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Structure, electronic properties, NBO, NLO and chemical reactivity of bis (1, 4-dithiafulvalene) derivatives: functional density theory study

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Abstract

In this work, through computational study based on density functional theory (DFT/B3LYP) using basis set 6-31G (d,p) a number of global and local reactivity descriptors for a series of molecules containing a TTF function which are bis (1,4-dithiafulvalene) derivatives. They were computed to predict the reactivity and the reactive sites on the molecules. The molecular geometry and the electronic properties in the ground state such as frontier molecular orbital (HOMO and LUMO), ionization potential (I) and electron affinity (A) were investigated to get a better insight of the molecular properties. Molecular electrostatic potential (MEP) for all compounds were determined to check their electrophilic or nucleophilic reactivity. Fukui index, polarizability, hyperpolarizability, second order NLO property and natural bond orbital (NBO) analyses have also employed to determine the reactivity of bis (1,4-dithiafulvalene) derivatives.

Keywords: Computational Chemistry; Density Functional Theory; Electronic Structure; Quantum Chemical Calculations; Tetrathiafulvalenes.

1. Introduction

Among the various candidates of organic materials for optoelectronic applications, (Wang et al. 2006; Mas-Torrent et al. 2006; Martín et al. 2007) tetrathiafulvalene (TTF) is most attractive because of its excellent electron-donating properties. The optoelectronic properties of these materials are clearly dependent on both the molecular structure and design within the solid state and so the TTF skeleton and peripheral substitutes has been extensively changed in order to reinforce dimensionality of the materials and/or to attain a suitable solid-state organization. (Otsubo et al. 1996; Schukat et al. 1996; Andreu et al. 1998) in addition, as a result of the strong electron-donating property of TTF, its derivatives are sometimes sensitive to air and light, which is one of the main drawbacks of TTF for practical applications. So as to overcome this barrier, heterocycle has been annulated to decrease its HOMO energy level, that suitable for organic semiconductors.

A variety of donor molecules are synthesized during which the TTF core is annulated to quinoline, furan, thiophene, pyridine or pyrazine units; all of these compounds have oxidation potentials appreciably higher than that of TTF itself. Among the heterocyclic-fused TTF donors, the pyridine-TTF derivatives showed the wonderful FET (field effect transistor) performances in thin films. Annulation of pyridine e rings to the TTF skeleton was effective to reinforce the intermolecular interaction, which was conjointly helpful to reinforce the stability of the FET device to oxygen (Naraso et al. 2005).

Materials having large second-order nonlinear optic (NLO) properties are in demand because of their potential applications in photonic devices and optical information processing (Kay et al. 2004; Bass et al. 2001; Prasad et al.1988). Organic NLO materials have drawn a lot of attention due to their engaging potential applications in optical data transmission and optical information processing (Kajzar et al. 2003). Compared with ancient inorganic and semiconductor materials, the organic NLO materials have several benefits like larger nonlinear optical coefficients, easier preparation and lower price (Hochberg et al. 2006). At a fundamental level, organic push pull NLO chromophores contain electron-donor and electron-acceptor groups at opposite ends of a π -conjugated spacer (Burland et al. 1994), and the overwhelming majority of known organic NLO compounds utilize aromatic linkers in the π -conjugated bridge (Hochberg et al. 2006).

In this work we set out theoretical investigation of the title compound described in literature (Abd El-Wareth et al. 2005). A detailed interpretation has been made on the basis of the calculated potential energy distribution and redistribution of electron density in various bonding and antibonding orbitals and stabilization energies have been calculated by natural bond orbital analysis to offer clear evidence of stabilization originating from the hyper conjugation of various intra-molecular interactions. HOMO and LUMO energies, the first and second order hyperpolarizabilities of this molecular system are calculated using density functional method.

2. Material and methods

The optimum geometry was determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints. The structural and spectroscopic characterization was carried out using Gaussian 09 program package on the personal computer. DFT computations were performed by using the closed-shell Becke-Lee-Yang-Parr hybrid exchange-correlation three-parameter functional (B3LYP) in combination with 6-31G (d, p) basis set to derive the complete geometry optimizations and normal-mode analysis on isolated entities. All optimized structures were confirmed to be minimum energy conformations.

3. Results and discussion

3.1. Molecular geometry

In order to find the global minimum energy, the energy calculations were carried out for various bis (1,4-dithiafulvalene). The various structures of bis (1, 4-dithiafulvalene) derivatives 1-4 are shown in Fig. 1. The most optimized structural parameters (bond length, and bond angle) calculated by B3LYP with 6-31G (d,p) basis set are presented in Table 1-4. The geometry of the compounds under investigation is considered by possessing C₁ point group symmetry. The absence of imaginary frequencies confirmed that the stationary points correspond to minima on the Potential Energy Surface. The internal coordinates describe the position of the atoms in terms of distances, angles and dihedral angles with respect to an origin atom.

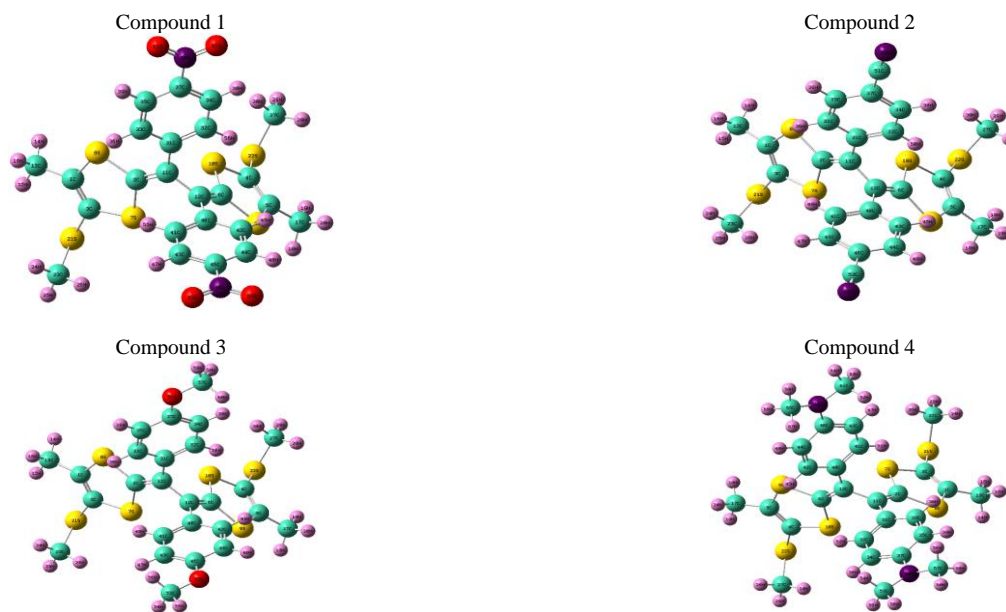


Fig. 1: Optimized Molecular Structure of Bis (1, 4-Dithiafulvalene) Derivatives 1-4.

Table 1: Optimized Geometric Parameters of Compound 1

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,3)	1.350	A(3,1,8)	116.253	D(13,1,3,7)	179.561
R(1,8)	1.772	A(3,1,13)	127.769	D(13,1,8,2)	179.992
R(1,13)	1.501	A(8,1,13)	115.978	D(3,1,13,16)	123.600
R(2,8)	1.781	A(7,2,8)	112.147	D(11,2,8,1)	177.211
R(2,11)	1.369	A(7,2,11)	121.689	D(21,3,7,2)	177.515
R(3,21)	1.774	A(1,3,21)	125.520	D(7,3,21,23)	75.448
R(11,12)	1.505	A(21,23,26)	111.004	D(10,4,5,17)	179.557
R(11,31)	1.480	A(24,23,26)	110.339	D(22,4,10,6)	177.520
R(13,15)	1.091	A(12,40,42)	122.991	D(4,5,17,20)	123.597
R(21,23)	1.839	A(40,41,43)	121.544	D(9,5,17,18)	63.317
R(23,25)	1.092	A(40,41,55)	119.251	D(2,11,12,6)	75.835
R(31,32)	1.412	A(43,46,44)	121.347	D(33,35,37,50)	179.610
R(32,56)	1.084	A(43,46,49)	119.332	D(12,40,42,44)	179.571
R(37,50)	1.465	A(46,49,54)	117.766	D(48,44,46,43)	178.256

Table 2: Optimized Geometric Parameters of Compound 2

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,3)	1.350	A(3,1,8)	116.268	D(13,1,3,7)	179.439
R(1,8)	1.772	A(3,1,13)	127.718	D(3,1,13,16)	123.976
R(1,13)	1.501	A(7,2,8)	112.140	D(8,1,13,14)	63.635
R(2,7)	1.776	A(7,2,11)	121.886	D(11,2,8,1)	177.900
R(2,11)	1.367	A(1,3,7)	117.393	D(21,3,7,2)	177.883
R(3,21)	1.774	A(2,11,12)	118.374	D(7,3,21,23)	74.911
R(11,12)	1.504	A(2,11,31)	124.689	D(10,4,5,17)	179.439
R(11,31)	1.482	A(12,11,31)	116.926	D(4,5,17,20)	123.975
R(13,14)	1.096	A(1,13,14)	111.031	D(12,6,9,5)	177.903
R(31,32)	1.411	A(21,23,24)	110.854	D(2,11,12,6)	75.417
R(32,34)	1.387	A(24,23,25)	109.485	D(4,22,27,28)	63.307
R(32,50)	1.084	A(31,32,50)	119.211	D(33,31,32,50)	178.894
R(35,37)	1.404	A(32,34,37)	120.144	D(11,31,33,35)	179.471
R(37,51)	1.432	A(37,34,38)	119.576	D(36,33,35,37)	177.676

Table 3: Optimized Geometric Parameters of Compound 3

Bond Length (Å)	Bond Angles (°)		Dihedral Angles (°)		
R(1,3)	1.350	A(3,1,8)	116.477	D(13,1,3,7)	179.419
R(1,8)	1.772	A(3,1,13)	127.548	D(13,1,8,2)	179.018
R(1,13)	1.501	A(8,1,13)	115.975	D(3,1,13,16)	124.026
R(2,8)	1.789	A(7,2,8)	112.214	D(8,1,13,14)	63.411
R(2,11)	1.361	A(1,3,7)	117.603	D(11,2,7,3)	179.766
R(3,21)	1.774	A(2,11,12)	119.748	D(11,2,8,1)	179.955
R(6,12)	1.361	A(2,11,31)	123.459	D(21,3,7,2)	178.590
R(11,12)	1.499	A(12,11,31)	116.761	D(22,4,10,6)	178.589
R(11,31)	1.489	A(1,13,16)	110.934	D(4,5,17,20)	124.028
R(13,14)	1.096	A(14,13,15)	108.444	D(9,5,17,18)	63.413
R(31,33)	1.409	A(11,31,32)	119.977	D(2,11,12,6)	71.877
R(33,36)	1.085	A(31,32,50)	119.129	D(33,31,32,50)	178.890
R(37,51)	1.366	A(37,34,38)	121.050	D(32,34,37,51)	179.881
R(51,57)	1.418	A(34,37,51)	124.811	D(35,37,57,60)	124.412

Table 4: Optimized Geometric Parameters of Compound 4

Bond Length (Å)	Bond Angles (°)		Dihedral Angles (°)		
R(1,3)	1.350	A(5,4,10)	117.650	D(13,1,3,7)	179.519
R(1,8)	1.772	A(5,4,22)	125.229	D(11,2,8,1)	178.720
R(1,13)	1.501	A(4,5,9)	116.506	D(21,3,7,2)	177.938
R(2,7)	1.784	A(9,6,10)	112.221	D(7,3,21,23)	74.278
R(3,7)	1.781	A(5,9,6)	97.149	D(10,4,5,17)	179.519
R(3,21)	1.775	A(6,12,40)	123.817	D(22,4,10,6)	177.937
R(11,12)	1.501	A(11,12,40)	116.855	D(17,5,9,6)	179.708
R(12,40)	1.486	A(22,27,28)	110.870	D(4,5,17,20)	124.123
R(13,14)	1.096	A(28,27,29)	109.508	D(12,6,9,5)	178.724
R(21,23)	1.839	A(40,41,51)	119.092	D(31,11,12,40)	69.723
R(23,24)	1.091	A(40,42,44)	122.061	D(3,21,23,24)	64.067
R(37,50)	1.392	A(43,46,49)	121.503	D(33,31,32,52)	178.262
R(43,47)	1.083	A(46,49,61)	119.160	D(39,35,37,34)	177.154
R(50,57)	1.453	A(46,49,65)	119.179	D(44,46,49,61)	168.527

3.2. Molecular electrostatic potential

Electrostatic potential maps are very useful, they enable us to visualize the charge distributions of molecules and charge related properties of molecules. They also allow us to visualize the size and shape of molecules. The different values of the electrostatic potential at the surface are represented by different colors. Potential increases in the ordered (most negative) < orange < yellow < green < blue (most positive). For investigating chemical reactivity of the molecule, molecular electrostatic potential (MEP) surface is plotted over the optimized electronic structure of bis (1, 4-dithiafulvalene) derivatives 1-4 using density functional B3LYP method with 6-31G (d,p) basis set. Because the computationally or experimentally observed MEP surface is directly provide information about the electrophilic (electronegative charge region) and nucleophilic (most positive charge region) regions. The electrostatic potential $V(r)$ at any point in space around a molecule by charge distribution is given by

$$V(r) = \sum Z_A / |R_A - r| - \int \rho(r') / |r' - r| d^3r'$$

Where $q(r)$ is the electron density function of the molecule, Z_A is the charge on the nucleus A located at R_A and r' is the dummy integration variable.

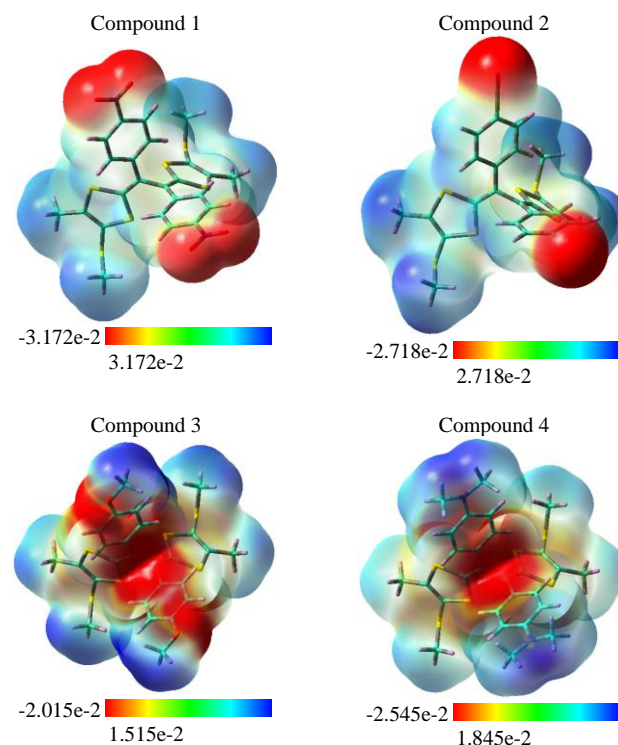


Fig. 2: Molecular Electrostatic Potential Surface of Bis (1, 4-Dithiafulvalene) Derivatives 1-4.

As seen from the Fig. 2 that, in all molecules, the regions exhibiting the negative electrostatic potential are localized near the TTF core and functional groupings (-NO₂, -CN, -OMe, -NMe₂) while the regions presenting the positive potential are localized vicinity of the hydrogen atoms of alkyl groups.

3.3. Frontier molecular orbitals (FMOs)

Molecular orbitals and their properties such as energy are very useful for physicists and chemists and are very important parameters for quantum chemistry. The most important orbitals in a mol-

ecule are the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Both the highest occupied molecular orbital and lowest unoccupied molecular orbital are the main orbital take part in chemical stability (Gunasekaran et al. 2008). The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. Recently, the energy gap between HOMO and LUMO has been used to prove the bioactivity from intra-molecular charge transfer (ICT) (Padmaja et al. 2009; Sagdinc et al. 2009), and describes the chemical reactivity, optical polarizability, kinetic stability, and chemical softness-hardness of a molecule. The molecules having a small energy gap are known as soft and having a large energy gap are known as hard molecules. The HOMO and LUMO energies of compound 1 calculated by the DFT level and B3LYP/6-31G (d,p) method are listed in Table 5. Besides, the pictorial representation of their HOMO-LUMO distribution and their respective positive and negative regions is shown in Fig. 3. The positive and negative phase is represented in green and red color, respectively.

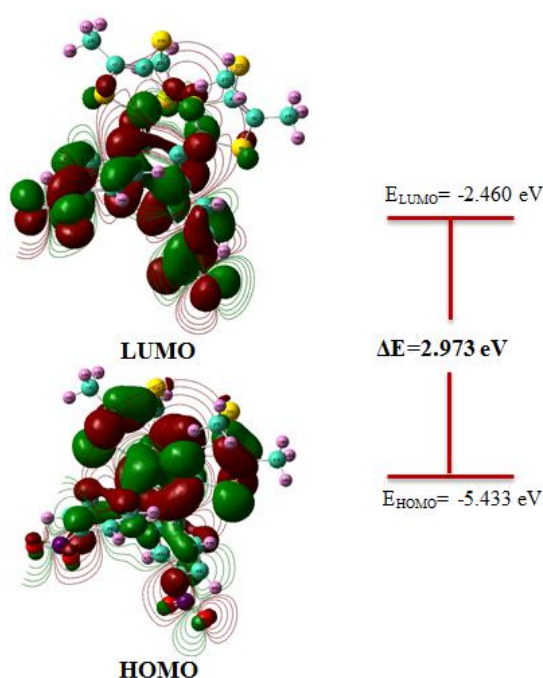


Fig. 3: HOMO-LUMO Structure with the Energy Level Diagram of Compound 1.

3.4. Global reactivity descriptors

The highest occupied molecular orbitals (HOMO) and the lowest-lying unoccupied molecular orbitals (LUMO), also called frontier molecular orbitals (FMOs), play an important role in many properties of a compound as well as in quantum chemistry and UV-VIS spectra. The energy gap between the HOMO and LUMO is very important for determining the electrical properties, kinetic stability, optical polarizability and chemical reactivity descriptors, such as hardness and softness of a molecule. The concept of hardness (η) and softness is related to a compound's reactivity and is a property that measures the extent of chemical reactivity to which the addition of a charge stabilizes the system. The chemical potential (μ) provide a global reactivity index and is related to charge transfer from a system of higher chemical potential to one of lower chemical potential. Electronegativity (χ) is the power to attract electrons and is directly related to all the previously mentioned properties. All these properties are defined as follows (Özdemir et al. 2013; Parr et al. 1989; Parr et al. 1999):

$$\chi = (E_{\text{HOMO}} - E_{\text{LUMO}}) / 2$$

$$\mu = -(IE + EA) / 2 = (E_{N+1} - E_{N-1}) / 2 = -\chi$$

$$\eta = (IE - EA) / 2 = (E_{N-1} - E_{N+1} - 2E_N) / 2$$

$$S = 1 / 2\eta$$

Where (A) is the ionization potential and (I) is the electron affinity of the molecule. The ionization energy and electron affinity are obtained from the HOMO and LUMO energies as $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$ according to the Janak theorem (Janak et al. 1978) and Perdew et al. (Perdew et al. 1982). In terms of chemical hardness, a large HOMO-LUMO gap indicates a hard molecule and is related to more stable molecules, whereas a small gap indicates a soft molecule and is related to a more reactive molecule. Another important descriptor is the electrophilicity index (ω) (Özdemir et al. 2013) that measures the energy lowering due to charge transfer. The electrophilicity index is defined as follows:

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

The energies of frontier molecular orbitals (E_{HOMO} , E_{LUMO}), energy gap ($E_{\text{LUMO}} - E_{\text{HOMO}}$), electronegativity (χ), chemical potential (μ), global hardness (η), global softness (S), and global electrophilicity index (ω) for compounds 1-4 are given in Table 5.

Table 5: Quantum Chemical Descriptors of Bis (1, 4-Dithiafulvalene) Derivatives 1-4

Parameters	compound 1	compound 2	compound 3	compound 4
E_{HOMO} (eV)	-5.433	-5.317	-4.533	-4.231
E_{LUMO} (eV)	-2.460	-1.803	-0.491	-0.262
ΔE_{gap} (eV)	2.973	3.514	4.042	3.969
IE (eV)	5.433	5.317	4.533	4.231
EA (eV)	2.460	1.803	0.491	0.262
μ (eV)	-3.947	-3.560	-2.512	-2.247
χ (eV)	3.947	3.560	2.512	2.247
η (eV)	1.487	1.757	2.021	1.984
S (eV)	0.336	0.285	0.247	0.252
ω (eV)	5.239	3.606	1.561	1.272

As shown in table 5, the compound which have the lowest energetic gap is the compound 1 ($\Delta E_{\text{gap}} = 2.973$ eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound 3 ($\Delta E_{\text{gap}} = 4.042$ eV). The compound that has the highest HOMO energy is the compound 4 ($E_{\text{HOMO}} = -4.231$ eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound 1 ($E_{\text{LUMO}} = -2.460$ eV) which signifies that it can be the best electron acceptor. The two properties like I (potential ionization) and A (affinity) are so important, the determination of these two properties allow us to calculate the absolute electronegativity (χ) and the absolute hardness (η). These two parameters are related to the one-electron orbital energies of the HOMO and LUMO respectively. Compound 4 has lowest value of the potential ionization ($I = 4.231$ eV), so that will be the better electron donor. Compound 1 has the largest value of the affinity ($A = 2.460$ eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound 1 ($\eta = 1.487$ eV, $S = 0.336$ eV) is lesser (greater) among all the molecules. Thus, compound 1 is found to be more reactive than all the compounds. Compound 1 possesses higher electronegativity value ($\chi = 3.947$ eV) than all compounds so; it is the best electron acceptor. The value of ω for compound 1 ($\omega = 5.239$ eV) indicates that it is the stronger electrophiles than all compounds. Compound 1 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

Fukui functions (FF) are used to depict the chemical reactivity and site selectivity of the molecule. Fukui function is reactive de-

scriptor to identify nucleophilic and electrophilic attack sites in particular molecule, perhaps it is also used to recognize the electron acceptor centre and donor centre. Thus, for an atom k in a molecule, three kinds of condensed Fukui function (for nucleophilic, electrophilic and radical attack) at atom k can be obtained depending upon the type of electron transfer. Which are defined by equations in finite difference approximation. According to Parr and Yang (Parr et al. 1984), the sites, which have highest values of Fukui function $f(r)$, are more reactive centers in chemical species.

$$f^+ = [q(N+1) - q(N)], \text{ for nucleophilic attack,}$$

$$f^- = [q(N) - q(N-1)], \text{ for electrophilic attack,}$$

$$f^0 = [q(N+1) - q(N-1)]/2, \text{ for radical attack.}$$

where, q is the gross charge of atom k in the molecule and N , $N+1$, $N-1$ are electron systems containing neutral, anion, cation form of molecule respectively. Where $+$, $-$, 0 signs show nucleophilic, electrophilic and radical attack respectively. Fukui functions for selected atomic sites in bis (1, 4-dithiafulvalene) derivatives 1-4 are shown in Tables 6-7.

Table 6: Order of the Reactive Sites on Compounds 1 and 2

Compound 1					Compound 2				
Ato	52	53	51	54	Ato	52	54	6 C	2 C
m	O	O	O	O	m	N	N		
f^+	0.19	0.19	0.19	0.19	f^+	0.22	0.22	0.13	0.13
	9	9	9	9		0	0	0	0
Ato	49	50	37	46	Ato	51	53	40	31
m	N	N	C	C	m	C	C	C	C
	-	-	-	-		-	-	-	-
f^-	0.36	0.36	0.21	0.21	f^-	0.16	0.16	0.13	0.13
	4	4	2	2		9	9	7	7
Ato	6 C	2 C	3 C	4 C	Ato	6 C	2 C	3 C	4 C
m					m				
	-	-	-	-		-	-	-	-
f^0	0.13	0.13	0.08	0.08	f^0	0.00	0.00	0.00	0.00
	6	6	8	8		6	6	9	9

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
π (C35 - C37)	1.63834	π^* (N50-O51)	0.63660	26.00	0.15	0.059
π (C44-C46)	1.63834	π^* (N49-O54)	0.63660	26.00	0.15	0.059
π (C31-C33)	1.60761	π^* (C35-C37)	0.39048	24.66	0.27	0.073
π (C40-C42)	1.60761	π^* (C44-C46)	0.39048	24.66	0.27	0.073
LP(2)S8	1.74078	π^* (C1-C3)	0.26434	23.41	0.26	0.069
LP(2)S9	1.74078	π^* (C4-C5)	0.26434	23.41	0.26	0.069
LP(2)S7	1.74072	π^* (C2-C11)	0.33205	22.27	0.26	0.069
LP(2)S10	1.74072	π^* (C6-C12)	0.33205	22.27	0.26	0.069
LP(2)S8	1.74078	π^* (C2-C11)	0.33205	21.39	0.26	0.068
LP(2)S9	1.74078	π^* (C6-C12)	0.33205	21.39	0.26	0.068
π (C35-C37)	1.63834	π^* (C32-C34)	0.28009	20.45	0.30	0.071
π (C44-C46)	1.63834	π^* (C41-C43)	0.28009	20.45	0.30	0.071
π (C32-C34)	1.66762	π^* (C31-C33)	0.37308	20.42	0.28	0.068
LP(2)S7	1.74072	π^* (C1-C3)	0.26434	19.68	0.25	0.063
LP(2)O51	1.89907	σ^* (N50-O52)	0.05684	19.24	0.70	0.105
LP(2)O54	1.89907	σ^* (N49-O53)	0.05684	19.24	0.70	0.105
π (C31-C33)	1.60761	π^* (C2-C11)	0.33205	12.06	0.25	0.050
π (C40-C42)	1.60761	π^* (C6-C12)	0.33205	12.06	0.25	0.050
π (N49- O54)	1.98559	LP(3)O53	1.45041	12.06	0.18	0.077
π (N50-O51)	1.98559	LP(3)O52	1.45041	12.06	0.18	0.077

Table 7: Order of the Reactive Sites on Compounds 3 and 4

Compound 3					Compound 4				
Ato	52	51	6 C	2 C	Ato	49	50	6 C	2 C
m	O	O			m	N	N		
f^+	0.33	0.33	0.11	0.11	f^+	0.27	0.27	0.12	0.12
	3	3	8	8		1	1	2	2
Ato	46	37	40	31	Ato	46	37	40	31
m	C	C	C	C	m	C	C	C	C
	-	-	-	-		-	-	-	-
f^-	0.25	0.25	0.11	0.11	f^-	0.25	0.25	0.12	0.12
	1	1	0	0		4	4	2	2
Ato	31	40	4 C	3 C	Ato	40	31	4 C	3 C
m	C	C			m	C	C		
	-	-	-	-		-	-	-	-
f^0	0.00	0.00	0.01	0.01	f^0	0.00	0.00	0.00	0.00
	4	4	0	0		2	2	8	8

From the tables 6-7, the parameters of local reactivity descriptors show that 52O is the more reactive site in compounds 1, 3 and 52N, 49N for compounds 2 and 4 respectively for nucleophilic attacks. The more reactive sites in radical attacks are 6C for compounds 1, 2 and 31C, 40C for compound 3 and compound 4 respectively. The more reactive sites for electrophilic attacks are 49N, 51C, 46C and 46C for compounds 1, 2, 3 and 4 respectively.

3.6. Natural bond orbital analysis (NBO)

The second order Fock matrix was carried out to evaluate the donor-acceptor interactions in the NBO analysis (Krishna Kumar et al. 2014). For each donor (i) and acceptor (j), the stabilization energy $E(2)$ associated with the delocalization $i - j$ is estimated as,

$$E(2) = \Delta E_{ij} = q_i \frac{F^2(i,j)}{E_j - E_i}$$

Where q_i is the donor orbital occupancy, i and j are diagonal elements and $F(i, j)$ is the off diagonal NBO Fock matrix element. The larger the $E(2)$ value, the more intensive is the interaction between electron donors and electron acceptors.

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
π (C31-C33)	1.61328	π^* (C35-C37)	0.39982	23.94	0.27	0.072
π (C40-C42)	1.61328	π^* (C44-C46)	0.39982	23.94	0.27	0.072
LP(2)S8	1.74588	π^* (C1-C3)	0.26481	23.32	0.26	0.069
LP(2)S9	1.74588	π^* (C4-C5)	0.26481	23.32	0.26	0.069
LP(2)S7	1.74635	π^* (C2-C11)	0.32677	21.94	0.26	0.069
LP(2)S10	1.74635	π^* (C6-C12)	0.32678	21.94	0.26	0.069
LP(2)S8	1.74588	π^* (C2-C11)	0.32677	21.04	0.26	0.068
LP(2)S9	1.74588	π^* (C6-C12)	0.32678	21.04	0.26	0.068
π (C35-C37)	1.64298	π^* (C32-C34)	0.28629	19.95	0.29	0.069
π (C44-C46)	1.64298	π^* (C41-C43)	0.28629	19.95	0.29	0.069
π (C32-C34)	1.67341	π^* (C31-C33)	0.37264	19.80	0.28	0.068
π (C41-C43)	1.67341	π^* (C40-C42)	0.37264	19.80	0.28	0.068
LP(2)S7	1.74635	π^* (C1-C3)	0.26481	19.63	0.25	0.063
LP(2)S10	1.74635	π^* (C4-C5)	0.26481	19.63	0.25	0.063
π (C35-C37)	1.64298	π^* (C31-C33)	0.37264	18.56	0.28	0.065
π (C44-C46)	1.64298	π^* (C40-C42)	0.37264	18.56	0.28	0.065
π (C32-C34)	1.67341	π^* (C35-C37)	0.39982	18.30	0.28	0.065
π (C41-C43)	1.67341	π^* (C44-C46)	0.39982	18.30	0.28	0.065
LP(1)N52	1.97021	σ^* (C37-C51)	0.03053	12.52	1.02	0.101
LP(1)N54	1.97021	σ^* (C46-C53)	0.03053	12.52	1.02	0.101

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)O51	1.84014	π^* (C34-C37)	0.39893	30.49	0.34	0.097
LP(2)O52	1.84014	π^* (C44-C46)	0.40097	27.54	0.34	0.092
LP(2)S8	1.76263	π^* (C1-C3)	0.26853	23.46	0.26	0.070
LP(2)S9	1.76263	π^* (C4-C5)	0.26853	23.46	0.26	0.070
π (C44-C46)	1.61779	π^* (C40-C42)	0.39791	23.18	0.29	0.073
π (C40-C42)	1.63471	π^* (C41-C43)	0.35554	23.15	0.27	0.071
π (C41-C43)	1.69661	π^* (C44-C46)	0.40097	22.45	0.28	0.072
π (C34-C37)	1.65490	π^* (C31-C32)	0.36856	22.18	0.30	0.073
π (C31-C32)	1.65388	π^* (C33-C35)	0.31741	21.52	0.28	0.070
LP(2)S7	1.76767	π^* (C2-C11)	0.30192	20.32	0.27	0.067
LP(2)S10	1.76767	π^* (C6-C12)	0.30193	20.32	0.27	0.067
π (C40-C42)	1.63471	π^* (C44-C46)	0.40097	19.62	0.27	0.065
LP(2)S7	1.76767	π^* (C1-C3)	0.26853	19.45	0.25	0.063
LP(2)S10	1.76767	π^* (C4-C5)	0.26853	19.45	0.25	0.063
LP(2)S8	1.76263	π^* (C2-C11)	0.30192	19.37	0.27	0.066
π (C33-C35)	1.71005	π^* (C31-C32)	0.36856	16.76	0.29	0.063
π (C34-C37)	1.65490	π^* (C33-C35)	0.31741	16.68	0.29	0.063
π (C41-C43)	1.69661	π^* (C40-C42)	0.39791	16.47	0.29	0.063
LP(1)O51	1.96375	σ^* (C34-C37)	0.02859	7.44	1.11	0.081
LP(1)O52	1.96375	σ^* (C43-C46)	0.02859	7.44	1.11	0.081

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(1)N49	1.74371	π^* (C44-C46)	0.42884	39.44	0.28	0.098
LP(1)N50	1.74371	π^* (C35-C37)	0.42884	39.44	0.28	0.098
π (C35-C37)	1.62704	π^* (C31-C33)	0.39573	23.92	0.29	0.074
π (C44-C46)	1.62704	π^* (C40-C42)	0.39573	23.92	0.29	0.074
LP(2)S8	1.76549	π^* (C1-C3)	0.26906	23.45	0.25	0.070
LP(2)S9	1.76549	π^* (C4-C5)	0.26906	23.45	0.25	0.070
π (C31-C33)	1.64871	π^* (C32-C34)	0.32807	22.54	0.28	0.071
π (C40-C42)	1.64871	π^* (C41-C43)	0.32806	22.54	0.28	0.071
π (C32-C34)	1.72230	π^* (C35-C37)	0.42884	20.72	0.28	0.070
π (C41-C43)	1.72230	π^* (C44-C46)	0.42884	20.72	0.28	0.070
LP(2)S7	1.77013	π^* (C2-C11)	0.30150	19.94	0.27	0.066
LP(2)S7	1.77013	π^* (C1-C3)	0.26906	19.54	0.25	0.063
LP(2)S8	1.76549	π^* (C2-C11)	0.30150	18.99	0.27	0.065
LP(2)S9	1.76549	π^* (C6-C12)	0.30150	18.99	0.27	0.065
π (C31-C33)	1.64871	π^* (C35-C37)	0.42884	17.99	0.27	0.063
π (C40-C42)	1.64871	π^* (C44-C46)	0.42884	17.99	0.27	0.063
π (C44-C46)	1.62704	π^* (C41-C43)	0.32806	15.96	0.29	0.061
π (C40-C42)	1.64871	π^* (C6-C12)	0.30150	10.81	0.26	0.048
π (C31-C33)	1.64871	π^* (C2-C11)	0.30150	10.80	0.26	0.048
LP(1)N49	1.74371	σ^* (C65-H67)	0.02489	7.62	0.67	0.068

intra molecular interaction for the title compounds is formed by the orbital overlap between: π (C35-C37) and π^* (N50-O51) for compound 1, π (C31-C33) and π^* (C35-C37) for compound 2, π (C44-C46) and π^* (C40-C42) for compound 3 and π (C35-C37) and π^* (C31-C33) for compound 4 respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of π (C35-C37) to π^* (N50-O51) for compound 1, π (C31-C33) to

π^* (C35-C37) for compound 2, π (C44-C46) to π^* (C40-C42) for compound 3 and π (C35-C37) to π^* (C31-C33) for compound 4 lead to highest stabilization of 26.00, 23.94, 23.18 and 23.92 kJ mol⁻¹ respectively. In case of LP(2)S8 orbital to the π^* (C1-C3) for compound 1, LP(2)S8 orbital to π^* (C1-C3) for compound 2, LP(2)O51 orbital to π^* (C34-C37) for compound 3, LP(1)N49 orbital to π^* (C44-C46) for compound 4 respectively, show the stabilization energy of 23.41, 23.32, 30.49 and 39.44 kJ mol⁻¹ respectively.

3.7. Nonlinear optical properties (NLO)

Nonlinear optical effects arise from the interactions of the electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristic from the incident fields [25], [26]. NLO is at the forefront of current research because of its importance in providing the key functions of frequency shifting; optical modulation, optical switching, optical logic and optical memory for the emerging technologies in area such as telecommunications, signal processing and optical inter connections [24]. Dipole moment is one of the important qualities which are of fundamental importance in structural chemistry. It can be used as a descriptor to illustrate the charge movement across the molecule. The first hyperpolarizability (β_0) of this novel molecular system and the related properties of bis (1, 4-dithiafulvalene) derivatives 1-4 are calculated using the B3LYP/6-31G (d,p) basis set based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first hyperpolarizability is a third-rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry. It can be given in the lower tetrahedral. The components of β are defined as the coefficient in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous this expansion becomes:

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

Where E^0 is the energy of the unperturbed molecule, F_i the field at the origin and μ_i , μ_{ij} and β_{ijk} are the components of dipole moment, polarizability and the first hyperpolarizability respectively. The total static dipole moment (μ), polarizability (α), mean polarizability ($\Delta\alpha$) and the mean first hyperpolarizability (β) using the (x,y,z) components are defined as follows:

$$\mu_{tot} = [\mu_x^2 + \mu_y^2 + \mu_z^2]^{1/2}$$

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

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

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

$$\beta_x = \beta_{xxx} + \beta_{xyx} + \beta_{xzx}$$

$$\beta_y = \beta_{yyy} + \beta_{xyy} + \beta_{yyz}$$

$$\beta_z = \beta_{zzz} + \beta_{xzz} + \beta_{zyz}$$

Table 12 lists the values of the electric dipole moment (Debye) and dipole moment components. Polarizabilities and hyperpolarizabilities of bis (1, 4-dithiafulvalene) derivatives 1-4 In addition to the isotropic polarizabilities and polarizabilities anisotropy invariant were also calculated.

Table 12: The Dipole Moments μ (D), Polarizability A, the Average Polarizability A (Esu), the Anisotropy of the Polarizability $\Delta\alpha$ (Esu), and the First Hyperpolarizability B (Esu) of Bis (1, 4-Dithiafulvalene) Derivatives 1-4 Calculated by B3LYP/6-31G (D, P) Method

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
β_{xxx}	193.3866	382.2072	122.8609	223.2427
β_{yyy}	-0.2441	0.0116	0.0119	0.0024
β_{zzz}	0.0825	-0.0020	0.0268	0.0065
β_{xyy}	302.7627	69.0013	-44.6374	39.1889
β_{xxy}	0.1097	0.0023	-0.0310	-0.0072
β_{xxz}	-0.0116	0.0011	-0.0071	-0.0097
β_{xzz}	109.1390	390.0507	54.5567	23.5363
β_{yzz}	-0.0010	0.0171	-0.0001	-0.0037
β_{yyz}	0.0261	-0.0017	-0.0086	0.0048
β_{xyz}	64.3172	-22.5447	43.1915	-80.4254
$\beta_{tot}(\text{esu}) \times 10^{-33}$	615.0252	841.2592	132.7802	285.9679
μ_x	9.2119	8.4084	1.6060	4.8671
μ_y	-0.0026	0.0003	-0.0001	-0.0001
μ_z	0.0015	-0.0001	0.0004	0.0002
$\mu_{tot}(\text{D})$	9.2119	8.4084	1.6060	4.8671
α_{xx}	-295.5875	-294.6684	-238.9058	-235.3163
α_{yy}	-284.5214	-191.1230	-207.4160	-232.2450
α_{zz}	-207.5975	-278.3674	-220.4466	-220.6181
α_{xy}	0.0052	-0.0044	0.0022	0.0005
α_{xz}	-0.0285	0.0003	-0.0001	0.0000
α_{yz}	-12.5171	-3.8179	17.9026	4.3814
$\alpha_0(\text{esu}) \times 10^{-24}$	85.7964	96.6603	41.3834	15.4246
$\Delta\alpha(\text{esu}) \times 10^{-24}$	12.7150	14.3251	6.1330	2.2859

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. = 0.1482×10^{-24} e.s.u., for β ; 1 a.u. = 8.6393×10^{-33} e.s.u.). The calculated values of dipole moment (μ) for the title compounds were found to be 9.2119, 8.4084, 1.6060 and 4.8671 D respectively, which are approximately 10 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 85.7964×10^{-24} , 96.6603×10^{-24} , 41.3834×10^{-24} and 15.4246×10^{-24} esu respectively; the values of anisotropy of the polarizability are 12.7150, 14.3251, 6.1334 and 2.2859 esu, respectively. The magnitude of the molecular hyperpolarizability (β) is one of important key factors in a NLO system. The DFT/6-31G (d,p) calculated first hyperpolarizability value (β) of tetrathiafulvalenes molecules are equal to 615.0252×10^{-33} , 841.2592×10^{-33} , 132.7802×10^{-33} and 285.9679×10^{-33} esu. The first hyperpolarizability of title molecules is approximately 1.79, 2.45, 0.04 and 0.83 times than those of urea (β of urea is 343.272×10^{-33} esu obtained by B3LYP/6-311G (d,p) method). This result indicates the non-linearity of the compounds 1 and 2 of bis (1,4-dithiafulvalene) derivatives 1-4 and indicates at the same time that compound 3 and 4 are not nonlinear.

4. Conclusion

From the whole of the results presented in this contribution it has been clearly demonstrated that the sites of interaction of the title compounds 1-4 can be predicted by using DFT-based reactivity descriptors such as the hardness, softness, and electrophilicity, as well as Fukui-function calculations. These descriptors were used in the characterization and successfully description of the preferred reactive sites and provide a firm explanation for the reactivity of bis (1, 4-dithiafulvalene) derivatives 1-4.

NLO behavior of the title molecule has been investigated by dipole moment, polarizability and first hyperpolarizability. The lowest singlet excited state of the molecule is mainly derived from the HOMO \rightarrow LUMO ($\pi \rightarrow \pi^*$) electron transition, NBO analysis reveals that the some important intramolecular charge transfer can

induce large nonlinearity to the title molecule and the intramolecular conjugative interaction around the tetrathiafulvalene core can induce the large conductivity in the compound. Finally we hope that these consequences will be of assistance in the quest of the experimental and theoretical evidence for the title compounds in molecular bindings.

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