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## Application of Density Functional Theory (DFT) to Study the Electronic Properties and First Hyperpolarizability of Tetrathiafulvalene (TTFs) Connected to Acceptor Moieties



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## ABSTRACT

The tetrathiafulvalene (TTFs) connected to acceptor moieties 1-4 have been studied in the best way in this investigation. Theoretical calculations were performed by the density functional theory DFT/B3LYP method using 6-31G (d,p) basis set. The optimized geometries and geometrical parameters of these compounds have been obtained by the same method. The electrophilic and nucleophilic sites are revealed from the molecular electrostatic potential map. The energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) have been calculated, and the obtained energies displayed that charge transfer occurs in molecules. Various reactivity and selectivity descriptors such as chemical hardness, chemical potential, softness, electrophilicity, and electronegativity have been discussed clearly. The analysis of Fukui indices is also carried out to distinguish the nucleophilic and electrophilic centers. The stability and charge delocalization of the molecule were also studied by natural bond orbital (NBO) analysis. A computation of the first hyperpolarizability indicates that the studied compounds may be a good candidate as an NLO material.

## **INTRODUCTION**

Tetrathiafulvalene (TTF) is a heterocyclic compound that has been widely exploited as a redox-active molecule in both materials and supramolecular chemistry owing to its electrondonating properties <sup>[1-6]</sup>. Recently, tetrathiafulvalenes TTFs have become an interesting topic of research due to their high electrical conductivity and superconducting properties <sup>[7, 8]</sup>. It has also been reported that tetrathiafulvalenes show good  $\pi$ -donor properties <sup>[9]</sup>. Tetrathiafulvalene (TTF) and its derivatives are well-established organic  $\pi$  -donors (D) which have been extensively studied for various applications, in particular, in the field of conducting organic materials involving intermolecular charge-transfer interactions with various  $\pi$ accepting molecules (A) <sup>[10]</sup>.

Density functional theory (DFT) is a widely used, advanced quantum mechanical modeling approach in analyzing the molecular structures, energies and vibrational frequencies theoretically. DFT offers a better compromise between computational cost and accuracy for medium size molecules, and hence it has been successfully applied in many previous studies <sup>[11-13]</sup>. Accordingly, it is necessary to underline that the theoretical approaches deduced form DFT/B3LYP calculation level is more effective and reliable as compared to those inferred from the other methods <sup>[14]</sup>.

The objective of this work is to investigate the computational study of the tetrathiafulvalene (TTFs) connected to acceptor moieties **1-4** reported in the literature <sup>[15]</sup> at DFT method with B3LYP/6-31G (d,p) basis set. The optimized geometries and the geometrical parameters are computed by the same method. The molecular electrostatic potential map (MEP) reveals the regions for electrophilic and nucleophilic attack on the investigating molecules. The information regarding charge transfer within the molecule has been reported by frontier molecular orbitals analysis. The nature of chemical reactivity and site selectivity of the title compounds have been determined on the basis of global and local reactivity descriptors. The natural bond orbital (NBO) analysis has been also performed. Nonlinear optical (NLO) analysis has also been done to calculate first hyperpolarizability.

## 1. MATERIALS AND METHODS

Calculations of (TTFs) connected to acceptor moieties **1-4** were carried out using Gaussian 09 software <sup>[16]</sup> by utilizing Becke's three-parameter hybrid model with the Lee-Yang-Parr

correlation functional (B3LYP) method. All the quantum chemical calculations are carried out with the DFT method with B3LYP/6-31G (d,p) level.

## 2. RESULTS AND DISCUSSION

## **2.1.Molecular Geometry**

The geometries of (TTFs) connected to acceptor moieties **1-4** in the ground state were optimized at B3LYP/6-31G (d,p) level. The optimized structures are shown in Figure 1 and the values of the geometrical parameters are listed in tables 1-4.



Figure 1. Optimized molecular structure of (TTFs) connected to acceptor moieties 1-4

Bond Longth (Å)		Rond Angles	(°)	Dihadral Angles (°)		
Donu Len	gin (A)	Donu Angles	()	Differential Aligie	5()	
R(1,4)	1.350	A(4,1,10)	124.046	D(11,1,4,9)	179.412	
R(1,11)	1.777	A(10,1,11)	112.282	D(4,1,11,3)	159.567	
R(2,3)	1.356	A(3,2,23)	125.651	D(23,2,3,11)	172.814	
R(2,23)	1.766	A(11,3,24)	117.519	D(23,2,10,1)	173.024	
<b>R</b> (3,11)	1.790	A(1,4,8)	123.722	D(3,2,23,29)	124.330	
R(4,9)	1.786	A(8,4,9)	113.251	D(11,3,24,25)	63.117	
R(5,7)	1.084	A(6,5,9)	119.367	D(1,4,9,5)	168.155	
R(6,8)	1.789	A(7,5,9)	116.462	D(9,5,6,12)	178.492	
R(12,13)	1.362	A(5,6,12)	127.259	D(12,6,8,4)	173.637	
R(13,15)	1.087	A(6,12,13)	126.563	D(15,13,16,18)	179.775	
R(16,17)	1.373	A(12,13,16)	121.738	D(13,16,17,19)	179.915	
R(16,18)	1.087	A(17,16,18)	116.890	D(18,16,17,20)	179.975	
R(17,20)	1.431	A(16,17,20)	121.567	D(2,23,29,30)	59.682	
R(20,22)	1.164	A(2,23,29)	101.793	D(2,23,29,31)	178.142	
R(24,25)	1.837	A(24,25,27)	111.468	D(3,24,25,28)	63.838	

Table 1. Optimized geometric parameters of compound 1

 Table 2. Optimized geometric parameters of compound 2

		3			
Bond Len	gth (Å)	Bond Angles	s (°)	Dihedral Angle	<b>s</b> (°)
R(1,4)	1.350	A(4,1,10)	123.938	D(4,1,11,3)	163.331
<b>R</b> (1,11)	1.781	A(10,1,11)	112.559	D(23,2,3,11)	176.100
R(2,3)	1.354	A(3,2,23)	125.913	D(23,2,10,1)	172.661
R(2,10)	1.787	A(10,2,23)	117.230	D(3,2,23,47)	111.689
R(2,23)	1.768	A(2,3,24)	127.813	D(2,3,24,43)	70.200
R(4,9)	1.786	A(11,3,24)	115.255	D(1,4,9,5)	169.257
R(6,8)	1.789	A(1,4,9)	122.978	D(9,5,6,12)	178.873
R(13,16)	1.425	A(8,4,9)	113.279	D(12,6,8,4)	174.037
R(15,26)	2.189	A(6,5,7)	123.931	D(5,6,12,14)	178.248
R(16,18)	1.089	A(7,5,9)	116.654	D(8,6,12,13)	176.402
R(17,19)	1.471	A(5,6,12)	126.995	D(6,12,13,16)	179.933
R(19,21)	1.408	A(8,6,12)	117.564	D(14,12,13,15)	179.890
R(20,22)	1.411	A(1,10,2)	95.043	D(15,13,16,18)	179.956
R(22,37)	1.485	A(6,12,13)	126.120	D(18,16,17,20)	179.938
R(36,38)	1.093	A(13,12,14)	117.865	D(19,17,20,26)	179.594

	0				
Bond Len	gth (A)	Bond Angles	s (°)	Dihedral Angle	<b>s</b> (°)
R(1,4)	1.346	A(4,1,10)	124.046	D(4,1,11,3)	163.203
<b>R</b> (1,10)	1.779	A(3,2,10)	116.692	D(22,2,3,11)	176.296
R(2,3)	1.350	A(3,2,22)	126.083	D(3,2,22,41)	107.613
R(2,22)	1.768	A(11,3,23)	115.340	D(1,4,9,5)	168.674
R(3,11)	1.779	A(1,4,9)	123.098	D(9,5,6,12)	178.871
R(4,9)	1.784	A(8,4,9)	113.131	D(12,6,8,4)	173.615
R(5,9)	1.737	A(6,5,9)	119.444	D(5,6,12,14)	176.303
R(6,12)	1.442	A(5,6,12)	127.298	D(8,6,12,13)	174.409
R(12,13)	1.359	A(13,12,14)	117.898	D(6,12,13,16)	179.660
R(13,15)	1.084	A(12,13,15)	121.396	D(14,12,13,15)	179.508
R(16,18)	1.087	A(16,17,19)	129.860	D(12,13,16,17)	179.293
R(17,20)	1.477	A(21,19,24)	119.617	D(18,16,17,20)	175.853
R(19,24)	1.476	A(17,20,35)	131.952	D(16,17,19,21)	174.207
R(20,36)	1.377	A(35,20,36)	122.080	D(20,17,19,24)	179.974
R(22,41)	1.837	A(19,21,36)	108.279	D(24,19,21,36)	179.330

Table 3. Optimized geometric parameters of compound 3

Table 4. Optimized geometric parameters of compound 4

Bond Len	gth (Å)	Bond Angles	; (°)	Dihedral Angle	<b>s</b> (°)
R(1,10)	1.782	A(4,1,10)	124.019	D(22,3,11,1)	172.836
R(2,3)	1.354	A(10,1,11)	112.549	D(2,3,22,39)	113.113
R(2,21)	1.774	A(3,2,10)	116.852	D(1,4,8,6)	168.956
R(3,22)	1.767	A(2,3,22)	125.811	D(7,5,6,8)	178.019
R(4,8)	1.781	A(11,3,22)	117.285	D(7,5,9,4)	174.632
R(5,7)	1.084	A(1,4,8)	123.724	D(14,12,13,15)	179.925
R(6,12)	1.442	A(8,4,9)	113.286	D(12,13,16,17)	179.780
R(13,15)	1.084	A(6,5,9)	119.414	D(16,17,19,28)	179.636
R(16,18)	1.085	A(5,6,12)	126.999	D(20,17,19,34)	179.736
R(17,19)	1.467	A(4,9,5)	95.200	D(28,19,34,36)	179.965
R(19,28)	1.486	A(1,11,3)	95.044	D(17,20,29,24)	179.862
R(20,29)	1.480	A(6,12,13)	126.061	D(2,21,43,46)	173.610
R(21,43)	1.836	A(28,19,34)	124.974	D(22,3,11,1)	172.836
R(24,25)	1.395	A(17,20,23)	128.052	D(2,3,22,39)	113.113
R(34,35)	1.429	A(2,21,43)	102.072	D(1,4,8,6)	168.956

## 2.2. Molecular Electrostatic Potential (MEP)

Molecular electrostatic potential (MEP) maps are often used to interpret the electrophilic and nucleophilic reactions <sup>[17]</sup>, rationalize intermolecular interactions between polar species, calculate the atomic charges <sup>[18]</sup> and define regions of local negative and positive potential in

the molecule <sup>[19]</sup>. This surface represents the distance from a molecule at which a positive test charge experiences a certain amount of attraction or repulsion and they highlight the bonding possibilities during complex formation. Molecular electrostatic potential V(r) is defined by

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

where  $Z_A$  is the charge of nucleus A, located R <sub>A</sub>,  $\rho(r')$  is the electronic density function of the molecule and r' is a dummy integration variable <sup>[20]</sup>. To investigate the reactive sites of the title compounds, the molecular electrostatic potentials were evaluated using the B3LYP/6-31G (d,p) method and shown in Figure 2. The negative (red) regions of MEP were related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity.



# Figure 2. The molecular electrostatic potential surface of (TTFs) connected to acceptor moieties 1-4

In these molecules, the regions exhibiting the negative electrostatic potential are localized around of the cyanide groups for compound **1**, the carbonyls of the amide functions and sulfur group for compound **2**, the carbonyl of the ester function and on the nitrogen atom for compound **3** and the carbonyl of ketone and on cyanide groups for compound **4**. While the regions presenting the positive potential are localized vicinity of the hydrogen atoms linked to TTF core and alkyl groups for all compounds.

## 2.3. Frontier Molecular Orbitals (FMOs)

The frontier orbital gap helps to characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is termed as soft molecule <sup>[21]</sup>. The frontier molecular orbitals play an important role in the electric and optical properties <sup>[22]</sup>. The conjugated molecules are characterized by a small value of HOMO, LUMO separation, which is the result of a significant degree of intramolecular charge transfer from end-capping electron-donor groups to the efficient electron-acceptor groups through the  $\pi$  conjugated path. The HOMO and LUMO energy are calculated by the B3LYP/6-31G (d,p) method. The frontier molecular orbitals of (TTFs) connected to acceptor moieties **1-4** are listed in Table 5. The distributions and energy levels of the HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1 and LUMO+2 orbitals of compound **4** with a small energy gap comparing with the test compounds are shown in Figure 3.



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

## 2.4. Global Reactivity Descriptors

The most fruitful and promising framework so far is probably the density functional theory of chemical reactivity so-called conceptual DFT <sup>[23]</sup>. Conceptual DFT is a subfield of DFT in which one tries to extract from the electronic density relevant concepts and principles that help to understand and predict the chemical behavior of a molecule. The calculated global

parameters <sup>[24,25]</sup> are obtained by the DFT method with B3LYP/6-31G (d,p) basis set and given in Table 5.

According to Mulliken<sup>[26]</sup>, chemical potential and the global hardness are calculated as

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

where I and A are the first ionization energy and electron affinity, respectively. I and A can be expressed through HOMO and LUMO orbital energies as  $I = -E_{HOMO}$  and  $A = -E_{LUMO}$ . The chemical potential and the absolute electronegativity are molecular properties and not the orbital properties. Electronegativity and softness of the molecule are calculated by

$$\chi = (I + A)/2$$
$$S = 1/2\eta$$

The electrophilicity index  $(\omega)$  defined as follows:

According to Parr et al., electrophilicity index ( $\omega$ ) is as a global reactivity index similar to the chemical hardness and chemical potential.

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

Table 5. Quantum chemical descriptors of (TTFs) connected to acceptor moieties 1-4

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
EHOMO (eV)	-5.291	-5.110	-5.257	-5.096
ELUMO (eV)	-3.275	-3.178	-3.296	-3.368
ΔEgap (eV)	2.016	1.932	1.961	1.728
I (eV)	5.291	5.110	5.257	5.096
An (eV)	3.275	3.178	3.296	3.368
μ (eV)	-4.283	-4.144	-4.276	-4.232
χ (eV)	4.283	4.144	4.276	4.232
η (eV)	1.008	0.966	0.981	0.864
S (eV)	0.496	0.518	0.510	0.579
ω (eV)	9.099	8.889	9.323	10.363

The compound which has the lowest energy gap is compound 4 ( $\Delta E_{gap} = 1.728$  eV). This lower gap allows it to be the softest molecule. The compound that has the highest energy gap

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is compound 1 ( $\Delta E_{gap} = 2.016 \text{ eV}$ ). The compound that has the highest HOMO energy is compound 4 ( $E_{HOMO} = -5.096 \text{ eV}$ ). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is compound 4 ( $E_{LUMO} = -3.368 \text{ eV}$ ) 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 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 4 has the lowest value of the potential ionization (I = 5.096 eV), so that will be the better electron donor. Compound 4 has the largest value of the affinity (A =  $(A = A)^{-1}$ ) 3.368 eV), so it is the better electron acceptor. The chemical reactivity varies with the structure of molecules. Chemical hardness (softness) value of compound 4 ( $\eta = 0.864 \text{ eV}$ , S = 0.579 eV) is lesser (greater) among all the molecules. Thus, compound 4 is found to be more reactive than all the compounds. Compound 1 possesses higher electronegativity value ( $\gamma =$ 4.283 eV) than all compounds so; it is the best electron acceptor. The value of  $\omega$  for compound 4 ( $\omega = 10.363$  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.

## **2.5.Local Reactivity Descriptors**

The local reactivity descriptor like the Fukui function indicates the preferred regions where a chemical species (molecule) will amend its density when the electron number is modified or indicates the tendency of the electron density to deform at a given position upon accepting or donating electrons <sup>[27]</sup>. The condensed or atomic Fukui functions on the kth atom site, for electrophilic ( $f_k$ ), nucleophilic ( $f_k$ ) and free radical ( $f_k^0$ ) attacks are defined as:

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$$f_i^- = q_i(N) - q_i(N-1)$$
 for nucleophilic attack

 $f_i^+ = q_i(N+1) - q_i(N)$  for electrophilic attack

$$f_j^0 = \frac{1}{2} \left[ q_j (N+1) - q_j (N-1) \right]$$
 for radical attack

where  $q_k$  is the atomic charge at the kth atomic site in the anionic (N+1), cationic (N-1) or neutral molecule (N). According to Parr and Yang <sup>[27]</sup>, the sites in chemical species with the

largest of Fukui Function ( $f_k$ ) values show high reactivity for corresponding attacks. The FF values for the title compounds are calculated at the B3LYP/6-31G (d,p) level and cited in tables 6-7.

	Compound 1				Compound 2				
Atom	3 C	4 C	6 C	29 C	Atom	4 C	22 N	21 N	2 C
$f^{\scriptscriptstyle +}$	0.053	0.045	0.013	0.006	$f^{\scriptscriptstyle +}$	0.039	0.019	0.018	0.007
Atom	2 C	12 C	6 C	1 C	Atom	27 C	26 O	3 C	12 C
$f^{-}$	0.033	0.011	0.009	0.005	$f^{-}$	0.019	0.008	0.006	0.000
Atom	4 C	3 C	2 C	6 C	Atom	4 C	27 C	3 C	21 N
$f^{ heta}$	0.013	0.004	0.003	0.002	$f^{ heta}$	0.012	0.006	0.004	0.003

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

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

	Со	mpoun	d 3		Compound 4				
Atom	4 C	6 C	2 C	24 C	Atom	4 C	3 C	6 C	2 C
$f^{\scriptscriptstyle +}$	0.030	0.021	0.013	0.001	$f^{\scriptscriptstyle +}$	0.034	0.010	0.009	0.000
Atom	29 C	3 C	35 O	17 C	Atom	23 O	2 C	20 C	29 C
$f^{-}$	0.014	0.007	0.003	0.001	$f^{-}$	0.012	0.006	0.006	0.004
Atom	4 C	29 C	3 C	6 C	Atom	4 C	2 C	3 C	6 C
$f^{ heta}$	0.008	0.007	0.004	0.004	$f^{ heta}$	0.011	0.003	0.003	0.002

The parameters of local reactivity descriptors show that 4C is the more reactive site in compounds 2, 3 and 4 and 3C is the more reactive site in compound 1 for nucleophilic attacks. The more reactive sites for electrophilic attacks are 2C, 27C, 29C and 23O for compounds 1, 2, 3 and 4 respectively. The more reactive site in radical attacks is 4C for all compounds.

## 2.6.Natural Bond Orbital Analysis (NBO)

NBO analysis investigates the delocalization of electron density and thus verifies the stability of different molecular structure <sup>[28]</sup>. The second order Fock matrix has been performed to evaluate the donor-acceptor interactions in NBO analysis <sup>[29]</sup>. The larger the E <sup>(2)</sup> value, the more intense is the interaction between electron donors and acceptors, i.e. a more donating tendency from electron donors to electron acceptors and a greater extent of conjugation of the whole system with delocalization of the electron density between occupied Lewis-type (bond or lone pairs). For each donor (i) and acceptor (j), the stabilization energy E <sup>(2)</sup> associates with electron delocalization between i and j are estimated as

$$E^{\left(\mathcal{2}\right)} = q_{j} \, \frac{F^{2}(i, j)}{\varepsilon_{j} - \varepsilon_{j}}$$

where  $q_i$  is the donor orbital occupancy,  $\varepsilon_i$  and  $\varepsilon_j$  are diagonal elements and  $F_{i,j}$  is the offdiagonal NBO Fock matrix element <sup>[30]</sup>. NBO analysis has been performed on the title molecules at the B3LYP/6-31G (d, p) level and shown in tables 8-11.

 Table 8. Second order perturbation theory analysis of Fock matrix on NBO of

 compound 1

Donor (i)	FD/a	Accoptor (i)	ED/a	E(2)	<b>E(j)-E(i)</b>	F(i.j)
Donor (I)	ED/e	Acceptor (J)	ED/e	Kcal/mol	a.u	a.u
LP (2) S9	1.71244	$\pi^{*}(C5-C6)$	0.29567	25.74	0.25	0.072
π (C12-C13)	1.78071	π*(C16-C17)	0.25830	23.27	0.29	0.074
π (C16-C17)	1.79317	π*(C19-N21)	0.08751	19.98	0.40	0.082
LP (2) S8	1.79350	$\pi^{*}(C5-C6)$	0.29567	19.55	0.25	0.064
π (C16-C17)	1.79317	$\pi^{*}(C20-N22)$	0.08445	19.33	0.39	0.080
LP (2) S11	1.78359	$\pi^{*}(C2-C3)$	0.31220	19.20	0.25	0.063
LP (2) S10	1.78617	$\pi^{*}(C2-C3)$	0.31220	19.06	0.25	0.063
LP (2) S9	1.71244	$\pi^{*}(C1-C4)$	0.38757	16.67	0.26	0.060
LP (2) S8	1.79350	$\pi^{*}(C1-C4)$	0.38757	16.66	0.25	0.061
LP (2) S11	1.78359	$\pi^{*}(C1-C4)$	0.38757	15.26	0.25	0.057
LP (2) S10	1.78617	$\pi^{*}(C1-C4)$	0.38757	15.17	0.25	0.057
π (C12-C13)	1.78071	$\pi^{*}(C5-C6)$	0.29567	14.54	0.28	0.058
π (C5-C6)	1.86368	π*(C12-C13)	0.18165	14.14	0.33	0.061
LP (1) N21	1.96938	<i>σ</i> *(C17-C19)	0.03339	12.94	1.02	0.102
LP (1) N22	1.96896	<i>σ</i> *(C17-C20)	0.03701	12.79	1.02	0.102
π (C16-C17)	1.79317	$\pi^{*}(C12-C13)$	0.18165	12.60	0.31	0.056
π (C20-N22)	1.95754	<b>π</b> *(C16-C17)	0.25830	8.40	0.34	0.051
π (C19-N21)	1.95530	π*(C16-C17)	0.25830	8.27	0.34	0.050
σ (C19-N21)	1.99553	<i>σ</i> *(C17-C19)	0.03339	6.37	1.54	0.089
σ (C20-N22)	1.99553	$\sigma^*(C17-C20)$	0.03701	6.14	1.54	0.088

Table	9.	Second	order	perturbation	theory	analysis	of	Fock	matrix	on	NBO	of
compo	un	d 2										

Donor (i)	FD/a	Accontor (i)	FD/o	E(2)	<b>E(j)-E(i)</b>	F(i.j)
Donor (I)	ED/e	Acceptor (j)	ED/e	Kcal/mol	a.u	a.u
LP (1) N21	1.58697	π*(C27-S28)	0.45401	75.59	0.19	0.108
LP (1) N22	1.58767	$\pi^{*}(C27-S28)$	0.45401	74.49	0.19	0.108
LP (1) N22	1.58767	π*(C20-O26)	0.31773	53.34	0.26	0.109
LP (1) N21	1.58697	π*(C19-O25)	0.30992	52.73	0.27	0.109
LP (2) O25	1.85860	$\sigma^*(C19-N21)$	0.09221	28.30	0.66	0.124
LP (2) O26	1.86275	$\sigma^*(\text{C20-N 22})$	0.09215	27.92	0.66	0.123
π (C16-C17)	1.73336	$\pi^{*}(C20-O26)$	0.31773	26.96	0.27	0.078
π (C16-C17)	1.73336	π*(C19-O25)	0.30992	26.80	0.28	0.078
LP (2) S9	1.71355	$\pi^{*}(C5-C6)$	0.29410	25.51	0.26	0.072
π (C12-C13)	1.75366	π*(C16-C17)	0.23442	23.97	0.30	0.076
LP (2) S11	1.76828	$\pi^{*}(C2-C3)$	0.30659	21.79	0.23	0.065
LP (2) S10	1.78075	$\pi^{*}(C2-C3)$	0.30659	20.27	0.24	0.063
LP (2) S8	1.79397	$\pi^{*}(C5-C6)$	0.29410	19.52	0.25	0.064
LP (2) O25	1.85860	$\sigma^*(C17-C19)$	0.06236	18.06	0.70	0.103
LP (2) O26	1.86275	<i>σ</i> *(C17-C20)	0.06049	17.04	0.72	0.101
LP (2) S8	1.79397	π*(C1-C4)	0.39301	17.03	0.25	0.061
LP (2) S9	1.71355	$\pi^{*}(C1-C4)$	0.39301	16.94	0.26	0.061
LP (2) S11	1.76828	$\pi^{*}(C1-C4)$	0.39301	16.31	0.25	0.059
LP (2) S10	1.78075	$\pi^{*}(C1-C4)$	0.39301	15.98	0.25	0.059
π (C12-C13)	1.75366	$\pi^{*}(C5-C6)$	0.29410	15.60	0.27	0.058

Donor (i)	FD/o	Accentor (i)	FD/e	E(2)	<b>E(j)-E(i)</b>	F(i.j)
	ED/C	Acceptor (J)		Kcal/mol	a.u	a.u
LP (2) O36	1.77075	π*(C20-O35)	0.27683	40.90	0.34	0.106
LP (2) O35	1.83213	$\sigma^*(C20-O36)$	0.11797	34.44	0.59	0.129
LP (2) S9	1.70345	$\pi^{*}(C5-C6)$	0.29922	25.62	0.26	0.072
LP (2) S11	1.75458	$\pi^{*}(C2-C3)$	0.31656	22.65	0.23	0.066
π (C12-C13)	1.76978	π*(C16-C17)	0.23537	22.00	0.31	0.073
π (C16-C17)	1.74759	$\pi^{*}(C20-O35)$	0.27683	21.49	0.30	0.072
LP (2) S10	1.76578	$\pi^{*}(C2-C3)$	0.31656	21.26	0.24	0.065
π (C27-C28)	1.65375	π*(C24-C29)	0.37412	21.11	0.28	0.069
π (C25-C26)	1.65359	$\pi^{*}(C27-C28)$	0.32644	21.03	0.28	0.069
π (C25-C26)	1.65359	π*(C24-C29)	0.37412	20.83	0.28	0.069
π (C16-C17)	1.74759	π*(C19-N21)	0.23000	20.28	0.30	0.070
π (C24-C29)	1.65472	$\pi^{*}(C27-C28)$	0.32644	19.97	0.29	0.068
LP (2) S8	1.78309	$\pi^{*}(C5-C6)$	0.29922	19.73	0.25	0.064
π (C27-C28)	1.65375	$\pi^*(C25-C26)$	0.30450	19.41	0.29	0.067
π (C24-C29)	1.65472	$\pi^{*}(C25-C26)$	0.30450	19.27	0.29	0.067
LP (2) S9	1.70345	π*(C1-C4)	0.41753	18.97	0.25	0.063
LP (2) S8	1.78309	π*(C1-C4)	0.41753	18.95	0.24	0.064
LP (2) S11	1.75458	π*(C1-C4)	0.41753	18.47	0.24	0.062
LP (2) S10	1.76578	π*(C1-C4)	0.41753	18.19	0.24	0.062
LP (2) O35	1.83213	$\sigma^*(C17-C20)$	0.07671	17.57	0.68	0.100

Table 10. Second order perturbation theory analysis of Fock matrix on NBO ofcompound 3

Donor (i)	ED/e	Acceptor (j)	ED/e	E(2)	E(j)-E(i)	F(i.j)
Donor (I)				Kcal/mol	a.u	a.u
LP (2) S9	1.70854	π*(C5-C6)	0.29700	25.72	0.25	0.072
π (C12-C13)	1.74814	π*(C16-C17)	0.24496	23.12	0.30	0.074
π (C16-C17)	1.72022	$\pi^*(C19-C34)$	0.30580	22.06	0.28	0.071
LP (2) S10	1.77148	$\pi^{*}(C2-C3)$	0.30773	21.49	0.24	0.065
π (C16-C17)	1.72022	π*(C20-O23)	0.20749	21.00	0.28	0.070
LP (2) O23	1.87726	$\sigma^*(C17-C20)$	0.07029	20.68	0.69	0.108
LP (2) S11	1.77701	$\pi^{*}(C2-C3)$	0.30773	20.45	0.24	0.063
LP (2) O23	1.87726	$\sigma^{*}(C20-C29)$	0.06639	20.25	0.71	0.109
π (C25-C26)	1.61773	π*(C27-C28)	0.35223	20.07	0.28	0.068
π (C24-C29)	1.61986	$\pi^{*}(C27-C28)$	0.35223	19.70	0.28	0.067
π (C25-C26)	1.61773	$\pi^{*}(C24-C29)$	0.33566	19.69	0.29	0.068
π (C27-C28)	1.61248	$\pi^{*}(C25-C26)$	0.31821	19.62	0.28	0.067
π (C27-C28)	1.61248	$\pi^{*}(C24-C29)$	0.33566	19.57	0.29	0.068
LP (2) S8	1.79342	$\pi^{*}(C5-C6)$	0.29700	19.53	0.25	0.064
π (C24-C29)	1.61986	π*(C25-C26)	0.31821	19.41	0.28	0.067
π (C24-C29)	1.61986	π*(C20-O23)	0.20749	18.87	0.27	0.067
LP (2) S8	1.79342	$\pi^{*}(C1-C4)$	0.39523	17.31	0.25	0.062
LP (2) S9	1.70854	$\pi^{*}(C1-C4)$	0.39523	17.26	0.26	0.061
π (C27-C28)	1.61248	$\pi^{*}(C19-C34)$	0.30580	17.04	0.27	0.062
LP (2) S10	1.77148	$\pi^{*}(C1-C4)$	0.39523	16.48	0.25	0.059

Table 11. Second order perturbation theory analysis of Fock matrix on NBO ofcompound 4

The intramolecular interaction for the title compounds is formed by the orbital overlap between:  $\pi$  (C12-C13) and  $\pi^*$ (C16-C17) for compound **1**,  $\pi$  (C16-C17) and  $\pi^*$ (C20-O26) for compound **2**,  $\pi$  (C12-C13) and  $\pi^*$ (C16-C17) for compound **3** and  $\pi$  (C12-C13) and  $\pi^*$ (C16-C17) for compound **4** respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intramolecular hyper conjugative interactions of  $\pi$ (C12-C13) to  $\pi^*$ (C16-C17) for compound **1**,  $\pi$  (C16-C17) to  $\pi^*$ (C20-O26) for compound **2**,  $\pi$ (C12-C13) to  $\pi^*$ (C16-C17) for compound **3** and  $\pi$  (C12-C13) to  $\pi^*$ (C16-C17) for compound **4** lead to highest stabilization of 23.27, 26.96, 22.00 and 23.12 kJ mol<sup>-1</sup> respectively. In case of LP (2) S9 orbital to the  $\pi^*$ (C5-C6) for compound **1**, LP (1) N21orbital to  $\pi^*$ (C27-S28) for compound **2**, LP (2) O36 orbital to  $\pi^*$ (C20-O35) for compound **3**, LP (2) S9 orbital to  $\pi^*$ (C5-C6) for compound **4** respectively, show the stabilization energy of 25.74, 75.59, 40.90 and 25.72 kJ mol<sup>-1</sup> respectively.

## 2.7.Nonlinear Optical Properties (NLO)

The search for new molecular systems possessing a large value of static first hyperpolarizability is an important stage for the optimization of new materials which are found applications in a wide spectrum from optical telecommunications, data storage; signal processing, logic technologies and sensor protection to modern optical computing <sup>[31]</sup>. In the presence of an applied electric field, the energy of a system is a function of the electric field. First order hyperpolarizability is a third rank tensor that can be described by the  $3\times3\times3$  matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Klein-man symmetry <sup>[32]</sup>. It can be given in the lower tetrahedral format. It is obvious that the lower part of the  $3\times3\times3$  matrixes is a tetrahedral. The component of  $\beta$  is defined as the coefficient in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, the expansion becomes:

$$\mathcal{E} = \mathcal{E}^{0} - \mu_{\alpha} \mathcal{F}_{\alpha} - \frac{1}{2} \alpha_{\alpha\beta} \mathcal{F}_{\alpha} \mathcal{F}_{\beta} - \frac{1}{6} \beta_{\alpha\beta\gamma} \mathcal{F}_{\alpha} \mathcal{F}_{\beta} \mathcal{F}_{\gamma} + \dots$$

where  $E^0$  is the energy of the unperturbed molecules,  $F_{\alpha}$  is the field at the origin.  $\mu_{\alpha}$ ,  $\alpha_{\alpha\beta}$  and  $\beta_{\alpha\beta\gamma}$  are the components of 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 the mean first order hyperpolarizability  $\beta_0$ , using the x, y, z components they are defined as:

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

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

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

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

Where

$$\beta_{X} = \beta_{XXX} + \beta_{XYY} + \beta_{XZZ}$$
$$\beta_{Y} = \beta_{YYY} + \beta_{XXY} + \beta_{YZZ}$$
$$\beta_{Z} = \beta_{ZZZ} + \beta_{XXZ} + \beta_{YYZ}$$

Theoretically calculated values of first order hyperpolarizability, dipole moments, total polarizability and anisotropy of the polarizability are calculated at the DFT method with B3LYP/6-31G (d,p) basis set and mentioned in table 12.

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
$\beta_{xxx}$	851.0470	-669.6495	415.3071	-314.7963
$\beta_{yyy}$	22.6590	36.5924	57.7922	-102.0355
$\beta_{zzz}$	19.6443	16.7838	18.8616	11.3465
$\beta_{xyy}$	128.7043	-17.1132	54.7675	-147.4217
$\beta_{xxy}$	-41.6795	-53.1582	306.5605	-340.9888
$\beta_{xxz}$	-32.9909	-4.4370	-39.6032	45.0165
$\beta_{xzz}$	43.4556	-4.5289	24.6004	-33.1287
$\beta_{yzz}$	1.2488	7.1350	-12.0716	8.1132
$\beta_{yyz}$	13.5248	5.8500	3.7198	27.6989
$\beta_{xyz}$	-7.5957	-55.2745	-55.8300	-50.5603
$\beta_{\theta}(\mathrm{esu}) \mathrm{x10}^{-33}$	1023.4986	691.5954	607.5320	664.5167
$\mu_x$	6.3471	-5.8364	5.0013	-3.2760
$\mu_y$	0.6473	1.2233	4.6642	-4.1691
$\mu_z$	1.4092	0.2104	0.4220	1.1308
$\mu(\mathbf{D})$	6.5338	5.9669	6.8517	5.4215
$\alpha_{xx}$	-249.0713	-231.7602	-212.2787	-199.2381
$\alpha_{yy}$	-165.8871	-222.5710	-215.2460	-239.3854
$\alpha_{zz}$	-169.3943	-224.8662	-211.0451	-226.7179
$\alpha_{xy}$	-2.1863	-2.8732	-35.4780	-44.5827
$\alpha_{xz}$	23.8888	-6.3127	9.5270	3.8037
$\alpha_{yz}$	1.1848	6.1716	-3.8891	6.7310
$\alpha_{\theta}(esu)x10^{-24}$	91.4918	18.0887	64.0915	86.0574
$\Delta \alpha(esu) \times 10^{-24}$	13.5591	2.6807	9.4984	12.7537

Table 12. Nonlinear optical properties of (TTFs) connected to acceptor moieties 1-4

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 6.5338, 5.9669, 6.8517 and 5.4215 D respectively, which are approximately two times more than 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 91.4918 x 10<sup>-24</sup>, 18.0887 x 10<sup>-24</sup>, 64.0915 x 10<sup>-24</sup> and 86.0574 x 10<sup>-24</sup> esu respectively; the values of

anisotropy of the polarizability are 13.5591, 2.6807, 9.4984 and 12.7537 esu, respectively. The magnitude of the molecular hyperpolarizability ( $\beta_0$ ) is one of the important key factors in an NLO system. The DFT/6-31G(d,p) calculated first hyperpolarizability value ( $\beta_0$ ) of (TTFs) connected to acceptor moieties molecules are equal to 1023.4986 x 10<sup>-33</sup>, 691.5954 x 10<sup>-33</sup>, 607.5320 x 10<sup>-33</sup> and 664.5167 x 10<sup>-33</sup> is. The first hyperpolarizability of title molecules is approximately 2.98, 2.01, 1.77 and 1.94 times than those of urea ( $\beta$  of urea is 343.272 x10<sup>-33</sup> esu obtained by B3LYP/6-311G (d,p) method). The above results show that (TTFs) connected to acceptor moieties **1-4** might have the NLO applications.

#### 3. CONCLUSION

In this work, we have calculated the geometric parameters of the (TTFs) connected to acceptor moieties **1-4** using the DFT/B3LYP method using 6-31G (d,p) basis set. By the same method, the reactivity sites are identified by mapping the molecular electrostatic potential (MEP) surface. The HOMO- LUMO energies describe the charge transfer takes place within the molecules by the frontier molecular orbital analysis. The calculation of quantum chemical descriptors indicates that compound **4** has the smaller frontier orbital gap which means that is the compound with a high chemical reactivity compared to other compounds. The local reactivity descriptors are also determined to provide the information on the electrophilic, nucleophilic and free radical prone reactive sites of the molecules. Complete NBO analysis was also carried out to find the intermolecular electronic interactions and their stabilization energies. The calculation of first order hyperpolarizability reveals that the title compounds possess good NLO properties.

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