

Theoretical Study of the Global Reactivity and Theoretical Characterization of the Preferential Sites of Reactivity of Five Derivatives of Tetrathiafulvalene

Fatogoma Diarrassouba^{1,*}, Affoué Lucie Bédé², Mabintou Kalo², Konan Charly Kouadio², Kafoumba Bamba¹, Nahossé Ziao¹

¹Laboratoire de Thermodynamique et Physico-Chimie du Milieu (LTPCM), UFR-SFA, Université Nangui Abrogoua, Abidjan, Côte-d'Ivoire

²Laboratoire de Constitution et de Réaction de la Matière (LCRM), UFR-SSMT, Université Félix Houphouët Boigny, Abidjan, Côte-d'Ivoire

Email address:

fatogomadiarras89@gmail.com (Fatogoma Diarrassouba)

*Corresponding author

To cite this article:

Fatogoma Diarrassouba, Affoué Lucie Bédé, Mabintou Kalo, Konan Charly Kouadio, Kafoumba Bamba et al. (2023). Theoretical Study of the Global Reactivity and Theoretical Characterization of the Preferential Sites of Reactivity of Five Derivatives of Tetrathiafulvalene. *American Journal of Chemical Engineering*, 11(6), 117-124. <https://doi.org/10.11648/j.ajche.20231106.12>

Received: November 24, 2023; Accepted: December 12, 2023; Published: December 26, 2023

Abstract: In this work, which had the general objective of carrying out a theoretical study of the overall reactivity and a theoretical characterization of the preferential sites of reactivity of certain Tetrathiafulvalene (TTF) derivatives, we can now retain that: The higher the conductivity of these transfer complexes charge (TTF-TCNQ) increase, the more the polarity of the TTF donor molecules increases. For the TTF_4 and TTF_5 molecules, the values of the determined reactivity quantities are approximately equal. This clearly shows that the TTF_4 and TTF_5 molecules have similar chemical reactivity properties. The substitution of the methyl group (–CH₃) by a hydrogen atom (–H) in the TTF_4 molecule does not substantially influence the reactive properties. This could explain the equality of the experimental difference between the first oxidation and second oxidation potentials ($\Delta E_{\text{exp}} = 0,23 \text{ V}$) for these two molecules. A decrease in the conductivity of charge-transfer complexes was also observed as the chemical reactivity of TTF increased. The choice of these two basic molecules significantly impacts the electrical conductivity of the charge transfer complexes (TTF-TCNQ). The nucleophilic sites of the molecules are the sulfur atoms of the central TTF core while the electrophilic sites are the carbon atoms of the bulky substituent. These different potential sites of reactivity can constitute the dimerization sites of these molecules with a view to extending the conjugation.

Keywords: Tetrathiafulvalene (TTF), Charge Transfer Complex, Nucleophile, Electrophile

1. Introduction

Tetrathiafulvalene (TTF) is a molecule made up of two 1,3-dithios heterocycles giving it a remarkable set of properties [1]. It can be oxidized in a reversible and sequential manner successively in species cation radical $\text{TTF}^{+\bullet}$ then dication TTF^{2+} in a window of potentials ($E_1^{1/2} = +0.45 \text{ V}$ and $E_2^{1/2} = +0.77 \text{ V}$) [2]. Both oxidized species are very stable. TTF is therefore a good π electron donor, which allows it to associate with electron acceptor molecules such as tetracyanoquinodimethane (TCNQ). Thanks to these properties, research on conductive organic materials has been devoted to increasing the electrical conductivity of charge transfer complexes within derivatives of this molecule. Therefore, many changes have been made on this

donor. This is the case with sulfur atoms replaced by atoms of selenium [3] or tellurium [4] or other heteroatoms [5]. The introduction of such atoms into the donor promotes intra- and inter-chain molecular interactions in the resulting charge transfer complexes. In fact, selenium and tellurium atoms have larger and more diffuse atomic orbitals than those of sulfur atoms. Likewise, organic chemists are currently interested in dimers of TTF molecules with a view to extending conjugation within complexes [5]. It is in this very perspective that we have set as the main objective in this work, to do a theoretical study of the overall reactivity and a theoretical characterization of the preferential sites of reactivity of these molecules. This study could therefore not only reduce the number of tests for experimental chemists but could also help them to have charge

transfer complexes with more improved electrical conductivities.

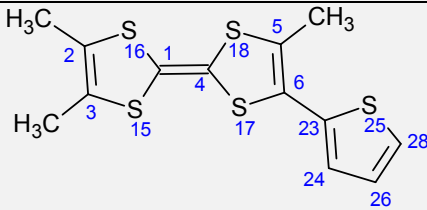
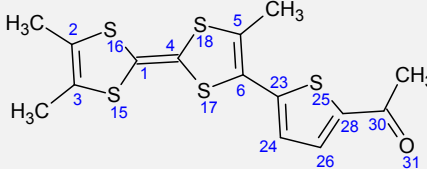
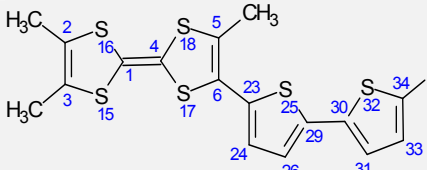
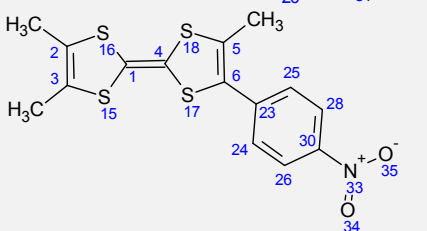
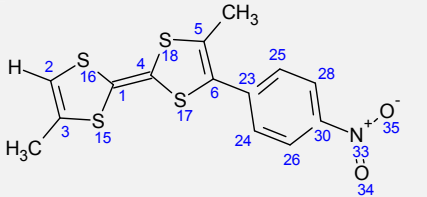
2. Materials and Methods

2.1. Series of Studied Molecules

As part of this chemical reactivity study, we were interested in a series of five (05) Tetrathiafulvalene

derivatives codified (TTF). These molecules were synthesized by Tahar Abbaz et al. [2]. The choice of these five (05) complexes is due to the availability of first and second oxidation potentials. The 2D structures of these molecules are shown in Table 1 with their first and second oxidation potentials expressed in volts (V).

Table 1. 2D structures and values of the first and second oxidation potentials of the analogous conjugated TTF- π studied molecules.

CODE	STRUCTURE	E_{exp}^1 (V)	E_{exp}^2 (V)
TTF_1		+0.365	+0.792
TTF_2		+0.408	+0.800
TTF_3		+0.371	+0.784
TTF_4		+0.500	+0.730
TTF_5		+0.520	+0.750

2.2. Used Software and Level of Theory

GaussView 5.0 software [6] was used to represent the 3D structure and visualize the studied molecules. Then, Gaussian 09 software [7] was used for the optimization and calculation of frequencies. As for the 2D structures, they were represented with the chemsketch software [8]. The used theory level is B3LYP/6-311G(d,p). The calculations were carried out under the temperature conditions $T=298.15$ Kelvin under pressure $P=1$ atm in vacuum.

2.3. Methodology of the Used Molecular Descriptors

Various global and local reactivity descriptors were used for this study. These descriptors are described as follows:

Energy gap ΔE_{gap}

The energy gap is the energy between the highest occupied molecular orbital and the lowest vacant molecular orbital. This is an important indicator of stability. This difference in energy serves as a measure of the excitability of a molecule. Thus, the lower the energy interval, the more the molecule will be able to interact with the environment. On the other hand, a large HOMO-LUMO gap implies high stability of the molecule and low reactivity in chemical reactions. Likewise, a small deviation implies a high reactivity of the molecule [9, 10].

$$\Delta E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (1)$$

Hardness (η) [11]

It expresses the resistance of a molecule to a change in its electron number or to charge transfer. The higher the hardness, the less reactive the molecule.

$$\eta = \frac{(PI - AE)}{2} \quad (2)$$

Softness (S) [11]

Softness is defined as the inverse of twice the hardness.

$$S = \frac{1}{2\eta} \quad (3)$$

Fukui function (f^+ et f^-)

The Fukui function [12] is defined as the response of electron density when the number of electrons changes. The Fukui function exists in three forms: the electrophilic Fukui function, the nucleophilic Fukui function and the radical Fukui function. These are local indices of chemical reactivity. However, we have limited ourselves to the first two functions in our work. The electrophilic Fukui function denoted f^+ is none other than the response of electron density to an electron gain. It gives information on the electrophilic sites with respect to nucleophilic attacks. Conversely, the nucleophilic Fukui function noted f^- is the response of the electron density to a loss of electrons. It gives information on the nucleophilic sites vis-à-vis electrophilic attacks. The condensed form of these two functions in the case of a molecule with N electrons has been proposed by Yang and Mortier [13].

$$f^+ = q_k(N+1) - q_k(N) \quad (4)$$

$$f^- = q_k(N) - q_k(N-1) \quad (5)$$

With $q_k(N)$, $q_k(N-1)$, $q_k(N+1)$ the net charges of the k^{th} atom of the molecule to N, N-1 and N+1 electrons, respectively. Net charges are determined using partial atomic charges obtained using population analysis techniques. It seems accepted that an atom having a high value of the electrophilic Fukui function is the site of nucleophilic attacks

while in a molecule, any atom having a high value of the nucleophilic Fukui function, is the preferential site of attacks. electrophiles. In general, various studies have shown the effectiveness of these local descriptors. Despite their performance during these studies, some cases have demonstrated the limits of these functions [14, 15]. To overcome this problem, Morell et al. [16, 17] have made their contribution by proposing a new dual descriptor with advantages over the previous functions.

Dual descriptor (Δf)

The dual descriptor denoted Δf is the difference between the electrophilic Fukui function and the nucleophilic Fukui function. It is an algebraic quantity.

$$\Delta f = f^+ - f^- \quad (6)$$

According to these authors, the electrophilic or nucleophilic behavior of an atom in a molecule is alternatively characterized by the sign and the amplitude of the Δf function. Indeed,

If $\Delta f > 0$, the site has an electrophilic character.

If $\Delta f < 0$, the site has a nucleophilic character.

When $\Delta f = 0$, the function of electrophilic Fukui

f^+ is equal to the nucleophilic function f^- and is even equal to the radical Fukui function f^0 . Under these conditions, the reactivity of the site is poorly defined, it is neither electrophile nor nucleophilic.

3. Results and Discussion

3.1. Global Reactivity of Conjugated TTF- π

For the study of the global chemical reactivity of analogous TTF molecules, global reactivity descriptors derived from Frontier Molecular Orbitals have been determined. The summary of these descriptors is given in Table 2.

Table 2. Values of global reactivity descriptors derived from Frontier Molecular Orbitals of TTF molecules and experimental electrical conductivities of charge transfer complexes TTF-TCNQ.

COMPOUND	ΔE_{exp} (V)	ΔE_{gap} (eV)	η (eV)	S (eV ⁻¹)	σ (S.cm ⁻¹)
TTF_1	0.427	3.3515	1.6758	0.2984	0.0050
TTF_2	0.392	2.6135	1.3067	0.3826	0.0370
TTF_3	0.413	2.8230	1.4115	0.3542	0.0085
TTF_4	0.230	2.1192	1.0596	0.4719	2.3000
TTF_5	0.230	2.1366	1.0683	0.4680	2.6000

$$\Delta E_{\text{exp}} = E_{\text{exp}}^2 - E_{\text{exp}}^1$$

Overall, there is a variation in the values of each determined quantity from one molecule to another. For the TTF_4 and TTF_5 molecules, the values of these reactivity quantities are appreciably equal. Under these conditions, it should be said that the TTF_4 and TTF_5 molecules have similar chemical reactivity properties. Substitution of the methyl group ($-\text{CH}_3$) by a hydrogen atom ($-\text{H}$) in the TTF_4 molecule does not substantially influence the reactive properties. This could explain the equality of the experimental difference between the

potentials of first oxidation and second oxidation ($\Delta E_{\text{exp}} = 0.23$ V) for these two molecules. This is a gap that measures the strength of the conjugation in these molecules. Regarding the energy gap ΔE_{gap} , this is an important parameter which gauges the overall reactivity towards an electron acceptor and the stability of a molecule. Considering the energy gap and the chemical hardness, the TTF_4 and TTF_5 molecules have the lowest values while the TTF_1 molecule has the highest values. These values show that the molecules TTF_4 and TTF_5 have high chemical activity, very low kinetic stability and are called soft molecules. As for the TTF_1 molecule, it is the hardest molecule. We see that the softness S and the energy gap evolve

inversely. Indeed, while the energy gap decreases, the softness increases. The TTF_4 and TTF_5 molecules have the highest softness values while the TTF_1 molecule has the lowest softness value. These data also confirm that the TTF_4 and TTF_5 molecules are the softest molecules and the TTF_1 molecule is the hardest. Taking into account all the global reactivity indices determined, the order of increasing stability of the five TTF molecules studied is as follows:

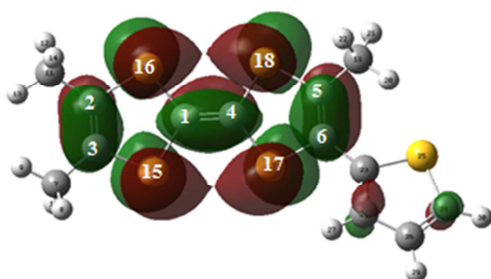
Growing stability : TTF_4 \approx TTF_5 < TTF_2 < TTF_3 < TTF_1

Regarding the difference ΔE_{exp} , the classification of molecules in increasing order of these values is as follows:

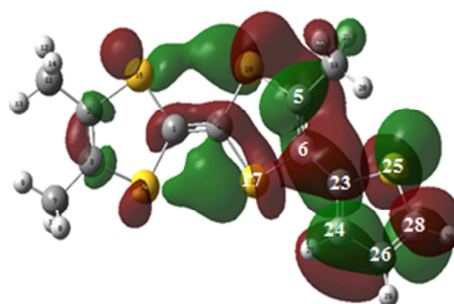
ΔE_{exp} : TTF_4 = TTF_5 < TTF_2 < TTF_3 < TTF_1

We get exactly same evolutionary sequences. It shows that difference between the potential of first oxidation and that of second oxidation increases as the stability of the molecules increases. With experimental electrical conductivity, the ranking of molecules in decreasing order of values is:

σ : (TTF_5, TCNQ) > (TTF_4, TCNQ) > (TTF_2, TCNQ)
> (TTF_3, TCNQ) > (TTF_1, TCNQ)



HOMO



LUMO

Figure 1. Isodensity maps of Frontier Molecular Orbitals of TTF_1 molecule.

By observing the isodensity maps of the Frontier Molecular Orbitals, we note that in the HOMO, the largest lobes entirely contain the atoms C₁, C₂, C₃, C₄, C₅, C₆, S₁₅, S₁₆, S₁₇ and S₁₈. These atoms therefore constitute the probable nucleophilic sites of this molecule. As for LUMO, it entirely contains the atoms C₅, C₆, S₁₇, S₁₈, C₂₃, C₂₄, S₂₅, C₂₆, and C₂₈. The latter are therefore the probable electrophilic sites of the TTF_1 molecule. For identification of sites of potential reactivity, the values of local Fukui reactivity indices and those of dual descriptor were calculated and are reported in Table 3.

Table 3. Values of local indices of reactivity of Fukui and those of dual descriptor of TTF_1.

Natural Population Analysis (NPA)			
ATOME	f^+	f^-	Δf
C ₁	0.0360	0.0122	0.0238
C ₂	0.0093	0.0373	-0.0280
C ₃	0.0142	0.0350	-0.0208
C ₄	0.0046	0.0089	-0.0044

Overall, it is noted that a decrease in ΔE_{gap} causes a gradual increase in the electrical conductivity of charge transfer complexes. Also, a notable reduction in this difference is noted for the TTF_4 and TTF_5 molecules due to a strong reduction in the intramolecular Coulomb repulsion between the positive charges created in the oxidized forms of the donors (radical cation TTF⁺ And dication TTF²⁺). This indicates a large extension of conjugation in these molecules [18]. Hence the strong electrical conductivity of the charge transfer complexes they form with unsubstituted TCNQ.

3.2. Local Reactivity of Conjugated TTF- π

Regarding the characterization of preferential sites of reactivity, the dual descriptor has been determined. First, isodensity maps of HOMO and LUMO Frontier Molecular Orbitals (FMO) were plotted and observed to identify sites of probable reactivity across lobe volumes. The electrophilic and nucleophilic Fukui functions were determined using natural charges (Natural Population Analysis) in order to determine the dual descriptor of the heavy atoms belonging to the large lobes.

Case of TTF_1 molecule

Natural Population Analysis (NPA)			
ATOME	f^+	f^-	Δf
C ₅	0.0684	0.0254	0.0429
C ₆	0.0161	0.0369	-0.0209
C ₇	0.0072	-0.0217	0.0289
S ₁₅	0.0700	0.1459	-0.0760
S ₁₆	0.0929	0.1461	-0.0531
S ₁₇	0.0699	0.1495	-0.0796
S ₁₈	0.1215	0.1437	-0.0222
C ₂₃	0.0499	-0.0598	0.1097
C ₂₄	0.0712	0.0410	0.0302
S ₂₅	0.0601	0.0808	-0.0207
C ₂₆	0.0402	-0.0185	0.0587
C ₂₈	0.0884	0.0382	0.0502

The data in Table 3 indicate that dual descriptor for sulfur atom S₁₇ is negative and weaker. Under these conditions, it is the seat of electrophilic attacks. Regarding the C₂₃ atom, we see that its dual descriptor is positive and higher. Therefore, any nucleophilic attack will preferably be on the C₂₃ atom.

Case of TTF_1 molecule

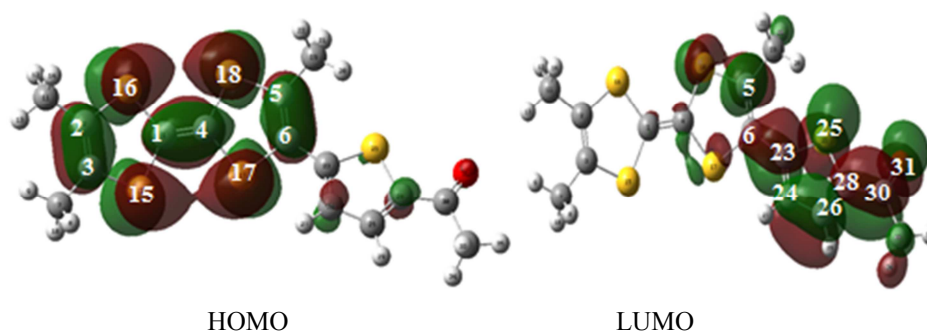


Figure 2. Isodensity maps of Frontier Molecular Orbitals of the TTF_2 molecule.

By observing the Frontier Molecular Orbitals isodensity maps, we note that in the HOMO, the largest lobes entirely contain the atoms C₁, C₂, C₃, C₄, C₅, C₆, S₁₅, S₁₆, S₁₇ and S₁₈. These atoms therefore constitute the probable nucleophilic sites of this molecule. For LUMO, the larger lobes completely contain the atoms C₅, C₆, C₂₃, C₂₄, S₂₅, C₂₆, C₂₈, C₃₀, and O₃₁. Consequently, the latter are the likely electrophilic sites of the TTF_2 molecule. For the identification of potential sites of reactivity, the values of the local Fukui reactivity indices and those of the dual descriptor were determined and are reported in Table 4.

Table 4. Values of the local indices of reactivity of Fukui and those of the dual descriptor of TTF_2.

Natural Population Analysis (NPA)			
ATOME	f^+	f^-	Δf
C ₁	0.0249	0.0118	0.0130
C ₂	0.0008	0.0368	-0.0360
C ₃	0.0005	0.0366	-0.0361
C ₄	-0.0115	0.0097	-0.0212
C ₅	0.0829	0.0174	0.0655
C ₆	-0.0244	0.0412	-0.0655
C ₇	0.0133	-0.0275	0.0408
S ₁₅	0.0346	0.1449	-0.1103
S ₁₆	0.0460	0.1465	-0.1004
S ₁₇	0.0322	0.1438	-0.1117
S ₁₈	0.0812	0.1418	-0.0606
C ₁₉	0.0167	-0.0356	0.0523
C ₂₃	0.0974	-0.0566	0.1540
C ₂₄	0.0322	0.0326	-0.0004
S ₂₅	0.0765	0.0927	-0.0162
C ₂₆	0.0917	-0.0175	0.1091

Natural Population Analysis (NPA)			
ATOME	f^+	f^-	Δf
C ₂₈	0.0333	0.0385	-0.0051
C ₃₀	0.1039	-0.0206	0.1245
O ₃₁	0.0960	0.0358	0.0602

Examination of the data in this table shows that the maximum magnitude of negative dual descriptor is attributed to the sulfur atom S₁₇ ($\Delta f = -0.1117$). Thus, it is the seat atom of electrophilic attacks. Regarding the positive dual, it is the C₂₃ carbon atom that displays the greatest value. As a result, nucleophilic attacks will preferably be on the C₂₃ atom. By focusing on the Fukui functions only, we notice that the carbon atom of the carbonyl group which displays the greatest value of f^+ , is the most electrophilic site while the oxygen atom O₃₁ of said group has a non-negligible electrophilic character with a value of $f^+ = 0.0960$, a value very close to the maximum value ($f^+ = 0.1039$). This is contrary to the experimental results [19]. However, this anomaly has just been corrected by the dual descriptor which is worth $\Delta f = 0.0602$ for the same oxygen atom, a fairly low value compared to the maximum value ($\Delta f = 0.1540$) but the carbon atom C₃₀ always remains electrophilic with a value of positive dual $\Delta f = 0.1245$ of the same order of magnitude as the maximum value. It should be noted that electrophilicity of the C₃₀ atom is due to the strong electronegativity of the oxygen of the C = O carbonyl group, which is a polar group.

Case of TTF_3 molecule

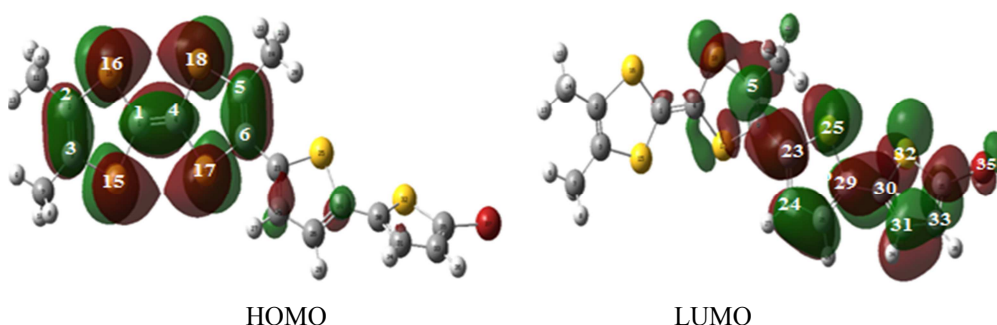


Figure 3. Isodensity maps of Frontier Molecular Orbitals of TTF_3 molecule.

By observing the Frontier Molecular Orbitals isodensity maps of this molecule, we note that in HOMO, the largest lobes entirely contain the atoms C₁, C₂, C₃, C₄, C₅, C₆, S₁₅,

S₁₆, S₁₇ and S₁₈. These atoms are therefore the probable nucleophilic sites of this molecule. As for LUMO, the large lobes completely contain the atoms C₅, C₆, C₂₃, C₂₄, S₂₅, C₂₆,

C₂₉, C₃₀, C₃₁, S₃₂, C₃₃ and C₃₅. The latter are therefore the probable electrophilic sites of the TTF_3 molecule. To identify the sites of potential reactivity, the values of the local Fukui reactivity indices and those of the dual were calculated and are reported in Table 5.

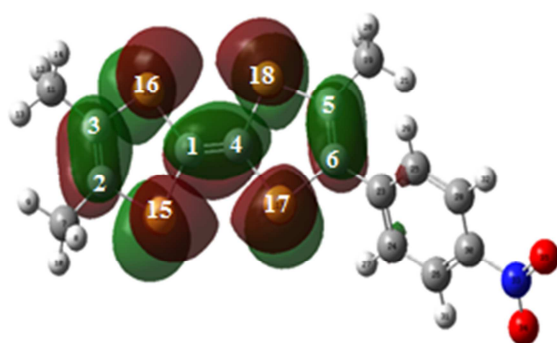
Table 5. Values of the local indices of reactivity of Fukui and those of the dual descriptor of TTF_3.

Natural Population Analysis (NPA)			
ATOME	f^+	f^-	Δf
C ₁	0.0236	0.0133	0.0103
C ₂	-0.0003	0.0349	-0.0352
C ₃	0.0018	0.0318	-0.0300
C ₄	-0.0095	0.0056	-0.0150
C ₅	0.0646	0.0255	0.0391
C ₆	-0.0167	0.0337	-0.0504
S ₁₅	0.0325	0.1307	-0.0982
S ₁₆	0.0456	0.1295	-0.0839
S ₁₇	0.0339	0.1275	-0.0936
S ₁₈	0.0764	0.1352	-0.0588

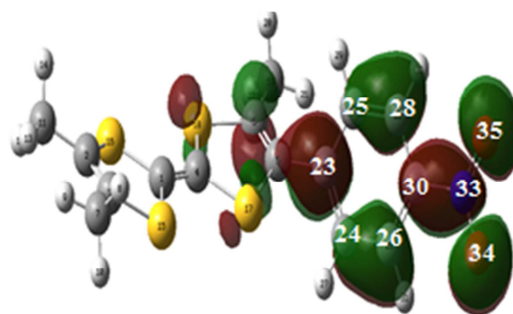
Natural Population Analysis (NPA)			
ATOME	f^+	f^-	Δf
C ₁₉	0.0193	-0.0372	0.0566
C ₂₃	0.0818	-0.0488	0.1306
C ₂₄	0.0382	0.0339	0.0044
S ₂₅	0.0731	0.0614	0.0116
C ₂₆	0.0588	-0.0142	0.0729
C ₂₉	0.0469	0.0397	0.0072
C ₃₀	0.0121	-0.0341	0.0462
C ₃₁	0.0737	0.0298	0.0439
S ₃₂	0.0545	0.0503	0.0041
C ₃₃	0.0312	-0.0153	0.0465
C ₃₅	0.0541	0.0172	0.0369

On analyzing the data in this table, we note that negative and smaller value of the dual descriptor belongs to the sulfur atom S₁₅. Regarding the carbon atom C₂₃, it displays a positive and maximum value of the dual index. Thus, any electrophilic attack occurs preferentially on the S₁₅ atom while any nucleophilic attack occurs on the C₂₃ atom.

Case of the TTF_4 molecule



HOMO



LUMO

Figure 4. Isodensity maps of Frontier Molecular Orbitals of TTF_4 molecule.

From the observation of the isodensity maps of the Frontier Molecular Orbitals, it emerges that in the HOMO, the larger lobes entirely contain the atoms C₁, C₂, C₃, C₄, C₅, C₆, S₁₅, S₁₆, S₁₇ and S₁₈. These atoms therefore constitute the probable nucleophilic sites of this molecule. As for the larger lobes in LUMO, they completely contain atoms C₂₃, C₂₄, C₂₅, C₂₆, C₂₈, C₃₀, N₃₃, O₃₄ and O₃₅. Thus, the latter are the likely electrophilic sites of the TTF_4 molecule. For the identification of potential sites of reactivity among the probable sites, the values of the local Fukui reactivity indices and those of the dual descriptor were determined and are reported in Table 6.

Table 6. Values of the local indices of reactivity of Fukui and those of the dual descriptor of TTF_4.

Natural Population Analysis (NPA)			
ATOME	f^+	f^-	Δf
C ₁	0.0286	0.0041	0.0245
C ₂	0.0000	0.0386	-0.0386
C ₃	0.0010	0.0369	-0.0359
C ₄	-0.0126	0.0181	-0.0307
C ₅	0.0607	0.0149	0.0458
C ₆	-0.0385	0.0473	-0.0858
S ₁₅	0.0389	0.1505	-0.1116

Natural Population Analysis (NPA)			
ATOME	f^+	f^-	Δf
S ₁₆	0.0468	0.1527	-0.1060
S ₁₇	0.0263	0.1610	-0.1346
S ₁₈	0.0772	0.1366	-0.0594
C ₁₉	0.0405	-0.0576	0.0981
C ₂₃	0.1248	-0.0567	0.1815
C ₂₄	0.0211	0.0170	0.0041
C ₂₅	0.0329	-0.0045	0.0374
C ₂₆	0.0711	-0.0174	0.0885
C ₂₈	0.0743	-0.0044	0.0786
C ₃₀	0.0278	0.0239	0.0039
N ₃₃	0.0191	0.0354	-0.0163
O ₃₄	0.0774	0.0833	-0.0060
O ₃₅	0.1957	-0.0351	0.2308

The data in Table 6 show that the S₁₇ atom has the value of its negative and minimum dual descriptor. Which makes him the seat of electrophilic attacks. Regarding the oxygen atom O₃₅ of the nitro moiety (-NO₂), it has the positive and higher dual descriptor indicating that oxygen O₃₅ is the preferred site of nucleophilic attacks. It is also noted that the descriptor attributes to the nitrogen atom N₃₃ a negligible nucleophilicity ($\Delta f = -0.0163$). Which is at odds with the experimental results. It should be noted that this case could resemble that of the C=O carbonyl group where the Fukui

functions presented limits. Indeed, the Fukui functions predicted carbon as the preferred site of electrophilic attacks but attribute to oxygen a significant electrophilic character. This is completely contrary to the experimental results [19]. Unfortunately, in our particular case, the dual descriptor does not correct this anomaly since its value always remains high for said oxygen atom O₃₅. Anyway, O₃₅ oxygen under these

conditions cannot be an electrophilic site due to the presence of its free doublets. It is in the interest of favoring the carbon atom C₂₃ whose value of the positive dual descriptor.

($\Delta f = 0.1815$) comes just after that of O₃₅. The latter will be the potential electrophilic site of the TTF_4 molecule as in the previous cases.

Case of TTF_5 molecule

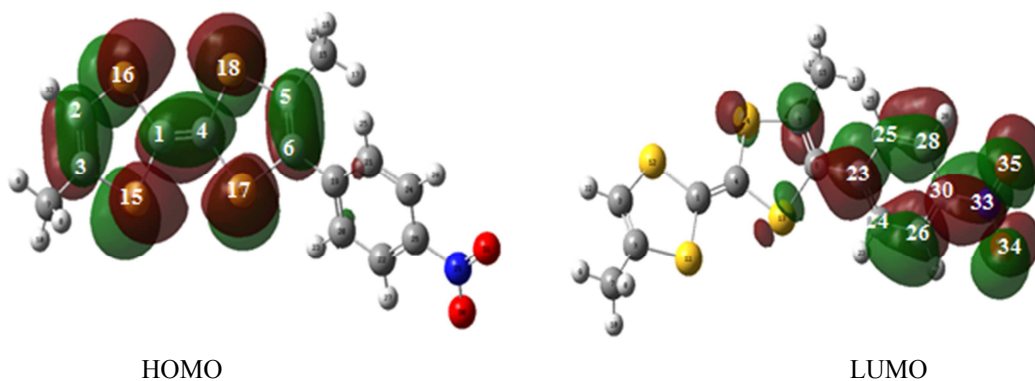


Figure 5. Isodensity maps of Frontier Molecular Orbitals of the TTF_5 molecule.

The observation of the isodensity maps of the Frontier Molecular Orbitals shows that in the HOMO, the larger lobes entirely contain the atoms C₁, C₂, C₃, C₄, C₅, C₆, S₁₅, S₁₆, S₁₇ and S₁₈. Thus, they constitute the probable nucleophilic sites of this molecule. In LUMO, only atoms C₂₃, C₂₄, C₂₅, C₂₆, C₂₈, C₃₀, N₃₃, O₃₄ and O₃₅ belong to the larger lobes. Under these conditions, these atoms are likely sites of electrophilic attack of the TTF_5 molecule. In order to identify potential sites of reactivity, the values of the local Fukui reactivity indices and those of the dual descriptor were determined and are reported in Table 7.

Table 7. Values of the local indices of reactivity of Fukui and those of the dual descriptor of TTF_5.

Natural Population Analysis (NPA)			
ATOME	f^+	f^-	Δf
C ₁	0.0248	0.0087	0.0161
C ₂	0.0073	0.0274	-0.0201
C ₃	0.0112	0.0347	-0.0235
C ₄	-0.0089	0.0132	-0.0221
C ₅	0.0608	0.0160	0.0448
C ₆	-0.0384	0.0482	-0.0866
S ₁₅	0.0421	0.1458	-0.1037
S ₁₆	0.0299	0.1710	-0.1411
S ₁₇	0.0261	0.1654	-0.1393
S ₁₈	0.0805	0.1389	-0.0584
C ₂₃	0.1255	-0.0580	0.1835
C ₂₄	0.0214	0.0174	0.0040
C ₂₅	0.0332	-0.0041	0.0373
C ₂₆	0.0713	-0.0174	0.0887
C ₂₈	0.0747	-0.0045	0.0792
C ₃₀	0.0284	0.0245	0.0039
N ₃₃	0.0190	0.0352	-0.0162
O ₃₄	0.0780	0.0835	-0.0056
O ₃₅	0.1963	-0.0348	0.2312

Based on the data in Table 7, we note that the S₁₆ atom has the negative and minimum value of the dual descriptor ($\Delta f = -0.1411$). Which makes him the seat of electrophilic attacks.

As for the oxygen atom O₃₅ (oxygen O₃₅ of the nitro group), it contains the positive and higher value of the dual descriptor showing that oxygen O₃₅ is the most electrophilic site. Also, negligible nucleophilicity is also attributed to nitrogen N₃₃ with a value of $\Delta f = -0.0162$. This differs from the experimental results. To explain this divergence of results, the arguments put forward in the case of the TTF_4 molecule are valid here. Thus, we are inclined to still favor the carbon atom C₂₃ whose value of the positive dual descriptor ($\Delta f = 0.1835$) comes just after that of O₃₅. The latter will also have an electrophilic character. A. Bendjeddou et al. [20] studied the chemical reactivity of six molecules of which the TTF_4 and TTF_5 molecules are part by examining the Fukui indices (f^+ , f^- and Δf). By analyzing these same indices in our case for these same molecules, we see that there is a discrepancy between the results. It should not be forgotten that these researchers developed their calculations using the so-called DFT method but with the theory level B3LYP/6-31G(d,p). The latter used the Mulliken atomic charges directly to determine the Fukui functions, unlike our case where they were calculated with the net charges from the natural population.

4. Conclusion

Our study aimed to study the chemical reactivity of five (05) derivatives of Tetrathiafulvalene (TTF). Regarding the overall reactivity of the five (05) analog TTF molecules, the difference between the potential of the second oxidation and that of the first reduction decreases when the reactivity increases, leading to a reduction of the Coulomb repulsion in these molecules and therefore to the extension of electronic conjugation. This causes an increase in the electrical conductivity of charge transfer complexes (TTF-TCNQ). As for the local reactivity of these same molecules, there is a

competition between the sulfur atoms of the TTF nucleus on the nucleophilic site. This competition is linked to the environment of these atoms within the molecule. On the other hand, the carbon atom of the bulky substituent (carbon directly linked to the TTF nucleus) is the electrophilic site of all the TTF molecules studied. It could also be the potential site for dimerization of TTF molecules.

Conflicts of Interest

The authors declare no conflicts of interest.

References

- [1] Bryce M. R., Functionalised tetrathiafulvalenes: new applications as versatile π -electron systems in materials chemistry, *J. Mater. Chem.*, 10, 589-598, 2000.
- [2] Taha Abbaz, Synthèse et étude de nouvelles donneur-II à grande extension spatiale, Thèse de Doctorat option chimie des matériaux organiques, Université Badji Mokhtar-Annaba d'Algérie, 2009.
- [3] Abdelkrim GOUASMIA, thèse de doctorat d'état, Académie de Montpellier, Université des Sciences et Technologiques de Languedoc Montpellier (France), 1988.
- [4] Peter W. Kenny, Prediction of planarity and reduction potential of derivatives of tetracyanoquinodimethane using ab initio molecular orbital theory, *J. chem. Soc. Perkin Trans. 2*, 1995.
- [5] Fatogoma Diarrassouba, Mawa Koné, Kafoumba Bamba, Yafigui Traoré, Mamadou Guy-Richard Koné, Edja Florentin Assanvo, Development of Predictive QSPR Model of the First Reduction Potential from a Series of Tetracyanoquinodimethane (TCNQ) Molecules by the DFT (Density Functional Theory) Method, *Computational Chemistry*, 7(4), 121-142, 2019.
- [6] R Dennington; T Keith and J Millam. GaussView, Version 5, Semichem Inc., Shawnee Mission, KS, 2009.
- [7] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA et al. Gaussian 09. Gaussian, Inc. Print, Wallingford, 2009.
- [8] ACDLABS 10, Advanced Chemistry Development Inc., Toronto, ON, Canada, 2015.
- [9] D. F. V. Lewis, C. Ioannides, and D. V. Parke, Interaction of a series of nitriles with the alcoholinducible isoform of P 450: Computer analysis of structure-activity relationships, *Xenobiotica*, 24(5), 401-408, 1994.
- [10] Z. Zhou and R. G. Parr, Activation hardness: new index for describing the orientation of electrophilic aromatic substitution, *Journal of the American Chemical Society*, 112(15), 5720-5724, 1990.
- [11] Reed A. E., Curtiss L. A., Weinhold F., Intermolecular Interactions from a Natural Bond Orbital, Donor-Acceptor Viewpoint, *Chem. Rev.*, 88, 899-926, 1988.
- [12] Parr RG., Yang W., Density functional approach to the frontier-electron theory of chemical reactivity, *J. Am. Chem. Soc.*, 106, 4049-4050, 1984.
- [13] W. Yang, W. J. Mortier, The use of global and local molecular parameters for the analysis of the gas-phase basicity of amines, *J. Am. Chem. Soc.*, 108, 5708-5711, 1986.
- [14] Langenaeker W., De Proft F., Geerlings P. J., Electron correlation effects on Fukui functions, *Mol Struct. (THEOCHEM)*, 362, 175-179, 1996.
- [15] De Proft, F.; Martin, J. M. L.; Geerlings P., Calculation of molecular electrostatic potentials and Fukui functions using density functional methods, *Chem. Phys. Lett.*, 256(4-5), 400-408, 1996.
- [16] Morell C., Grand A., Toro-Labbé, New Dual Descriptor for Chemical Reactivity, *A. Chem. Phys. Chem. A*, 109(1), 205-212, 2005.
- [17] Morell C., Grand A., Toro-Labbé A., Theoretical support for using the $\Delta f(r)$ descriptor, *Chem. Phys. Chem. Lett.*, 425, (4-6), 342-346, 2006.
- [18] J. Ferraris, D. O. Cowan, V. V. Walatka, J. H. Perlstein, Electron transfer in a new highly conducting donor-acceptor complex, *J. Am. Chem. Soc.*, 95, 948-949, 1973.
- [19] C. Morell, Un nouveau descripteur de la réactivité chimique: Etude théorique et applications à la sélectivité de quelques réactions chimiques, Doctorat Chimie et Sc. du Vivant, Université J. Fourier-Grenoble I, 2006.
- [20] A. Bendjeddou, T. Abbaz, R. Khammar, Electronic structure and reactivity analysis of some TTF-donor substituted molecules, *Der Pharmacia Lettre*, 8(4), 151-160, 2016.