



## Density Functional Theory Calculations and Chemical Reactivity of a Series of Dibenzylaminophenyl Benzene-fused bis tetrathiafulvalenes

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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 ( $\omega$ ), 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; Quantum chemical calculations.

### INTRODUCTION

The discovery of tetrathiafulvalene (TTF) in 1970 by Wudl<sup>1</sup> initiated more intensive research into the field. Today, the family of molecular conductors based on TTF and its derivatives consists of thousands of known compounds.<sup>2</sup> TTF represents a prototype structure, ripe for structural and elemental modifications, that has provided a fertile ground for synthetic chemists to explore new methodologies. The use of the general TTF framework is likely to remain an important theme in the ongoing search for new electron donor systems and research into advanced materials in the future. In the search for new organic superconductors, it is imperative to eliminate disorder and to avoid structural modification on cooling, whilst maintaining a 2-D chalcogen atom network. When a large number of atoms or molecules are brought together to form a crystalline solid, Langmuir-Blodgett film, or polymer, and sufficient mixing of the constituent atomic or molecular orbitals occurs, an energy band will form. This supramolecular orbital provides a mechanism for conductive delocalization of electrons, by producing a conduction band, whose width is dependent upon the mixing of the molecular orbitals of neighboring molecules.

The occupancy of these bands is very important. When the energy gap between the highest occupied (valence) band and the lowest unoccupied (conduction) band is large the material is an insulator. An intrinsic semiconductor is formed when the gap decreases, thus allowing thermal excitation of electrons from the valence band into the conduction band. As the gap between the bands becomes very small, and a large number of charge carriers move easily from the highest occupied state

(Fermi level) into higher energy states within the band, the material adopts metallic behavior. The understanding of the chemical processes often requires simulations performed at different levels of theory. Quantum chemical calculations represent now a powerful tool able to answer many questions related to different molecular properties. The knowledge of reactivity on a molecule is an essential concept; it is of a crucial interest because it allows understanding interactions that are operating during a reaction mechanism. In particular electrostatic interactions have been successfully explained by the use of the molecular electrostatic potential.<sup>3,4</sup> On the other hand, there is no a unique tool to quantify and rationalize covalent interactions, however since 2005 a descriptor of local reactivity whose name is simply dual descriptor,<sup>5,6</sup> has allowed to rationalize reaction mechanisms in terms of overlapping nucleophilic regions with electrophilic regions in order to get a maximum stabilization thus leading to final products or intermediates; all those favorable nucleophilic–electrophilic interactions have been explained as a manifestation of the Principle of Maximum Hardness.<sup>7</sup>

For instance, quantum chemistry approaches are used to determine the mechanism of a given reaction, the molecular transition states involved, the assignment and interpretation of subtle features of a particular spectrum, molecular structures, vibrational frequencies, atomization energies, ionization energies, electric and magnetic properties, reaction paths.

In this paper density functional theory method was used to study HOMO-LUMO energies and global reactivity descriptors of a serie of dibenzylaminophenyl benzene-fused bis tetrathiafulvalenes at level of B3LYP theory and

6-31G(d,p) basis set. In fact the present work is a good chance to test the capability of the most recent reactivity descriptors coming from the Conceptual DFT,<sup>8-11</sup> therefore the framework of this conceptual theory will be presented in the next section.

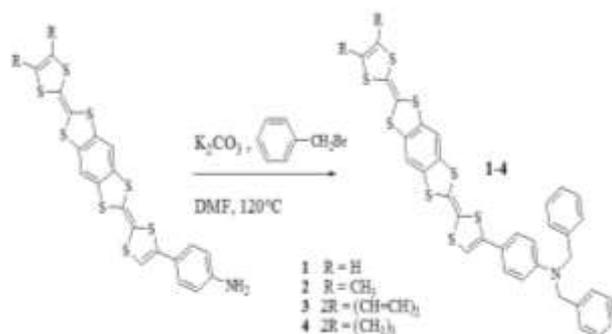
## MATERIALS AND METHODS

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 6.31 G(d,p) basis set. Gaussian output files were visualized by means of GAUSSIAN VIEW 05 software. Principal component analysis (PCA) and Hierarchical cluster analysis (HCA) are two chemometric methods were performed using software XLSTAT.

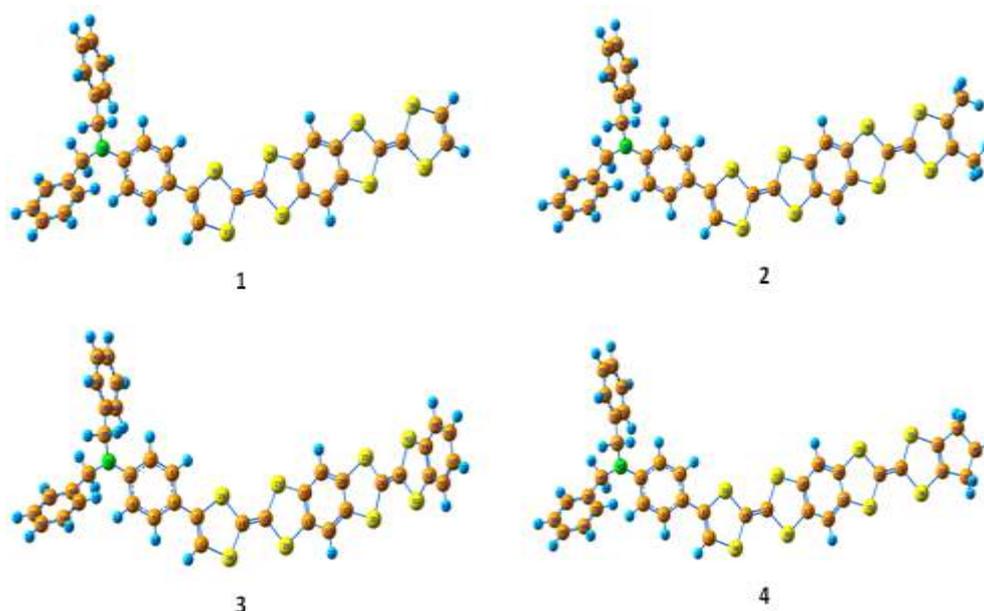
## RESULTS AND DISCUSSION

### Chemistry

In a previous work,<sup>12</sup> we have described the synthesis of new serie of dibenzylaminophenyl benzene-fused bis tetrathiafulvalenes **1-4** indicated in Scheme 1.



**Scheme 1:** Synthetic route for the preparation of dibenzylaminophenyl benzene-fused bis TTFs **1-4**



**Figure 1:** Optimized molecular structure of dibenzylaminophenyl benzene-fused bis TTFs (**1-4**)

The synthesis of these electron donors was carried out using a alkylation reaction of various *p*-aminophenyl benzene-fused bis tetrathiafulvalene derivatives by treatment with  $K_2CO_3$  (2 equiv.) and with 2 equivalents of benzyl bromide in DMF at reflux, these electron donors was obtained in 87%, 95%, 93% and 85% yields, respectively.

### Molecular Geometry

The optimized parameters (bond lengths and bond angles) of dibenzylaminophenyl benzene-fused bis tetrathiafulvalenes **1-4** have been obtained using the B3LYP/6-31G(d,p) method. No solvent corrections were made with these calculations. The computations were converged upon a true energy minimum, which were supported by the absence of imaginary frequencies. The chemical structure of the title molecules are shown in scheme 1 and the final optimized molecular structures of compounds in accordance with the atom numbering scheme were shown in Figure 1. Some selected geometrical parameters calculated are listed in Table 1 and 2.

### Molecular Electrostatic Potential

Molecular electrostatic potential has been found to be a very useful tool in the investigation of the correlation between molecular structures with its physicochemical property relationship, including biomolecules and drugs.<sup>13,14</sup> The MEP has been plotted for dibenzylaminophenyl benzene-fused bis tetrathiafulvalenes molecules at the B3LYP/6-31G(d,p) basis set as shown in Figure 2.

**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)	1.35	A(1,2,4)	126.71	R(1,2)	1.35	A(1,2,34)	115.26
R(2,4)	1.47	A(1,2,36)	115.25	R(2,4)	1.47	A(4,2,34)	118.00
R(2,36)	1.79	A(7,11,38)	121.47	R(2,34)	1.79	A(7,11,36)	121.46
R(11,38)	1.39	A(15,14,36)	123.33	R(11,36)	1.39	A(15,14,34)	123.34
R(14,15)	1.35	A(36,14,37)	113.22	R(14,15)	1.35	A(34,14,35)	113.21
R(14,36)	1.78	A(18,16,34)	123.02	R(14,34)	1.78	A(18,16,32)	123.02
R(16,18)	1.40	A(18,20,32)	122.98	R(16,18)	1.40	A(18,20,30)	123.01
R(18,20)	1.40	A(2,36,14)	95.51	R(18,20)	1.40	A(28,27,65)	114.97
R(27,29)	1.08	A(39,38,42)	115.83	R(27,65)	1.50	A(2,34,14)	95.50
R(38,42)	1.46	A(38,39,56)	116.05	R(36,40)	1.46	A(37,36,40)	115.79

**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)	1.35	A(2,1,3)	124.08	R(1,2)	1.35	A(2,1,3)	124.06
R(1,3)	1.08	A(1,2,29)	115.24	R(1,3)	1.08	A(1,2,29)	115.27
R(2,29)	1.79	A(4,2,29)	118.06	R(2,4)	1.47	A(4,2,29)	118.02
R(11,31)	1.39	A(7,11,31)	121.43	R(2,29)	1.79	A(7,11,45)	121.46
R(14,15)	1.35	A(15,14,29)	123.38	R(11,45)	1.39	A(15,14,29)	123.37
R(14,29)	1.78	A(29,14,30)	113.24	R(14,15)	1.35	A(29,14,30)	113.21
R(16,18)	1.40	A(18,16,27)	123.04	R(14,29)	1.78	A(18,16,27)	123.02
R(18,20)	1.40	A(18,20,25)	122.96	R(16,18)	1.40	A(18,20,25)	122.98
R(31,35)	1.45	A(2,29,14)	95.52	R(33,42)	1.51	A(2,29,14)	95.49
R(54,56)	1.39	A(32,31,35)	115.88	R(45,47)	1.46	A(46,45,47)	115.80

**Table 3:** Energetic parameters of dibenzylaminophenyl benzene-fused bis TTFs

Compounds	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)	ΔE <sub>gap</sub> (eV)	I(eV)	A(eV)
1	-4.569	-1.128	3.441	4.569	1.128
2	-4.516	-1.065	3.451	4.516	1.065
3	-4.586	-1.164	3.422	4.586	1.164
4	-4.519	-1.063	3.456	4.519	1.063

**Table 4:** Quantum chemical descriptors of dibenzylaminophenyl benzene-fused bis TTFs

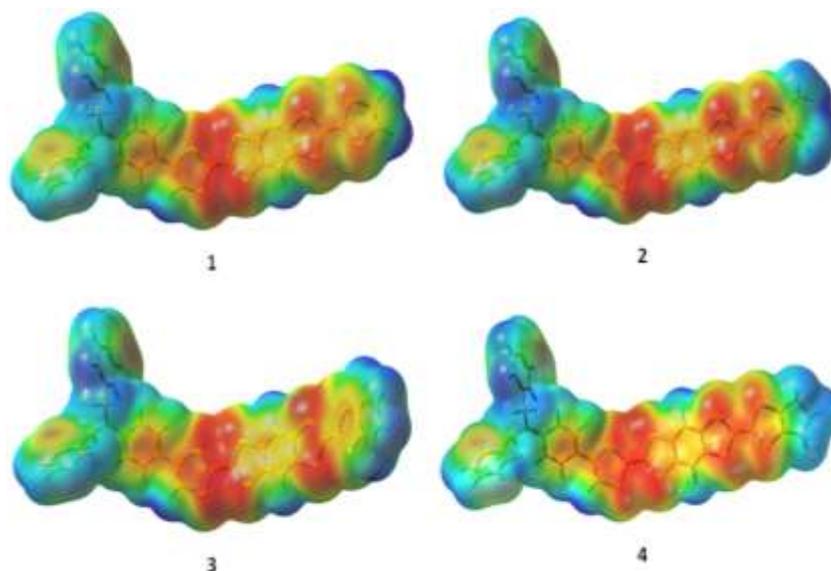
Compounds	μ(eV)	χ(eV)	η(eV)	S(eV)	ω(eV)
1	-2.848	2.848	1.721	0.291	2.358
2	-2.790	2.790	1.726	0.290	2.256
3	-2.875	2.875	1.711	0.292	2.415
4	-2.791	2.791	1.728	0.289	2.253

**Table 5:** Values of the Fukui function of compounds 1 and 2

Compound 1						Compound 2					
Atom	24 C	15 C	58 C	47 C	56 C	Atom	24 C	15 C	56 C	45 C	27 C
$f^+$	0.027	0.022	0.011	0.011	0.003	$f^+$	0.025	0.021	0.011	0.010	0.004
Atom	14 C	24 C	58 C	47 C	16 C	Atom	14 C	24 C	56 C	45 C	2 C
$f^-$	0.018	0.012	0.011	0.011	0.009	$f^-$	0.016	0.010	0.010	0.010	0.008
Atom	24 C	15 C	58 C	47 C	14 C	Atom	24 C	15 C	56 C	45 C	14 C
$f^0$	0.019	0.012	0.011	0.011	0.009	$f^0$	0.018	0.012	0.010	0.010	0.008

**Table 6:** Values of the Fukui function of compounds **3** and **4**

Compound 3						Compound 4					
Atom	15 C	24 C	51 C	40 C	64 C	Atom	24 C	15 C	55 C	57 C	32 C
$f^+$	0.022	0.020	0.010	0.009	0.006	$f^+$	0.027	0.021	0.011	0.011	0.005
Atom	24 C	14 C	40 C	51 C	16 C	Atom	14 C	55 C	57 C	31 C	24 C
$f^-$	0.019	0.017	0.011	0.011	0.009	$f^-$	0.016	0.010	0.010	0.008	0.008
Atom	24 C	15 C	51 C	40 C	14 C	Atom	24 C	15 C	55 C	57 C	14 C
$f^0$	0.020	0.012	0.010	0.010	0.007	$f^0$	0.017	0.013	0.010	0.010	0.009

**Figure 2:** Molecular electrostatic potential surface of dibenzylaminophenyl benzene-fused bis TTFs (**1-4**)

The MEP superimposed on top of the total energy density as a shell. Because of the usefulness feature to study reactivity given that an approaching electrophile will be attracted to negative regions (where the electron distribution effect is dominant). The different electrostatic potential values of the surface are represented by different colors: red represents regions of most negative electrostatic potential, blue represents regions of most positive electrostatic potential, and green represents regions of zero potential. Potential increases in the order: red < orange < yellow < green < blue. In all cases, the shape of the electrostatic potential surface is influenced by the structure and charge density distributions in the molecule with sites close to the oxygen atom, showing regions of most negative electrostatic potential. In the present work, as can be seen from the Figure 2, the calculated result shows that the negative potentials are mainly over the electron negative sulfur atoms. Positive potentials are over the nucleophilic reactive hydrogen atoms. This result gives information for the region from where the compound can have intermolecular interaction. The MEP provides a visual representation of the chemically active sites and comparative reactivity of atoms. As we have mentioned earlier, the electrostatic potential has been used primarily for predicting sites and relative reactivity towards electrophilic attack, and in studies of biological recognition and hydrogen bonding interactions.<sup>15,16</sup>

### Frontier Molecular Orbitals (FMOs)

The properties of the frontier molecular orbitals (FMOs) like energy and electron densities are very important quantum chemical parameters.

The electron densities of these FMOs were used for predicting the most reactive position in  $\pi$ -electron systems and also explained several types of reactions in conjugated system.<sup>17</sup> Moreover, the energies of the lowest unoccupied molecular orbital ( $E_{LUMO}$ ) and the highest occupied molecular orbital ( $E_{HOMO}$ ) and their energy gap ( $\Delta E$ ) reflect the chemical reactivity of the molecule.

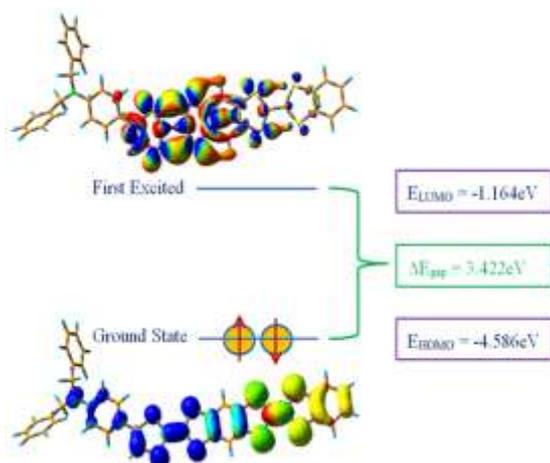
A molecule having high frontier orbital gap ( $\Delta E$ ) is less polarizable and is generally associated with a low chemical reactivity and high kinetic stability.<sup>18</sup> Recently, the energy gap between HOMO and LUMO has been used to prove the bioactivity from intramolecular charge transfer (ICT).<sup>19,20</sup>

The  $E_{HOMO}$ ,  $E_{LUMO}$  and  $\Delta E$  values of the studied compound were calculated by B3LYP/6-31G(d,p) method. The HOMO and LUMO picture for compound **3** is shown in Figure 3.

The electron densities of the HOMO and LUMO are mainly localized on the TTF-atom.

The LUMO of all the studied systems is mainly localized on the  $\pi$ -system of the TTF-ring. In general, the presence

of dibenzylaminophenyl substituent on the TTF-ring stabilizes both HOMO and LUMO levels.



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

### Global Reactivity Descriptors

Several new chemical reactivity descriptors have been proposed from time to time for understanding various aspects of pharmacological sciences including drug design and the possible ecotoxicological characteristics of the drug molecules. Conceptual DFT based descriptors have helped in many ways to understand the structure of molecules and their reactivity. Various reactivity descriptors as chemical potential, global hardness, electrophilicity have been calculated using the standard working equations and listed in Table 3 and 4.

The chemical potential,  $\mu$ , of a system is useful for describing physical phenomena and processes, such as phase transitions, the stratification of gases in a gravitational field and electric currents in semi-conductor junctions and nuclear reactions, to mention just a few. In equilibrium it has been defined as the derivative of the energy with respect to the number of electrons at fixed molecular geometry:<sup>21</sup>

$$\mu = \left[ \frac{\partial E}{\partial N} \right]_V$$

Here  $E$  is expressed as function of the number of electrons,  $N$ , i.e., functional of  $N$ ,  $E(N)$ .

It is seen that the chemical potential of dibenzylaminophenyl benzene-fused bis TTFs (**1-4**) molecules is negative. It means that these substances are stable. They do not decompose spontaneously into the elements they are made up of.

Those substances, which have a positive potential are difficult to synthesize and conserve. They are metastable at best.

The hardness signifies the resistance towards the deformation of electron cloud of chemical systems under small perturbation encountered during chemical processes. The principle of hardness works in Chemistry and Physics but it is not physical observable. Soft systems

are large and highly polarizable, while hard systems are relatively small and much less polarizable.

The absolute hardness,  $\eta$  of the density functional theory is defined as:<sup>22</sup>

$$\eta = 1/2 \left[ \frac{\partial \mu}{\partial N} \right]_V = 1/2 \left[ \frac{\partial^2 E}{\partial N^2} \right]_V$$

Although mathematical formulae were suggested, but rigorous evaluation of chemical potential and hardness in terms of suggested formula, this equation has not been possible. However, calculus of finite difference approximation was invoked to suggest approximate and operational formula of hardness and chemical potential as under:<sup>23</sup>

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

where 'I' and 'A' are the first ionization potential (I) and electron affinity (A) of the chemical species.

The amount of energy required to remove an electron from an isolated gaseous atom is known as ionization potential or ionization energy.

The electron affinity of an element is the energy given off when a neutral atom in the gas phase gains an extra electron to form a negatively charged ion. I energies are directly proportional to the electrochemical oxidation potentials of the compounds whereas A energies give an idea about the stability of free radicals and anions and are of great importance in the determination of biochemical pathways for electron transfer, photosynthesis, oxidative phosphorylation, and oxidative stress.<sup>24</sup>

The ionization energy and electron affinity can be expressed through HOMO and LUMO orbital energies by connecting it with Hartree-Fock SCF theory and invoking Koopmans' theorem as:<sup>25</sup>

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

$$\eta = (-E_{HOMO} + E_{LUMO})/2, \quad \mu = (E_{HOMO} + E_{LUMO})/2$$

Recently, Parr<sup>26</sup> have proposed the global electrophilicity power of a ligand and also its propensity to soak up electrons:

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

This index measures the stabilization in energy when the system acquires an additional electronic charge from the environment.

By definition, it encompasses both the ability of an electrophile to acquire additional electronic charge and the resistance of the system to exchange electronic charge with the environment.

Electrophilicity contains information about both electron transfer (chemical potential) and stability (hardness), it is expected to be a better descriptor of global chemical reactivity.

### Local Reactivity Descriptors

At a local level, electronic density is the first local reactivity descriptor to be used when electrostatic interactions are predominant between molecules; within the framework of Conceptual DFT it is defined as follows:

$$\rho(r) = [\partial E / \partial v(r)]_N$$

But when chemical reactions are governed by interactions mainly of covalent nature, in such a case a second order local reactivity descriptors (LRD) called Fukui function is used instead of electronic density.<sup>10</sup>

Fukui function is defined in terms of the derivative of  $\rho(r)$  with respect to  $N$ ; through a Maxwell relation, the same descriptor is interpreted as the variation of  $\mu$  with respect to  $u(r)$ :<sup>10</sup>

$$f(r) = (\delta\rho(r) / \delta N)_{v(r)} = [\partial\mu / \partial v(r)]_N$$

The function  $f(r)$  reflects the ability of a molecular site to accept or donate electrons. High values of  $f(r)$  are related to a high reactivity at point  $r$ .<sup>10</sup>

Since the number of electrons  $N$  is a discrete variable,<sup>27</sup> right and left derivatives of  $\rho(r)$  with respect to  $N$  have emerged.

By applying a finite difference approximation to the above equation, three definitions of Fukui functions depending on total electronic densities are obtained:

For nucleophilic attack

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

For electrophilic attack

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

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  $\rho$  is the electron density of atom ( $k$ ) in the molecule and ( $q$ ) is the gross charge of atom ( $k$ ) in the molecule.

The behavior of molecules as an electrophilic and nucleophilic attack during reaction depends on the local behavior of molecule.

The electrophilic, nucleophilic and radical attack order for the title compounds are given in Table 5 and 6.

### Principal Component Analysis (PCA)

Principal component analysis (PCA) is probably the most popular multivariate statistical technique and it is used by almost all scientific disciplines.

It is also likely to be the oldest multivariate technique. In this work, we auto scaled all calculated variables in order to compare them in the same scale.

Afterwards, PCA (principal component analysis) was used to reduce the number of variables and select the most relevant ones, i.e. those responsible for the tetrathiafulvalenes derivatives reactivity.

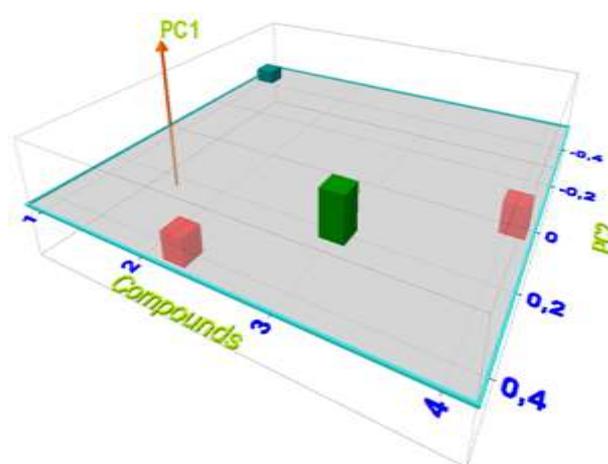
After performing many tests, a good separation is obtained between more active and less active tetrathiafulvalenes compounds using ten variables:  $I, A, \chi, \eta, \sigma, \mu, \omega, \text{EHOMO}, \text{ELUMO}, \Delta E_{\text{gap}}$  (see Tables 3 and 4).

We can observe from PCA results that the first three principal components (PC1, PC2 and PC3) describe 99.17% of the overall variance as follows: PC1 = 94.30%, PC2 = 3.95% and PC3 = 0.92%.

The score plot of the variances is a reliable representation of the spatial distribution of the points for the data set studied after explaining almost all of the variances by the first two PCs.

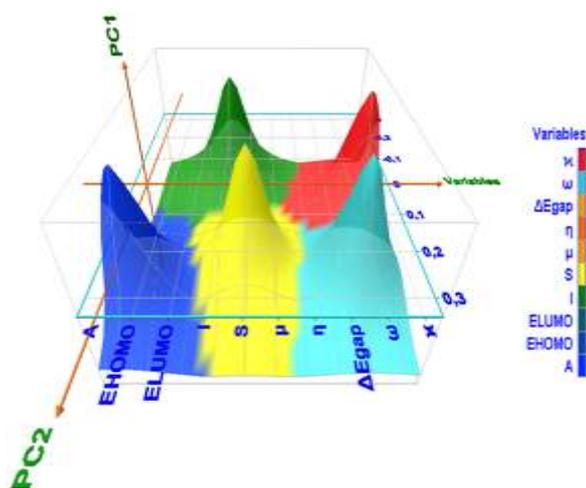
The most informative score plot is presented in Figure 4 (PC1 versus PC2) and we can see that PC1 alone is responsible for the separation between more active **1** and **3** and less active compounds **2** and **4** where  $\text{PC1} > 0$  for the more active compounds and  $\text{PC1} < 0$  for the less active ones.

The same results follow in the case of global reactivity trend based on  $\omega$ .



**Figure 4:** Score plot of dibenzylaminophenyl benzene-fused bis TTFs (**1-4**) in gas phase

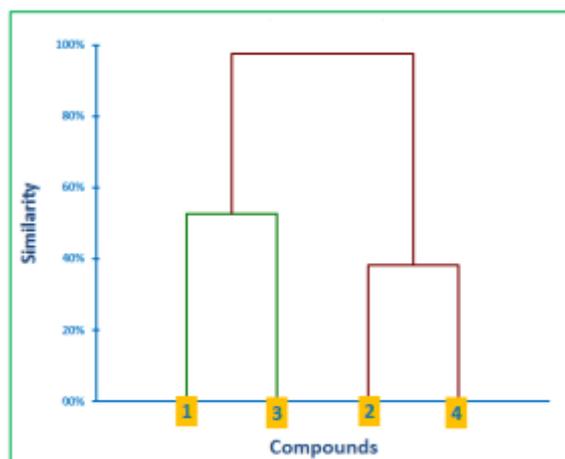
The loading vectors for the first two principal components (PC1 and PC2) are displayed in Figure 5. We can see that more active compounds ( $\text{PC1} > 0$ ) can be obtained when we have higher  $A, I, S, \chi, \omega$ , values. In this way, some important features on the more active compounds can be observed.



**Figure 5:** Loading plot for the variables responsible for the classification of dibenzylaminophenyl benzene-fused bis TTFs studied.

### Hierarchical Cluster Analysis (HCA)

Figure 6 shows HCA analysis of the current study. The horizontal lines represent the compounds and the vertical lines the similarity values between pairs of compounds, a compound and a group of compounds and among groups of compounds. We can note that HCA results are very similar to those obtained with the PCA analysis, i.e. the compounds studied were grouped into two categories: more active compounds **1** and **3** and less active compounds **2** and **4**.



**Figure 6:** Dendrogram obtained for dibenzylaminophenyl benzene-fused bis TTFs studied.

### CONCLUSION

Molecular structure and quantum chemical calculation studies have been performed on dibenzylaminophenyl benzene-fused bis tetrathiafulvalenes in order to identify their structural features. The title compounds were theoretically optimized using B3LYP/6-31G(d,p) method. Information about the charge density distribution and site of chemical activity of the molecules has been obtained by reactivity descriptors and MEP surface. From PCA results, Consistency between the results obtained through the reactivity descriptors and those that

determined from PCA analysis has been proved. 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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