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Density functional theory studies on the structure and first order molecular hyperpolarizability of di (tert-butylbenzylthio) tetrathiafulvalene derivatives

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Abstract
The molecular structure of di(tert-butylbenzylthio) tetrathiafulvalene derivatives was investigated by density functional theory employing Becke's three parameter hybrid exchange functional with Lee-Yang-Parr (B3LYP) co-relational functional involving 6-31G(d,p) basis set. The non-linear optical (NLO) properties of the title molecules are computed. The first order hyperpolarizability (β_0) of the molecular system and related properties (β, α_0 and $\Delta\alpha$) are calculated using DFT method on the basis of finite-field approach. The molecular electrostatic potential (MEP) surface maps are plotted and explained in detail. The significant changes in occupancies and the energies of bonding and antibonding orbital have been explained in detail. Reactivity descriptors, Fukui functions and electrophilic sites are found and discussed.

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

1. Introduction

Tetrathiafulvalene (TTF) and its derivatives are well-known as π-electron-donor materials within the field of organic conductors [1]. As a result of progress in synthetic TTF chemistry, TTFs are incorporated into variety of macrocyclic, molecular, and supramolecular systems so as to form multifunctional materials with desired structures, stability, and physical properties [1-3]. So, considerable efforts are presently devoted to the modification of the TTF core with substituents like pyridine-type Heterocycles [4], acetylacetonates [5], and phosphines [6], all of which are well tailored for a chelating coordination function toward varied transition metal ions. On the opposite hand, TTFs are often used as donor units in donor-acceptor (D-A) ensembles, which are of significant research interest thanks to their potential applications in sensors, optoelectronics, and molecular devices [3, 7]. D-π-A systems have gained increasing attention as the π-conjugated spacer might optimize the communication between the D and A units [3, 8].

Development of nonlinear optical materials has been enhanced over the past few years as a result of their applications such as frequency conversion, frequency mixing, optical data storage, electro-optical modulation, optical parametric oscillation, etc [9]. particularly, the organic materials are more appropriate for the above applications, as a result of they have high nonlinear optical susceptibility compared to inorganic compounds because of delocalized electrons at π - π* orbitals. In organic materials, the hyperpolarizability of molecules tends to the macroscopic nonlinear response and additionally it's proper orientation in solid state facilitate high frequency conversion efficiency [10].

Metal-organic materials show good thermal stability and wide optical transmittance compared to organic materials and the mechanical behavior of these materials has been improved compared to inorganic materials [11]. Metal-organic materials have conjointly advantages over organic and inorganic ones due to the structural modifiability of organic ligands and the diversity of electronic properties tunable by virtue of the coordinated metal center. Up to now, the nonlinear optical (NLO) properties of various classes of organic materials are investigated within the search for new and more effective NLO materials [12, 13].

In this paper and in the objective to study the properties of a series of di(tert-butylbenzylthio) tetrathiafulvalene derivatives 1-4 molecules described in literature [14] and to predict their

applications, we provides a complete description of the molecular geometry and also the electronic properties such as HOMO-LUMO energy gap, nonlinear optical properties (NLO), chemical hardness, and chemical potential.

2. Materials and methods

All calculations were performed using the Gaussian 09W package. The traditional hybrid Becke, three-parameter, Lee-Yang-Parr (B3LYP) exchange correlation functions of the Density Functional Theory (DFT) was applied using 6-31G(d,p) basis set. The geometry of di(tert-butylbenzylthio) tétrathiafulvalènes derivatives was fully optimized at the afore mentioned levels of theory.

3. Results and discussion

3.1 Molecular Geometry

The molecular structure of di(tert-butylbenzylthio) tetrathiafulvalene derivatives 1-4 belongs to C1 point group symmetry. The optimized molecular structure of the title molecule shown in Figure 1 was obtained using Gaussian 09 program. The optimized bond lengths, bond angles and torsional angles of compounds 1-4 are listed in Tables 1-4. To the best of our knowledge, exact theoretical data on the geometrical parameters of di(tert-butylbenzylthio) tetrathiafulvalene derivatives is not available in the literature.

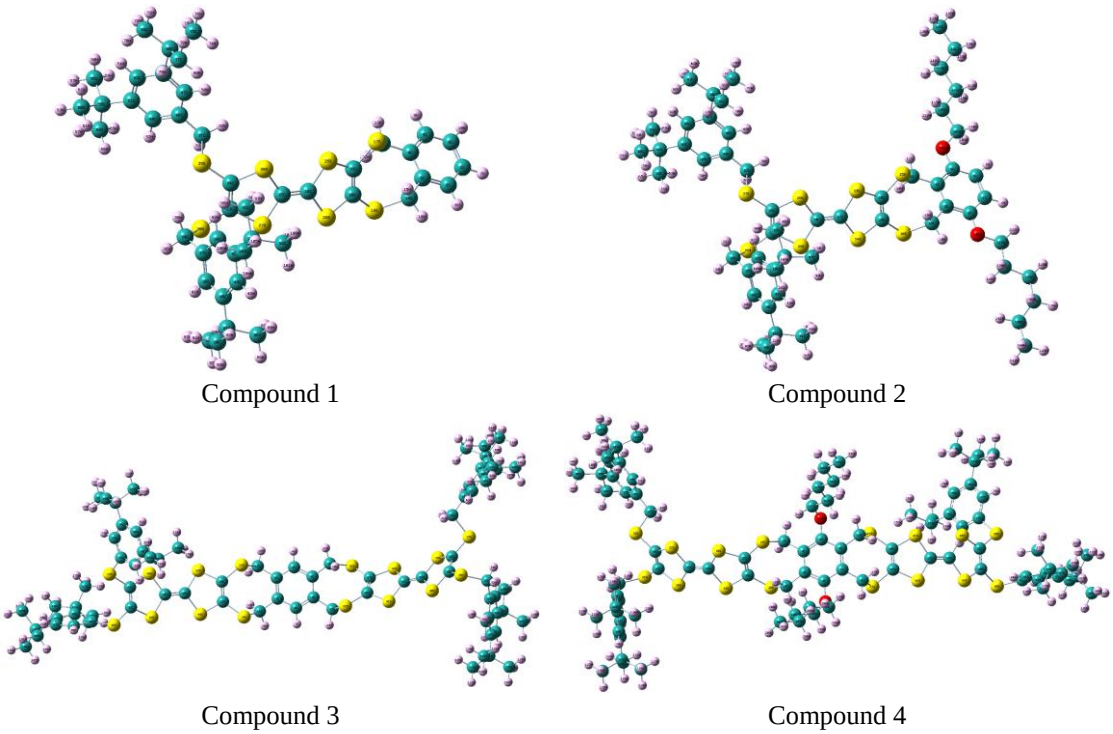

Fig 1: Optimized molecular structure of di(tert-butylbenzylthio) tetrathiafulvalene derivatives 1-4.

Table 1: Optimized geometric parameters of compound 1

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.395	A(2,1,6)	119.434	D(7,1,2,3)	179.756
R(1,7)	1.086	A(6,1,7)	120.589	D(2,3,4,11)	176.460
R(3,14)	1.510	A(1,2,3)	121.795	D(2,3,14,15)	114.693
R(14,18)	1.859	A(2,3,14)	117.727	D(4,3,14,16)	177.224
R(19,22)	1.349	A(4,11,17)	115.277	D(3,4,11,13)	177.008
R(19,25)	1.779	A(12,11,13)	107.629	D(5,4,11,12)	114.429
R(20,21)	1.353	A(15,14,18)	106.538	D(4,5,6,10)	179.739
R(22,28)	1.781	A(25,19,26)	113.101	D(13,11,17,21)	127.370
R(23,30)	1.771	A(17,21,20)	129.624	D(16,14,18,20)	127.682
R(29,31)	1.871	A(20,21,25)	116.636	D(26,19,22,28)	178.615
R(31,46)	1.505	A(24,23,30)	127.779	D(22,19,26,20)	164.959
R(39,43)	1.084	A(27,23,30)	115.320	D(26,20,21,17)	177.650
R(46,47)	1.394	A(28,24,29)	117.221	D(19,22,28,24)	160.764
R(51,55)	1.541	A(69,68,77)	108.129	D(35,34,37,38)	157.165
R(55,56)	1.547	A(78,77,80)	107.722	D(34,37,38,40)	179.463

Table 2: Optimized geometric parameters of compound 2

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.393	A(2,1,7)	120.856	D(7,1,2,3)	179.776
R(1,7)	1.083	A(1,2,106)	123.354	D(106,2,3,4)	179.944
R(2,106)	1.371	A(2,3,12)	117.539	D(3,2,106,119)	179.145
R(3,12)	1.510	A(4,9,15)	115.585	D(2,3,4,9)	177.129
R(12,16)	1.860	A(13,12,16)	106.409	D(12,3,4,5)	176.961
R(17,20)	1.349	A(20,17,23)	123.288	D(2,3,12,13)	114.716
R(17,23)	1.779	A(23,17,24)	113.231	D(4,3,12,14)	177.199
R(18,19)	1.353	A(16,18,19)	129.910	D(3,4,5,105)	179.999
R(20,25)	1.783	A(15,19,23)	113.510	D(3,4,9,11)	177.281
R(22,26)	1.787	A(17,20,26)	123.786	D(5,4,9,10)	114.959
R(27,29)	1.871	A(26,22,27)	117.199	D(4,5,105,107)	177.974
R(49,53)	1.541	A(22,27,29)	101.323	D(11,9,15,19)	127.250
R(51,52)	1.083	A(30,29,31)	109.174	D(14,12,16,18)	126.600
R(106,119)	1.426	A(5,105,107)	119.112	D(24,17,20,26)	178.263
R(119,120)	1.522	A(119,120,123)	112.256	D(20,17,24,18)	167.148

Table 3: Optimized geometric parameters of compound 3

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.398	A(2,1,6)	118.379	D(18,1,6,5)	179.738
R(2,3)	1.398	A(6,1,18)	122.882	D(6,1,18,20)	160.082
R(4,9)	1.509	A(5,4,9)	117.878	D(2,3,4,9)	176.915
R(6,15)	1.505	A(6,5,8)	118.333	D(12,3,4,5)	176.724
R(9,21)	1.860	A(1,6,15)	122.863	D(2,3,12,13)	114.840
R(15,23)	1.872	A(3,12,13)	111.950	D(4,3,12,14)	177.189
R(22,26)	1.773	A(16,15,23)	104.670	D(3,4,9,11)	176.247
R(25,34)	1.349	A(19,18,20)	107.518	D(5,4,9,10)	113.834
R(26,27)	1.353	A(9,21,27)	102.661	D(4,5,6,15)	179.028
R(28,44)	1.783	A(34,25,42)	123.499	D(8,5,6,1)	179.705
R(31,45)	1.781	A(21,27,42)	113.766	D(5,6,15,17)	140.948
R(34,40)	1.782	A(31,28,43)	123.952	D(11,9,21,27)	127.567
R(49,50)	1.092	A(23,30,29)	127.396	D(14,12,22,26)	127.799
R(55,56)	1.394	A(28,31,45)	123.665	D(16,15,23,30)	133.531
R(60,62)	1.407	A(33,32,45)	116.884	D(1,18,24,29)	105.892

Table 4: Optimized geometric parameters of compound 4

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.408	A(2,1,6)	118.940	D(2,1,6,13)	179.891
R(2,190)	1.384	A(2,1,16)	119.377	D(16,1,6,5)	174.054
R(4,7)	1.508	A(1,2,190)	118.987	D(6,1,16,18)	161.448
R(7,8)	1.090	A(4,3,10)	123.113	D(1,2,3,10)	175.137
R(7,19)	1.860	A(3,10,11)	112.048	D(190,2,3,4)	179.650
R(19,25)	1.777	A(12,10,20)	104.473	D(2,3,4,7)	172.135
R(23,32)	1.349	A(1,16,18)	111.342	D(10,3,4,5)	176.402
R(24,25)	1.353	A(13,21,28)	102.994	D(2,3,10,11)	116.107
R(34,35)	1.768	A(20,24,39)	112.669	D(4,3,10,12)	176.256
R(35,47)	1.871	A(29,26,41)	123.754	D(5,4,7,8)	118.339
R(50,62)	1.503	A(37,32,38)	112.379	D(5,6,13,15)	147.858
R(56,102)	1.541	A(29,44,31)	94.661	D(9,7,19,25)	123.746
R(98,101)	1.096	A(35,47,53)	109.313	D(12,10,20,24)	128.542
R(115,116)	1.547	A(47,53,55)	120.067	D(14,13,21,28)	134.071
R(120,122)	1.095	A(54,56,102)	119.619	D(190,191,192,195)	178.169

3.2 Molecular Electrostatic Potential

The Molecular Electrostatic Potential (MEP) is a plot of electrostatic potential mapped onto the constant electron density surface. The MEP has been used primarily for predicting sites and relative reactivities towards electrophilic attack, in studies of chemical recognition and hydrogen bonding interactions [15, 16]. The different values of the electrostatic potential at the surface are represented by different colors; red represents regions of most negative electrostatic potential (preferred site for electrophilic attack), blue represents regions of most positive electrostatic potential (preferred site for nucleophilic attack) and green represents regions of zero potential. Potential increases in the order red < orange < yellow < green < blue. To predict reactive sites for electrophilic and nucleophilic attack for di(tert-butylbenzylthio) tetrathiafulvalene derivatives 1-4, the MEP at the B3LYP/6-31G(d,p) method was calculated and 3D plots of MEP is illustrated in Figure 2.

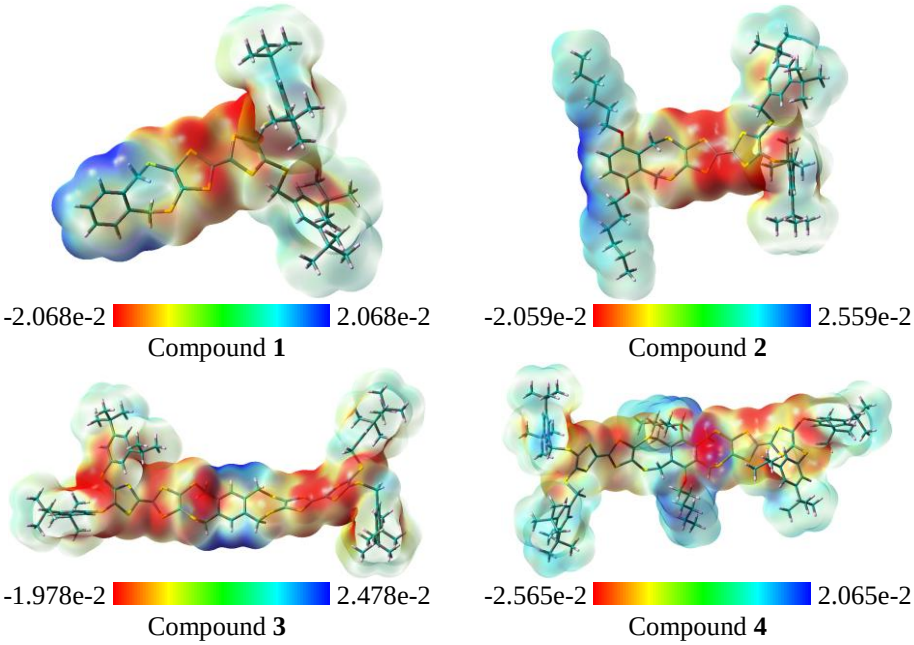

Fig 2: Molecular electrostatic potential surface of di(tert-butylbenzylthio) tetrathiafulvalene derivatives 1-4

As seen from the figure that, in all molecules, the regions exhibiting the negative electrostatic potential are localized near the TTF core and groups that contain sulfur atoms while the regions presenting the positive potential are localized vicinity of the hydrogen atoms of alkyl groups.

3.3 Frontier Molecular Orbitals (FMOs)

The most important orbitals in a molecule are the frontier molecular orbitals, called lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO). The HOMO energy represents the ability to donate an electron while the LUMO as an electron acceptor represents the ability to obtain an electron. The gap between the HOMO and LUMO determines the chemical stability and electrical transport properties of the molecule [17]. A molecule with a small frontier orbital gap is more polarizable (reactive), and is generally associated with a high chemical reactivity (less stable) [18]. The HOMO - LUMO plots of compound 3 are given in Figure 3. According to Figure 3, the positive phase is shown as blue color region whereas the orange one is provided as green color region. Table 5 illustrates the change of $\Delta E_{LUMO - HOMO}$ (E_{gap}) energy gap value of title compound. The low value of gap represents the high reactivity of the molecule in chemical reactions [19]. Also, the lowering of the energy gap describes that the eventual charge transfer takes place within the molecule [20].

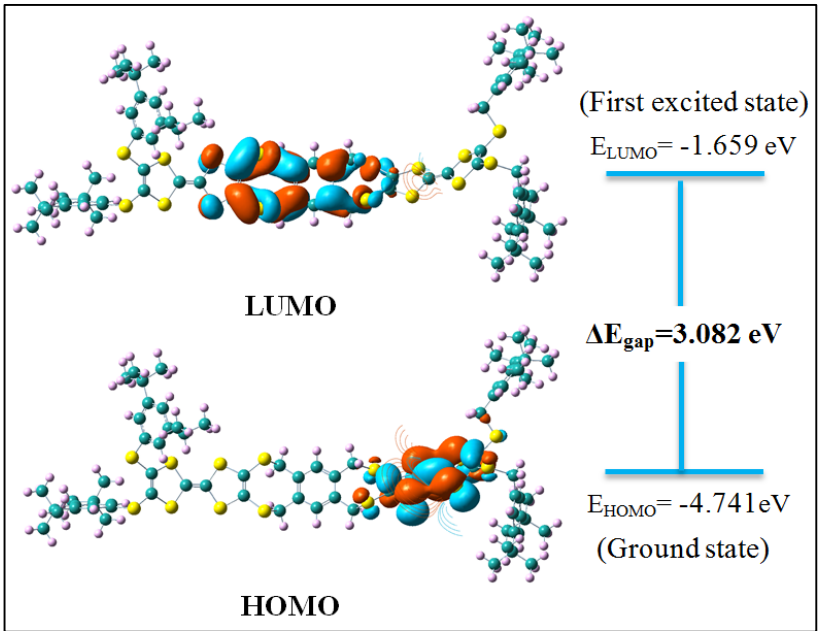

Fig 3: HOMO-LUMO Structure with the energy level diagram of compound 3

3.4 Global Reactivity Descriptors

The energies of frontier molecular orbitals (E_{HOMO}, E_{LUMO}), energy band gap (E_{HOMO} - E_{LUMO}), electronegativity (χ), chemical potential (μ), global hardness (η), global softness (S) and global electrophilicity index (ω) [21-23] of di(tert-butylbenzylthio) tetrathiafulvalene derivatives are listed in

Table 5. On the basis of E_{HOMO} and E_{LUMO}, these are calculated by using the below equations.

$$\chi = (E_{HOMO} - E_{LUMO})/2$$
$$\mu = -(IE + EA)/2 = (E_{N+1} - E_{N-1})/2 = -\chi$$
$$\eta = (IE - EA)/2 = (E_{N-1} - E_{N+1} - 2E_N)/2$$
$$S = 1/2\eta$$
$$\omega = \mu^2/2\eta$$

Electrophilicity index is one of the important quantum chemical descriptors in describing chemical reactivity of the molecules in the context of development of Quantitative Structure Activity Relationship (QSAR) parlance. Quantitative Structure-Activity Relationship methodology is one of the most powerful tools for describing the relationships between biological activity and the physicochemical characteristics of molecules. The molecular descriptor is the final result of a logic and mathematical procedure which transforms chemical information encoded within a symbolic representation of a molecule into a useful number or the result of some standardized experiment. Many of the descriptors are based directly on the results of quantum-mechanical calculations or can be derived from the electronic wave function or electrostatic field of the molecule [24]. Since the electrophilicity index is a chemical reactivity descriptor and it has been used as appropriate descriptor of QSAR study. Recently the electrophilicity index has been used as a possible descriptor of chemical reactivity confirming the fact that the electrophilicity properly quantifies the chemical activity.

Table 5: Quantum chemical descriptors of di(tert-butylbenzylthio) tetrathiafulvalene derivatives 1-4

Parameters	compound 1	compound 2	compound 3	compound 4
E_{HOMO} (eV)	-4.682	-4.494	-4.741	-4.688
E_{LUMO} (eV)	-1.120	-1.013	-1.659	-1.573
ΔE_{gap} (eV)	3.562	3.480	3.082	3.115
IE (eV)	4.682	4.494	4.741	4.688
EA (eV)	1.120	1.013	1.659	1.573
μ (eV)	-2.901	-2.753	-3.200	-3.131
χ (eV)	2.901	2.753	3.200	3.131
η (eV)	1.781	1.740	1.541	1.557
S (eV)	0.281	0.287	0.324	0.321
ω (eV)	2.363	2.178	3.323	3.147

As presented in table 5, the compound which have the lowest energetic gap is the compound 3 (ΔE_{gap} = 3.082 eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound 1 (ΔE_{gap} = 3.562 eV).The compound that has the highest HOMO energy is the compound 2 (E_{HOMO} = -4.494 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} = -1.659 eV) which signifies that it can be the best electron acceptor. The two properties like I (potential ionization) and A (affinity) are so important, the determination of these two properties allow us to calculate the absolute electronegativity (χ) and the absolute hardness (η). These two parameters are related to the one-electron orbital energies of the HOMO and LUMO respectively. Compound 2 has lowest value of the potential ionization (I = 4.494 eV), so that will be the better electron donor. Compound 3 has the largest value of the affinity (A = 1.659 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 = 1.541 eV, S = 0.324 eV) is lesser (greater) among all the molecules. Thus, compound 3 is found to be more reactive than all the compounds. Compound 3 possesses higher electronegativity value (χ = 3.200 eV) than all compounds so; it is the best electron acceptor. The value of ω for compound 3 (ω = 3.323 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

Fukui function (FF) [24-27] is one of the widely used local density functional descriptors to model chemical reactivity and site selectivity. The condensed Fukui functions (f^+_k, f^-_k, f^0_k) [28] have been calculated by following equation.

$$f^+ = [q(N+1) - q(N)]$$, for nucleophilic attak,

$$f^- = [q(N) - q(N-1)]$$, for electrophilic attak,

$$f^0 = [q(N+1) - q(N-1)]/2$$, for radical attak.

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. (+, -, 0) signs show nucleophilic, electrophilic and radical attack respectively. Fukui functions for selected atomic sites in compounds 1-4 are shown in Tables 6-7.

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

Compound 1					Compound 2				
Atom	22 C	19 C	68 C	94 C	Atom	105 O	106 O	20 C	17 C
f^+	0.089	0.075	0.067	0.067	f^+	0.361	0.360	0.100	0.085
Atom	42 C	40 C	49 C	51 C	Atom	5 C	2 C	119 C	107 C
f^-	0.155	0.149	0.147	0.145	f^-	0.243	0.242	0.139	0.137
Atom	94 C	81 C	55 C	68 C	Atom	138 C	92 C	79 C	53 C
f^0	0.023	0.018	0.011	0.007	f^0	0.043	0.039	0.035	0.025

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

Compound 3					Compound 4				
Atom	73 C	32 C	28 C	34 C	Atom	210 O	190 O	29 C	32 C
f^+	0.108	0.108	0.107	0.097	f^+	0.293	0.286	0.127	0.105
Atom	85 C	3 C	69 C	4 C	Atom	38 S	46 S	74 C	76 C
f^-	0.142	0.136	0.135	0.135	f^-	0.514	0.407	0.375	0.368
Atom	83 C	75 C	82 C	176 C	Atom	89 C	76 C	74 C	5 C
f^0	0.004	0.001	0.001	0.001	f^0	0.131	0.112	0.109	0.108

From the tables 6-7, the parameters of local reactivity descriptors show that 22C, 105O, 73C and 210O are the more reactive sites in compounds 1, 2, 3 and 4 respectively, for nucleophilic attacks. The more reactive sites for electrophilic attacks are 42C, 5C, 85C and 38S for compounds 1, 2, 3 and 4 respectively. The more reactive sites in radical attacks are 94C, 138C, 83C and 89C for compounds 1, 2, 3 and 4 respectively.

3.6 Nonlinear Optical Properties (NLO)

The NLO phenomena have attracted much attention in recent years because of their potential applications in optical communication, optical signal processing and transmission, optical data acquisition and storage, optical computing, and especially optical limiting effects utilized in the protection of optical sensors and human eyes from high intensity laser beams [29-34]. Many types of polarizabilities and hyperpolarizabilities have been discussed in the literature [34]. They determine not only the strength of molecular interactions, the cross sections of different scattering and collision processes, but also the NLO properties of the system [35]. In order to investigate the relationships among photocurrent generation, molecular structures and NLO, the polarizabilities and hyperpolarizabilities of di(tert-butylbenzylthio) tetrathiafulvalene derivatives was calculated using DFT-B3LYP method and 6-31G(d,p) basis set, based on the finite-field approach. First hyperpolarizability is a third rank tensor that can be described by a (3 × 3 × 3) matrix. The 27 components of the 3D-matrix can be reduced to 10 components due to the Kleinmann [35] symmetry. It can be given in the lower tetrahedral format. It is obvious that the lower part of the (3 × 3 × 3) matrix is a tetrahedral. The components of first hyperpolarizability β_0 are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous this expansion becomes:

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

Where E^0 is the energy of the unperturbed molecules, F_i is the field at the origin and μ_i, α_{ij}, β_{ijk} are the components of dipole moment, polarizability, and first hyperpolarizability, respectively. The total static dipole moment (μ_0), anisotropy of the polarizability (α_0), mean polarizability ($\Delta\alpha$) and the total first hyperpolarizability (β_0) using (x, y, z) components are defined as [36].

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

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

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

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

$$\beta_x = \beta_{xxx} + \beta_{xyz} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

Since the x, y, z components of α_0 and β_0 of Gaussian 09 output are reported in atomic mass unit (a.u.), the calculated values have been converted into electrostatic unit (esu) using conversion factor as (for α_0 : 1 a.u. = 0.1482 × 10^{-24} esu; for β_0 : 1 a.u. = 0.0086393 × 10^{-30} esu). The total molecular dipole moment and first order hyperpolarizability are depicted in Table 8. The first order hyperpolarizability is 13 times greater than that of urea (β of urea 0.3728×10^{-30} esu) obtained by B3LYP/6-31G (d,p) method. Therefore, investigated molecules will show NLO response and might be used for NLO materials in future.

Table 8: The dipole moments μ (D), polarizability α (esu), the anisotropy of the polarizability Δα (esu), and the first hyperpolarizability β (esu) of di(tert-butylbenzylthio) tetrathiafulvalene derivatives 1-4 calculated by B3LYP/6-31G(d,p) method.

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
β_{xxx}	-413.8203	733.0595	-295.9824	387.3405
B_{yyy}	-2.9853	76.6059	106.0465	0.6729
B_{zzz}	17.6626	11.7113	10.3244	109.3456
B_{xyy}	-47.9077	135.4162	167.7646	-116.1941
B_{xxy}	-208.2808	152.6740	425.2452	399.6284
B_{xxz}	-48.0654	-54.0145	-12.4729	5.8131
B_{xzz}	73.1650	-25.1805	-1.0386	-99.0576
B_{yzz}	8.0940	8.9914	17.2876	8.2532
B_{yyz}	-13.9651	1.7841	8.8109	67.6457
B_{xyz}	-43.6751	-28.4675	-113.8020	-124.2914
B_{tot}(esu)x10^{-33}	414.7549	877.2467	563.6407	479.5298
μ_x	-0.8157	4.3919	0.3360	-0.7655
μ_y	-1.9158	2.3943	2.7219	0.1405
μ_z	0.0846	0.1780	-2.4737	6.1250
μ_{tot}(D)	*2.0840*	*5.0053*	*3.6933*	*6.1743*
α_{xx}	-314.7979	-365.6471	-627.0326	-730.0619
α_{yy}	-344.3191	-422.1585	-648.4797	-716.0348
α_{zz}	-371.8758	-460.7647	-670.1077	-748.1236
α_{xy}	6.4963	2.1357	-0.2586	-3.2532
α_{xz}	-1.4204	1.7828	8.5031	13.3129
α_{yz}	2.2081	-1.6228	6.5989	-11.8432
α_0(esu)x10^{-24}	50.9084	83.0469	41.7055	41.9592
$\Delta\alpha$(esu)x10^{-24}	7.5446	12.3075	6.1808	6.2183

Since the values of the polarizabilities (Δα) 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 *2.0840*, *5.0053*, *3.6933* and *6.1743* D respectively, which are approximately six 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 50.9084 x 10^{-24}, 83.0469 x 10^{-24}, 41.7055 x 10^{-24} and 41.9592 x 10^{-24} esu respectively; the values of anisotropy of the polarizability are 7.5446, 12.3075, 6.1808 and 6.2183 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 414.7549 x 10^{-33}, 877.2467 x 10^{-33}, 563.6407 x 10^{-33} and 479.5298 x 10^{-33} esu. The first hyperpolarizability of title molecules is approximately 1.21, 2.55, 1.64 and 1.40 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 the non-linearity of the di(tert-butylbenzylthio) tetrathiafulvalene derivatives 1-4.

4. Conclusion

B3LYP level with the 6-31G(d,p) basis set is utilized to conduct a detailed study of the structures, geometrical parameters and molecular electrostatic potential map of di(tert-butylbenzylthio) tetrathiafulvalene derivatives 1-4. The lowering of the HOMO-LUMO energy gap value has substantial influence on the intra molecular charge transfer and reactivity of the molecules. The MEP map is agrees well with the ground state interaction. The highest electro negativity and electrophilicity were found for compounds 3 and the lowest ones for compounds 2 respectively. The charge distribution has been calculated from the atomic charges by non-linear optical (NLO). The energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels and the molecular electrostatic potential (MEP) energy surface studies evidenced the existence of intramolecular charge transfer (ICT) within the molecules.

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6. References

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