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DFT study including NBO, NLO response and reactivity descriptor of bis and tris (1, 3-dithiole) tetrathiafulvalene

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ABSTRACT

We present a density functional theory (DFT) study on the reactivity of bis and tris (1,3-dithiole) TTF **1-4** by using B3LYP/6-31G (d,p) level. The possible electrophile and nucleophile attacking sites of the title compounds is identified using MEP surface plot study. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy gaps were calculated to explain the frontier molecular orbitals and to predict the quantum chemical descriptors. Local reactivity properties have been investigated using average local ionization energies and Fukui functions. Natural Bond Orbital analysis was computed and possible transitions were correlated with the electronic transitions. The calculated first hyperpolarizability (β_0) of bis and tris (1,3-dithiole) TTF molecules, indicates that investigated molecules might have not the NLO applications.

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

1. INTRODUCTION

The tetrathiafulvalene (TTF) derivatives are one kind of organic semiconductors that have been paid considerable attention as potential charge transfer materials in organic electronic devices in recent years[1-5]. They have been widely explored in both materials and supramolecular chemistry[6]. The π-electron donor tetrathiafulvalene (TTF) and its derivatives have been studied extensively for their use in a variety of applications such as organic metals and superconductors[7], Langmuir-Blodgett films[8], molecular sensors[9], non-linear optics[10], field effect transistors[11] and photovoltaics[10].

Density functional theory based on the Becke's three parameter hybrid exchange functional combined with the Lee e Yang e Parr non-local correlation function level of theory displays good achievement on the characterization of the organic molecules[12-14] as a consequence of the recovering of the electron correlation in the self-consistent Kohn e Sham procedure throughout the electron density functions[15-17].

The present research work predominantly focused on the computational study of bis and tris (1,3-dithiole) TTF **1-4** reported in literature[18] by DFT/B3LYP method within 6-31G (d,p) basis set. The optimized structural parameters such as bond lengths, bond angles and dihedral angles have been computed using the same method cited above. The global reactivity descriptors, namely, hardness (η), chemical potential (μ) and electrophilicity index (ω) are also calculated to understand the reactive nature of the investigated compounds. Fukui functions are determined to predict the reactive sites in these molecules. In addition the

molecular electrostatic potential, the frontier molecular orbital, the intramolecular charge transfer and non-linear optical activity of the title compounds have been also studied clearly.

2. MATERIALS AND METHODS

The theoretical calculations were performed using the Gaussian 09W program package[19] and B3LYP (Becke's Three parameter Hybrid Functional Using the LYP Correlation Functional) approach in conjunction with the 6-31G (d,p) basis set.

3. RESULTS AND DISCUSSION

3.1. Molecular Geometry

The optimized structural parameters such as bond lengths, bond angles and dihedral angles of bis and tris (1,3-dithiole) TTF **1-4** are determined by theoretical B3LYP method with 6-31G (d,p) basis set and presented in Tables 1-4 in accordance with the atom numbering scheme as given in Figure 1.
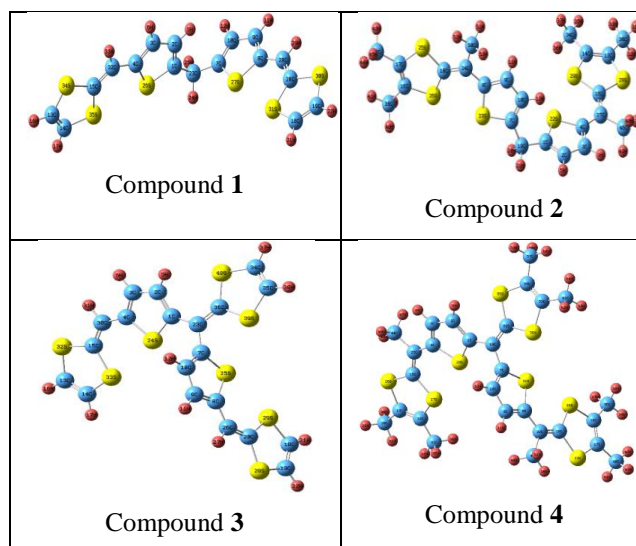

Figure 1: Optimized molecular structure of bis and tris (1,3-dithiole) TTF **1-4**

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

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.370	A(2,1,23)	129.406	D(23,1,2,3)	177.320
R(1,23)	1.512	A(2,1,26)	110.547	D(26,1,2,5)	179.740
R(1,26)	1.749	A(23,1,26)	119.993	D(2,1,23,7)	23.443
R(2,3)	1.419	A(1,2,3)	113.604	D(2,1,23,24)	147.495
R(2,5)	1.083	A(1,2,5)	122.485	D(26,1,23,25)	79.958
R(4,32)	1.440	A(3,4,32)	125.136	D(2,3,4,32)	179.771
R(8,28)	1.441	A(10,7,23)	128.063	D(26,4,32,33)	179.630
R(13,14)	1.337	A(27,8,28)	125.444	D(10,7,23,24)	128.525
R(13,16)	1.083	A(7,10,12)	122.462	D(10,7,23,25)	14.070
R(13,34)	1.756	A(14,13,34)	117.694	D(27,7,23,1)	72.330
R(15,32)	1.355	A(16,13,34)	117.401	D(27,8,9,11)	179.991
R(15,34)	1.789	A(34,15,35)	112.921	D(9,8,28,20)	179.803
R(18,21)	1.083	A(21,18,31)	117.059	D(34,13,14,17)	179.950
R(18,31)	1.761	A(4,32,15)	130.874	D(32,15,34,13)	179.722
R(32,33)	1.088	A(13,34,15)	95.816	D(30,20,28,8)	179.945

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

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.369	A(2,1,19)	128.179	D(19,1,2,3)	179.886
R(1,19)	1.503	A(2,1,22)	110.304	D(22,1,19,20)	50.080
R(1,22)	1.746	A(19,1,22)	121.516	D(22,1,19,21)	164.577
R(2,3)	1.419	A(1,2,3)	113.869	D(1,2,3,6)	179.581
R(2,5)	1.085	A(1,2,5)	122.604	D(3,4,27,46)	4.751
R(3,4)	1.385	A(3,4,27)	125.713	D(22,4,27,15)	6.453
R(3,6)	1.082	A(10,7,23)	110.430	D(10,7,19,21)	96.551
R(4,27)	1.457	A(8,9,11)	122.827	D(23,7,19,1)	159.052
R(13,14)	1.344	A(14,13,28)	116.772	D(23,7,19,20)	34.986
R(13,28)	1.773	A(14,13,30)	128.006	D(19,7,23,8)	177.556
R(13,30)	1.503	A(17,16,38)	128.105	D(24,8,9,10)	179.753
R(15,27)	1.364	A(1,19,20)	110.142	D(9,8,24,18)	171.027
R(15,28)	1.787	A(4,27,15)	126.311	D(23,8,24,50)	172.444
R(19,20)	1.097	A(4,27,46)	114.418	D(8,9,10,12)	179.526
R(27,46)	1.517	A(15,27,46)	119.258	D(14,13,30,31)	121.645

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

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.385	A(2,1,23)	131.383	D(32,15,30,4)	179.947
R(1,23)	1.457	A(2,1,24)	109.638	D(21,18,29,20)	179.903
R(1,24)	1.763	A(23,1,24)	118.977	D(32,13,14,17)	179.841
R(2,3)	1.410	A(1,2,3)	113.932	D(33,15,30,31)	179.820
R(2,5)	1.082	A(1,2,5)	123.377	D(2,3,4,30)	179.604
R(3,4)	1.385	A(3,2,5)	122.616	D(11,9,10,7)	179.533
R(4,30)	1.438	A(3,4,30)	124.796	D(37,34,35,39)	179.414
R(13,14)	1.337	A(14,13,16)	124.948	D(23,1,2,3)	179.252
R(13,16)	1.083	A(14,13,32)	117.622	D(30,15,32,13)	178.743
R(13,32)	1.756	A(1,23,7)	117.676	D(23,7,10,9)	178.631
R(15,30)	1.357	A(1,23,36)	124.336	D(23,36,39,35)	176.280
R(15,32)	1.788	A(7,23,36)	117.987	D(1,23,36,39)	174.988
R(20,26)	1.356	A(4,30,15)	130.782	D(24,1,23,36)	159.435
R(23,36)	1.369	A(13,32,15)	95.810	D(10,7,23,36)	103.254
R(30,31)	1.088	A(25,8,26)	125.557	D(25,7,23,1)	101.121

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

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.383	A(2,1,19)	131.255	D(22,8,9,10)	179.996
R(1,19)	1.458	A(2,1,20)	109.539	D(36,16,24,18)	178.514
R(1,20)	1.760	A(19,1,20)	119.202	D(26,15,25,4)	177.710
R(2,3)	1.412	A(1,2,3)	113.981	D(20,1,2,5)	176.619
R(4,25)	1.455	A(1,2,5)	123.372	D(8,22,48,50)	173.146
R(7,19)	1.484	A(3,4,20)	108.950	D(4,25,44,45)	165.085
R(13,14)	1.344	A(3,4,25)	125.587	D(20,1,19,52)	157.119
R(13,26)	1.773	A(14,13,26)	116.719	D(14,13,28,29)	122.273
R(13,28)	1.503	A(14,13,28)	128.005	D(17,16,36,37)	119.322
R(15,25)	1.365	A(26,13,28)	115.273	D(13,14,32,34)	118.285
R(15,26)	1.786	A(1,19,7)	117.679	D(18,22,48,51)	113.118
R(19,52)	1.369	A(1,19,52)	124.006	D(15,25,44,46)	104.471
R(25,44)	1.518	A(7,19,52)	118.312	D(21,7,19,1)	102.748
R(44,46)	1.097	A(13,26,15)	97.280	D(56,53,61,63)	62.465
R(1,2)	1.383	A(25,15,26)	122.080	D(24,16,36,38)	58.651

3.2. Molecular Electrostatic Potential (MEP)

The MEP is a very useful feature to study reactivity given that an approaching electrophile will be attracted to negative regions (the electron distribution in where effect is dominant). In the majority of the MEPs, while the maximum negative region which preferred site for electrophilic attack indications as red color, the maximum positive region which preferred site for nucleophilic attack symptoms as blue color. The importance of MEP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative and neutral electrostatic potential (MEP) of bis and tris (1,3-dithiole) TTF **1-4** is calculated by B3LYP/6-31G (d,p) and shown in Figure 2. The MEP is a plot of electrostatic potential mapped onto the constant electron density surface. The different values of the electrostatic potential at the surface are represented by different colors. Potential increases in the order red < orange < yellow < green < blue.

As observed from the figure **2** that, in all molecules, the regions exhibiting the negative electrostatic potential are localized near the thiophene spacer units while the regions presenting the positive potential are localized vicinity of the hydrogen atoms and alkyl groups.
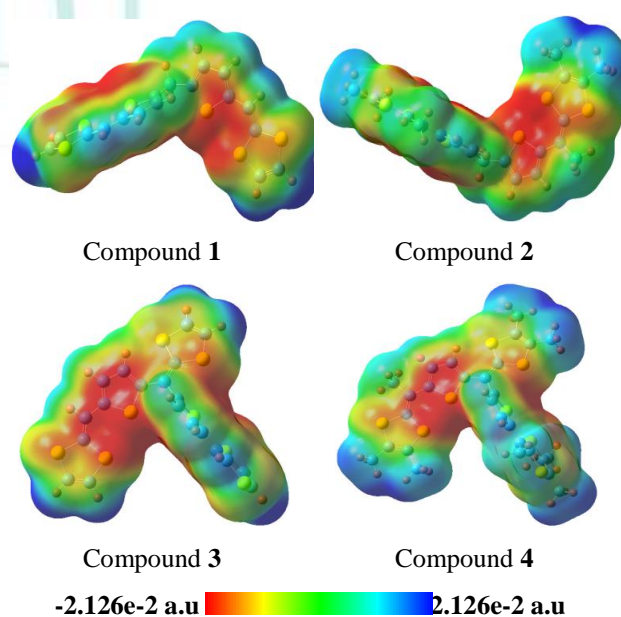

Compound **1**   Compound **2**

Compound **3**   Compound **4**

-2.126e-2 a.u ▮▮▮▮ 2.126e-2 a.u

Figure 2: Molecular electrostatic potential surface of bis and tris (1, 3-dithiole) TTF **1-4**

3.3. Frontier Molecular Orbitals (FMOs)

The properties of the frontier molecular orbitals (FMOs) like energy are very applied for physicists and chemists. The electron densities of these FMOs were used for predicting the most reactive position in π-electron systems and also explained several types of reaction in conjugated system[20]. Moreover, eigen values of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) and their energy gap reflect the chemical reactivity of the molecule. Recently the energy gap between HOMO and LUMO has been used to prove the bioactivity from intramolecular charge transfer (ICT)[21,22]. The HOMO-LUMO energy gap for the studied compounds were calculated by B3LYP/6-31G (d,p) method. The HOMO-1, HOMO, LUMO and LUMO+1 picture of compound **3** with a small energy gap is shown in Figure 3.
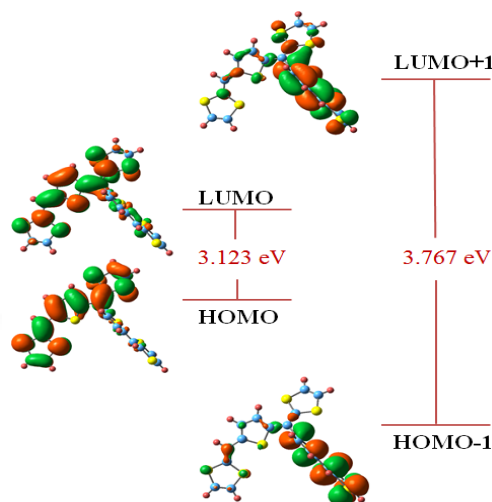

Figure 3: HOMO-LUMO Structure with the energy level diagram of compound **3**

3.4. Global Reactivity Descriptors

Based on the energies of the frontier molecular orbitals, various chemical reactivity descriptors such as electronegativity (χ), chemical potential (μ), chemical hardness (η), global softness (S) and global electrophilicity index (ω)[23-27] were proposed for understanding the different pharmacological aspects of drug molecules. These descriptors are calculated using equations given below:

$$\chi = \frac{(I + A)}{2}$$

$$\mu = -\chi = -\frac{(I + A)}{2}$$

$$\eta = \frac{(I - A)}{2}$$

$$S = \frac{1}{2\eta}$$

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

The chemical hardness is a measure of the resistance to charge transference[28], while the electronegativity is a measure of the tendency to attract electrons in a chemical bond, as is defined as the negative of the chemical potential in DFT[28]. The electrophilicity index (ω) contains information about both electron transfer (chemical potential) and stability (hardness) and is a better descriptor of global chemical reactivity. For the studied compounds, the chemical reactivity descriptors are computed by B3LYP/6-31G (d,p) method and given in Table 5.

Table 5: Quantum chemical descriptors of bis and tris (1,3-dithiole) TTF **1-4**

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
E_{HOMO} (eV)	-4.699	-4.531	-4.349	-4.165
E_{LUMO} (eV)	-0.988	-0.771	-1.226	-0.983
ΔE_{gap} (eV)	3.711	3.759	3.123	3.182
IE (eV)	4.699	4.531	4.349	4.165
A (eV)	0.988	0.711	1.226	0.983
μ (eV)	-2.844	-2.651	-2.787	-2.574
χ (eV)	2.844	2.651	2.787	2.574
η (eV)	1.855	1.880	1.561	1.591
S (eV)	0.269	0.266	0.320	0.314
ω (eV)	2.179	1.870	2.488	2.082

The compound which have the lowest energetic gap is the compound **3** (ΔE_{gap} = 3.123 eV). This lower gap allows it to be the softest molecule. The compound that has the highest energy gap is the compound **2** (ΔE_{gap} = 3.759 eV).The compound that has the highest HOMO energy is the compound **4** (E_{HOMO} = -4.165 eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound **3** (E_{LUMO} = -1.226 eV) which signifies that it can be the best electron acceptor. The two properties like I (potential ionization) and A (affinity) are so important, the determination of these two properties allow us to calculate the absolute electronegativity (χ) and the absolute hardness (η). These two parameters are related to the one-electron orbital energies of the HOMO and LUMO respectively. Compound **4** has lowest value of the potential ionization (I = 4.165 eV), so that will be the better electron donor. Compound **3** has the largest value of the affinity (A = 1.226 eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound **3** (η = 1.561 eV, **S** =

0.320 eV) is lesser (greater) among all the molecules. Thus, compound **3** is found to be more reactive than all the compounds. Compound **1** possesses higher electronegativity value (χ = 2.844 eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **3** (ω = 2.488 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.

3.5. Local Reactivity Descriptors

Parr and Yang[29] have demonstrated that most of the frontier-electron density theory of chemical reactivity can be rationalized from the DFT. Parr and Yang defined a Fukui function (f_k) to describe electrophilic attack (f_k^-), nucleophilic attack (f_k^+) and neutral (radical) attack (f_k^0). Yang and Mortier proposed a finite

difference approach to calculate Fukui function indices[30]. In a finite difference approximation, the condensed Fukui function values are given Yang et al. as

$$f_j^- = q_j(N) - q_j(N-1) \text{ for nucleophilic attack}$$

$$f_j^+ = q_j(N+1) - q_j(N) \text{ for electrophilic attack}$$

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

where q_k is the gross charge of the kth atom in the neutral (N), anionic (N+1) and cationic (N-1) molecule, respectively, all with the ground state geometry of the N electron molecule. Gross charges may be determined by Mulliken, Hirschfeld and Natural charge analysis. The reactive sites on bis and tris (1,3-dithiole) TTF **1-4** are calculated by the DFT/B3LYP method with 6-31G (d,p) basis set and shown in Tables 6-7.

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

	Compound 1					Compound 2			
Atom	4 C	8 C	1 C	15 C	**Atom**	8 C	4 C	14 C	16 C
f^+	0.043	0.042	0.008	0.004	f^+	0.030	0.025	0.001	0.001
Atom	28 C	32 C	7 C	27 S	**Atom**	24 C	27 C	1 C	17 C
f^-	0.010	0.009	0.003	0.002	f^-	0.036	0.033	0.018	0.010
Atom	4 C	8 C	7 C	1 C	**Atom**	17 C	13 C	16 C	14 C
f^0	0.002	0.003	0.008	0.008	f^0	0.002	0.002	0.001	0.001

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

	Compound 3					Compound 4			
Atom	36 C	1 C	8 C	10 C	**Atom**	52 C	1 C	10 C	8 C
f^+	0.097	0.057	0.046	0.036	f^+	0.094	0.045	0.035	0.031
Atom	23 C	7 C	26 C	30 C	**Atom**	19 C	7 C	22 C	25 C
f^-	0.178	0.065	0.031	0.013	f^-	0.177	0.070	0.036	0.034
Atom	7 C	4 C	23 C	8 C	**Atom**	7 C	53 C	13 C	22 C
f^0	0.010	0.010	0.008	0.005	f^0	0.008	0.004	0.002	0.002

The parameters of local reactivity descriptors show that 4C, 8C, 36C and 52C are the more reactive sites in compounds **1**, **2**, **3** and **4** respectively for nucleophilic attacks. The more reactive sites for electrophilic attacks are 28C, 24C, 23C and 19C for compounds **1**, **2**, **3** and **4** respectively. The more reactive sites in radical attacks are 4C, 17C, for compounds **1**, **2** respectively and 7C for the both compounds **3** and **4**.

3.6. Natural Bond Orbital Analysis (NBO)

A useful aspect of the NBO method is that it gives information about intra and intermolecular bonding and interactions among bonds and also provides a convenient basis for investigating the interactions in both filled and virtual orbital spaces along with charge transfer and conjugative interactions in molecular system. Some electron donor orbital, acceptor orbital and the interacting stabilization energies resulting from the second-order micro-disturbance theory are reported[31,32].The large value of second order stabilization energy ($E^{(2)}$) shows that the more donating

tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system[33]. In order to characterize the intra and intermolecular interactions quantitatively, a second-order perturbation theory is applied that gives the energy lowering associated with such interactions. For each donor NBO(i) and acceptor NBO(j), stabilization energy ($E^{(2)}$) associated with electron delocalization between donor and acceptor is estimated by an equation as[34,35].

$$E^{(2)} = -q_i \frac{\left(F_{ij}\right)^2}{\varepsilon_i - \varepsilon_j}$$

where q_i is the donor orbital occupancy; ε_i, ε_j are orbital energies of donor and acceptor NBO orbitals, respectively; F_{ij} is the off-diagonal Fock or Kohn-Sham matrix element. The results of second-order perturbation theory analysis of the Fock Matrix of bis and tris (1,3-dithiole) TTF **1-4** at B3LYP/6-31G (d,p) level of theory are presented 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) S34	1.76226	π*(C13-C14)	0.22006	22.85	0.25	0.068
LP(2) S30	1.76003	π*(C18-C19)	0.21963	22.77	0.25	0.068
LP(2) S35	1.75627	π*(C13-C14)	0.22006	22.21	0.25	0.067
LP(2) S31	1.75279	π*(C18-C19)	0.21963	22.20	0.25	0.067
LP(2) S27	1.66431	π*(C7-C10)	0.31685	21.18	0.27	0.068
LP(2) S26	1.67209	π*(C1-C2)	0.31139	20.95	0.28	0.068
LP(2) S27	1.66431	π*(C8-C9)	0.36906	20.87	0.27	0.067
LP(2) S26	1.67209	π*(C3-C4)	0.36665	20.18	0.27	0.067
LP(2) S31	1.75279	π*(C20-C28)	0.32339	20.11	0.27	0.067
LP(2) S35	1.75627	π*(C15-C32)	0.32218	19.80	0.27	0.067
π (C3-C4)	1.80546	π*(C15-C32)	0.32218	19.23	0.27	0.067
π (C8-C9)	1.80282	π*(C20-C28)	0.32339	18.97	0.27	0.066
LP(2) S30	1.76003	π*(C20-C28)	0.32339	17.66	0.27	0.063
LP(2) S34	1.76226	π*(C15-C32)	0.32218	17.45	0.27	0.063
π (C8-C9)	1.80282	π*(C7-C10)	0.31685	16.92	0.29	0.065
π (C3-C4)	1.80546	π*(C1-C2)	0.31139	16.61	0.29	0.064
π (C1-C2)	1.84789	π*(C3-C4)	0.36665	15.32	0.29	0.063
π (C7-C10)	1.85043	π*(C8-C9)	0.36906	14.95	0.29	0.063
π (C20-C28)	1.91327	π*(C8-C9)	0.36906	11.72	0.32	0.059
π (C15-C32)	1.91577	π*(C3-C4)	0.36665	11.51	0.32	0.058

Table 9: Second order perturbation theory analysis of Fock matrix on NBO of compound **2**

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F(i.j) a.u
LP(2) S22	1.66342	π*(C1-C2)	0.31620	21.41	0.27	0.068
LP(2) S23	1.67140	π*(C7-C10)	0.30949	21.10	0.28	0.068
LP(2) S29	1.76658	π*(C13-C14)	0.23691	20.44	0.27	0.066
LP(2) S28	1.77803	π*(C13-C14)	0.23691	20.40	0.27	0.067
LP(2) S22	1.66342	π*(C3-C4)	0.36960	20.39	0.27	0.066
LP(2) S25	1.77979	π*(C16-C17)	0.23695	20.39	0.27	0.067
LP(2) S26	1.77026	π*(C16-C17)	0.23695	20.37	0.27	0.066
LP(2) S23	1.67140	π*(C8-C9)	0.36558	19.71	0.27	0.066
LP(2) S29	1.76658	π*(C15-C27)	0.32738	19.24	0.27	0.066
LP(2) S26	1.77026	π*(C18-C24)	0.32525	18.88	0.27	0.066
LP(2) S28	1.77803	π*(C15-C27)	0.32738	17.90	0.27	0.064
LP(2) S25	1.77979	π*(C18-C24)	0.32525	17.60	0.28	0.064
π (C8-C9)	1.81785	π*(C18-C24)	0.32525	17.18	0.28	0.064
π (C3-C4)	1.81440	π*(C15-C27)	0.32738	17.08	0.28	0.064
π (C3-C4)	1.81440	π*(C1-C2)	0.31620	16.77	0.29	0.064
π (C8-C9)	1.81785	π*(C7-C10)	0.30949	16.41	0.29	0.064
π (C7-C10)	1.84992	π*(C8-C9)	0.36558	15.43	0.29	0.063
π (C1-C2)	1.85238	π*(C3-C4)	0.36960	15.05	0.29	0.063
π (C15-C27)	1.89677	π*(C3-C4)	0.36960	11.90	0.31	0.058
π (C18-C24)	1.89983	π*(C8-C9)	0.36558	11.55	0.31	0.058

The intra molecular interaction for the title compounds is formed by the orbital overlap between: π (C3-C4) and π*(C15-C32) for compound **1**, π (C8-C9) and π*(C18-C24) for compound **2**, π (C3-C4) and π*(C15-C30) for compound **3** and π (C18-C22) and π*(C8-C9) for compound **4** respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of π (C3-C4) to π*(C15-C32) for compound **1**, π (C8-C9) to π*(C18-C24) for compound **2**, π (C3-C4) to π*(C15-C30) for compound **3** and π (C18-C22) to π*(C8-C9) for compound **4** lead to highest stabilization of 19.23, 17.18, 19.83 and 11.87 kJ mol^{-1} respectively. In case of LP(2) S34 orbital to the π*(C13-C14) for compound **1**, LP(2) S22 orbital to π*(C1-C2) for compound **2**, LP(2) S39 orbital to π*(C34-C35) for compound **3**, LP(2) S21 orbital to π*(C8-C9) for compound **4** respectively, show the stabilization energy of 22.85, 21.41, 23.07 and 21.23 kJ mol^{-1} respectively.

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) S39	1.73999	π*(C34-C35)	0.22026	23.07	0.25	0.069
LP(2) S32	1.75980	π*(C13-C14)	0.22068	22.76	0.25	0.068
LP(2) S28	1.75851	π*(C18-C19)	0.21995	22.75	0.25	0.068
LP(2) S33	1.75045	π*(C13-C14)	0.22068	22.37	0.25	0.068
LP(2) S29	1.75001	π*(C18-C19)	0.21995	22.25	0.25	0.067
LP(2) S40	1.74741	π*(C34-C35)	0.22026	21.92	0.26	0.067
LP(2) S25	1.65108	π*(C8-C9)	0.37672	21.74	0.27	0.068
LP(2) S24	1.66989	π*(C3-C4)	0.38553	20.90	0.27	0.068
LP(2) S29	1.75001	π*(C20-C26)	0.32384	20.25	0.27	0.067
LP(2) S33	1.75045	π*(C15-C30)	0.33086	19.99	0.27	0.067
π (C3-C4)	1.77776	π*(C15-C30)	0.33086	19.83	0.27	0.067
LP(2) S25	1.65108	π*(C7-C10)	0.33037	19.82	0.27	0.065
LP(2) S24	1.66989	π*(C1-C2)	0.38247	19.80	0.27	0.066
LP(2) S40	1.74741	π*(C23-C36)	0.35872	19.63	0.27	0.067
LP(2) S39	1.73999	π*(C23-C36)	0.35872	19.44	0.27	0.066
π (C8-C9)	1.78802	π*(C20-C26)	0.32384	19.17	0.27	0.066
π (C8-C9)	1.78802	π*(C7-C10)	0.33037	18.29	0.29	0.067
LP(2) S28	1.75851	π*(C20-C26)	0.32384	17.73	0.27	0.063
LP(2) S32	1.75980	π*(C15-C30)	0.33086	17.46	0.27	0.063
π (C3-C4)	1.77776	π*(C1-C2)	0.38247	17.20	0.28	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) S21	1.65040	π*(C8-C9)	0.37846	21.23	0.27	0.067
LP(2) S56	1.75601	π*(C53-C54)	0.23801	21.13	0.27	0.067
LP(2) S27	1.76480	π*(C13-C14)	0.23753	20.62	0.27	0.066
LP(2) S24	1.76488	π*(C16-C17)	0.23737	20.53	0.27	0.066
LP(2) S20	1.66868	π*(C3-C4)	0.38460	20.41	0.27	0.067
LP(2) S23	1.77809	π*(C16-C17)	0.23737	20.41	0.27	0.067
LP(2) S26	1.77806	π*(C13-C14)	0.23753	20.34	0.27	0.067
LP(2) S55	1.76189	π*(C53-C54)	0.23801	20.20	0.27	0.066
LP(2) S55	1.76189	π*(C19-C52)	0.35390	20.06	0.27	0.067
LP(2) S20	1.66868	π*(C1-C2)	0.37698	20.03	0.27	0.066
LP(2) S21	1.65040	π*(C7-C10)	0.32854	19.97	0.27	0.066
LP(2) S56	1.75601	π*(C19-C52)	0.35390	19.90	0.26	0.067
LP(2) S24	1.76488	π*(C18-C22)	0.32765	19.28	0.27	0.066
LP(2) S27	1.76480	π*(C15-C25)	0.33286	19.02	0.27	0.066
LP(2) S23	1.77809	π*(C18-C22)	0.32765	17.92	0.27	0.064
LP(2) S26	1.77806	π*(C15-C25)	0.33286	17.54	0.28	0.064
π (C18-C22)	1.89540	π*(C8-C9)	0.37846	11.87	0.31	0.059
π (C19-C52)	1.89205	π*(C1-C2)	0.37698	9.89	0.32	0.054
σ (C25-C44)	1.96695	σ*(C15-S27)	0.03776	5.73	0.78	0.060
σ (C22-C48)	1.96686	σ*(C18-S24)	0.03792	5.71	0.78	0.060

3.7. Nonlinear Optical Properties (NLO)

NLO techniques are considered as one among the most structure sensitive method to study molecular structure and assemblies since the potential or organic materials for NLO device have been proven. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing, and dynamic image processing[36]. DFT has been extensively used as an effective method to investigate NLO properties of organic materials. In order to gain insight into NLO property of title compound, the first static hyperpolarizability (β) were calculated by the finite field perturbation method in vacuum as well as incorporating the solvent factors with increasing polarity. First hyperpolarizability is a third rank tensor that can be described by a 3×3×3 matrix. The 27 components of the 3D-matrix can be reduced to 10 components due to the Kleinman symmetry[37]. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous this expansion becomes:

$$E = E^0 - \mu_i F_i - 1/2\, \alpha_{ij} F_i F_j - 1/6\, \beta_{ijk} F_i F_j F_k + 1/24 \gamma_{ijkl}$$

where E^0 is the energy of the unperturbed molecules, F_i the field at the origin and μ_i, α_{ij}, β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability, and the first hyperpolarizability respectively. Using the x, y and z components of β obtained from Gaussian 09 output, the magnitude of the mean first hyperpolarizability tensor can be calculated.

The total static dipole moment is $\mu_{tot} = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2}$

The mean polarizability is $\alpha_0 = \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)/3$

The anisotropy polarizability is

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

and the mean first hyperpolarizability is

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

and

$$\beta_x = \left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)$$
$$\beta_y = \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)$$
$$\beta_z = \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)$$

The first static hyperpolarizability (β₀) and its related properties of title compounds have been computed using B3LYP/6-31G (d,p) level based on finite field approach and shown in Table 12.

Table 12: The dipole moments μ_{tot} (D), polarizability α_0 (esu), the anisotropy of the polarizability $\Delta\alpha$ (esu) and the first hyperpolarizability β_0 (esu) of bis and tris (1,3-dithiole) TTF **1-4**.

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
β_{xxx}	-121.5512	-150.1263	5.0493	-3.0010
β_{yyy}	-19.5719	37.1972	18.3092	24.5356
β_{zzz}	-2.5386	-1.0018	1.3466	-3.9574
β_{xyy}	84.3712	95.7305	34.7951	80.9100
β_{xxy}	-162.6516	189.3376	-102.0284	-85.5066
β_{xxz}	-54.4601	-53.0192	-64.0034	-80.8182
β_{xzz}	-45.8577	-55.8834	56.4871	54.2933
β_{yzz}	-3.3246	5.5184	-20.5327	-36.1668
β_{yyz}	-8.3396	-8.4140	-67.0276	-78.0401
β_{xyz}	16.5318	9.4698	20.8458	25.4880
β_0 (esu)x10^{-33}	247.9135	310.4428	185.6699	204.5481
μ_x	-0.0649	-0.3470	1.5926	2.0672
μ_y	-1.2689	2.3490	-1.1695	-1.7797
μ_z	-0.3978	-0.4539	-1.0008	-1.6486
μ_{tot} (D)	1.3313	2.4175	2.2149	3.1873
α_{xx}	-137.2983	-168.2622	-192.9694	-235.6603
α_{yy}	-161.0968	-195.0899	-174.4119	-218.5017
α_{zz}	-171.5538	-208.6007	-211.9540	-260.3748
α_{xy}	-2.8168	1.7521	3.5466	11.4015
α_{xz}	8.8212	10.4312	-6.9355	-9.0632
α_{yz}	2.4475	-2.5874	-0.1302	0.9577
α (esu)x10^{-24}	34.6380	40.2549	35.2022	44.3672
$\Delta\alpha$ (esu)x10^{-24}	5.1334	5.9658	5.2170	6.5752

Since the values of the polarizabilities ($\Delta\alpha$) and the hyperpolarizabilities (β_0) of the GAUSSIAN 09 output are obtained in atomic units (a.u.), the calculated values have been converted into electrostatic units (e.s.u.) (for α; 1 a.u = 0.1482 x 10^{-24} e.s.u., for β; 1 a.u = 8.6393 x 10^{-33} e.s.u.). The calculated values of dipole moment (μ_{tot}) for the title compounds were found to be 1.3313, 2.4175, 2.2149 and 3.1873 D respectively, which are approximately three times than to the value for urea (μ = 1.3732 D). Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore, it has been used frequently as a threshold value for comparative purposes. The calculated values of polarizability are 34.6380 x 10^{-24}, 40.2549 x 10^{-24}, 35.2022 x 10^{-24} and 44.3672 x 10^{-24} esu respectively; the values of anisotropy of the polarizability are 5.1334, 5.9658, 5.2170 and 6.5752 esu, respectively. The magnitude of the molecular hyperpolarizability (β_0) is one of important key factors in a NLO system. The DFT/6-31G (d,p) calculated first

hyperpolarizability value (β_0) of bis and tris (1,3-dithiole) TTF molecules are equal to 247.9135 x 10^{-33}, 310.4428 x 10^{-33}, 185.6699 x 10^{-33} and 204.5481 x 10^{-33} esu. The first hyperpolarizability of title molecules is approximately 0.72, 0.90, 0.54 and 0.60 times than those of urea (β of urea is 343.272 x10^{-33} esu obtained by B3LYP/6-311G (d,p) method). The above results show that bis and tris (1,3-dithiole) TTF **1-4** might have not the NLO proprieties.

4. CONCLUSION

In this investigation we reported a detailed theoretical study of bis and tris (1,3-dithiole) TTF **1-4** at DFT/B3LYP method with 6-31G (d,p) basis set. Molecular parameters such as bond length, bond angle and dihedral angle were calculated with the same method. MEP predicts the most reactive part in the molecules. The difference in HOMO and LUMO energy supports the charge transfer interaction within the molecule. The chemical reactivity and site selectivity of

the molecules have been determined with the help of global and local reactivity descriptors. The stabilization energies have been calculated from second order perturbation theory. The predicted NLO properties of title compounds are much smaller than those of urea which indicates that have not the NLO materials.

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