

Theoretical Study of the Effect of Substituting Nitrogen Atom in Tetracyanoquinodimethane (TCNQ), Using Density Functional Theory

دراسة نظرية لتأثير استبدال ذرة النيتروجين في جزيئة (TCNQ), باستخدام نظرية دالة الكثافة

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Abstract:

The optimized geometrical structures and the electronic properties of the Tetracyanoquinodimethane molecule (TCNQ) and its derivative have been calculated using density functional theory with (B3LYP) and 6-31G** level. The aim of this work is to determine the effects of substituting the nitrogen atom in mentioned molecule with trivalent atoms (phosphorus P and arsenic As). The results show that the both HOMO and LUMO energy decrease whenever the trivalent atom substitute instead of nitrogen atom. The energy gap decrease when replace nitrogen atom with trivalent atom. With respect to electron affinity then any nitrogen atom has been replaced with trivalent atom, the formed molecule will has more positive electron affinity, this new molecule will be a good electron acceptor.

الخلاصة:

تم حساب التراكيب الهندسية المثلى والخواص الالكترونية لجزيئة (TCNQ) ومشتقاتها باستخدام نظرية دالة الكثافة و دالة (B3LYP) لحساب طاقة التبادل والارتباط الالكترونية. اما دوال الاساس فقد تم استخدام دوال من النوع (6-31G**). ان هدف الدراسة هو تحديد تأثير استبدال ذرة النيتروجين في جزيئة (TCNQ) بذرة ثلاثية التكافؤ مثل (الفسفور او الزرنيخ) و بالتالي امكانية الحصول على خواص مرغوبة في التطبيقات الالكترونية المختلفة للجزيئات العضوية. أظهرت النتائج التي تم الحصول عليها ان طاقة اعلى مستوى في حزمة التكافؤ واطأ مستوى في حزمة التوصيل تتناقص كلما تم استبدال ذرة من ذرات النيتروجين بذرة ثلاثية التكافؤ. اظهرت الحسابات كذلك ان فجوة الطاقة للجزيئات المدروسة تتناقص بزيادة عدد ذرات النيتروجين المستبدلة. اما بالنسبة للألفة الالكترونية فأن الجزيئات المتكونة من استبدال ذرات النيتروجين يكون لها الفة الكترونية اكثر ايجابية من الجزيئة السابقة لها, وبالتالي تمتلك هذه الجزيئة صفة مستقبل الكترون اي لها القابلية على استقبال الالكترونات.

Introduction:

The organic semiconductor molecules had been widely studied as they have been used in many electronic devices, such these devices are organic field effect transistors (OFET) which can be prepared either by vacuum evaporation, by solution-casting, or by mechanical transfer of a peeled single-crystalline organic layer onto a substrate. These devices have been developed to realize low-cost, large-area electronic products and biodegradable electronics [1,2]. OFETs have been fabricated with various device geometries. The most commonly used device geometry is bottom gate with top drain and source electrodes, because this geometry is similar to the thin-film silicon transistor (TFT) using thermally grown SiO₂ as gate dielectric. Organic polymers, such as polymethylmethacrylate (PMMA), can also be used as dielectric.[3,4]. While Organic light-emitting diodes (OLED) in which the emitting layer is a thin film of organic compound , when it subjected to electric current will emits light. This thin film of organic semiconductor is situated between two electrodes, at least one of these electrodes is transparent. There are two types of Organic light-emitting diodes: those based on small molecules and those employing polymers. Adding mobile ions to an OLED creates a light-emitting electrochemical cell (LEC) which has a slightly different mode of operation [5,6]. In addition the organic semiconductors is used in organic photovoltaic cells is a type of polymer solar cell that uses organic electronics for light absorption and charge

transport to produce electric current from sunlight by the photovoltaic effect. [7,8]. These wide application of organic semiconductors because some of their suitable properties such as low cost, easy fabrication and mechanical flexibility [9]. Therefore, the develop of high-performance organic semiconductor materials is crucial for the development of organic electronics. (TCNQ) is the organic compound with the formula $(\text{NC})_2\text{CC}_6\text{H}_4\text{C}(\text{CN})_2$. This molecule is supposed as an electron acceptor that accepts electrons transferred to it from another compound. It is an oxidizing agent that, by virtue of its accepting electrons, is itself reduced in the process. The typical oxidizing agents undergo constant chemical alteration through covalent or ionic reaction, resulting in the complete and irreversible transfer of one or more electrons. In many chemical Conditions, nevertheless, the transfer of electronic charge from an electron donor may be only fractional, that is mean an electron is not completely transferred, but results in an electron resonance between the donor and acceptor. This leads to the modeling of charge transfer complexes in which the components largely retain their chemical identities. The electron accepting power of an acceptor molecule is measured by its electron affinity which is the energy released when filling the lowest unoccupied molecular orbital (LUMO) [10].

Theoretical Details:

In this study, it had been used the density functional theory (DFT) (Kohn Sham equations), where the electronic energy has the following form [11]:

$$E = E^T + E^V + E^J + E^{XC} \quad (1)$$

Where E^T is the electrons kinetic energy term, E^V is the potential energy of the nuclear attraction and the repulsion between nuclei, E^J is the repulsion between electrons and E^{XC} is the exchange correlation term.

These terms are functions of electron density (ρ), except the nuclear-nuclear repulsion. E^J is given by the following [11]:

$$E^J = \frac{1}{2} \iint \rho(\vec{r}_1) (\Delta r_{12})^{-1} \rho(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (2)$$

Where $(\Delta r_{12})^{-1}$ is displacement between two electrons, $d\vec{r}_1$ is integration element of first electron, and $d\vec{r}_2$ is integration element of second electron.

E^{XC} is approximated as an integral involving the spin densities and their gradients [11]:

$$E^{XC}(\rho) = \int f(\rho_\alpha(\vec{r}), \rho_\beta(\vec{r}), \nabla \rho_\alpha(\vec{r}), \nabla \rho_\beta(\vec{r})) d^3\vec{r} \quad (3)$$

where ρ_α refer to α spin density, ρ_β refer to β spin density, and ρ refer to total electron density ($\rho_\alpha + \rho_\beta$). The term E^{XC} is consist of two terms, and these are: [11]

$$E^{XC}(\rho) = E^X(\rho) + E^C(\rho) \quad (4)$$

where $E^X(\rho)$ is the exchange functionals, and $E^C(\rho)$ is the correlation functionals. In this work it had been used Becke three Lee Yang Parr functional, this is called a hybrid functional and this functional has the form [11,12]:

$$E_{B3LYP}^{XC} = E_{LDA}^X + c_0(E_{HF}^X - E_{LDA}^X) + c_x \Delta E_{B88}^X + E_{VWN3}^C + c_c(E_{LYP}^C - E_{VWN3}^C) \quad (5)$$

Where $c_0 = 0.2$, $c_x = 0.72$, $c_c = 0.81$

The E_{LDA}^X is the local exchange and it has the form [12]:

$$E_{\text{LDA}}^{\text{X}} = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int \rho^{4/3} d\vec{r} \quad (6)$$

The E_{HF}^{X} is the Hartree Fock exact exchange functional, and has the form [12]:

$$E_{\text{HF}}^{\text{X}} = -\frac{1}{2} \sum_{i,j} \iint \phi_i^*(\vec{r}_1) \phi_j^*(\vec{r}_1) \frac{1}{r_{12}} \phi_i(\vec{r}_2) \phi_j(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (7)$$

while the Becke functional ($E_{\text{B88}}^{\text{X}}$) has the following form [13]:

$$E_{\text{B88}}^{\text{X}} = E_{\text{LDA}}^{\text{X}} - \beta \sum \int \frac{\rho^{4/3} x^2}{(1 + 6\gamma \sinh^{-1} x)} d^3\vec{r} \quad (8)$$

where $x = \rho^{-4/3} |\nabla \rho|$

β is a parameter chosen to fit known exchange energies of inert gas atoms, and its value equal (0.0042) Hartree.

$E_{\text{VWN3}}^{\text{C}}$ is Vosko-Wilk-Nusair correlation functional, and it has the form [13]:

$$E_{\text{VWN3}}^{\text{C}}(\rho_{\alpha}, \rho_{\beta}) = \int \rho \epsilon_{\text{VWN3}}^{\text{C}}(\rho_{\alpha}, \rho_{\beta}) d\vec{r} \quad (9)$$

Results and Discussion:

The optimization structures for all molecules have been performed using density functional theory with (6-31G**) level, these structures are shown in figure (1).

The first group of investigated molecules is TCQN molecule and four molecules contained from one to four a phosphorus atom. The lowest unoccupied Molecular orbitals (LUMO) and highest occupied molecular orbitals (HOMO) for TCNQ molecule and for molecules contained phosphorus atoms, are shown in figure (2), from this figure we note that the both HOMO and LUMO energy decrease whenever the phosphorus atom substitute instead of nitrogen atom, and we note that the 4P-TCNQ has the lowest HOMO and LUMO energies.

This approaching between HOMO and LUMO led to that the energy gap decrease as shown in figure (3), and this mean when we replace nitrogen atom with phosphorus the energy gap had been decreased. We know that both nitrogen and phosphorus are trivalent, but the unique difference is that phosphorus has electrons more than nitrogen.

For the second group of investigated molecules which is TCQN molecule and four molecules contained from one to four a arsenic atom. The lowest unoccupied Molecular orbitals (LUMO) and highest occupied molecular orbitals (HOMO) for TCNQ molecule and for molecules contained arsenic atoms, are shown in figure (4), from this figure we note that the both HOMO and LUMO energy decrease whenever the arsenic atom substitute instead of nitrogen atom, and we note that the 4As-TCNQ has the lowest HOMO and LUMO energies.

This decrease in energy of HOMO and LUMO led to that the energy gap decrease as shown in figure (5), and this mean when we replace nitrogen atom with arsenic the energy gap had been decreased. This result is similar to that of phosphorus group. And the reason is the same where the unique difference is that arsenic has electrons more than nitrogen.

The electron affinity of first group is shown in figure (6) decrease when number of phosphorus atom is increase. This mean that when we replace the nitrogen with phosphorus. In this figure we see that 4P-TCNQ molecule has electron affinity more positive than what the TCNQ molecule, and this make the 4P-TCNQ is an electron acceptor compare with TCNQ molecule which in this case is an electron donor.

In the second group the electron affinity decrease when number of arsenic atom is increase, this is similar to first group. Where the 4As-TCNQ has electron affinity more than TCNQ molecule, and this also make 4As-TCNQ is an electron acceptor compare with TCNQ molecule.

The ionization energy (IE) mean the minimum amount of energy required to remove an electron from the atom or molecule. The result show for the first group that ionization energy decrease with increasing of phosphorus atoms, where 4P-TCNQ molecule has (IE) less than another molecules figure (8), and this is maybe happened because when we replace the nitrogen atom with phosphorus that the electronic molecular orbitals be away from the center of positive charge for nucleus, thus it easy to remove an electron from the molecule

For the second group where the arsenic atom is substituted in place of nitrogen atom, that this process make the molecules have little ionization energy as shown in figure (9), and this decreasing in (IE) due to the same reason in first group, where the arsenic atom has number of electrons more than the nitrogen, these electrons are far from nucleus. However, the amount of energy required to remove an electron from 4As-TCNQ is less than the energy for the another molecules.

The values for the properties have been shown above are listed in table (1) below. We note that the energy gap for 4As-TCNQ is the least from other molecules, and the same molecule has the least electron affinity, thus this molecule can be considered to be an electron acceptor in comparing with other molecules.

Table (1): The E_{LUMO} , E_{HOMO} , E_{Gap} , Ionization energy (IE) and Electron affinity (EA) for molecule under study in (eV)

<i>Molecule</i>	<i>E_{LUMO}</i>	<i>E_{HOMO}</i>	<i>E_{Gap}</i>	<i>(IE)</i>	<i>(EA)</i>
TCNQ	-5.12	-7.63	2.50	7.63	-5.12
1P-TCNQ	-4.80	-7.00	2.20	7.00	-4.80
2P-TCNQ	-4.55	-6.55	1.99	6.55	-4.55
3P-TCNQ	-4.19	-5.92	1.73	5.92	-4.19
4P-TCNQ	-4.03	-5.60	1.57	5.60	-4.03
1As-TCNQ	-4.55	-6.62	2.07	6.62	-4.55
2As-TCNQ	-4.33	-6.05	1.71	6.05	-4.33
3As-TCNQ	-4.13	-5.65	1.52	5.65	-4.13
4As-TCNQ	-3.96	-5.30	1.34	5.30	-3.96

Conclusions:

In the first group of molecules, it has been noted that the (4P-TCNQ) has the least energy gap comparing with molecules of this group, and so on for the molecule (4As-TCNQ) in second group, this property make both molecules useful for electronic applications such that in organic field effect transistors (OFET), Organic light-emitting diodes (OLED) or in organic solar cells (OSC).

With respect to electron affinity for (4P-TCNQ) has the least value comparing with molecules of first group, and so on for the molecule (4As-TCNQ) in second group, thus both two molecules can be considered as electron acceptor, but when we compare between them then the (4As-TCNQ) is the best between all the molecules under study.

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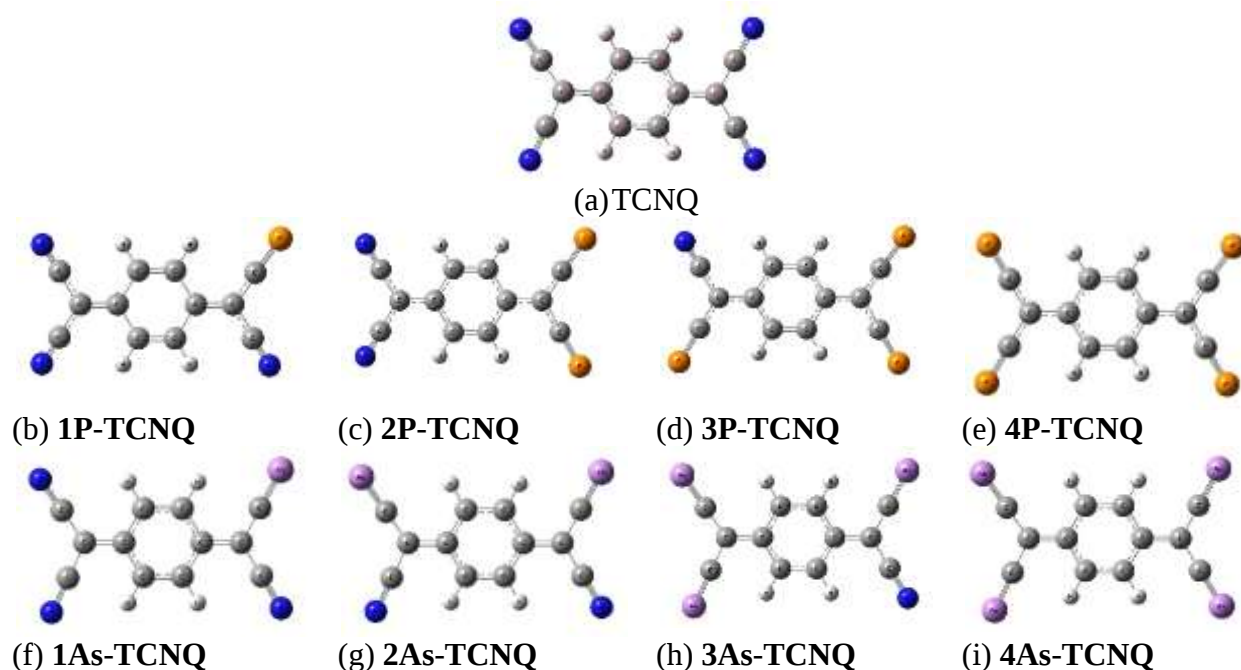


Figure (1): The optimized structures for molecules under study.

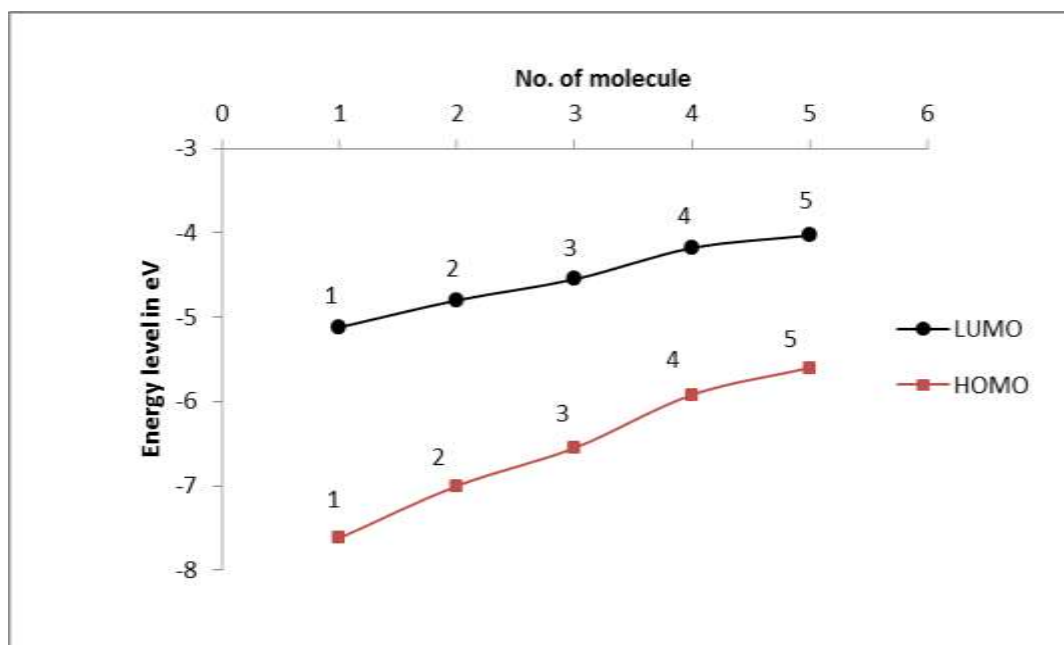


Figure (2): Relation between LUMO & HOMO energy and No. of molecule, where (1 is TCNQ molecule), (2 is 1P-TCNQ molecule), (3 is 2P-TCNQ molecule), (4 is 3P-TCNQ molecule), and (5 is 4P-TCNQ molecule).

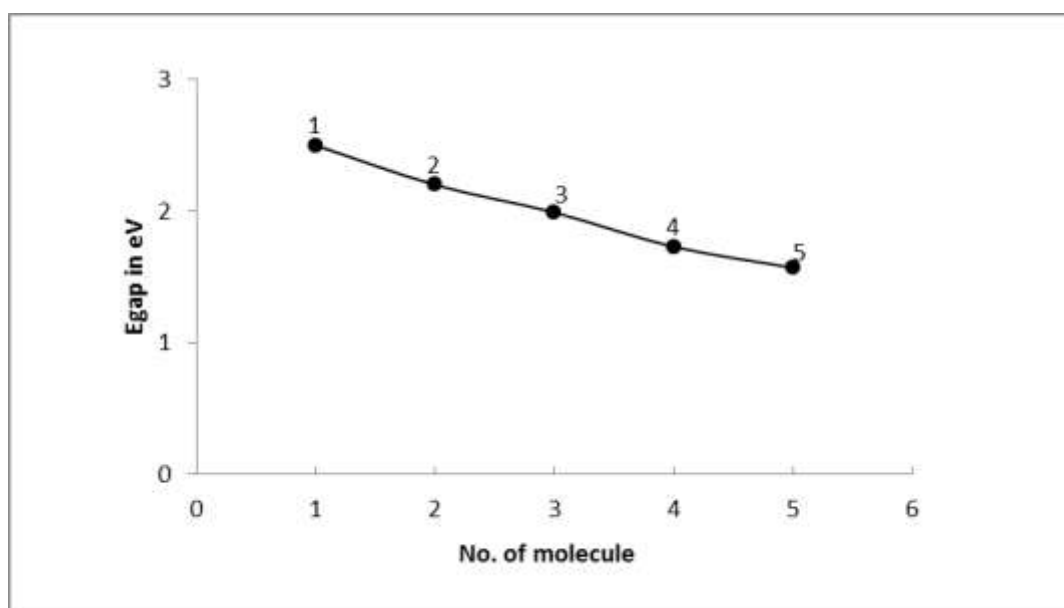


Figure (3): Relation between energy gap and No. of molecule, where (1 is TCNQ molecule), (2 is 1P-TCNQ molecule), (3 is 2P-TCNQ molecule), (4 is 3P-TCNQ molecule), and (5 is 4P-TCNQ molecule).

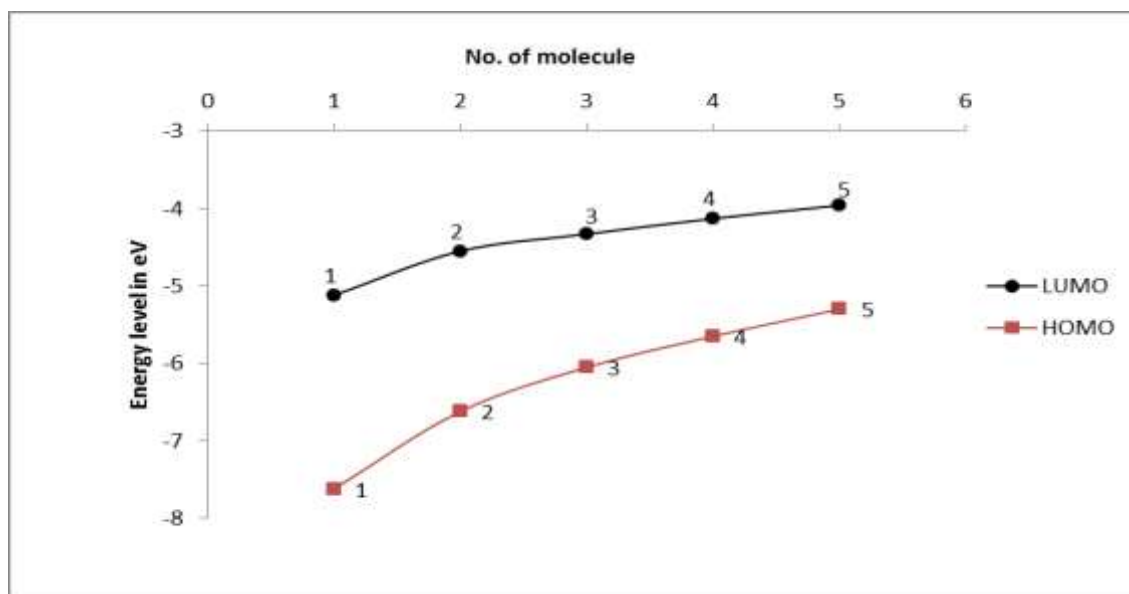


Figure (4): Relation between LUMO & HOMO energy and No. of molecule, where (1 is TCNQ molecule), (2 is 1As-TCNQ molecule), (3 is 2 As -TCNQ molecule), (4 is 3 As -TCNQ molecule), and (5 is 4 As -TCNQ molecule).

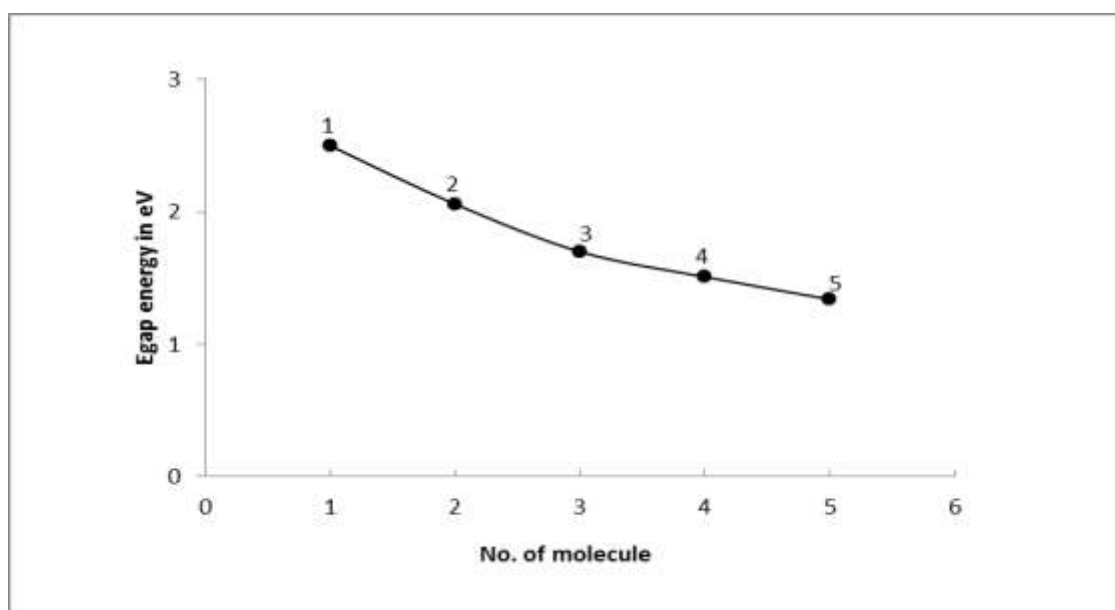


Figure (5): Relation between energy gap and No. of molecule, where (1 is TCNQ molecule), (2 is 1As-TCNQ molecule), (3 is 2 As -TCNQ molecule), (4 is 3 As -TCNQ molecule), and (5 is 4 As -TCNQ molecule).

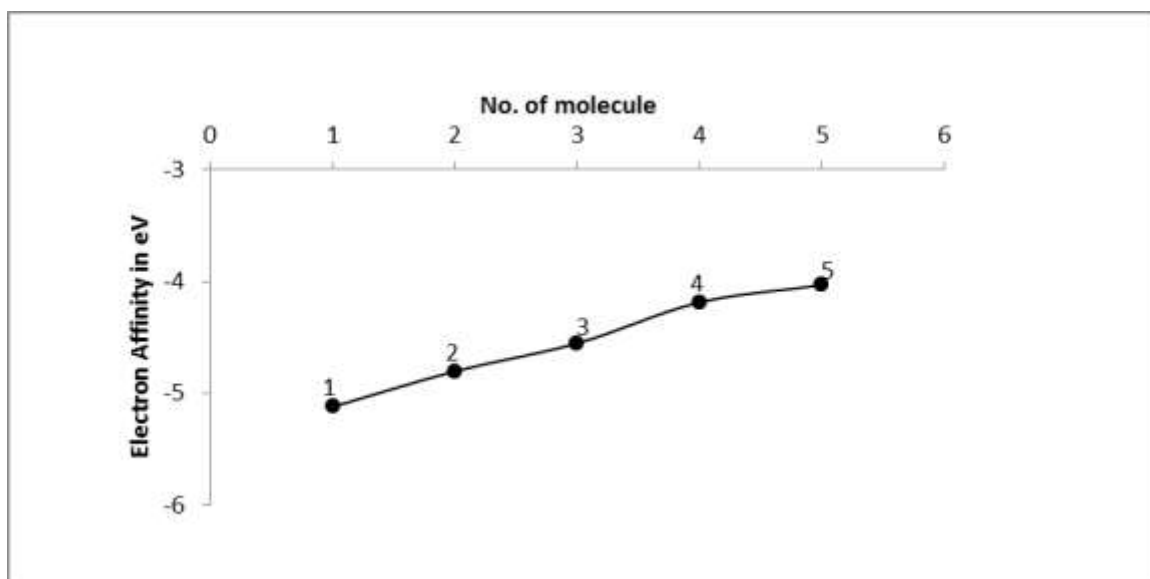


Figure (6): Relation between electron affinity and No. of molecule, where (1 is TCNQ molecule), (2 is 1P-TCNQ molecule), (3 is 2P-TCNQ molecule), (4 is 3P-TCNQ molecule), and (5 is 4P-TCNQ molecule).

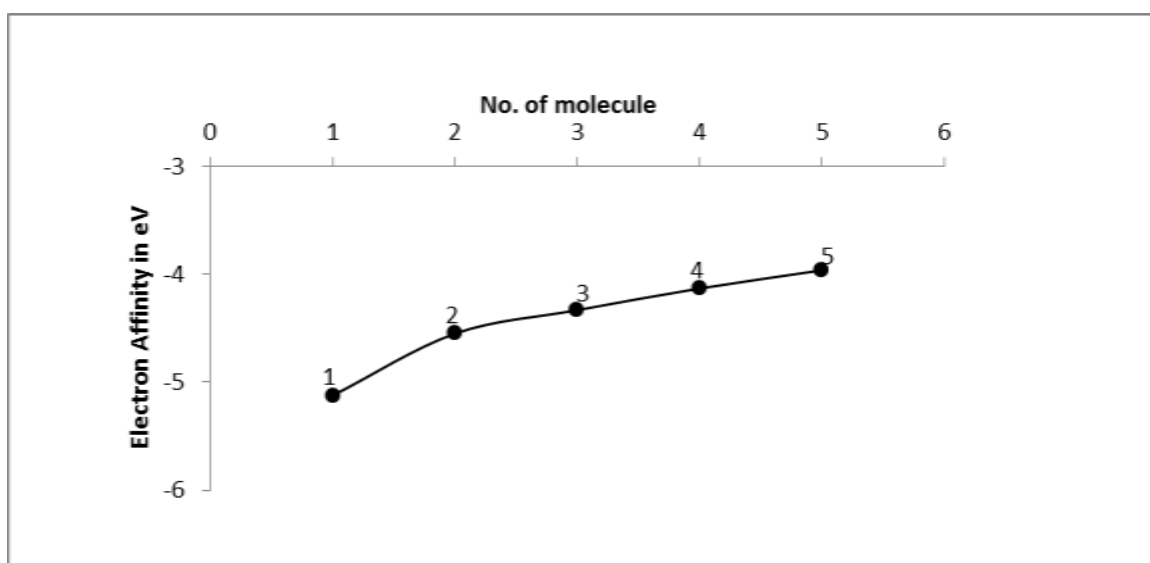


Figure (7): Relation between electron affinity and No. of molecule, where (1 is TCNQ molecule), (2 is 1As-TCNQ molecule), (3 is 2 As -TCNQ molecule), (4 is 3 As -TCNQ molecule), and (5 is 4 As -TCNQ molecule).

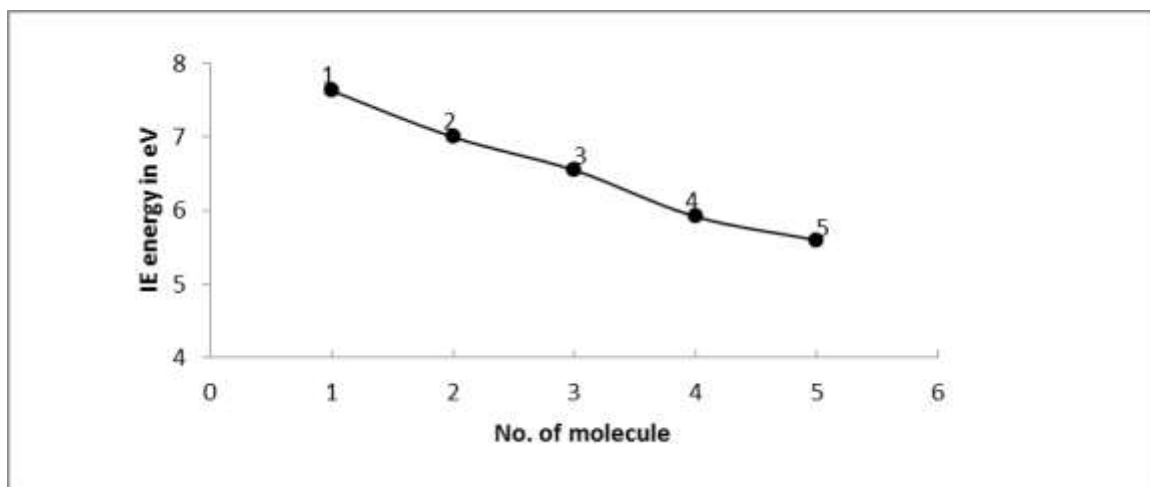


Figure (8): Relation between ionization energy and No. of molecule, where (1 is TCNQ molecule), (2 is 1P-TCNQ molecule), (3 is 2P-TCNQ molecule), (4 is 3P-TCNQ molecule), and (5 is 4P-TCNQ molecule).

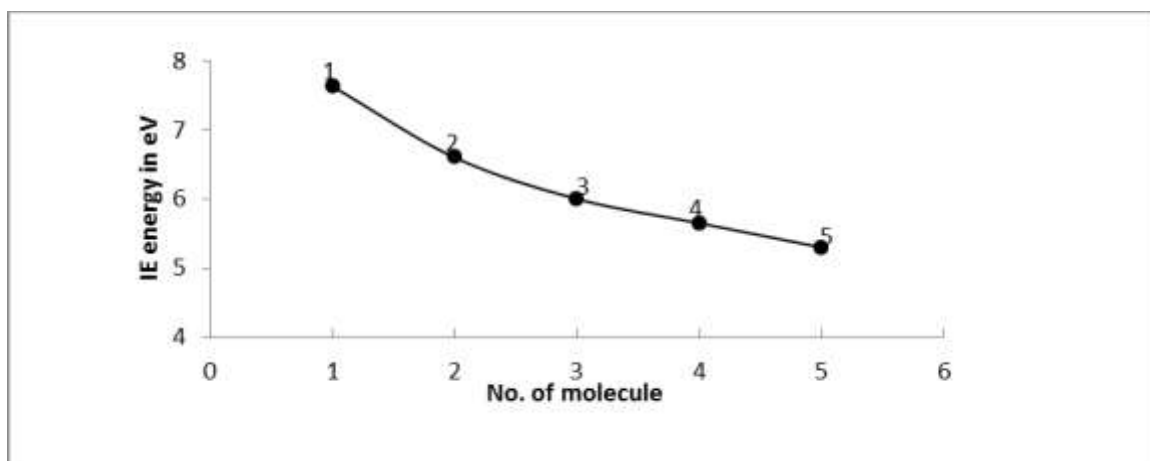


Figure (9): Relation between ionization energy and No. of molecule, where (1 is TCNQ molecule), (2 is 1As-TCNQ molecule), (3 is 2 As -TCNQ molecule), (4 is 3 As -TCNQ molecule), and (5 is 4 As -TCNQ molecule).