Study of the global reactivity and characterization of the preferential sites of reactivity of eight (08) derivatives of Tetracyanoquinodimethane (TCNQ) at the theory level B3LYP/6-311G(d,p)

Abstract:

In this work, it was a question of carrying out a theoretical study of the global reactivity and a characterization of the preferential sites of reactivity of eight (08) derivatives of Tetracyanoquinodimethane (TCNQ). It emerges from this study that the oxidizing power of the eight (08) molecules increases with the electrophilic character and electro-acceptor power. In terms of local reactivity, in general, nucleophilicity concerns terminal nitrogen atoms. Electrophilicity concerns the central ring carbon atoms of analogous TCNQ.

Keywords: Tetracyanoquinodimethane (TCNQ), Nucleophile, Electrophile, Oxidizing power

1. INTRODUCTION

The development of conductive organic materials is a new field of investigation open to organic chemistry. It is with this in mind that Cowan et al. **[1]** discovered in 1973 the charge transfer complex resulting from Tetrathiafulvalene (TTF) and Tetracyanoquinodimethane (TCNQ). This complex exhibited interesting electrical properties making it the first true organic electrical conductor. However, it undergoes a conductor-to-insulator transition below 58 K. This is explained by a structural distortion known as the "Peierls transition" **[2]**, encountered in one-dimensional systems. This discovery had a major impact and opened up new perspectives. Several lines of research have been developed in order to find the best access conditions and above all to stabilize the conductive state, or even to reach the superconducting state at lower temperatures. Consequently, intense research on the preparation of materials derived from TTF type derivatives led in 1980 to the development of the first true superconductor at T = 1.2 K under 10 kbar. This is Bechgaard's salt (TMTSF)2 (PF6)**[3]**.7,7,8,8-Tetracyano-p-quinodimethane**[4]** or more simply Tetracyanoquinodimethane (TCNQ) **[5]** is a good electron acceptor due to the presence of cyano groups and the possibility of conjugation of the electrons of the π-system **[6]**.It is easily reduced to the anion radical ($TCNQ^{-\bullet}$) then to the dianion ($TCNQ^{2-}$). A number of strategies have been studied to modify the properties of TCNQ. Indeed, the extension of the π system reduces the Coulomb repulsion thus leading to more stable and larger radical anions to achieve high electrical conductivity. Also, by replacing the hydrogen atoms with an alkyl, alkoxy, thioalkyl, halo and cyano group, a variation of the filling band is recorded. Introducing heteroatoms into the π system reduces Coulomb repulsion. These heteroatoms also interact with each other thus suppressing the conductor-insulator transition. Removing this transition results in an electrical conductivity greater than that of organic conductors, such as the thiophene-TCNQ molecule **[7]**. In our work in particular, it is a question of making a theoretical study of the global reactivity and a theoretical characterization of the preferential sites of a series of molecules derived from the TCNQ in order to improve the electrical conductivity of the charge transfer complexes TTF-TCNQ.

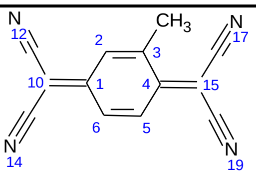
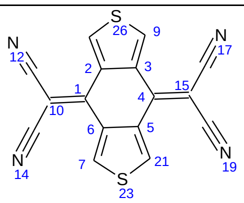
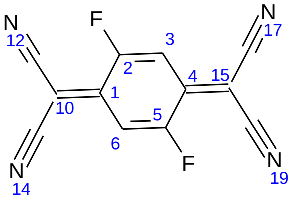
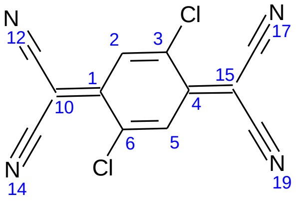
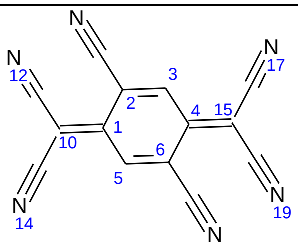
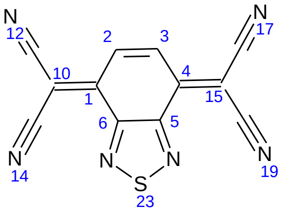
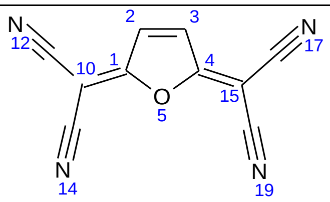
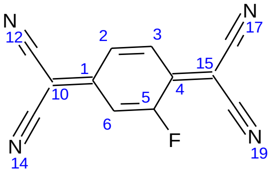
2. MATERIAL AND METHODS

2.1 Series of studied molecules

This reactivity study focuses on eight (08) Tetracyanoquinodimethane molecules codified TCNQ with their available experimental first reduction potentials. These molecules have been synthesized by several groups of researchers **[8,9,10,11,12,13]**. **Table 1** shows the 2D structures of these molecules as well as their experimental first reduction potentials expressed in volts (V).

Table 1. The 2D structures and experimental first reduction potentials of studies TCNQ molecules

CODE	STRUCTURE	$\mathbf{E^{1}_{exp}(V)}$

TCNQ_1		**+0.170**
TCNQ_2		**-0.470**
TCNQ_3		**+0.300**
TCNQ_4		**+0.410**
TCNQ_5		**+0.650**
TCNQ_6		**+0.120**
TCNQ_7		**+0.030**
TCNQ_8		**+0.260**

2.1. Used software and theory levels

Three software were used. GaussView 5.0 software **[14]** was used to represent the 3D structure and visualize the studied molecules. Then, Gaussian 09 software **[15]** was used for the optimization and calculation of frequencies under the conditions of temperature T= 298.15 Kelvin under pressure P=1atm in vacuum. The used theory level is B3LYP/6-311G(d,p). 2D structures have been represented with chemsketch software**[16]**.

2.2. Methodology for calculating the used molecular descriptors

Various molecular descriptors have been calculated, analyzed and interpreted. These molecular descriptors are described as follows:

- **Electro-acceptor power(ω^+)[17,18]**

From the ionization potential and the electron affinity, the electro-acceptor power has been defined:

$$\omega^+ = \frac{(PI+3.AE)^2}{16(PI-AE)}$$

A larger value of ω^+ corresponds to a better capacity to accept the charge while a smaller value of ω^+ of a system makes it a better electron donor **[19].**

- **Electrophilic index(ω)[20]**

It is the stabilizing energy of a molecule saturated with electrons from its surroundings.

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

With regard to the classification of electrophiles established by Domingo et al. **[21]**, a compound is said to be strongly electrophilic, when $\omega > 1.50$. Any compound having $0.80 < \omega < 1.50$ is a moderate electrophile. On the other hand, a compound is said to be marginal electrophilic if $\omega < 0.80$.

3. RESULTS AND DISCUSSION

3.1. Global reactivity of TCNQ molecules

Regarding the global reactivity, the summary of the values of the global descriptors deriving from the Frontier Molecular Orbitals is given in **Table 2.**

Table 2. Values of global reactivity descriptors and experimental first reduction potentials of studies TCNQ molecules

COMPOUND	E^1_{exp}(V)	ω^+ (eV)	ω (eV)
TCNQ_1	+0.170	12.0910	15.0274
TCNQ_2	**-0.470**	**6.3710**	**8.9866**

TCNQ_3	+0.300	13.8567	16.9587
TCNQ_4	+0.410	14.1729	17.2695
TCNQ_5	**+0.650**	**16.6889**	**20.0110**
TCNQ_6	+0.120	11.1465	14.1239
TCNQ_7	+0.030	10.2492	13.2109
TCNQ_8	+0.260	13.2512	16.2980

With regard to the overall reactivity of analog TCNQ, the molecular descriptors used are: ω^{+}, ω. We present the values of these descriptors in diagram form below for better visibility.

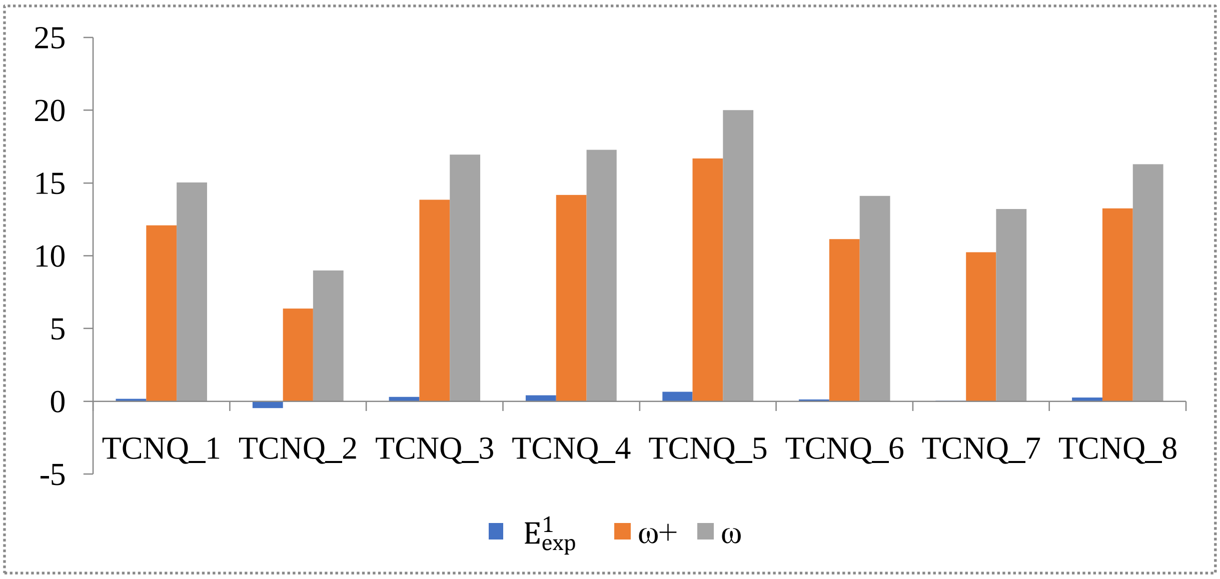


Figure 1. Diagram of the values of the global reactivity descriptors of TCNQ molecules

In this diagram, we note a variation in the value of each quantity from one molecule to another. In our series of molecules, we see that the TCNQ_5 molecule displays the highest value for electro-acceptor power when the TCNQ_2 molecule has the lowest value for electro-acceptor power. Electro-acceptor power (ω^{+}) by definition is the ability of a system to accept electrons and this magnitude is greater the more the system is able to accept electrons. It therefore appears clearly that in this series of studied molecules, the TCNQ_5 molecule is more acceptor while TCNQ_2 is less acceptor. The redox potential is a thermodynamic quantity that measures the oxidizing or reducing power of a system. In fact, the more oxidizing a system, the higher its redox potential. On the other hand, the more it is reducing the more it is able to oxidize by giving up electrons and the lower its redox potential. The classification of these molecules in decreasing order of the values of the first reduction potential is as follows:

$$\mathbf{E^{1}_{exp}}: \mathbf{TCNQ\_5} > TCNQ\_4 > TCNQ\_3 > TCNQ\_8 > TCNQ\_1 > TCNQ\_6 > TCNQ\_7 > \mathbf{TCNQ\_2}$$

From this evolutionary sequence, we note that the TCNQ_5 molecule which displays a remarkably high value of the redox potential is the most oxidizing while the TCNQ_2 molecule having the lowest value of the redox potential is the least oxidizing. With electro-acceptor power, the classification of molecules in the same order is:

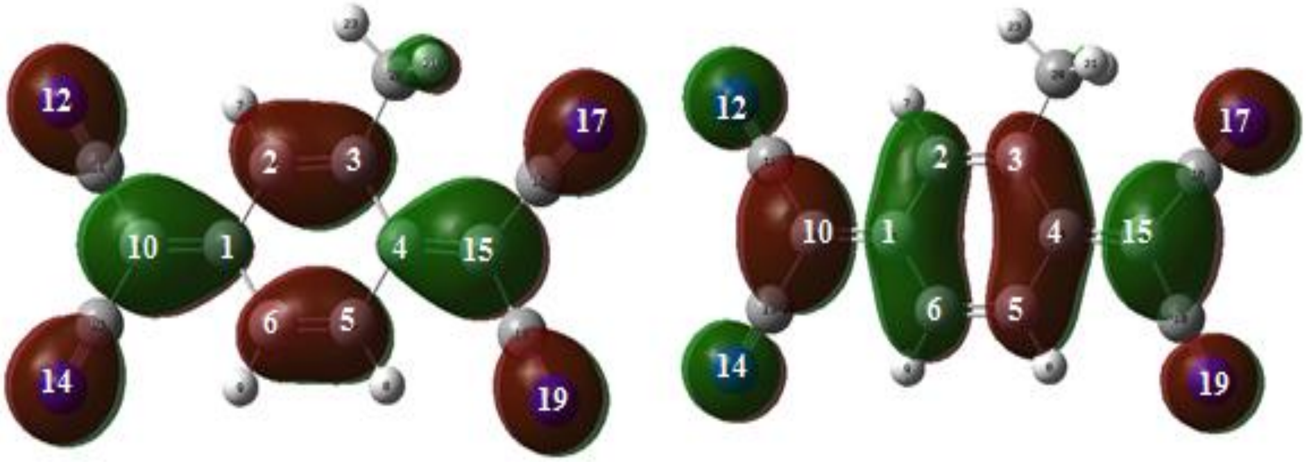
$$\boldsymbol{\omega^{+}}\text{: } \mathbf{TCNQ\_5} > TCNQ\_4 > TCNQ\_3 > TCNQ\_8 > TCNQ\_1 > TCNQ\_6 > TCNQ\_7 > \mathbf{TCNQ\_2}$$

We get exactly the same evolutionary sequence as with the first reduction potential. Thus, the electro-acceptor power of the molecules increases in the direction of the increasing oxidizing power. As for the electrophilic index, it is an index indicating the energy stability due to the transfer of electrons. It is the ability of a molecule to bind strongly to a nucleophile through electron transfer. It makes it possible to compare the electrophilic power of two species and therefore has a relative power. In the series of TCNQ derivatives studied, it is well above 1.50. This means that these compounds are strongly electrophilic. Also, this index decreases as the reduction potential decreases. The TCNQ_5 molecule displays the highest value of the electrophilic index when the lowest value is due to the TCNQ_2 molecule. This parameter further confirms that the TCNQ_5 molecule is the most oxidizing while the molecule TCNQ_2 is the least oxidizing and also increases in the direction of the increasing oxidizing power of the series.

3.2. Local reactivity of TCNQ molecules

Concerning the characterization of the 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 molecule TCNQ_1



HOMO LUMO

Figure 2. Isodensity maps of Frontier Molecular Orbitals of the TCNQ_1 molecule

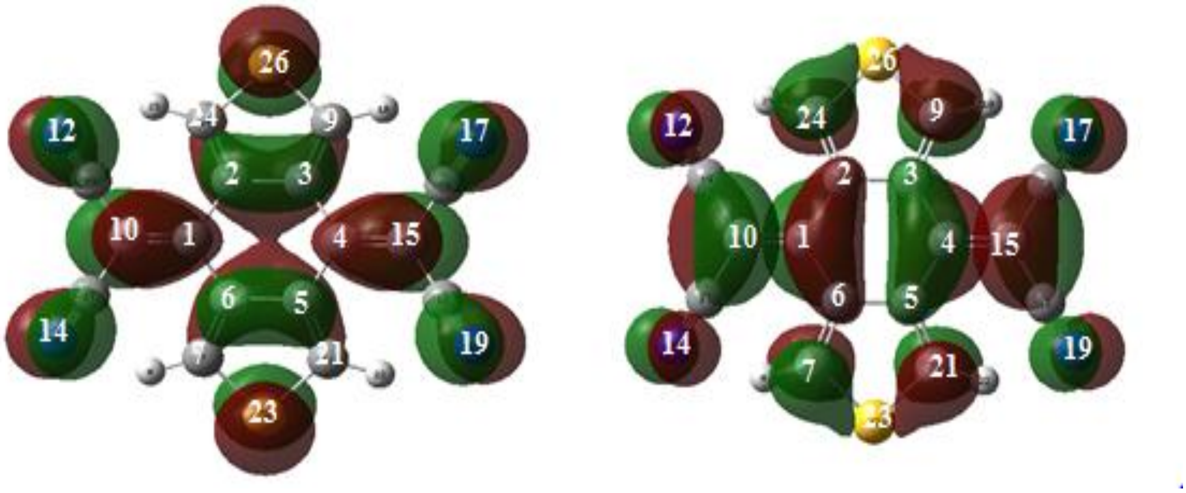
By observing the isodensity maps of the Frontier Molecular Orbitals (HOMO and LUMO) of the TCNQ_1 molecule, we note that the larger lobes completely contain the atoms C_1, C_2, C_3, C_4, C_5, C_6, C_{10}, N_{12}, N_{14} , C_{15}, N_{17} and N_{19}. These atoms therefore constitute the probable electrophilic and nucleophilic sites of the TCNQ_1 molecule.

Table 3. Values of the local Fukui reactivity indices and those of the dual descriptor of TCNQ_1.

Natural Population Analysis (NPA)			
ATOME	f^+	f^-	Δf
C_1	0.0291	0.0037	0.0254
C_2	0.0251	0.0485	-0.0234
C_3	0.0253	0.0690	-0.0436
C_4	0.0716	-0.0429	**0.1145**
C_5	0.0191	0.0579	-0.0387
C_6	0.0496	0.0225	0.0271
C_{10}	0.1599	0.1321	0.0278
N_{12}	0.1106	0.1593	-0.0487
N_{14}	0.1095	0.1629	-0.0534
C_{15}	0.1518	0.1372	0.0146
N_{17}	0.1005	0.1716	**-0.0711**
N_{19}	0.1105	0.1535	-0.0430

As for the molecule TCNQ_1, the C_4 atom has the positive and higher value of the dual descriptor. This is the site of the lowest electron density. Also, we notice that the terminal nitrogen N_{17} contains the negative and weakest dual descriptor: it is the potential nucleophilic site of the molecule. As for the C_4 atom, it is favorable to any nucleophilic attack.

Case of TCNQ_2 molecule



HOMO **LUMO**

Figure 3. Isodensity maps of Frontier Molecular Orbitals of the TCNQ_2 molecule

Observation of the isodensity maps of Frontier Molecular Orbitals (HOMO and LUMO), shows that the largest lobes entirely contain the atoms C_1, C_2, C_3, C_4, C_5, C_6, C_9, C_{10}, N_{12}, N_{14} C_{15}, N_{17} , N_{19}, C_{21}, S_{23}, C_{24} and S_{26}. These atoms are therefore the probable electrophilic and nucleophilic sites of the TCNQ_2 molecule.

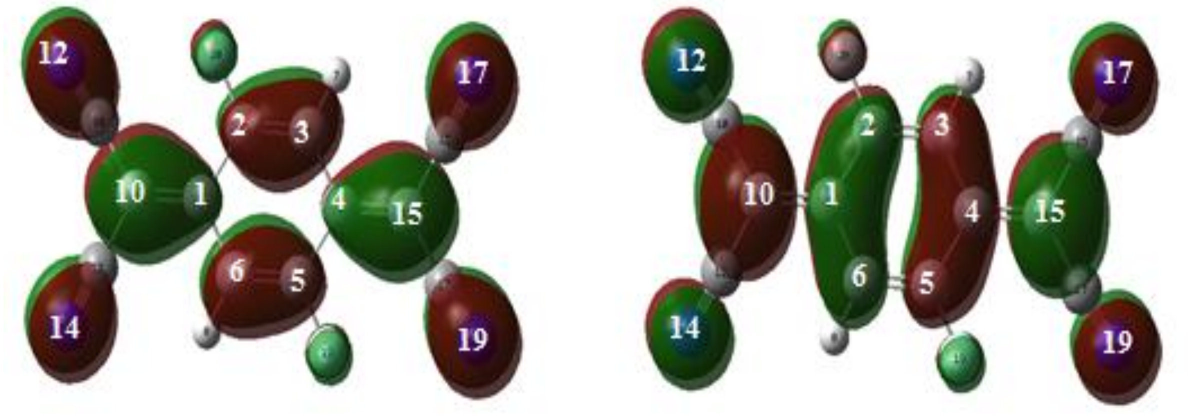
Table 4. Values of the local Fukui reactivity indices and those of the dual descriptor of TCNQ_2.

	Natural Population Analysis (NPA)		
ATOME	f^+	f^-	Δf
C_1	0.0499	0.0226	0.0272
C_2	-0.0024	0.0141	-0.0165
C_3	-0.0025	0.0141	-0.0166
C_4	0.0500	0.0225	0.0275
C_5	-0.0025	0.0141	-0.0166
C_6	-0.0025	0.0141	-0.0166
C_7	0.0715	-0.0135	**0.0851**
C_9	0.0715	-0.0136	**0.0851**
C_{10}	0.1197	0.0902	0.0295
N_{12}	0.0772	0.1381	-0.0608
N_{14}	0.0772	0.1381	-0.0609
C_{15}	0.1196	0.0904	0.0292
N_{17}	0.0773	0.1381	-0.0608
N_{19}	0.0772	0.1381	-0.0608
C_{21}	0.0715	-0.0135	**0.0850**
S_{23}	0.0033	0.1911	**-0.1878**
C_{24}	0.0715	-0.0135	**0.0850**

S_{26}	0.0033	0.1912	**-0.1879**

Based on the data reported in this table, only atoms C_7, C_9, C_{21}, and C_{24} have equal, positive, and higher values of the dual descriptor. These are the sites of the lowest electron density of the studied molecule. These equal values of the dual descriptor for these carbon atoms indicate that they are equivalent. With regard to the sulfur atoms S_{23} and S_{26}, their dual descriptors are equal, negative and higher. These sulfur atoms are therefore equivalent and constitute the sites of highest electron density. This proves that the S_{23} and S_{26} atoms are the sites of nucleophilic attacks while any electrophilic attack will be on the carbon atom C_7, C_9, C_{21} and C_{24} preferably. The equal descriptors for these atoms confirm that the studied molecule is point group symmetric with symmetric (GPS) D2h.

Case of TCNQ_3 molecule



HOMO **LUMO**

Figure 4. Isodensity maps of Frontier Molecular Orbitals of the TCNQ_3 molecule

Regardless of the Frontier Molecular Orbitals, the larger lobes completely contain the atoms, C_1, C_2, C_3, C_4, C_5, C_6, C_{10}, N_{12}, N_{14}, C_{15}, N_{17}, and N_{19}. Therefore, these different atoms are the probable electrophilic and nucleophilic sites of this molecule.

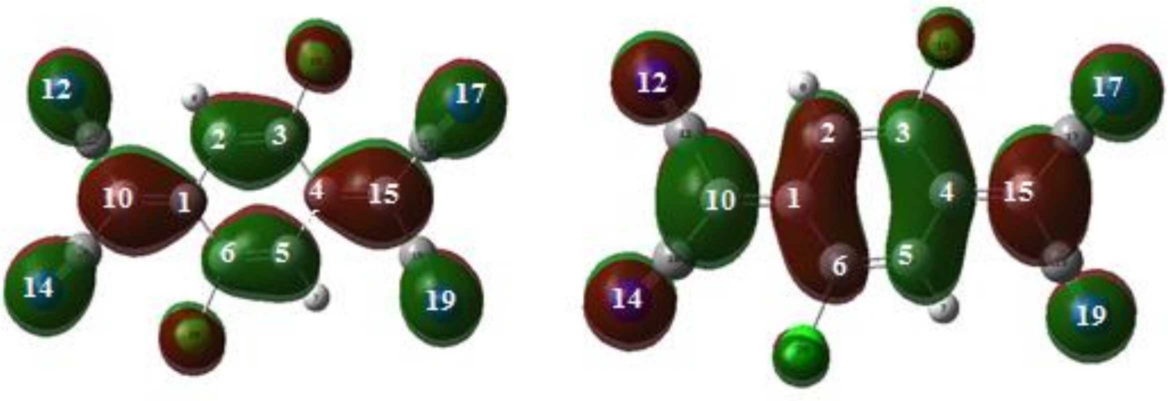
Table 5. Values of the local Fukui reactivity indices and those of the dual descriptor of TCNQ_3

Natural Population Analysis (NPA)			
ATOME	f^{+}	f^{-}	Δf
C_1	0.0327	-0.0009	0.0337
C_2	0.0342	0.0347	-0.0005
C_3	0.0257	0.0559	-0.0302
C_4	0.0562	-0.0244	**0.0805**

C_5	0.0220	0.0469	-0.0249
C_6	0.0343	0.0472	-0.0129
C_{10}	0.1663	0.1232	0.0431
N_{12}	0.1142	0.1680	-0.0538
N_{14}	0.1137	0.1555	-0.0418
C_{15}	0.1658	0.1236	0.0421
N_{17}	0.1135	0.1557	-0.0422
N_{19}	0.1126	0.1695	**-0.0569**

The data in **Table 5** indicate that the terminal nitrogen atom N_{19} has its negative and weaker dual descriptor. This is the site of the most electron-rich molecule. As for the C_4 carbon atom, it displays a positive and higher dual descriptor: it is the potential electrophilic site of the molecule and the terminal nitrogen atom N_{19} is favorable to any electrophilic attack.

Case of TCNQ_4 molecule



HOMO **LUMO**

Figure 5. Isodensity maps of Frontier Molecular Orbitals of the TCNQ_4 molecule

The observation of the isodensity maps of all the HOMO and LUMO Frontier Molecular Orbitals shows that the largest lobes definitely contain only the atoms C_1, C_2, C_3, C_4, C_5, C_6, C_{10}, N_{12}, N_{14}, N_{17}, C_{15} and N_{19}. Thus, it is highly likely that they are the electrophilic and nucleophilic sites of the TCNQ_4 molecule.

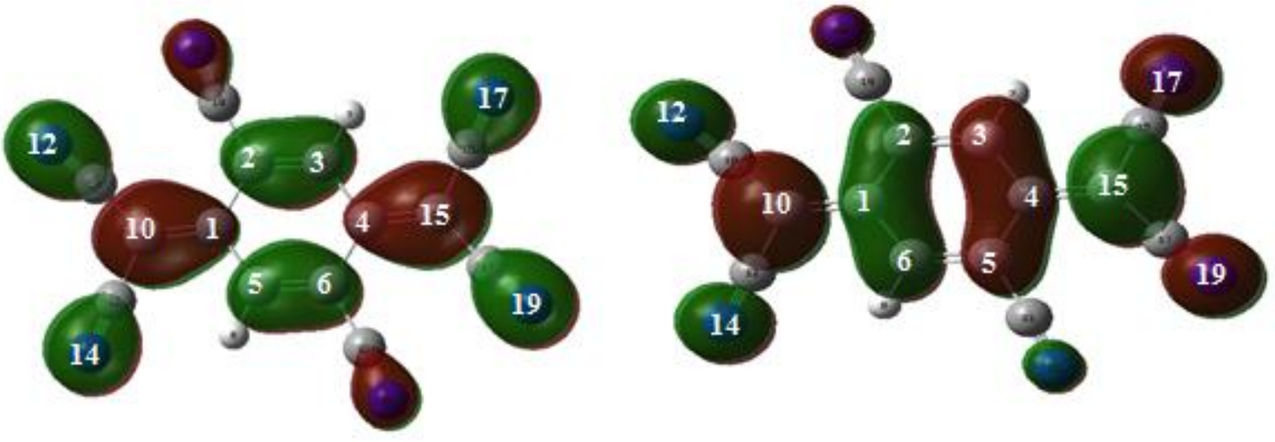
Table 6. Values of the local Fukui reactivity indices and those of the dual descriptor of TCNQ_4.

Natural Population Analysis (NPA)			
ATOME	f^+	f^-	Δf
C_1	0.0385	-0.0098	0.0483
C_2	0.0220	0.0460	-0.0240
C_3	0.0030	0.0425	-0.0395

C_4	0.0656	-0.0370	**0.1027**
C_5	0.0125	0.0556	-0.0432
C_6	0.0161	0.0293	-0.0132
C_{10}	0.1571	0.1207	0.0364
N_{12}	0.1060	0.1469	-0.0410
N_{14}	0.0915	0.1736	-0.0821
C_{15}	0.1573	0.1204	0.0369
N_{17}	0.0921	0.1730	**-0.0809**
N_{19}	0.1056	0.1473	-0.0417

The values in **Table 6**show that the case of the TCNQ_4 molecule is exactly the same as that of the molecule TCNQ_1. Consequently, the arguments put forward in the case of the TCNQ_1 molecule remain valid for this molecule.

Case of TCNQ_5 molecule



HOMO **LUMO**

Figure 6. Isodensity Maps of Frontiers Molecular Orbital of the TCNQ_5 molecule

From the observation of all the isodensity maps of Frontier Molecular Orbitals (HOMO and LUMO), it appears that the largest lobes entirely contain the atoms C_1, C_2, C_3, C_4, C_5, C_6, C_{10}, N_{12}, N_{14} , C_{15}, N_{17} and N_{19}. Consequently, these different atoms constitute the probable electrophilic and nucleophilic sites of this molecule.

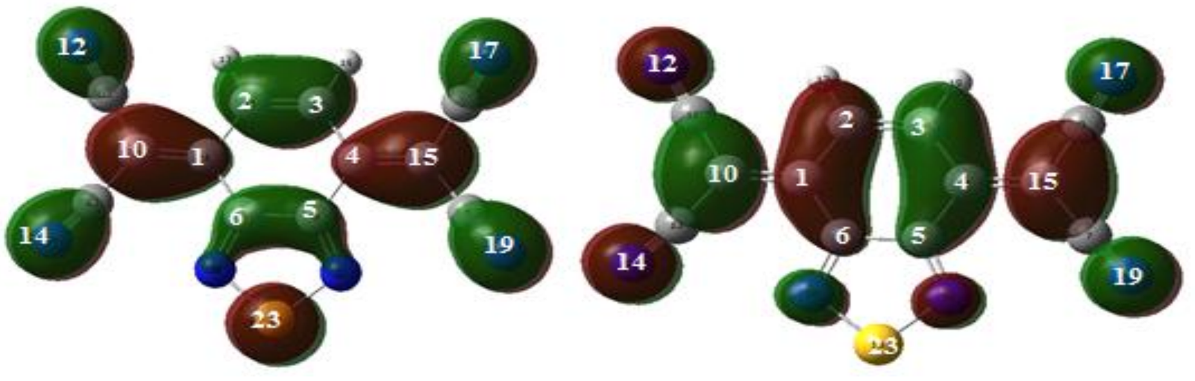
Table 7. Values of the local Fukui reactivity indices and those of the dual descriptor of TCNQ_5.

	Natural Population Analysis (NPA)		
Atome	f^+	f^-	Δf
C_1	0.0155	0.0098	0.0057
C_2	0.0745	0.0157	0.0588
C_3	0.0004	0.0638	**-0.0634**
C_4	0.0420	-0.0167	0.0587

C_5	0.0595	0.0308	0.0287
C_6	0.0119	0.0523	-0.0404
C_{10}	0.1613	0.1116	0.0497
N_{12}	0.1046	0.1544	-0.0497
N_{14}	0.1009	0.1531	-0.0522
C_{15}	0.1671	0.1058	**0.0612**
N_{17}	0.1038	0.1502	-0.0464
N_{19}	0.1044	0.1546	-0.0503

The values reported in this table indicate that the C_{15} atom has the value of its positive and higher dual descriptor. It is therefore the site of the lowest electron density of the studied molecule. As for C_3 carbon, it has the greatest negative value. This site has a high electron density. It is concluded that the C_{15} atom is the site of nucleophilic attacks while any electrophilic attack will preferably be on the C_3 carbon atom.

Case of TCNQ_6 molecule



HOMO **LUMO**

Figure 7. Isodensity maps of Frontier Molecular Orbitals of the TCNQ_6 molecule

The observation of the isodensity maps of the high occupied and low vacant Frontier Molecular Orbitals shows that the largest lobes entirely contain the atoms C_1, C_2, C_3, C_4, C_5, C_6, C_{10}, N_{12}, N_{14}, C_{15}, N_{17}, N_{19} and S_{23}. This proves that these atoms are therefore the probable electrophilic and nucleophilic sites of the TCNQ_6 molecule.

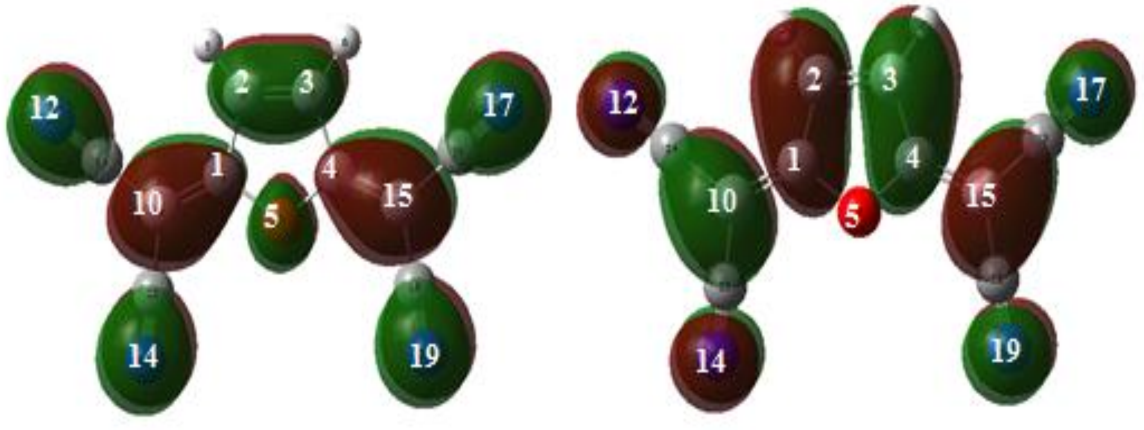
Table 8. Values of the local Fukui reactivity indices and those of the dual descriptor of TCNQ_6.

Natural Population Analysis (NPA)			
ATOME	f^+	f^-	Δf
C_1	0.0314	0.0191	0.0123
C_2	0.0498	0.0481	0.0017
C_3	0.0498	0.0481	0.0017
C_4	0.0314	0.0191	0.0123

C_5	0.0162	-0.0129	0.0291
C_6	0.0162	-0.0129	0.0291
C_{10}	0.1574	0.1048	**0.0526**
N_{12}	0.1044	0.1462	-0.0418
N_{14}	0.1088	0.1500	-0.0413
C_{15}	0.1574	0.1048	**0.0526**
N_{17}	0.1045	0.1462	-0.0417
N_{19}	0.1088	0.1501	-0.0413
S_{23}	-0.0189	0.2326	**-0.2514**

The data reported in this table indicates that atoms C_{10} and C_{15} have equal, positive, and higher values of the dual descriptor. These are the low electron density sites within the studied molecule. Regarding the sulfur atom S_{23}, it displays the smallest negative value of the dual descriptor. This is the high electron density site. It is concluded that the C_{10} and C_{15} atoms are the sites of nucleophilic attacks while the electrophilic attacks will preferably be on the sulfur atom S_{23}.

Case of TCNQ_7 molecule



HOMO

LUMO

Figure 8. Isodensity maps of Frontier Molecular Orbitals of the TCNQ_7 molecule

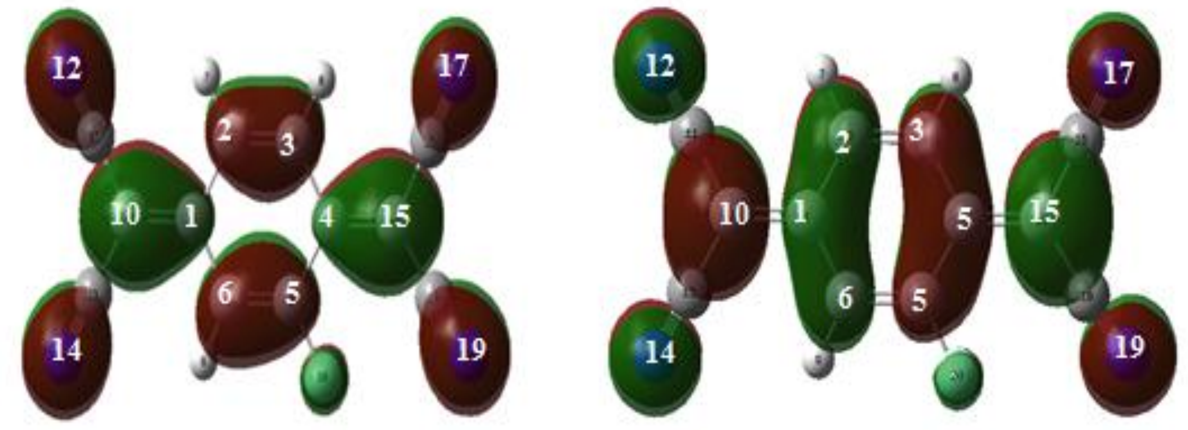
Observation of the isodensity maps of Frontier Molecular Orbitals (HOMO and LUMO), shows that the larger lobes entirely contain the atoms C_1, C_2, C_3, C_4, O_5, C_{10}, N_{12}, N_{14}. C_{15}, N_{17} and N_{19}. These atoms are therefore the probable electrophilic and nucleophilic sites of the TCNQ_7 molecule.

Table 9. Values of the local Fukui reactivity indices and those of the dual descriptor of TCNQ_7.

Natural Population Analysis (NPA)			
ATOME	f^{+}	f^{-}	Δf
C_1	0.0181	0.0110	0.0071
C_2	0.0981	0.0438	**0.0543**
C_3	0.0981	0.0438	**0.0543**
C_4	0.0180	0.0110	0.0070
O_5	-0.0072	0.0635	**-0.0707**
C_{10}	0.16161	0.1331	0.0285
N_{12}	0.1201	0.1680	-0.0479
N_{14}	0.1128	0.1701	-0.0582
C_{15}	0.1617	0.1330	0.0287
N_{17}	0.1201	0.1680	-0.0479
N_{19}	0.1127	0.1710	-0.0583

Analysis of the results indicate that atoms C_2 and C_3 have equal, positive, and higher values of the dual descriptor. These are the low electron density sites of the studied molecule. The smaller negative value is attributed to the oxygen atom O_5. This is the high electron density site. Thus, the C_2 and C_3 atoms will be sensitive to the approach of a nucleophile while the electrophilic attacks will preferably be on the oxygen atom O_5.

Case of TCNQ_8 molecule



HOMO **LUMO**

Figure 9. Isodensity maps of Frontier Molecular Orbitals of the TCNQ_8 molecule

Regarding the TCNQ_8 molecule, the observation of the isodensity maps of the Frontier Molecular Orbitals (HOMO and LUMO) indicates that the larger lobes entirely contain the atoms C_1, C_2, C_3, C_4, C_5, C_6, C_{10} , N_{12}, N_{14}, C_{15}, N_{17}, N_{19}. These atoms therefore constitute the probable electrophilic and nucleophilic sites of this molecule.

Table 10. Values of the local Fukui reactivity indices and those of the dual descriptor of TCNQ_8.

	Natural Population Analysis (NPA)		
ATOME	f^+	f^-	Δf
C_1	0.0188	0.0082	0.0106
C_2	0.0530	0,0247	0.0283
C_3	0.0193	0,0583	-0.0390
C_4	0.0693	-0.0350	**0.1043**
C_5	0.0107	0.0606	-0.0500
C_6	0.0442	0.0423	0.0019
C_{10}	0.1651	0.1314	0.0337
N_{12}	0.1119	0.1647	-0.0528
N_{14}	0.1129	0.1628	-0.0499
C_{15}	0.1626	0.1266	0.0359
N_{17}	0.1134	0.1561	-0.0426
C_{18}	-0.0236	-0.0330	0.0093
N_{19}	0.1135	0.1683	**-0.0548**

The values in **Table 10** show that the case of the TCNQ_8 molecule is exactly the same as that of the TCNQ_21 molecule. Thus, the arguments put forward in the case of the TCNQ_21 molecule are also valid for TCNQ_8.

4. CONCLUSION

This work is concerned with the theoretical study of the chemical reactivity of a series of eight (08) molecules derived from Tetracyanoquinodimethane (TCNQ). Regarding the overall reactivity, the TCNQ_5 moleculeis more acceptor (more oxidizing) when the molecule TCNQ_2 is less acceptor (less oxidizing). The oxidizing power of these molecules is so high as the electrophilic index and the electro-acceptor power increase. In the case of local reactivity, in general, nucleophilic concerns the terminal nitrogen atoms. For electrophilic attack sites, they relate to the central ring carbon atoms of analogous TCNQ. These different sites could also constitute sites for dimerization of these molecules. This would extend the conjugation of molecules and therefore improve the conductivity of the TTF-TCNQ charge transfer complexes.

REFERENCES

[1]Ferraris, J., Cowan, D. O., Walatka, V., & Perlstein, J. H., *Electron transfer in a new highly conducting donor-acceptor complex. Journal of the American Chemical Society, 95(3), 948–949,* **1973**

[2]Coleman, L. B., Cohen, M. J., Sandman, D. J., Yamagishi, F. G., Garito, A. F., & Heeger, A. J., *Superconducting fluctuations and the peierls instability in an organic solid. Solid State Communications, 12(11), 1125–1132,* **1973**

[3] Abdelkrim GOUASMIA, thèse de doctorat d'état, Académie de Montpellier, Université des Sciences et Technologiques de Languedoc Montpellier (France), **1988**

[4]Melby, L. R., Harder, R. J., Hertler, W. R., Mahler, W., Benson, R. E., & Mochel, W. E., *Substituted Quinodimethans. II. Anion-radical Derivatives and Complexes of 7,7,8,8-Tetracyanoquinodimethan. Journal of the American Chemical Society, 84(17), 3374–3387,* **1962**

[5] M.P. Le Paillard, A.Robert, G. Garrigou-Lagrange, P.Delhaes, p.Le Maguerés, L. Ouahab et L. Toupet, *Synthetic Metals*, 1993, 58, 223,232.

[6] K.EL. Kacemi et M. Lamache, *Electrochimca acta*., 1986, 31,7,845,849.

[7]M.Fujil, Y.Aso, T.Otsubo et F.Ogura, *Synthetic Metals* ., 1993,55,57,1910,1913.

[8]James J. Delaney B., Sc., *Synthesis of New Heterocyclic TCNQ Analogues, Doctorate of Philosophy, Dublin City University* (School of Chemical Sciences), 202 p, **1997**.

[9]J R Andersen, O Jorgensen, *Organic Metals;Mono- and 2,5-Di-substituted 7,7,8,8-tetracyano-pquinodimethanes and Conductivities of their Charge-transfer Complexes*, J. Chem Soc. Perkin Trans I, 3095-3098, **1979**.

[10]R. C. Wheland, J. L. Gillson, *Synthesis of Electrically Conductive Organic Solids*, J. Am. Chem. Soc., 98, 3916-3925, **1976**.

[11] J. P. Ferraris, G. Saito, *Organic Metals with Asymmetric Acceptors :The Monofluorotetracyanoquino-dimethane Anion*, J. Chem. Soc., Chem. Comm., 992-993, **1978**.

[12]G. Saito, J. P. Ferraris, *Difluorotetracyanoquinodimethane :Electron Affinity Cut -off for 'Metallic' Behaviour in a Tetrathiafulvalene Salt,* J. Chem. Soc., Chem. Comm., 1027-1029, **1979**.

[[13]Y. Yamashita, *Novel Electron Acceptors and Donors Containing Fused-heterocycles*, J. Org. Syn. Chem., 47(12), 1108-1117, **1989**

[14] R Dennington; T Keith and J Millam. GaussView, Version 5, Semichem Inc., Shawnee Mission, KS, **2009**.

[15] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi,

J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

[16] ACDLABS 10, Advanced Chemistry Development Inc., Toronto, ON, Canada, **2015**.

[17] J. L. Gazquez, A. Cedillo and A. Vela, *Electrodonating and Electroaccepting Powers* J. Phys. Chem. A, 111, 1966–1970, **2007**

[18] A. Martínez, *Donator Acceptor Map of Psittacofulvins and Anthocyanins: Are They Good Antioxidant Substances?* J. Phys. Chem. B, 113(14), 4915-4921, **2009**

[19]L. R. Domingo, P. Pérez, *The nucleophilicity N index in organic chemistry*, Org. Biomol. Chem., 9, 7168–7175, **2011**

[20] Parr R.G., Szentpaly L.V., Liu S., *Electrophillicity index.* J. Am. Chem. Soc., 121, 1922-1924, **1999**

[21]L. R. Domingo, M. J. Aurell, P. Perez and R. Contreras, *Quantitative characterization of the global electrophilicity power of common diene/dienophile pairs in Diels-Alder reactions*,Tetrahedron, *58*, 4417-4423, **2002**