A Computational Investigation of a Series Ofdimeric and Trimetric Tetrathiafulvalenes Using DFT Method

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Abstract: *In this perspective article, density functional theory (DFT) calculations are used to investigate themolecular stability and bond strengths of dimeric and trimeric tetrathiafulvalenes **1-4** by applying the natural bond orbital analysis. The indication about the size, shape, charge density distribution and site of chemical reactivity of the molecules has been obtained by mapping electron density with molecular electrostatic potential (MEP).The HOMO and LUMO energies determined showed that the serious charge transfer occurs in the title molecules studied. NLO properties such as dipole moment, polarizability, first static hyperpolarizability were also calculated to predict their Non-linear optical behavior.*
Keywords: *tetrathiafulvalenes; density functional theory; computational chemistry; electronic structure; quantum chemical calculations.*

I.   Introduction

Tetrathiafulvalene (TTF) is a fascinating planar π-electron- donor molecule with a broad range of potential applications [1]. Tetrathiafulvalene (TTF) derivatives [2] are very versatile electro-active molecules widely used as building blocks to prepare organic metals, for supramolecular functions [3] and in molecular electronics [4].Recently, donor–acceptor type dyads using a tetrathiafulvalene (TTF) framework have received considerable interest as materials for fluorescence switches, chemical sensors, molecular rectification, and photovoltaic and NLO applications [5-10].

Quantum chemical calculation is one of the recent emerging tools in unraveling physical and chemical properties of molecules. Recently, density functional theory (DFT) has been emerged as a powerful tool for study of electronic properties of polyatomic molecules. The application of DFT to chemical systems has received much attention because of faster convergence in time than traditional quantum mechanical correlation methods [11].

In order to understand the electronic properties ofdimeric and trimeric tetrathiafulvalenes **1-4**illustrate in literature [12], the theoretical calculations have been computed by DFT/B3LYP method with 6-31G (d,p) basis. This study investigated the characterization of the molecular structures, molecular electrostatic potential (MEP), frontier molecular orbital analysis properties, quantum chemical descriptors,the Fukui functions, second order perturbation theory analysis (NBO) and first order hyperpolarizability (β) using the calculation method quoted above.

II.   Materials and Methods

All calculations have been performed by using Gaussian 09W [13] program package at the DFT level of theory by using the hybrid functional B3LYP [14] with 6-31G (d,p) basis set. The calculated results have been visualized by using Gauss View 5 [15] software.

III. Results and Discussion

3.1 Molecular Geometry:

The atomic numbering scheme the theoretical geometric structures of dimeric and trimeric tetrathiafulvalenes **1-**4 are shown in Figure 1. The optimized parameters (bond lengths, bond angles and dihedral angles) of the title compounds were obtained using DFT and the B3LYP/6-31G (d,p) method. The results are given in Tables 1-4.

Figure 1. Optimized molecular structure of dimeric and trimeric tetrathiafulvalenes **1-4**

Table 1. Optimized geometric parameters of compound **1**
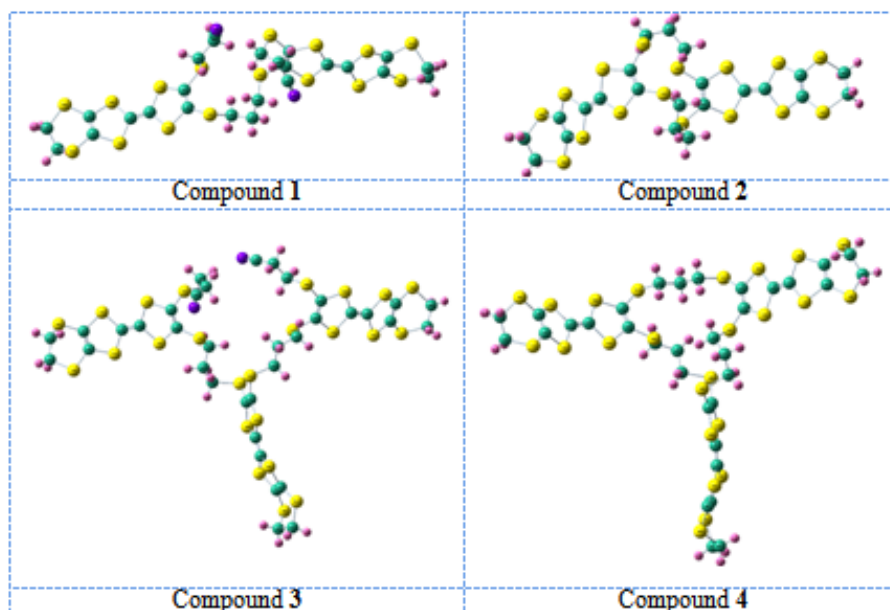
Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,4)	1.327	A(4,1,17)	123.323	D(17,1,4,19)	179.758
R(1,17)	1.842	A(3,2,24)	126.329	D(18,1,4,20)	179.712
R(2,17)	1.837	A(17,2,24)	115.169	D(4,1,17,2)	171.292
R(3,18)	1.835	A(2,3,23)	127.115	D(17,2,24,32)	110.522
R(4,20)	1.842	A(18,3,23)	114.547	D(23,3,18,1)	173.995
R(5,6)	1.331	A(1,4,20)	123.331	D(18,3,23,45)	112.910
R(5,53)	1.812	A(6,5,53)	126.747	D(1,4,19,6)	159.747
R(6,52)	1.813	A(5,6,52)	123.286	D(53,5,6,19)	178.851
R(7,13)	1.843	A(19,6,52)	117.883	D(53,5,20,4)	168.347
R(8,9)	1.331	A(10,7,13)	123.452	D(20,5,53,63)	144.346
R(8,13)	1.841	A(10,7,14)	123.548	D(14,7,10,15)	179.347
R(8,50)	1.813	A(13,7,14)	113.001	D(10,7,13,8)	159.183
R(9,51)	1.813	A(9,8,13)	118.077	D(7,10,16,12)	176.535
R(10,16)	1.842	A(13,8,50)	115.192	D(11,22,39,40)	110.534
R(11,12)	1.332	A(8,9,14)	118.410	D(2,24,32,35)	175.268

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

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,4)	1.328	A(4,1,14)	123.208	D(4,1,13,2)	160.708
R(1,13)	1.841	A(13,1,14)	113.180	D(13,2,3,41)	178.827
R(2,3)	1.331	A(3,2,13)	118.425	D(41,3,14,1)	168.713
R(2,13)	1.839	A(3,2,42)	123.371	D(14,3,41,43)	144.977
R(3,14)	1.841	A(13,2,42)	117.824	D(1,4,16,6)	159.164
R(4,15)	1.837	A(2,3,41)	126.814	D(24,5,6,16)	175.458
R(5,6)	1.335	A(14,3,41)	115.078	D(24,5,15,4)	170.782
R(5,15)	1.851	A(1,4,15)	123.685	D(6,5,24,26)	128.812
R(6,16)	1.850	A(1,4,16)	124.055	D(19,7,10,18)	179.527
R(7,10)	1.328	A(6,5,15)	117.534	D(39,9,20,7)	168.391
R(8,9)	1.331	A(15,5,24)	116.679	D(20,9,39,49)	144.653
R(8,40)	1.813	A(5,6,16)	117.681	D(7,10,18,12)	162.900
R(9,20)	1.841	A(16,6,23)	115.523	D(22,11,17,10)	174.636
R(9,39)	1.813	A(10,7,19)	123.650	D(12,11,22,32)	118.750
R(10,17)	1.838	A(19,7,20)	113.098	D(11,22,32,34)	112.589

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

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,18)	1.842	A(4,1,18)	123.332	D(18,1,4,20)	179.363
R(2,3)	1.332	A(17,1,18)	113.374	D(4,1,17,2)	174.306
R(2,17)	1.836	A(3,2,17)	118.505	D(17,2,24,32)	104.544
R(3,18)	1.837	A(17,2,24)	115.388	D(23,3,18,1)	176.771
R(4,19)	1.842	A(2,3,23)	126.081	D(1,4,19,6)	159.225
R(5,6)	1.331	A(18,3,23)	115.597	D(51,5,6,19)	178.829
R(5,20)	1.841	A(1,4,19)	123.603	D(51,5,20,4)	168.169
R(6,50)	1.813	A(1,4,20)	123.395	D(20,5,51,61)	144.418
R(7,13)	1.843	A(6,5,51)	126.744	D(10,7,13,8)	158.730

R(7,14)	1.842	A(20,5,51)	115.172	D(49,9,14,7)	173.888
R(8,13)	1.842	A(5,6,50)	123.277	D(14,9,49,52)	128.336
R(9,14)	1.839	A(19,6,50)	117.873	D(7,10,16,12)	172.579
R(10,16)	1.837	A(10,7,13)	123.473	D(15,11,12,21)	177.934
R(11,12)	1.332	A(10,7,14)	123.562	D(22,11,15,10)	173.968
R(11,15)	1.842	A(13,7,14)	112.965	D(11,22,38,39)	147.661

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

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,18)	1.842	A(4,1,17)	123.349	D(17,1,4,19)	179.832
R(2,3)	1.333	A(17,1,18)	113.403	D(18,1,4,20)	179.388
R(2,17)	1.836	A(3,2,24)	126.296	D(4,1,17,2)	173.085
R(3,23)	1.822	A(17,2,24)	115.274	D(17,2,24,28)	112.221
R(4,19)	1.842	A(2,3,18)	118.433	D(23,3,18,1)	175.521
R(5,6)	1.331	A(18,3,23)	115.245	D(18,3,23,40)	106.144
R(5,20)	1.842	A(1,4,19)	123.512	D(1,4,19,6)	159.279
R(5,46)	1.813	A(19,4,20)	113.014	D(46,5,6,19)	178.758
R(6,45)	1.813	A(6,5,46)	126.693	D(46,5,20,4)	168.226
R(7,10)	1.327	A(20,5,46)	115.221	D(20,5,46,56)	144.181
R(8,9)	1.331	A(5,6,45)	123.275	D(14,7,10,15)	179.794
R(8,43)	1.813	A(19,6,45)	117.877	D(13,8,9,44)	172.903
R(9,14)	1.838	A(10,7,13)	123.387	D(44,9,14,7)	174.303
R(9,44)	1.813	A(13,7,14)	113.054	D(7,10,16,12)	176.078
R(10,15)	1.841	A(9,8,43)	126.971	D(15,11,12,21)	177.298

3.2 Molecular Electrostatic Potential (MEP):

The molecular electrostatic potential (MEP) has been used as a useful method in research of molecular structure with its physicochemical property relationship [16]. The molecular electrostatic potential, V(r), at a given point r (x,y,z) in the vicinity of a molecule, is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and a positive test charge (a proton) located at r. It is defined by:

$$V(r) = \sum_A \frac{Z_A}{(R_A - r)} - \int \frac{\rho(r')}{(r' - r)} dr'$$

In which Z_A is the charge of nucleus A, located at R_A and $\rho(r')$ is the electronic density function for the molecule and r' is the dummy integration variable [17,18]. The MEP has been used for predicting sites and relative reactivity toward electrophilic attack and in the studies of biological recognition and hydrogen bonding interactions [19].Potential increases in the order red < orange < yellow < green < blue. To predict reactivesites for electrophilic and nucleophilic attack for the title molecules,MEP was calculated at the B3LYP/6-31G(d,p) optimized geometries.The negative (red) regions of MEP were related to electrophilicreactivity and the positive (bleu) regions to nucleophilic reactivity illustrated in Figure 2.
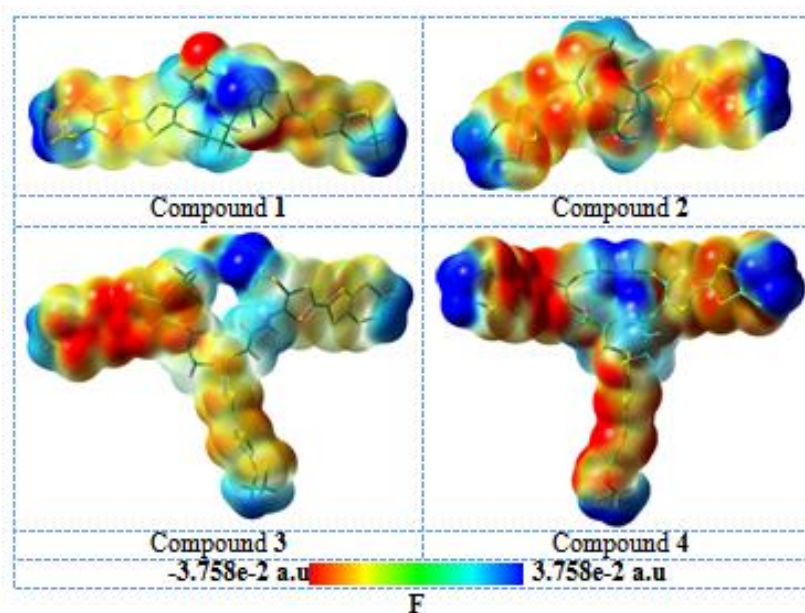

Figure 2. Molecular electrostatic potential surface of dimeric and trimeric tetrathiafulvalenes **1-4**

As seen from the figure above that, in all molecules, the regions exhibiting the negative electrostatic potential are localized near the TTF core and the nitrile function in compound **1** 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):

The highest occupied molecular orbitals (HOMOs) and the lowest-lying unoccupied molecular orbitals (LUMOs) are named as Frontier Molecular Orbitals (FMOs). The FMOs play an important role in the optical and electric properties, as well as in quantum chemistry. HOMO, LUMO energy characterizes the ability of electron accepting. The eigenvalues of HOMO and LUMO and their energy gap reflect the biological activity of the molecule. These orbitals are a pair of orbitals in the compound, which allows them to interact more strongly. The frontier orbital gap helps characterize the chemical reactivity and the kinetic stability of the molecule. A molecule having a small frontier orbitals gap is more polarizable and is generally associated with a high chemical reactivity and low kinetic stability [20–22]. The HOMO and LUMO orbitals of compound **3** with a small energy gap were computed by the DFT/B3LYP method with 6-31G (d,p) basis set and visualized in Figure 3.
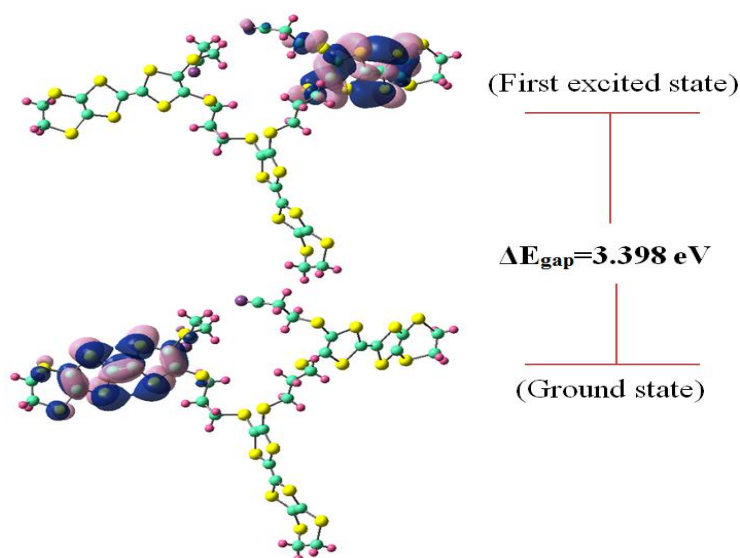

Figure 3. HOMO-LUMO Structure with the energy level diagram of compound **3**

3.4 Global Reactivity Descriptors:

Density functional theory method concept the chemical reactivity and site selectivity of the molecular systems. The energies of frontier molecular orbitals (E_{HOMO}, E_{LUMO}), energy band gap which explains the eventual charge transfer interaction within the molecule, electronegativity (χ), chemical potential (μ), global hardness (η), global softness (S) and global electrophilicity index (ω) [23,24] of dimeric and trimeric tetrathiafulvalenes **1-4** are computed by the DFT/B3LYP method with 6-31G (d,p) basis set and listed in Table 5.

$$\chi = -1/2\left(E_{LUMO} + E_{HOMO}\right)$$
$$\mu = -\chi = 1/2\left(E_{LUMO} + E_{HOMO}\right)$$
$$\eta = 1/2\left(E_{LUMO} - E_{HOMO}\right)$$
$$S = 1/2\eta$$
$$\omega = \mu^2/2\eta$$

The large HOMO-LUMO gap means a hard molecule and small HOMO-LUMO gap means a soft molecule. One can also relate the stability of the molecule to hardness, which means that the molecule with least HOMO-LUMO gap means it is more reactive.

Table 5. Quantum chemical descriptors of dimeric and trimeric tetrathiafulvalenes **1-4**

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
E_{HOMO} (eV)	-5.187	-5.212	-5.044	-5.142
E_{LUMO} (eV)	-1.518	-1.423	-1.647	-1.478
ΔE_{gap} (eV)	3.668	3.789	3.398	3.663
IE (eV)	5.187	5.212	5.044	5.142
A (eV)	1.518	1.423	1.647	1.478
μ (eV)	-3.353	-3.317	-3.345	-3.310

χ **(eV)**	3.353	3.317	3.345	3.310
η **(eV)**	1.834	1.895	1.699	1.832
S (eV)	0.273	0.264	0.294	0.273
ω **(eV)**	3.064	2.904	3.294	2.990

As presented in table 5, the compound which have the lowest energetic gap is the compound **3** (ΔE_{gap} = 3.398 eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound **2** (ΔE_{gap} = 3.789 eV).The compound that has the highest HOMO energy is the compound **3** (E_{HOMO} = -5.044 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} = -1.647 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 **3** has lowest value of the potential ionization (I = 5.044 eV), so that will be the better electron donor. Compound **3** has the largest value of the affinity (A = 1.647 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 = 1.699 eV, **S** = 0.294 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 = 3.353 eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **3** (ω = 3.294 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:

The Fukui function is a local reactivity descriptor that gives the preferred regions where a chemical species will change its density when the number of electrons is changed and it shows the propensity of the electronic density to deform at a given position upon accepting or donating electrons [25-27]. Also, the condensed or atomic Fukui functions on the *j*th atom site is given as,

$$f_j^- = q_j(N) - q_j(N-1)$$

$$f_j^+ = q_j(N+1) - q_j(N)$$

$$f_j^0 = \frac{1}{2}[q_j(N+1) - q_j(N-1)]$$

For an electrophilic $f_j^-(r)$, nucleophilic or free radical attack $f_j^+(r)$, on the reference molecule, respectively. In these equations, q_j is the atomic charge at the jth atomic site is the neutral (N), anionic (N+1) or cationic (N-1) chemical species. Chattarajet al. [28] proposed the concept of generalized philicity and it contains almost all information about the known different global and local reactivity and selectivity descriptor, in addition to the information regarding electrophilic/nucleophilic power of a given atomic site in a molecule. Morell et al. [29] proposed a dual descriptor ($\Delta f(r)$), which is defined as the difference between the nucleophilic and electrophilic Fukuifunction and is given by,

$$\Delta f(r) = |f^+(r) - f^-(r)|$$

Δf (r) > 0, then the site is favored for a nucleophilic attack, whereas if$\Delta f(r)$< 0, then the site may be favored for an electrophilic attack. Under this situation, dual descriptors $\Delta f(r)$ gives a clear difference between nucleophilic and electrophilic attack at a particular region with their sign and it provides positive value for site prone for nucleophilic attack and a negative value prone for electrophilic attack. Fukui functions for selected atomic sites dimeric and trimeric tetrathiafulvalenes **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	10 C	1 C	8 C	5 C	**Atom**	10 C	4 C	26 C	9 C
f^+	0.139	0.112	0.084	0.083	f^+	0.146	0.099	0.095	0.083
Atom	23 S	24 S	52 S	53 S	**Atom**	23 S	24 S	42 S	41 S
f^-	0.126	0.110	0.095	0.095	f^-	0.124	0.107	0.097	0.096
Atom	10 C	1 C	9 C	11 C	**Atom**	10 C	24 S	4 C	8 C
f^0	0.022	0.015	0.006	0.006	f^0	0.027	0.018	0.011	0.006

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

Compound 3					Compound 4			
Atom	92 C	66 C	14 S	13 S	**Atom**	10 C	1 C	65 C	67 C
f^+	0.103	0.088	0.079	0.074	f^+	0.454	0.426	0.425	0.412
Atom	64 S	81 C	82 C	2 C	**Atom**	25 C	12 C	9C	61 C

f^-	0.155	0.073	0.066	0.063	f^-	0.212	0.088	0.070	0.067
Atom	66 C	23 S	22 S	32 C	**Atom**	10 C	65 C	1 C	3 C
f^0	0.067	0.033	0.020	0.016	f^0	0.249	0.241	0.241	0.237

From the tables 6-7, the parameters of local reactivity descriptors show that 10C is the more reactive site in compounds **1**, **2** and **4** and 92C in compound **3** respectively for nucleophilic attacks. The more reactive sites in radical attacks are 10C for compounds **1**, **2** and **4** and 66C for compounds **3** respectively.The more reactive sites for electrophilic attacks are 23S for compounds **1**, **2** and 64S, 25C for compounds **3** and **4**respectively.

3.6 Natural Bond Orbital Analysis (NBO):

NBO analysis helps in identifying individual bonds and the energies associated with lone–pair electrons that play a vital role in the chemical processes [30–32]. It helps in studying hybridization, hydrogen bonding as well as hyper-conjugative interactions between occupied Lewis type (bonding or lone pair) and unoccupied (anti-bonding or Rydberg) orbitals which further help in studying inter and intramolecular interactions among various bonds. Stabilization energy ($E^{(2)}$) associated as a result of electron delocalization between donor NBO (i) and acceptor NBO (j), is estimated by equation [33,34]

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

whereq_i is the donor orbital occupancy; $E(i)$ and $E(j)$ are orbital energies of donor and acceptor NBO orbitals and F_{ij} is the off-diagonal Fock matrix. Extent of hyper-conjugation depends upon the donating ability of Lewis type orbitals and accepting ability of non Lewis type orbitals and this is measured in terms of the interaction energy $E^{(2)}$.The second-order perturbation theory analysis of Fock matrix in NBO basis of dimeric and trimeric tetrathiafulvalenes **1-4** is given 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) S18	1.81120	π*(C2-C3)	0.26532	18.51	0.23	0.059
LP (2) S15	1.80820	π*(C11-C12)	0.25684	18.28	0.23	0.059
LP (2) S17	1.81414	π*(C 2-C3)	0.26532	18.12	0.23	0.059
LP (2) S16	1.81266	π*(C11-C12)	0.25684	17.79	0.23	0.058
LP (2) S19	1.83399	π*(C5-C6)	0.30332	16.42	0.24	0.058
LP (2) S14	1.83631	π*(C8-C9)	0.30341	16.41	0.24	0.058
LP (2) S13	1.83730	π*(C8-C9)	0.30341	16.20	0.24	0.057
LP (2) S20	1.83543	π*(C5-C6)	0.30332	16.18	0.24	0.057
LP (2) S50	1.88883	π*(C8-C9)	0.30341	11.98	0.24	0.050
LP (2) S53	1.88865	π*(C5-C6)	0.30332	11.95	0.24	0.050
LP (2) S15	1.80820	π*(C7-C10)	0.26415	9.81	0.34	0.053
LP (2) S16	1.81266	π*(C7-C10)	0.26415	9.64	0.35	0.053
LP (2) S17	1.81414	π*(C1-C4)	0.26811	9.21	0.34	0.051
LP (2) S18	1.81120	π*(C1-C4)	0.26811	9.12	0.34	0.050
LP (1) N49	1.96400	π*(C28-C31)	0.02069	8.93	0.93	0.082
LP (1) N48	1.96609	π*(C35-C38)	0.02128	8.78	0.94	0.082
LP (2) S51	1.90087	π*(C8-C9)	0.30341	6.90	0.24	0.038
LP (2) S52	1.90059	π*(C5-C6)	0.30332	6.89	0.24	0.038
LP (2) S19	1.83399	π*(C1-C4)	0.26811	6.57	0.33	0.043
LP (2) S 20	1.83543	π*(C1-C4)	0.26811	6.50	0.33	0.043

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	1.83161	π*(C8-C9)	0.30295	16.44	0.24	0.058
LP (2) S13	1.82967	π*(C2-C3)	0.30342	16.42	0.24	0.058
LP (2) S17	1.82062	π*(C11-C12)	0.25034	16.28	0.24	0.057
LP (2) S14	1.83055	π*(C2-C3)	0.30342	16.26	0.24	0.057
LP (2) S20	1.83338	π*(C8-C9)	0.30295	16.20	0.24	0.057
LP (2) S18	1.81870	π*(C11-C12)	0.25034	16.12	0.24	0.057
LP (2) S16	1.82761	π*(C5-C6)	0.25918	15.27	0.25	0.056
LP (2) S15	1.82966	π*(C5-C6)	0.25918	15.02	0.25	0.056
LP (2) S41	1.88865	π*(C2-C3)	0.30342	12.09	0.24	0.050
LP (2) S39	1.88913	π*(C8-C9)	0.30295	11.97	0.24	0.050
LP (2) S18	1.81870	π*(C7-C10)	0.28112	9.49	0.30	0.049
LP (2) S17	1.82062	π*(C7-C10)	0.28112	9.37	0.30	0.049
LP (2) S13	1.82967	π*(C1-C4)	0.28344	9.27	0.29	0.048
LP (2) S14	1.83055	π*(C1-C4)	0.28344	9.19	0.29	0.047
LP (2) S16	1.82761	π*(C1-C4)	0.28344	9.13	0.29	0.047
LP (2) S15	1.82966	π*(C1-C4)	0.28344	8.88	0.29	0.047

LP (2) S19	1.83161	π*(C7-C10)	0.28112	8.41	0.30	0.046
LP (2) S20	1.83338	π*(C7-C10)	0.28112	8.31	0.30	0.046
LP (2) S42	1.90109	π*(C2-C3)	0.30342	6.91	0.24	0.038
LP (2) S40	1.90115	π*(C8-C9)	0.30295	6.87	0.24	0.038

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) S67	1.80896	π*(C65-C66)	0.26403	19.01	0.23	0.059
LP (2) S68	1.81359	π*(C65-C66)	0.26403	18.48	0.23	0.059
LP (2) S17	1.81224	π*(C2-C3)	0.25390	18.31	0.23	0.059
LP (2) S18	1.81201	π*(C2-C3)	0.25390	18.30	0.23	0.059
LP (2) S16	1.81536	π*(C11-C12)	0.26478	17.12	0.24	0.058
LP (2) S15	1.81938	π*(C11-C12)	0.26478	16.51	0.24	0.057
LP (2) S76	1.83294	π*(C81-C82)	0.30339	16.50	0.24	0.058
LP (2) S19	1.83561	π*(C5-C6)	0.30333	16.49	0.24	0.058
LP (2) S14	1.83576	π*(C8-C9)	0.30304	16.46	0.24	0.058
LP (2) S20	1.83765	π*(C5-C6)	0.30333	16.18	0.24	0.057
LP (2) S13	1.83732	π*(C8-C9)	0.30304	16.17	0.24	0.057
LP (2) S77	1.83539	π*(C81-C82)	0.30339	16.15	0.24	0.057
LP (2) S84	1.88855	π*(C81-C82)	0.30339	11.92	0.24	0.050
LP (2) S51	1.88936	π*(C5-C6)	0.30333	11.91	0.24	0.050
LP (2) S48	1.88935	π*(C8-C9)	0.30304	11.85	0.24	0.050
LP (2) S15	1.81938	π*(C7-C10)	0.27158	9.98	0.33	0.052
LP (2) S16	1.81536	π*(C7-C10)	0.27158	9.86	0.33	0.052
LP (2) S18	1.81201	π*(C1-C4)	0.26564	9.51	0.34	0.052
LP (2) S17	1.81224	π*(C1-C4)	0.26564	9.49	0.34	0.052
LP (2) S67	1.80896	π*(C70-C72)	0.26048	8.69	0.35	0.050

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) S18	1.81211	π*(C2-C3)	0.26179	18.30	0.23	0.059
LP (2) S17	1.81223	π*(C2-C3)	0.26179	18.27	0.23	0.059
LP (2) S63	1.81296	π*(C60-C61)	0.26923	18.21	0.23	0.059
LP (2) S62	1.81348	π*(C60-C61)	0.26923	18.15	0.23	0.059
LP (2) S16	1.81180	π*(C11-C12)	0.25501	17.86	0.23	0.059
LP (2) S15	1.81843	π*(C11-C12)	0.25501	17.03	0.24	0.058
LP (2) S19	1.83511	π*(C5-C6)	0.30333	16.51	0.24	0.058
LP (2) S14	1.83596	π*(C8-C9)	0.30367	16.44	0.24	0.058
LP (2) S71	1.83514	π*(C75-C76)	0.30322	16.33	0.24	0.057
LP (2) S20	1.83708	π*(C5-C6)	0.30333	16.21	0.24	0.057
LP (2) S13	1.83818	π*(C8-C9)	0.30367	16.13	0.24	0.057
LP (2) S72	1.83684	π*(C75-C76)	0.30322	16.05	0.24	0.057
LP (2) S43	1.88867	π*(C8-C9)	0.30367	12.22	0.24	0.051
LP (2) S78	1.88823	π*(C75-C76)	0.30322	12.17	0.24	0.051
LP (2) S46	1.88949	π*(C5-C6)	0.30333	11.75	0.24	0.050
LP (2) S63	1.81296	π*(C65-C67)	0.27036	9.64	0.33	0.051
LP (2) S62	1.81348	π*(C65-C67)	0.27036	9.54	0.33	0.051
LP (2) S17	1.81223	π*(C1-C4)	0.26659	9.44	0.34	0.052
LP (2) S18	1.81211	π*(C1-C4)	0.26659	9.40	0.34	0.051
LP (2) S15	1.81843	π*(C7-C10)	0.25936	9.24	0.36	0.053

The intra molecular interaction for the title compounds is formed by the orbital overlap between: LP(2) S18 orbital to the π*(C2-C3) for compound **1**, LP(2) S19 orbital to π*(C8-C9) for compound **2**, LP(2) S67 orbital to π*(C65-C66) for compound **3**,LP(2) S18 orbital to π*(C2-C3) for compound **4** respectively, show the stabilization energy of 18.51, 16.44, 19.01 and 18.30 kJ mol^{-1} respectively.

3.7 Nonlinear Optical Properties (NLO):

The NLO activity provide the key functions for frequency shifting, optical modulation, optical switching and optical logic for the developing technologies in areas such as communication, signal processing and optical interconnections [35,36].In the presence of an applied electric field, the energy of a system is a function of the electric field and the 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 because of the Kleinman symmetry [37]. The matrix can be given in the lower tetrahedral format. It is obvious that the lower part of the 3×3×3 matrices is a tetrahedral. 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 is given below:

$$E = E^0 - \mu_\alpha F_\alpha - 1/2\alpha_{\alpha\beta}F_\alpha F_\beta - 1/6\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma + \ldots$$

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

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

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

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

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

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

$$\beta_0 = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2\right]^{1/2}$$

The first static hyperpolarizability (β_0) and its related properties (β, α_0 and $\Delta\alpha$) of dimeric and trimeric tetrathiafulvalenes **1-4** have been calculated using B3LYP/6-31G (d,p) level based on finite field approach and given in Table 12.

Table 12. The dipole moments μ (D), polarizability α_0 (esu), the anisotropy of the polarizability $\Delta\alpha$ (esu) and the first hyperpolarizability β_0 (esu) of dimeric and trimeric tetrathiafulvalenes **1-4**.

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
β_{xxx}	-289.0559	303.5919	316.8736	300.0018
β_{yyy}	-79.5692	-5.7775	1228.0452	-4.7664
β_{zzz}	-7.7440	-2.0174	1.9232	-5.1026
β_{xyy}	75.8515	-69.4989	215.6755	-70.5067
β_{xxy}	-618.0880	-355.2097	-229.4884	-289.3058
β_{xxz}	68.9535	-54.2634	993.0575	-60.2438
β_{xzz}	-2.4739	8.2827	15.4279	6.2766
β_{yzz}	42.5474	-0.3585	-79.9362	-0.2685
β_{yyz}	48.4056	-49.3465	-35.9478	-50.6867
β_{xyz}	11.4459	-14.3233	-17.1372	-12.5286
β_0 (esu)x10^{-33}	740.7538	447.7430	1436.6234	394.5737
μ_x	-0.9366	1.9896	5.5572	2.8974
μ_y	-2.3713	-1.3325	0.5104	-2.4638
μ_z	1.8636	-0.6400	0.2692	-0.5007
μ(D)	3.1580	2.4787	5.5870	4.0045
α_{xx}	-245.2820	-222.4729	53.1231	-200.3258
α_{yy}	-369.6545	-341.8921	9.4303	-300.0147
α_{zz}	-383.6559	-352.3766	-62.5535	-236.2566
α_{xy}	2.8362	21.1364	-12.7626	19.1258
α_{xz}	22.3699	9.6055	-24.2787	8.8025
α_{yz}	2.9674	-15.8246	15.8894	-16.5625
α_0(esu)x10^{-24}	137.6871	134.1313	115.1101	98.9939
$\Delta\alpha$(esu)x10^{-24}	20.4052	19.8783	17.0593	14.6709

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 3.1580, 2.4787, 5.5870 and 4.0045 D respectively, which are approximately four 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 137.6871 x 10^{-24}, 134.1313 x 10^{-24}, 115.1101 x 10^{-24} and 98.9939 x 10^{-24} esu respectively; the values of anisotropy of the polarizability are 20.4052, 19.8783, 17.0593 and 14.6709 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 dimeric and trimeric tetrathiafulvalenes molecules are equal to 740.7538 x 10^{-33}, 447.7430 x 10^{-33}, 1436.6234 x 10^{-33} and 394.5737 x 10^{-33} esu. The first hyperpolarizability of title molecules is approximately 2.16, 1.30, 4.19 and 1.49 times than those of urea (β of urea is 343.272 x10^{-33} esu obtained by B3LYP/6-311G (d,p) method). This result indicates that dimeric and trimeric tetrathiafulvalenes **1-4** are nonlinear.

IV. Conclusion
In the present study, molecular structure, geometrical parameters, Molecular electrostatic potential map of dimeric and trimeric tetrathiafulvalenes **1-4** has been studied using DFT/B3LYP method with 6-31G (d,p) basis set. The frontier molecular orbital analysis provides information regarding ionization potential, chemical potential and other chemical descriptors.Fukui function also computed to predict reactive sites for electrophilic and nucleophilic attacks in the studied molecules. The NBO analysis obviously illustrates the stability of the molecular structure that arises from conjugative interactions, charge delocalization and E(2) energies confirm the occurrence of intra-molecular charge transfer. The calculated dipole moment and first order hyperpolarizability results indicate that the title compounds is a good candidate of NLO material.

Acknowledgments

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