A Quantum Chemical Study of Dendralene and Radialene Tetrathiafulvalene Analogues

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Abstract The computations were performed at DFT levels of theory to get the optimized geometries of the title compounds using Gaussian09 software. The calculated HOMO and LUMO energies show the chemical activity of the molecules. The global quantities: electronic chemical potential, electrophilicity index, chemical hardness and softness based on HOMO and LUMO energy eigenvalues are also computed at B3LYP/6-31G(d,p) level of theory.

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

1. Introduction

Tetrathiafulvalenes (TTFs) have been of great interest in recent years due to their use for 'organic metals'[1]. One of the trends in TTF research has been and still is the incorporation of various spacer groups into the central double bond as a means to achieve better overlap between the molecules in the solid state, as well as lowering electron-electron repulsion in the molecule [2,3].

Tetrathiafulvalene (TTF) is a fascinating planar π-electron- donor molecule with a broad range of potential applications [4]. Since its preparation in 1970 by Wudl et al. [5], there has been an unabated interest in this molecule for the preparation of unconventional materials exhibiting electrical, optical, magnetic properties. The parent TTF is a non-aromatic (14π- electrons) molecule which is easily oxidized to form reversibly the in the search of electrically conducting and superconducting materials [6]. The field of TTF-based organic conductors was reviewed [7].

An enormous number of studies have been devoted during the past four decades to improve the conductivity and T_c of organic conductors and superconductors. Among them, a series of cross-conjugated compounds such as radialenes, dendralenes, tetraethynylethane (TEE), radia annulene, and so on, containing TTF or 1,3-dithiole (DT) moieties have been prepared [8-10].

This paper presents a theoretical study of dendralene and radialene TTF analogues **1-4** described in literature [11]. This investigation makes use of electronic descriptors such as the energy of the highest occupied molecular orbital (HOMO), the energy of the lowest unoccupied molecular orbital (LUMO), the gap energy HOMO-LUMO. The optimized structural parameters, First hyperpolarizability, chemical reactivity and Fukui functions are obtained using the Density Functional Theory (DFT), performing B3LYP/6-31G(d,p) level of calculations.

2. Materials and Methods

The quantum computational works of the compound are performed using DFT method and basis set 6-31G(d,p). All these calculations are performed using the GAUSSIAN 09W [12] program package on i7 processor in a personal computer. Becke's three-parameter hybrid function (B3) combined with the Lee-Yang-Parr correlation function constitute B3LYP [13,14]. The optimized molecular structure of the studied molecules is shown in Fig 1.

3. Results and Discussion

3.1. Molecular Geometry

The bond parameters (bond length, bond angles and dihedral angles) of dendralene and radialene TTF analogues molecules are listed in Tables 1-4 using DFT/B3LYP method with6-31G(d,p) basis set. The optimized molecular structure of a title compounds are obtained from Gaussian 09Wand Gauss View 5.0programs are shown in Fig 1.
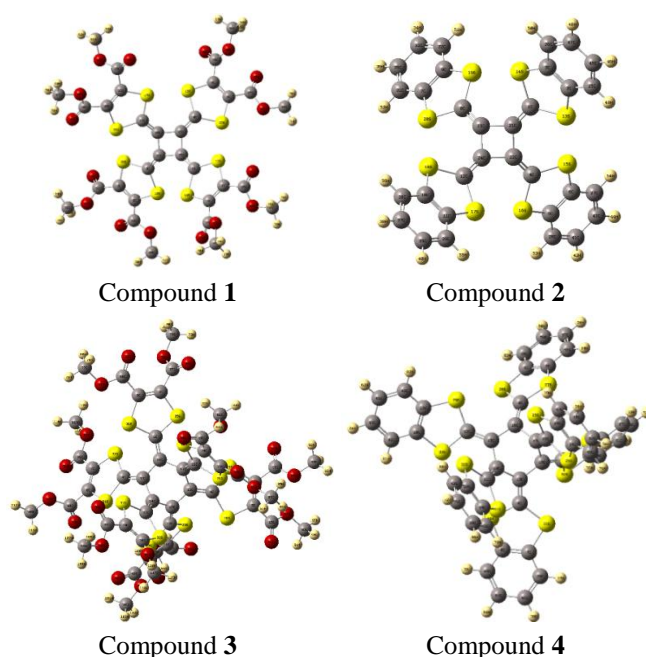

Compound **1**   Compound **2**

Compound **3**   Compound **4**

*Figure 1: Optimized molecular structure of dendralene and radialene TTF analogues **1-4***

Table 1: Optimized geometric parameters of compound **1**

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,13)	1.784	A(13,1,14)	113.387	D(21,1,13,2)	175.239
R(1,21)	1.354	A(2,3,14)	117.531	D(14,1,21,22)	163.522
R(2,13)	1.764	A(15,4,16)	113.038	D(25,2,13,1)	175.536
R(3,14)	1.760	A(15,4,22)	123.575	D(22,4,15,6)	179.610
R(4,16)	1.785	A(16,4,22)	123.066	D(22,4,16,5)	179.627
R(4,22)	1.354	A(15,6,27)	118.647	D(6,5,28,36)	123.418
R(5,16)	1.752	A(9,7,31)	126.603	D(5,6,27,43)	171.896
R(6,15)	1.770	A(19,8,23)	123.585	D(15,6,27,35)	165.401
R(7,9)	1.352	A(20,8,23)	123.037	D(31,7,9,19)	178.658
R(7,20)	1.752	A(7,9,32)	123.848	D(31,7,20,8)	177.004
R(8,19)	1.784	A(19,9,32)	118.809	D(23,8,19,9)	179.435
R(8,20)	1.785	A(11,10,18)	117.445	D(19,8,23,24)	162.868
R(9,19)	1.770	A(11,10,30)	129.239	D(18,10,30,46)	153.540
R(10,11)	1.353	A(18,10,30)	113.252	D(24,12,18,10)	178.017
R(10,18)	1.765	A(10,11,17)	117.452	D(6,27,43,69)	177.662

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

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(2,3)	1.386	A(13,1,14)	112.981	D(21,1,14,3)	160.141
R(2,25)	1.385	A(14,1,21)	123.451	D(13,1,21,23)	164.636
R(3,14)	1.766	A(3,2,25)	120.333	D(25,2,3,14)	178.746
R(3,26)	1.385	A(13,2,25)	123.211	D(25,2,13,1)	171.447
R(4,16)	1.774	A(2,3,26)	120.333	D(3,2,25,49)	179.639
R(5,6)	1.386	A(14,3,26)	123.211	D(13,2,25,45)	178.472
R(6,15)	1.766	A(15,4,22)	123.454	D(22,4,16,5)	160.104
R(6,27)	1.385	A(16,4,22)	123.456	D(16,5,6,27)	178.741
R(7,9)	1.386	A(6,5,28)	120.333	D(27,6,15,4)	171.428
R(8,19)	1.774	A(15,6,27)	123.212	D(31,7,9,19)	178.746
R(10,18)	1.766	A(9,7,31)	120.333	D(31,7,20,8)	171.456
R(11,17)	1.766	A(20,7,31)	123.210	D(9,7,31,52)	179.639
R(2,3)	1.386	A(19,8,23)	123.451	D(20,7,31,35)	178.475
R(2,25)	1.385	A(20,8,23)	123.453	D(20,8,23,21)	164.630
R(3,14)	1.766	A(11,10,18)	116.443	D(30,10,11,17)	178.741

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

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,18)	1.376	A(18,1,35)	121.386	D(18,1,36,3)	177.840
R(1,36)	1.779	A(3,2,35)	117.732	D(35,2,3,38)	175.901
R(2,3)	1.353	A(3,2,37)	125.951	D(3,2,37,49)	117.136
R(4,28)	1.783	A(35,2,37)	116.296	D(35,2,37,72)	115.620
R(5,28)	1.764	A(2,3,38)	123.634	D(2,3,38,71)	173.344
R(6,27)	1.756	A(36,3,38)	119.007	D(36,3,38,50)	167.582
R(7,39)	1.478	A(16,4,27)	121.073	D(27,4,16,15)	160.903
R(17,22)	1.376	A(6,5,45)	129.131	D(28,4,16,17)	150.462
R(19,20)	1.354	A(28,5,45)	113.366	D(16,4,27,6)	172.178
R(19,31)	1.766	A(5,6,46)	128.881	D(28,5,6,46)	175.704
R(19,41)	1.490	A(8,7,39)	123.299	D(45,5,6,27)	173.405
R(20,32)	1.764	A(33,7,39)	119.546	D(6,5,45,57)	155.649
R(21,31)	1.784	A(7,8,40)	125.284	D(8,7,39,61)	174.673
R(21,32)	1.783	A(34,8,40)	117.153	D(33,7,39,51)	173.140
R(22,26)	1.776	A(13,9,33)	125.986	D(40,8,34,9)	175.240

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

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,18)	1.347	A(18,1,35)	121.906	D(18,1,36,3)	162.640
R(1,36)	1.775	A(35,2,37)	123.635	D(37,2,3,36)	179.036
R(2,35)	1.759	A(2,3,36)	116.569	D(37,2,35,1)	172.120
R(4,28)	1.775	A(36,3,38)	122.980	D(3,2,37,73)	179.706
R(5,28)	1.763	A(6,5,45)	120.441	D(35,2,37,49)	178.262
R(6,27)	1.759	A(13,9,34)	121.125	D(27,4,16,15)	173.313
R(7,8)	1.385	A(11,10,30)	116.048	D(28,4,16,17)	151.676
R(7,39)	1.386	A(11,10,43)	120.281	D(16,4,27,6)	162.518
R(8,34)	1.761	A(30,10,43)	123.659	D(6,5,45,83)	179.812
R(12,29)	1.777	A(10,11,29)	116.723	D(28,5,45,59)	178.794
R(13,14)	1.499	A(10,11,44)	120.373	D(40,8,34,9)	171.352
R(14,21)	1.346	A(29,11,44)	122.895	D(7,8,40,78)	179.426
R(15,16)	1.483	A(15,12,29)	126.533	D(34,8,40,67)	178.181
R(16,17)	1.517	A(9,13,14)	121.468	D(44,11,29,12)	171.904
R(17,18)	1.517	A(9,13,18)	127.401	D(10,11,44,82)	179.855

3.2. Molecular Electrostatic Potential (MEPS)

The molecular electrostatic potential surface (MEPS) is a method of mapping electrostatic potential onto the iso-electron density surface which in turn enables a simultaneous display of electrostatic potential (electrons+nuclei) distribution, molecular shape, size and dipole moments of the molecule. Consequently, it can

emerge as a useful descriptor for understanding the sites for electrophilic and nucleophilic reactions as well as hydrogen-bonding interactions [22]. The electrostatic potential V(r) is also applicable for reflecting the reactivity map of the molecule based on the ''recognition'' of one molecule by another, as in drug-receptor, and enzyme-substrate interactions, because it is through their potentials that the two species first ''see'' each other [18-23]. The total electron density surface mapped with the electrostatic potential of dendralene and radialene TTF analogues **1-4**, as obtained from calculation at B3LYP/6-31G(d,p) level, is shown in Fig 2 along with the projection of the electrostatic potential contour map [15-18]. The color scheme for the MEPS is as follows: red: electron rich, partially negative charge; yellow: slightly electron rich region; blue: electron deficient, partially positive charge; light blue: slightly electron deficient region; green: neutral, respectively. Thus it is obvious that the red and yellow regions in the MEPS can be related to electrophilic reactivity and the blue regions to nucleophilic reactivity of the molecules.
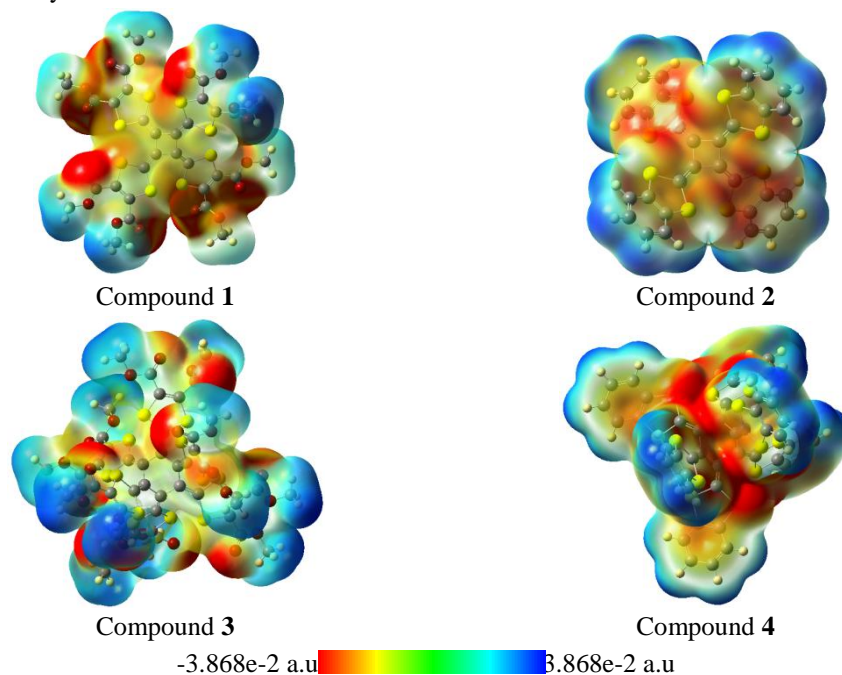

Compound **1**   Compound **2**

Compound **3**   Compound **4**

-3.868e-2 a.u   3.868e-2 a.u

Figure 2: Molecular electrostatic potential surface of dendralene and radialene TTF analogues 1-4

As seen from the figure 2 that, the regions exhibiting the negative electrostatic potential are localized near the TTF core in compounds **2** and **4**and the carbonyl of ester function for compounds **1** and **3**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)

HOMO-LUMO band gap plays a very crucial role in determining the chemical reactivity, stability of the molecule, chemical reactions, electrical and optical properties. LUMO energy means the ability to accept an electron while HOMO energy means ability to donate an electron. The conjugated molecules are characterized by a highest occupied molecular orbital-lowest unoccupied molecular orbital gap (HOMO-LUMO), which is the result of a significant degree of intermolecular charge transfer from the end capping electron-donor groups to the efficient electron-acceptorgroups through a π-conjugated path. The strong charge transfer interaction through π-conjugated bridge results in substantial ground state donor-acceptor mixing the appearance of a charge transfer band in the electronic spectrum. Therefore, an electron density transfers occurs from the more aromatic part of the pi-conjugated system in the electron-donor side to its electron-withdrawing part. The energy gap between the HOMO and LUMO is a critical parameter in determining molecular electrical transport properties and for predicting the most reactive position in π-electron systems and also explains several types of reaction in conjugated system. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the compound **1** are shown in Fig 3.
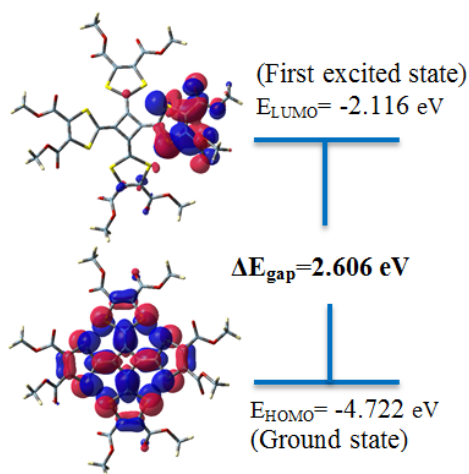
Figure 3: HOMO-LUMO Structure with the energy level diagram of compound 1

3.4. Global Reactivity Descriptors

The energy gap between HOMO and LUMO is a critical parameter to determine molecular electrical transport properties. By using HOMO and LUMO energy values for a molecule, the global chemical reactivity descriptors of molecules such as hardness, chemical potential, softness, electronegativity and electrophilicity index as well as local reactivity have been defined [24-28]. Pauling introduced the concept of electronegativity as the power of an atom in a molecule to attract electrons to it. Hardness (η), chemical potential (μ) and electronegativity (χ) and softness are defined follows.

$$\eta = \frac{1}{2}\left(\frac{\partial_2 E}{\partial N_2}\right)V(r) = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)V(r)$$

$$\mu = \left(\frac{\partial E}{\partial N}\right)V(r)$$

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)V(r)$$

Where E and V(r) are electronic energy and external potential of an n-electron system respectively. Softness is a property of molecule that measures the extent of chemical reactivity. It is the reciprocal of hardness.

$$S = 1/2\eta$$

Using Koopman's theorem for closed-shell molecules, η, μ and χ can be defined as

$$\eta = (I - A)/2$$
$$\mu = -(I + A)/2$$
$$\chi = (I + A)/2$$

Where A and I are the ionization potential and electron affinity ofthe molecules respectively. The ionization energy and electron affinity can be expressed through HOMO and LUMO orbital energies as I = -E $_{HOMO}$ and A = -E $_{LUMO}$. Electron affinity refers to the capability of a ligand to accept precisely one electron from a donor. Considering the chemical hardness, 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. Parret al. [24] have defined a new descriptor to quantify the global electrophilic power of the molecule as electrophilicity index (ω), which defines a quantitative classification of the global electrophilic nature of a molecule Parr et al. [24] have proposed electrophilicity index (ω) as a measure of energy lowering due to maximal electron flow between donor and acceptor. They defined electrophilicity index (ω) as follows:

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

Using the above equations, the chemical potential, hardness and electrophilicity index have been calculated for dendralene and radialene TTF analogues **1-4** and their values are shown in Table 5.

Table 5. Quantum chemical descriptors of dendralene and radialene TTF analogues **1-4**

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
E_{HOMO} (eV)	-4.722	-6.750	-4.662	-6.552
E_{LUMO} (eV)	-2.116	1.759	-1.999	2.157
ΔE_{gap} (eV)	2.606	8.509	2.663	8.709
IE (eV)	4.722	6.750	4.662	6.552
A (eV)	2.116	-1.759	1.999	-2.157
μ (eV)	-3.419	-2.495	-3.331	-2.197
χ (eV)	3.419	2.495	3.331	2.197
η (eV)	1.303	4.254	1.331	4.354
S (eV)	0.384	0.118	0.376	0.115
ω (eV)	4.487	0.732	4.167	0.554

As presented in table 5, the compound which have the lowest energetic gap is the compound **1** (ΔE_{gap} = 2.606 eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound **4** (ΔE_{gap} = 8.709 eV).The compound that has the highest HOMO energy is the compound **3** (E_{HOMO} = -4.662 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_{LUMO} = -2.116 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* = 4.662 eV), so that will be the better electron donor. Compound **1** has the largest value of the affinity (A = 2.116 eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound **1** (η = 1.303 eV, S = 0.384 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 (χ = 3.419 eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **1** (ω = 4.487 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

The study of population of electrons around the atoms in a molecule is also much useful to analyze the stability of the molecule. Complete pictures of electronic charge density of the molecule are viewed through Mullikan population analysis and the procedure given by Yang and Mortier [29] have been used to calculate the condensed Fukui function f_k at DFT/ B3LYP/6-31G(d,p) level of theory. For a system of N electrons, independent calculations are made corresponding to N-1; N and N+1 electron systems with the same molecular geometry. The Mullikan population analysis yields $q_k(N-1)$, $q_k(N)$ and $q_k(N+1)$ for all atoms k: In a finite difference approximation, the f_k values are calculated by using Yang and Mortier procedure.

The optimization of the title compounds are performed at three different charge states, i.e., neutral, singly positively and negatively charged. All these calculations were performed at the equilibrium geometries of the neutral charge state of the molecules. In a molecular system, the atomic sites which possess highest condensed Fukui function favor the higher reactivity. Lee et al. [30] have studied the condensed Fukui function and concluded that the most reactive site during the chemical reaction has the higher value of f_k. The calculated Fukui function values are given in Tables6-7 and indicate that there is a significant difference in the charge between the atoms.

From the tables 6-7, the parameters of local reactivity descriptors show that 45O, 22C, 9C and 12C are the more reactive sites in compounds **1**, **2**, **3** and **4** respectively for nucleophilic attacks. The more reactive sites in radical attacks are 46O, 22C, 14C and 17C for compounds **1**, **2**, **3** and **4** respectively. The more reactive sites for electrophilic attacks are 28C, 18S, 47C, 32S for compounds **1**, **2**, **3** and **4** respectively.

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

	Compound 1				Compound 2			
Atom	45 O	42 O	46 O	41 O	**Atom**	22 C	24 C	21 C	23 C
f^+	0.305	0.303	0.303	0.302	f^+	0.021	0.020	0.020	0.019
Atom	28 C	31 C	32 C	27C	**Atom**	18S	15 S	14S	16 S
f^-	0.381	0.381	0.376	0.375	f^-	0.085	0.084	0.084	0.084
Atom	46 O	42 O	45 O	47O	**Atom**	22C	24 C	21C	23 C
f^0	0.006	0.006	0.005	0.005	f^0	0.018	0.018	0.018	0.018

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

	Compound 3				Compound 4			
Atom	9 C	21 C	69O	1C	**Atom**	12 C	9 C	21 C	4 C
f^+	0.310	0.288	0.285	0.284	f^+	0.291	0.291	0.241	0.227
Atom	47 C	39 C	44C	46C	**Atom**	32 S	31 S	33 S	29 S
f^-	0.389	0.367	0.356	0.356	f^-	0.176	0.176	0.156	0.156
Atom	14 C	61 O	13C	69O	**Atom**	17 C	14 C	6 C	2 C
f^0	0.003	-0.001	-0.002	-0.002	f^0	0.018	0.010	0.000	0.000

3.6. Nonlinear Optical Properties (NLO)

Organic molecules can able to manipulate photonic signal efficiently are of importance in technologies such as optical communication and computing process [31,32]. Nonlinear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristic from the incident fields. In this context, the first hyperpolarizability of the title compounds is also calculated in the present study. The first order hyperpolarizability (β) of the title molecule is calculated using B3LYPmethod. First order hyperpolarizability is a third rank tensor that can be described by $3 \times 3 \times 3$ matrices. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [33]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the $3 \times 3 \times 3$ matrices isa 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 homogenous, this expansion becomes:

$$E = E_0 - \sum_i \mu_i F^i - \frac{1}{2}\sum \alpha_{ij}F^i F^i - \frac{1}{6}\sum \beta_{ijk}F^i F^j F^k - \frac{1}{24}\sum_{ijkl} \gamma_{ijkl}F^i F^j F^k F^l + ...$$

where E_0 is the energy of the unperturbed molecule, F^i is the field at the origin, μ_{ij} , α_{ij} , β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability, the first hyperpolarizabilities, and second hyperpolarizabilities, respectively. The total static dipole moment μ, the mean polarizability α_0 and the anisotropy of the polarizability $\Delta\alpha$ using the x-, y- and z-components are defined as

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

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

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

First order hyperpolarizability is

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

Where

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

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

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

The total molecular dipole moment (μ), mean polarizability (α_0) and anisotropy polarizability (Δα) and first hyperpolarizability (β_{total}) of symmetrical acetylenic analogues of dendralene and radialene TTF analogues **1-4** are computed and are depicted in Table 8.

Table 8: The dipole moments μ (D), polarizability α, the average polarizability α (esu), the anisotropy of the polarizability Δα (esu), and the first hyperpolarizability β (esu) of dendralene and radialene TTF analogues **1-4** calculated by B3LYP/6-31G(d,p) method

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
β_{xxx}	-13.4025	-0.0459	21.6060	172.9494
B_{yyy}	22.2639	0.0631	94.2273	0.0302
B_{zzz}	186.7631	-0.0001	353.4592	197.2694
B_{xyy}	62.0403	-0.0268	-39.9616	-136.5064
B_{xxy}	70.8476	0.0573	-292.3512	-0.0460
B_{xxz}	341.8918	-6.8492	-64.5379	-58.3298
B_{xzz}	128.0935	-0.0022	-65.0671	-53.4075
B_{yzz}	-71.9393	0.0147	47.9933	-0.0500
B_{yyz}	-77.9735	6.8495	-315.4043	-72.1736
B_{xyz}	23.3023	160.8188	21.2253	0.0159
B_{tot}(esu)x10^{-33}	532.2399	160.7708	173.7812	68.8876
μ_x	3.2200	-0.0015	-0.6862	-0.0941
μ_y	0.1473	0.0027	-0.5572	-0.0011
μ_z	4.8578	0.0000	-1.1229	1.5826
μ_{tot}(D)	5.8299	0.0031	1.4290	1.5854
α_{xx}	-271.8087	-256.9747	-474.4498	-365.2236
α_{yy}	-334.5163	-256.9763	-497.4833	-393.7374
α_{zz}	-367.3879	-253.1399	-487.8304	-396.7018
α_{xy}	3.0352	0.0001	-35.0959	-0.0070
α_{xz}	-15.2700	0.0007	5.7090	-4.4598
α_{yz}	-13.5619	-0.0004	1.4711	-0.0024
α(esu)x10^{-24}	91.3948	3.8356	64.8137	31.0809
$\Delta\alpha$(esu)x10^{-24}	13.5447	0.5684	9.6054	4.6062

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 5.8299, 0.0031, 1.4290 and 1.5854 D respectively, which are approximately 4.25, 0.01, 1.04 and 1.15 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 91.3948 x 10^{-24}, 3.8356 x 10^{-24}, 64.8137 x 10^{-24} and 31.0809 x 10^{-24} esu respectively; the values of anisotropy of the polarizability are 13.5447, 0.5684, 9.6054 and 4.6062 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 dendralene and radialene TTF analogues molecules are equal to 532.2399 x 10^{-33}, 160.7708 x 10^{-33}, 173.7812 x 10^{-33} and 68.8876 x 10^{-33} esu. The first hyperpolarizability of title molecules is approximately 1.55, 0.46, 0.50 and 0.20 times than those of urea (β of urea is 343.272 x10^{-33} esu obtained by B3LYP/6-311G (d,p) method). The above results show that only compound **1** might have the NLO applications.

Conclusion

The computations were performed at B3LYP/6-31G(d,p) levels of theory to get the optimized geometries of TTF analogues **1-4**. The HOMO and LUMO analysis is used to determine the charge transfer within the molecule. From the MEP it is evident that the negative charge covers the TTF core in compounds **2** and **4**and the carbonyl of ester function for compounds **1** and **3** and the positive charge is over the of the hydrogen atoms of

alkyl and cycled groups. The more electronegativity in the carbonyl for compounds **1** and **3** makes it the most reactive part in these molecules. The calculated first hyperpolarizability of the title compounds were found to be 532.2399×10^{-33} esu for compound **1**which is comparable with the reported values of similar derivatives and which is 1.55 times that of the standard NLO material urea, so only compound **1** might have the NLO applications.

Acknowledgments

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