

Theoretical study of the charge transfer of five derivatives of Tetrathiafulvalene complexed with unsubstituted Tetracyanoquinodimethane

Abstract:

Our work consisted of a theoretical study of the charge transfer of five Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ) complexes. Global reactivity and charge transfer descriptors were determined at theory level B3LYP/6-311G (d,p). These descriptors revealed that the Tetrathiafulvalene (TTF) has a reducing character when the Tetracyanoquinodimethane (TCNQ) has an oxidizing character, the oxidation-reduction reaction between these two molecules is a polar reaction characterized by a high charge transfer, the electronic flow moves from TTF to TCNQ and the conductivity of these charge transfer complexes increases when the $\text{HOMO}_{\text{TTF}}\text{-LUMO}_{\text{TCNQ}}$ energy gap decreases. When the dipole moment of TTF molecules increases, the conductivity of the complexes they form with unsubstituted TCNQ increases and leads to high charge transfer. We intend to deepen this study by proposing new complexes with more improved electrical properties

Keywords: Tetrathiafulvalene (TTF); Tetracyanoquinodimethane (TCNQ); charge transfer; Charge transfer complex

1. INTRODUCTION

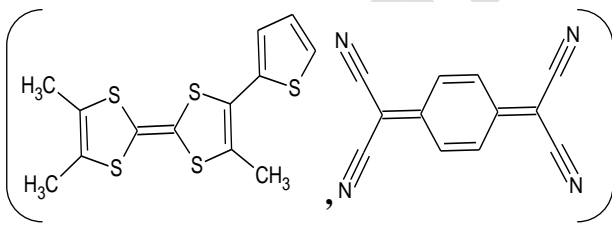
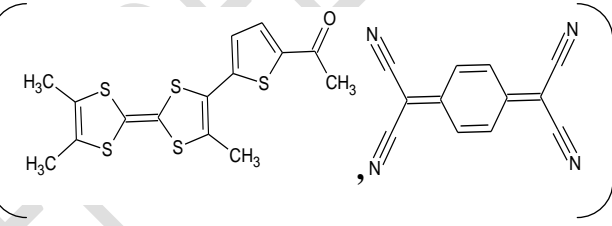
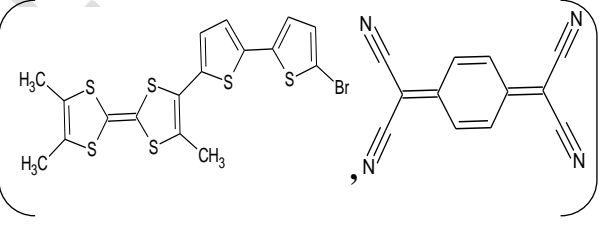
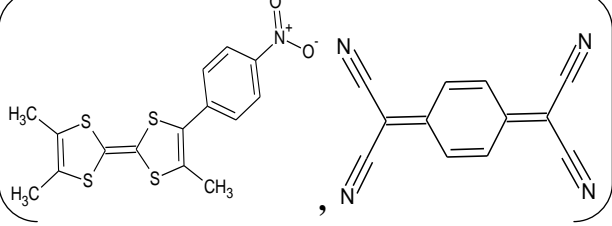
Since the first synthesis of Tetrathiafulvalene (TTF) [1] and the discovery of the electrical conductivity of the first charge transfer complexes, studies of TTF derivatives and their analogues have received much attention [2,3]. Since then, great efforts have been made to improve and understand the properties of the TTF-TCNQ complex. Various TTF derivatives, the most important of which is Bis(Ethylenedithio)Tetrathiafulvalene (BEDT-TTF) have been synthesized and their charge transfer salts with Tetracyanoquinodimethane (TCNQ) or monovalent anions have been prepared [4,5,6]. They exhibit interesting electrical properties such as superconductivity at very low temperature, conductivity and semiconductivity [7]. These properties depend on the choice of both molecules TTF and TCNQ [8]. They therefore give them a particular interest in biochemistry, bioelectrochemical energy transfer, biology and drug receptor binding mechanism [9]. The transfer of charge is therefore a very important phenomenon. Our work consists of a study of the charge transfer of five TTF-TCNQ charge transfer complexes by the Density Functional Theory (DFT) method in order to propose new charge transfer complexes with more improved electrical conductivities.

2. MATERIAL AND METHODS

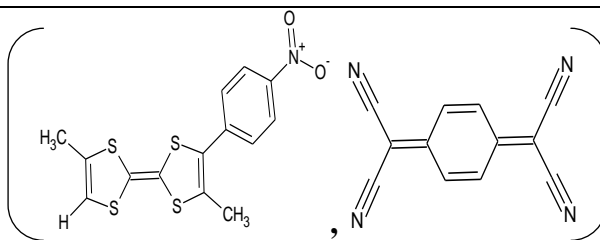
2.1. Presentation of the studied charge transfer complexes

The charge transfer of five Tetrathiafulvalene –Tetracyanoquinodimethane (TTF-TCNQ) charge transfer complexes was investigated. The choice of these complexes stems from the availability of their experimental electrical conductivities and the availability of the experimental redox potentials of TTF. All these charge transfer complexes were synthesized by Tahar Abbaz et al. [10] in Algeria. The **Table 1** presents their 2D structures with their respective experimental electrical conductivities expressed in $S \cdot cm^{-1}$.

Table 1. 2D structures of the studied TTF-TCNQ charge transfer complexes and their respective experimental electrical conductivities

CODE	STRUCTURE	σ ($S \cdot cm^{-1}$)
(TTF_1, TCNQ)		0.0050
(TTF_2, TCNQ)		0.0370
(TTF_3, TCNQ)		0.0085
(TTF_4, TCNQ)		2.3000

(TTF_5, TCNQ)



2.6000

2.2. Software and theory level

GaussView 5.0 software [11] was used to represent 3D structures and visualize the studied molecules. Then, Gaussian 09 software [12] was used for geometric optimization and frequency calculation. The used theory level is B3LYP/6-31G(d,p). The calculations were carried out under the conditions of Temperature T=298.15 Kelvin under pressure P=1atm in vacuum. The 2D structures were represented with the chemsketch software [13].

2.3. Methodology for calculating of used global reactivity molecular descriptors

To carry out this charge transfer study, various global molecular descriptors of reactivity were calculated, analyzed and interpreted. These descriptors are described as follows:

- **Dipole moment (μ_D)**

The dipole moment is related to the asymmetric distribution of charges within a molecule. It is therefore a quantity that characterizes the polar or nonpolar nature of a molecule. Indeed, a molecule is said to be polar, when its dipole moment is non-zero. On the other hand, when the dipole moment is zero, the molecule has an apolar character. The dipole moment is frequently involved in studies of Quantitative Structure-Activity Relationship/Quantitative Structure - Property Relationship (QSAR/QSPR).

- **Frontier molecular orbitals energies HOMO/LUMO**

They play a major role in many chemical reactions and in reaction mechanisms. The energies of these orbitals are very popular molecular descriptors in quantum chemistry and in Quantitative Structure-Property Relationship/Quantitative Structure-Activity Relationship (QSPR/QSAR) studies [14,15].

- **Ionization potential (IP) / Electronic affinity (EA)**

According to the Koopmans approximation [16], the ionization potential is the opposite of the energy of HOMO while the electronic affinity is the opposite of that of LUMO.

$$AE = -E_{LUMO} \quad (1) \quad \text{et} \quad PI = -E_{HOMO} \quad (2)$$

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

From the ionization potential and the electronic affinity, the definition of the electro-acceptor power is:

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

A greater 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 donor of electrons [19].

- **Hardness (η) / Softness (S) [20]**

Hardness 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 will be.

$$\eta = \frac{(PI - AE)}{2} \quad (4)$$

Softness is defined as the inverse of twice the hardness.

$$S = \frac{1}{2\eta} \quad (5)$$

- **Electronegativity(χ)/Chemical potential (μ)[21,22]**

Electronegativity measures the tendency of a chemical species to attract electrons. Regarding the chemical potential, it measures the tendency of the electron cloud to escape from the molecule. It is assumed to be the opposite of electronegativity:

$$\mu = -\frac{(PI + AE)}{2} = -\chi \quad (6)$$

- **Electrophilic index (ω)[23]**

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

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \quad (7)$$

With regard to the classification of electrophiles established by Domingo et al. [24], 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 $\omega < 0.80$.

- **Nucleophilic index (N)**

In order to propose a simple descriptor for nucleophilic, Domingo et al. [25] used the highest occupied molecular orbital (HOMO) obtained within the limits of the Kohn-Sham scheme [26]. They introduced the nucleophilicity index (N) as:

$$N(\text{Nu}) = E_{\text{HOMO}}(\text{Nu}) - E_{\text{HOMO}}(\text{TCE}) \text{ in (eV)} \quad (8)$$

Where Tetracyanoethylene (TCE) was taken as a reference. In this scale, the nucleophilicity index of TCE is $N = 0.0$ eV, presenting the lowest HOMO energy of a long series of organic molecules already considered. Studies [27] have shown that organic molecules with nucleophilicity indices strictly greater than 3.00 eV are strong nucleophiles ($N > 3.00$ eV). When $2.00 \text{ eV} < N < 3.00 \text{ eV}$, organic compounds are said to be moderate nucleophiles. Any organic compound is a marginal nucleophile if $N < 2.00$ eV.

- **Dual indices (γ_1 , γ_2 et $\Delta\gamma_{12}$) [28,29]**

The direction of electron flow during a reaction can be determined using the dual indices γ_1 , γ_2 et Δ_{12} . Consider two reactants A and B and set:

$$\gamma_1 = \omega_A + N_B \quad (9) \quad \gamma_2 = \omega_B + N_A \quad (10) \quad \Delta_{12} = \gamma_1 - \gamma_2 \quad (11)$$

Thus, if $\gamma_1 > \gamma_2$, the electronic flow evolves from B to A while if $\gamma_1 < \gamma_2$, the process is characterized by an electronic flow moving from A to B. For a large and positive difference $\Delta\gamma_{12} = \gamma_1 - \gamma_2$, the reaction is said polar and is characterized by a relatively high charge transfer. A negative difference $\Delta\gamma_{12} = \gamma_1 - \gamma_2$ with a relatively high value also indicates that the reaction is polar and is characterized by a relatively high charge transfer.

The processes characterized by negligible values of $\Delta\gamma_{12}$ are systematically said to be nonpolar with negligible charge transfer.

3. RESULTS AND DISCUSSION

3.1. Highlighting of the oxidizing and reducing character of TTF and TCNQ molecules

The global molecular descriptors of the reactivity of the isolated TTF and of the unsubstituted TCNQ forming the complexes were determined in order to demonstrate their oxidizing and reducing characteristics. The values of these descriptors are collated in **Table 2**.

Table 2. Values of global molecular descriptors of reactivity of TTF and unsubstituted TCNQ forming charge transfer complexes.

DESCRIPTORS	TTF_1	TTF_2	TTF_3	TTF_4	TTF_5	TCNQ
E_{HOMO}	-4.6638	-4.8255	-4.7373	-4.8682	-4.9096	-7.5772
PI	4.6638	4.8255	4.7373	4.8682	4.9096	7.5772
E_{LUMO}	-1.3123	-2.2120	-1.9143	-2.7490	-2.7729	-5.0214
AE	1,3123	2.2120	1.9143	2.7490	2.7729	5.0214
ω	2.6640	4.7377	3.9182	6.8447	6.9058	15.5263
ω^+	1.3795	3.1416	2.4317	5.0728	5.1187	12.5363
N	4.7052	4.5435	4.6317	4.5008	4.4594	1.7918
χ	2.9881	3.5188	3.3258	3.8086	3.8413	6.2993
μ	-2.9881	-3.5188	-3.3258	-3.8086	-3.8413	-6.2993
μ_{D}	1.8195	4.9247	3.4097	5.7947	5.1572	0,0016

On analysis of the data in **Table 2**, all these quantities vary and show the same sign when we switch each time from a TTF molecule to the unsubstituted TCNQ molecule. Regarding HOMO, it is the energy of the highest occupied molecular orbital. It therefore contains the electrons that are easier to give up. This is related to the electron donor character of a molecule. A large energy value of HOMO indicates the tendency of this molecule to donate electrons to a suitable acceptor. In the case of our study, it is found that TTF molecules have the highest HOMO energy values ranging from -4.9096 eV to -4.6638 eV. As a result, TTF molecules will easily give up electrons. As for LUMO, it provides information on the electron acceptor character of a molecule. Its energy indicates the ability of this molecule to accept electrons. The TCNQ molecule has the lowest energy value of LUMO ($E_{\text{LUMO}} = -5.0214$ eV). Knowing that the probability that a molecule will accept electrons is as high as this energy is low, we deduce that the TCNQ molecule can therefore easily accept electrons against TTF. Also, we note that the HOMO of TTF and LUMO of TCNQ are very close in

energy, reflecting a high mobility of charge carriers (electrons) between these two types of molecules.

The charge transfer created between the TTF and TCNQ entities depends on both the ionization (IP) and oxidation potential of the TTF as well as the electron affinity (EA) and reduction potential of the TCNQ. TTF molecules have the smallest values of electron affinity (1.3123 eV to 2.7729 eV) while the TCNQ molecule has the largest value of ionization potential (7.5772eV). This also means that TTF molecules will easily give up electrons during the redox reaction. As for the TCNQ molecule, it can easily accept electrons.

Along with the electrophilic and nucleophilic indices, the unsubstituted TCNQ molecule displays the highest value of the electrophilic index when the TTF molecules display the highest values of the nucleophilic index. Thus, faced with the unsubstituted TCNQ molecule, the TTF molecules will behave like nucleophiles. As for the unsubstituted TCNQ molecule, it will have an electrophilic character during the redox reaction. It is useful to note that the nucleophilicity indices of TTF (4.4594 eV to 4.7052 eV) are all greater than 3.00 eV while that of TCNQ is less than 2 eV. Accordingly, the TTF molecules studied are strong nucleophiles while TCNQ is a marginal nucleophile. As for the electrophilic index ω , its value is greater than 1.50 for all the studied molecules. This means they are strong electrophiles. However, the TCNQ molecule is electrophilic than TTF with a very high electrophilic index ($\omega = 15.5263$ eV).

The role of electro-attractors groups is to attract electron density towards them. This leads to a lowering of the energy of the HOMO and a depletion of electrons in the rest of the molecule. This high value of the electrophilic index for the TCNQ is therefore explained by the grafting of the cyano group (-CN) which is an electro-atttractor group. This group has a very strong mesomeric attracting effect (-M). Faced with TTF, the latter will be more able to attract electrons. The greater capacity of the TCNQ molecule to accept electrons is justified by the high value of the electro-acceptor power ($\omega^+ = 12.5363$ eV).

Chemical potential is the ability of a molecule to release its electrons. A high value of the chemical potential indicates a high reactivity of the molecule. In contrast, electronegativity is the ability of a molecule to acquire and store electrons. The higher values of the chemical potential of TTF molecules (-3.8413 eV to -2.9881 eV) make them the most reactive molecules. The higher value of the electronegativity of the TCNQ molecule, shows

that the latter is more electronegative. TTF molecules will therefore have a reducing character when the unsubstituted TCNQ molecule has an oxidizing character during the redox reaction.

Electric dipole moment is a measure of the separation of positive and negative charges within a system, that is, a measure of the overall polarity of the system. In our case, we notice that TTF have non-zero and high dipole moment values ranging from 1.8195 D to 5.7947 D. It is therefore clear that TTF molecules are all polar molecules. These high values of the dipole moments prove the existence of a very important separation of charges in these molecules. Also, the TTF_1 molecule which displays the smallest value of the dipole moment is the least polar and the TTF_5 molecule which has the largest value of the dipole moment is the most polar. As for the TCNQ molecule, the value of its dipole moment is located in the vicinity of zero (0.0016 D), thus reflecting the nonpolar character of the TCNQ molecule. This nonpolar character of the TCNQ molecule is explained by the fact that the latter is a symmetrical molecule. This will cause a coincidence of the barycenters of the positive charges and the negative charges within this molecule. However, the proximity of polar TTF molecules during the redox reaction will induce charge separation on the originally apolar TCNQ molecule. The theoretical results obtained agree well with the experimental results of these different molecules. This agreement with the experiment therefore reflects the adequacy of the used theory level to develop our various calculations.

Also, as part of the study of charge transfer between these molecules, other reactivity indices called dual indices (γ) were also analyzed in order to know the direction of the electron flow and the polarity of the reaction. These indices have already experienced remarkable growth in the theoretical study of intra- and inter-molecular Diels-Alder reactions (studies of charge transfer, reaction polarity and direction of electron flow) [30]. The summary of the values of these indices is given in **Table 3**.

3.2. Direction of electronic flow in TTF-TCNQ charge transfer complexes

In TTF-TCNQ charge transfer complexes, there is always an electronic flow displacement. In order to highlight the direction of this flow, the dual indices of each charge transfer complex were determined. The summary of the values of these indices is given in **Table 3**.

Table 3. Values of experimental electrical conductivities ($S \cdot cm^{-1}$) and dual indices (eV) of charge transfer complexes TTF-TCNQ and dipole moments of TTF molecules (D)

CTC	γ_1	γ_2	$\Delta\gamma_{12}$	$\mu_D(\text{TTF})$	σ
(TTF_1, TCNQ)	4.4558	20.2315	-15.7757	1.8195	0.0050
(TTF_2, TCNQ)	6.5295	20.0698	-13.5404	4.9247	0.0370
(TTF_3, TCNQ)	5.7100	20.1580	-14.4481	3.4097	0.0085
(TTF_4, TCNQ)	8.6365	20.0271	-11.3906	5.7947	2.3000
(TTF1_5, TCNQ)	8.6976	19.9857	-11.2881	5.1572	2.6000

Examination of the values in **Table 3** shows that except for the values of $\Delta\gamma_{12}$, the values of the other quantities are all positive. Regarding the dual index γ_1 , it is lower than the dual index γ_2 . So the redox reaction between these two molecules is a polar reaction and the electron flow will take place from the TTF molecules to the TCNQ molecule. The higher values of the chemical potential of the TTF molecules compared to those of the TCNQ confirm that the electron flow will take place from the TTF molecules to the TCNQ molecule. As for the deviation $\Delta\gamma_{12}$, its value is negative and high; which confirms that the redox reaction between these two molecules is a polar reaction characterized by a high charge transfer. Regarding the conductivity σ and the difference $\Delta\gamma_{12}$, the ranking in descending order of the values is as follows:

$\sigma, \Delta\gamma_{12}$: (TTF_5, TCNQ) > (TTF_4, TCNQ) > (TTF_2, TCNQ) > (TTF_3, TCNQ) > (TTF_1, TCNQ)
 As for the dipole moment of TTF molecules, the classification of molecules according to the same order of values is:

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

By permuting (TTF_4, TCNQ) and (TTF_5, TCNQ) in the second classification, we obtain exactly the same sequence of evolution as the first. From these two similar evolutionary sequences, we note that overall, when the dipole moment of TTF molecules increases, the conductivity of the complexes they form with unsubstituted TCNQ increases and leads to high charge transfer. It therefore appears clearly that the electrical conductivity of the formed complexes is as high as the polarity of the TTF electron donors increases.

3.3. Evolution of the experimental electrical conductivity of the TTF-TCNQ charge transfer complexes as a function of the energy difference $\Delta\varepsilon = \text{HOMO}_{\text{TTF}} - \text{LUMO}_{\text{TCNQ}}$

The evolution of the experimental conductivity of these same charge transfer complexes was studied based on $\Delta\varepsilon$, the energy difference between the HOMO of TTF and the LUMO of unsubstituted TCNQ. The summary of these values is given in **Table 4**.

Table 4. Values of the $\text{HOMO}_{\text{TTF}}\text{-LUMO}_{\text{TCNQ}}$ energy differences (eV) and experimental electrical conductivities of the TTF-TCNQ charge transfer complexes ($\text{S}\cdot\text{cm}^{-1}$)

CTC	$E_{\text{HOMO}}^{\text{TTF}}$	$E_{\text{LUMO}}^{\text{TCNQ}}$	$\Delta\varepsilon$	σ
(TTF_1, TCNQ)	-4.6638		0.3576	0.0050
(TTF_2, TCNQ)	-4.8255		0.1959	0.0370
(TTF_3, TCNQ)	-4.7373	-5.0214	0.2841	0.0085
(TTF_4, TCNQ)	-4.8682		0.1532	2.3000
(TTF_5, TCNQ)	-4.9096		0.1119	2.6000

With regard to the conductivity scale established by DO Cown et al. [31], when the electrical conductivity of a material is between $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ and $1 \text{ S}\cdot\text{cm}^{-1}$, this material has a semiconductor behavior. On the other hand, a compound having an electrical conductivity greater than 1 is an electrical conductor. We speak of a superconductor when the resistance of the material is almost zero (extremely high electrical conductivity). Under these conditions, apart from the charge transfer complexes (TTF_4, TCNQ) and (TTF_5, TCNQ), which are conductors, all others appear as semiconductors. Also, we note in this table a variation of each quantity from one complex to another. Regarding the energy difference $\Delta\varepsilon$, the classification of the complexes in decreasing order of values is as follows:

$$\Delta\varepsilon: (\text{TTF}_1, \text{TCNQ}) > (\text{TTF}_3, \text{TCNQ}) > (\text{TTF}_2, \text{TCNQ}) > (\text{TTF}_4, \text{TCNQ}) >$$

(TTF_5, TCNQ). As for the electrical conductivity, the classification of molecules according to the same order of values is presented as following:

$$\sigma: (\text{TTF}_1, \text{TCNQ}) < (\text{TTF}_3, \text{TCNQ}) < (\text{TTF}_2, \text{TCNQ}) < (\text{TTF}_4, \text{TCNQ}) < (\text{TTF}_5, \text{TCNQ})$$

We obtain sequences of evolution in opposite directions. It emerges from these two evolution sequences that the complex (TTF_1, TCNQ) has the highest value of the energy difference with a low conductivity while the complex (TTF_5, TCNQ) displays the greatest value of the conductivity with a low energy gap. It emerges from this comparison that the conductivity of the charge transfer complex increases when the energy difference $\Delta\varepsilon$ decreases. With a small

energy gap, charge carriers will tend to move easily from the TTF donor HOMO to the TCNQ acceptor LUMO.

4. CONCLUSION

In this study which consisted in studying the charge transfer of five Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ) complexes, we can retain that the TTF molecules have a reducing character while the unsubstituted TCNQ molecule has an oxidizing character. The redox reaction between these two types of molecules is a polar reaction characterized by high charge transfer. It also results in the electronic flux moving from the TTF to the TCNQ. When the dipole moment of TTF molecules increases, the conductivity of the complexes they form with unsubstituted TCNQ increases and leads to high charge transfer. In addition, the conductivity of these charge transfer complexes has been found to increase as the $\text{HOMO}_{\text{TTF}}\text{-LUMO}_{\text{TCNQ}}$ energy gap decreases. Therefore, we plan to deepen this study in order to propose new complexes with more improved electrical properties.

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