Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(3):117-127
(http://derpharmachemica.com/archive.html)

Computational studies of global and local reactivity descriptors of some trimethyltetrathiafulvalenylthiophene molecules (tMeTTF-TP) by density functional theory (DFT)

Mounira Benazzouz[1], Tahar Abbaz[1,2*], Amel Bendjeddou[1], Abdelkrim Gouasmia[2] and Didier Villemin[3]

[1]Laboratory of Aquatic and Terrestrial Ecosystems, Organic and Bioorganic Chemistry group, University of Mohamed-Cherif Messaadia, Souk Ahras, Algeria
[2]Laboratory of Organic Materials and Heterochemistry, University of Tebessa, Algeria
[3]Laboratory of Molecular and Thio-Organic Chemistry, UMR CNRS 6507, INC3M, FR 3038, Labex EMC3, ensicaen & University of Caen, Caen 14050, France

---

ABSTRACT

In this work we have been calculated global and local DFT reactivity descriptors for trimethyl-tetrathiafulvalenylthiophenes (tMeTTF-TP) such as: the ionization potential (I), electron affinity (A), electronegativity (x), electrophicility (ω), and hardness (η) have been calculated using density functional theory (DFT) approach with B3LYP/6-31G(d,p) level of theory. The plots of frontier molecular orbital and molecular electrostatic potential (MEP) have been demonstrated. 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, Reactivity descriptors, Principal Component Analysis and Hierarchical Cluster Analysis

---

INTRODUCTION

The reactivity descriptors, defined within the framework of density functional theory, are chemical potential, global hardness, softness, electrophilicity index etc. [1]. These descriptors have been tested and studied in the literature by several research groups and are found to be very useful in rationalizing the reactivity patterns of the molecular systems [2-10]. In general, the descriptors are classified as global reactivity descriptors or local reactivity descriptors. The global reactivity descriptors describe about the overall stability of the system. On the other hand, the local counterpart describes the site reactivity and selectivity. Since most of these descriptors are the derivatives of energy and electron density variables, it is expected that they will provide the information of reactivity in the molecular systems [11-13]. Geerlings et al. and Chattaraj et al. have recently reviewed the theoretical basis for these descriptors and their applications in various molecular systems [14-15]. Recently, the exact conditions for which the electrophilicity index experiences an extremum along an arbitrary reaction path were studied [16-17]. In recent years, the impact of DFT in quantum chemistry has increased enormously [18-19] . Hence, in this article, we have made an effort to investigate a quantum chemical for molecular similarity indices in terms of global and local reactivity within the framework of density functional theory (DFT) [20].

MATERIALS AND MEHTODS

By employing the B3LYP functional [21] of the density functional theory [22] (DFT) with 6 31G (d, p) basis set, the geometries of all trimethyltetrathiafulvalenylthiophene compounds investigated (scheme 1) were completely optimized. The imaginary frequencies are absent which confirms that the structures are true minima on the potential energy surface. In this work all the calculations were performed in the Gaussian 09W package [21] program. Vibrational frequency assignments were made with a high degree of accuracy by combining the results of the Gauss view program [22] with symmetry considerations. Density functional theory based descriptors have found immense usefulness in the prediction of reactivity of atoms and molecules as well as site selectivity [23]. The resourcefulness of density functional descriptors in the development of QSAR has been recently reviewed by Chattaraj and al [24]. The global reactivity descriptors are: Chemical hardness (η), chemical potential (μ), electrophilicity index (ω) and softness(s). A new descriptor was defined recently by parr et al [25] used to quantify the global electrophilic power of the molecule; it is the electrophilicity index (ω), which defines a quantitative classification of the global electrophilic nature of a molecule in a relative scale.

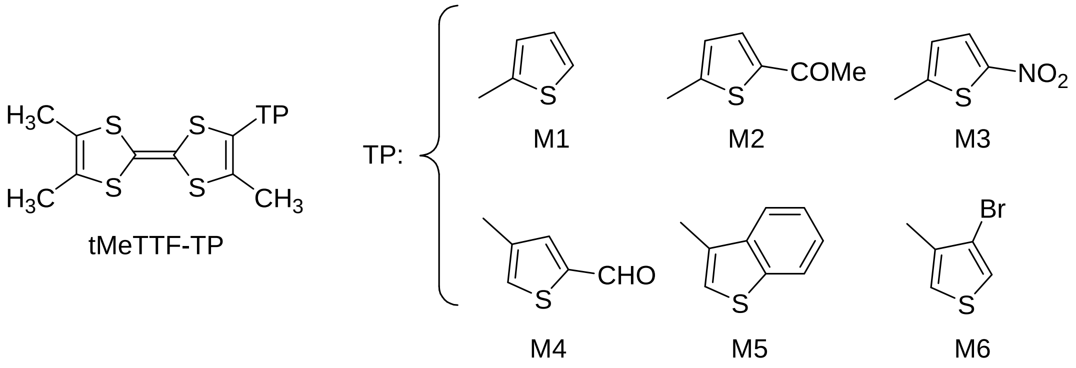
Principal component analysis (PCA) and Hierarchical cluster analysis (HCA) are two important techniques in multivariate analysis to analyze data that corresponds to more than one variable. The main objective of PCA [26, 27] and HCA are to study how the variables are related to one another, and how they work in combination to distinguish between multiple cases of observations. All chemometric methods were performed using software XLSTAT Premium.

RESULTS AND DISCUSSION

Synthesis:

In a previous work [28], we have described the synthesis of new trimethyl-tetrathiafulvalenylthiophene (tMeTTF-TP) M1-M6 indicated in Scheme 1. The synthesis of these electron donors was carried out using a palladium-catalyzed reaction involving various bromothiophene and the tributylstannyltrimethyltetrathiafulvalene (tMeTTF-$SnBu_3$). The latter was previously synthesized in 79% yield [29] by using lithiation of trimethyltetrathiafulvalene (tMeTTF) [30] followed by treatment with tributyltin chloride.

Scheme 1. Structure of trimethyltetrathiafulvalenylthiophene M1-M6



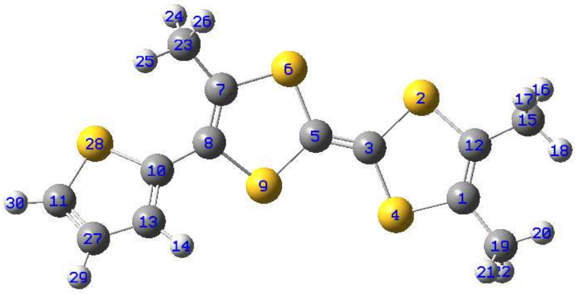
Theoretical calculation:

The structure of a molecule contains the features responsible for its physical, chemical, and biological properties, and that variations in the fate within a series of similar structures can be correlated with changes in descriptors that reflect their molecular properties.

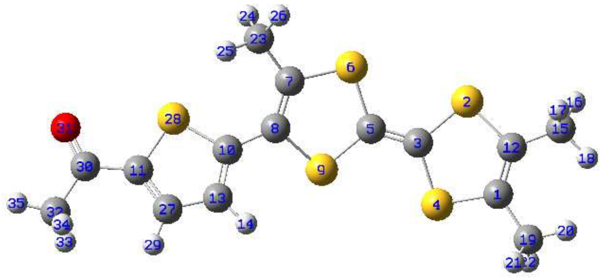
Geometries Optimization:

Geometry optimization is an important part of most quantum chemical calculations; it is a key component of most computational chemistry studies that are concerned with the structure and/or reactivity of molecules. Many of physical and chemical properties are determined from the geometry of molecule. The optimization of the geometry for the molecules M1-M6 has been achieved by energy minimization, using DFT at the B3LYP level, employing the basis set 6-31G (d, p).The following figure 1 and tables 1-3 represent the schemes of the optimized molecules, their bond lengths and their angle measurement.

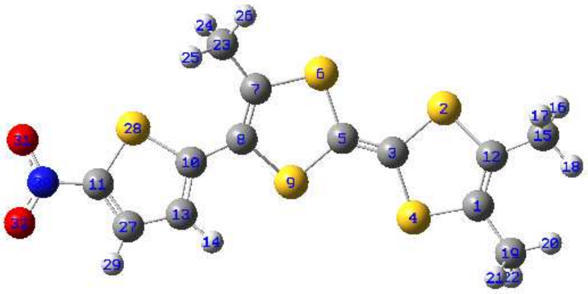
Fig. 1. Optimized molecular structure of the minimum energy structure of tMeTTF-SnBu$_3$ obtained at B3LYP/6-31G(d,p) level



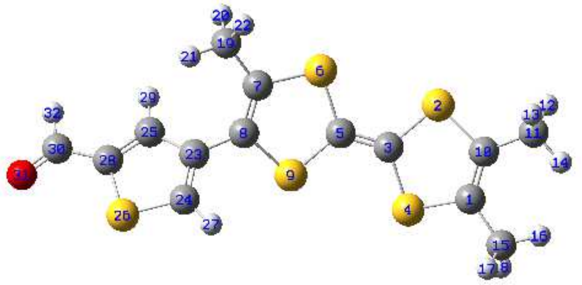
Coumpond M1



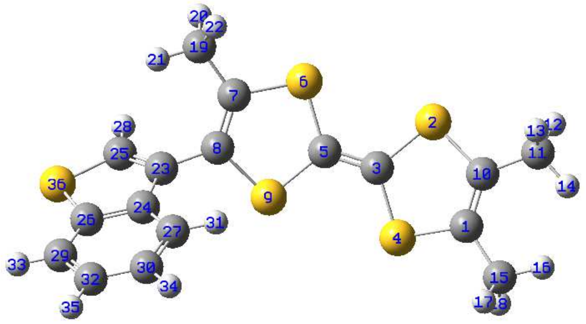
Coumpond M2



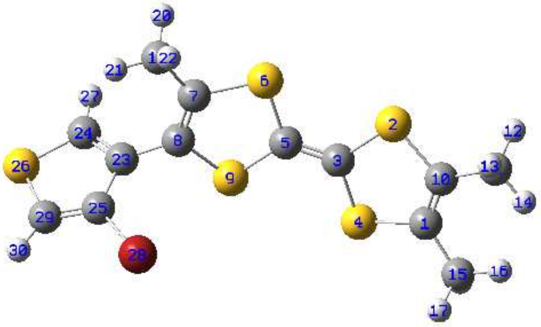
Coumpond M3



Coumpond M4



Coumpond M5



Coumpond M6

Table 1: Optimized geometric parameters of compound M1 and M2

M1				M2			
Bond length(Å)		**Angles(°)**		**Bond length(Å)**		**Angles(°)**	
C_1S_4	1.784	$C_1C_{12}S_2$	116.998	C_1S_4	1.784	$C_{19}C_1C_{12}$	127.967
C_1C_{12}	1.344	$C_{12}C_1S_4$	117.001	C_1C_{12}	1.344	$S_4C_1C_{19}$	115.025
C_1C_{19}	1.502	$C_1S_4C_3$	95.550	C_1C_{19}	1.502	$C_1S_4C_3$	95.598
$C_{12}S_2$	1.784	$S_2C_3S_4$	112.965	S_2C_{12}	1.784	$C_1C_{12}S_2$	116.995
$C_{12}C_{15}$	1.502	$C_{12}S_2C_3$	95.557	S_2C_3	1.777	$S_2C_3S_4$	113.029
C_3S_2	1.778	$S_6C_5S_9$	112.563	C_3C_5	1.349	$S_6C_5S_9$	112.531
C_3S_4	1.778	$C_5S_6C_7$	95.585	C_5S_6	1.777	$C_5S_6C_7$	95.727
C_7C_8	1.352	$C_7C_8S_9$	116.611	$C_{30}O_{31}$	1.224	$C_5S_9C_8$	95.095
$C_{13}C_{27}$	1.423	$C_8C_{10}S_{28}$	122.732	C_8S_9	1.796	$C_{12}S_2C_3$	95.606
$C_{10}S_{28}$	1.757	$C_{10}S_{28}C_{11}$	91.904	C_7C_8	1.356	$C_{11}C_{30}O_{31}$	120.741

Table 2: Optimized geometric parameters of compound M3 and M4

M3				M4			
Bond length(Å)		**Angles(°)**		**Bond length(Å)**		**Angles(°)**	
C_1C_{12}	1.344	$S_4C_1C_{12}$	116.995	C_1C_{15}	1.502	$S_2C_{10}C_1$	117.012
C_1S4	1.784	$C_1C_{12}S_2$	116.979	C_1S_4	1.784	C_{10} C_1S_4	116.994
C_1C_{19}	1.502	$C_{12}S_2C_3$	95.672	C_1C_{10}	1.344	$C_{10}S_2C_3$	95.606
S_2C_{12}	1.784	$C_1S_4C_3$	95.662	C_{10} S_2	1.784	$S_2C_3C_5$	123.575
C_3S_4	1.776	$S_2C_3C_5$	123.583	C_3C_5	1.349	$S_6C_7C_8$	116.733
C_3C_5	1.350	$C_{23}C_7C_8$	127.854	C_8C_{23}	1.472	$C_7C_8C_{23}$	127.312
C_5S_6	1.777	$S_{28}C_{11}C_{30}$	119.798	$C_{25}C_{28}$	1.377	$C_8C_7C_{19}$	127.626
C_8C_{10}	1.452	$C_{11}C_{30}O_{31}$	117.096	$C_{24}H_{27}$	1.082	$C_8C_{23}C_{25}$	125.217
$C_{30}O_{31}$	1.237	$C_7C_8C_{10}$	128.763	$C_{30}O_{31}$	1.218	$C_{28}C_{30}O_{31}$	124.626
C_{10} S_{28}	1.756	31C30O32	125.337	C_{24}S26	1.721	$C_{24}S_{26}C_{28}$	90.914

Table 3: Optimized geometric parameters of compound M5 and M6

M5				M6			
Bond length(Å)		**Angles(°)**		**Bond length(Å)**		**Angles(°)**	
C_1C_{10}	1.344	$C_{10}C_1S_4$	117.034	C_1C_{10}	1.344	$C_{10}C_1S_4$	117.037
C_1S_4	1.784	$C_1S_4C_3$	95.596	C_1C_{15}	1.502	$C_{10}S_2C_3$	95.577
C_1C_{15}	1.502	$S_2C_3C_5$	123.528	C_1S_4	1.784	$C_5S_9C_8$	94.968
S_2C_3	1.778	$S_6C_7C_8$	116.964	S_2C_3	1.778	$S_6C_7C_{19}$	116.178
C_3C_5	1.350	$C_7C_8C_{23}$	126.393	C_3C_5	1.350	$S_9C_8C_{23}$	116.614
C_5S_9	1.778	$C_8C_{23}C_{25}$	123.205	C_5S_9	1.778	$Br_{28}C_{25}C_{23}$	122.775
C_7C_{19}	1.502	$C_{25}S_{36}C_{26}$	90.824	C_7C_{19}	1.501	$C_7C_8C_{23}$	125.999
C_8C_{23}	1.475	$C_{30}C_{32}C_{29}$	120.746	C_8C_{23}	1.475	$C_{24}S_{26}C_{29}$	91.593
$C_{24}C_{26}$	1.415	$C_{23}C_{24}C_{27}$	132.562	$C_{25}Br_{28}$	1.893	$C_{15}C_1C_{10}$	127.930
$C_{26}S_{36}$	1.459	$S_6C_7C_{19}$	115.838	$C_{24}S_{26}$	1.731	$C_{23}C_{24}S_{26}$	112.671

Energetic properties:

The values of the calculated quantum chemical parameters such as the energy of the highest occupied molecular orbital (EHOMO), energy of the lowest unoccupied molecular orbital (ELUMO), energy gap (ΔEgap), ionization energy (I), electron affinity (A) are presented in table 4.

The value of HOMO energy determines the ability of electron to be donated. When the value of E_{HOMO} is high it indicates the ease of donating electron to the unoccupied orbital of the receptor molecule. When the value of E_{LUMO} is small, this means that it have a small resistance to accept electrons so it will be more able to accept electron. The HOMO and LUMO energy values are related to the ionization potential ($I= - E_{HOMO}$) and electron affinities ($A = - E_{LUMO}$). The difference between HOMO and LUMO energy values gives the HOMO-LUMO energy gap.

Table 4: Energetic parameters of tMeTTF-SnBu$_3$ calculated with B3LYP/6-31G(d,p)

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_{gap} (eV)	I (eV)	A (eV)
M1	- 4 ,482	-1,118	3,364	4,482	1,118
M2	- 4,646	-2,005	2,641	4,646	2,005
M3	- 4,879	-2,724	2,155	4,879	2,724
M4	- 4,635	-2,099	2,536	4,635	2,099
M5	- 4,465	-0,979	3,486	4,465	0,979
M6	- 4,461	-0,946	3,515	4,461	0,946

As shown in table 4, the molecule which have the lowest energetic gap is the molecule M3 (ΔEgap = 2,155). This lower gap allows it to be the softest molecule. The molecule that have the highest energy gap is the molecule M6 (ΔEgap = 3,515).

The molecule that has the highest HOMO energy is the molecule M6 ($E_{HOMO} = - 4{,}461$). This higher energy allows it to be the best electron donor. The molecule that has the lowest LUMO energy is the molecule M3 ($E_{LUMO} = - 2{,}724$) 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. The more I is lower, the molecule will be the better electron donor. The more A is larger the molecule will be the better electron acceptor.

Figures 2 and 3 represent the frontier molecular orbitals of M3 and its electrostatic potential mapping on the electronic density.

Fig. 2. Highest occupied molecular orbitals and lowest unoccupied molecular orbitals of M3

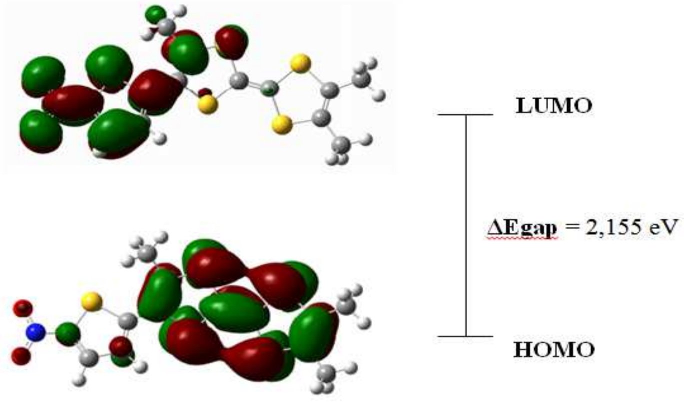
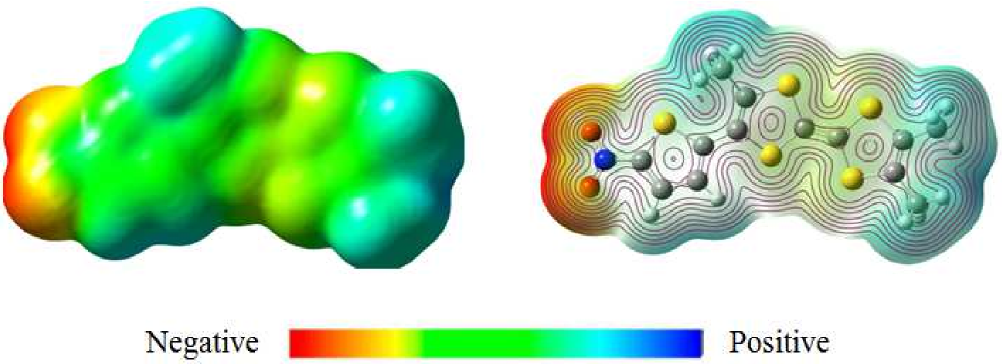


Fig. 3. Electrostatic potential mapping on the electron density of compound M3



Global reactivity descriptors:

According to Koopmans theorem [31], global properties can be obtained by the Frontier Molecular Orbital (FMO) energies. The Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) plots of tMeTTF-SnBu$_3$ molecule are presented in Fig. 2. In DFT, chemical potential (l) is defined as the first derivative of energy with respect to the number of electrons [32]:

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

and global hardness (η) [33,34] as:

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})}$$

Where E is the energy and N is the number of electrons of an electronic system at constant external potential. These equations are related with the electronegativity (**x**), describes the ability of a molecule to attract electrons towards itself in a covalent bond; and the global hardness, measure the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction, through the following relation:

$$\chi = \frac{(I + A)}{2}$$

global softness (S) is defined as:

$$S = \frac{1}{2\eta}$$

Global electrophilicity index is a combined descriptor involving chemical potential and hardness which expresses propensity of a species to accept electron. This index [35,36] is expressed as

$$\omega = \frac{\mu^2}{2\eta}$$

The values of the calculated quantum chemical parameters like global hardness (η) global softness (S), electronegativity (χ), chemical potential (μ) and electrophilicity index (ω) are summarized in table 5.

Table 5: Ouantum chemical descriptors of tMeTTF-SnBu$_3$ calculated with B3LYP/6-31G(d,p)

Compounds	μ(eV)	x(eV)	η(eV)	S(eV)	ω(eV)
M1	-2,800	2,800	1,682	0,297	2,330
M2	-3,325	3,325	1,327	0,377	4,165
M3	-3,801	3,801	1,077	0,464	6,707
M4	-3,367	3,367	1,268	0,394	4,470
M5	-2,722	2,722	1,743	0,287	2,125
M6	-2,703	2,703	1,757	0,284	2,079

All these parameters for compounds M1-M6 have been listed in Table 5. According to these parameters, the chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound M3 is lesser (greater) among all the molecules. Thus, compound M3 is found to be more reactive than all the molecules. Compound M3 possesses higher electronegativity value than all compounds so; it is the best electron acceptor.

The values of ω for compounds M1-M6 indicate that they are two groups, group 1 (M2, M3 and M4) and group 2 (M1, M5 and M6). Group 1 has the high value of electrophilicity index which, shows that the compounds of this group are a strong electrophiles than compounds of group 2.

Table 6: Values of the Fukui function considering NBO charges of the molecules M_1 and M_2 calculated with B3LYP/6-31G(d,p)

	M1				**M2**		
Atom	f^+	f^-	f^0	**Atom**	f^+	f^-	f^0
C1	0,001	0,007	0,004	**C1**	0,002	0,007	0,005
S2	-0,077	-0,157	-0,117	**S2**	-0,045	-0,155	-0,100
C3	-0,012	0,006	-0,003	**C3**	-0,020	0,009	-0,006
S4	-0,069	-0,156	-0,113	**S4**	-0,036	-0,155	-0,096
C5	**0,049**	0,004	**0,027**	**C5**	**0,036**	0,001	**0,019**
S6	-0,160	-0,163	-0,162	**S6**	-0,096	-0,153	-0,125
C7	-0,039	**0,012**	-0,014	**C7**	-0,049	0,005	-0,022
C8	0,003	0,006	0,005	**C8**	0,002	0,011	0,007
S9	-0,144	-0,156	-0,15	**S9**	-0,056	-0,126	-0,106
C10	0,010	0,005	0,008	**C10**	-0,012	**0,016**	0,002
C11	-0,032	-0,014	-0,023	**C11**	-0,007	-0,006	-0,007
C12	0,002	0,006	0,004	**C12**	0,002	0,006	0,004
C13	-0,039	0,004	-0,022	**C13**	-0,024	-0,011	-0,018
H 14	-0,046	-0,013	-0,030	**H14**	-0,055	-0,008	-0,032
C15	0,008	0,007	0,008	**C15**	0,005	0,008	0,007
H 16	-0,02	-0,033	-0,027	**H16**	-0,015	-0,033	-0,024
H 17	-0,021	-0,029	-0,025	**H17**	-0,011	-0,028	-0,020
H 18	-0,025	-0,032	-0,029	**H18**	-0,017	-0,032	-0,025
C19	0,006	0,007	0,007	**C19**	0,005	0,008	0,007
H20	-0,025	-0,032	-0,029	**H20**	-0,018	-0,032	-0,025
H21	-0,02	-0,029	-0,025	**H21**	-0,01	-0,028	-0,019
H22	-0,019	-0,032	-0,026	**H22**	-0,014	-0,033	-0,024
C23	0,024	0,007	0,016	**C23**	0,019	0,004	0,012
H24	-0,042	-0,036	-0,039	**H24**	-0,042	-0,031	-0,037
H25	-0,021	-0,033	-0,027	**H25**	-0,005	-0,028	-0,017
H26	-0,048	-0,021	-0,0345	**H26**	-0,042	-0,021	-0,032
C27	0,000	0,006	-0,003	**C27**	-0,014	-0,005	-0,010
S28	-0,122	-0,054	-0,088	**S28**	-0,142	-0,045	-0,094
H 29	-0,058	-0,035	-0,047	**H29**	-0,059	-0,028	-0,044
H30	-0,063	-0,037	-0,050	**C30**	-0,056	-0,014	-0,035
				O31	-0,117	-0,029	-0,073
				C32	0,027	0,004	0,0155
				H33	-0,057	-0,012	-0,035
				H34	-0,038	-0,010	-0,024
				H35	-0,045	-0,023	-0,034

Local reactivity descriptors:

Fukui Function [37] is one of the widely used local density functional descriptors to model chemical reactivity and site selectivity. The atom with the highest FF is highly reactive compared to the other atoms in the molecule. Fukui function is defined as the derivative of the electron density ρ(r) with respect to the total number of electrons N in the system, at constant external potential ν(r) acting on an electron due to all the nuclei in the system where **μ** is the chemical potential of the system.

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

The electronic chemical potential is the derivative of the total energy E with respect to the electron density. It is more convenient to represent the FF values around each atomic site into a single value that characterizes the atoms in a molecule. Depending on the electron transfer, three types of the FF are defined:

$$f^+(\vec{r}) = \rho_{N+1}(\vec{r}) - \rho_N(\vec{r})$$
$$f^-(\vec{r}) = \rho_N(\vec{r}) - \rho_{N-1}(\vec{r})$$
$$f^0(\vec{r}) = \frac{1}{2}\left[\rho_{N+1}(\vec{r}) - \rho_{N-1}(\vec{r})\right]$$

However, for studying the reactivity at the atomic level, a more convenient way of calculating the Fukui function is through the condensed forms of the Fukui function for an atom k in a molecule which are expressed as: [38]

$$f_k^+ = q_k(N+1) - q_k(N) \quad \text{for nucleophilic attak,}$$
$$f_k^- = q_k(N) - q_k(N-1) \quad \text{for electrophilic attak,}$$
$$f_k^0 = [q_k(N+1) - q_k(N-1)]/2 \quad \text{for radical attak.}$$

In these equations, q_k is the atomic charge (evaluated from the Mulliken population, electrostatic-derived charge, etc.) at the k^{th} atomic site in the neutral (N), anionic (N+1) or cationic (N–1) chemical species.

Table 7: Values of the Fukui function considering NBO charges of the molecules M_3 and M_4 calculated with B3LYP/6-31G(d,p)

	M3				**M4**		
Atom	f^+	f^-	f^0	**Atom**	f^+	f^-	f^0
C1	0,002	0,006	0,004	**C1**	0,002	0,007	0,005
S2	-0,042	-0,160	-0,101	**S2**	-0,053	-0,160	-0,107
C3	-0,020	0,013	-0,004	**C3**	-0,016	0,008	-0,004
S4	-0,035	-0,157	-0,096	**S4**	-0,042	-0,160	-0,101
C5	**0,033**	-0,004	**0,015**	**C5**	**0,024**	0,002	**0,013**
S6	-0,088	-0,144	-0,116	**S6**	-0,084	-0,159	-0,122
C7	-0,041	-0,004	-0,0223	**C7**	-0,019	0,006	-0,007
C8	0,007	0,018	0,013	**C8**	0,009	0,007	0,008
S9	-0,045	-0,156	-0,101	**S9**	-0,050	-0,160	-0,105
C10	-0,029	**0,028**	-0,001	**C10**	0,003	0,006	0,005
C11	0,031	-0,011	0,01	**C11**	0,005	0,008	0,007
C12	0,002	0,006	0,004	**H12**	-0,015	-0,033	-0,024
C13	-0,009	-0,019	-0,014	**H13**	-0,014	-0,029	-0,022
H14	-0,055	-0,009	-0,032	**H14**	-0,017	-0,033	-0,025
C15	0,004	0,008	0,006	**C15**	0,004	0,008	0,006
H16	-0,015	-0,033	-0,024	**H16**	-0,018	-0,033	-0,026
H17	-0,010	-0,029	-0,020	**H17**	-0,012	-0,029	-0,021
H18	-0,017	-0,032	-0,025	**H18**	-0,013	-0,033	-0,023
C19	0,004	0,008	0,006	**C19**	0,014	0,005	0,010
H20	-0,017	-0,032	-0,025	**H20**	-0,026	-0,032	-0,029
H21	-0,009	-0,029	-0,019	**H21**	0,006	-0,034	-0,014
H22	-0,014	-0,033	-0,024	**H22**	-0,041	-0,022	-0,0315
C23	0,019	0,001	0,010	**C23**	0,006	**0,018**	0,012
H24	-0,041	-0,025	-0,033	**C24**	-0,057	-0,003	-0,030
H25	-0,007	-0,021	-0,014	**C25**	-0,032	-0,009	-0,021
H26	-0,038	-0,024	-0,031	**S26**	-0,179	-0,067	-0,123
C27	-0,036	-0,007	-0,022	**H27**	-0,065	-0,006	-0,036
S28	-0,139	-0,046	-0,0925	**C28**	0,021	0,005	0,013
H29	-0,059	-0,027	-0,043	**H29**	-0,059	-0,011	-0,035
N30	-0,089	-0,018	-0,054	**C30**	-0,077	-0,011	-0,044
O31	-0,121	-0,029	-0,075	**O31**	-0,122	-0,031	-0,077
O32	-0,130	-0,037	-0,084	**H32**	-0,084	-0,021	-0,053

The values of the condensed Fukui function for Nucleophilic and electrophilic condensed Fukui functions over the atoms are reported in Tables 6-8. It was observed that for compounds M1 and M2 the more reactive sites for nucleophilic and free radical attacks is 5C and for electrophilic attack 7C and 10C respectively (table 6). For compounds M3 and M4, the more reactive sites for nucleophilic and free radical attacks is 5C and for electrophilic attack 10C and 23C respectively (table 7). Finally, the more reactive sites for nucleophilic and free radical attacks in compound 5 is 5C and for electrophilic attack is 7C and for compound 6 the more reactive sites for electrophilic attack is 7C and for nucleophilic and free radical attacks is 23C (table 8).

Table 8: Values of the Fukui function considering NBO charges of the molecules M5 and M6 calculated with B3LYP/6-31G(d,p)

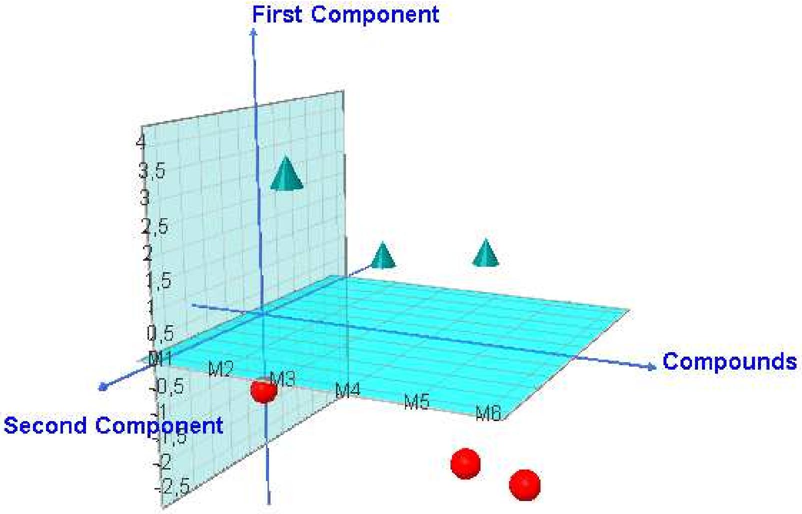
	M5				M6		
Atom	f^+	f^-	f^0	**Atom**	f^+	f^-	f^0
C1	0,002	0,007	0,005	**C1**	0,002	0,007	0,005
S2	-0,077	-0,159	-0,118	**S2**	-0,093	-0,162	-0,128
C3	-0,008	0,004	-0,002	**C3**	-0,004	0,006	0,001
S4	-0,068	-0,159	-0,114	**S4**	-0,081	-0,161	-0,121
C5	**0,041**	0,001	**0,021**	**C5**	0,035	0,002	0,019
S6	-0,138	-0,158	-0,148	**S6**	-0,142	-0,156	-0,149
C7	-0,044	**0,018**	-0,013	**C7**	-0,051	**0,018**	-0,017
C8	0,021	-0,006	0,008	**C8**	0,009	-0,002	0,004
S9	-0,145	-0,156	-0,151	**S9**	-0,132	-0,165	-0,149
C10	0,001	0,008	0,006	**C10**	0,002	0,008	0,005
C11	0,007	0,007	0,007	**C11**	0,008	0,008	0,008
H12	-0,017	-0,033	-0,025	**H12**	-0,019	-0,033	-0,026
H13	-0,022	-0,029	-0,026	**H13**	-0,024	-0,03	-0,027
H14	-0,024	-0,032	-0,028	**H14**	-0,026	-0,033	-0,030
C15	0,006	0,007	0,007	**C15**	0,007	0,008	0,008
H16	-0,024	-0,032	-0,028	**H16**	-0,025	-0,034	-0,030
H17	-0,021	-0,029	-0,025	**H17**	-0,024	-0,029	-0,027
H18	-0,017	-0,032	-0,025	**H18**	-0,018	-0,033	-0,026
C19	0,020	0,006	0,013	**C19**	0,019	0,007	0,013
H20	-0,04	-0,032	-0,036	**H20**	-0,038	-0,033	-0,036
H21	-0,015	-0,032	-0,024	**H21**	-0,014	-0,032	-0,023
H22	-0,038	-0,023	-0,031	**H22**	-0,048	-0,023	-0,036
C23	0,013	0,012	0,0125	**C23**	**0,051**	0,001	**0,026**
C24	-0,003	-0,005	-0,004	**C24**	-0,069	0,000	-0,035
C25	-0,065	-0,007	-0,036	**C25**	-0,028	0,010	-0,009
C26	0,011	0,008	0,010	**S26**	-0,130	-0,075	-0,103
C27	-0,017	0,006	-0,004	**H27**	-0,048	-0,014	-0,031
H28	-0,034	-0,013	-0,024	**Br28**	-0,066	-0,029	-0,048
C29	-0,013	-0,006	-0,010	**C29**	-0,004	-0,004	-0,004
C30	-0,002	-0,005	-0,004	**H30**	-0,047	-0,027	-0,037
H31	-0,028	0,016	-0,006				
C32	-0,018	-0,004	-0,011				
H33	-0,040	-0,025	-0,033				
H34	-0,042	-0,02	-0,031				
H35	-0,047	-0,028	-0,038				
S36	-0,116	-0,074	-0,095				

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 tetrathiafulvalenylthiophenes reactivity. After performing many tests, a good separation is obtained between more active and less active tetrathiafulvalenylthiophenes compounds using ten variables: I, A, χ , η, s, μ, ω, E_{HOMO} , E_{LUMO} , ΔE_{gap} (see Table 4-5).

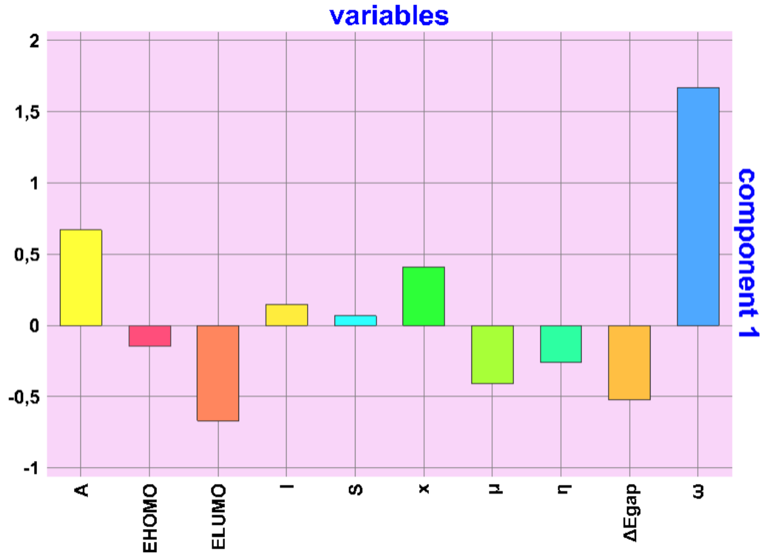
We can observe from PCA results that the first three principal components (PC1, PC2 and PC3) describe 99.99% of the overall variance as follows: PC1 = 99, 32%, PC2 = 0, 66% and PC3 = 0,01%. The score plot of the variances is a reliable representation of the spatial distribution of the points for the 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 (M2, M3, M4) and less active compounds (M1, M5, M6) 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 ω.

Fig. 4. Score plot for trimethyltetrathiafulvalenylthiophenes 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, χ, ω, values. In this way, some important features on the more active compounds can be observed.

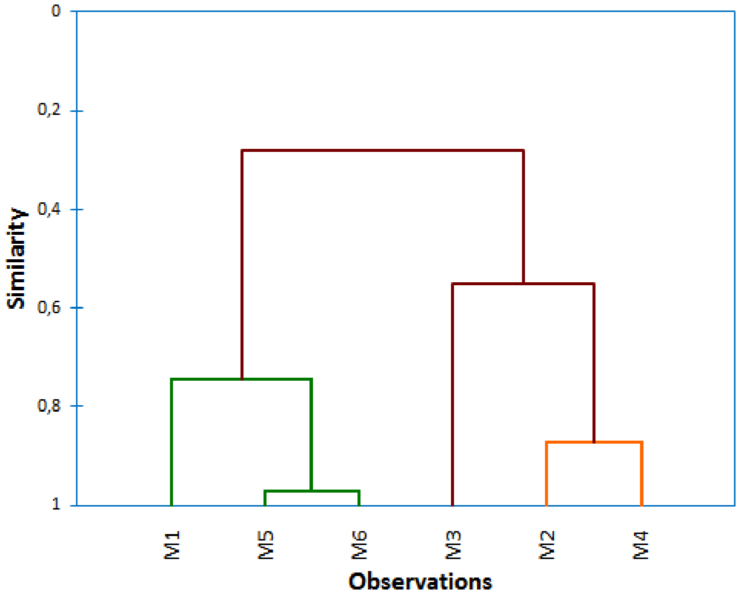
Fig. 5. Loading plot for the variables responsible for the classification of the tMeTTF-SnBu$_3$ studied



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 actives (compounds: M2, M3, M4) and less active (compounds M1, M5, M6).

Fig. 6. Dendrogram obtained for trimethyltetrathiafulvalenylthiophenes studied



CONCLUSION

In the present work we have calculated the geometrical parameters and frontier orbitals and it found that these theoretical results are in good agreement with the experimental data. Information about the charge density distribution and site of chemical activity of the molecule has been obtained by reactivity descriptors and MEP surface. Theoretical results from reactivity descriptors show that 5C is more reactive site for nucleophilic and free radical attacks in compounds M1, M2 M3 M4 and M5 and the more reactive site for electrophilic attack is 7C in M1, M5 and M6, 10C for M2 and M3, and 23C for M4. Chemometric methods shows the separation between more active (M2, M3, M4) and less active compounds (M1, M5, M6).

Acknowledgments
This work was generously supported by the (General Directorate for Scientific Research and Technological Development, DGRS-DT) and Algerian Ministry of Scientific Research.

REFERENCES

[1] R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, NewYork, Oxford University Press, **1989**.
[2] T. Mineva, T. Heine, *J. Phys. Chem. A*. 108 (**2004**) 11086.
[3] G. Molteni, A. Ponti, *Chem. Eur. J*. 9 (**2003**) 2770.
[4] R.K. Roy, *J. Phys. Chem. A*. 107 (**2003**) 397.
[5] J. Melin, F. Aparicio, V. Subramanian, M. Galvan, P.K. Chattaraj, *J. Phys.Chem. A*. 108 (**2004**) 2487.
[6] S. Shetty, R. Kar, D.G. Kanhere, S. Pal, *J. Phys. Chem. A*. 110 (**2006**) 252.
[7] T. Mineva, *J. Mol. Struct.* 762 (**2006**) 79.
[8] J.S.M. Anderson, J. Melin, P.W. Ayers, *J. Chem. Th. Comp*. 3 (**2007**) 375.
[9] M.L. Romero, F. Mendez, *J. Phys. Chem. A*. 107 (**2003**) 5874.
[10] G. Madjarova, A. Tadjer, T.P. Cholakova, A.A. Dobrev, T. Mineva, *J. Phys.Chem. A*. 109 (**2005**) 387.
[11] G. Roos, P. Geerlings, J. Messens, *J. Phys. Chem. B*. 113 (**2009**) 13465.
[12] R. Kar, S. Pal, *Int. J. Quant. Chem*. 110 (**2009**) 1642.
[13] H.S. De, S. Krishnamurty, S. Pal, *J. Phys. Chem. C*. 113 (**2009**) 7101.
[14] P. Geerlings, F. De Proft, W. Langenaekar, *Chem. Rev*. 103 (**2003**) 1793.
[15] P.K. Chattaraj, U. Sarkar, D.R. Roy, *Chem. Rev*. 106 (**2006**) 2065.
[16] E. Chamorro, P.K. Chattaraj, P. Fuentealba, *J. Phys. Chem. A*. 107 (**2003**) 7068.
[17] R. Parthasarathi, M. Elango, V. Subramanian, P.K. Chattaraj, *Theor. Chem. Acc*. 113 (**2005**) 257.
[18] R.G. Parr, W. Yang, Annu. *Rev. Phys. Chem*. 46 (**1995**) 710.
[19] W. Kohn, A.D. Becke, R.G. Parr, *J. Phys. Chem*. 100 (**1996**) 12974.
[20] R.G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules, Oxford University Press, New York, NY,**1989**.

[21] C. Lee, W. Yang, R. G. Paar, *Phys. Rev*. B37 (**1988**)785.
[22] R. G. Parr, W. Wang, Density-Functional Theory of Atoms and Molecules, Oxford University Press: New York, **1994**.
[23] R. G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, UK. **1989**.
[24] P. K. Chattaraj, S. Nath, B. Maiti, Reactivity Descriptors In Computational Medicinal Chemistry for Drug Discovery, Eds. Marcel Dekker, New York, Chap. 11(**2003)** 295-322.
[25] R. G. Parr, L. V. Szentpaly, S. J. Liu, *Am. Chem. Soc*. (**1999**)121.
[26] A. D. Becke, *J. Chem. Phys*. 98 (**1993**) 5648.
[27] T. Koopmans, *Physica*. 1 (**1993**) 104.
[28] T. Abbaz, A.K. Gouasmia, H. Fujiwara, T. Hiraoka, T. Sugimoto, M. Taillefer, J.M. Fabre. *Synthetic Metals* 157 (**2007)** 508–516.
[29] S. Bouguessa, A.K. Gouasmia, S. Golhen, L. Ouahab, J.M. Fabre, *Tetrahedron Lett*. 44 (**2003)** 9275.
[30] A.J. Moore, M.R. Bryce, A.S. Batsanov, J.C. Cole, A.K. Howard, Synthesis (**1995)** 675.
[31] T. Koopmans, Ordering of wave functions and Eigen energies to the individual electrons of an atom, *Physica* (**1933**) 104–113.
[32] R.G. Parr, R.A. Donnelly, M. Levy, W.E. Palke, *J. Chem. Phys*. 68 (**1978**) 3801-38017.
[33] R.G. Parr, R.G. Pearson, *J. Am. Chem. Soc*. 105 (**1983**) 7512–7516.
[34] R.G. Pearson, *J. Am. Chem. Soc*. 107 (**1985**) 6801–6806.
[35] R.G. Parr, L. Von Szentpaly, S. Liu, *J. Am. Chem. Soc*. 121(**1999**) 1922–1924.
[36] P.K. Chattaraj, U. Sarkar, D.R. Roy, *Chem. Rev*. 106 (**2006**)2065–2091.
[37] R.G. Parr, R.G. Pearson, *J. Am. Chem. Soc*. 105 (**1983**) 7512.
[38] W. Yang, W.J. Mortier, *J. Am. Chem. Soc*. 108 (**1986**) 5708.