

Quantum Investigation of Structure Electronic and Non-Linear Optical Properties of TTF Separated by Thiophene

ABSTRACT

We investigate in this study, the quantum chemical computations of a series of TTF separated by Thiophene **1-4** using the DFT/B3LYP method with 6-31G (d,p) basis set. The optimized structures and geometrical parameters were determined by same method cited above. The chemical reactivity parameters (chemical hardness and softness, electronegativity, chemical potential and electrophilicity index) were discussed clearly. To find out most reactive sites of the title molecules, condensed Fukui functions have been also calculated. In addition, a molecular electrostatic potential map (MEP) has been analyzed for predicting the reactive sites. Stability of the compounds arising from hyper-conjugative interaction and charge delocalization has been analyzed using Natural bond orbital (NBO) analysis. NLO properties related to polarizability and hyperpolarizability are also discussed.

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

1. INTRODUCTION

Among sulfur-rich π -conjugated molecules, thiophene and tetrathiafulvalene (TTF) which are two extraordinary candidates, which show remarkable electronic properties and ample application potentials. Thiophene is the essential repeat unit for a class of well-known conducting polymers (CPs), poly/oligo-thiophenes [1-3], while TTF and its derivatives are excellent organic electron donors widely applicable in various fields ranging from charge-transfer complexes, nonlinear optical materials, organic transistors, to molecular switches and sensors [4-7]. Tetrathiafulvalene and its derivatives have been extensively investigated as electron-donating unit in molecular conductors due to strong intermolecular π - π stacking [8,9].

Density functional theory (DFT) is a quantum mechanical method used in chemistry and physics to calculate the electronic structure of atoms, molecules and solids and it has been very popular in computational chemistry since the late 1980s and 1990s. Within this context density functional theory (DFT) is a source whose importance is increasing in terms of computational techniques [10].

In this Letter, we describe a global computational study on a series of TTF separated by thiophene **1-4** illustrate in literature [11] by using DFT/B3LYP method with 6-31G (d,p) basis set. We have determine the optimized molecular structures and parameters, the second order perturbation theory analysis, molecular electrostatic potential surface and frontier molecular orbitals (FMOs). The nature of chemical reactivity and site selectivity of these molecules has been determined on the basis of Global and Local reactivity descriptors. The first hyperpolarizability (β_0) has been computed to indicate suitability for non-linear optical response.

2. MATERIAL AND METHODS

All computational calculations have been performed on personal computer using the Gaussian 09W program packages developed by Frisch and coworkers [10]. The Becke's three parameter hybrid functional using the LYP correlation functional (B3LYP), one of the most robust functional of the hybrid family, was herein used for all the calculations, with 6.31G (d,p) basis set. Gaussian output files were visualized by means of GAUSSIAN VIEW 05 software.

3. RESULTS AND DISCUSSION

3.1. Molecular Geometry

The optimized molecular structures of TTF separated by thiophene **1-4** with atom numbering scheme adopted in this study is shown in Figure 1. The optimized geometries parameters, namely bond lengths, bond angles and dihedral angles were calculated by B3LYP/6-31G (d,p) method are listed in Tables 1-4.

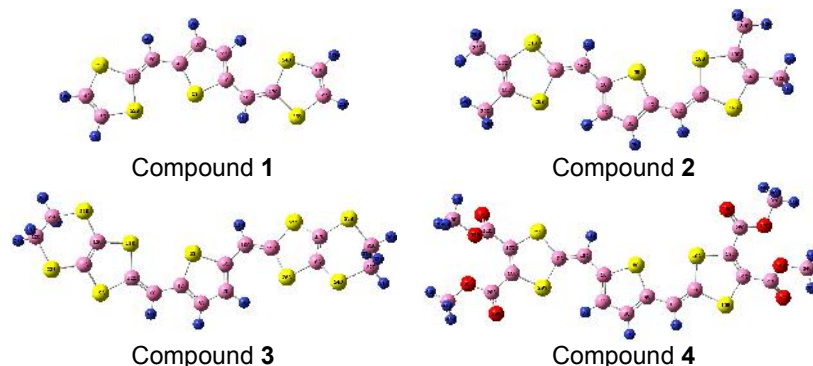


Fig. 1. Optimized molecular structure of TTF separated by thiophene 1-4

Table 1. Optimized geometric parameters of compound 1

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.387	A(2,1,5)	109.610	D(5,1,2,3)	56.001
R(1,5)	1.763	A(2,1,10)	132.790	D(10,1,2,3)	179.999
R(1,10)	1.440	A(5,1,10)	117.600	D(2,1,10,17)	47.002
R(2,3)	1.411	A(1,2,3)	113.782	D(6,2,3,4)	179.997
R(2,6)	1.082	A(1,2,6)	123.664	D(7,3,4,5)	180.000
R(4,5)	1.757	A(5,4,8)	125.711	D(8,4,5,1)	179.999
R(8,12)	1.358	A(1,5,4)	92.695	D(3,4,8,9)	86.014
R(10,11)	1.088	A(4,8,12)	130.859	D(5,4,8,12)	78.018
R(10,17)	1.358	A(1,10,11)	115.474	D(1,10,17,25)	179.997
R(12,22)	1.783	A(11,10,17)	115.652	D(8,12,22,13)	179.994
R(13,14)	1.338	A(22,12,23)	112.979	D(22,13,14,16)	179.999
R(13,15)	1.083	A(14,13,15)	125.019	D(16,14,23,12)	179.997
R(17,24)	1.781	A(14,13,22)	117.896	D(10,17,24,18)	180.002
R(18,20)	1.083	A(18,19,25)	117.725	D(25,17,24,18)	55.004
R(18,24)	1.761	A(21,19,25)	117.385	D(21,19,25,17)	180.002

Table 2. Optimized geometric parameters of compound 2

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(2,3)	1.411	A(2,1,5)	109.599	D(10,1,5,4)	180.000
R(2,6)	1.082	A(2,1,10)	132.753	D(6,2,3,4)	179.993
R(3,4)	1.387	A(5,1,10)	117.648	D(7,3,4,5)	179.999
R(3,7)	1.085	A(1,2,3)	113.785	D(8,4,5,1)	180.000
R(4,5)	1.758	A(1,2,6)	123.598	D(3,4,8,12)	179.999
R(4,8)	1.438	A(3,2,6)	122.618	D(5,4,8,9)	179.999
R(8,9)	1.089	A(2,3,4)	114.601	D(8,12,18,13)	179.992
R(8,12)	1.358	A(2,3,7)	123.461	D(14,13,34,36)	120.294
R(10,11)	1.088	A(4,3,7)	121.938	D(18,13,34,35)	180.000
R(10,15)	1.358	A(3,4,5)	109.307	D(18,13,34,37)	59.705
R(12,18)	1.774	A(3,4,8)	124.985	D(30,14,19,12)	179.994
R(12,19)	1.780	A(5,4,8)	125.709	D(13,14,30,31)	120.264
R(13,14)	1.346	A(1,5,4)	92.709	D(19,14,30,32)	59.695
R(13,18)	1.780	A(4,8,9)	113.194	D(19,14,30,33)	179.979
R(13,34)	1.503	A(4,8,12)	130.816	D(10,15,20,16)	179.986

Table 3. Optimized geometric parameters of compound 3

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,10)	1.440	A(2,1,5)	109.842	D(5,1,2,6)	176.969
R(2,6)	1.083	A(2,1,10)	131.829	D(10,1,2,3)	178.908
R(3,4)	1.387	A(5,1,10)	118.324	D(2,1,10,11)	163.802
R(3,7)	1.085	A(1,2,3)	113.707	D(5,1,10,15)	162.758
R(4,5)	1.756	A(1,2,6)	123.415	D(1,2,3,7)	179.230
R(4,8)	1.438	A(3,2,6)	122.814	D(2,3,4,8)	179.926
R(8,9)	1.089	A(2,3,4)	114.391	D(8,4,5,1)	179.957
R(8,12)	1.357	A(2,3,7)	123.582	D(3,4,8,12)	179.050
R(10,11)	1.088	A(4,3,7)	122.019	D(5,4,8,9)	178.780
R(10,15)	1.357	A(3,4,5)	109.585	D(4,8,12,19)	176.395
R(12,18)	1.778	A(3,4,8)	124.761	D(9,8,12,18)	179.704
R(12,19)	1.784	A(5,4,8)	125.654	D(1,10,15,21)	174.384
R(13,14)	1.350	A(4,8,9)	113.287	D(11,10,15,20)	176.650
R(13,18)	1.780	A(4,8,12)	130.757	D(19,12,18,13)	18.3890
R(14,22)	1.766	A(9,8,12)	115.956	D(8,12,19,14)	164.026

Table 4. Optimized geometric parameters of compound 4

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(4,8)	1.438	A(3,2,6)	122.658	D(10,1,5,4)	179.560
R(8,9)	1.089	A(2,3,4)	114.429	D(6,2,3,4)	177.663
R(8,12)	1.357	A(2,3,7)	123.512	D(7,3,4,5)	179.518
R(10,11)	1.088	A(4,3,7)	122.056	D(8,4,5,1)	179.963
R(10,15)	1.357	A(3,4,5)	109.523	D(8,12,18,13)	177.895
R(12,18)	1.780	A(3,4,8)	124.880	D(25,13,18,12)	177.172
R(12,19)	1.784	A(5,4,8)	125.597	D(22,14,19,12)	175.300
R(13,14)	1.354	A(4,8,9)	113.226	D(10,15,20,16)	173.348
R(13,18)	1.769	A(4,8,12)	130.703	D(28,16,20,15)	178.902
R(13,25)	1.488	A(9,8,12)	116.071	D(31,17,21,15)	173.854
R(14,19)	1.757	A(1,10,11)	115.847	D(22,24,34,36)	62.336
R(14,22)	1.496	A(1,10,15)	128.132	D(25,27,38,40)	61.652
R(17,21)	1.757	A(11,10,15)	116.019	D(16,28,30,42)	179.919
R(17,31)	1.498	A(8,12,18)	126.266	D(28,30,42,44)	61.352
R(22,23)	1.213	A(8,12,19)	120.372	D(31,33,46,48)	62.571

3.2. Molecular Electrostatic Potential (MEP)

Molecular electrostatic used extensively for interpreting potentials have been and predicting the reactive behavior of a wide variety of chemical system in both electrophilic and nucleophilic reactions, the study of biological recognition processes and hydrogen bonding interactions [13]. $V(r)$, 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 positive test charge (a proton) located at r . Unlike many of the other quantities used at present and earlier as indices of reactivity, $V(r)$ is a real physical property that can be determined experimentally by diffraction or by computational methods. For the systems studied the MEP values were calculated as described previously, using the equation [14]:

$$V(r) = \sum \frac{Z_A}{R_{A-r}} - \int \frac{\rho(r')}{|r-r'|} dr'$$

Where the summation runs over all the nuclei A in the molecule and polarization and reorganization effects is neglected. Z_A is the charge of the nucleus A , located at R_A and $\rho(r')$ is the electron density function of the molecule. To predict reactive sites for electrophilic and nucleophilic attack for the investigated molecules, molecular electrostatic potential (MEP) was calculated at B3LYP/6-31G (d,p) optimized geometries. Red and blue areas in the MEP map refer to the regions of negative and positive potentials and correspond to the electron-rich and electron-poor regions, respectively, whereas the green color signifies the neutral electrostatic potential. The MEP surface provides necessary information about the reactive sites. The electron total density onto which the electrostatic potential surface has been mapped is shown in Figure 2.

88

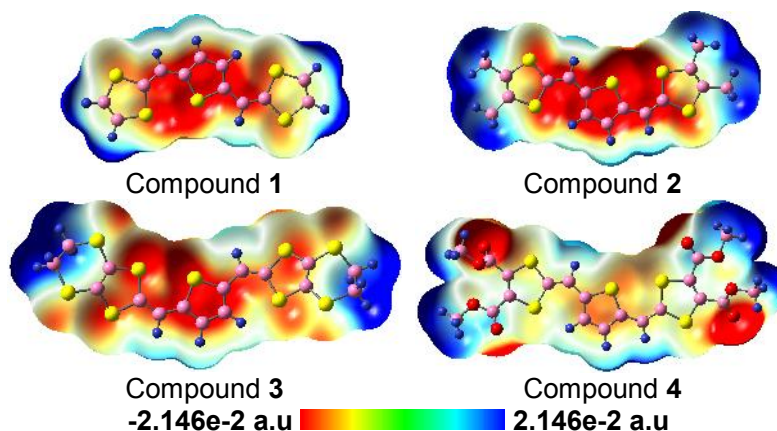


Fig 2. Molecular electrostatic potential surface of TTF separated by thiophene 1-4

As seen from the figure 2 that, in all molecules, the regions exhibiting the negative electrostatic potential are localized near the thiophene, except compound 4 the region exhibiting the negative electrostatic potential is localized in carbonyl of ester function while the regions presenting the positive potential are localized vicinity of the hydrogen atoms.

3.3. Frontier Molecular Orbitals (FMOs)

The most important frontier molecular orbitals (FMOs) such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) plays a crucial part in the chemical stability of the molecule [15]. The HOMO represents the ability to donate an electron and LUMO as an electron acceptor represents the ability to accept an electron. The energy gap between HOMO and LUMO also determines the chemical reactivity, optical polarizability and chemical hardness-softness of a molecule [16]. The energy gap between various occupied and unoccupied molecular orbitals of TTF separated by thiophene 1-4 calculated at B3LYP/6-31G (d,p) level is given in Table 5 reflects the chemical reactivity of the molecules. The energies HOMO, LUMO, LUMO+1 and HOMO-1 and the ΔE_{gap} of compound 4 are calculated and shown in Figure 3.

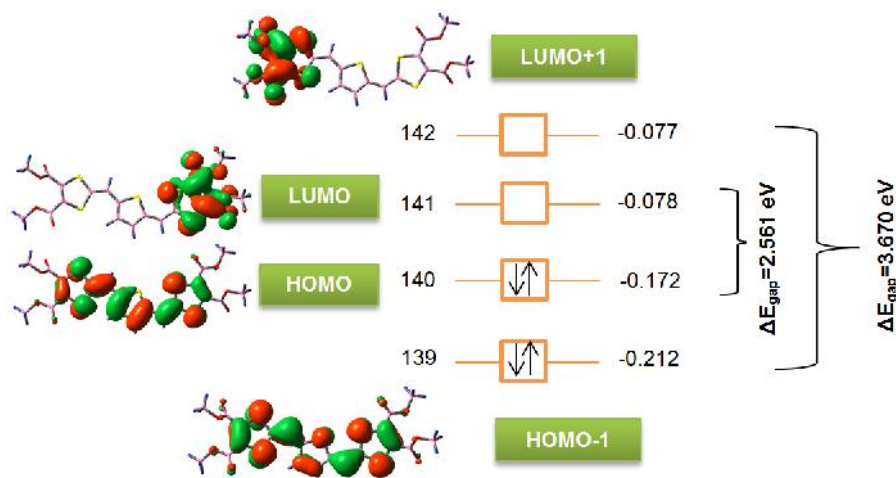


Fig 3. HOMO-LUMO Structure with the energy level diagram of compound 4

3.4. Global Reactivity Descriptors

The chemical reactivity and site selectivity of the molecular systems have been determined by the conceptual density functional theory [17]. Electronegativity (χ), chemical potential (μ), global hardness (η), global softness (S) and electrophilicity index (ω) are global reactivity descriptors, highly successful

in predicting global reactivity trends. On the basis of Koopman's theorem [17], global reactivity descriptors are calculated using the energies of frontier molecular orbitals E_{HOMO} , E_{LUMO} and given by the equations below [18-22].

$$\begin{aligned} \chi &= -1/2(E_{\text{LUMO}} + E_{\text{HOMO}}) \\ \mu &= -\chi = 1/2(E_{\text{LUMO}} + E_{\text{HOMO}}) \\ \eta &= 1/2(E_{\text{LUMO}} - E_{\text{HOMO}}) \\ S &= 1/\eta \\ \omega &= \mu^2/\eta \end{aligned}$$

According to Parr et al., electrophilicity index (ω) [21] is a global reactivity index similar to the chemical hardness and chemical potential. The global reactivity descriptors of TTF separated by thiophene **1-4** are computed by DFT/B3LYP method with 6-31G (d,p) basis set and listed in Table 5.

Table 5. Quantum chemical descriptors of TTF separated by thiophene 1-4

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
E_{HOMO} (eV)	-4.402	-4.220	-4.553	-4.698
E_{LUMO} (eV)	-1.274	-1.099	-1.522	-2.136
ΔE_{gap} (eV)	3.128	3.121	3.031	2.561
IE (eV)	4.402	4.220	4.553	4.698
A (eV)	1.274	1.099	1.522	2.136
μ (eV)	-2.838	-2.660	-3.038	-3.417
χ (eV)	2.838	2.660	3.038	3.417
η (eV)	1.564	1.560	1.515	1.281
S (eV)	0.320	0.320	0.330	0.390
ω (eV)	2.575	2.267	3.044	4.559

As presented in table 5, the compound which have the lowest energetic gap is the compound **4** ($\Delta E_{\text{gap}} = 2.561$ eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound **1** ($\Delta E_{\text{gap}} = 3.128$ eV). The compound that has the highest HOMO energy is the compound **2** ($E_{\text{HOMO}} = -4.220$ eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound **4** ($E_{\text{LUMO}} = -2.136$ 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 ($I = 4.220$ eV), so that will be the better electron donor. Compound **4** has the largest value of the affinity ($A = 2.136$ eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound **4** ($\eta = 1.281$ eV, $S = 0.390$ eV) is lesser (greater) among all the molecules. Thus, compound **4** is found to be more reactive than all the compounds. Compound **4** possesses higher electronegativity value ($\chi = 3.417$ eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **4** ($\omega = 4.559$ eV) indicates that it is the stronger electrophiles than all compounds. Compound **4** 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:

DFT is one of the important tools of quantum chemistry to understand popular chemical concepts such as electronegativity, electron affinity, chemical potential and ionization potential [23]. The electron density-based local reactivity descriptors such as Fukui functions are proposed to explain the chemical selectivity or reactivity at a particular site of a chemical system [24]. Electron density is a property that contains all the information about the molecular system and plays an important role in calculating almost all these chemical quantities. Parr and Yang [25] proposed a finite difference approach to calculate Fukui function indices, i.e. nucleophilic, electrophilic and radical attacks. Fukui indices are, in short, reactivity indices; they give us information about which atoms in a molecule have a larger tendency to either loose or accept an electron, which we chemist interpret as which are more

prone to undergo a nucleophilic or an electrophilic attack, respectively. The Fukui function is defined as [26]

$$f(r) = \frac{\partial \rho(r)}{\partial N}$$

where $\rho(r)$ is the electronic density, N is the number of electrons and r is the external potential exerted by the nucleus. The Fukui function is a local reactivity descriptor that indicates the preferred regions where a chemical species will change its density when the number of electrons is modified. Therefore, it indicates the propensity of the electronic density to deform at a given position upon accepting or denoting electrons [26-28]. Also, it is possible to define the corresponding condensed or atomic Fukui functions on the k th atom site as,

$$f_j^- = q_j(N) - q_j(N-1) \text{ for nucleophilic attack}$$

$$f_j^+ = q_j(N+1) - q_j(N) \text{ for electrophilic attack}$$

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

where +, -, 0 signs show nucleophilic, electrophilic and radical attack, respectively. In these equations, q_k is the atomic charge (evaluated from Mulliken population analysis, electrostatic derived charge, etc.) at the k th atomic site is the neutral (N), anionic ($N+1$) or cationic ($N-1$) chemical species. The Fukui function allows determining the pin point distribution of the active sites on a molecule, the value of this function is completely dependent of the kind of charges used. The reactive sites on TTF separated by thiophene **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	4 C	1 C	12 C	13 C	Atom	4 C	1 C	13 C	17 C
f^+	0.036	0.023	0.022	0.022	f^+	0.035	0.022	0.014	0.001
Atom	17 C	8 C	12 C	5 S	Atom	15 C	16 C	8 C	14 C
f^-	0.015	0.009	0.003	0.003	f^-	0.015	0.014	0.012	0.010
Atom	4 C	1 C	12 C	17 C	Atom	17 C	14 C	13 C	16 C
f^0	0.028	0.027	0.015	0.011	f^0	0.005	0.004	0.002	0.002

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

Compound 3					Compound 4				
Atom	13 C	14 C	17 C	16 C	Atom	4 C	25 C	28 C	12 C
f^+	0.022	0.018	0.016	0.013	f^+	0.059	0.050	0.035	0.033
Atom	17 C	15 C	14 C	12 C	Atom	16 C	8 C	14 C	17 C
f^-	0.007	0.006	0.005	0.000	f^-	0.030	0.022	0.022	0.021
Atom	17 C	14 C	13 C	16 C	Atom	12 C	15 C	4 C	31 C
f^0	0.008	0.006	0.005	0.003	f^0	0.004	0.003	0.002	0.000

From the tables 6-7, the parameters of local reactivity descriptors show that 4C is the more reactive site in compounds **1**, **2** and **4** and 13C is the more reactive site in compounds **3** for nucleophilic attacks. The more reactive sites for electrophilic attacks are 17C for compound **1** and **3** and 15C, 16C for compounds **2** and **4** respectively. The more reactive sites in radical attacks are 4C, 12C for compounds **1**, **4** respectively and 17C for the both compounds **2** and **3**.

3.6. Natural Bond Orbital Analysis (NBO)

NBO provides an accurate method for studying interaction and also gives an efficient basis for investigating charge transfer or conjugative interaction in various molecular systems [29]. The bonding-anti bonding interaction can be quantitatively described in terms of the NBO approach that is expressed by means of second-order perturbation interaction energy $E(2)$ [30-33]. The stabilization energy $E^{(2)}$ associated with $i(\text{donor}) \rightarrow j(\text{acceptor})$ delocalization is estimated from the second-order perturbation approach as given below:

$$E_2 = \Delta E_j = q_i \frac{F(i, j)^2}{\epsilon_j - \epsilon_i}$$

where q_i is the donor orbital occupancy, ϵ_i and ϵ_j are diagonal elements (orbital energies) and $F(i,j)$ is the off-diagonal Fock matrix element. The larger the $E^{(2)}$ value, the more intensive is the interaction between electron donors and electron acceptors, i.e. the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. The second order perturbation theory of Fock-matrix in the NBO analysis shows intramolecular hyper conjugative interactions of TTF separated by thiophene **1-4** is calculated at the B3LYP/6-31G (d,p) level and presented 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) S25	1.75744	$\pi^*(C18-C19)$	0.21950	22.95	0.25	0.068
LP (2) S23	1.75910	$\pi^*(C13-C14)$	0.22022	22.84	0.25	0.068
LP (2) S22	1.75262	$\pi^*(C13-C14)$	0.22022	22.23	0.25	0.067
LP (2) S24	1.75566	$\pi^*(C18-C19)$	0.21950	21.98	0.25	0.067
LP (2) S5	1.68016	$\pi^*(C3-C4)$	0.38743	20.16	0.27	0.067
$\pi(C3-C4)$	1.77763	$\pi^*(C8-C12)$	0.33250	19.99	0.27	0.068
$\pi(C1-C2)$	1.78450	$\pi^*(C10-C17)$	0.33315	17.28	0.27	0.063
$\pi(C1-C2)$	1.78450	$\pi^*(C3-C4)$	0.38743	16.93	0.29	0.065
$\pi(C3-C4)$	1.77763	$\pi^*(C1-C2)$	0.39208	16.80	0.29	0.065
$\pi(C10-C17)$	1.90945	$\pi^*(C1-C2)$	0.39208	11.73	0.32	0.059
$\pi(C8-C12)$	1.90871	$\pi^*(C3-C4)$	0.38743	11.61	0.32	0.059
$\sigma(C8-H9)$	1.95724	$\sigma^*(C12-S22)$	0.04506	8.45	0.68	0.068
$\sigma(C10-H11)$	1.96456	$\sigma^*(C17-S24)$	0.04484	8.38	0.68	0.068
$\sigma(C8-H9)$	1.95724	$\sigma^*(C4-S5)$	0.03060	6.94	0.72	0.063
$\sigma(C14-H16)$	1.97566	$\sigma^*(C13-S22)$	0.02299	5.36	0.77	0.057
$\sigma(C4-C8)$	1.97555	$\sigma^*(C8-C12)$	0.01584	5.02	1.32	0.073
$\sigma(C12-S23)$	1.97695	$\sigma^*(C4-C8)$	0.02459	4.93	1.18	0.068
LP (1) S23	1.97577	$\sigma^*(C12-S22)$	0.04506	3.99	0.82	0.051
LP (1) S25	1.97556	$\sigma^*(C17-S24)$	0.04484	3.99	0.82	0.051
LP (1) S22	1.97062	$\sigma^*(C12-S23)$	0.03707	3.89	0.81	0.050

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) S21	1.77296	$\pi^*(C16-C17)$	0.23736	20.80	0.27	0.067
LP (2) S19	1.77433	$\pi^*(C13-C14)$	0.23797	20.68	0.27	0.067
LP (2) S18	1.76565	$\pi^*(C8-C12)$	0.33259	20.44	0.27	0.068
LP (2) S20	1.76847	$\pi^*(C10-C15)$	0.33300	20.40	0.27	0.068
LP (2) S18	1.76565	$\pi^*(C13-C14)$	0.23797	20.30	0.27	0.066
LP (2) S5	1.68159	$\pi^*(C3-C4)$	0.38784	20.12	0.27	0.067
LP (2) S20	1.76847	$\pi^*(C16-C17)$	0.23736	20.05	0.27	0.066
$\pi(C3-C4)$	1.77932	$\pi^*(C8-C12)$	0.33259	19.74	0.27	0.067
LP (2) S5	1.68159	$\pi^*(C1-C2)$	0.39166	19.23	0.27	0.066
LP (2) S21	1.77296	$\pi^*(C10-C15)$	0.33300	18.07	0.27	0.064
LP (2) S19	1.77433	$\pi^*(C8-C12)$	0.33259	17.93	0.27	0.064
$\pi(C1-C2)$	1.78574	$\pi^*(C10-C15)$	0.33300	17.09	0.27	0.063
$\pi(C1-C2)$	1.78574	$\pi^*(C3-C4)$	0.38784	16.91	0.28	0.065
$\pi(C3-C4)$	1.77932	$\pi^*(C1-C2)$	0.39166	16.75	0.29	0.065
$\pi(C10-C15)$	1.90789	$\pi^*(C1-C2)$	0.39166	11.88	0.32	0.059
$\pi(C8-C12)$	1.90712	$\pi^*(C3-C4)$	0.38784	11.78	0.32	0.059
$\sigma(C8-H9)$	1.95776	$\sigma^*(C12-S18)$	0.04174	8.41	0.69	0.068
$\sigma(C10-H11)$	1.96509	$\sigma^*(C15-S20)$	0.04156	8.35	0.69	0.068
$\sigma(C8-H9)$	1.95776	$\sigma^*(C4-S5)$	0.03066	6.94	0.72	0.063
$\sigma(C17-S21)$	1.97334	$\sigma^*(C16-C22)$	0.01857	5.25	1.04	0.066

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) S5	1.67255	$\pi^*(C3-C4)$	0.38364	20.54	0.27	0.067
LP (2) S19	1.77914	$\pi^*(C13-C14)$	0.37234	20.54	0.23	0.064
LP (2) S21	1.77647	$\pi^*(C16-C17)$	0.37137	20.41	0.23	0.064
$\pi(C3-C4)$	1.77318	$\pi^*(C8-C12)$	0.31691	20.33	0.27	0.068
LP (2) S18	1.76974	$\pi^*(C13-C14)$	0.37234	20.22	0.23	0.064
LP (2) S20	1.77404	$\pi^*(C16-C17)$	0.37137	20.06	0.24	0.064
LP (2) S5	1.67255	$\pi^*(C1-C2)$	0.38500	19.68	0.27	0.066
LP (2) S24	1.85838	$\pi^*(C16-C17)$	0.37137	18.70	0.24	0.063
LP (2) S18	1.76974	$\pi^*(C8-C12)$	0.31691	18.30	0.27	0.064
LP (2) S22	1.85843	$\pi^*(C13-C14)$	0.37234	18.30	0.24	0.062
LP (2) S20	1.77404	$\pi^*(C10-C15)$	0.31454	18.27	0.27	0.064
$\pi(C1-C2)$	1.78085	$\pi^*(C3-C4)$	0.38364	16.91	0.29	0.065
LP (2) S21	1.77647	$\pi^*(C10-C15)$	0.31454	16.69	0.27	0.061
$\pi(C1-C2)$	1.78085	$\pi^*(C10-C15)$	0.31454	16.24	0.27	0.061
$\pi(C8-C12)$	1.90516	$\pi^*(C3-C4)$	0.38364	11.44	0.32	0.058
LP (2) S25	1.87701	$\pi^*(C16-C17)$	0.37137	11.35	0.23	0.049
LP (2) S23	1.87584	$\pi^*(C13-C14)$	0.37234	11.06	0.23	0.048
$\pi(C10-C15)$	1.90672	$\pi^*(C1-C2)$	0.38500	10.73	0.32	0.056
$\sigma(C8-H9)$	1.95749	$\sigma^*(C12-S18)$	0.04653	8.46	0.69	0.068
$\sigma(C10-H11)$	1.96437	$\sigma^*(C15-S20)$	0.04777	8.34	0.69	0.068

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) O30	1.78743	$\pi^*(C28-O29)$	0.27013	49.69	0.33	0.116
LP (2) O27	1.78509	$\pi^*(C25-O26)$	0.26494	49.56	0.33	0.116
LP (2) O24	1.77831	$\pi^*(C22-O23)$	0.25002	49.27	0.33	0.115
LP (2) O33	1.77686	$\pi^*(C31-O32)$	0.24527	48.97	0.34	0.115
LP (2) O29	1.84271	$\sigma^*(C28-O30)$	0.10131	32.85	0.64	0.131
LP (2) O26	1.84194	$\sigma^*(C25-O27)$	0.10161	32.81	0.64	0.131
LP (2) O23	1.84023	$\sigma^*(C22-O24)$	0.10231	32.49	0.64	0.130
LP (2) O32	1.83869	$\sigma^*(C31-O33)$	0.10277	32.39	0.64	0.130
LP (2) S21	1.72333	$\pi^*(C16-C17)$	0.28552	24.15	0.26	0.070
LP (2) S19	1.72690	$\pi^*(C13-C14)$	0.28688	23.99	0.25	0.070
LP (2) S18	1.73539	$\pi^*(C13-C14)$	0.28688	22.38	0.25	0.067
LP (2) S20	1.74326	$\pi^*(C16-C17)$	0.28552	21.80	0.25	0.066
$\pi(C3-C4)$	1.77512	$\pi^*(C8-C12)$	0.32582	20.28	0.27	0.068
$\pi(C1-C2)$	1.78238	$\pi^*(C10-C15)$	0.32279	16.91	0.27	0.062
$\pi(C3-C4)$	1.77512	$\pi^*(C1-C2)$	0.38606	16.90	0.29	0.065
$\pi(C1-C2)$	1.78238	$\pi^*(C3-C4)$	0.38321	16.86	0.29	0.065
$\pi(C16-C17)$	1.88204	$\pi^*(C28-O29)$	0.27013	14.43	0.31	0.062
$\pi(C13-C14)$	1.88140	$\pi^*(C25-O26)$	0.26494	13.35	0.31	0.060
$\pi(C8-C12)$	1.91008	$\pi^*(C3-C4)$	0.38321	11.38	0.32	0.058
$\pi(C10-C15)$	1.91092	$\pi^*(C1-C2)$	0.38606	11.05	0.32	0.058

The intra molecular interaction for the title compounds is formed by the orbital overlap between: $\pi(C3-C4)$ and $\pi^*(C8-C12)$ for compound 1, $\pi(C3-C4)$ and $\pi^*(C8-C12)$ for compound 2, $\pi(C3-C4)$ and $\pi^*(C8-C12)$ for compound 3 and $\pi(C3-C4)$ and $\pi^*(C8-C12)$ for compound 4 respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of $\pi(C3-C4)$ to $\pi^*(C8-C12)$ for compound 1, $\pi(C3-C4)$ to $\pi^*(C8-C12)$ for compound 2, $\pi(C3-C4)$ to $\pi^*(C8-C12)$ for compound 3 and $\pi(C3-C4)$ to $\pi^*(C8-C12)$ for compound 4 lead to highest stabilization of 19.99, 19.74, 5.89 and 5.85 kJ mol⁻¹ respectively. In case of LP (2) S25 orbital to the $\pi^*(C18-C19)$ for compound 1, LP (2) S21 orbital to $\pi^*(C16-C17)$ for compound 2, LP (2) S5 orbital to $\pi^*(C3-C4)$ for compound 3, LP (2) O30 orbital to $\pi^*(C28-O29)$ for compound 4 respectively, show the stabilization energy of 22.95, 20.80, 20.54 and 49.69 kJ mol⁻¹ respectively.

3.7. Nonlinear Optical Properties (NLO)

Hyperpolarizabilities and polarizabilities determine the strength of molecular interactions, cross sections of different scattering and collision processes and the non-linear optical properties (NLO) of the system [34]. NLO is the current research as it provides the key functions of frequency shifting; optical modulation and optical memory for the emerging technologies in areas such as telecommunication, signal processing and optical inter connections [35]. The first order hyperpolarizability is a third rank tensor described by 3×3×3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [36]. The expression of the external Electric field when it becomes weak and homogeneous is

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

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

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

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

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

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

and

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

$$\beta_y = \beta_{yyx} + \beta_{xyy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzx} + \beta_{xzz} + \beta_{yzz}$$

The total molecular dipole moment (μ), mean polarizability (α_0) and anisotropy polarizability ($\Delta\alpha$) and first hyperpolarizability (β_0) of TTF separated by thiophene **1-4** are computed at DFT/B3LYP method with 6-31G (d,p) basis set and depicted in Table 12.

Table 12. The dipole moments μ (D), polarizability α (esu), the anisotropy of the polarizability $\Delta\alpha$ (esu) and the first hyperpolarizability β_0 (esu) of TTF separated by thiophene 1-4

Parameters	compound 1	compound 2	compound 3	compound 4
β_{xxx}	48.5662	-51.9869	126.1306	-150.8761
β_{yyy}	-0.2756	1.0471	-13.4868	25.4100
β_{zzz}	-0.0004	0.0152	3.6041	27.0772
β_{xyy}	-11.2293	5.7014	-40.8498	35.2859
β_{xxy}	-39.1565	52.7500	121.2337	208.1845
β_{xxz}	0.0199	0.1282	-9.5819	262.2399
β_{xzz}	-0.3967	-0.2834	4.0342	16.5712
β_{yzz}	-1.8508	4.4583	5.8608	15.7364
β_{yyz}	0.0044	0.0004	-6.1300	3.0308
β_{xyz}	0.0127	0.0186	-0.1152	-95.2099
$\beta_0(\text{esu}) \times 10^{-33}$	54.3223	74.5813	145.0189	396.7845
μ_x	0.4356	-0.5659	0.5192	-0.2091
μ_y	-0.2164	0.6528	0.3412	1.1751
μ_z	0.0004	0.0021	-1.0835	1.9530
μ (D)	0.4864	0.8640	1.2490	2.2888
α_{xx}	-88.5127	-96.2797	-118.8895	-122.3996
α_{yy}	-123.3393	-149.1197	-205.0181	-220.7949
α_{zz}	-141.6035	-166.3713	-216.4466	-225.1946
α_{xy}	8.1613	9.4463	-19.5411	18.6919
α_{xz}	-0.0013	-0.0038	3.1610	-2.0543
α_{yz}	-0.0003	0.0007	-0.2701	3.6653
$\alpha(\text{esu}) \times 10^{-24}$	48.8096	65.3372	98.5334	105.9954

$\Delta\alpha(\text{esu})\times 10^{-24}$	7.2336	9.6830	14.6026	15.7085
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Since the values of the polarizabilities ($\Delta\alpha$) and the hyperpolarizabilities (β_0) of the GAUSSIAN 09 output are obtained in atomic units (a.u.), the calculated values have been converted into electrostatic units (e.s.u.) (for α ; 1 a.u. = 0.1482×10^{-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 0.4864, 0.8640, 1.2490 and 2.2888 D respectively, which are approximately two 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 48.8096×10^{-24} , 65.3372×10^{-24} , 98.5334×10^{-24} and 105.9954×10^{-24} esu respectively; the values of anisotropy of the polarizability are 7.2336, 9.6830, 14.6026 and 15.7085 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 TTF separated by thiophene molecules are equal to 54.3223×10^{-33} , 74.5813×10^{-33} , 145.0189×10^{-33} and 396.7845×10^{-33} esu. The first hyperpolarizability of title molecules is approximately 0.16, 0.22, 0.42 and 1.16 times than those of urea (β of urea is 343.272×10^{-33} esu obtained by B3LYP/6-311G (d,p) method). The above results show that only compound **4** might have the NLO applications.

4. CONCLUSION

A complete theoretical analysis of TTF separated by thiophene **1-4** was performed by DFT/B3LYP method with 6-31G (d,p) basis set. The geometrical structures and parameters have been optimized by DFT method. The HOMO and LUMO analysis is used to determine the charge transfer within the molecules. The NBO analysis have been made with which the stability and intra molecular interactions have been interpreted and the transactions give stabilization to the structure have been identified by second order perturbation energy calculations. The analysis of Fukui indices is also carried out to distinguish the nucleophilic and electrophilic centers. MESP confirmed the different negative and positive potential sites of the molecules in accordance with the total electron density surface. From global reactivity descriptors, compound **4** has a low kinetic stability and high chemical reactivity as compare to others. The total and partial dipole moment, polarizability and hyperpolarizability of the title compounds are calculated and it is found that the compound **4** is candidate NLO material.

REFERENCES

1. Fichou D (ed). Handbook of Oligo and Polythiophenes, Weinheim: Wiley-VCH, (1999). ISBN: 9783527294459.
2. Roncali J. Conjugated Poly(thiophenes): Synthesis, Functionalization, and Applications. Chem. Rev. 1992; 92(4): 711-738. Available: <http://dx.doi.org/10.1021/cr00012a009>.
3. Mishra A, Ma CQ, Bäuerle P. Functional Oligothiophenes: Molecular Design for Multidimensional Nanoarchitectures and Their Applications. Chem. Rev. 2009; 109(3): 1141-1276. Available: <http://dx.doi.org/10.1021/cr8004229>.
4. Yamada J, Sugimoto T. TTF Chemistry: Fundamentals and Applications of Tetrathiafulvalene, Tokyo: Kodansha; Berlin; New York: Springer-Verlag, 2004. 3540210040.
5. Segura JL, Martín N. New Concepts in Tetrathiafulvalene Chemistry. Angew. Chem., Int. Ed. 2001; 40(8): 1372-1409. Available: [http://dx.doi.org/10.1002/1521-3773\(20010417\)40:8<1372::AID-ANIE1372>3.0.CO;2-I](http://dx.doi.org/10.1002/1521-3773(20010417)40:8<1372::AID-ANIE1372>3.0.CO;2-I).
6. Bryce MR. Functionalised Tetrathiafulvalenes: New Applications as Versatile π -electron Systems in Materials Chemistry. J. Mater. Chem. 2000; 10(3): 589-598. Available: <http://dx.doi.org/10.1039/A908385E>.
7. Mas-Torrent M, Durkut M, Hadley P, Ribas X, Rovira C. High Mobility of Dithiophene-Tetrathiafulvalene Single-Crystal Organic Field Effect Transistors. J. Am. Chem. Soc. 2004; 126(4): 984-985. Available: <http://dx.doi.org/10.1021/ja0393933>.
8. Nishida S, Morita Y, Fukui K, Sato K, Shiomi D, Takui T et al. Spin transfer and Solvato-/Thermochromism Induced by Intramolecular Electron Transfer in a Purely Organic Open-Shell System. Angew Chem Int Ed. 2005; 117(44): 7443-7446. Available: <http://dx.doi.org/10.1002/ange.200502180>.
9. Olaya AJ, Ge P, Gonthier FJ, Pechy P, Corminboeuf C, Girault HH. Four electron oxygen reduction by tetrathiafulvalene. J Am Chem Soc. 2011; 133(31): 12115-12123. Available: <http://dx.doi.org/10.1021/ja203251u>.

10. Geerlings P, De Proft F. Chemical Reactivity as Described by Quantum Chemical Methods. *Int. J. Mol. Sci.* 2002; 3(4): 276-309. Available: <http://dx.doi.org/10.3390/i3040276>.
11. Lakshmikantham MV, Cava PM. Synthesis and Properties of Novel π -electron Donors-Variants of Tetrathiafulvalene. *Current Science*. 1994; 66(1): 28-34.
12. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR et al. Gaussian 09, Revision C.01; Gaussian Inc.: Wallingford, CT, USA 2010.
13. Beveridge DL, Lavery R. Theoretical Biochemistry and Molecular Biophysics: DNA; Proteins. Adenine Press, 1990. ISBN: 0940030284.
14. Politzer P, Murray J. The Fundamental Nature and Role of the Electrostatic Potential in Atoms and Molecules. *Theor.Chem. Acc.* 2002; 108(3): 134-142. Available: <http://dx.doi.org/10.1007/s00214-002-0363-9>.
15. Kosar B, Albayrak C. Spectroscopic Investigations and Quantum Chemical Computational Study of (E)-4-methoxy-2-[(p-tolylimino)methyl]phenol. *Spectrochim. Acta A.* 2011; 78(1): 160-167. Available: <http://dx.doi.org/10.1016/j.saa.2010.09.016>.
16. Senthil Kumar P, Vasudevan K, Prakasam A, Geetha M, Anbarasan PM. Quantum Chemistry Calculations of 3-Phenoxyphthalonitrile Dye Sensitizer for Solar Cells. *Spectrochim. Acta A.* 2010; 77(1): 45-50. Available: <http://dx.doi.org/10.1016/j.saa.2010.04.021>.
17. Parr RG, Yang W. Density Functional Theory of Atoms and Molecules, Oxford University Press, Oxford, New York, 1989. Available: <https://doi.org/10.1002/qua.560470107>
18. Pearson RG. Absolute Electronegativity and Hardness: Applications to Organic Chemistry. *J. Org. Chem.* 1989; 54(6): 1430-1432. Available: <http://dx.doi.org/10.1021/jo00267a034>.
19. Parr RG, Pearson RG. Absolute Hardness: Companion Parameter to Absolute Electronegativity. *J. Am. Chem. Soc.* 1983; 105(26): 7512-7516. Available: <http://dx.doi.org/10.1021/ja00364a005>.
20. Geerlings P, De Proft F, Langenaeker W. Conceptual Density Functional Theory. *Chem. Rev.* 2003; 103(5): 1793-1873. Available: <http://dx.doi.org/10.1021/cr990029p>.
21. Parr RG, Szentpály L, Liu S. Electrophilicity Index. *J. Am. Chem. Soc.* 1999; 121(9): 1922-1924. Available: <http://dx.doi.org/10.1021/ja983494x>.
22. Chattaraj PK, Sarkar U, Roy DR. Electrophilicity Index. *Chem. Rev.* 2006; 106(6): 2065-2091. Available: <http://dx.doi.org/10.1021/cr040109f>.
23. Hohenberg P, Kohn W. Inhomogeneous Electron Gas. *Phys. Rev.* 1964; 136(3B): B864-B871. Available: <http://dx.doi.org/10.1103/PhysRev.136.B864>.
24. Yang W, Parr RG. Hardness, Softness, and the Fukui Function in the Electronic Theory of Metals and Catalysis. *Proc. Natl. Acad. Sci. USA.* 1985; 82(20): 6723-6726. Available: <http://dx.doi.org/10.1073/pnas.82.20.6723>.
25. Parr RG, Yang W. Density Functional Approach to the Frontier-Electron Theory of Chemical Reactivity. *J. Am. Chem. Soc.* 1984; 106(14): 4049-4050. Available: <http://dx.doi.org/10.1021/ja00326a036>.
26. Parr RG, and Yang W. Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989. Available: <https://doi.org/10.1002/qua.560470107>
27. Ayers PW, Parr RGJ. Variational Principles for Describing Chemical Reactions: The Fukui Function and Chemical Hardness Revisited. *Am. Chem. Soc.* 2000; 122(9): 2010-2018. Available: <http://dx.doi.org/10.1021/ja9924039>.
28. Parr RG, Yang WJ. Density Functional Approach to the Frontier-Electron Theory of Chemical Reactivity. *Am. Chem. Soc.* 1984; 106(14): 4049-4050. Available: <http://dx.doi.org/10.1021/ja00326a036>.
29. Snehathalatha IM, Ravikumar C, Joe Hubert I, Sekar N, Jayakumar VS. Spectroscopic Analysis and DFT Calculations of a Food Additive Carmoisine. *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* 2009; 72(3): 654-662. Available: <http://dx.doi.org/10.1016/j.saa.2008.11.017>.
30. Reed AE, Weinhold F. Natural Localized Molecular Orbitals. *J. Chem. Phys.* 1985; 83(4): 1736. Available: <http://dx.doi.org/10.1063/1.449360>.
31. Reed AE, Weinhold RB, Weinhold F. Natural Population Analysis. *J. Chem. Phys.* 1985; 83(2): 735. Available: <http://dx.doi.org/10.1063/1.449486>.
32. Reed AE, Weinhold F. Natural Bond Orbital Analysis of Near-Hartree-Fock Water Dimer. *J. Chem. Phys.* 1983; 78(6): 4066. Available: <http://dx.doi.org/10.1063/1.445134>.
33. Foster JP, Weinhold F. Natural Hybrid Orbitals. *J. Am. Chem. Soc.* 1980; 102(24): 7211-7218. Available: <http://dx.doi.org/10.1021/ja00544a007>.

- 382 34. Sun Y, Chen X, Sun L, Guo X, Lu W. Nanoring Structure and Optical Properties of Ga₈As₈.
383 Chem. Phys. Lett. 2003; 381(3-4): 397-403. Available:
384 <http://dx.doi.org/10.1016/j.cplett.2003.09.115>.
385 35. Geskin VM, Lambert C, Bredas JL. Origin of High Second- and Third-Order Nonlinear Optical
386 Response in Ammonio/Borato Diphenylpolyene Zwitterions: the Remarkable Role of
387 Polarized Aromatic Groups. J. Am. Chem. Soc. 2003; 125(50): 15651-15658. Available:
388 <http://dx.doi.org/10.1021/ja035862p>.
389 36. Kleinman DA. Nonlinear Dielectric Polarization in Optical Media. Phys. Rev. 1962; 126(6):
390 1977-1979. Available: <http://dx.doi.org/10.1103/PhysRev.126.1977>.