



Study of the Molecular Structure and Chemical Reactivity of a Series of *p*-Nitrophenyl Benzene-fused bis tetrathiafulvalenes by DFT Calculations

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ABSTRACT

By using density functional method at the level of B3LYP theory and 6-31G(d,p) basis set the molecular geometry of dibenzylaminophenyl benzene-fused bis tetrathiafulvalenes 1-4 in the ground state have been calculated. The electron density based local reactivity descriptor such as Fukui functions were calculated to explain the chemical reactivity site in the molecule. The electronic properties, such as excitation energies, HOMO and LUMO energies were performed which confirms the charge transfer of the molecule. The molecular electrostatic potential has also been computed. According to the electrophilicity index (ω), compound 3 is a good electrophile which is acting as a better, nucleophile. The chemometric methods PCA and HCA were employed to find the subset of variables that could correctly classify the compounds according to their reactivity.

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

INTRODUCTION

Molecular simulation methods have become an important technique in many areas of chemistry with the recent advent of effective and widespread software for molecular mechanics, molecular dynamics, and Monte Carlo simulations, along with procedures for the estimation of free energy differences. This advance has been mainly thanks to the modern tools and the available experimental techniques which have reached the ability to control the size, composition and functionality of matter and also to perform a complete and more accurate characterization of its physical and chemical properties. Density functional theory (DFT) is a powerful, formally exact reformulation of Quantum mechanics¹⁻³. It is distinct from quantum chemical methods because in its revolutionary perspective the electronic density, rather than the many-electron wave function, plays the central role⁴. Chemical reactivity is most often described in terms of energy profiles along a certain reaction path, i.e., in terms of the change in energy associated with a certain change in the atomic arrangement. For the prediction of such paths, one has to be able to calculate the energy of a molecular system starting from the first principles of quantum mechanics. DFT is a well-established tool to rationalize chemical reactivity⁵. Properties such as chemical potential⁶, chemical hardness⁷ and the Fukui function⁸, allowing us to gain deep insights into the nature of chemical reactions, can be obtained on a ground theoretical basis.

Tetrathiafulvalene (TTF) and its derivatives have been extensively studied for more than 25 years as π -electron donors in intermolecular charge-transfer materials, the

intriguing potential of TTF as a donor in an intra-molecular sense has recently been developed⁹ and many versatile, functionalized TTF building blocks are now readily available. Tetrathiafulvalene (TTF) and its derivatives are versatile building blocks in many areas of materials chemistry¹⁰. They play essential role in cation sensors, liquid crystals, intra molecular charge-transfer and nonlinear optical materials, supra molecular switches and devices, and redox polymers (main-chain, side-chain and dendritic systems). In this context and in the aim to create a database on the geometrical parameters of molecules based on TTF, in this paper, we give a complete description of the molecular geometry and we evaluate the global, local reactivity descriptors and MEP features of the title compound to get a better understanding the chemical behavior of these important precursors of organic materials.

MATERIAL AND METHODS

All computational calculations have been performed on personal computer using the Gaussian 09W program packages developed by Frisch and coworkers. 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.



Table 1: Optimized geometric parameters of compound 1 and 2

Compound 1				Compound 2			
Bond Length (Å)		Bond Angles (°)		Bond Length (Å)		Bond Angles (°)	
R(1,2)	1.348	A(2,1,3)	124.118	R(1,2)	1.348	A(2,1,3)	124.119
R(1,3)	1.083	A(2,1,40)	119.370	R(1,3)	1.083	A(1,2,4)	125.801
R(2,4)	1.470	A(1,2,39)	115.480	R(2,4)	1.470	A(3,1,38)	116.507
R(1,40)	1.757	A(4,2,39)	118.701	R(2,37)	1.788	A(2,1,38)	119.369
R(11,14)	1.469	A(2,39,17)	95.164	R(11,14)	1.468	A(1,38,17)	94.573
R(14,15)	1.232	A(18,17,40)	123.309	R(14,15)	1.232	A(9,11,14)	119.102
R(17,18)	1.350	A(39,17,40)	113.287	R(17,18)	1.350	A(18,17,38)	123.317
R(17,40)	1.784	A(22,25,36)	123.005	R(17,37)	1.781	A(37,17,38)	113.274
R(20,22)	1.395	A(15,14,16)	124.697	R(22,25)	1.395	A(30,28,39)	128.030
R(28,31)	1.083	A(30,28,31)	124.964	R(28,39)	1.503	A(15,14,16)	124.688

Table 2: Optimized geometric parameters of compound 3 and 4

Compound 3				Compound 4			
Bond Length (Å)		Bond Angles (°)		Bond Length (Å)		Bond Angles (°)	
R(1,2)	1.348	A(2,1,33)	119.369	R(1,2)	1.348	A(1,2,4)	125.809
R(1,3)	1.083	A(3,1,33)	116.501	R(1,3)	1.083	A(2,1,33)	119.372
R(2,4)	1.470	A(7,11,14)	119.186	R(2,4)	1.470	A(1,2,32)	115.472
R(1,33)	1.752	A(1,33,17)	94.580	R(1,33)	1.752	A(7,11,14)	119.193
R(11,14)	1.469	A(15,14,16)	124.702	R(11,14)	1.468	A(1,33,17)	94.577
R(14,15)	1.232	A(18,17,33)	123.312	R(14,16)	1.231	A(18,17,33)	123.319
R(17,18)	1.350	A(32,17,33)	113.287	R(17,18)	1.350	A(32,17,33)	113.279
R(17,33)	1.784	A(22,20,31)	122.941	R(17,33)	1.784	A(15,14,16)	124.690
R(22,25)	1.395	A(11,14,15)	117.625	R(35,42)	1.506	A(37,35,42)	128.698
R(37,40)	1.086	A(35,36,45)	116.506	R(39,45)	1.558	A(35,42,39)	101.692

Molecular electrostatic potential

Electrostatic potential maps are very useful three dimensional diagrams used to visualize the charge distributions and charge related properties of molecules. The MEP is typically visualized through mapping its values

onto the surface reflecting the molecules boundaries so it allows us to visualize the size and shape of molecules. MEP diagram has been also used to predict the reactive sites for electrophilic and nucleophilic attack, and in studies of biological recognition and hydrogen bonding



interactions [12]. The MEP of the studied compounds calculated using B3LYP method with 6-31G(d,p) basis set is shown in Fig. 2. This Figure provides a visual representation of the chemically active sites and comparative reactivity of atoms. Potential increases in the

order red < orange < yellow < green < blue. For all the studied compounds, the negative regions (red) are mainly localized over the oxygen atoms. The maximum positive regions (blue) are localized on the hydrogen atom.

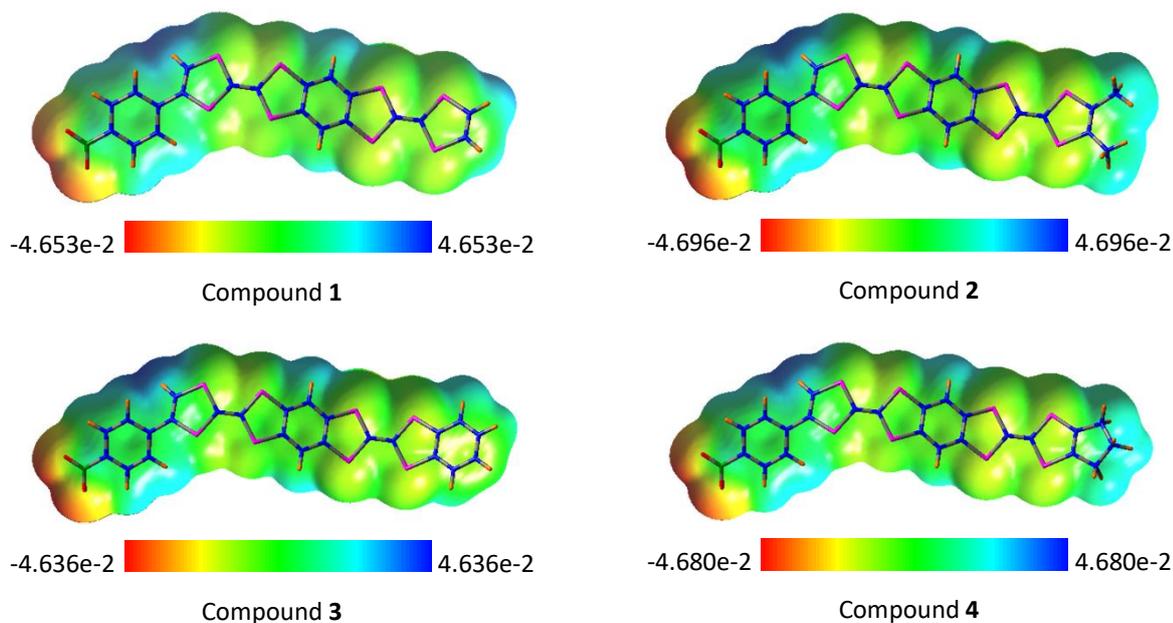


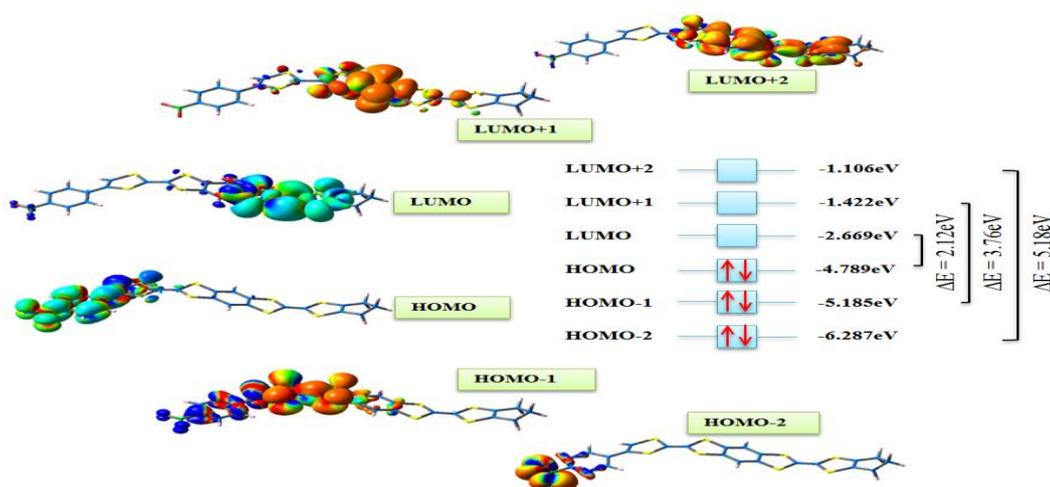
Figure 2: Molecular electrostatic potential surface of *p*-nitrophenyl benzene-fused bis tetrathiafulvalenes **1-4**

Frontier molecular orbitals (FMOs)

The frontier molecular orbital determine the way in which the molecule interacts with other species. HOMO (highest occupied molecular orbital), which can be thought the outermost orbital containing electrons, tends to give these electrons such as an electron donor. On the other hand, LUMO (lowest unoccupied molecular orbital) can be thought the innermost orbital containing free places to accept electrons [13]. Therefore, while the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structures [14], in this case, the order of stability of the

title compounds is **3**, **1**, **2** and **4**. HOMO-LUMO helps to characterize the chemical reactivity and kinetic stability of the molecule [15]. A molecule with a small gap is more polarized and is known as soft molecule. Recently, the energy gap between HOMO and LUMO has been used to prove the bioactivity from intramolecular charge transfer (ICT) [16,17] because it is a measure of electron conductivity. The frontier orbital (HOMO, LUMO) of *p*-nitrophenyl benzene-fused bis tetrathiafulvalene **4**, with B3LYP/6-31G(d,p) method is plotted in Fig. 3. The HOMO and LUMO energy gap of *p*-nitrophenyl benzene-fused bis tetrathiafulvalenes (**1-4**) calculated by B3LYP/6-31G(d,p) method are given in Table 3.

Figure 3: HOMO-LUMO Structure with the energy level diagram of compound **4**



Global reactivity descriptors

According to the frontier molecular orbital theory, the energy of the highest occupied molecular orbital (E_{HOMO}) and lowest unoccupied molecular orbital (E_{LUMO}) are important quantum chemical indices for predicting the reactivity of a chemical species [18]. The ionization potential (I) and electron affinity (A) can also be expressed through HOMO and LUMO orbital energies. The higher HOMO energy corresponds to the more reactive molecule in the reactions with electrophiles, while lower LUMO energy is essential for molecular reactions with nucleophiles. An electronic system with larger HOMO-LUMO energy gap means a harder and less

reactive molecule [18]. The Eigen value of HOMO, LUMO and their energy gap reflect the chemical activity of the molecule. LUMO as electron acceptors represents the ability to obtain an electron whereas HOMO as electron donor represents the ability to donate electron. Smaller the HOMO-LUMO energy gaps, easier it is for HOMO electrons to be excited. Higher the HOMO energies, easier it is for HOMO to donate electrons. Lower the LUMO energies; the easier it is for LUMO to accept electrons. The calculated HOMO, LUMO with the band gap (ΔE) of *p*-nitrophenyl benzene-fused bis tetrathiafulvalenes **1-4** are given in Table 3.

Table 3: Energetic parameters of *p*-nitrophenyl benzene-fused bis tetrathiafulvalenes

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_{gap} (eV)	I(eV)	A(eV)
1	-4.900	-2.683	2.217	4.900	2.683
2	-4.806	-2.664	2.142	4.806	2.664
3	-4.976	-2.688	2.288	4.976	2.688
4	-4.789	-2.669	2.121	4.789	2.669

As shown in table 3, the compound which have the lowest energetic gap is the compound **2** ($\Delta E_{\text{gap}} = 2,142$ eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound **3** ($\Delta E_{\text{gap}} = 2,288$ eV). The compound that has the highest HOMO energy is the compound **4** ($E_{\text{HOMO}} = -4,789$ eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound **3** ($E_{\text{LUMO}} = -4,976$ 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 electro negativity (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 ($I = 4.789$ eV), so that will be the better electron donor. Compound **3** has the largest value of the affinity ($A = 2.688$ eV), so it is the better electron acceptor.

Density functional theory (DFT) [19] has now emerged as the most significant quantum mechanical technique in providing theoretical insights into the chemical reactivity and selectivity, in terms of popular qualitative chemical concepts like electronegativity (χ), hardness (η), softness(S), electrophilicity index (ω) and local reactivity descriptors such as Fukui function, $f(r)$ and local softness, $S(r)$. The relationships between the chemical potential of DFT with the first derivative of the energy with respect to the number of electrons, and therefore with the negative of the electronegativity (χ) was established by Parr et al [6]. and is given by the relation:

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

Where $v(r)$ and μ are the external and electronic chemical potentials respectively. Ionization potential (I), electron affinity (A), electro negativity (χ), global hardness (η) and softness (S) may be defined in terms of the energy of the HOMO and the LUMO using Koopman's theorem [5].

Ionization potential (I) and Electron affinity (A) [20] are given as:

$$I = -E_{\text{HOMO}} \quad \text{and} \quad A = -E_{\text{LUMO}}$$

Using the values of I and A, one can determine electro negativity (χ) [21] and the global hardness (η) [22] of the molecule:

$$\chi = \frac{I + A}{2} \quad \text{and} \quad \eta = \frac{I - A}{2}$$

Chemical softness (S) [21] and electro philicity index (ω) which was proposed by Parr et al [23]. are given as:

$$S = \frac{1}{\eta} \quad \text{and} \quad \omega = \frac{\mu^2}{2\eta}$$

According to these parameters, the chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound **4** ($\eta = 1.060$ eV) is lesser (greater) among all the molecules.

Table 4: Quantum chemical descriptors of *p*-nitrophenyl benzene-fused bis tetrathiafulvalenes

Compounds	μ (eV)	χ (eV)	η (eV)	S(eV)	ω (eV)
1	-3.792	3.792	1.109	0.451	6.484
2	-3.735	3.735	1.071	0.467	6.513
3	-3.832	3.832	1.144	0.437	6.417
4	-3.729	3.729	1.060	0.472	6.557

Thus, compound **4** is found to be more reactive than all the compounds. Compound **3** possesses higher electro negativity value ($\chi = 3.832$ eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **4** ($\omega = 6.557$ 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.

Local reactivity descriptors

The site selectivity of a chemical system cannot, however, be studied using the global descriptors of reactivity. For this, appropriate local descriptors need to be defined such as the Fukui function $f(r)$ ²⁴. To describe the reactivity of an atom in a molecule, it is necessary to condense the values of $f(r)$ around each atomic site into a single value that characterizes the atomic contribution in a molecule. Thus, for an atom k in a molecule, depending upon the types of electron transfer, three kinds of condensed Fukui function of the atom k can be obtained. According to Parr and Yang [4] the sites which have the highest values of Fukui Function $f(r)$ are more reactive centers in chemical species. The Fukui function is defined as:

$$f(r) = (\delta\rho / \delta v)_N = (\delta\rho / \delta N)_v$$

where (r) is the electronic chemical potential, (N) is the number of electrons, (ρ) corresponds to the electron density and (v) 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 donating electrons [25-28].

The second formula for $f(r)$, $[(\delta\rho(r) / \delta N)_v]$ is a quantity involving the electron density of the atoms or in its frontier valence regions. For an N -electron system, independent calculations have been made on $N-1$, N and $N+1$ electronic system with the same molecular geometry. Various population schemes yield $q_k(N-1)$, $q_k(N)$ and $q_k(N+1)$ for all the atoms. Then these values were substituted in the following equations and the corresponding Fukui function values for f_k^+ , f_k^- and f_k^0 , were obtained. In a finite-difference approximation, the values are calculated as:

$$\begin{aligned} f_k^+(r) &= (\delta\rho(r) / \delta N)_v^+ \\ &= [\rho_{N+1}(r) - \rho_N(r)] \\ &= [q_k(N+1) - q_k(N)] \end{aligned}$$

For nucleophilic attack

$$\begin{aligned} f_k^-(r) &= (\delta\rho(r) / \delta N)_v^- \\ &= [\rho_N(r) - \rho_{N-1}(r)] \\ &= [q_{k1}(N) - q_k(N-1)] \end{aligned}$$

For electrophilic attack

For radical attack

$$\begin{aligned} f_k^0(r) &= (\delta\rho(r) / \delta N)_v^0 \\ &= 1/2 [\rho_{N+1}(r) - \rho_{N-1}(r)] \\ &= 1/2 [q_k(N+1) - q_k(N-1)] \end{aligned}$$

where (ρ) is the electron density of atom (k) in the molecule and (q) is the gross charge of atom (k) in the molecule.

Table 5: Order of the reactive sites on compounds **1** and **2**

Compound 1						Compound 2					
Atom	17 C	11 C	27 C	20 C	19 C	Atom	17 C	11 C	27 C	20 C	19 C
f^+	0.033	0.015	0.013	0.007	0.006	f^+	0.033	0.015	0.013	0.007	0.006
Atom	18 C	4 C	29 C	27 C	23 C	Atom	18 C	29 C	4 C	23 C	25 C
f^-	0.016	0.010	0.010	0.008	0.007	f^-	0.017	0.011	0.010	0.009	0.009
Atom	17 C	27 C	11 C	20 C	19 C	Atom	17 C	27 C	11 C	20 C	19 C
f^0	0.017	0.010	0.006	0.005	0.005	f^0	0.017	0.009	0.006	0.005	0.005

Table 6: Order of the reactive sites on compounds 3 and 4

Compound 3						Compound 4					
Atom	17 C	11 C	27 C	20 C	19 C	Atom	17 C	11 C	27 C	20 C	19 C
f^+	0.031	0.015	0.014	0.006	0.005	f^+	0.034	0.015	0.012	0.007	0.006
Atom	18 C	27 C	35 C	36 C	4 C	Atom	18 C	34 C	4 C	23 C	25 C
f^-	0.015	0.015	0.011	0.011	0.010	f^-	0.017	0.013	0.010	0.009	0.009
Atom	17 C	27 C	35 C	36 C	11 C	Atom	17 C	27 C	11 C	20 C	19 C
f^0	0.017	0.014	0.007	0.007	0.006	f^0	0.018	0.007	0.006	0.005	0.005

The molecules under investigation mainly give reduction reactions on the nitro group. In the carbon atoms of title compounds, the tendency of the electrophilic attack, nucleophilic attack and free radical attacks is given in Tables 5 and 6.

Natural bond orbital analysis

NBO analysis has been performed on the title molecules at B3LYP/6-31G (d,p) level of theory. Natural bond orbital (NBO) analysis is a useful tool for understanding delocalization of electron density from occupied Lewis-type (donor) NBOs to properly unoccupied non-Lewis type (acceptor) NBOs within the molecule. The stabilization of orbital interaction is proportional to the difference energy between the interacting orbitals. Therefore, the interaction having strongest stabilization takes place between effective donors and effective acceptors. The interaction between bonding and anti-bonding molecular orbitals can be quantitatively described in terms of NBO approach that is expressed by means of second-order

perturbation interaction energy $E(2)$. This energy represents the estimate of the off-diagonal NBO Fock matrix element. The stabilization energy $E(2)$ associated with i (donor) $\rightarrow j$ (acceptor) delocalization is estimated from the second-order perturbation approach as given below:

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

where q_i is the donor orbital occupancy, E_i and E_j are diagonal elements (orbital energies) and $F(i, j)$ is the off-diagonal Fock matrix element.

In NBO analysis large $E(2)$ value shows the intensive interaction between electron-donors and electron-acceptors, and greater the extent of conjugation of the whole system, the possible intensive interaction are given in Tables 7-10.

Table 7: 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
$\pi^*(C_{23}-C_{25})$	0.48742	$\pi^*(C_{20}-C_{22})$	0.41377	308.84	0.01	0.083
$\pi^*(C_{23}-C_{25})$	0.48742	$\pi^*(C_{19}-C_{21})$	0.41366	307.73	0.01	0.083
LP(3)O ₁₅	1.44617	$\pi^*(N_{14}-O_{16})$	0.63127	163.21	0.14	0.139
$\pi^*(C_1-C_2)$	0.25754	$\pi^*(C_4-C_5)$	0.36945	127.47	0.01	0.060
$\pi(C_7-C_{11})$	1.63904	$\pi^*(N_{14}-O_{16})$	0.63127	24.95	0.15	0.059
$\pi(C_4-C_5)$	1.61406	$\pi^*(C_7-C_{11})$	0.37833	23.70	0.28	0.072
LP(2)S ₄₀	1.75451	$\pi^*(C_1-C_2)$	0.25754	22.23	0.26	0.068
LP(2)S ₃₃	1.77509	$\pi^*(C_{28}-C_{30})$	0.21338	21.60	0.26	0.067
LP(2)S ₃₄	1.77520	$\pi^*(C_{28}-C_{30})$	0.21338	21.58	0.26	0.067
$\pi(C_6-C_9)$	1.66742	$\pi^*(C_4-C_5)$	0.36945	20.69	0.28	0.069
$\pi(C_7-C_{11})$	1.63904	$\pi^*(C_6-C_9)$	0.28053	20.57	0.29	0.071
LP(2)S ₃₉	1.79047	$\pi^*(C_1-C_2)$	0.25754	19.29	0.26	0.064
$\pi(C_{23}-C_{25})$	1.66826	$\pi^*(C_{20}-C_{22})$	0.41377	19.26	0.29	0.068
LP(2)O ₁₆	1.89798	$\sigma^*(N_{14}-O_{15})$	0.05683	19.26	0.71	0.105
$\pi(C_{23}-C_{25})$	1.66826	$\pi^*(C_{19}-C_{21})$	0.41366	19.25	0.29	0.068
LP(2)O ₁₅	1.89821	$\sigma^*(N_{14}-O_{16})$	0.05666	19.22	0.71	0.105
$\pi(C_6-C_9)$	1.66742	$\pi^*(C_7-C_{11})$	0.37833	18.93	0.28	0.066
$\pi^*(N_{14}-O_{16})$	0.63127	$\pi^*(C_7-C_{11})$	0.37833	18.76	0.14	0.064
$\pi(C_{19}-C_{21})$	1.69325	$\pi^*(C_{23}-C_{25})$	0.48742	18.68	0.27	0.066
$\pi(C_{20}-C_{22})$	1.69351	$\pi^*(C_{23}-C_{25})$	0.48742	18.66	0.27	0.066

Table 8: 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
$\pi^*(C_{23}-C_{25})$	0.48688	$\pi^*(C_{20}-C_{22})$	0.41475	323.17	0.01	0.083
$\pi^*(C_{23}-C_{25})$	0.48688	$\pi^*(C_{19}-C_{21})$	0.41464	321.93	0.01	0.083
LP(3)O ₁₅	1.44637	$\pi^*(N_{14}-O_{16})$	0.63146	163.16	0.14	0.139
$\pi^*(C_1-C_2)$	0.25774	$\pi^*(C_4-C_5)$	0.36949	129.31	0.01	0.060
$\pi(C_7-C_{11})$	1.63910	$\pi^*(N_{14}-O_{16})$	0.63146	25.00	0.15	0.059
$\pi(C_4-C_5)$	1.61374	$\pi^*(C_7-C_{11})$	0.37860	23.73	0.28	0.072
LP(2)S ₃₈	1.75457	$\pi^*(C_1-C_2)$	0.25774	22.25	0.26	0.068
$\pi(C_6-C_9)$	1.66777	$\pi^*(C_4-C_5)$	0.36949	20.67	0.28	0.069
$\pi(C_7-C_{11})$	1.63910	$\pi^*(C_6-C_9)$	0.28050	20.57	0.29	0.071
LP(2)S ₃₁	1.78871	$\pi^*(C_{28}-C_{30})$	0.23230	19.61	0.27	0.066
LP(2)S ₃₂	1.78877	$\pi^*(C_{28}-C_{30})$	0.23230	19.61	0.27	0.066
$\pi(C_{23}-C_{25})$	1.66627	$\pi^*(C_{19}-C_{21})$	0.41464	19.35	0.29	0.068
$\pi(C_{23}-C_{25})$	1.66627	$\pi^*(C_{20}-C_{22})$	0.41475	19.35	0.29	0.068
LP(2)S ₃₇	1.79091	$\pi^*(C_1-C_2)$	0.25774	19.28	0.26	0.064
LP(2)O ₁₆	1.89802	$\sigma^*(N_{14}-O_{15})$	0.05683	19.26	0.71	0.105
LP(2)O ₁₅	1.89825	$\sigma^*(N_{14}-O_{16})$	0.05666	19.22	0.71	0.105
$\pi(C_6-C_9)$	1.66777	$\pi^*(C_7-C_{11})$	0.37860	18.92	0.28	0.066
$\pi^*(N_{14}-O_{16})$	0.63146	$\pi^*(C_7-C_{11})$	0.37860	18.76	0.14	0.064
$\pi(C_{19}-C_{21})$	1.69375	$\pi^*(C_{23}-C_{25})$	0.48688	18.61	0.27	0.066
$\pi(C_{20}-C_{22})$	1.69401	$\pi^*(C_{23}-C_{25})$	0.48688	18.60	0.27	0.066

Table 9: 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
$\pi^*(C_{23}-C_{25})$	0.48763	$\pi^*(C_{20}-C_{22})$	0.41267	303.07	0.01	0.083
$\pi^*(C_{23}-C_{25})$	0.48763	$\pi^*(C_{19}-C_{21})$	0.41256	302.07	0.01	0.083
$\pi^*(C_{36}-C_{38})$	0.40279	$\pi^*(C_{39}-C_{41})$	0.34460	191.47	0.02	0.083
$\pi^*(C_{35}-C_{37})$	0.40281	$\pi^*(C_{39}-C_{41})$	0.34460	191.41	0.02	0.083
LP(3)O ₁₅	1.44610	$\pi^*(N_{14}-O_{16})$	0.63124	163.24	0.14	0.139
$\pi^*(C_1-C_2)$	0.25746	$\pi^*(C_4-C_5)$	0.36949	126.69	0.01	0.060
$\pi(C_7-C_{11})$	1.63901	$\pi^*(N_{14}-O_{16})$	0.63124	24.94	0.15	0.059
$\pi(C_4-C_5)$	1.61411	$\pi^*(C_7-C_{11})$	0.37823	23.69	0.28	0.072
LP(2)S ₃₃	1.75439	$\pi^*(C_1-C_2)$	0.25746	22.22	0.26	0.068
$\pi(C_{39}-C_{41})$	1.66046	$\pi^*(C_{35}-C_{37})$	0.40281	21.86	0.26	0.069
$\pi(C_{39}-C_{41})$	1.66046	$\pi^*(C_{36}-C_{38})$	0.40279	21.86	0.26	0.069
$\pi(C_6-C_9)$	1.66739	$\pi^*(C_4-C_5)$	0.36949	20.69	0.28	0.069
$\pi(C_7-C_{11})$	1.63901	$\pi^*(C_6-C_9)$	0.28053	20.57	0.29	0.071
LP(2)S ₃₂	1.79025	$\pi^*(C_1-C_2)$	0.25746	19.29	0.26	0.064
LP(2)O ₁₆	1.89797	$\sigma^*(N_{14}-O_{15})$	0.05683	19.26	0.71	0.105
LP(2)O ₁₅	1.89820	$\sigma^*(N_{14}-O_{16})$	0.05667	19.23	0.71	0.105
$\pi(C_{23}-C_{25})$	1.66934	$\pi^*(C_{19}-C_{21})$	0.41256	19.19	0.29	0.068
$\pi(C_{23}-C_{25})$	1.66934	$\pi^*(C_{20}-C_{22})$	0.41267	19.19	0.29	0.068
$\pi(C_6-C_9)$	1.66739	$\pi^*(C_7-C_{11})$	0.37823	18.93	0.28	0.066
$\pi(C_{36}-C_{38})$	1.68292	$\pi^*(C_{35}-C_{37})$	0.40281	18.80	0.28	0.066

Table 10: 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
$\pi^*(C_{23}-C_{25})$	0.48716	$\pi^*(C_{20}-C_{22})$	0.41440	317.53	0.01	0.083
$\pi^*(C_{23}-C_{25})$	0.48716	$\pi^*(C_{19}-C_{21})$	0.41429	316.36	0.01	0.083
LP(3)O ₁₅	1.44631	$\pi^*(N_{14}-O_{16})$	0.63142	163.18	0.14	0.139
$\pi^*(C_1-C_2)$	0.25776	$\pi^*(C_4-C_5)$	0.36952	128.51	0.01	0.060
$\pi(C_7-C_{11})$	1.63909	$\pi^*(N_{14}-O_{16})$	0.63142	24.99	0.15	0.059
$\pi(C_4-C_5)$	1.61381	$\pi^*(C_7-C_{11})$	0.37852	23.72	0.28	0.072
LP(2)S ₃₃	1.75448	$\pi^*(C_1-C_2)$	0.25776	22.25	0.26	0.068
LP(2)S ₃₈	1.78265	$\pi^*(C_{35}-C_{36})$	0.24195	21.44	0.28	0.069
LP(2)S ₃₇	1.78279	$\pi^*(C_{35}-C_{36})$	0.24195	21.42	0.28	0.069
$\pi(C_6-C_9)$	1.66772	$\pi^*(C_4-C_5)$	0.36952	20.67	0.28	0.069
$\pi(C_7-C_{11})$	1.63909	$\pi^*(C_6-C_9)$	0.28049	20.57	0.29	0.071
$\pi(C_{23}-C_{25})$	1.66707	$\pi^*(C_{19}-C_{21})$	0.41429	19.30	0.29	0.068
$\pi(C_{23}-C_{25})$	1.66707	$\pi^*(C_{20}-C_{22})$	0.41440	19.30	0.29	0.068
LP(2)S ₃₂	1.79075	$\pi^*(C_1-C_2)$	0.25776	19.29	0.26	0.064
LP(2)O ₁₆	1.89801	$\sigma^*(N_{14}-O_{15})$	0.05683	19.26	0.71	0.105
LP(2)O ₁₅	1.89824	$\sigma^*(N_{14}-O_{16})$	0.05667	19.22	0.71	0.105
$\pi(C_6-C_9)$	1.66772	$\pi^*(C_7-C_{11})$	0.37852	18.92	0.28	0.066
$\pi^*(N_{14}-O_{16})$	0.63142	$\pi^*(C_7-C_{11})$	0.37852	18.76	0.14	0.064
$\pi(C_{19}-C_{21})$	1.97569	$\pi^*(C_{23}-C_{25})$	0.48716	18.63	0.27	0.066
$\pi(C_{20}-C_{22})$	1.97569	$\pi^*(C_{23}-C_{25})$	0.48716	18.62	0.27	0.066

The intra-molecular interaction is formed by the orbital overlap between $\pi^*(C_{23}-C_{25})$, $\pi^*(C_{20}-C_{22})$, $\pi^*(C_{19}-C_{21})$, $\pi^*(N_{14}-O_{16})$, $\pi^*(C_1-C_2)$, $\pi^*(C_4-C_5)$ for compound 1 and 2, and between $\pi^*(C_{23}-C_{25})$, $\pi^*(C_{20}-C_{22})$, $\pi^*(C_{19}-C_{21})$, $\pi^*(N_{14}-O_{16})$, $\pi^*(C_1-C_2)$, $\pi^*(C_4-C_5)$, $\pi^*(C_{36}-C_{38})$, $\pi^*(C_{35}-C_{37})$, $\pi^*(C_{39}-C_{41})$ for compound 3 and between $\pi^*(C_{23}-C_{25})$, $\pi^*(C_{20}-C_{22})$, $\pi^*(C_{19}-C_{21})$, $\pi^*(N_{14}-O_{16})$, $\pi^*(C_1-C_2)$, $\pi^*(C_4-C_5)$ for compound 4 and LP(3)O₁₅ which result into intermolecular charge transfer (ICT) causing stabilization of the system. The most important interactions in compound 1 having $\pi^*(C_{23}-C_{25})$ to $\pi^*(C_{20}-C_{22})$ and $\pi^*(C_{19}-C_{21})$, $\pi^*(C_1-C_2)$ to $\pi^*(C_4-C_5)$ lead to stabilization energy of 308.84, 307.73 and 127.47 kJ mol⁻¹ respectively, the same interactions in compound 2 lead to stabilization energy of 323.17, 321.93 and 129.31 kJ mol⁻¹ respectively. Compound 3 have $\pi^*(C_{23}-C_{25})$ to $\pi^*(C_{20}-C_{22})$ and $\pi^*(C_{19}-$

$C_{21})$, $\pi^*(C_{36}-C_{38})$ and $\pi^*(C_{35}-C_{37})$ to $\pi^*(C_{39}-C_{41})$ and $\pi^*(C_1-C_2)$ to $\pi^*(C_4-C_5)$ lead to stabilization energy of 303.07, 302.07, 191.47, 191.41 and 126.69 kJ mol⁻¹ respectively. Compound 4 have $\pi^*(C_{23}-C_{25})$ to $\pi^*(C_{20}-C_{22})$ and $\pi^*(C_{19}-C_{21})$, $\pi^*(C_1-C_2)$ to $\pi^*(C_4-C_5)$ lead to stabilization energy of 317.53, 316.36 and 128.51 kJ mol⁻¹, respectively. The intra molecular hyper conjugative interactions in compound 1 of $\pi(C_7-C_{11})$ to $\pi^*(N_{14}-O_{16})$ and $\pi(C_4-C_5)$ to $\pi^*(C_7-C_{11})$ lead to highest stabilization of 24.95 and 23.70 kJ mol⁻¹. In compound 2 $\pi(C_7-C_{11})$ to $\pi^*(N_{14}-O_{16})$ and $\pi(C_4-C_5)$ to $\pi^*(C_7-C_{11})$ lead to highest stabilization of 25.00 and 23.73 kJ mol⁻¹. For compound 3 $\pi(C_7-C_{11})$ to $\pi^*(N_{14}-O_{16})$ and $\pi(C_4-C_5)$ to $\pi^*(C_7-C_{11})$ lead to highest stabilization of 24.94 and 23.69 kJ mol⁻¹. In compound 4 of $\pi(C_7-C_{11})$ to $\pi^*(N_{14}-O_{16})$ and $\pi(C_4-C_5)$ to $\pi^*(C_7-C_{11})$ lead to highest stabilization of 24.99 and 23.72 kJ mol⁻¹. In case of LP(3) orbital to the

$\pi^*(N_{14}-O_{16})$ in all compounds **1-4**, show the stabilization energy of 163.21, 163.16, 163.24 and 163.18 kJ mol⁻¹, respectively.

Non-linear optical effects

The nonlinear optical effects arise due to the interactions of electromagnetic fields in various media to produce new fields which are altered in frequency, phase and amplitude or other propagation characteristics from the incident fields. Computational approach is an inexpensive, yet an effective way to design molecules by analyzing their potential which helps to determine the molecular NLO properties. In this direction, The first static hyper polarizability (β_{tot}) and its related properties (α , β and $\Delta\alpha$) of *p*-nitrophenyl benzene-fused bis tetrathiafulvalenes **1-4** have been calculated using B3LYP/6-31G (d,p) method based on finite-field approach and are presented in Table 11. To calculate all the electric dipole moment and the first hyper polarizability tensor components for a given system will depend on the choice of the Cartesian coordinate system (x, y, z)=(0, 0, 0) was chosen at own centre of mass of molecule. The polarizability of this novel molecular system for which $\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$ is said to be isotropic. The polarizability is isotropic or is the same in all directions for a molecular system whose electron density is spherically symmetrical. If the molecule is perfectly isotropic (P) and (E) will have the same direction and is then a simple scalar quantity. The polarizability of this

novel molecular system for which $\alpha_{xx} \neq \alpha_{yy} \neq \alpha_{zz}$ (P) will no longer have the same direction as (E).

In the presence of an applied electric field, the energy of a system is a function of the electric field and the first order hyperpolarizability is a third rank tensor that can be described by a 3×3×3 matrices. The 27 components of the 3D matrix can be reduced to 10 components because of the Kleinman symmetry. It can be given in the lower tetrahedral format. It is obvious that the lower part of the 3×3×3 matrices is tetrahedral. The components of β are defined as the coefficients in the Taylor series expansion of energy in an external electric field. 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 molecules, F_i is the field at the origin and μ_i , α_{ij} , β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability and the hyper polarizability, respectively. The total static dipole moment (μ), the mean polarizability (α), the anisotropy of the polarizability ($\Delta\alpha$) and the mean first hyperpolarizability (β_{tot}), using the x, y, z components can be calculated using the following equations:

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

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

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

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

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

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

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

Since the values of the polarizabilities ($\Delta\alpha$) and the hyperpolarizabilities (β_{tot}) of the GAUSSIAN 09 output are obtained in atomic units (a.u.), the calculated values have been converted into electrostatic units (e.s.u.) (for α ; 1 a.u. = 0.1482 x 10⁻²⁴ e.s.u., for β ; 1 a.u. = 8.6393 x 10⁻³³ e.s.u.). The calculated values of dipole moment (μ) for the title compounds were found to be 5.8762, 6.9688, 5.8157 and 6.7681 D respectively, which are approximately 5 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 -35.2043 x 10⁻²⁴, -36.5913 x 10⁻²⁴, -

38.6931 x 10⁻²⁴ and -37.5382 x 10⁻²⁴ esu respectively; the values of anisotropy of the polarizability are 8.6080, 9.5715, 9.4450 and 9.2513 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 *p*-nitrophenyl benzene-fused bis tetrathiafulvalenes are equal to 11716.5789 x 10⁻³³, 19771.3617 x 10⁻³³, 17998.0358 x 10⁻³³ and 19155.5391 x 10⁻³³ esu. The first hyperpolarizability of title molecules is approximately 34.13, 57.59, 52.43 and 55.80 times than those of urea (β of urea is 343.272 x 10⁻³³ esu obtained by HF/6-311G (d,p) method).

Table 11: The dipole moments μ (D), polarizability α , the average polarizability α (esu), the anisotropy of the polarizability $\Delta\alpha$ (esu), and the first hyperpolarizability β (esu) of *p*-nitrophenyl benzene-fused bis tetrathiafulvalenes **1-4** calculated by B3LYP/6-31 G(d,p) method

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
β_{xxx}	1366.6463	1624.4777	1500.7274	1627.9474
β_{yyy}	8.0816	7.0809	6.3441	10.3755
β_{zzz}	-7.2820	-4.4926	-7.7794	-3.6608
β_{xyy}	22.5566	35.4803	47.6151	28.0236
β_{xxy}	261.9580	301.3163	356.5226	317.5352
β_{xxz}	115.6044	136.5765	149.2141	106.5772
β_{xzz}	-41.7978	-28.2344	-48.0756	-24.2577
β_{yzz}	-9.3005	-10.6542	-10.6807	-11.0222
β_{yyz}	-0.1218	1.1470	2.9792	-0.2544
β_{xyz}	1.6408	5.4749	-4.3522	12.5524
β_{tot} (esu) $\times 10^{-33}$	11716.5789	19771.3617	17998.0358	19155.5391
μ_x	5.4217	6.5669	5.2677	6.3758
μ_y	2.2259	2.2056	2.3823	2.2133
μ_z	0.4241	0.7585	0.6308	0.5068
μ_{tot} (D)	5.8762	6.9688	5.8157	6.7681
α_{xx}	-246.9321	-249.4635	-274.5660	-257.7476
α_{yy}	-226.6631	-239.4626	-246.5028	-245.6174
α_{zz}	-239.0437	-251.7905	-262.1926	-256.5176
α_{xy}	-31.1056	-33.7059	-32.9527	-34.8885
α_{xz}	3.7538	5.3153	5.3375	3.0999
α_{yz}	-6.2078	-5.7711	-6.4618	-5.2493
α (esu) $\times 10^{-24}$	-35.2043	-36.5913	-38.6931	-37.5382
$\Delta\alpha$ (esu) $\times 10^{-24}$	8,6080	9,5715	9,4450	9,2513

CONCLUSION

In summary, we have successfully 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. The chemical reactivity and the Fukui function are found to be the most efficient descriptors to characterize the regio-selectivity that might be driving to different reactions. Compound **3** is the better electron acceptor, while compound **4** is more polarizable and is associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule that confirm the results of electrical conductivity and electrochemical study obtained in our previous work [11] where it's proved that these compounds have a high conductivity and a low oxidation potential. NLO behavior of the title molecule has been investigated by dipole moment, polarizability and first hyperpolarizability. The calculated first hyper polarizability of the title compound are 11.71×10^{-30} esu, 19.77×10^{-30} esu, 17.99×10^{-30} esu and 19.15×10^{-30} esu, respectively implies that the title molecule may be useful as a nonlinear optical material. 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 intra molecular charge transfer can induce large nonlinearity to the title molecule and the intra molecular conjugative interaction around the tetrathia fulvalene 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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