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QUANTUM CHEMICAL STUDIES ON MOLECULAR STRUCTURE AND REACTIVITY DESCRIPTORS OF SOME *p*-NITROPHENYL TETRATHIAFULVALENES BY DENSITY FUNCTIONAL THEORY (DFT)

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ABSTRACT

The main purpose of this study was the determination of chemical reactivity and sites selective of the title compounds (**A**-**F**). Molecular geometries have been studied using the density functional theory (DFT) with B3LYP/6-31G (d,p) basis set. In addition, the molecular electrostatic potential maps and frontier molecular orbitals were performed at B3LYP/6-31G (d,p) level of theory. DFT global chemical reactivity descriptors (chemical hardness, energy, electronic chemical potential and electrophilicity) are calculated for the title molecules and used to predict their relative stability and reactivity. The active sites for nucleophilic and electrophilic attacks have been chosen by relating them to the Fukui function. The chemometric method PCA was employed to find the subset of variables that could correctly classify the compounds according to their reactivity.

Key words: Tetrathiafulvalenes, Density functional Theory, Reactivity descriptors, Principal component analysis and Hierarchical cluster analysis

INTRODUCTION

With the development of computational chemistry, the quantum chemistry presents insights into electronic structures of molecules and strongly propels the development of the traditionally experimental chemistry.[1] Density functional theory (DFT) has been very popular for calculations in theoretical modeling since the 1970s. A search of the Science Citation Index for articles published in 1986 with the words "Density functional theory" in the title or abstract yields less than 50 entries. Repeating this search for 1996 and 2006 gives more than 1100 and 5600 entries, respectively.[2] Today, these numbers beyond 10,000s. In many cases the results of DFT calculations for solid-state systems agreed quite satisfactorily with experimental data. DFT predicts a great variety of molecular properties: molecular structures, vibrational

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frequencies, atomization energies, ionization energies, electric and magnetic properties, reaction paths, etc. The reactivity descriptors, defined within the framework of density functional theory are global hardness, global electrophilicity, chemical potential, local softness, Fukui functions etc.[3] 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.[4-6] Chattaraj et al.[7] have reviewed the theoretical basis for these descriptors and their applications. In general, the descriptors are classified to refer to the whole system, called "global reactivity descriptors", or to refer a local part of the system, called "local reactivity descriptors". Some of the recent developments and applications in this area of research are highly appreciable.[8] Since most of these descriptors are the derivatives of energy and electron density variables. The objective of this work focused on the performance of a detailed calculation of the molecular structure and chemical reactivity of some *p*-nitrophenyl tetrathiafulvalene.

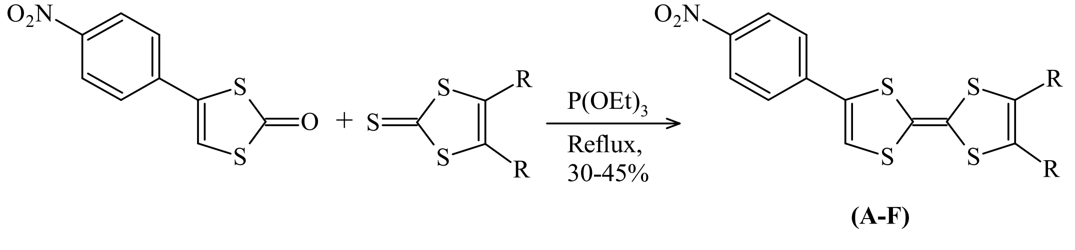
EXPERIMENTAL

Materials and mehtods

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)[13,14] is a chemometric method was performed using software XLSTAT.

RESULTS AND DISCUSSION

In a previous work[15], we have described the synthesis of new unsymmetrical tetrathiafulvalenes (TTF) containing nitrophenyl rings **(A-F)** indicated in **Scheme 1**. The synthesis of these electron donors was carried out using a cross-coupling method of the respective 4,5-dialkyl-1,3-dithiole-2-one with 4-(p-nitrophenyl)-1,3-dithiole-2-thione.



(A-F)

(A) R = SCH_3, (B) R = SCH_2S, (C) 2R = $S(CH_2)_2S$, (D) 2R = $S(CH_2)_3S$, (E) 2R= $O(CH_2)_2O$,
(F) 2R = $Se(CH_2)_2Se$

Scheme 1: Synthetic route for the preparation of *p*-nitrophenyl tétrathiafulvalènes (A-F)

Molecular geometry

The geometric parameters of title compounds **A-F** were optimized with B3LYP method at 6-31G (d,p) level. 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 compounds **A-F** are shown in **Scheme 1** and the final optimized molecular structures of compounds in accordance with the atom numbering scheme were shown in Fig. 1. The optimized energy for compounds varies between -86324.8 and -67677.5 eV, which indicate that these compounds were stable. Based on these, some structural parameters such as bond distances and bond angles have been calculated. From the optimized geometries, various molecular properties such as energy of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), energy gap ΔE_{gap}, ionization potential (I), electron affinity (A) and global reactivity parameters such as chemical hardness (η), softness, electronegativity, chemical potential (μ) and electrophilicity index (ω) were also calculated to analyze the reactivity of title molecules. The optimized geometrical parameters, namely Bond length and Bond Angles calculated with 6-31G (d, p) basis set were listed in Table 1-3.

Table 1: Selected molecular structure parameters of compound A and B

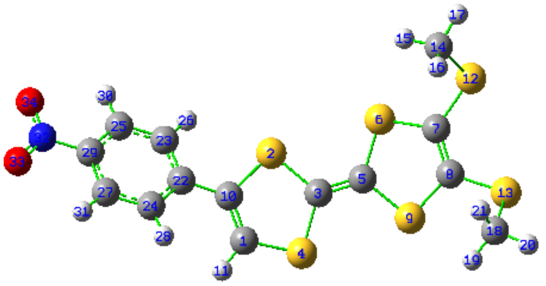
Compound A				**Compound B**			
Bond length (Å)		**Bond angles (°)**		**Bond length (Å)**		**Bond angles (°)**	
1C4S	1.75	10C1C4S	119.55	1C4S	1.75	10C1C4S	119.53
10C2S	1.79	1C4S3C	94.79	10C2S	1.79	1C4S3C	94.78
3C2S	1.78	10C2S3C	95.37	3C2S	1.78	10C2S3C	95.37
5C6S	1.78	34O32N33O	124.69	5C6S	1.79	29O27N28O	124.72
7C12S	1.77	5C6S7C	94.63	7C12S	1.77	5C6S7C	93.04
12S14C	1.84	7C12S14C	101.76	12S14C	1.85	7C12S14C	91.43
8C13S	1.77	7C8C13S	125.58	8C13S	1.77	7C8C13S	117.96
13S18C	1.84	8C13S18C	101.81	13S14C	1.84	12S14C13S	109.15
8C9S	1.79	2S3C4S	113.61	8C9S	1.76	4S3C2S	113.67
10C22C	1.47	6S5C9S	112.15	10C17C	1.47	9S5C6S	113.63

Table 2: Selected molecular structure parameters of compound C and D

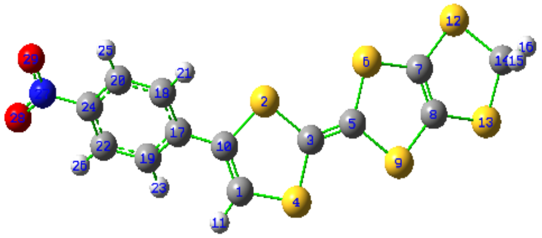
Compound C				**Compound D**			
Bond length (Å)		**Bond angles (°)**		**Bond length (Å)**		**Bond angles (°)**	
1C19S	1.75	14C1C19S	119.35	1C19S	1.75	14C1C19S	119.37
14C18S	1.79	1C19S2C	94.55	14C18S	1.79	1C19S2C	94.53
2C18S	1.78	14C18S2C	95.14	2C18S	1.78	14C18S2C	95.10
20C23S	1.78	16O15N17O	124.67	20C34S	1.78	16O15N17O	124.66
22C25S	1.76	20C23S22C	93.57	22C23S	1.77	20C34S22C	94.61
25S27C	1.84	22C25S27C	96.30	23S25C	1.84	22C23S25C	103.08
30C26S	1.86	22C21C26S	127.71	31C24S	1.84	22C21C24S	117.24
27C30C	1.52	21C26S30C	103.80	31C28C	1.53	25C28C31C	115.77
21C24S	1.79	19S2C18S	113.32	28C25C	1.53	19S2C18S	112.28
4C14C	1.47	24S20C23S	112.78	4C14C	1.47	35S20C34S	112.51

Table 3: Selected molecular structure parameters of compound E and F

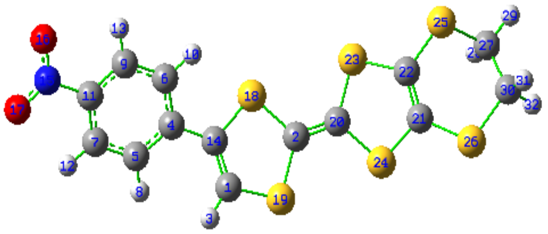
Compound E				Compound F			
Bond length (Å)		Bond angles (°)		Bond length (Å)		Bond angles (°)	
1C4S	1.75	5C1C4S	119.35	1C22S	1.79	2C1C22S	115.62
5C2S	1.79	1C4S3C	94.50	2C21S	1.75	1C22S20S	95.28
3C2S	1.78	5C2S3C	95.07	20C21S	1.78	2C21S20C	94.71
20C23S	1.79	19O17N18O	124.66	17C23S	1.79	15O14N16O	124.67
21C23S	1.77	20C23S21C	93.07	19C23S	1.77	17C23S19C	93.99
25O21C	1.37	21C25O27C	110.36	19C25Se	1.89	19C25Se30C	100.80
22C26O	1.37	21C22C26O	27.36	18C26Se	1.89	19C18C26Se	121.98
27C30C	1.53	22C26O30C	110.86	27C30C	1.52	18C26Se27C	92.86
22C24S	1.77	23S20C24S	115.11	18C24S	1.77	23S17C24S	112.92
5C7C	1.47	2S3C4S	113.27	1C4S	1.47	21S20C22S	113.60



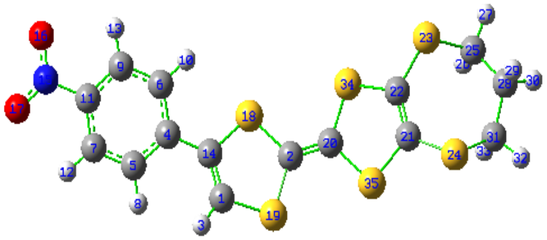
Compound A



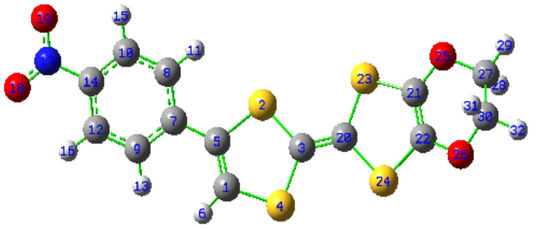
Compound B



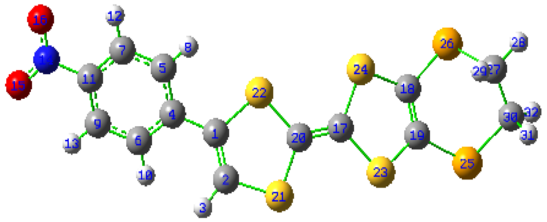
Compound C



Compound D



Compound E



Compound F

Fig. 1: The optimized structure of compounds A-F calculated with the B3LYP/6-31G (d, p)

Global reactivity descriptors

In Table 4, it is reported the values of the electronic energies calculated for all studied compounds in order to describe their reactivity**.** The energy corresponding to HOMO represents the ionization potential of the molecule and LUMO the corresponding electron affinity value. Using the Koopmans' theorem[16-17] (I) and (A) values can be correlated with the Frontier orbitals by the relation: I = -E_{HOMO} and A = -E_{LUMO}.

Table 4: Energetic parameters of *p*-Nitrophenyl tetrathiafulvalenes (A-F)

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_{gap} (eV)	I (eV)	A (eV)
A	-5.06	-2.68	2.38	5.06	2.68
B	-5.01	-2.70	2.31	5.01	2.70
C	-5.01	-2.65	2.36	5.01	2.65
D	-5.00	-2.63	2.38	5.00	2.63
E	-4.81	-2.62	2.19	4.81	2.62
F	-4.96	-2.63	2.33	4.96	2.63

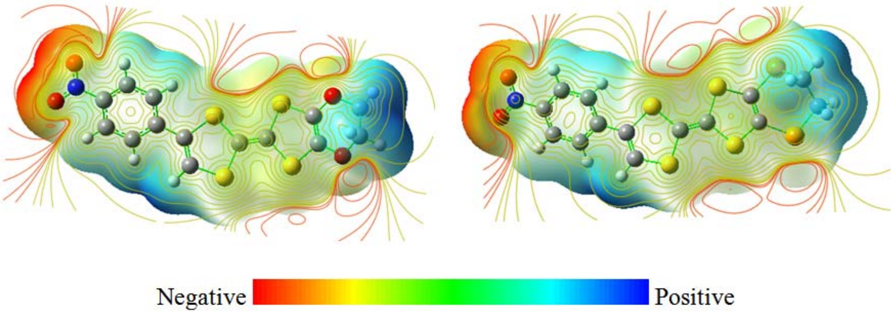


Fig. 2: Molecular electrostatic potential surface of compounds E and F

The frontier orbitals, HOMO and LUMO were the most important orbitals in a molecule. These orbitals determine the way how the molecule interacts with other species and give information about reactivity/stability of specific regions of the molecule. The energy of HOMO characterizes electron donating ability of a molecule while LUMO energy determines the ability to accept an electron. Therefore, higher values of E_{HOMO} indicate better tendency towards the donation of electron, As can be seen in Table 4 that the molecule (B) is the most molecule has the ability to accept electrons while (E) has the highest HOMO energy (E_{HOMO} = -4,81eV) that allows him to be the best electron donor molecule.

The energy gap between the HOMO and LUMO is very important in determining the chemical reactivity of the molecule. The high value of the energy gap indicates that the molecule shows high chemical stability, while a small HOMO-LUMO gap means small excitation energies to the manifold of excited states.

Ionization potential (I), which is defined as the amount of energy needed to remove an electron from a molecule. High ionization energy indicates high stability and chemical inertness and small ionization energy indicates high reactivity of the atoms and molecules. Compound (**E**) has the lowest ionization potential value (I = 4,81eV), which indicate that it is the best electron donor. The electronic affinity (A) is defined as the energy released when an electron is added to a neutral molecule. A molecule with high (A) values tend to take electrons easily. From Table 4 it is clear that Compound (**B**) is the best reactive.

The global chemical reactivity descriptors, chemical potential (μ), electronegativity (χ), hardness (η), softness (S), and electrophilicity index (ω) wich calculated from HOMO and LUMO energies were obtained at the level of theory B3LYP/6-31G and incorporated in Table 5. According to these parameters, the chemical reactivity varies with the structural configuration of molecules.

Global reactivity descriptors are described as:[18-22] Chemical potential are described ($\mu = -\chi$), the absolute electronegativity (χ) is given by the relation ($\chi = (IP + EA)/2$), global hardness and global softness (S) are defined as ($\eta = (E_{LUMO} - E_{HOMO})/2$) and ($S = 1/2\eta$), the electrophilicity (ω) can be calculated using the electronic chemical potential and the chemical hardness ($\omega = \mu^2/2\eta$)

Table 5: Quantum chemical descriptors of *p*-Nitrophenyl tétrathiafulvalènes (A-F)

Compounds	μ (eV)	x (eV)	η (eV)	S (eV)	ω (eV)
A	-3.87	3.87	1.19	0.42	6.30
B	-3.85	3.85	1.16	0.43	6.42
C	-3.83	3.83	1.18	0.42	6.21
D	-3.81	3.81	1.19	0.42	6.12
E	-3.72	3.72	1.10	0.46	6.31
F	-3.80	3.80	1.16	0.43	6.19

The chemical potential μ (eV) measures the escaping tendency of an electron and it can be associated with the molecular electronegativity[23] then, as μ becomes more negative, it is more difficult to lose an electron but easier to gain one. As shown in Table 5, compound E is the least stable and the most reactive among all the compounds.

Electronegativity (χ), representing the ability of molecules to attract electrons, The (χ) values displayed in Table 2 shows that Compound **A** has higher electronegativity value compared to all the molecules.

Hardness (η) and softness (S) are a useful concept for understanding the behaviour of chemical systems. A hard molecule has a large energy gap and a soft molecule has a small energy gap.[24] Therefore, soft molecules will be more polarizable than hard molecules. From theoretical calculations established, it was found that the molecule **A** has the highest hardness value (η = 2.19 eV), which indicates that is the hardest molecule. The molecules **E** has the highest softness (S = 0,46 eV), so it is the softest molecule.

Electrophilicity (ω), 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 (ω), while higher values indicate the presence of a good electrophile. Our results indicate that, molecule **D** has lower values of (ω), so that compound is good nucleophile. However molecule **B** is a good electrophile.

Local reactivity descriptors

In a chemical reaction, a change in the number of electrons involves the addition or subtraction of at least one electron in the frontier orbitals. Thus, calculating Fukui functions helps us determine the active sites of a molecule, based on the electronic density changes experienced by it during a reaction.

Fukui functions $f^{+}(\overrightarrow{r})$, $f^{-}(\overrightarrow{r})$ and $f^{0}(\overrightarrow{r})$ are calculated using the following equations as:[25-28]

$f^{+} = [q(N+1) - q(N)]$, for nucleophilic attack,

$f^{-} = [q(N) - q(N-1)]$, for electrophilic attack,

$f^{0} = [q(N+1) - q(N-1)]/2$, for radical attack.

Where q(N) is the charge on kth atom for neutral molecule while q(N + 1) and q(N - 1) are the same for its anionic and cationic species, respectively. The value of descriptors calculated at B3LYP/6-31G (d, p) level using Mulliken charges on atoms in molecules are presented in Table 6, 7 and 8.

Table 6 shows that at the DFT level the most susceptible site to a nucleophilic attack for compound **A** is located on 32N. In the case of an electrophilic attack, the most reactive site is on 29C. For a free radical attack the most reactive site is on 7C. For compound **B** the more susceptible sites to nucleophilic attacks is 3C, while 14C is the most susceptible sites for electrophilic and free radical attacks. Compound C and D (Table 7) show that the most susceptible sites to nucleophilic and free radical attacks are 2C while 30C and 25C will be preferred site for the electrophilic attack, respectively. For the Compound **E** (Table 8) our results reported that a preferred site for nucleophilic attack is the 3C while 30C represents the preferred sites for electrophilic and radical attack. For the Compound **F**, 20 C implies that this will be preferred site for the nucleophilic and free radical attacks, while an electrophilic attack is more probable on 4 S.

Table 6: Values of the Fukui function of the molecules A and B

Compound A				Compound B			
Atom	f^+	f^-	f^0	**Atom**	f^+	f^-	f^0
1 C	-0.089	0.004	-0.042	1 C	-0.049	-0.006	-0.028
2 S	-0.259	-0.044	-0.152	2 S	-0.057	-0.124	-0.091
3 C	0.248	-0.044	0.102	3 C	**0.023**	0.002	0.012
4 S	-0.217	-0.103	-0.159	4 S	-0.097	-0.124	-0.110
5 C	0.085	-0.116	-0.016	5 C	-0.012	0.014	0.001
6S	-0.183	-0.103	-0.143	6 S	-0.017	-0.160	-0.089
7 C	0.182	-0.091	**0.046**	7 C	-0.001	0.007	0.003
8 C	0.071	-0.087	-0.007	8 C	-0.001	0.007	0..003
9 S	-0.153	-0.105	-0.129	9 S	-0.027	-0.163	-0.095
10 C	0.094	-0.099	-0.002	10 C	-0.003	0.007	0.002
11 H	0.039	-0.083	-0.022	11 H	-0.034	-0.046	-0.040
12 S	-0.115	0.044	-0.036	12 S	-0.030	-0.112	-0.071
13 S	-0.144	0.045	-0.049	13 S	-0.034	-0.112	-0.073
14 C	-0.040	0.056	0.008	14 C	0.005	**0.032**	**0.018**
15 H	0.026	-0.045	-0.009	15 H	-0.008	-0.034	-0.020
16 H	0.033	-0.044	-0.006	16 H	-0.016	-0.042	-0.029
17 H	0.027	-0.044	-0.009	17 C	-0.020	0.019	-0.001

Cont…

Compound A				Compound B			
Atom	f^+	f^-	f^0	**Atom**	f^+	f^-	f^0
18 C	-0.028	0.055	0.013	18 C	-0.012	-0.009	-0.011
19 H	0.018	-0.046	-0.014	19 C	-0.010	-0.008	-0.009
20 H	0.021	-0.047	-0.013	20 C	-0.027	-0.008	-0.018
21H	0.024	-0.041	-0.009	21 H	-0.052	-0.005	-0.029
22 C	-0.077	0.108	0.016	22 C	-0.021	-0.008	-0.015
23 C	-0.139	0.034	-0.053	23 H	-0.055	-0.016	-0.036
24 C	-0.150	0.052	-0.049	24 C	0.015	-0.005	0.005
25 C	0.102	-0.053	0.024	25 H	-0.053	-0.022	-0.037
26 H	0.026	-0.052	-0.013	26 H	-0.053	-0.024	-0.039
27 C	0.095	-0.052	0.022	27 N	-0.099	-0.015	-0.057
28 H	0.038	-0.072	-0.017	28 O	-0.126	-0.023	-0.075
29C	-0.630	**0.429**	-0.1002	29 O	-0.126	-0.022	-0.074
30 H	-0.002	-0.048	-0.025				
31 H	-0.001	-0.050	-0.025				
32N	**0.481**	-0.438	0.021				
33 O	-0.191	0.038	-0.077				
34 O	-0.192	0.039	-0.076				

Table 7: Values of the Fukui function of the molecules C and D

Compound C				Compound D			
Atom	f^+	f^-	f^0	**Atom**	f^+	f^-	f^0
1 C	-0.055	-0.003	-0.029	1 C	-0.054	-0.003	-0.029
2 C	**0.032**	0.011	**0.022**	2 C	**0.031**	0.007	**0.019**
3 H	-0.033	-0.047	-0.040	3 H	-0.033	-0.048	-0.040
4 C	-0.013	0.013	-0.0002	4 C	-0.014	0.012	-0.001
5 C	-0.012	-0.006	-0.009	5 C	-0.012	-0.006	-0.009
6 C	-0.014	-0.008	-0.011	6 C	-0.013	-0.008	-0.011
7 C	-0.022	-0.008	-0.015	7 C	-0.021	-0.008	-0.015
8 H	-0.055	-0.017	-0.036	8 H	-0.055	-0.017	-0.036
9 C	-0.029	-0.008	-0.018	9 C	-0.028	-0.008	-0.018
10 H	-0.055	-0.003	-0.029	10 H	-0.054	-0.004	-0.029
11 C	0.016	-0.005	0.006	11 C	0.016	-0.005	0.005
12 H	-0.053	-0.025	-0.039	12 H	-0.052	-0.026	-0.039

Cont…

Compound C				Compound D			
Atom	f^+	f^-	f^0	**Atom**	f^+	f^-	f^0
13 H	-0.053	-0.022	-0.038	13 H	-0.052	-0.023	-0.038
14 C	-0.007	0.009	0.001	14 C	-0.006	0.011	0.002
15 N	-0.101	-0.015	-0.058	15 N	-0.100	-0.016	-0.058
16 O	-0.128	-0.023	-0.075	16 O	-0.126	-0.023	-0.075
17 O	-0.128	-0.024	-0.076	17 O	-0.127	-0.025	-0.076
18 S	-0.040	-0.135	-0.088	18 S	-0.042	-0.146	-0.094
19 S	-0.081	-0.132	-0.107	19 S	-0.082	-0.144	-0.113
20 C	-0.023	0.007	-0.008	20 C	-0.021	0.004	-0.008
21 C	-0.005	0.026	0.010	21 C	0.002	0.011	0.007
22 C	0.015	0.013	0.014	22 C	0.003	0.011	0.007
23 S	-0.025	-0.160	-0.093	23 S	-0.023	-0.070	-0.047
24 S	-0.040	-0.160	-0.099	24 S	-0.027	-0.071	-0.049
25 S	-0.014	-0.104	-0.059	25 C	0.006	**0.016**	0.011
26 S	-0.039	-0.095	-0.067	26 H	-0.004	-0.013	-0.009
27 C	0.020	0.022	0.021	27 H	-0.016	-0.034	-0.025
28 H	-0.017	-0.027	-0.022	28 C	0.006	0.013	0.009
29 H	-0.015	-0.040	-0.027	29 H	-0.036	-0.021	-0.029
30 C	-0.007	**0.035**	0.014	30 H	0.009	-0.035	-0.013
31 H	-0.001	-0.030	-0.016	31 C	0.007	0.016	0.012
32 H	-0.019	-0.039	-0.029	32 H	-0.017	-0.034	-0.026
				33 H	-0.005	-0.013	-0.009
				34 S	-0.024	-0.149	-0.086
				35 S	-0.035	-0.150	-0.093

Table 8: Values of the Fukui function of the molecules E and F

Compound E				Compound F			
Atom	f^+	f^-	f^0	**Atom**	f^+	f^-	f^0
1 C	-0.054	-0.002	-0.028	1 C	-0.004	0.008	0.002
2 S	-0.043	-0.134	-0.089	2 C	-0.053	-0.006	-0.029
3 C	**0.034**	-0.005	0.014	3 H	-0.033	-0.047	-0.040
4 S	-0.085	-0.131	-0.108	4 C	-0.019	**0.019**	0.001
5 C	-0.005	0.009	0.002	5 C	-0.013	-0.009	-0.011
6 H	-0.033	-0.047	-0.040	6 C	-0.010	-0.008	-0.009

Cont…

Compound E				**Compound F**			
Atom	f^+	f^-	f^0	**Atom**	f^+	f^-	f^0
7 C	-0.015	0.013	-0.001	7 C	-0.028	-0.008	-0.018
8 C	-0.013	-0.008	-0.011	8 H	-0.053	-0.005	-0.029
9 C	-0.012	-0.006	-0.008	9 C	-0.021	-0.008	-0.015
10 C	-0.029	-0.008	-0.018	10 H	-0.056	-0.017	-0.036
11 H	-0.055	-0.003	-0.029	11 C	0.016	-0.005	0.006
12 C	-0.022	-0.008	-0.015	12 H	-0.053	-0.023	-0.038
13 H	-0.055	-0.017	-0.036	13 H	-0.053	-0.025	-0.039
14 C	0.017	-0.005	0.006	14 N	-0.101	-0.016	-0.058
15 H	-0.053	-0.023	-0.038	15 O	-0.128	-0.025	-0.076
16 H	-0.053	-0.025	-0.039	16 O	-0.127	-0.023	-0.075
17 N	-0.102	-0.016	-0.059	17 C	-0.019	0.001	-0.009
18 O	-0.129	-0.025	-0.077	18 C	0.006	0.019	0.012
19 O	-0.129	-0.023	-0.076	19 C	0.005	0.014	0.009
20 C	-0.022	0.022	-0.0002	20 C	**0.033**	0.003	**0.018**
21 C	-0.007	-0.029	-0.018	21 S	-0.086	-0.135	-0.111
22 C	-0.009	-0.029	-0.019	22 S	-0.047	-0.135	-0.091
23 S	-0.032	-0.163	-0.097	23 S	-0.033	-0.149	-0.091
24 S	-0.042	-0.164	-0.103	24 S	-0.024	-0.154	-0.089
25 O	-0.003	-0.027	-0.015	25 Se	-0.031	-0.092	-0.062
26 O	-0.005	-0.028	-0.016	26 Se	-0.029	-0.089	-0.059
27 C	0.009	0.020	0.015	27 C	0.004	0.013	0.008
28 H	-0.024	-0.035	-0.029	28 H	-0.017	-0.038	-0.027
29 H	-0.008	-0.048	-0.028	29 H	-0.002	-0.011	-0.007
30 C	0.009	**0.025**	**0.017**	30 C	0.005	0.013	0.009
31 H	-0.026	-0.034	-0.030	31 H	-0.014	-0.032	-0.023
32 H	-0.003	-0.048	-0.026	32 H	-0.015	-0.033	-0.024

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

We can observe from PCA results that the first three principal components (PC1, PC2 and PC3) describe 99.91% of the overall variance as follows: PC1 = 66.64%, PC2 = 33.27% and PC3 = 0.07%. 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 Fig. 3 (PC1 versus PC2) and we can see that PC1 alone is responsible for the separation between more active (E, F) and less active compounds (A, B, C, D) 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.

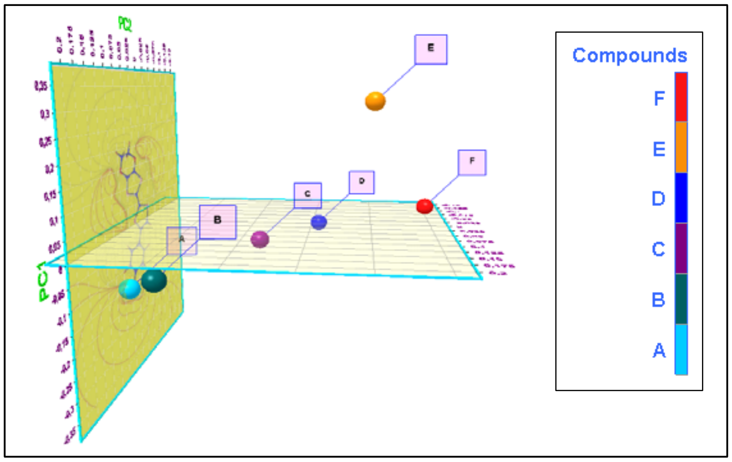


Fig. 3: Score plot for *p*-nitrophenyl tetrathiafulvalene in gas phase

The loading vectors for the first two principal components (PC1 and PC2) are displayed in Fig. 4. We can see that more active compounds (PC1 > 0) can be obtained when we have higher E_{HOMO}, E_{LUMO}, μ, s, ω values. In this way, some important features on the more active compounds can be observed.

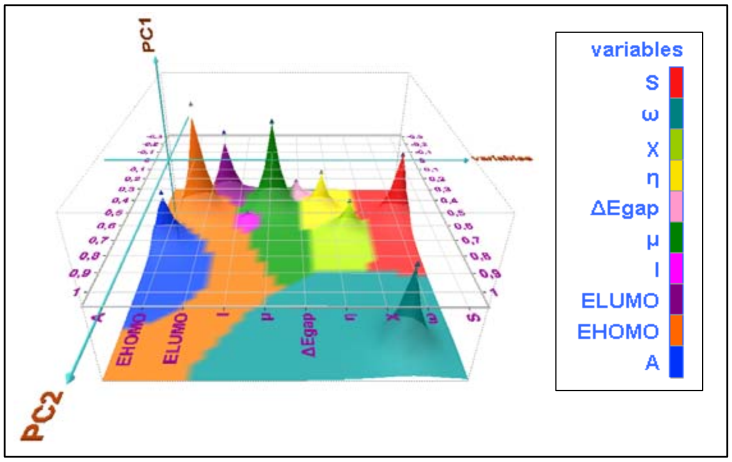


Fig. 4: Loading plot for the variables responsible for the classification of the *p*-Nitrophenyl tetrathiafulvalene studied

CONCLUSION

From the whole of the results presented in this contribution it has been clearly demonstrated that the sites of interaction of the title compounds (**A-F**) can be predicted by using DFT-based reactivity descriptors such as the hardness, softness, and electrophilicity, as well as Fukui-function calculations. These descriptors were used in the characterization and successfully description of the preferred reactive sites and provide a firm explanation for the reactivity of the p-nitrophenyl tétrathiafulvalènes molecule.

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