The global reactivity descriptors of title compounds are computed by the DFT/B3LYP method with 6-31G (d,p) basis set and listed in Table 5.

As presented in Table 5, the compound which has the lowest energy gap is the compound 4 ( $\Delta E_{\text{gap}} = 2.561 \text{ eV}$ ). This lower gap allows it to be the softest molecule. The compound that has the highest energy gap is the compound 1 ( $\Delta E_{\text{gap}} = 3.128 \text{ eV}$ ). The compound that has the highest HOMO energy is the compound 2 ( $E_{\text{HOMO}} = -4.220 \text{ eV}$ ). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound 4 ( $E_{\text{LUMO}} = -2.136 \text{ eV}$ ) which signifies that it can be the

**Table 5. Quantum chemical descriptors of TTF separated by thiophene 1-4**

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
$E_{\text{HOMO}}$ (eV)	-4.402	-4.220	-4.553	-4.698
$E_{\text{LUMO}}$ (eV)	-1.274	-1.099	-1.522	-2.136
$\Delta E_{\text{gap}}$ (eV)	3.128	3.121	3.031	2.561
$I$ (eV)	4.402	4.220	4.553	4.698
$A$ (eV)	1.274	1.099	1.522	2.136
$\mu$ (eV)	-2.838	-2.660	-3.038	-3.417
$\chi$ (eV)	2.838	2.660	3.038	3.417
$\eta$ (eV)	1.564	1.560	1.515	1.281
$S$ (eV)	0.320	0.320	0.330	0.390
$\omega$ (eV)	2.575	2.267	3.044	4.559

best electron acceptor. The two properties like  $I$  (potential ionization) and  $A$  (affinity) are so important, the determination of these two properties allows us to calculate the absolute electronegativity ( $\chi$ ) and the absolute hardness ( $\eta$ ). These two parameters are related to the one-electron orbital energies of the HOMO and LUMO respectively. Compound 2 has the lowest value of the potential ionization ( $I = 4.220$  eV), so that will be the better electron donor. Compound 4 has the largest value of the affinity ( $A = 2.136$  eV), so it is the better electron acceptor. The chemical reactivity varies with the structure of molecules. Chemical hardness (softness) value of compound 4 ( $\eta = 1.281$  eV,  $S = 0.390$  eV) is lesser (greater) among all the molecules. Thus, compound 4 is found to be more reactive than all the compounds. Compound 4 possesses higher electronegativity value ( $\chi = 3.417$  eV) than all compounds so; it is the best electron acceptor. The value of  $\omega$  for compound 4 ( $\omega = 4.559$  eV) indicates that it is the stronger electrophiles than all compounds. Compound 4 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 a soft molecule.

### 3.5 Local Reactivity Descriptors

DFT is one of the important tools of quantum chemistry to understand popular chemical concepts such as electronegativity, electron affinity, chemical potential and ionization potential [23]. The electron density-based local reactivity descriptors such as Fukui functions are proposed to explain the chemical selectivity or reactivity at a particular site of a chemical system [24]. Electron density is a property that contains all the information about the molecular system and plays an important role in calculating almost all these chemical quantities. Parr and Yang [25] proposed a finite difference approach to calculate

Fukui function indices, i.e. nucleophilic, electrophilic and radical attacks. Fukui indices are, in short, reactivity indices; they give us information about which atoms in a molecule have a larger tendency to either lose or accept an electron, which we chemist interpret as which are more prone to undergo a nucleophilic or an electrophilic attack, respectively. The Fukui function is defined as [26].

$$f(r) = \frac{\partial \rho(r)}{\partial N}$$

where  $\rho(r)$  is the electronic density,  $N$  is the number of electrons and  $r$  is the external potential exerted by the nucleus. The Fukui function is a local reactivity descriptor that indicates the preferred regions where a chemical species will change its density when the number of electrons is modified. Therefore, it indicates the propensity of the electronic density to deform at a given position upon accepting or denoting electrons [26-28]. Also, it is possible to calculate the atomic condensed Fukui function indices based on Mulliken population analysis (MPA) and on three possible forward, backward, and central finite difference approximations to the derivatives of Fukui function, and can be written as,

$$f_j^- = q_j(N) - q_j(N-1) \quad \text{governing electrophilic attack,}$$

$$f_j^+ = q_j(N+1) - q_j(N) \quad \text{governing nucleophilic attack,}$$

$$f_j^0 = \frac{1}{2} [q_j(N+1) - q_j(N-1)] \quad \text{governing radical attack,}$$

where  $f_j^-$  and  $f_j^+$  describe the ability of an atom to accommodate an extra electron or to cope with the loss of an electron and  $f_j^0$  is then

considered an indicator for radical reactivity. In these equations,  $q_j$  is the atomic charge (evaluated from Mulliken population analysis, electrostatic derived charge, etc.) at the  $j^{\text{th}}$  atomic site is the neutral (N), anionic (N+1) or cationic (N-1) chemical species. The Fukui function allows determining the pinpoint distribution of the active sites on a molecule, the value of this function is completely dependent of the kind of charges used. The reactive sites on TTF separated by thiophene 1-4 are calculated by the DFT/B3LYP method with 6-31G (d,p) basis set and shown in Tables 6-7.

From the Tables 6-7, the parameters of local reactivity descriptors show that 4C is the more reactive site in compounds 1, 2 and 4 and 13C is the more reactive site in compounds 3 for nucleophilic attacks. The more reactive sites for electrophilic attacks are 17C for compound 1 and 3 and 15C, 16C for compounds 2 and 4 respectively. The more reactive sites in radical attacks are 4C, 12C for compounds 1, 4 respectively and 17C for both compounds 2 and 3.

### 3.6 Natural Bond Orbital Analysis (NBO)

NBO provides an accurate method for studying interaction and also gives an efficient basis for investigating charge transfer or conjugative interaction in various molecular systems [29]. The bonding-anti bonding interaction can be quantitatively described in terms of the NBO approach that is expressed by means of second-order perturbation interaction energy  $E^{(2)}$  [30-33]. The stabilization energy  $E^{(2)}$  associated with  $i(\text{donor}) \rightarrow j(\text{acceptor})$  delocalization is estimated

from the second-order perturbation approach as given below:

$$E_2 = -E_{ij} = q_i \frac{F(i,j)^2}{\epsilon_j - \epsilon_i}$$

where  $q_i$  is the donor orbital occupancy,  $\epsilon_i$  and  $\epsilon_j$  are diagonal elements (orbital energies) and  $F(i,j)$  is the off-diagonal Fock matrix element. The larger the  $E^{(2)}$  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. The second order perturbation theory analysis of Fock-matrix on NBO for TTF separated by thiophene 1-4 presented in Tables 8-11.

The intramolecular interaction for the title compounds is formed by the orbital overlap between:  $\pi(\text{C3-C4})$  and  $\pi^*(\text{C8-C12})$  for compound 1,  $\pi(\text{C3-C4})$  and  $\pi^*(\text{C8-C12})$  for compound 2,  $\pi(\text{C3-C4})$  and  $\pi^*(\text{C8-C12})$  for compound 3 and  $\pi(\text{C3-C4})$  and  $\pi^*(\text{C8-C12})$  for compound 4 respectively, which result intermolecular charge transfer (ICT) causing stabilization of the system. The intramolecular hyper conjugative interactions of  $\pi(\text{C3-C4})$  to  $\pi^*(\text{C8-C12})$  for compound 1,  $\pi(\text{C3-C4})$  to  $\pi^*(\text{C8-C12})$  for compound 2,  $\pi(\text{C3-C4})$  to  $\pi^*(\text{C8-C12})$  for compound 3 and  $\pi(\text{C3-C4})$  to  $\pi^*(\text{C8-C12})$  for compound 4 lead to highest stabilization of 19.99, 19.74, 5.89 and 5.85  $\text{kJ mol}^{-1}$  respectively. In case of LP (2) S25 orbital to the  $\pi^*(\text{C18-C19})$  for compound 1, LP (2) S21 orbital to  $\pi^*(\text{C16-C17})$  for compound 2, LP (2) S5 orbital to

**Table 6. Order of nucleophilic ( $f^+$ ), electrophilic ( $f^-$ ) and radical ( $f^0$ ) attack on compounds 1-2**

Compound 1					Compound 2				
Atom	4 C	1 C	12 C	13 C	Atom	4 C	1 C	13 C	17 C
$f^+$	0.036	0.023	0.022	0.022	$f^+$	0.035	0.022	0.014	0.001
Atom	17 C	8 C	12 C	5 S	Atom	15 C	16 C	8 C	14 C
$f^-$	0.015	0.009	0.003	0.003	$f^-$	0.015	0.014	0.012	0.010
Atom	4 C	1 C	12 C	17 C	Atom	17 C	14 C	13 C	16 C
$f^0$	0.028	0.027	0.015	0.011	$f^0$	0.005	0.004	0.002	0.002

**Table 7. Order of nucleophilic ( $f^+$ ), electrophilic ( $f^-$ ) and radical ( $f^0$ ) attack on compounds 3-4**

Compound 3					Compound 4				
Atom	13 C	14 C	17 C	16 C	Atom	4 C	25 C	28 C	12 C
$f^+$	0.022	0.018	0.016	0.013	$f^+$	0.059	0.050	0.035	0.033
Atom	17 C	15 C	14 C	12 C	Atom	16 C	8 C	14 C	17 C
$f^-$	0.007	0.006	0.005	0.000	$f^-$	0.030	0.022	0.022	0.021
Atom	17 C	14 C	13 C	16 C	Atom	12 C	15 C	4 C	31 C
$f^0$	0.008	0.006	0.005	0.003	$f^0$	0.004	0.003	0.002	0.000



**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) S25	1.75744	$\pi^*(C18-C19)$	0.21950	22.95	0.25	0.068
LP (2) S23	1.75910	$\pi^*(C13-C14)$	0.22022	22.84	0.25	0.068
LP (2) S22	1.75262	$\pi^*(C13-C14)$	0.22022	22.23	0.25	0.067
LP (2) S24	1.75566	$\pi^*(C18-C19)$	0.21950	21.98	0.25	0.067
LP (2) S5	1.68016	$\pi^*(C3-C4)$	0.38743	20.16	0.27	0.067
$\pi(C3-C4)$	1.77763	$\pi^*(C8-C12)$	0.33250	19.99	0.27	0.068
$\pi(C1-C2)$	1.78450	$\pi^*(C10-C17)$	0.33315	17.28	0.27	0.063
$\pi(C1-C2)$	1.78450	$\pi^*(C3-C4)$	0.38743	16.93	0.29	0.065
$\pi(C3-C4)$	1.77763	$\pi^*(C1-C2)$	0.39208	16.80	0.29	0.065
$\pi(C10-C17)$	1.90945	$\pi^*(C1-C2)$	0.39208	11.73	0.32	0.059
$\pi(C8-C12)$	1.90871	$\pi^*(C3-C4)$	0.38743	11.61	0.32	0.059
$\sigma(C8-H9)$	1.95724	$\sigma^*(C12-S22)$	0.04506	8.45	0.68	0.068
$\sigma(C10-H11)$	1.96456	$\sigma^*(C17-S24)$	0.04484	8.38	0.68	0.068
$\sigma(C8-H9)$	1.95724	$\sigma^*(C4-S5)$	0.03060	6.94	0.72	0.063
$\sigma(C14-H16)$	1.97566	$\sigma^*(C13-S22)$	0.02299	5.36	0.77	0.057
$\sigma(C4-C8)$	1.97555	$\sigma^*(C8-C12)$	0.01584	5.02	1.32	0.073
$\sigma(C12-S23)$	1.97695	$\sigma^*(C4-C8)$	0.02459	4.93	1.18	0.068
LP (1) S23	1.97577	$\sigma^*(C12-S22)$	0.04506	3.99	0.82	0.051
LP (1) S25	1.97556	$\sigma^*(C17-S24)$	0.04484	3.99	0.82	0.051
LP (1) S22	1.97062	$\sigma^*(C12-S23)$	0.03707	3.89	0.81	0.050

**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) S21	1.77296	$\pi^*(C16-C17)$	0.23736	20.80	0.27	0.067
LP (2) S19	1.77433	$\pi^*(C13-C14)$	0.23797	20.68	0.27	0.067
LP (2) S18	1.76565	$\pi^*(C8-C12)$	0.33259	20.44	0.27	0.068
LP (2) S20	1.76847	$\pi^*(C10-C15)$	0.33300	20.40	0.27	0.068
LP (2) S18	1.76565	$\pi^*(C13-C14)$	0.23797	20.30	0.27	0.066
LP (2) S5	1.68159	$\pi^*(C3-C4)$	0.38784	20.12	0.27	0.067
LP (2) S20	1.76847	$\pi^*(C16-C17)$	0.23736	20.05	0.27	0.066
$\pi(C3-C4)$	1.77932	$\pi^*(C8-C12)$	0.33259	19.74	0.27	0.067
LP (2) S5	1.68159	$\pi^*(C1-C2)$	0.39166	19.23	0.27	0.066
LP (2) S21	1.77296	$\pi^*(C10-C15)$	0.33300	18.07	0.27	0.064
LP (2) S19	1.77433	$\pi^*(C8-C12)$	0.33259	17.93	0.27	0.064
$\pi(C1-C2)$	1.78574	$\pi^*(C10-C15)$	0.33300	17.09	0.27	0.063
$\pi(C1-C2)$	1.78574	$\pi^*(C3-C4)$	0.38784	16.91	0.28	0.065
$\pi(C3-C4)$	1.77932	$\pi^*(C1-C2)$	0.39166	16.75	0.29	0.065
$\pi(C10-C15)$	1.90789	$\pi^*(C1-C2)$	0.39166	11.88	0.32	0.059
$\pi(C8-C12)$	1.90712	$\pi^*(C3-C4)$	0.38784	11.78	0.32	0.059
$\sigma(C8-H9)$	1.95776	$\sigma^*(C12-S18)$	0.04174	8.41	0.69	0.068
$\sigma(C10-H11)$	1.96509	$\sigma^*(C15-S20)$	0.04156	8.35	0.69	0.068
$\sigma(C8-H9)$	1.95776	$\sigma^*(C4-S5)$	0.03066	6.94	0.72	0.063
$\sigma(C17-S21)$	1.97334	$\sigma^*(C16-C22)$	0.01857	5.25	1.04	0.066

$\pi^*(C3-C4)$  for compound 3, LP (2) O30 orbital to  $\pi^*(C28-O29)$  for compound 4 respectively, show the stabilization energy of 22.95, 20.80, 20.54 and 49.69 kJ mol<sup>-1</sup> respectively.

### 3.7 Nonlinear Optical Properties (NLO)

Hyperpolarizabilities and polarizabilities determine the strength of molecular interactions,

cross sections of different scattering and collision processes and the non-linear optical properties (NLO) of the system [34]. NLO is the current research as it provides the key functions of frequency shifting; optical modulation and optical memory for the emerging technologies in areas such as telecommunication, signal processing and optical interconnections [35]. The first order

hyperpolarizability is a third rank tensor described by 3×3×3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [36]. The expression of the external Electric field when it becomes weak and homogeneous is

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{\alpha_{\alpha\beta}} F_\alpha F_\beta + \frac{1}{\beta_{\alpha\beta\gamma}} F_\alpha F_\beta F_\gamma$$

$E^0$  is the energy of the unperturbed molecules,  $F_\alpha$  is the field of the origin,  $\mu_\alpha$ ,  $\alpha_{\alpha\beta}$  and  $\beta_{\alpha\beta\gamma}$  are the components of the dipole moment, polarizability and the first order hyperpolarizability respectively. The total static dipole moment  $\mu$ , the mean polarizability  $\alpha_0$ , the anisotropy of the polarizability  $\Delta\alpha$  and mean first order hyperpolarizability  $\beta_0$  using the x, y and z components are defined as follows.

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

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

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

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

and

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

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

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

The total molecular dipole moment ( $\mu$ ), mean polarizability ( $\alpha_0$ ) and anisotropy polarizability ( $\Delta\alpha$ ) and first hyperpolarizability ( $\beta_0$ ) of TTF separated by thiophene 1-4 are computed at DFT/B3LYP method with 6-31G (d,p) basis set and depicted in Table 12.

Since the values of the polarizabilities ( $\Delta\alpha$ ) and the hyperpolarizabilities ( $\beta_0$ ) 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  $\alpha$ ; 1 a.u. = 0.1482 x 10<sup>-24</sup> e.s.u., for  $\beta$ ; 1 a.u. = 8.6393 x 10<sup>-33</sup> e.s.u.). The calculated values of dipole moment ( $\mu$ ) for the title compounds were found to be 0.4864, 0.8640, 1.2490 and 2.2888 D respectively, which are approximately two 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 48.8096 x 10<sup>-24</sup>, 65.3372 x 10<sup>-24</sup>, 98.5334 x 10<sup>-24</sup> and 105.9954 x 10<sup>-24</sup> esu respectively; the values of anisotropy of the polarizability are 7.2336, 9.6830, 14.6026 and 15.7085 esu, respectively. The magnitude of the molecular hyperpolarizability ( $\beta_0$ ) is one of the

**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) S5	1.67255	$\pi^*(C3-C4)$	0.38364	20.54	0.27	0.067
LP (2) S19	1.77914	$\pi^*(C13-C14)$	0.37234	20.54	0.23	0.064
LP (2) S21	1.77647	$\pi^*(C16-C17)$	0.37137	20.41	0.23	0.064
$\pi(C3-C4)$	1.77318	$\pi^*(C8-C12)$	0.31691	20.33	0.27	0.068
LP (2) S18	1.76974	$\pi^*(C13-C14)$	0.37234	20.22	0.23	0.064
LP (2) S20	1.77404	$\pi^*(C16-C17)$	0.37137	20.06	0.24	0.064
LP (2) S5	1.67255	$\pi^*(C1-C2)$	0.38500	19.68	0.27	0.066
LP (2) S24	1.85838	$\pi^*(C16-C17)$	0.37137	18.70	0.24	0.063
LP (2) S18	1.76974	$\pi^*(C8-C12)$	0.31691	18.30	0.27	0.064
LP (2) S22	1.85843	$\pi^*(C13-C14)$	0.37234	18.30	0.24	0.062
LP (2) S20	1.77404	$\pi^*(C10-C15)$	0.31454	18.27	0.27	0.064
$\pi(C1-C2)$	1.78085	$\pi^*(C3-C4)$	0.38364	16.91	0.29	0.065
LP (2) S21	1.77647	$\pi^*(C10-C15)$	0.31454	16.69	0.27	0.061
$\pi(C1-C2)$	1.78085	$\pi^*(C10-C15)$	0.31454	16.24	0.27	0.061
$\pi(C8-C12)$	1.90516	$\pi^*(C3-C4)$	0.38364	11.44	0.32	0.058
LP (2) S25	1.87701	$\pi^*(C16-C17)$	0.37137	11.35	0.23	0.049
LP (2) S23	1.87584	$\pi^*(C13-C14)$	0.37234	11.06	0.23	0.048
$\pi(C10-C15)$	1.90672	$\pi^*(C1-C2)$	0.38500	10.73	0.32	0.056
$\sigma(C8-H9)$	1.95749	$\sigma^*(C12-S18)$	0.04653	8.46	0.69	0.068
$\sigma(C10-H11)$	1.96437	$\sigma^*(C15-S20)$	0.04777	8.34	0.69	0.068

**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) O30	1.78743	$\pi^*(C28-O29)$	0.27013	49.69	0.33	0.116
LP (2) O27	1.78509	$\pi^*(C25-O26)$	0.26494	49.56	0.33	0.116
LP (2) O24	1.77831	$\pi^*(C22-O23)$	0.25002	49.27	0.33	0.115
LP (2) O33	1.77686	$\pi^*(C31-O32)$	0.24527	48.97	0.34	0.115
LP (2) O29	1.84271	$\sigma^*(C28-O30)$	0.10131	32.85	0.64	0.131
LP (2) O26	1.84194	$\sigma^*(C25-O27)$	0.10161	32.81	0.64	0.131
LP (2) O23	1.84023	$\sigma^*(C22-O24)$	0.10231	32.49	0.64	0.130
LP (2) O32	1.83869	$\sigma^*(C31-O33)$	0.10277	32.39	0.64	0.130
LP (2) S21	1.72333	$\pi^*(C16-C17)$	0.28552	24.15	0.26	0.070
LP (2) S19	1.72690	$\pi^*(C13-C14)$	0.28688	23.99	0.25	0.070
LP (2) S18	1.73539	$\pi^*(C13-C14)$	0.28688	22.38	0.25	0.067
LP (2) S20	1.74326	$\pi^*(C16-C17)$	0.28552	21.80	0.25	0.066
$\pi(C3-C4)$	1.77512	$\pi^*(C8-C12)$	0.32582	20.28	0.27	0.068
$\pi(C1-C2)$	1.78238	$\pi^*(C10-C15)$	0.32279	16.91	0.27	0.062
$\pi(C3-C4)$	1.77512	$\pi^*(C1-C2)$	0.38606	16.90	0.29	0.065
$\pi(C1-C2)$	1.78238	$\pi^*(C3-C4)$	0.38321	16.86	0.29	0.065
$\pi(C16-C17)$	1.88204	$\pi^*(C28-O29)$	0.27013	14.43	0.31	0.062
$\pi(C13-C14)$	1.88140	$\pi^*(C25-O26)$	0.26494	13.35	0.31	0.060
$\pi(C8-C12)$	1.91008	$\pi^*(C3-C4)$	0.38321	11.38	0.32	0.058
$\pi(C10-C15)$	1.91092	$\pi^*(C1-C2)$	0.38606	11.05	0.32	0.058

**Table 12. Nonlinear optical properties of TTF separated by thiophene 1-4**

Parameters	compound 1	compound 2	compound 3	compound 4
$\beta_{xxx}$	48.5662	-51.9869	126.1306	-150.8761
$\beta_{yyy}$	-0.2756	1.0471	-13.4868	25.4100
$\beta_{zzz}$	-0.0004	0.0152	3.6041	27.0772
$\beta_{xyy}$	-11.2293	5.7014	-40.8498	35.2859
$\beta_{xxy}$	-39.1565	52.7500	121.2337	208.1845
$\beta_{xxz}$	0.0199	0.1282	-9.5819	262.2399
$\beta_{xzz}$	-0.3967	-0.2834	4.0342	16.5712
$\beta_{yzz}$	-1.8508	4.4583	5.8608	15.7364
$\beta_{yyz}$	0.0044	0.0004	-6.1300	3.0308
$\beta_{xyz}$	0.0127	0.0186	-0.1152	-95.2099
$\beta_0(\text{esu}) \times 10^{-33}$	54.3223	74.5813	145.0189	396.7845
$\mu_x$	0.4356	-0.5659	0.5192	-0.2091
$\mu_y$	-0.2164	0.6528	0.3412	1.1751
$\mu_z$	0.0004	0.0021	-1.0835	1.9530
$\mu$ (D)	0.4864	0.8640	1.2490	2.2888
$a_{xx}$	-88.5127	-96.2797	-118.8895	-122.3996
$a_{yy}$	-123.3393	-149.1197	-205.0181	-220.7949
$a_{zz}$	-141.6035	-166.3713	-216.4466	-225.1946
$a_{xy}$	8.1613	9.4463	-19.5411	18.6919
$a_{xz}$	-0.0013	-0.0038	3.1610	-2.0543
$a_{yz}$	-0.0003	0.0007	-0.2701	3.6653
$\alpha(\text{esu}) \times 10^{-24}$	48.8096	65.3372	98.5334	105.9954
$\Delta\alpha(\text{esu}) \times 10^{-24}$	7.2336	9.6830	14.6026	15.7085

important key factors in an NLO system. The DFT/6-31G (d,p) calculated first hyperpolarizability value ( $\beta_0$ ) of TTF separated by thiophene molecules are equal to  $54.3223 \times 10^{-33}$ ,  $74.5813 \times 10^{-33}$ ,  $145.0189 \times 10^{-33}$  and

$396.7845 \times 10^{-33}$  esu. The first hyperpolarizability of title molecules is approximately 0.16, 0.22, 0.42 and 1.16 times than those of urea ( $\beta$  of urea is  $343.272 \times 10^{-33}$  esu obtained by B3LYP/6-311G (d,p) method). The above results show

that only compound 4 might have the NLO applications.

#### 4. CONCLUSION

A complete theoretical analysis of TTF separated by thiophene 1-4 was performed by DFT/B3LYP method with 6-31G (d,p) basis set. The HOMO and LUMO analysis is used to determine the charge transfer within the molecules. NBO analysis reveals that the important intramolecular charge transfer causing stabilization of the system to the title molecule and the intramolecular conjugative interaction lead to highest stabilization. The analysis of Fukui indices is also carried out to distinguish the nucleophilic and electrophilic centres. The MEP map contour shows the regions exhibiting the negative electrostatic potential are localized near the thiophene in all molecules, except compound 4 where it is localized in carbonyl of the ester function while the regions presenting the positive potential are localized vicinity of the hydrogen atoms. The results of quantum chemical descriptors show that compound 4 has a low kinetic stability and high chemical reactivity as compared to others. The total and partial dipole moment, polarizability and hyperpolarizability of the title compounds found that the compound 4 is a candidate for NLO material.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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