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# Studies on Chemical Reactivity of *p*-aminophenyl Benzene-Fused Bis Tetrathiafulvalenes Through Quantum Chemical Approaches

Amel Bendjeddou<sup>1, \*</sup>, Tahar Abbaz<sup>1</sup>, Abdelkrim Gouasmia<sup>2</sup>, Didier Villemin<sup>3</sup>

<sup>1</sup>Aquatic and Terrestrial Ecosystems Laboratory, Mohamed-Cherif Messaadia University, Souk Ahras, Algeria

<sup>2</sup>Organic Materials and Heterochemistry Laboratory, Larbi Tebessi University, Tebessa, Algeria

<sup>3</sup>Molecular and Thio-Organic Chemistry Laboratory, Ensicaen & Caen University, Caen, France

## Email address:

amel.bendjeddou@univ-soukahras.dz (A. Bendjeddou)

\*Corresponding author

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**Abstract:** The theoretical study on the molecular structure of a serie of *p*-aminophenyl benzene-fused bis tetrathiafulvalenes is presented. Optimized geometry of the title compound was calculated using DFT method at the level of B3LYP theory and 6-31G(d,p) basis set. The HOMO and LUMO analysis were used to determine the charge transfer within the molecule and some molecular properties such as ionization potential, electron affinity, electronegativity, chemical potential, hardness, softness and global electrophilicity index. Molecular electrostatic potential map was performed by the DFT method. 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

## 1. Introduction

The heterocyclic compounds are extensively distributed in nature and are essential to life in various ways [1]. The chemistry of heterocyclic compounds is one of the most complex branches of organic chemistry. It is evenly interesting for its theoretical implications, for the diversity of its synthetic procedures, and for the physiological and industrial significance of heterocyclic compounds. The studies of heterocyclic compounds have been an interesting field for a long time in medicinal chemistry. A number of heterocyclic derivatives containing sulphur or (and) nitrogen atom serve as a unique and versatile scaffolds for experimental drug design [2]. Thiophene and a number of its derivatives [3-5] are significant in fine chemical industries as intermediates to many products for pharmaceutical, agrochemical, dyestuffs, and electronic applications.

With the development of computer techniques and computational chemistry, the quantum chemistry presents insights into electronic structures of molecules and strongly propels the development of the traditionally experimental chemistry [6]. Currently, density functional theory (DFT) method has been accepted as a popular approach for the computation of structural characteristics and energies of molecules by the community [7] and for the efficiency and accuracy with respect to the evaluation of a number of molecular properties [8]. A suitable quantum chemical study is helpful to insightfully clarify experimental phenomena and to economically predict material properties.

In this paper, we present the synthesis, molecular structure, HOMO, LUMO and molecular electrostatic potential (MESP) map of a serie of *p*-aminophenyl benzene-fused bis tetrathiafulvalenes. Calculations were performed by using DFT-B3LYP method with 6-31G(d,p) basis set. The electronic properties of the title molecule were calculated

from the total energies and the Koopmans' theorem. These are related to especially Frontier molecular orbitals. The other important quantities such as ionization potential (I), electron affinity (A), electrophilicity index ( $\omega$ ), chemical potential ( $\mu$ ), electronegativity ( $\chi$ ), chemical hardness ( $\eta$ ), and softness (S) are also evaluated in the way of molecular orbital framework.

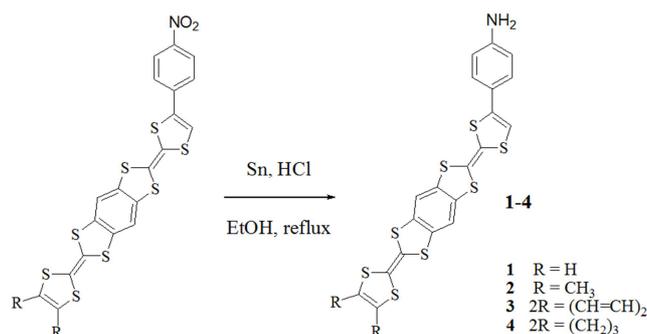
## 2. Materials and Methods

All computational calculations have been performed on personal computer using the Gaussian 09W program packages developed by Frisch and coworkers [9]. 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 [10-11]. Gaussian output files were visualized by means of GAUSSIAN VIEW 05 software [12]. Principal component analysis (PCA) [13] and Hierarchical cluster analysis (HCA) are two chemometric methods were performed using software XLSTAT.

## 3. Results and Discussion

### 3.1. Chemistry

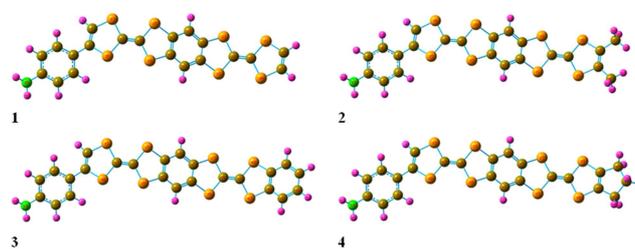
In a previous work [14], we have described the synthesis of new serie of *p*-aminophenyl benzene-fused bis tetrathiafulvalenes 1-4 indicated in Scheme 1. The synthesis of these electron donors was carried out using a reduction reaction. The nitro group of *p*-nitrophenyl benzene-fused bis tetrathiafulvalenes was reduced at reflux in the presence of tin and hydrochloric acid into an amino group in ethanol. The *p*-aminophenyl benzene-fused bis tetrathiafulvalene 1-4 derivatives were obtained after purification by column chromatography in 74%, 77%, 79% and 71% yields, respectively.



**Scheme 1.** Synthetic route for the preparation of *p*-aminophenyl benzene-fused bis tetrathiafulvalenes 1-4.

### 3.2. Molecular Geometry

The optimized geometry of *p*-aminophenyl benzene-fused bis tetrathiafulvalenes which performed by B3LYP methods with atoms numbering as shown in Figure 1. The global minimum energies obtained by DFT/B3LYP method with 6-31G(d,p) basis set for compounds 1-4 are -4008.96, -4087.61, -4162.62 and -4125.71 a.u., respectively. Some selected optimized geometrical parameters of entitled compounds have been obtained by using the above method and they are presented in Tables 1 and 2. In the present work, geometry optimization parameters for *p*-aminophenyl benzene-fused bis tetrathiafulvalenes have been employed without symmetry constraint.



**Figure 1.** Optimized structures of *p*-aminophenyl benzene-fused bis tetrathiafulvalenes at the B3LYP/6-31G(d,p) level.

**Table 1.** Optimized geometric parameters of compound 1 and 2.

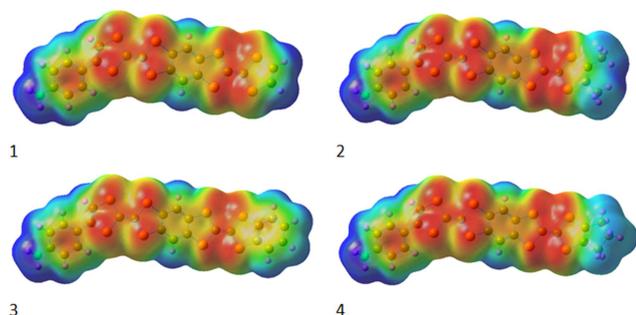
Compound 1				Compound 2			
Bond Length (Å)		Bond Angles (°)		Bond Length (Å)		Bond Angles (°)	
R(1,2)	1.34	A(2,4,6)	120.79	R(1,2)	1.34	A(1,2,4)	126.62
R(2,4)	1.46	A(1,2,4)	126.63	R(1,3)	1.08	A(2,1,3)	124.07
R(1,37)	1.76	A(3,1,2)	124.08	R(2,4)	1.47	A(2,1,36)	119.32
R(37,14)	1.78	A(2,1,37)	119.32	R(1,36)	1.76	A(1,36,15)	94.53
R(14,15)	1.35	A(1,37,14)	94.54	R(36,15)	1.78	A(36,15,35)	113.19
R(11,38)	1.39	A(37,14,15)	123.21	R(15,16)	1.35	A(36,15,16)	123.39
R(25,28)	1.08	A(37,14,36)	113.21	R(11,14)	1.39	A(34,18,20)	123.03
R(38,39)	1.01	A(35,17,19)	123.02	R(14,16)	1.01	A(46,14,45)	112.47
R(17,19)	1.39	A(31,25,28)	117.10	R(26,37)	1.50	A(11,14,46)	115.84
R(20,22)	1.40	A(39,38,40)	112.50	R(18,17)	1.40	A(30,26,37)	114.97

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)	1.34	A(6,4,2)	120.78	R(1,4)	1.46	A(4,2,1)	126.63
R(1,3)	1.08	A(4,2,1)	126.63	R(1,2)	1.34	A(2,1,3)	124.08
R(2,4)	1.46	A(2,1,3)	124.08	R(1,3)	1.08	A(2,1,31)	119.32
R(4,6)	1.40	A(2,1,31)	119.32	R(1,31)	1.76	A(1,31,15)	94.53
R(1,31)	1.76	A(1,31,15)	94.54	R(31,15)	1.78	A(31,15,16)	123.39
R(15,16)	1.35	A(46,14,45)	112.50	R(15,16)	1.35	A(29,18,20)	123.03
R(31,15)	1.78	A(45,14,11)	115.86	R(18,20)	1.39	A(29,18,17)	116.40
R(11,14)	1.39	A(31,15,30)	113.21	R(33,40)	1.50	A(34,33,40)	112.68
R(14,46)	1.01	A(31,15,16)	123.37	R(11,14)	1.39	A(11,14,46)	115.83
R(18,20)	1.39	A(20,23,27)	122.95	R(14,47)	1.01	A(46,14,47)	112.48

### 3.3. Molecular Electrostatic Potential (MEP) Diagrams

The computed 3D plot of molecular electrostatic potential (MEP) for *p*-aminophenyl benzene-fused bis tetrathiafulvalenes are shown in Figure 2, which is based on the electron density at different points on the molecule. The red colour in the map indicates the negatively charged portion and the blue colour indicates the positive region, while the green colour indicates the neutral region. The potential values in this molecule ranges from  $-4.50 \text{ e-}3 \text{ a.u.}$  (deepest red) to  $+4.50 \text{ e-}3 \text{ a.u.}$  (deepest blue). As can be seen from the map, the regions surrounding the sulfur atoms are strongly negative, while the H atoms in the ring and amine groups are positive; among them the H atoms in the amines are more positive than them in ring groups.

Figure 2. MEP plot of *p*-aminophenyl benzene-fused bis tetrathiafulvalenes.

### 3.4. Frontier Molecular Orbitals (FMOs)

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters. We can determine the way the molecule interacts with other species; hence, they are the frontier orbitals. Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the main orbitals to take part in chemical stability. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The second highest and highest occupied MO's (HOMO and HOMO-1), the lowest and the second lowest unoccupied MO's (LUMO and LUMO+1) energies for compound 1 calculated by B3LYP/6-31G(d,p) method are shown in Figure 3.

The electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

The HOMO is located mostly on the benzene-fused bis tetrathiafulvalenes. The excitation of electron from HOMO to LUMO implies an electron density transfer from benzene-fused to ring groups. The 3D plots of highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are shown Figure 3.

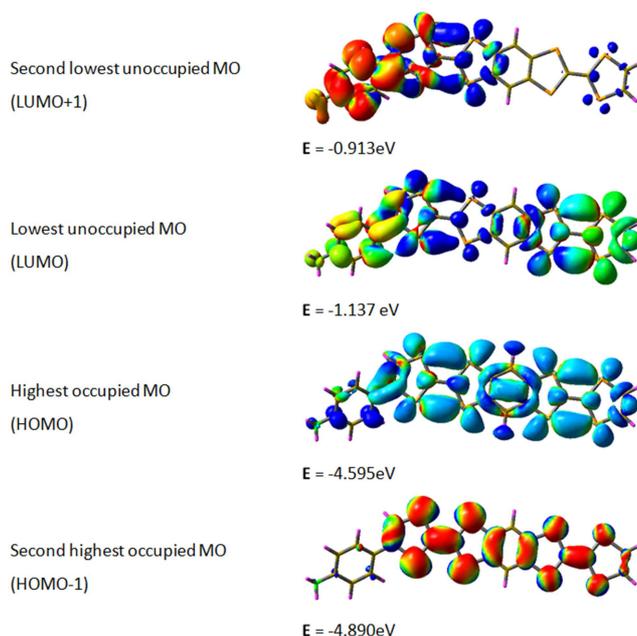


Figure 3. Spin density of second highest and highest occupied MO's and lowest and the second lowest unoccupied MO's of compound 1.

### 3.5. Global Reactivity Descriptors

The HOMO and LUMO energy values are related to the ionization potential (IP) and electron affinities (EA) as [15]:

$$IP = -E_{HOMO}, \quad AP = -E_{LUMO}$$

The difference between HOMO and LUMO energy values gives the HOMO-LUMO energy gap. By using these

HOMO-LUMO energy values, the important properties like global hardness ( $\eta$ ), global softness ( $S$ ), electronegativity ( $\chi$ ), chemical potential ( $\mu$ ) and electrophilicity index ( $\omega$ ) were calculated. The sections below describe the theoretical backgrounds of above said properties.

In the simplest terms, the hardness of a species (atom, ion, or molecule) is a qualitative indication of how polarizable it is, in another way how much its electron cloud is distorted in an electric field. The hardness and softness were suggested in literature [16, 17] to denote resistance to deformation by mechanical force. This explains the changes in the energy linked with the transition state to ground-state using different descriptors. The softness is simply the reciprocal of the hardness. The global hardness ( $\eta$ ) and softness ( $S$ ) of a chosen molecule calculates the energy gap between the HOMO and LUMO orbitals. The mathematical expression of ( $\eta$ ) and ( $S$ ) can be written as:

$$\eta = (-E_{HOMO} + E_{LUMO}) / 2, \quad S = 1 / 2\eta$$

Molecules with large HOMO-LUMO gap are hard which implies higher stability and opposing charge transfer, since they oppose changes in their electron density and distribution. On the contrary a molecule which requires a small energy gap for its excitation is also termed as soft molecules. Hence, they are highly polarizable in nature. In terms of chemical change, soft molecules are more reactive than hard molecules.

Electronegativity is the tendency of molecules to attract electrons [18]. Parr and Yang attempted to quantify this very descriptor [19]. This is found by the average of HOMO and LUMO energy values, as represented by CHELPG [19]. It can be expressed in terms of orbital energies:

$$\chi = (E_{HOMO} - E_{LUMO}) / 2$$

From this point of view the electronegativity of a molecule is the drop in energy when an infinitesimal amount of electronic charge is added to the system. It is a measure of resistance of an atom or ion, or a group or atoms in a molecule for an entering electronic charge.

Chemical potential denotes the affinity of an electron to flee and is defined as the first derivative of the total energy with respect to the number of electrons in a molecule [20]. By the expression of MO theory,  $\mu$  is simply the negative of electronegativity value. It is given as:

$$\mu = (E_{HOMO} + E_{LUMO}) / 2$$

The capability of a substance to accept electrons is quantified as electrophilicity index ( $\omega$ ). Parr et al. defined the electron affinity as the capability of a substance to have only one electron from the surroundings. This index measures the energy lowering of a substance due to the electron flow between donor and acceptor. Parr and co-workers suggested that  $\omega$  can be measured through the equation [21]:

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

**Table 3.** Energetic parameters of *p*-aminophenyl benzene-fused bis tetraiafulvalenes 1-4.

Compounds	$E_{HOMO}(eV)$	$E_{LUMO}(eV)$	$\Delta E_{gap}(eV)$	$I(eV)$	$A(eV)$
1	-4.595	-1.137	3.458	4.595	1.137
2	-4.539	-1.075	3.465	4.539	1.075
3	-4.629	-1.167	3.462	4.629	1.167
4	-4.539	-1.074	3.466	4.539	1.074

**Table 4.** Quantum chemical descriptors of *p*-aminophenyl benzene-fused bis tetraiafulvalenes 1-4.

Compounds	$\mu(eV)$	$\chi(eV)$	$\eta(eV)$	$S(eV)$	$\omega(eV)$
1	-2.866	2.866	1.729	0.2892	2.376
2	-2.807	2.807	1.732	0.2887	2.274
3	-2.898	2.898	1.731	0.2889	2.426
4	-2.807	2.807	1.733	0.2886	2.273

From theoretical calculations established, it was found that the molecule 4 has the highest hardness value ( $\eta = 1.729$  eV), which indicates that is the hardest molecule. The molecules 1 has the highest softness ( $S = 0.289$  eV), so it is the softest molecule.

Electrophilicity ( $\omega$ ), that gives an idea of the stabilization energy when the system gets saturated by electrons which come from the external environment. These reactivity information shows if a molecule is capable of donating charge. A good, more reactive, nucleophile is characterized by a lower value of ( $\omega$ ), while higher values indicate the presence of a good electrophile. Our results indicate that, molecule 4 has lower values of ( $\omega$ ), so that compound is good nucleophile. However molecule 3 is a good electrophile. Compound 1 has the smaller frontier orbital gap so, it is more polarizable and is associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule.

### 3.6. Local Reactivity Descriptors

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 [22]:

$$f(r) = (\delta\rho(r) / \delta N)r$$

where  $\delta(r)$  is the electronic density.  $N$  is the number of electrons and  $r$  is the external potential exerted by the nuclease. Fukui function (FF) is he one of the widely used local density functional descriptors to model chemical reactivity and selectivity. The Fukui function is a local reactivity descriptor that indicates the preferred where a chemical species will change its density when the number of electron is modified. Therefore, it indicates the propensity of the electronic density to perform at a given position upon accepting or donating electrons [23, 24]. Also, it is possible to define the corresponding condensed or atomic Fukui functions on the  $j^{\text{th}}$  atom site as:

$$f_k^+ = [q_k(N+1) - q_k(N)]$$

$$f_k^- = [q_k(N) - q_k(N-1)]$$

$$f_k^0 = [q_k(N+1) - q_k(N-1)]/2$$

where  $f_k^+$ ,  $f_k^-$  and  $f_k^0$  are nucleophilic, electrophilic and free radical on the reference molecule, respectively. In these equations,  $q_k$  is the atomic charge (evaluated from Mulliken population, electrostatic derived charge, etc.) at the  $j^{\text{th}}$  atomic site is the neutral (N), anionic (N+1) or cationic (N-1) chemical species.

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

Compound 1					Compound 2						
Atom	24 C	15 C	17 C	20 C	22 C	Atom	25 C	16 C	28 C	26 C	18 C
$f^+$	0.028	0.023	0.001	0.001	0.001	$f^+$	0.026	0.022	0.004	0.004	0.001
Atom	14 C	24 C	16 C	17 C	2 C	Atom	15 C	25 C	17 C	27 C	2 C
$f^-$	0.015	0.012	0.009	0.008	0.008	$f^-$	0.014	0.010	0.007	0.007	0.007
Atom	24 C	15 C	14 C	17 C	16 C	Atom	25 C	16 C	15 C	18 C	17 C
$f^0$	0.020	0.013	0.007	0.005	0.005	$f^0$	0.018	0.014	0.007	0.004	0.004

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

Compound 3					Compound 4						
Atom	16 C	25 C	33 C	34 C	21 C	Atom	25 C	16 C	33 C	34 C	18 C
$f^+$	0.023	0.021	0.006	0.006	0.003	$f^+$	0.028	0.023	0.005	0.005	0.002
Atom	25 C	15 C	17 C	33 C	34 C	Atom	15 C	32 C	25 C	17 C	2 C
$f^-$	0.019	0.015	0.009	0.009	0.009	$f^-$	0.014	0.008	0.008	0.007	0.007
Atom	25 C	16 C	33 C	34 C	15 C	Atom	25 C	16 C	15 C	18 C	17 C
$f^0$	0.020	0.013	0.007	0.007	0.005	$f^0$	0.018	0.014	0.007	0.005	0.004

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 Table 5 and 6.

### 3.7. Principal Component Analysis (PCA)

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,  $\chi$ ,  $\eta$ ,  $s$ ,  $\mu$ ,  $\omega$ ,  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ ,  $\Delta E_{\text{gap}}$  (see tables 3 and 4).

We can observe from PCA results that the first three principal components (PC1, PC2 and PC3) describe 99.92% of the overall variance as follows: PC1 = 98.89%, PC2 = 1.01% and PC3 = 0.02%. 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 PC1 > 0 for the more active compounds and PC1 < 0 for the less active ones. The same results follow in the case of global reactivity trend based on  $\omega$ .

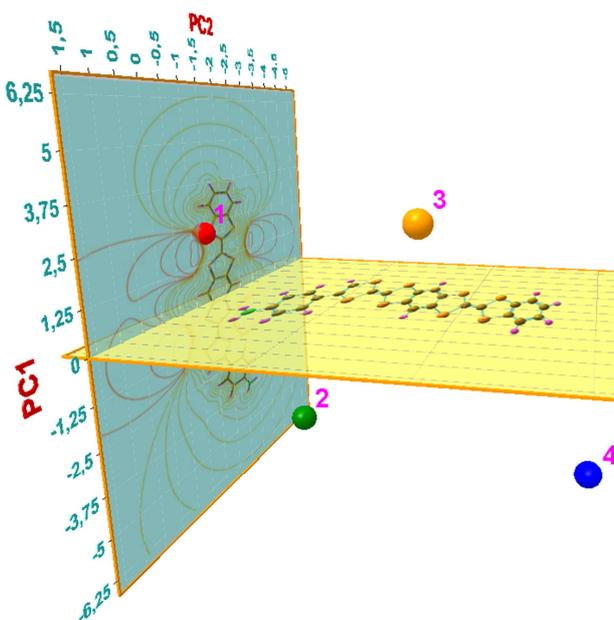


Figure 4. Score plot for *p*-aminophenyl benzene-fused bis tetrathiafulvalenes 1-4 in gas phase.

The loading vectors for the first two principal components (PC1 and PC2) are displayed in figure 5. We can see that more active compounds (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.

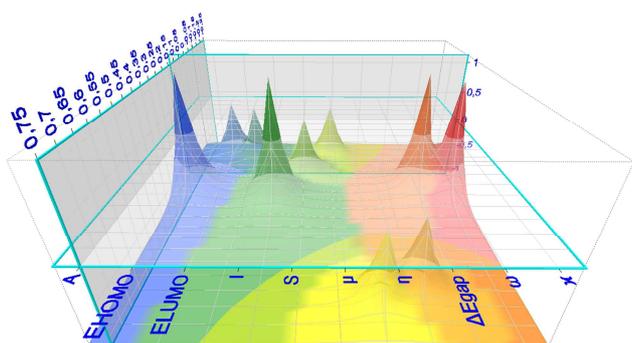


Figure 5. Loading plot for the variables responsible for the classification of the *p*-aminophenyl benzene-fused bis tetrathiafulvalenes studied

### 3.8. 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.

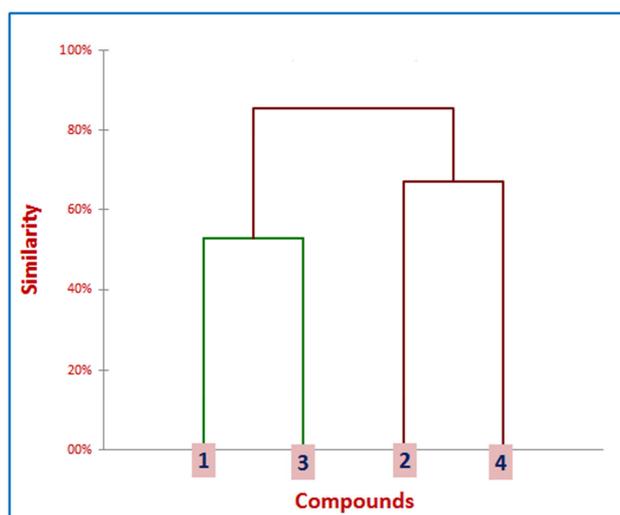


Figure 6. Dendrogram obtained for *p*-aminophenyl benzene-fused bis tetrathiafulvalenes studied.

## 4. Conclusions

This paper reports a comprehensive computational structural study on *p*-aminophenyl benzene-fused bis tetrathiafulvalenes. A number of reactivity parameters have been done by employing density functional theory (DFT) with 6-31G(d,p) as the basis sets. Reactivity reflects the susceptibility of the title compounds towards a specific chemical reaction and plays a key role in, for example, the design of new molecules and understanding material science. The chemical reactivity of molecules shows that compound 1 is more polarizable and is associated with a high chemical reactivity, low kinetic stability and is also termed as soft

molecule. The results reported in the present paper can help in the experimental investigations on the origin of the design of new molecules in the field of organic materials.

## Acknowledgements

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