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Determination of reactive properties of polyene TTF analogues employing DFT method

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Abstract

The present paper reports the detailed computational study of a series of Polyene TTF analogues 1-4 within DFT method and B3LYP/6-31G (d,p) basis set. The calculated HOMO and LUMO energies show that charge transfer within the molecules. Stability of the molecules arising from hyperconjugative interactions, charge delocalization have been analyzed using natural bond orbital analysis (NBO). The dipole moment (μ), polarizability (Δα) and first order hyperpolarizability (β) of the molecules were calculated. Molecular electrostatic potential (MEP) and Fukui functions were also performed.

Keywords: tetrathiafulvalenes, density functional theory, computational chemistry, electronic structure, quantum chemical calculations

1. Introduction

Recently, tetrathiafulvalenes TTFs have become an interesting topic of research due to their highly electrical conductivity and superconducting properties [1, 2]. It has also been reported that tetrathiafulvalenes show good π-donor properties [3]. The synthesis of two dithiole rings separated by a conjugated spacer has received great attention as a consequence of the potential of these compounds in the preparation of substances with nonlinear optical properties or as semiconductors. The synthesis of derivatives and analogues of dithiafulvalene (DTF) and tetrathiafulvalene (TTF) is of considerable interest [4, 5].

Tetrathiafulvalene [6] is redox active electron rich heterocyclic compound that can be oxidized in a stepwise manner giving first a stable radical cation and then a dication. Initially, tetrathiafulvalene (TTF) and its derivatives were extensively studied in the context of organic electronics due to the ability to form conductive, semi conductive, and superconductive solid-state phases [7]. Later, due to their unique electron-donating [8] and electrochemical properties, TTFs found use as building blocks in diverse molecular and supramolecular systems [9], ranging from polymers [10], dendrimers [9], and ion sensors [9] to Langmuir-Blodgett films [9] and charge-transfer systems [11], commonly playing the role of redox-switchable groups [12].

Quantum chemical calculations have been performed by density functional theory (DFT) using B3LYP functional and 6-31G (d,p) basis set. Atoms in molecules (AIM) theory have been extensively applied to classify and understand hydrogen bonding interactions and π-electron delocalization in a molecule [13]. Energy gap between HOMO and LUMO characterized the chemical stability and charge transfer interaction in the molecules. Development of materials with large nonlinear optical (NLO) property has been of great interest because of their application as an ultrafast image-processing, optical data processing, transmission, and storage [14].

Therefore, the present paper aims to give a complete description of the molecular geometry, chemical shifts, intramolecular interactions, electronic transitions, global reactivity descriptors and non-linear optical (NLO) features of Polyene TTF analogues 1-4 described in literature [15].

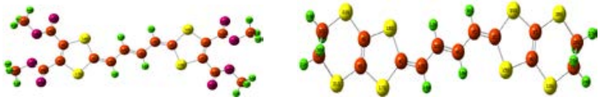
2. Materials and Methods

The optimized molecular structure, NBO analysis, NLO properties, atomic charges and frontier molecule orbitals (HOMO, LUMO) of Polyene TTF analogues 1-4 have been calculated by using DFT/B3LYP method with 6-31G(d,p) basis set. All quantum chemical calculations were carried out by using Gaussian 09 program package and the Gauss View molecular visualization program [16, 17]. The molecular structure of the title compounds was computed by using Becke-3-Lee Yang Parr (B3LYP) [18, 19] density functional method with 6-31G (d,p) basis set in ground state.

3. Results and Discussion

3.1. Molecular Geometry

The optimized geometric parameters (bond lengths, bond angles and dihedral angles) of the title molecules are given in Tables 1-4 using DFT/B3LYP with 6-31G (d,p) basis set. The atom numbering scheme adopted in this study is given in Fig 1



Compound 1 **Compound 2**

Compound 3 **Compound 4**

Fig 1: Optimized molecular structure of Polyene TTF analogues **1-4**

Table 1: Optimized geometric parameters of compound 1

Bond Length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
R(1,3)	1.337	A(3,1,4)	124.934	D(4,1,3,19)	180.000
R(1,4)	1.083	A(3,1,20)	117.713	D(4,1,20,2)	179.999
R(1,20)	1.759	A(4,1,20)	117.353	D(19,2,11,12)	179.999
R(2,11)	1.358	A(11,2,19)	124.491	D(20,2,11,13)	179.999
R(2,19)	1.786	A (11,2,20)	122.398	D(11,2,19,3)	179.998
R(2,20)	1.785	A (19,2,20)	113.111	D(19,2,20,1)	60.002
R(3,19)	1.762	A (1,3,19)	117.894	D(1,3,19,2)	50.001
R(6,17)	1.358	A(17,6,21)	122.398	D(17,6,21,8)	179.998
R(6,21)	1.785	A(17,6,22)	124.491	D(9,7,8,21)	180.000
R(6,22)	1.786	A(21,6,22)	113.111	D(9,7,22,6)	179.999
R(7,8)	1.337	A(8,7,9)	124.965	D(7,8,21,6)	80.001
R(11,12)	1.089	A(8,7,22)	117.894	D(2,11,13,15)	179.998
R(11,13)	1.434	A(9,7,22)	117.141	D(12,11,13,14)	179.997
R(13,14)	1.090	A(11,13,15)	124.129	D(13,15,17,18)	40.002
R(13,15)	1.362	A(13,15,17)	124.129	D(16,15,17,6)	59.003

Table 2: Optimized geometric parameters of compound 2

Bond Length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
R(1,3)	1.346	A(3,1,17)	116.819	D(17,1,3,20)	179.999
R(1,17)	1.778	A(3,1,24)	127.892	D(24,1,17,2)	179.997
R(1,24)	1.503	A(17,1,24)	115.289	D(3,1,24,26)	120.280
R(2,8)	1.359	A(8,2,16)	124.721	D(17,1,24,25)	179.985
R(2,16)	1.777	A(8,2,17)	122.662	D(17,1,24,27)	59.691
R(2,17)	1.776	A(16,2,17)	112.618	D(8,2,17,1)	180.001
R(3,16)	1.780	A(1,3,16)	117.014	D(1,3,20,21)	120.311
R(3,20)	1.503	A(1,3,20)	127.926	D(16,3,20,22)	59.695
R(4,14)	1.358	A(16,3,20)	115.060	D(14,4,18,6)	179.998
R(5,33)	1.500	A(5,6,7)	124.006	D(33,5,6,18)	179.996
R(6,7)	1.084	A(7,6,18)	117.033	D(33,5,19,4)	180.004
R(8,10)	1.434	A(2,8,10)	125.817	D(6,5,33,34)	120.133
R(10,12)	1.362	A(10,12,14)	124.141	D(19,5,33,35)	59.991
R(12,14)	1.435	A(13,12,14)	117.740	D(7,6,18,4)	179.996
R(14,15)	1.089	A(4,14,12)	sss	D(2,8,10,12)	179.997

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

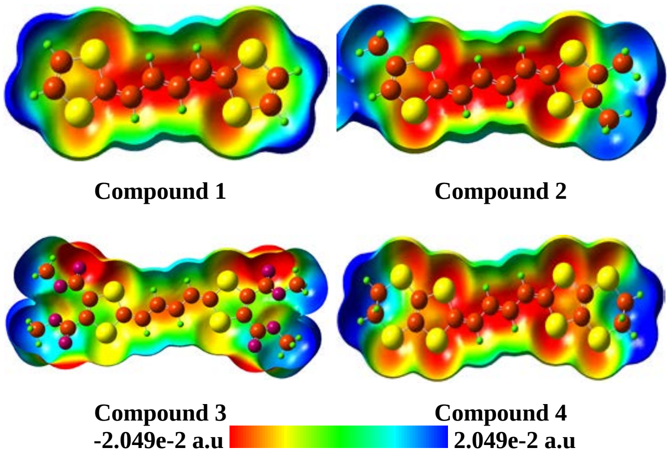
Bond Length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
R(1,3)	1.354	A(3,1,16)	117.344	D(16,1,3,21)	174.711
R(1,16)	1.762	A(3,1,22)	129.051	D(22,1,3,15)	175.100
R(1,22)	1.492	A(16,1,22)	113.589	D(3,1,16,2)	92.461
R(2,7)	1.357	A(7,2,15)	124.319	D(3,1,22,26)	149.185
R(2,15)	1.783	A(7,2,16)	122.155	D(16,1,22,27)	143.605
R(2,16)	1.780	A(15,2,16)	113.526	D(15,2,7,8)	179.875
R(3,15)	1.766	A(1,3,15)	117.486	D(16,2,7,9)	179.852
R(3,21)	1.490	A(13,4,17)	122.155	D(7,2,15,3)	179.453
R(5,20)	1.490	A(17,6,19)	113.589	D(7,2,16,1)	179.207
R(6,19)	1.492	A(2,7,8)	117.242	D(1,3,21,23)	152.473
R(7,8)	1.089	A(2,7,9)	125.737	D(15,3,21,28)	146.624
R(7,9)	1.435	A(8,7,9)	117.020	D(6,5,20,30)	31.458
R(20,30)	1.343	A(5,20,25)	122.734	D(18,5,20,25)	29.447
R(21,23)	1.214	A(5,20,30)	112.712	D(19,6,17,4)	176.187
R(30,43)	1.440	A(25,20,30)	124.427	D(5,6,19,29)	34.847

Table 4: Optimized geometric parameters of compound 4

Bond Length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
R(1,3)	1.347	A(3,1,16)	117.100	D(16,1,3,19)	179.031
R(1,16)	1.778	A(3,1,20)	128.845	D(20,1,3,15)	179.094
R(1,20)	1.776	A(16,1,20)	114.053	D(3,1,20,26)	14.633
R(2,7)	1.358	A(7,2,15)	124.301	D(15,2,7,8)	179.839
R(2,15)	1.779	A(7,2,16)	122.264	D(16,2,7,9)	179.791
R(2,16)	1.777	A(15,2,16)	113.435	D(7,2,16,1)	179.800
R(3,15)	1.780	A(1,3,15)	117.304	D(1,3,19,23)	14.768
R(3,19)	1.776	A(1,3,19)	128.831	D(13,4,18,5)	179.876
R(4,13)	1.358	A(15,3,19)	113.862	D(22,5,18,4)	179.335
R(4,17)	1.777	A(8,7,9)	117.021	D(21,6,17,4)	179.139
R(11,13)	1.434	A(7,9,10)	117.781	D(17,6,21,29)	165.939
R(13,14)	1.089	A(4,13,11)	125.788	D(7,9,11,13)	179.997
R(19,23)	1.833	A(4,13,14)	117.191	D(9,11,13,4)	179.925
R(20,26)	1.833	A(19,23,24)	103.902	D(12,11,13,14)	179.972
R(29,30)	1.092	A(25,23,26)	111.053	D(3,19,23,25)	75.319

3.2. Molecular Electrostatic Potential (MEP)

MEP is expounded to the ED and is a very helpful descriptor in understanding sites for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions [20, 21]. The electrostatic potential V(r), additionally compatible for analyzing processes, supported the ‘‘recognition’’ of one molecule by another, as in drug-receptor, and enzyme–substrate interactions and as a result it is through their potentials that the two species first ‘‘see’’ each other [22, 23]. To predict reactive sites of electrophilic and nucleophilic attacks for the investigated molecules, MEP at the B3LYP/6-31G (d,p) optimized geometries were calculated. The negative (red and yellow) regions of MEP were associated with electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity as presented in Fig 2.



Compound 1 **Compound 2**

Compound 3 **Compound 4**

Fig 2: Molecular electrostatic potential surface of Polyene TTF analogues 1-4

As seen from the figure **2** that, in all molecules, the regions exhibiting the negative electrostatic potential are localized near the conjugated chain of alkenes and in the carbonyl of 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 orbitals in molecule is the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These orbitals determine the way the molecule interacts with other species. 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 also termed as soft molecule [24]. The low values of frontier orbital gap in compound 3 make it more reactive and less stable. The energy gap between various occupied and unoccupied molecular orbitals of Polyene TTF analogues 1-4 calculated at B3LYP/6-31G (d,p) level is given in Table 5. The HOMO and LUMO orbitals of compound 3 were visualized in Fig 3.

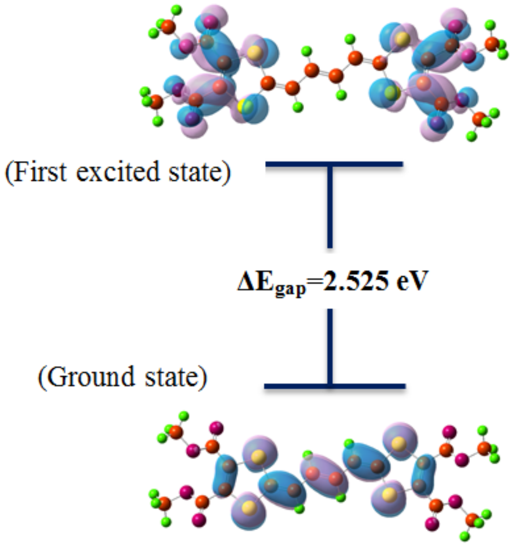


Fig 3: HOMO-LUMO Structure with the energy level diagram of compound 3

3.4. Global reactivity descriptors

The chemical reactivity of the molecular systems has been determined by the conceptual density functional theory [25]. Electronegativity (χ), chemical potential (μ), global hardness (η), global softness (S) and electrophilicity index (ω) are global reactivity descriptors, highly successful in predicting global reactivity trends. On the basis of Koopmans's theorem [26], global reactivity descriptors are calculated using the energies of frontier molecular orbitals ε_{HOMO}, ε_{LUMO} as

$$\chi = -1/2\left(\varepsilon_{LUMO} + \varepsilon_{HOMO}\right)$$

$$\mu = -\chi = 1/2\left(\varepsilon_{LUMO} + \varepsilon_{HOMO}\right)$$

$$\eta = 1/2\left(\varepsilon_{LUMO} - \varepsilon_{HOMO}\right)$$

$$S = 1/2\eta$$

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

The energies of frontier molecular orbitals (ε_{HOMO}, ε_{LUMO}) and global reactivity descriptors for Polyene TTF analogues 1-4 are listed in Table 5. The frontier orbital gap helps to characterize molecular electrical transport properties [27, 28], the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is generally associated with a high chemical reactivity and low kinetic stability.

Table 5: Quantum chemical descriptors of Polyene TTF analogues 1-4

Parameters	**Compound 1**	**Compound 2**	**Compound 3**	**Compound 4**
E_{HOMO} (eV)	-4.348	-4.190	-4.663	-4.342
E_{LUMO} (eV)	-1.199	-1.048	-2.139	-1.248
ΔE_{gap} (eV)	3.149	3.142	2.525	3.094
IE (eV)	4.348	4.190	4.663	4.342
A (eV)	1.199	1.048	2.139	1.248
μ (eV)	-2.774	-2.619	-3.401	-2.795
χ (eV)	2.774	2.619	3.401	2.795
η (eV)	1.575	1.571	1.262	1.547
S (eV)	0.318	0.318	0.396	0.323
ω (eV)	2.443	2.183	4.581	2.524

As presented in table 5, the compound which have the lowest energetic gap is the compound 3 (ΔE_{gap} = 2.525 eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound 1 (ΔE_{gap} = 3.149 eV).The compound that has the highest HOMO energy is the compound 2 (E_{HOMO}= -4.190 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} = -2.139 eV) which signifies that it can be the best electron acceptor. The two properties like I (potential ionization) and A (affinity) are so important, the determination of these two properties allow us to calculate the absolute electronegativity (χ) and the absolute hardness (η). These two parameters are related to the one-electron orbital energies of the HOMO and LUMO respectively. Compound 2 has lowest value of the potential ionization (I = 4.190 eV), so that will be the better electron donor. Compound 3 has the largest value of the affinity (A = 2.139 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 = 1.262 eV, S = 0.396 eV) is lesser (greater) among all the molecules. Thus, compound 3 is found to be more reactive than all the compounds. Compound 3 possesses higher electronegativity value (χ = 3.401 eV) than all compounds so; it is the best electron acceptor. The value of ω for compound 3 (ω = 4.581 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

To describe the chemical reactivity of an atom in a molecule, it is necessary to obtain the values of condensed Fukui function (FF) around each atomic site. Thus, for an atom k in a molecule, three kinds of condensed FF, namely, f_k^+, f_k^- and f_k^0 can be used to describe the electrophilic, nucleophilic and radical reactivity, respectively, which are defined by Eqs. (1)–(3) in a finite difference approximation [29]. The higher FF values indicate more reactivity of this atom than other ones.

For nucleophilic attack

For nucleophilic attack $f_k^{+}(r)=[\rho_{N+1}(r)-\rho_N(r)]=[q_k(N+1)-q_k(N)]$ (1)

For electrophilic attack $f_k^{-}(r)=[\rho_{N-1}(r)-\rho_N(r)]=[q_k(N)-q_k(N-1)]$ (2)

For radical attack $f_k^{0}(r)=1/2[\rho_{N+1}(r)-\rho_{N-1}(r)]=1/2[q_k(N+1)-q_k(N-1)]$ (3)

where ρ is the electron density of atom *k* in the molecule and *q* is the gross charge of atom *k* in the molecule.

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

Compound 1					Compound 2				
Atom	20 S	21 S	13 C	15 C	Atom	18 S	17 S	10 C	12 C
f^+	0.106	0.106	0.092	0.092	f^+	0.099	0.097	0.091	0.090
Atom	2 C	6 C	1 C	8 C	Atom	1 C	5 C	3 C	28 C
f^-	-0.064	-0.064	-0.100	-0.100	f^-	0.012	0.009	0.005	-0.005
Atom	2 C	6 C	1 C	8 C	Atom	5 C	1 C	3 C	28 C
f^0	-0.002	-0.002	-0.026	-0.026	f^0	0.006	0.006	0.004	0.000

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

Compound 3					Compound 4				
Atom	16 S	17 S	26 O	24 O	Atom	9 C	11 C	16 S	17 S
f^+	0.069	0.069	0.068	0.068	f^+	0.089	0.089	0.088	0.088
Atom	4 C	2 C	27 O	29 O	Atom	6 C	1 C	3 C	5 C
f^-	0.003	0.003	-0.009	-0.009	f^-	0.013	0.013	0.006	0.006
Atom	6 C	1 C	5 C	3 C	Atom	6 C	1 C	3 C	5 C
f^0	0.013	0.013	0.012	0.012	f^0	0.004	0.004	0.002	0.002

From the tables 6-7, the parameters of local reactivity descriptors show that 20S, 18S, 16S and 9C are the more reactive sites in compounds 1, 2, 3 and 4 respectively for nucleophilic attacks. The more reactive sites in radical attacks are 2C, 5C, for compounds 1, 2 respectively and 6C for the both compounds 3 and 4. The more reactive sites for electrophilic attacks are 2C, 1C, 4C and 6C for compounds 1, 2, 3 and 4 respectively.

3.6. Natural Bond Orbital Analysis (NBO)

NBOs give the most convenient 'natural Lewis structure' picture of ψ, because all orbitals are mathematically chosen in such a way to include the highest possible percentage of the electron density (ED). A useful aspect of the NBOs is that it provides an accurate method for studying intramolecular bonding and interaction among bonds, and also gives an efficient basis for investigating charge transfer or conjugative interaction in various molecular systems [30]. The large value of second order stabilization energy($E^{(2)}$) shows that the interaction is more intense 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 delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydgberg) non-Lewis NBO orbitals correspond to a stabilizing donor–acceptor interaction. 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), the strength of various types of interactions or stabilization energy ($E^{(2)}$) associated with electron delocalization between donor and acceptor is estimated by the second order energy lowering equation and it is described below [31, 32].

$$E^{(2)} = -q_i \frac{F^2(i, j)}{\varepsilon_j - \varepsilon_i}$$

Where q_i is the population of donor orbital or 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 between i and j NBO orbitals. Various intramolecular conjugative and hyperconjugative interactions are generated due to the various types of ''orbital–orbital'', ''loan pair–orbital'' overlap.

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) S20	1.75832	π*(C1-C3)	0.21898	22.53	0.25	0.068
LP (2) S21	1.75832	π*(C7-C8)	0.21898	22.53	0.25	0.068
LP (2) S19	1.76241	π*(C1-C3)	0.21898	22.36	0.25	0.067
LP (2) S22	1.76241	π*(C7-C8)	0.21898	22.36	0.25	0.067
LP (2) S19	1.76241	π*(C2-C11)	0.33044	19.18	0.27	0.066
LP (2) S22	1.76241	π*(C6-C17)	0.33044	19.18	0.27	0.066
π(C13-C15)	1.82760	π*(C2-C11)	0.33044	18.95	0.27	0.067
π(C13-C15)	1.82760	π*(C6-C17)	0.33044	18.95	0.27	0.067
LP (2) S20	1.75832	π*(C2-C11)	0.33044	17.82	0.27	0.064
LP (2) S21	1.75832	π*(C6-C17)	0.33044	17.82	0.27	0.064
π(C2-C11)	1.89629	π*(C13-C15)	0.22178	13.40	0.33	0.062
π(C6-C17)	1.89629	π*(C13-C15)	0.22178	13.40	0.33	0.062
σ(C11-H12)	1.96640	σ*(C2-S19)	0.04603	7.93	0.68	0.066
σ (C17-H18)	1.96640	σ*(C6-S22)	0.04603	7.93	0.68	0.066
σ(C1-H4)	1.97595	σ*(C3-S19)	0.01874	5.35	0.76	0.057
σ(C8-H10)	1.97595	σ*(C7-S22)	0.01874	5.35	0.76	0.057
σ(C3-H5)	1.97608	σ*(C1-S20)	0.01736	5.30	0.76	0.057
σ(C7-H9)	1.97608	σ*(C8-S21)	0.01736	5.30	0.76	0.057
σ(C13-H14)	1.97478	σ*(C15-H16)	0.01745	4.34	0.98	0.058
σ(C15-H16)	1.97478	σ*(C13-H14)	0.01745	4.34	0.98	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) S19	1.77240	π*(C5-C6)	0.22970	21.86	0.26	0.068
LP (2) S18	1.76391	π*(C5-C6)	0.22970	21.44	0.26	0.067
LP (2) S17	1.77167	π*(C1-C3)	0.23710	20.49	0.27	0.066
LP (2) S16	1.77551	π*(C1-C3)	0.23710	20.27	0.27	0.066
LP (2) S16	1.77551	π*(C2-C8)	0.33095	19.75	0.27	0.067
LP (2) S19	1.77240	π*(C4-C14)	0.32997	19.26	0.27	0.066
π(C10-C12)	1.82839	π*(C4-C14)	0.32997	18.96	0.27	0.067
π(C10-C12)	1.82839	π*(C2-C8)	0.33095	18.73	0.27	0.066
LP (2) S17	1.77167	π*(C2-C8)	0.33095	18.37	0.27	0.065
LP (2) S18	1.76391	π*(C4-C14)	0.32997	17.93	0.27	0.064
π(C2-C8)	1.89400	π*(C10-C12)	0.22291	13.6	0.33	0.062
π(C4-C14)	1.89664	π*(C10-C12)	0.22291	13.36	0.33	0.061
σ(C14-H15)	1.96640	σ*(C4-S19)	0.04298	7.96	0.68	0.066
σ(C8-H9)	1.96698	σ*(C2-S16)	0.04275	7.89	0.69	0.066
σ(C6-H7)	1.97410	σ*(C5-S19)	0.03222	6.02	0.75	0.060
σ(C33-H36)	1.98363	σ*(C5-S19)	0.03222	5.42	0.71	0.056
σ(C1-S17)	1.97331	σ*(C3-C20)	0.01859	5.23	1.04	0.066
σ(C3-S16)	1.97298	σ*(C1-C24)	0.01852	5.21	1.04	0.066
σ(C1-C24)	1.97901	σ*(C1-C3)	0.02996	5.15	1.29	0.073

σ(C3-C20)	1.97911	σ*(C1-C3)	0.02996	5.13	1.29	0.073

Table 10: Second order perturbation theory analysis of Fock matrix on NBO of compound 3

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F(i.j) a.u
LP (2) O30	1.78241	π*(C20-O25)	0.25961	49.42	0.33	0.115
LP (2) O30	1.78241	π*(C20-O25)	0.25961	49.42	0.33	0.115
LP (2) O27	1.78085	π*(C22-O26)	0.25588	49.40	0.33	0.115
LP (2) O29	1.78085	π*(C19-O24)	0.25588	49.40	0.33	0.115
LP (2) O23	1.84172	σ*(C21-O28)	0.10190	32.69	0.64	0.131
LP (2) O25	1.84172	σ*(C20-O30)	0.10190	32.69	0.64	0.131
LP (2) O24	1.84139	σ*(C19-O29)	0.10203	32.63	0.64	0.131
LP (2) O26	1.84139	σ*(C22-O27)	0.10203	32.63	0.64	0.131
LP (2) S16	1.72868	π*(C1-C3)	0.28654	23.50	0.25	0.069
LP (2) S17	1.72868	π*(C5-C6)	0.28654	23.50	0.25	0.069
LP (2) S15	1.73833	π*(C1-C3)	0.28654	22.83	0.25	0.068
LP (2) S18	1.73833	π*(C5-C6)	0.28654	22.83	0.25	0.068
LP (2) O24	1.84139	σ*(C6-C19)	0.07236	20.12	0.66	0.106
LP (2) O26	1.84139	σ*(C1-C22)	0.07236	20.12	0.66	0.106
LP (2) O23	1.84172	σ*(C3-C21)	0.07178	19.95	0.67	0.105
LP (2) O25	1.84172	σ*(C5-C20)	0.07178	19.95	0.67	0.105
LP (2) S15	1.73833	π*(C2-C7)	0.32461	19.67	0.27	0.066
LP (2) S18	1.73833	π*(C4-C13)	0.32461	19.67	0.27	0.066
π(C9-C11)	1.82646	π*(C2-C7)	0.32461	19.07	0.27	0.067
π(C9-C11)	1.82646	π*(C4-C13)	0.32461	19.07	0.27	0.067

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) S16	1.77596	π*(C1-C3)	0.37471	20.45	0.24	0.064
LP (2) S17	1.77596	π*(C5-C6)	0.37471	20.45	0.24	0.064
LP (2) S15	1.78019	π*(C1-C3)	0.37471	20.22	0.23	0.064
LP (2) S18	1.78019	π*(C5-C6)	0.37471	20.22	0.23	0.064
LP (2) S22	1.86890	π*(C5-C6)	0.37471	20.17	0.24	0.066
LP (2) S19	1.86891	π*(C1-C3)	0.37471	20.16	0.24	0.066
LP (2) S20	1.86933	π*(C1-C3)	0.37471	20.14	0.24	0.066
LP (2) S21	1.86934	π*(C5-C6)	0.37471	20.13	0.24	0.066
LP (2) S15	1.78019	π*(C2-C7)	0.32979	19.37	0.27	0.067
LP (2) S18	1.78019	π*(C4-C13)	0.32979	19.37	0.27	0.067
π(C9-C11)	1.82705	π*(C2-C7)	0.32979	18.99	0.27	0.067
π(C9-C11)	1.82705	π*(C4-C13)	0.32979	18.99	0.27	0.067
LP (2) S16	1.77596	π*(C2-C7)	0.32979	18.02	0.27	0.064
LP (2) S17	1.77596	π*(C4-C13)	0.32979	18.02	0.27	0.064
π(C2-C7)	1.89605	π*(C9-C11)	0.22097	13.38	0.33	0.062
π(C4-C13)	1.89605	π*(C9-C11)	0.22097	13.38	0.33	0.062
σ(C7-H8)	1.96621	σ*(C2-S15)	0.04460	7.95	0.68	0.066
σ(C13-H14)	1.96621	σ*(C4-S18)	0.04459	7.95	0.68	0.066
σ(C1-S16)	1.97037	σ*(C3-S19)	0.03117	5.96	0.83	0.063
σ(C6-S17)	1.97037	σ*(C5-S22)	0.03117	5.96	0.83	0.063

The intra molecular interaction for the title compounds is formed by the orbital overlap between: π(C13-C15) and π*(C2-C11) for compound 1, π(C10-C12) and π*(C4-C14) for compound 2, π(C9-C11) and π*(C2-C7) for compound 3 and σ(C7-S14) and σ*(C9-O28) for compound 4 respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of π(C13-C15) to π*(C2-C11) for compound 1, π(C10-C12) to π*(C4-C14) for compound 2, π(C9-C11) to π*(C2-C7) for compound 3 and π(C9-C11) to π*(C2-C7) for compound 4 lead to highest stabilization of 18.95, 18.96, 19.07 and 18.99 kJ mol^{-1} respectively. In case of LP (2) S20 orbital to the π*(C1-C3) for compound 1, LP (2) S19 orbital to π*(C5-C6) for compound 2, LP (2) O30 orbital to π*(C20-O25) for compound 3, LP (2) S16 orbital to π*(C1-C3) for compound 4 respectively, show the stabilization energy of 22.53, 21.86, 49.42 and 20.45 kJ mol^{-1} respectively.

3.7. Nonlinear Optical Properties (NLO)

In order to investigate the relationships among molecular structures and non-linear optic properties (NLO), the polarizabilities and first order hyperpolarizabilities of the MPP compound was calculated using DFT/B3LYP method with 6-31G(d,p) basis set, based on the finite-field approach. The polarizability and hyperpolarizability tensors (α_{xx}, α_{xy}, α_{yy},α_{xz}, α_{yz}, α_{zz} and β_{xxx}, β_{xxy}, β_{xyy}, β_{yyy}, β_{xxz}, β_{xyz}, β_{yyz}, β_{xzz}, β_{yzz}, β_{zzz}) can be obtained by a frequency job output file of Gaussian. The mean polarizability (α_{tot}), anisotropy of polarizability (Δα) and the average value of the first order hyperpolarizability (β_{tot}) can be calculated using the equations.

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

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

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

In Table 12, the calculated parameters described above and electronic dipole moment {μ_i (i = x, y, z) and total dipole moment μ} for Polyene TTF analogues 1-4 are listed. The total dipole moment can be calculated using the following equation.

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

It is well known that the higher values of dipole moment, molecular polarizability, and first order hyperpolarizability are important for more active NLO properties. The first order hyperpolarizability (β_{tot}) and the component of hyperpolarizability β_x, β_y and β_z of MPP along with related properties (μ, α_{tot} and $\Delta\alpha$) are reported in Table 12.

Table 12: The dipole moments μ (D), polarizability α, the average polarizability α (esu), the anisotropy of the polarizability Δα (esu), and the first hyperpolarizability β (esu) of Polyene TTF analogues 1-4 calculated by B3LYP/6-31G(d,p) method

Parameters	compound 1	compound 2	compound 3	compound 4
β_{xxx}	0.0000	-46.2570	-0.0412	0.0080
B_{yyy}	0.0000	-0.2427	-0.0220	0.0077
B_{zzz}	0.0000	0.0509	0.0070	0.0675
B_{xyy}	0.0000	-4.6425	0.0007	-0.0243
B_{xxy}	0.0000	-5.3195	-0.0107	0.0030
B_{xxz}	0.0000	-0.0932	0.0571	0.7159
B_{xzz}	0.0000	-1.1104	0.0044	0.0162
B_{yzz}	0.0000	-1.0161	0.0010	-0.0155
B_{yyz}	0.0000	-0.0490	0.0019	-0.0206
B_{xyz}	0.0000	-0.0209	-0.0131	-0.0131
B_{tot}(esu)x10^{-33}	0.0000	47.8427	0.0886	0.7628
μ_x	0.0000	-0.3537	-0.0003	-0.0001
μ_y	0.0000	-0.2275	-0.0009	-0.0001
μ_z	0.0000	-0.0007	0.0007	0.0059
μ_{tot}(D)	0.0000	0.4205	0.0012	0.0059
α_{xx}	-70.9576	-84.7516	-114.5164	-93.0679
α_{yy}	-104.7648	-132.6944	-199.0222	-190.2551
α_{zz}	-117.2456	-143.7289	-208.3095	-191.2968
α_{xy}	-6.0959	-7.5733	-10.7042	-12.8984
α_{xz}	-0.0006	0.0149	-6.5034	-0.4656
α_{yz}	0.0003	-0.0029	-19.1026	-0.9140
α(esu)x10^{-24}	42.8032	55.8691	97.8655	100.2493
$\Delta\alpha$(esu)x10^{-24}	6.3434	8.2798	14.5036	14.8569

Since the values of the polarizabilities ($\Delta\alpha$) and the hyperpolarizabilities (β_{tot}) of the GAUSSIAN 09 output are obtained in atomic units (a.u.), the calculated values have been converted into electrostatic units (e.s.u.) (for α; 1 a.u = 0.1482 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) for the title compounds were found to be 0.0000, 0.4205, 0.0012 and 0.0059 D respectively, which are approximately zero times than to the value for urea ($\mu = 1.3732$ D). Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore, it has been used frequently as a threshold value for comparative purposes. The calculated values of polarizability are 42.8032 x 10^{-24}, 55.8691 x 10^{-24}, 97.8655 x 10^{-24} and 100.2493 x 10^{-24} esu respectively; the values of anisotropy of the polarizability are 6.3434, 8.2798, 14.5036 and 14.8569 esu, respectively. The magnitude of the molecular hyperpolarizability (β) is one of important key factors in a NLO system. The DFT/6-31 G (d,p) calculated first hyperpolarizability value (β) of Polyene TTF analogues molecules are equal to 0.0000 x 10^{-33}, 47.8427 x 10^{-33}, 0.0886 x 10^{-33} and 0.7628 x 10^{-33} esu. The first hyperpolarizability of title molecules is inferior 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 Polyene TTF analogues 1-4 might have not the NLO applications.

4. Conclusion

Theoretical studies, based on density functional theory, provided valuable information on the geometry, the stability, the electrochemistry, the reactivity and the selectivity of Polyene TTF analogues compounds. NBO analysis was made and it is indicating the intra molecular charge transfer between the bonding and anti-bonding orbitals. The calculated HOMO and LUMO energy gap are confirm the presence of charge transfer within the molecules. The calculated HOMO and LUMO energies can be used to semi quantitatively estimate the ionization potential, electron affinity, electro negativity, electro philicity index, hardness, and chemical potential. The predicted MESP contour map shows the negative regions the conjugated chain of alkenes and in the carbonyl of ester function; they are subjected to the electrophilic attack of these compounds.

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6. References

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