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Structural Studies, NBO Analysis and Reactivity Descriptors of π-Extended Tetrathiafulvalene (exTTF) Connected to Thiophene Derivative

Tahar Abbaz[1*], Amel Bendjeddou[1] and Didier Villemin[2]

[1]Laboratory of Aquatic and Terrestrial Ecosystems, Organic and Bioorganic Chemistry Group, University of Mohamed-Cherif Messaadia, Souk Ahras, 41000, Algeria.
[2]Laboratory of Molecular and Thio-Organic Chemistry, UMR CNRS 6507, INC3M, FR 3038, Labex EMC3, Ensicaen & University of Caen, Caen 14050, France.

Authors' contributions

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

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ABSTRACT

We report here a quantum chemical study of π-extended tetrathiafulvalene (exTTF) connected to thiophene derivative 1-4 performed at DFT/B3LYP with 6-31G (d,p) basis set using Gaussian 09w program package. The optimized parameters (bond lengths, bond angles and dihedral angles) are determined in this investigation. The most reactive sites for electrophilic and nucleophilic attack are also predicted from the MEP analysis and the results show clearly that the regions reveal the negative electrostatic potential are localized in the nitro functional group while the regions presenting the positive potential are localized in the hydrogen atoms of alkyl and cycled groups. The possible electronic transitions are determined by HOMO–LUMO orbital shapes and their energies, although HOMO-1, HOMO are confined on the π-conjugated spacer of TTF core and delocalized over the part of thiophene derivative, and LUMO, LUMO+1 are confined the part of

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**Corresponding author: Email: tahar.abbaz@univ-soukahras.dz;*

thiophene derivative and delocalized on the π-conjugated spacer of TTF core which explained the charge transfer process in the molecular system. Global reactivity parameters of the studied molecules are also calculated it indicate that compound 2 is the more reactive. The natural bond orbital analysis indicates that the nonlinear optical activity of the molecules arises due to the $\pi \to \pi^*$ transitions. The predicted NLO properties of the title compounds are much greater than the ones of urea, which means that are an attractive object for future studies of nonlinear optics.

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

1. INTRODUCTION

The extended TTFs, in which a π-conjugated spacer is incorporated between the two dithiole rings, exhibit enhanced π-donor properties and stabilization of the dication state [1]. Extended tetrathiafulvalenes have attracted much attention due to their low oxidation potentials when compared to simple tetrathiafulvalene (TTF) derivatives; in fact, the larger extension of the π-framework in the former allows not only the easy generation of the cation radical state, but also that of di- and higher polycationic states, due to the decreased on site Coulomb repulsions [2]. Tetrathiafulvalene (TTF) derivatives with extended π-electron conjugation are versatile building blocks in supramolecular and materials chemistry [3]. The π-extended TTF have recently received particular attention as a consequence of their potential interest in the preparation of materials with increased dimensionality [4], nonlinear optical properties or as small-gap semiconductors [5].

Density functional theory (DFT) has been widely used in literature because of its efficiency and accuracy with respect to the evaluation of a number of molecular properties [6-8]. DFT has proved to be extremely useful in treating electronic structure of molecules. B3LYP is one of the most commonly used exchange-correlation energy functional, in which Becke three parameter hybrid functional combined [9] with the Lee-Yang-Parr correlation functional [10].

The present paper deals with a complete description on the molecular geometry, electronic features of π-extended tetrathiafulvalene (exTTF) connected to thiophene derivative 1-4 reported in literature [11] by using DFT/B3LYP method and 6-31G (d,p) basis set. These calculations provide insight into molecular parameters, the natural bond orbital (NBO) and molecular electrostatic potential (MESP). The density plots over the highest occupied molecular orbital (LUMO) energy surface directly identified the donor and acceptor atom in the title molecules and it also provided information about the charge transfer within the molecules. The molecular quantities as the chemical hardness (η), softness (*S*) and electrophilicity (ω), electronegativity (χ) are calculated. The NLO characteristics were also outlined.

2. MATERIALS AND METHODS

All computational calculations have been performed on personal computer using the Gaussian 09W program packages developed by Frisch and coworkers [12]. The Becke's three parameter hybrid functional using the LYP correlation functional (B3LYP), one of the most robust functional of the hybrid family, was herein used for all the calculations, with 6.31G (d,p) basis set. Gaussian output files were visualized by means of GAUSSIAN VIEW 05 software.

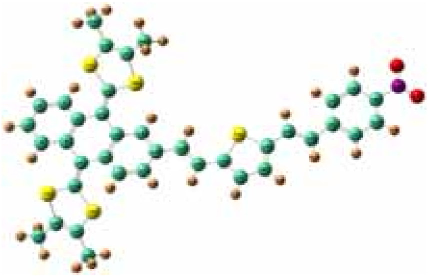
3. RESULTS AND DISCUSSION

3.1 Molecular Geometry

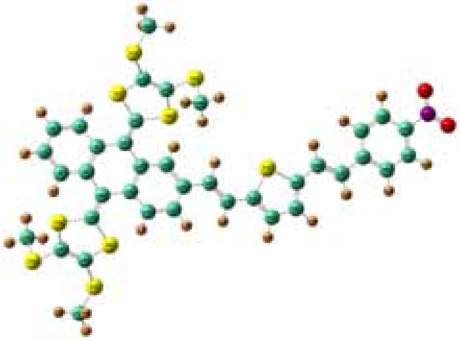
Among the different compounds (exTTF) connected to thiophene derivative, we have selected four compounds 1-4 which have the same structure and main chain and differ only in the group directly liked in the TTF core, those molecules have a potential interest in the preparation of compounds with nonlinear optical properties and widely used as semiconductors. The molecular structures of (exTTF)-thiophene 1-4 along with numbering of atoms are shown in Fig. 1.

The optimized geometrical parameters (bond lengths, bond angles and dihedral angles) obtained by the DFT method and B3LYP/6-31G (d,p) basis set are presented in Tables 1-4.

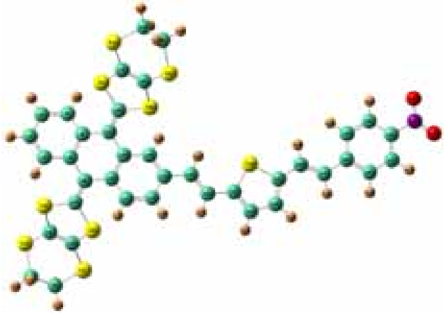
Compound **1**



Compound **2**



Compound **3**



Compound **4**

Fig. 1. Optimized molecular structure of (exTTF)-thiophene 1-4

Table 1. Optimized geometric parameters of compound 1

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.395	A(2,1,6)	119.819	D(6,1,2,8)	176.307
R(1,6)	1.393	A(2,1,7)	119.740	D(7,1,6,5)	178.405
R(1,7)	1.086	A(1,2,8)	119.190	D(1,2,3,20)	178.767
R(3,20)	1.482	A(3,2,8)	119.601	D(2,3,4,21)	177.450
R(14,15)	1.397	A(2,3,20)	123.211	D(3,4,5,9)	176.370
R(15,21)	1.481	A(4,3,20)	117.745	D(5,4,21,15)	140.409
R(21,27)	1.365	A(3,4,5)	119.033	D(16,11,12,18)	179.437
R(27,34)	1.792	A(4,5,9)	119.559	D(17,11,16,15)	176.364
R(28,29)	1.336	A(6,5,9)	119.234	D(11,12,13,36)	178.710
R(28,30)	1.083	A(1,6,10)	120.426	D(12,13,14,19)	176.422
R(28,34)	1.759	A(5,6,10)	119.762	D(14,15,16,20)	177.429
R(36,37)	1.354	A(12,11,16)	121.660	D(11,16,20,3)	140.872
R(37,56)	1.441	A(12,11,17)	118.802	D(15,16,20,22)	139.458
R(54,55)	1.409	A(11,12,13)	120.733	D(3,20,22,32)	175.392
R(56,57)	1.752	A(15,14,19)	119.256	D(20,22,33,24)	168.295

Table 2. Optimized geometric parameters of compound 2

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.394	A(2,1,6)	119.216	D(6,1,2,8)	178.989
R(15,16)	1.428	A(1,2,8)	118.476	D(7,1,2,3)	179.667
R(21,25)	1.383	A(2,3,20)	122.415	D(2,1,6,10)	174.478
R(25,30)	1.787	A(3,4,21)	119.713	D(7,1,6,5)	174.356
R(26,27)	1.343	A(1,6,5)	119.178	D(2,3,4,21)	160.619
R(26,60)	1.503	A(12,13,32)	124.130	D(20,3,4,5)	161.250
R(32,33)	1.355	A(13,14,15)	123.448	D(4,5,6,10)	179.732
R(32,34)	1.090	A(28,22,29)	110.158	D(9,5,6,1)	179.303

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(39,43)	1.397	A(26,27,31)	116.603	D(16,11,12,18)	178.943
R(43,46)	1.463	A(33,32,34)	118.146	D(12,11,16,20)	165.677
R(46,48)	1.233	A(32,33,52)	126.485	D(17,11,16,15)	166.155
R(49,53)	1.759	A(39,43,41)	121.422	D(32,13,14,15)	179.218
R(49,56)	1.441	A(47,46,48)	124.402	D(13,14,15,21)	166.611
R(56,57)	1.356	A(49,50,51)	113.661	D(19,14,15,16)	166.991
R(60,61)	1.096	A(27,64,65)	111.266	D(14,15,21,4)	160.543

Table 3. Optimized geometric parameters of compound 3

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.394	A(2,1,6)	119.254	D(6,1,2,8)	178.600
R(15,16)	1.427	A(12,11,17)	118.190	D(7,1,6,5)	174.373
R(21,25)	1.381	A(13,14,19)	117.566	D(20,3,4,5)	161.116
R(25,30)	1.791	A(16,20,22)	120.790	D(16,11,12,18)	178.799
R(26,27)	1.351	A(28,22,29)	109.931	D(17,11,16,15)	166.173
R(26,60)	1.771	A(23,24,29)	116.448	D(13,14,15,21)	166.462
R(32,33)	1.354	A(30,25,31)	109.943	D(11,16,20,3)	161.880
R(32,34)	1.090	A(27,26,60)	126.495	D(15,16,20,22)	144.263
R(39,43)	1.397	A(25,30,26)	97.329	D(20,22,29,24)	160.734
R(43,46)	1.463	A(32,33,52)	126.660	D(63,23,28,22)	171.191
R(46,48)	1.233	A(43,46,47)	117.786	D(60,26,30,25)	174.259
R(49,53)	1.758	A(33,52,51)	126.244	D(57,36,37,39)	179.793
R(49,56)	1.442	A(51,52,53)	109.790	D(36,38,41,45)	179.960
R(56,57)	1.356	A(57,56,58)	118.962	D(39,43,46,47)	179.988
R(60,64)	1.838	A(61,68,70)	105.712	D(56,49,50,51)	179.763

Table 4. Optimized geometric parameters of compound 4

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.394	A(2,1,6)	119.270	D(2,3,4,21)	160.430
R(15,16)	1.427	A(1,2,8)	118.481	D(20,3,4,5)	160.916
R(20,22)	1.384	A(2,3,20)	122.547	D(4,5,6,10)	179.675
R(25,30)	1.792	A(3,4,21)	119.590	D(9,5,6,1)	178.729
R(26,27)	1.345	A(6,5,9)	118.591	D(16,11,12,18)	178.813
R(26,60)	1.768	A(12,13,32)	123.956	D(12,11,16,20)	165.578
R(32,34)	1.090	A(13,14,15)	123.302	D(32,13,14,15)	179.281
R(33,52)	1.440	A(28,23,62)	114.451	D(13,14,15,21)	166.348
R(39,43)	1.397	A(26,27,31)	117.014	D(19,14,15,16)	166.329
R(46,47)	1.233	A(33,32,34)	118.302	D(62,23,28,22)	171.065
R(49,53)	1.758	A(32,33,52)	126.662	D(28,23,62,70)	159.924
R(49,56)	1.442	A(39,37,40)	118.585	D(60,26,30,25)	170.900
R(56,58)	1.088	A(47,46,48)	124.422	D(2,3,4,21)	160.430
R(61,67)	1.840	A(49,50,51)	113.626	D(20,3,4,5)	160.916
R(62,70)	1.856	A(60,64,65)	107.224	D(4,5,6,10)	179.675

3.2 Molecular Electrostatic Potential (MEP)

At any given point r (x, y, z) in the vicinity of a molecule, the molecular electrostatic potential, V(r) is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and a positive test charge (a proton) located at r [13]. The MEP is related to the electron density and a very useful descriptor for determining sites for electrophilic and nucleophilic attack as well as hydrogen-bonding interactions [14]. For the systems studied the molecular electrostatic potential values were calculated as described using the equation:

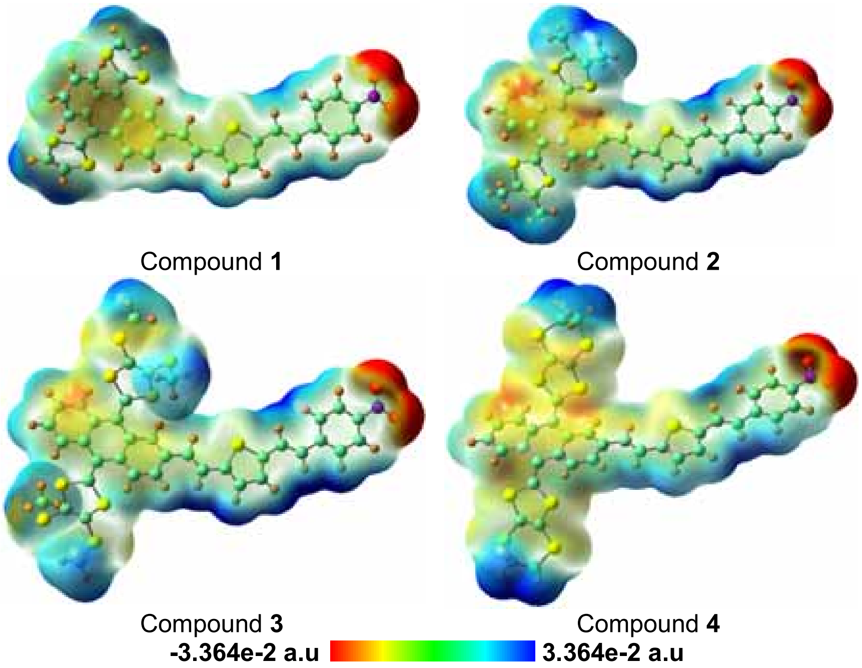
$$V(r) = \sum \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')}{|r' - r|} dr \qquad (1)$$

where the summation runs over all the nuclei A in the compound and polarization and reorganization effects are neglected. Z_A is the charge of the nucleus A, located at R_A and $\rho(r')$ is the electron density function of the molecule. The molecular electrostatic potential map for positive and negative sites of (exTTF)-thiophene 1-4 are computed by B3LYP/6-31G (d,p) basis set and shown in Fig. 2. The MEP is a plot of electrostatic potential mapped onto the constant electron density surface. Different values of the electrostatic potential are represented by different colors. Red represents the regions of the most negative electrostatic potential and blue represent the regions of the most positive electrostatic potential. Potential increases in the order red < orange < yellow < green < blue. The color grading of resulting surface simultaneously displays molecular size, shape and electrostatic potential value which are very useful in research of molecular structure with its physiochemical property relationship [15]. The importance of MESP lies within the undeniable fact that it at the same time displays the molecular size and form moreover because the electricity potential regions in terms of the color grading theme that is extremely helpful within the investigation of the foremost probable binding receptor site in conjunction with the size and form of the molecules.

As seen from the Fig. 2 that, in all molecules, the regions exhibiting the negative electrostatic potential are localized near the nitro functional group while the regions presenting the positive potential are localized vicinity of the hydrogen atoms of alkyl and cycled groups.

3.3 Frontier Molecular Orbitals (FMOs)

Knowledge of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and their properties such as their energy is very useful to gauge the chemical reactivity of the molecule. The ability of the molecule to donate an electron is associated with the HOMO and the characteristic of the LUMO is associated with the molecule's electron affinity. The HOMO and LUMO energies are very useful for physicists and chemists and are very important terms in quantum chemistry [16,17]. The electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the HOMO to the LUMO. Compound 2 have a small energy gap what explains the high reactivity comparing with the rest compounds, their energetic distributions of the HOMO-1,HOMO, LUMO and LUMO+1 orbitals computed at the B3LYP/6-31G (d,p) level are shown in Fig. 3.


Compound **1**

Compound **2**

Compound **3**

Compound **4**

Fig. 2. Molecular electrostatic potential surface of (exTTF)-thiophene 1-4

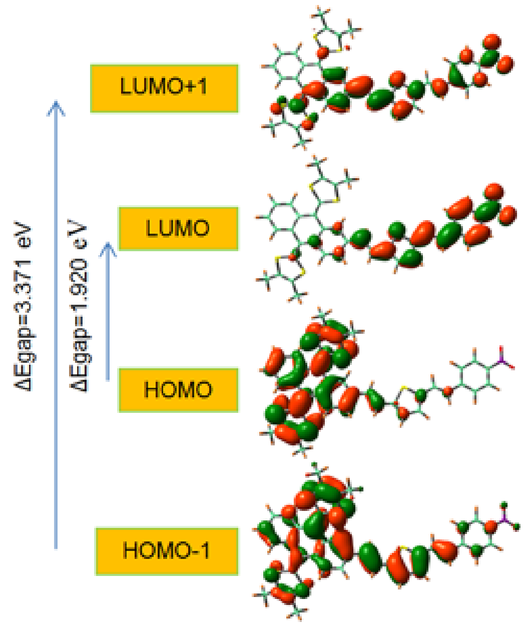


Fig. 3. HOMO-LUMO structure with the energy level diagram of compound 2

HOMO-1,HOMO are confined on the π-conjugated spacer of TTF core and delocalized over the part of thiophene derivative, while LUMO, LUMO+1 are confined the part of thiophene derivative and delocalized on the π-conjugated spacer of TTF core which gives charge transfer process in the molecular system.

3.4 Global Reactivity Descriptors

Based on the density functional theory (DFT) is possible to define ionization potential (*I*), electron affinity (*A*), chemical potential (μ), electronegativity (χ), global hardness (η), global softness (*S*) and global electrophilicity (ω) values can be described as followed [18]. In simple molecule orbital theory approaches, the HOMO energy (E_{HOMO}) is related to ionization potential (*I*) by Koop-man's theorem and LUMO energy (E_{LUMO}) is related to electron affinity (*A*) [19]. By the following relations:

$$\text{Ionization potential } (I) = -E_{HOMO} \tag{2}$$

$$\text{Electron affinity } (A) = -E_{LUMO} \tag{3}$$

Absolute electronegativity (χ) is related to average value of HOMO and LUMO energies defined by Mulliken [20].

$$\text{Electronegativity } (\chi) = \left(\frac{I+A}{2}\right) \tag{4}$$

The softness (*S*) is reciprocal of the hardness (η) [21]

$$\text{Global hardness } (\eta) = \left(\frac{I-A}{2}\right) \tag{5}$$

$$\text{Global softness } (S) = \frac{1}{\eta} \tag{6}$$

Parr et al. [22] defined global electrophilicity index (ω)

$$\text{Electrophilicity index } (\omega) = \frac{\mu^2}{2\eta} \tag{7}$$

where μ is the chemical potential takes the average value of ionization potential (*I*) and electron affinity (*A*) [23].

$$\text{Chemical potential } \mu = -\left(\frac{I+A}{2}\right) \tag{8}$$

The frontier molecular orbital analysis and global reactivity parameters of the studied molecules in B3LYP method with 6-31G (d,p) basis set are presented in Table 5.

Table 5. Quantum chemical descriptors of (exTTF)-thiophene 1-4

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
E_{HOMO} (eV)	-4.751	-4.523	-4.780	-4.700
E_{LUMO} (eV)	-2.654	-2.602	-2.661	-2.642
ΔE_{gap} (eV)	2.096	1.920	2.119	2.057
I (eV)	4.751	4.523	4.780	4.700
A (eV)	2.654	2.602	2.661	2.642
μ (eV)	-3.703	-3.563	-3.720	-3.671
χ (eV)	3.703	3.563	3.720	3.671
η (eV)	1.048	0.960	1.059	1.029
S (eV)	0.477	0.521	0.472	0.486
ω (eV)	6.540	6.610	6.531	6.551

As presented in Table 5, Compound 2 is characterized by the presence of the lowest energy gap (ΔEgap = 1,920 eV) and the highest HOMO energy (E_{HOMO} = -4,523 eV) which allows it to be the softest molecule and the best electron donor. On the other hand, compound 3 is characterized by the highest energy gap (ΔE_{gap} = 2.119 eV) and the lowest LUMO energy (E_{LUMO} = -2.661eV), which means that it can be the best acceptor of electrons. 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 (χ) and the absolute hardness (η). These two parameters are related to the one-electron orbital energies of the HOMO and LUMO respectively. The lowest value of the potential ionization (I=4.523 eV) for compound 2 confirm that is the better electron donor and the largest value of the affinity (A = 2.661 eV) for compound 3 confirm that is the better electron acceptor. The chemical reactivity varies with the structure of molecules. Chemical hardness (softness) value of compound 2 (η=0.960 eV, S= 0.521 eV) is lesser (greater) among all the molecules. Thus, compound 2 is found to be more reactive than all the compounds. Compound 3 possesses higher electronegativity value (χ=3.720 eV) than all compounds so; it is the best electron acceptor. The value of ω for compound 2 (ω=6.610 eV) indicates that it is the stronger electrophiles than all compounds. Compound 2 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. Therefore, we highlight that the relationship between the structure and the properties of the molecules is as follows, when the molecules contains π-conjugated electrons or a donor groups, they are characterized by higher reactivity.

3.5 Natural Bond Orbital Analysis (NBO)

Natural bond orbital analysis is a competent method to examine the charge transfer property, intra and intermolecular bonding nature of a molecular system. The electron delocalization can be described as a charge transfer from a Lewis valence orbital (donor) with a decrease in its occupancy, to a non-Lewis orbital (acceptor). Second order Fock matrix was carried out to evaluate the donor [i], acceptor [j] interactions in the NBO basis [24]. The stabilization energy $E^{(2)}$ associated with the electron delocalization between donor and acceptor (i → j) is estimated as [25,26]

$$E^{(2)} = \Delta E_{ij} = -q_i \frac{F^2(i,j)}{\varepsilon_i - \varepsilon_j} \tag{9}$$

where q_i is the donor orbital occupancy, ε_i and ε_j are the diagonal elements and F_{ij} is the Fock matrix element. If the $E^{(2)}$ value is larger, then we can observe the more intensive in the interaction between electron donor and electron acceptor. The larger interaction energy $E^{(2)}$ value, the more intensive is the interaction between electron donors and electron acceptors and bigger is that the tendency of electron donation from donor to acceptor. As a result, the larger is the extent of conjugation within the entire molecular system. The possible intensive interactions are calculated by B3LYP/6-31G (d,p) level and given in Tables 6-9.

Table 6. 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 (3) O51	1.45248	π*(N50-O52)	0.63981	161.82	0.14	0.138
π (C45-C47)	1.63825	π*(N50-O52)	0.63981	29.48	0.15	0.063
π (C40-C42)	1.58971	π*(C45-C47)	0.39306	25.00	0.27	0.074
LP (2) S33	1.75317	π*(C23-C24)	0.21696	22.35	0.26	0.068
LP (2) S35	1.75684	π*(C28-C29)	0.21638	22.29	0.26	0.068
LP (2) S32	1.75495	π*(C23-C24)	0.21696	22.26	0.26	0.068
LP (2) S34	1.75787	π*(C28-C29)	0.21638	22.21	0.26	0.068
LP (2) S57	1.65937	π*(C55-C56)	0.37292	21.44	0.27	0.068
π (C15-C16)	1.58858	π*(C13-C14)	0.39477	21.23	0.27	0.068
π (C13-C14)	1.61485	π*(C15-C16)	0.41632	20.90	0.28	0.069
LP (2) S57	1.65937	π*(C53-C54)	0.37378	20.47	0.27	0.066
π (C4-C5)	1.65011	π*(C1-C6)	0.33741	20.33	0.28	0.068
π (C45-C47)	1.63825	π*(C41-C43)	0.27214	20.31	0.29	0.071
π (C2-C3)	1.65112	π*(C1-C6)	0.33741	20.29	0.28	0.068

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F(i.j) a.u
π (C1-C6)	1.65795	π*(C2-C3)	0.36116	20.24	0.28	0.068
π (C1-C6)	1.65795	π*(C4-C5)	0.36071	20.22	0.28	0.068
π (C41-C43)	1.68322	π*(C40-C42)	0.38056	20.10	0.28	0.069
π (C15-C16)	1.58858	π*(C11-C12)	0.30895	19.40	0.28	0.067
π (C4-C5)	1.65011	π*(C2-C3)	0.36116	19.21	0.28	0.066
π (C2-C3)	1.65112	π*(C4-C5)	0.36071	19.18	0.28	0.066

Table 7. 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 (3) O48	1.45304	π*(N46-O47)	0.64092	161.48	0.14	0.138
π (C41-C43)	1.63823	π*(N46-O47)	0.64092	26.44	0.15	0.060
π (C36-C38)	1.58892	π*(C41-C43)	0.39462	25.12	0.27	0.074
π (C15-C16)	1.56408	π*(C13-C14)	0.41068	21.62	0.27	0.069
LP (2) S53	1.66142	π*(C51-C52)	0.37497	21.39	0.27	0.068
LP (2) S29	1.75109	π*(C23-C24)	0.23487	20.45	0.27	0.067
π (C4-C5)	1.64346	π*(C1-C6)	0.34244	20.40	0.28	0.068
π (C1-C6)	1.66136	π*(C2-C3)	0.37638	20.38	0.28	0.068
π (C41-C43)	1.63823	π*(C37-C39)	0.27214	20.33	0.29	0.071
LP (2) S28	1.75251	π*(C23-C24)	0.23487	20.33	0.27	0.067
LP (2) S31	1.75251	π*(C26-C27)	0.23401	20.33	0.27	0.067
LP (2) S53	1.66142	π*(C49-C50)	0.37589	20.31	0.27	0.066
LP (2) S30	1.75759	π*(C26-C27)	0.23401	20.29	0.27	0.067
π (C1-C6)	1.66136	π*(C4-C5)	0.37631	20.27	0.28	0.068
π (C2-C3)	1.64553	π*(C1-C6)	0.34244	20.25	0.28	0.068
π (C37-C39)	1.68450	π*(C36-C38)	0.38155	20.05	0.28	0.069
π (C13-C14)	1.61854	π*(C15-C16)	0.42803	19.52	0.28	0.066
π (C15-C16)	1.56408	π*(C11-C12)	0.31917	19.43	0.27	0.067
π (C13-C14)	1.61854	π*(C11-C12)	0.31917	18.61	0.28	0.066
LP (2) S29	1.75109	π*(C20-C22)	0.36539	18.43	0.27	0.065

Table 8. 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 (3) O47	1.45249	π*(N46-O48)	0.63984	161.82	0.14	0.138
π (C41-C43)	1.63819	π*(N46-O48)	0.63984	29.47	0.15	0.063
π (C36-C38)	1.58964	π*(C41-C43)	0.39316	25.00	0.27	0.074
LP (2) S28	1.73440	π*(C23-C24)	0.30583	22.91	0.24	0.066
LP (2) S31	1.73655	π*(C26-C27)	0.30560	22.89	0.24	0.066
LP (2) S29	1.73944	π*(C23-C24)	0.30583	21.91	0.24	0.065
LP (2) S30	1.74431	π*(C26-C27)	0.30560	21.65	0.24	0.065
LP (2) S53	1.65902	π*(C51-C52)	0.37381	21.42	0.27	0.068
π (C15-C16)	1.56689	π*(C13-C14)	0.40834	21.28	0.27	0.068
LP (2) S53	1.65902	π*(C49-C50)	0.37434	20.50	0.27	0.067
π (C1-C6)	1.65877	π*(C2-C3)	0.37561	20.47	0.28	0.068
π (C1-C6)	1.65877	π*(C4-C5)	0.37517	20.39	0.28	0.068
π (C41-C43)	1.63819	π*(C37-C39)	0.27210	20.31	0.29	0.071
π (C4-C5)	1.64411	π*(C1 -C6)	0.33686	20.17	0.28	0.068
π (C37-C39)	1.68310	π*(C36-C38)	0.38071	20.10	0.28	0.069
π (C2-C3)	1.64500	π*(C1-C6)	0.33686	20.07	0.28	0.068
π (C13-C14)	1.61674	π*(C15-C16)	0.42914	19.78	0.28	0.067
π (C15-C16)	1.56689	π*(C11-C12)	0.32000	19.47	0.27	0.067
π (C13-C14)	1.61674	π*(C11-C12)	0.32000	18.60	0.28	0.066
π (C11-C12)	1.69334	π*(C13-C14)	0.40834	18.49	0.29	0.067

Table 9. 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 (3) O48	1.45251	π*(N46-O47)	0.64020	161.60	0.14	0.138
π (C41-C43)	1.63819	π*(N46-O47)	0.64020	26.34	0.15	0.060
π (C36-C38)	1.58933	π*(C41-C43)	0.39362	25.04	0.27	0.074
LP (2) S53	1.65877	π*(C51-C52)	0.37393	21.44	0.27	0.068
π (C15-C16)	1.56524	π*(C13-C14)	0.40943	21.27	0.27	0.068
LP (2) S29	1.75486	π*(C23-C24)	0.37047	20.64	0.24	0.064
LP (2) S28	1.75912	π*(C23-C24)	0.37047	20.53	0.24	0.065
LP (2) S31	1.75888	π*(C26-C27)	0.36942	20.53	0.24	0.064
LP (2) S53	1.65877	π*(C49-C50)	0.37483	20.50	0.27	0.067
π (C1-C6)	1.65893	π*(C2-C3)	0.37539	20.45	0.28	0.068
LP (2) S30	1.76170	π*(C26-C27)	0.36942	20.43	0.24	0.065
π (C1-C6)	1.65893	π*(C4-C5)	0.37539	20.40	0.28	0.068
π (C41-C43)	1.63819	π*(C37-C39)	0.27214	20.31	0.29	0.071
π (C37-C39)	1.68356	π*(C36-C38)	0.38086	20.08	0.28	0.069
π (C4-C5)	1.64374	π*(C1-C6)	0.33478	20.07	0.28	0.068
π (C2-C3)	1.64495	π*(C1-C6)	0.33478	20.00	0.28	0.068
LP (2) S62	1.85773	π*(C23-C24)	0.37047	19.99	0.24	0.065
π (C13-C14)	1.61450	π*(C15-C16)	0.43040	19.84	0.27	0.067
LP (2) S60	1.85782	π*(C26-C27)	0.36942	19.72	0.24	0.065
π (C15-C16)	1.56524	π*(C11-C12)	0.32086	19.44	0.27	0.067

The intra molecular interaction for the title compounds is formed by the orbital overlap between: π (C45-C47) and π*(N50-O52) for compound 1, π (C41-C43) and π*(N46-O47) for compound 2, π (C41-C43) and π*(N46-O48) for compound 3 and π (C41-C43) and π*(N46-O47) for compound 4 with electron densities 1.638e → 0.639e, 1.638e → 0.640e, 1.638e → 0.63984e and 1.638e → 0.640e for compounds 1, 2, 3 and 4 respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of π (C45-C47) to π*(N50-O52) for compound 1, π (C41-C43) to π*(N46-O47) for compound 2, π (C41-C43) to π*(N46-O48) for compound 3 and π (C41-C43) to π*(N46-O47) for compound 4 lead to highest stabilization of 29.48, 26.44, 29.47 and 26.34 kJ mol^{-1} respectively. In case of LP (3) O51 orbital to the π*(N50-O52) for compound 1, LP (3) O48 orbital to π*(N46-O47) for compound 2, LP (3) O47 orbital to π*(N46-O48) for compound 3, LP (3) O48 orbital to π*(N46-O47) for compound 4 respectively, show the stabilization energy of 161.82, 161.48, 161.82 and 161.60 kJ mol^{-1} and electron densities 1.452e → 0.639e, 1.453e → 0.640e, 1.452e → 0.639e and 1.452e → 0.640e for compounds 1, 2, 3 and 4 respectively. The results calculated of natural orbital occupancy suggest that the bond lengths of these compounds are essentially controlled by the π character of these hybrid orbitals and also by the nature of the bonds.

3.6 Nonlinear Optical Properties (NLO)

The first order hyperpolarizability (β) is a measure of induced dipole in a molecule in the presence of an electric field. The large value of hyperpolarizability is a measure of the non-linear optical activity of the molecular system and is associated with the intermolecular charge transfer resulting from the electron cloud movement through π conjugated frame work from electron donor to electron acceptor groups. Non-linear optical (NLO) responses induced in various materials are of great interest in recent years because of the potential applications in photonic technologies such as optical communication, computing data storage and image processing [27]. Recent efforts have been focused to develop organic molecules with large molecular non-linear optical response, improved optical transparency and good thermal stability [28]. The first order hyperpolarizability is a third rank tensor described by 3×3×3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [29]. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. The expression of the external Electric field when it becomes weak and homogeneous is

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2\alpha_{\alpha\beta} F_\alpha F_\beta} + \frac{1}{6\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma} \quad (10)$$

E^0 is the energy of the unperturbed molecules, F_α is the field at the origin, μ_α, $\alpha_{\alpha\beta}$ & $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first order hyperpolarizability respectively. The total static dipole moment μ, the mean polarizability α_0, the anisotropy of the polarizability Δα and mean first order hyperpolarizability β_0 using the x, y and z components are defined as follows.

$$\mu = \left[\mu_x^2 + \mu_y^2 + \mu_z^2\right]^{1/2} \quad (11)$$

$$\alpha_0 = \frac{\left[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right]}{3} \quad (12)$$

$$\Delta\alpha = 2^{-1/2}\left[\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2 + 6\alpha_{xx}^2\right]^{1/2} \quad (13)$$

$$\beta_0 = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2} \quad (14)$$

and

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \quad (15)$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz} \quad (16)$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz} \quad (17)$$

Organic molecules having extended π-conjugation systems and electron donating groups possess higher NLO properties. The first order hyperpolarizability (β_0) of (exTTF)-thiophene 1-4 along with related properties were calculated using DFT/B3LYP method with 6-31G (d,p) basis set are presented in Table 10.

Since the values of the polarizabilities (Δα) 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 = 0.1482x 10^{-24} e.s.u., for β; 1 a.u = 8.6393x10^{-33} e.s.u.). The calculated values of dipole moment (μ) for the title compounds were found to be 8.6436, 8.8282, 8.0061 and 8.0732 D respectively, which

Table 10. The dipole moments μ (D), polarizability α (esu), the anisotropy of the polarizability Δα (esu) and the first hyperpolarizability β_0 (esu) of (exTTF)-thiophene 1-4

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
β_{xxx}	-2048.4570	2200.8385	2390.6171	2524.7211
β_{yyy}	12.8731	40.3127	10.0563	88.3574
β_{zzz}	-32.2800	11.9835	9.3349	10.3116
β_{xyy}	-62.2317	126.0724	-28.3763	78.1508
β_{xxy}	-495.5386	-393.2239	-169.0781	-299.0757
β_{xxz}	-45.1631	-222.4676	-263.3376	-344.3301
β_{xzz}	-42.2537	3.3112	65.1427	-11.2875
β_{yzz}	39.0669	-6.0853	1.7678	-8.0891
β_{yyz}	-67.1139	-30.9025	-20.2635	-21.9922
β_{xyz}	-42.8880	-36.7125	-16.2450	-26.5901
β_0(esu)x10^{-33}	2220.7201	2370.0382	2447.8851	2625.0581
μ_x	-8.0124	8.3193	7.6014	7.6771
μ_y	-2.8036	-2.2541	-1.5547	-1.4449
μ_z	-1.6285	-1.9093	-1.9747	-2.0373
μ (D)	8.6436	8.8282	8.0061	8.0732
α_{xx}	-360.8495	-399.1534	-461.4420	-447.6323
α_{yy}	-243.0608	-243.3060	-315.6182	-272.8413
α_{zz}	-268.8080	-301.9968	-338.8383	-354.1333
α_{xy}	-26.8955	4.5014	-5.8745	-32.8438
α_{xz}	7.5640	30.0732	34.8026	23.3111
α_{yz}	-0.8634	-1.7152	13.7394	13.9438
α(esu)x10^{-24}	117.6790	146.1815	150.7356	168.5255
$\Delta\alpha$(esu)x10^{-24}	17.4400	21.6641	22.3390	24.9755

are approximately eight times more than 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 $117.6790\text{x}10^{-24}$, $146.1815\text{x}\ 10^{-24}$, $150.7356\text{x}10^{-24}$ and $168.5255\text{x}10^{-24}$ esu respectively; the values of anisotropy of the polarizability are 17.4400, 21.6641, 22.3390 and 24.9755 esu, respectively. The magnitude of the molecular hyperpolarizability (β_0) is one of the important key factors in a NLO system. The DFT/6-31G (d,p) calculated first hyperpolarizability value (β_0) of (exTTF)-thiophene molecules are equal to $2220.7201 \text{ x } 10^{-33}$, $2370.0382 \text{ x } 10^{-33}$, $2447.8851 \text{ x } 10^{-33}$ and $2625.0581 \text{ x } 10^{-33}$ esu. The first hyperpolarizability of title molecules is approximately 6.47, 6.90, 7.13 and 7.65 times than those of urea (β of urea is $343.272 \text{ x}10^{-33}$ esu obtained by B3LYP/6-311G (d,p) method). The above results show that (exTTF)-thiophene 1-4 might have the NLO applications.

4. CONCLUSION

The π-extended tetrathiafulvalene (exTTF) connected to thiophene derivative 1-4 have been investigated theoretically at DFT/B3LYP method with 6-31G (d,p) basis set to predict their electronic proprieties and their applications. The optimized geometrical parameters and structures are obtained by same method cited above. From the MEP plot, it is evident that the negative charge covers the nitro functional group and the positive region is over the hydrogen atoms of alkyl and cycled groups. Furthermore the FMOs analyses shows that HOMO-1,HOMO are confined on the π-conjugated spacer of TTF core and delocalized over the part of thiophene derivative, while LUMO, LUMO+1 are confined the part of thiophene derivative and delocalized on the π-conjugated spacer of TTF core which gives charge transfer process in the molecular system. The lowering of HOMO-LUMO energy gap in compound 2 in the quantum chemical descriptors, explains that has a high chemical reactivity compared to other compounds. NBO analysis has been computed to determine the stability of the molecules arising from hyper-conjugative interactions and the results exhibits intramolecular conjugative interactions as $\pi \rightarrow \pi^*$, which are responsible for π-electron delocalization within molecules. On the other hand, due to the growing interest of organic materials for nonlinear optical devices, the Non Linear Optical (NLO) properties of the title compounds have also been studied revealing that are a good candidate as a NLO material.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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