



Sudan University of Science and Technology
College of Graduate Studies



**Computational Chemistry Study on the Corrosion
Inhibitor Performance Of 1,3,4-Oxidizole Derivatives Against The
Corrosion Of Mild Steel In Chloric Acid**

دراسة الكيمياء الحاسوبية على أداء مثبطات التآكل لمشتقات 1,3,4- الأوكسيديازول
على تآكل الفولاذ المطاوع في حمض الهيدروكلوريك

A Thesis Submitted In Partial Fulfilment for the
Requirements of M.SC in Chemistry

By

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بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِیْمِ

قال تعالى:

(بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِیْمِ (1) الْحَمْدُ لِلّٰهِ رَبِّ الْعَالَمِیْنَ
(2) الرَّحْمٰنِ الرَّحِیْمِ (3) مَالِكِ یَوْمِ الدِّیْنِ (4) اِیَّاكَ
نَعْبُدُ وَ اِیَّاكَ نَسْتَعِیْنُ (5) اِهْدِنَا الصِّرَاطَ الْمُسْتَقِیْمَ (6)
صِرَاطَ الَّذِیْنَ اَنْعَمْتَ عَلَیْهِمْ غَیْرِ الْمَغْضُوْبِ عَلَیْهِمْ
وَ لَا الضَّالِّیْنَ (7))

صدق الله العظيم

سورة الفاتحة

Dedication

I dedicate this work :

To my family,

My parents,

My sisters and brother,

And to my husband.

Acknowledgment

Foremost, I am highly grateful to Allah for his blessing that continue to flow into my life, and because of you.

I take this opportunity to express my profound gratitude and deep regards to my supervisor doctor Mohammed Suleiman Altoum for his advices throughout the time (it took me to complete this research).

I am making this research not only to have for marks but also to increase my knowledge).

Abstract

The objective of this research is to use computational chemistry through the study of three heterocyclic compounds of 1,3,4-oxadiazole derivatives.

Quantum chemical calculations based on density function theory (DFT) method were performed on three nitrogen-bearing heterocyclic compounds used as corrosion inhibitors for the mild steel in acid media to determine the relationship between the molecular structure of inhibitors and inhibition efficiency. The structural parameters, such as energy and distribution of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the charge distribution of the studied inhibitors, the absolute electronegativity (χ) values, and the fraction of electrons (ΔN) transfer from inhibitors to mild steel were also calculated and correlated with inhibition efficiencies. The results showed that the inhibition efficiency of inhibitors increased with the increase in energy of HOMO and decrease in energy gap of frontier molecular orbital, and the areas containing N and O atoms are most possible sites for bonding the steel surface by donating electrons to the mild steel.

مستخلص البحث

يهدف هذا البحث الى دراسة الكيمياء الحاسوبية من خلال دراسة مركبات حلقيه غير متجانسه وهي مشتقات 1,3,4-الأوكسيديازول.

تم اجراء الحسابات الكيمائية الكمييه على اساس طريقة نظرية الدالة الوظيفية للكثافة (DFT) على ثلاثه مركبات حلقيه غير متجانسه محتويه على ذرات النايتروجين تستخدم كمثبطات للتآكل للمعدن الصلب في الاوساط الحمضية لتحديد العلاقة بين البنية الجزيئية للمثبطات وكفاءة التثبيط.

عن طريق الكيمياء الحاسوبية تم حساب الطاقة وتوزيع اعلى المدارات الجزيئية المشغولة (HOMO) واقل مدارات جزيئية غير مشغولة (LUMO) وتوزيع الشحنة للمثبطات المدروسة وقيم الكهروسالبية (X) وجزء من الالكترونات (ΔN).

تم ايضاً حساب الترابط بين المثبطات وكفاءة التثبيط.

اظهرت النتائج ان كفاءة تثبيط المثبطات إزدادت مع زيادة طاقة HOMO وانخفاض في فجوة الطاقة في المدار الجزئي ، والمنطقة المحتوية على ذرة الN وال O هي اكثر المواقع الممكنة للارتباط بسطح المعدن الصلب عن طريق منح الالكترونات للمعدن.

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Chapter One

Introduction & Literature review

1. Introduction to Computational Chemistry and its Methods:

Computational chemistry is a branch of chemistry that uses computer simulation to assist in solving chemical problems. It uses methods of theoretical chemistry incorporated into efficient computer programs to calculate the structures and properties of molecules and solids [1][2].

1.1 Computational Chemistry:

Using computational chemistry we can find (or predict) energy, molecular geometry for transition state, bond energy, chemical energy, molecular orbitals, dipole moments, multipole moments, atom charges, vibrations frequency, spectroscopic IR, RAMAN and NMR, polarizations, thermochemistry properties, interaction method [1][2].

1.1.1 Molecular Structure:

Molecular structure can be found in equilibrium point and from transition state and energy of reactants and products can predict rate of reaction of any reactant [1].

1.1.2 Chemical Reactivity:

From knowledge of where position of electrons in molecular, that can be found position of nuclei and position of electrons. And can calculate atomic energy and, dipole moment or multipole moment and thermochemistry properties such as Gibbs energy and enthalpy [2].

1.1.3 Spectroscopic:

Computational chemistry can predict and calculate different spectroscopic such as IR, NMR, RAMAN, specially of unknown compounds and new compounds [1][2].

1.1.4 Methods of Computational Chemistry:

There are many methods that can be applied in computational chemistry, some of these methods depend on theoretical solution and equations totally. Other methods

depend on theoretic calculations, empirical values, theory of quantum mechanics and classical mechanics. Below, the fundamental methods that used in computational chemistry are listed [2].

1.1.4.1 Molecular Mechanics Methods:

These methods are considered as the simplest and fastest method used, but their results are less accurate when compared to quantum mechanics methods. Their importance lies in their fastness, they are used for compounds with relatively large structure, such as proteins and steroids. In this methods, molecules are seen as set of connected balls with each other like springs, thus when you know the true length between the lungs and its angle and the energy needed to tighten the chain of this association (springs), then the energy of this group of springs and balls can be calculated, ie in other words, the structure geometry is changed to the molecular so get the least possible energy (geometry optimization) [2].

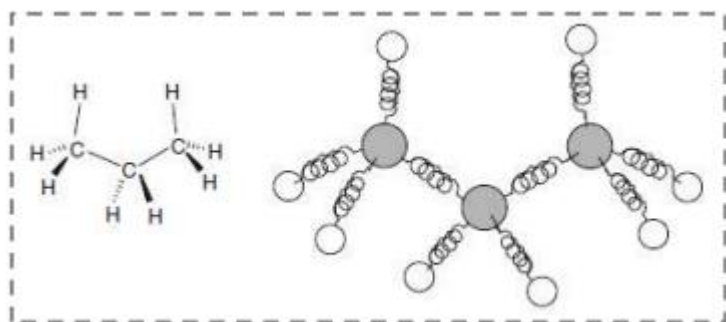


Figure (1.1) molecular mechanics methods

The disadvantages of this method, never illuminate electrons (molecular is part of the balls are connected to the springs do not exist for electrons), so it is not possible to know the chemical properties of electrons such as charging electrons dipole moment and effective places (love and hate of electrons).

In this method molecular energy is the sum of the energies of bonding and non-bonding. Energy of bonding is the energy produced by the direct effect by bonding such as the energy of the bond (tensile force) and angle energy and the force of the torsion.

The energy of non-bonding is the energy produced by the influence of the neighboring environment such as static electricity and strong Vander Wales [2].

$$E = E_{\text{Bond}} + E_{\text{Nonbond}}$$

$$E = \sum_{\text{Bond}} E_{\text{Stretch}} + \sum_{\text{Angles}} E_{\text{Bend}} + \sum_{\text{Dihedrals}} E_{\text{Torsion}} + \sum_{\text{Pairs}} E_{\text{Nonbond}}$$

Molecular mechanics method differ when power fields was different.

These methods was developed to the following:

- AMBER: Assisted Model Building Energy Refinement.
- CHARMM: Chemistry at HARvard Macromolecular Mechanics.
- OPLS: Optimized Potential for Liquid Simulations.
- MMFF: Merck Molecular Force Field.
- UFF: Universal Force Field.
- Dreiding: The Dreiding force field.

1.1.4.2 AB Initio:

Ab initio is a Latin word, which means from the beginning.

This is the basis of this set of methods. It depends on Schrodinger's equation, it is based on the theories of quantum mechanics and it solutions. This equation (Schrodinger equation) describes the movement of the electron within the molecule, when solved, we get the energy and the wave. The resulting wavform is a mathematical equation that expresses the electronic distribution of electrons in the molecule. Knowing this distribution we can calculate the polarity compound (molecule). It can also calculate the structure of molecular geometry, vibrations, ionization, electron beam, bipolar and other properties.

Schrodinger's equation is considered as basis of fundamental quantum physics and theoretical chemistry. Written by the world Orion Schrodinger in (1925) and

published in (1926). Through it was the first description of the electron as wave [3] [4].

$$H\Psi(r) = E\Psi(r)$$

Whereas:-

- H: The Hamiltonian operator
- Ψ : The wave function
- E: The energy, Eigen value of the Hamiltonian operator

The Hamiltonian factor (H) can be expressed as the total kinetic energy of the nuclei and electron as in the following equation:

$$H = T_n + T_e + V_{en} + V_{ee} + V_{nn}$$

Whereas:

T_n : coefficient represent the kinetic energy of nucleus

T_e : coefficient represent the kinetic energy of the electron

V_{en} : coefficient represent the mutual effect between electrons and nuclei

V_{ee} : coefficient represent the mutual effect between electron and electron

V_{nn} : coefficient represent the mutual effect between nuclei and nuclei

It can be expressed mathematically as follows:

$$\hat{H} = -\frac{1}{2} \sum_i^{\text{electrons}} \nabla_i^2 - \frac{1}{2} \sum_A^{\text{nuclei}} \frac{1}{M_A} \nabla_A^2 - \sum_i^{\text{electrons}} \sum_A^{\text{nuclei}} \frac{Z_A}{r_{iA}} + \sum_{i < j}^{\text{electrons}} \sum_j \frac{1}{r_{ij}} + \sum_{A < B}^{\text{nuclei}} \sum_B \frac{Z_A Z_B}{R_{AB}}$$

Where as:-

- Z: Charges
- M_A : Mass of nuclei (A) to the mass of electron
- R_{AB} : The dimension between the nucleus (A) and the nucleus (B)
- r_{ij} : The dimension between the electron (i) and electron (j)
- r_{iA} : The dimension between the electron (i) and nucleus (A)

It is known that Schrodinger's equation is an equation that cannot be solved except for electron-like system such as hydrogen or atoms similar to it. So it is necessary to provide some mathematical approximations to solve this equation. One of the

simplest approximations is approximation of (Hartree-fock). This approximation depends on the principle of the central field.

This means that the ambiguity of electronic antithesis is calculated on the basis of the integration of all electrons, thus, the result is obtained electronically and does not take into account the effect of electrons between them.

-The most important characteristic of this theory (method) is that it distributes the Schrodinger equation of multiple electron to a few simple equation of electron, thus, when solving the equation of single electron, produces a wave form called orbit, and the energy is called the orbit energy.

-The disadvantage of this method (Theory) is neglecting the electronic effect, so number of theories and methods have been developed from the theory of Hartree-Fock[4].

1.1.4.3 Semi-Empirical Methods:-

This type of calculation resembles ab initio method, it depends on Schrodinger's equation, but the difference is that this kind of calculations replaces the complex integrations used in the ab initio methods with experimental transactions and integration. These integrations are withdrawn from the library (Data base) of integration (with good results and high precision and are often taken from high level theory calculations such as DFT). That means the Schrodinger equation is solved using experimental equation and this is the difference between the type of this group of calculations, where the base of the data used for any transactions and experimental integrations.

- These methods are relatively faster than Ab initio methods but it is slower than the molecular mechanics methods[3].

And below some of these methods:

- CNDO: Complete neglect of differential overlap.
- INDO: Intermediate neglect of differential overlap.
- MNDO: Modified neglect of differential overlap.
- AM1: Austin Model1.
- PM3: Parametric Model number3.

1.1.4.4 Density functional Theory (DFT):-

Also experimental method in terms of its dependence on the Schrodinger equation, but the difference lies in the waveform, instead of using the wavefunction, it is replaced by direct electronic distribution (electronic density) functional method is a function that results in solving another function, i.e., a function of a function. And therefore energy is considered a function of density. This method is similar to Ab initio method and semi [1][5].

Can express energy of earth $E[\rho(\vec{r})]$ through the following equation:

$$E[p(\vec{r})] = T_s[p(\vec{r})] + J[p(\vec{r})] + E_{xc}[p(\vec{r})] + E_{Ne}[p]$$

Where:

- $T_s[p(\vec{r})]$: Kinetic energy of non-interacting system.
- $J[p(\vec{r})]$: Electron-Electron repulsion energy.
- $E_{Ne}[p]$: External potential.

$E_{xc}[p(\vec{r})]$: Exchange-Correlation energy functional.

Exchange – correlation energy functional $E_{xc}[p(\vec{r})]$ includes all non – obtainable information, it is usually calculated as total function of the functional interchange $E_x[p(\vec{r})]$ and functional of correlation $E_c[p(\vec{r})]$

$$E_{xc}[p(\vec{r})] = E_x[p(\vec{r})] + E_c[p(\vec{r})]$$

- **Hybrid functional theory:**

These methods combine the theory of density functional theory (DFT) with Hartree – Fock theory to describe the functional function of exchange energy such as

- B3LYP: (Becke's 3 parameter exchange correlation functional)

Which uses 3 parameters) and LYP (The Lee, Yang and Parr correlation functional)[6].

1.1.5 Basis sets:

Basis sets is a set of functions used to express the shape of molecule orbitals through linear composition of these functions,

We can find electronic distribution around the nucleus using several methods such as the use of hydrogen-like functions which depend on Schrodinger's equation of the hydrogen atom, or via multiple functions with adjustable parameters, added to this are our slater functions and the Gauss functions (Gaussian)[7]

- The orbits of slater species called STOs
- The orbits of Gaussian called GTOs
- ❖ Gauss and slater functions are simple function mathematically
- ❖ The slater orbits have good results compared to Gaussian orbits
- ❖ Gaussian orbits are considered simpler and faster compared to slater orbits
- ❖ Slater orbits can be expressed by approximating them using Gaussian orbits
- ❖ STO-3G is a slater type that is approximated . using three Gauss orbits

The classification for these groups:-

1.1.5.1 minimal basis sets:

- ❖ It is used to take initial properties of molecule
- ❖ The weakness lies in this sets is that they classify electrons as being just as important
- ❖ General shape is STO-nG
- ❖ STO-3G is example of this sets (slater type that approximated it using three Gauss orbits)[8]

1.1.5.2 split- valence Basis sets:

One of the problems of minimal sets is classifying all electrons as equals. But in fact the electrons of the inner casing and the outer casing are uneven, so that it is necessary for the method to compare between electrons of atomic orbits.

Solving this problem by making quick and simple calculations on the external causing electronics. Thus it is done by multiplying the number of slater orbits called DZ Double Zeta[9]

Example:

3-21G is split- valence basis sets, here use Gaussian orbits to approximate slater orbits, where found in two parts, "first number- second number G"

- ❖ First part 3 that means slater orbits is approximated by three Gaussian orbit
- ❖ Second part 21 that means Double Zeta it is calculated in two stage, first approximated by two Gaussian orbit, second approximated by one Gauss orbit. That means each electrons in the external layer is calculated twice, first used STO-2G and second used STO-1G for the same electron.
- ❖ One important example for triple Zeta sets :

6-311G basis set

6-311G++ basis set

1.1.5.3 Diffuse functions basis sets:

The probability of the presence of the electron near nucleus is very high. Thus probability decreases when we move away from the nucleus and at large distance we may find electrons in it , but in some system especially electrolytes and atoms in the case of propagation, we must use the diffuse function to ensure an increased distance in which we calculate the presence of the electron[5].

When added diffuse functions symbolizes the following symbols:

+: for heavy atoms except hydrogen

++: for heavy atoms and hydrogen

Example:

6-31+G: split- valence function for heavy atoms except hydrogen

6-31++G: split- valence function for heavy atom and hydrogen

1.1.5.4 Polarization function basis sets:

In some cases, the electron may polarize from its orbit to another orbit, so the polarization should be considered.

The polarization function gives more accurate explanation of where the electron is located or where it may be located[5].

The following symbols are added to the definition of polarization:

*for all atom except hydrogen

** For all atom and hydrogen

Or can add the name of orbit d or d,p

Example:

(6-31G*) or (6-31G(d)) is split- valence function and polarization for all atoms except hydrogen

(6-31G**) or (6-31G(d,p)) is split- valence function and polarization for all atoms and hydrogen

1.1.5.5 Effective core potential:

At large atoms normal base sets cannot be used so this method has been developed. They replace the electrons in inner layers with semi-negligible approximation. And attention to the external layers where it expresses all the chemical properties such as the strength of the association and ionization energy[1].

1.1.5.6 Combination of basis sets:

When doing a calculation, we can use more than a basic set, the condition specifies the program used[5].

1.2 The use quantum chemical method in corrosion inhibitor studies:

1.2.1 Quantum chemical parameters:

The quantum chemical parameters can be subdivided as follows:

1.2.1.1 Atomic charges:

Mulliken population analysis is mostly used for the calculation of the charge distribution in a molecule. These numerical quantities are easy to obtain and they provide at least a qualitative understanding of structure and reactivity of molecules. Furthermore, atomic charges are used for the description of the molecular polarity of molecules[10].

1.2.1.2 Molecular orbital energies:

Highest occupied molecular orbital energy (E_{HOMO}) and lowest unoccupied molecular orbital energy (E_{LUMO}) are very popular quantum chemical parameters.

These orbitals, also called the frontier orbitals, determine the way the molecule interacts with other species.

The HOMO is the orbital that could act as an electron donor, since it is the outermost (highest energy) orbital containing electrons.

The LUMO is the orbital that could act as the electron acceptor, since it is the innermost (lowest energy) orbital that has room to accept electrons[13].

According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between the frontier orbitals (HOMO and LUMO) of reactants.

The energy of HOMO is directly related to the ionization potential and the energy of the LUMO is directly related to the electron affinity.

The HOMO-LUMO gap, i.e. the difference in energy between the HOMO and LUMO, is an important stability index.

A large HOMO-LUMO gap implies high stability for the molecule in chemical reaction.

The concept of "activation hardness" has been also defined on the basis of the HOMO-LUMO energy gap.

The qualitative definition of hardness is closely related to the polarization of the molecule[13].

1.2.1.3 Dipole moment:

Used to describe the polarity, dipole moment is the measure of polarity of polar covalent bond.

It is defined as the product of charge on the atoms and the distance between the two bonded atoms.

The total dipole moment, however, reflects only the global polarity of a molecule[11].

For a complete molecule the total molecular dipole moment may be approximated as the vector sum of individual bond dipole moments.

1.2.1.4 Energy:

The total energy calculated by quantum chemical methods is also a beneficial parameter.

The total energy of system is composed of the internal, potential, and kinetic energy.

Hohenberg and kohn proved that the total energy of a system including that of the many body effects of electrons (exchange and correlation) in presence of static external potential is a unique functional of the charge density.

The minimum value of the total energy functional is the ground state energy of the system[12].

The electronic charge density which yields the minimum is then the exact single particle ground state energy.

1.3 Mild Steel:

Mild steel is the most widely used steel which is not brittle and cheap in price. Mild steel is not readily tempered or hardened but possesses enough strength.

1.3.1 Characteristic of mild steel:

The study of mild steel becomes more significant for a student of mechanical engineering or metallurgical engineering. Mild steel is an alloy. And alloy is a product made by mixing metals and non metals. Sometimes a pure metal cannot fulfill all the properties needed for manufacturing product. So additives are included in the pure metal to obtain some specific properties necessary for the production. Mild steel is made by adding carbon and other elements in the iron. These elements improve the hardness, ductility and tensile strength of the metal[13]

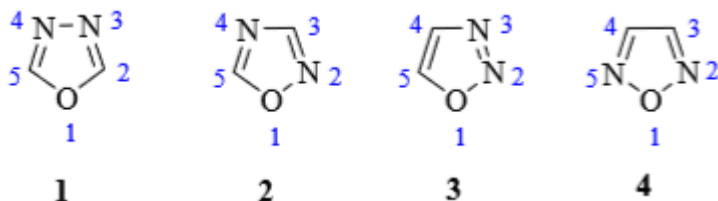
1.3.2 Mild steel properties:

- ❖ A small amount of carbon makes mild steel to change its properties. Different amount of carbon produces different types of steels. There are small spaces between the iron lattices. Carbon atoms get attached to these spaces and makes it stronger and harder. The harder the steel the lesser the ductility.
- ❖ The modulus of elasticity calculated for the industry grade mild steel is 210,000 Mpa. It has an average density of about 7860 kg/m³.
- ❖ Mild steel is a great conductor of electricity. So it can be used easily in the welding process.
- ❖ Because of its malleability, mild steel can be used for constructing pipelines and other construction materials. Even domestic cookwares are made of mild steel. It is ductile and not brittle but hard.
- ❖ Mild steel can be easily magnetized because of its ferromagnetic properties. So electrical devices can be made of mild steel.

- ❖ Mild steel is very much suitable as structural steel. Different automobile manufacturers also use mild steel for making the body and parts of the vehicle.
- ❖ Mild steel can be easily machined in the lathe, shaper, drilling or milling machine. Its hardness can be increased by the application of carbon.
- ❖ Mild steel is very much prone to rust because it has high amount of carbon. When rust free products are needed people prefer stainless steel over mild steel [13].

1.4 Pharmacological Activity of 1,3,4-Oxadiazoles

1,3,4-Oxadiazole (1, Figure 1.2) is a heterocyclic compound containing an oxygen atom and two nitrogen atoms in a five-membered ring. It is derived from furan by substitution of two methylene groups (=CH) with two pyridine type nitrogen's (-N=) [14][15]. There are three known isomers: 1,2,4-oxadiazole (2), 1, 2,3-oxadiazole (3) and 1,2,5-oxadiazole (4) (Figure 1.2). However, 1,3,4-oxadiazole and 1,2,4-oxadiazole are better known, and more widely studied by researchers because of their many important chemical and biological properties.



Figure(1.2) oxidizole Isomers

Among heterocyclic compounds, 1,3,4-oxadiazole has become an important construction motif for the development of new drugs. Compounds containing 1,3,4-oxadiazole cores have a broad biological activity spectrum including antibacterial, antifungal, analgesic, anti-inflammatory, antiviral, anticancer, antihypertensive, anticonvulsant, and anti-diabetic properties. They have also attracted interest in medicinal chemistry as surrogates (bioisosteres) for carboxylic acids, esters and carboxamides [15]. The ability of 1,3,4-oxadiazole heterocyclic compounds to undergo various chemical reactions has made them important for molecule

planning because of their privileged structure, which has enormous biological potential. Two examples of compounds containing the 1,3,4-oxadiazole unit currently used in clinical medicine are: Raltegravir® (5), an antiretroviral drug [16] and Zibotentan® (6) an anticancer agent [17] (Figure 1.3) .

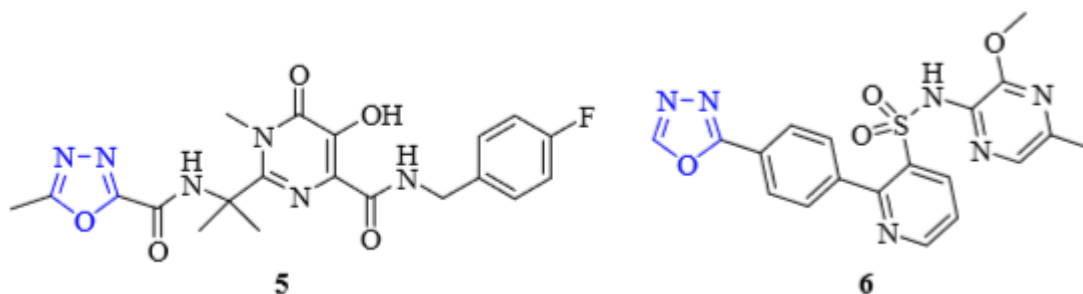
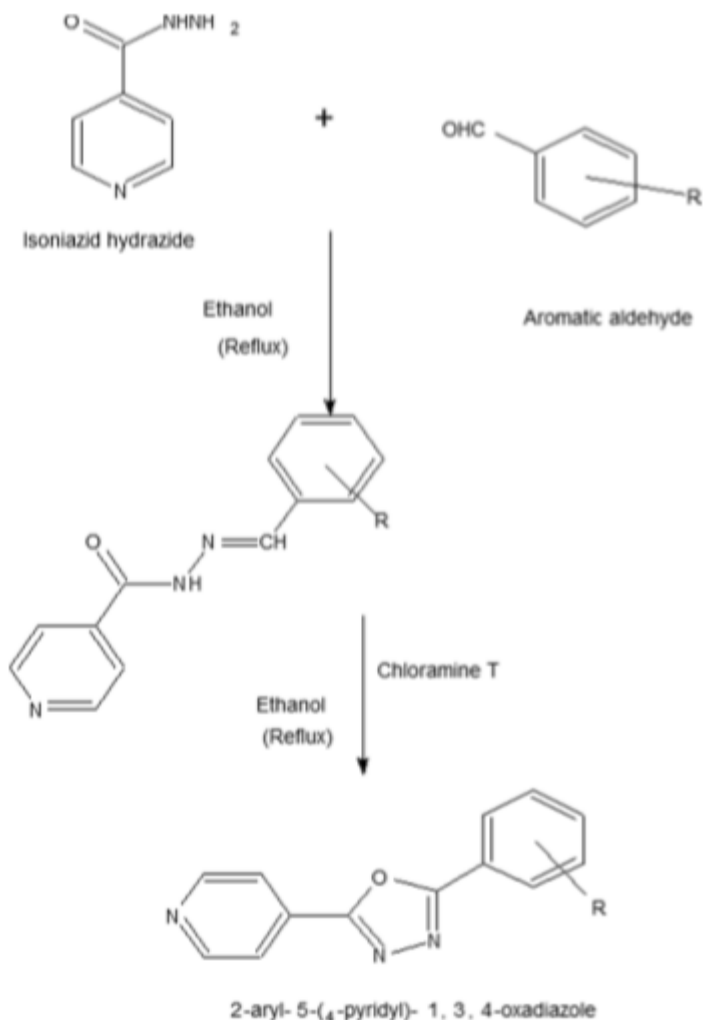


Figure (1.3). Structures of raltegravir and zibotentan, drugs that are in late stage clinical development

1.4.1 Synthesis of 1,3,4-Oxadiazole Derivatives

1,3,4-Oxadiazoles form a biologically important group of compounds having activities like analgesic, anti-inflammatory, bactericidal, antifungal, anticonvulsant, psychotropic, plant growth regulating and mono amino oxidase inhibition. 1,3,4-Oxadiazole derivatives were synthesized by microwave-assisted synthesis[18]



Figure(1.4): Synthetic scheme of 1,3,4 oxadiazole derivative

1.5 Introduction to computational work:

Acid solutions are widely used in industry, for example, chemical cleaning, descaling, and pickling, which leads to corrosive attack. Therefore, the consumption of inhibitors to reduce corrosion has increased in recent years [19][22]. The majority of the well-known inhibitors are organic compounds containing heteroatoms, such as oxygen, nitrogen, or sulphur[20], and multiple bonds, which allow an adsorption on the metal surface. In any case, adsorption is generally over the metal surface forming an adsorption layer that functions as a barrier protecting the metal from the corrosion [21].

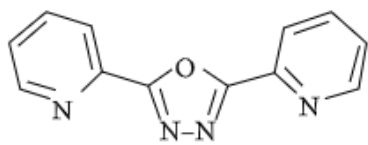
In order to evaluate compounds as corrosion inhibitors and to design novel inhibitors, much more research works were concentrated on the studies of the relationship between structural characteristics of the organic compounds and their inhibiting effects [23]. It had been suggested that the most effective factors for the inhibiting effects are the electronegative atoms (such as, N, S, P, and O)[24], the unsaturated bonds (such as double bonds or triple bonds)[25], and the plane conjugated systems including all kinds of aromatic cycles, of which they can offer special active electrons or vacant orbital to donate or accept electrons. Heterocyclic compounds, kind of effective inhibitors [27], have at least two factors within their structures, which is the reason of their effective inhibiting. The planarity (¶) and the lonely electron pairs in the heteroatoms are important features that determine the adsorption of these molecules on the metallic surface by transferring electrons from the organic compounds to the metal and forming a coordinate covalent bond during the chemical adsorption [25].

Theoretical chemistry has been used recently to explain the mechanism of corrosion inhibition, such as quantum chemical calculation [28][31]. Quantum chemical calculations have been proved to be a very powerful tool for studying the mechanism [32]. The objective of this work is to present a theoretical study on electronic and molecular structures of three heterocyclic compounds (1-pox, 2-pox, and 3-pox) and to determine relationship between molecular structure of the compounds and inhibition efficiency. The structural parameters, such as energy and distribution of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the charge distribution of the studied inhibitors, the absolute electronegativity (χ) values, and the fraction of electrons (ΔN) transfer from inhibitors to mild steel were also calculated and correlated with inhibition efficiencies. This work has great significance for the investigation of inhibition mechanism in theory. And it will be helpful to provide reference for screening corrosion inhibitors before the experiment.

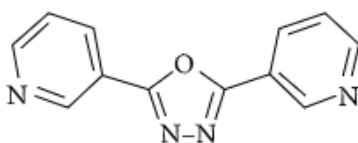
Objective of the research:

The goal of this study is to:

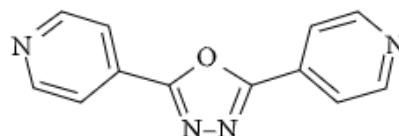
- 1- Evaluate the corrosion inhibition performance of the 1,3,4-oxidizole derivatives on the mild steel using density functional theory (DFT)
- 2- Determine the most effective corrosion inhibition among the oxidizole cpds theoretically



1-pox



2-pox



3pox

- This is chemical structure of oxidizole drivative

Chapter two

Material and Methods

2.. Materials and Methods

2.1 Materials

2.1.2 Instruments and programs

1. GaussView 5.0.9
2. Gaussian 09w Revision-B.01-SMP
3. Not pad ++
4. Microsoft Word 2013
5. Microsoft excel 2013
6. Snipping tool

2.2 Methods

- **2.2.1 Theory and Computational Detail**

Density functional theory (DFT) methods were used in this study. These methods have become very popular in recent years because they can reach exactitude similar to other methods in less time and they are less expensive from the computational point of view. In agreement with the DFT results, energy of the fundamental state of a polyelectronic system can be expressed through the total electronic density, and, in fact, the use of electronic density instead of wave function for calculating the energy constitutes the fundamental base of DFT[34]. All the calculations were done by GAUSSIAN 09W software[35], using the B3LYP functional[36] and a 6-31G basis set. The B3LYP, a version of DFT method, uses Beche's three-parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang, and Parr (LYP)[37]. This approach is shown to yield favorable geometries for a wide variety of systems. This basis set gives good geometry optimizations.

2.3 Procedure

- Gaussian view was turned first and the molecular structure of the compound was drawn. Then the ring format was clicked, then the structure was chosen and click in (G1:M1:V1-New) and the structure was drawn.

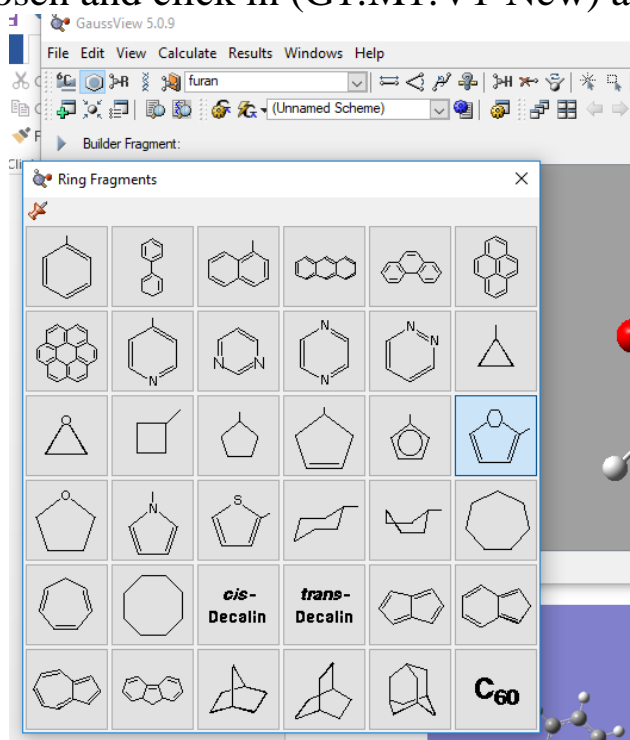


Figure (2.1) ring fragments to choose structure

- The structure of compound was drawn.

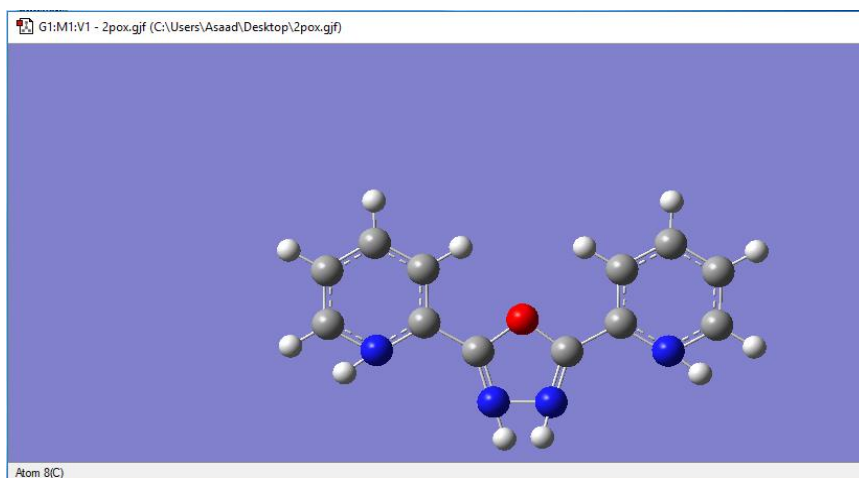


Figure (2.2) photo of 1,3,4 oxidizole

- click on calculate and chose Gaussian calculation setup

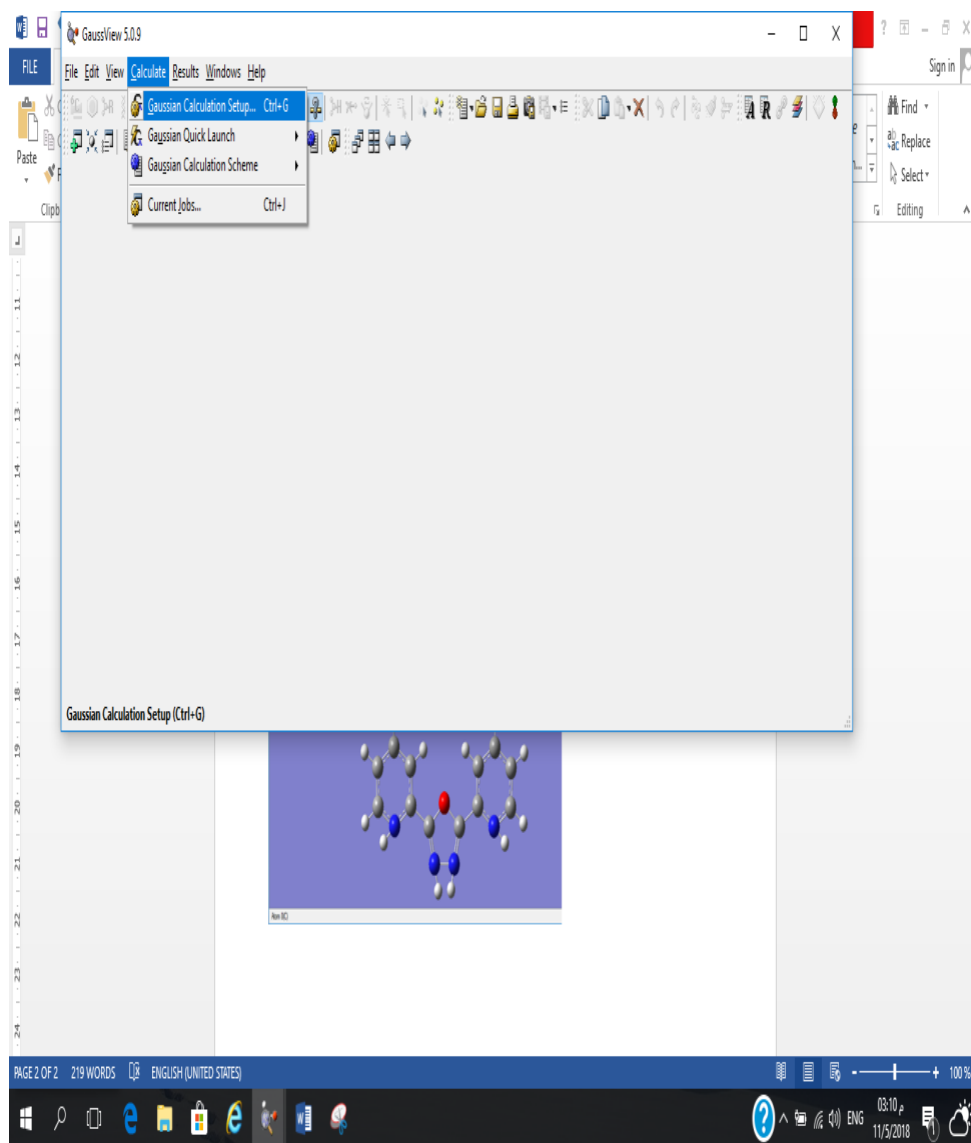


Figure (2.3) setup of calculation

- Method status was changed to DFT and B3LYB
- Basis set was changed to 6-31G+, then the file was submitted and saved the file in Gaussian program

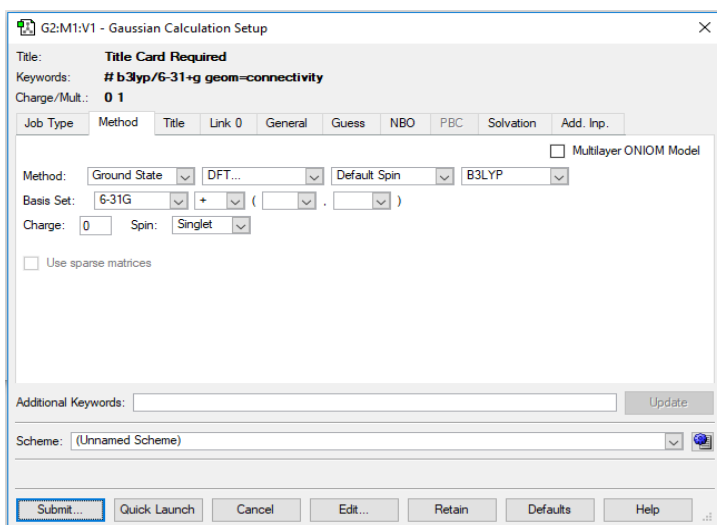


Figure (2.4) setup of method and input file

- The input file was calculated in Gaussian program and the results was sent to gauss View.

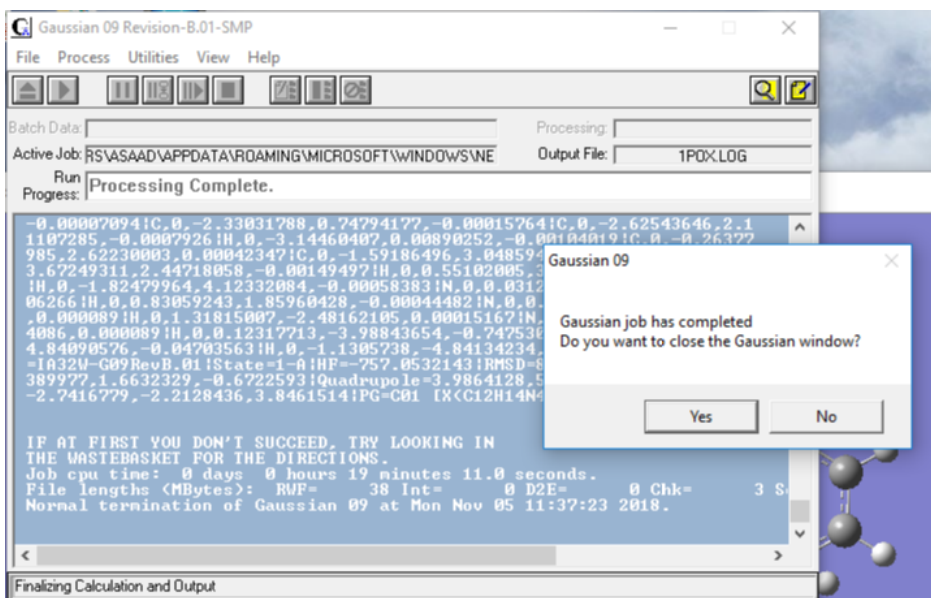


Figure (2.5) photo of Gaussian program

- The result was found in gauss view by click of result on summery

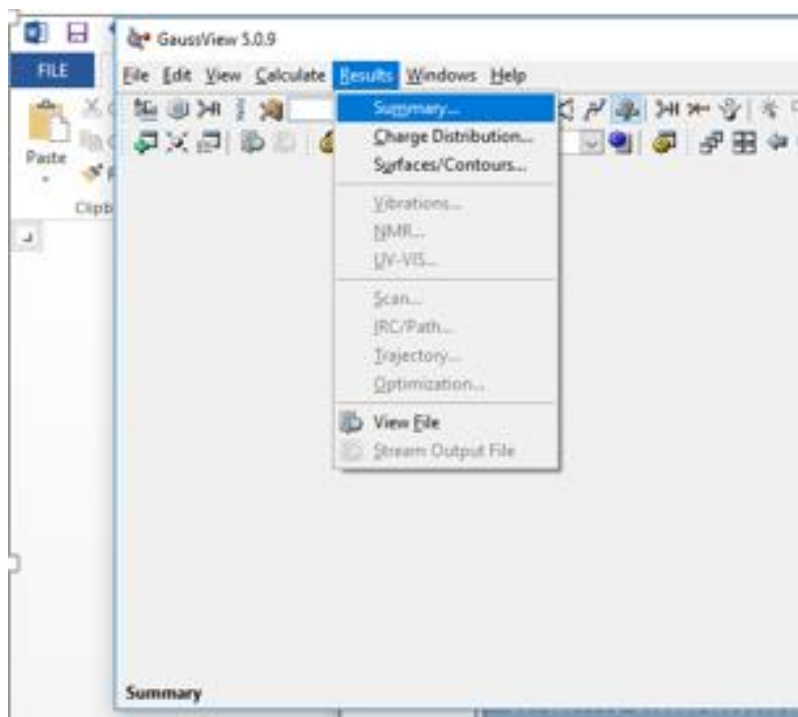


Figure (2.6) results of calculations

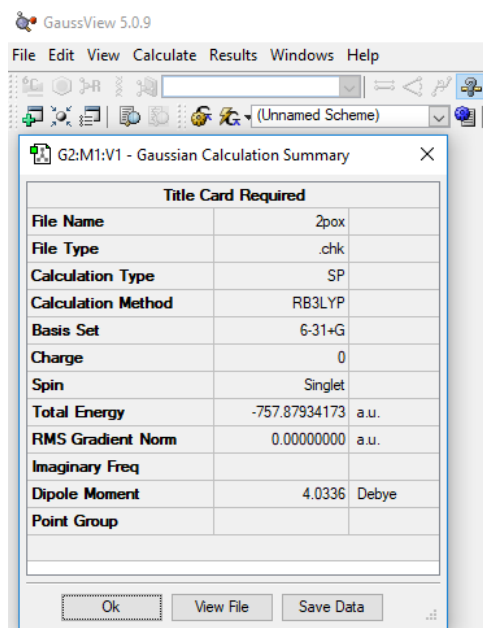


Figure (2.7) results of calculations

2.3.1 Millikan charge

- Millikan charge also was calculated by Gaussian program and found in result in Gaussian view.

After Gaussian job was completed, Gaussian view was opened and click on (Result) and click on (charge distribution), then the result of Millikan charge was founded.

It can be seen that the area of nitrogen and oxygen atoms charged a large electron density and might form adsorption

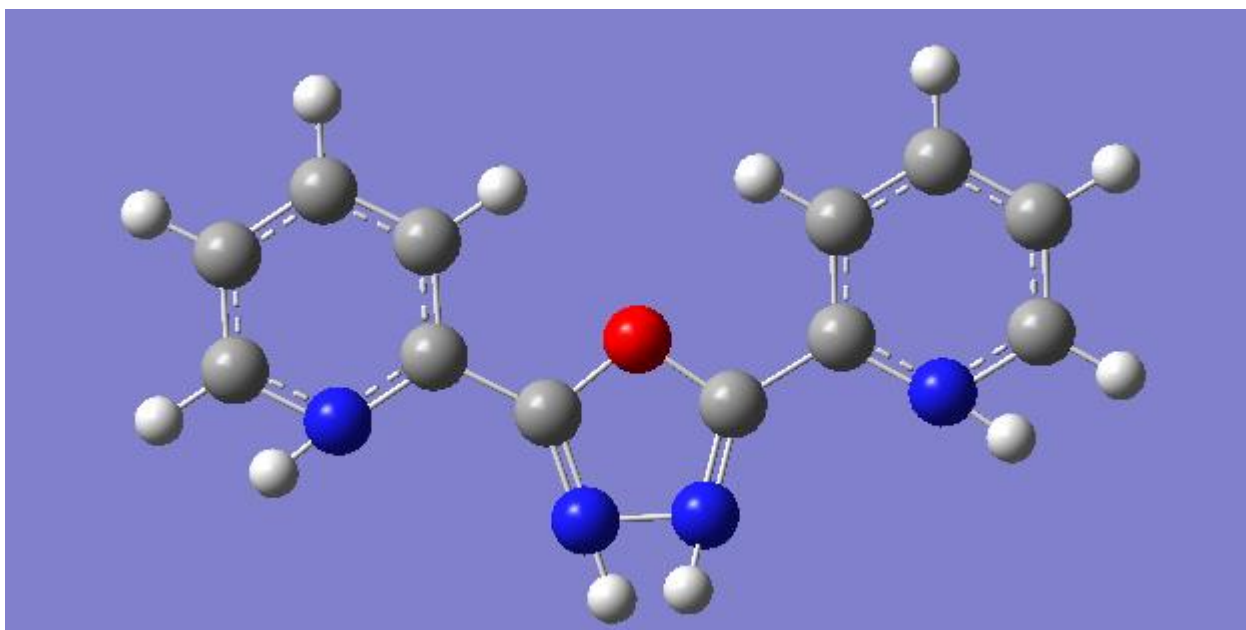


Figure (2.8) millikan charge of 1-pox

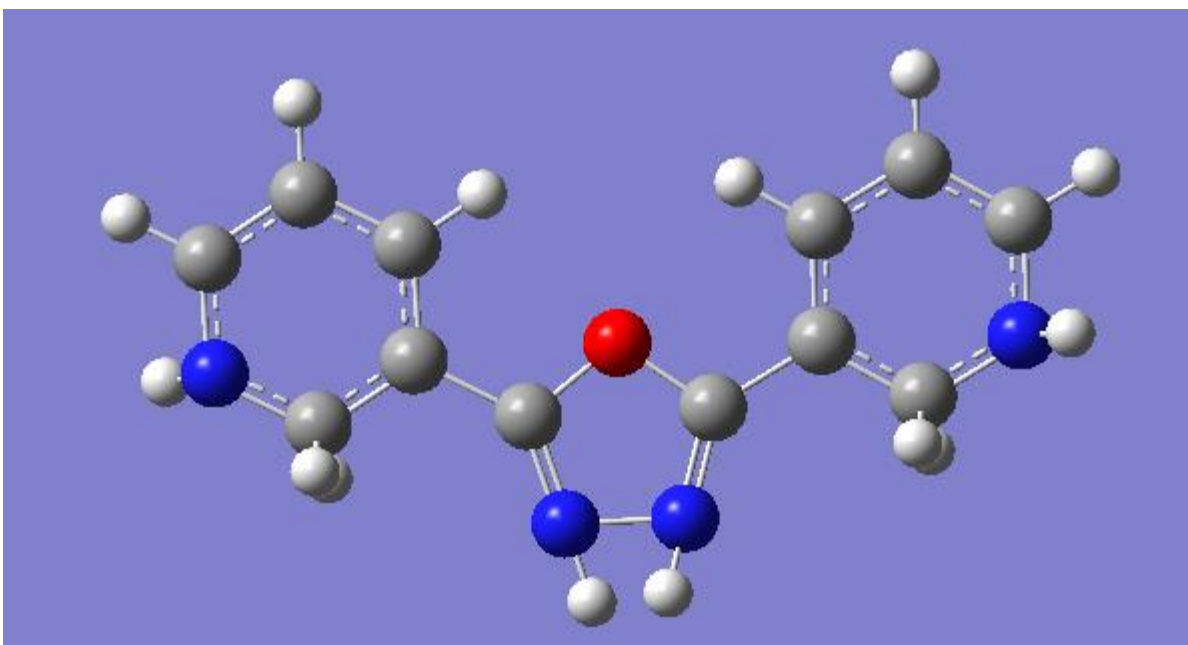


Figure (2.9) millikan charge of 2-pox

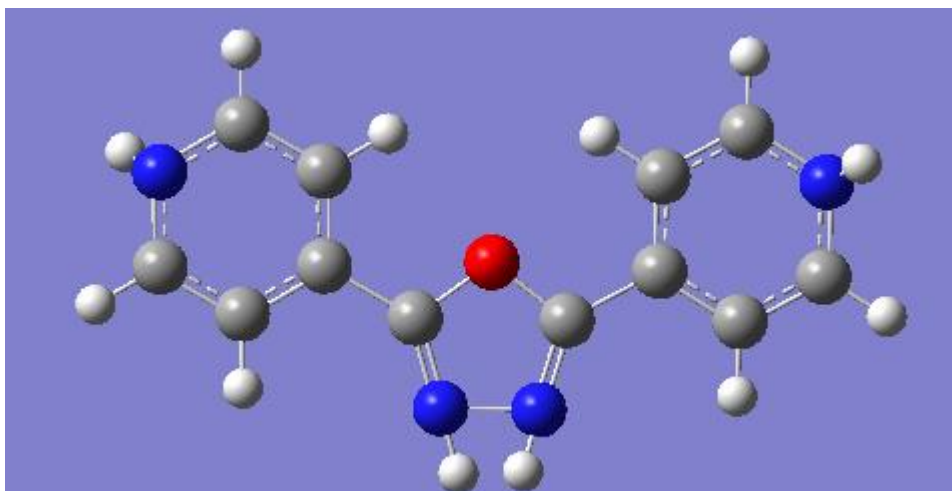


Figure (2.10) millikan charge of 3-pox

2.3.2 Molecular orbital

- After Gaussian job was completed, molecular orbital was found in Gaussian view by opened and click on (MO Editor).
- Energy and distribution of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) was calculated as below screen shot

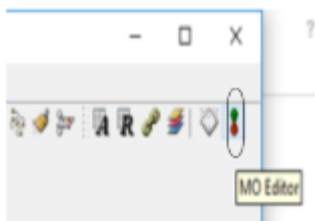


Figure (2.11) setup of molecular orbital

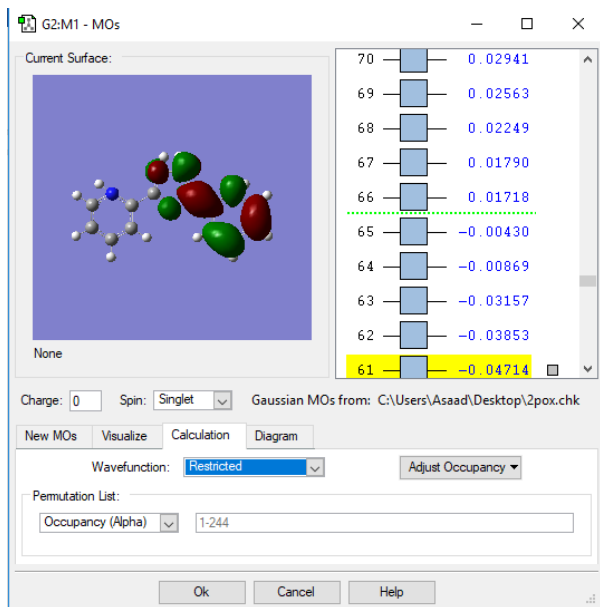


Figure (2.12) "HOMO" molecular orbital of 1-pox

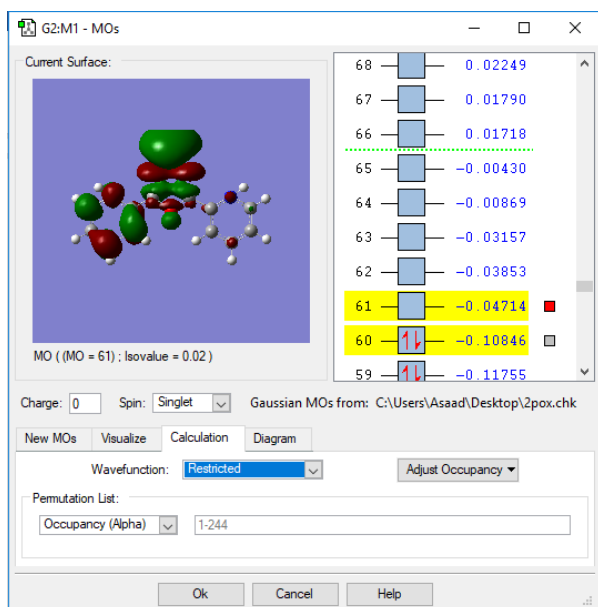


Figure (2.13) LUMO molecular orbital of 1-pox

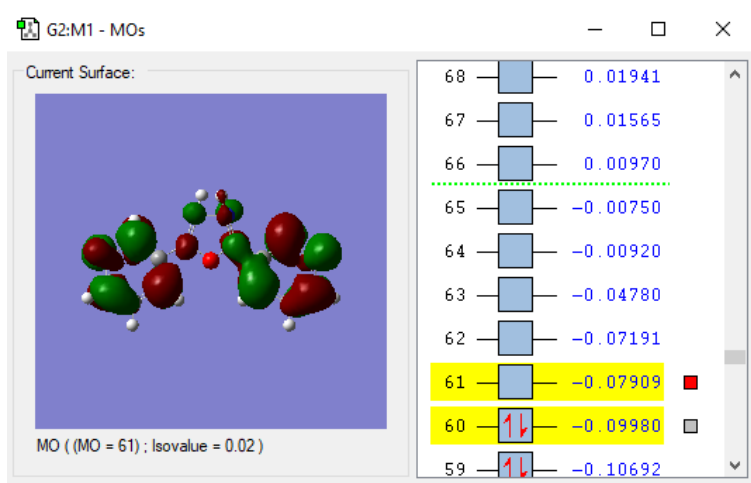


Figure (2.14) HOMO molecular orbital of 2-pox

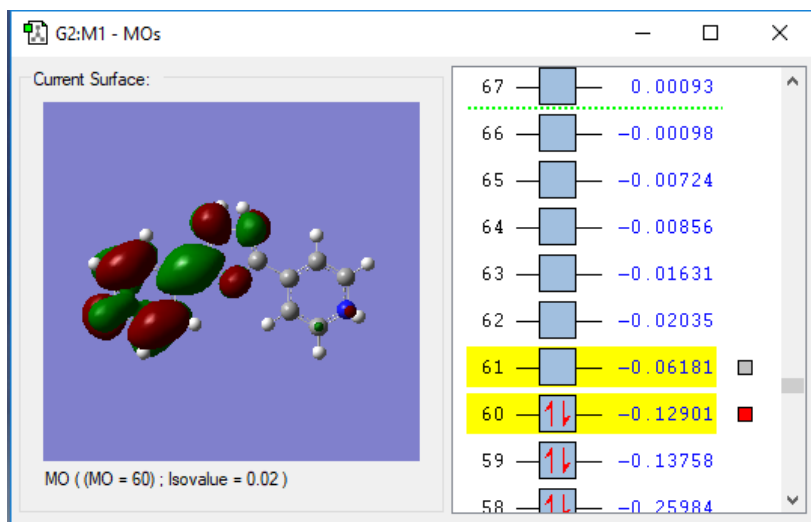


Figure (2.15) HOMO molecular orbital of 3-pox

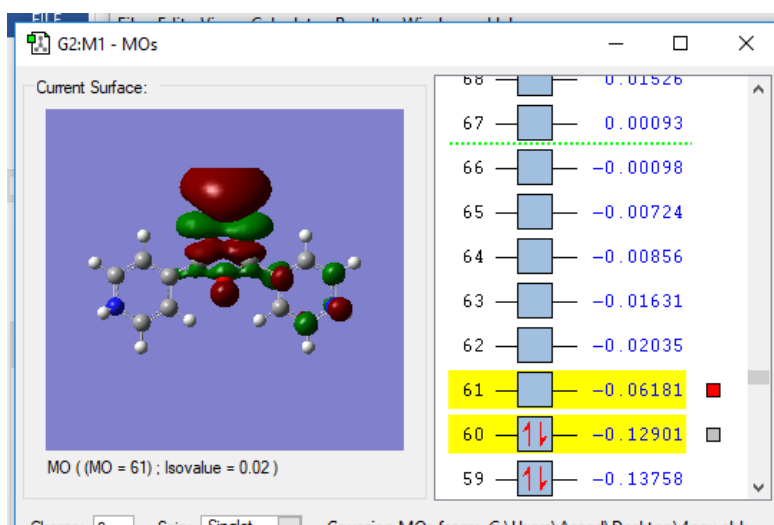


Figure (2.16) LUMO molecular orbital of 3-pox

2.3.3 Dipole moment

- Dipole moment was found in NotPad++ program by opening file log in

Chapter three

Results and Discussion

3. Result and Discussion

3.1 Results

The results related to methods discussed in chapter two

3.1.1 Millikan Charge

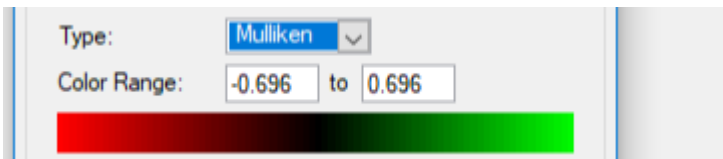


Figure (3.1) millikan charge result of 1-pox

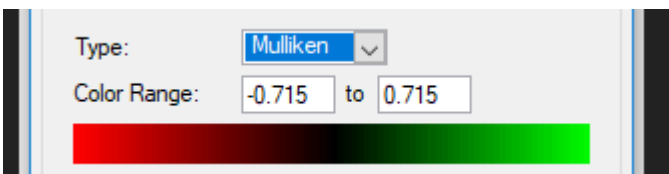


Figure (3.2) millikan charge result of 2-pox

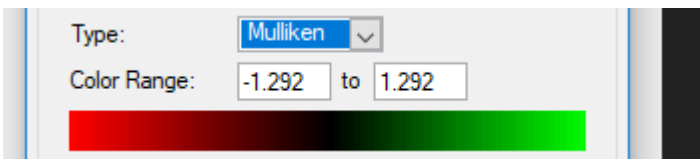


Figure (3.3) millikan charge result Of 3-pox

3.1.2 Molecular orbital

The frontier molecule orbital density distributions of three n-POXs were presented below. As seen , the distributions of HOMO and LUMO were mainly average around the whole compound structure, but the population densities of three compounds' frontier orbitals have a more obvious difference.

1-POX and 2-POX have higher and more uniform population densities than 3-POX.

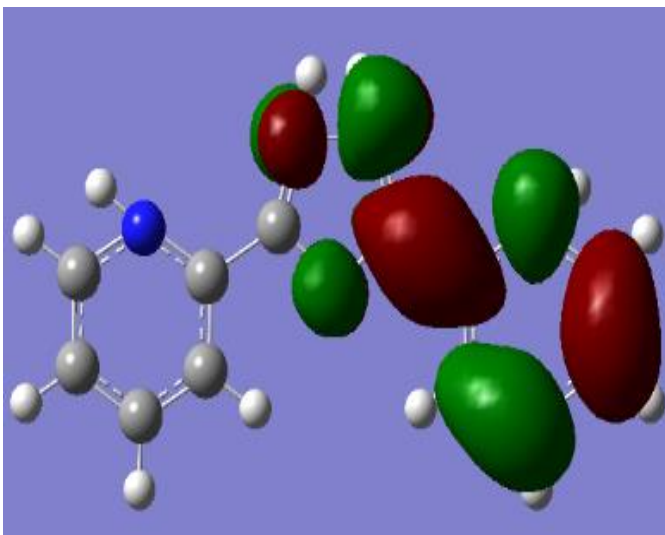


Figure (3.4) HOMO of 1-POX

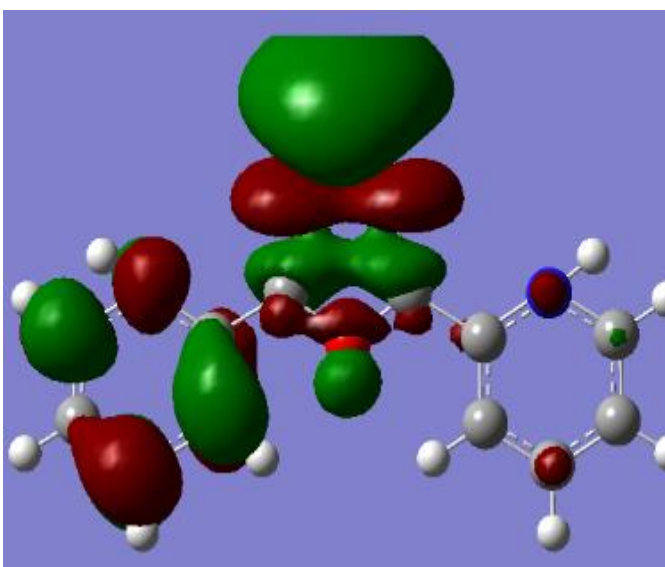


Figure (3.5) LUMO of 1-POX

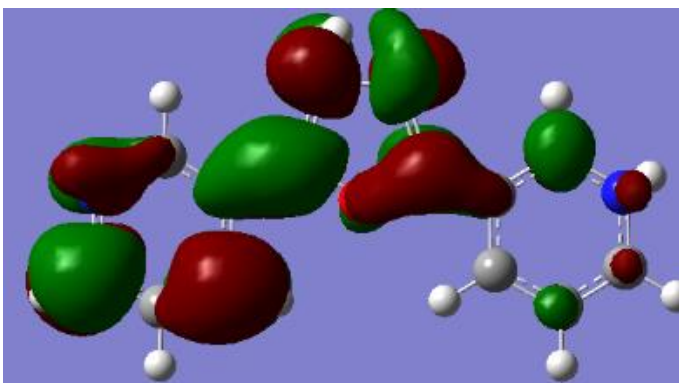


Figure (3.6) HOMO of 2-POX

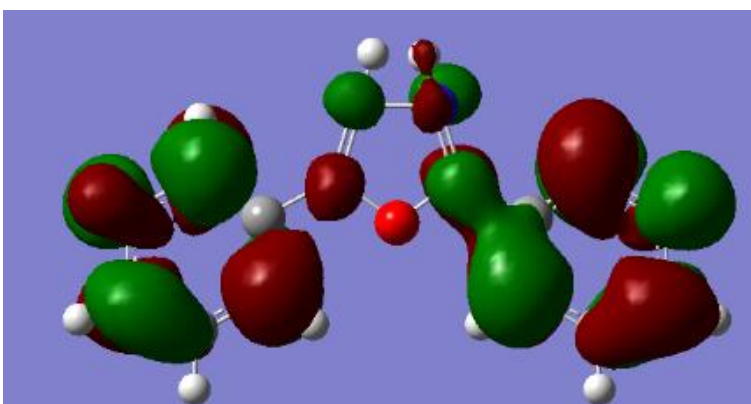


Figure (3.7) LUMO of 2-POX

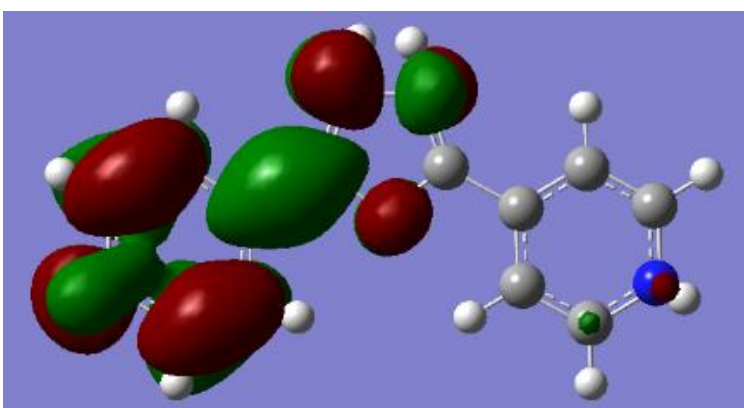


Figure (3.8) HOMO of 3-POX

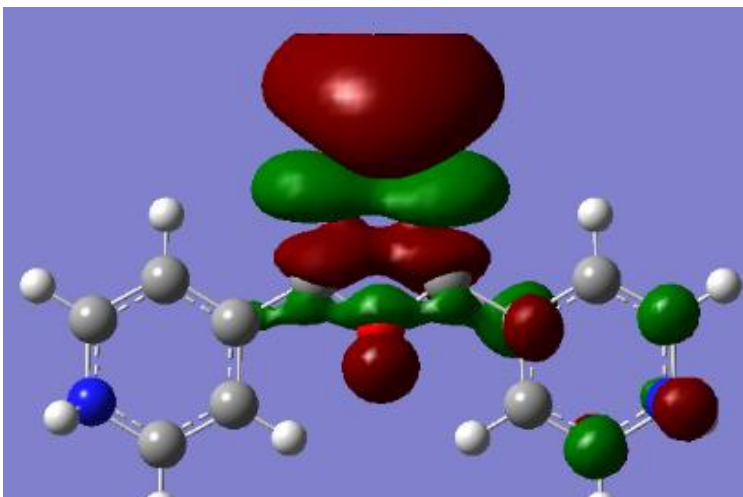


Figure (3.9) LUMO of 3-POX

3.1.3 Dipole moment

Dipole moment (field-independent basis, Debye):						
X=	-0.9348	Y=	3.8716	Z=	0.6372	Tot= 4.0335

Figure (3.10) dipole moment of 1-pox

Dipole moment (field-independent basis, Debye):						
X=	0.2532	Y=	4.5876	Z=	0.5756	Tot= 4.6305
Quadrupole moment (field-independent basis, Debye-Ang):						

Figure (3.11) dipole moment of 2-pox

Charge= 0.0000 electrons						
Dipole moment (field-independent basis, Debye):						
X=	0.8652	Y=	2.7205	Z=	0.6325	Tot= 2.9240

Figure (3.12) dipole moment of 3-pox

3.2 calculation

- Table 3.1 presents the calculated parameters of E_{HOMO} & E_{LUMO} and dipole moment for 3 Hetro Cyclic from Gaussian program:

Inhibitor	E_{HOMO} {A.U}	E_{LUMO} {A.U}	DIPOLE MOMENT
1-pox	-0.10046	-0.04714	4.0335
2-pox	-0.09980	-0.07909	4.6305
3-pox	-0.12901	-0.06181	2.924

Table (3.1) calculated parameters of E_{HOMO} and E_{LUMO} and dipole moment of 3poxs

- 1 hartree = 27.2114 eV Gaussian produce results in unit of atomic units (A.U) or hartree

$$-0.10046 * 27.2114 = -2.7336 \text{ eV}$$

$$-0.04714 * 27.2114 = -1.2827 \text{ eV}$$

$$-0.09980 * 27.2114 = -2.7157 \text{ eV}$$

$$-0.07909 * 27.2114 = -2.1521 \text{ eV}$$

$$-0.12901 * 27.2114 = -3.5105 \text{ eV}$$

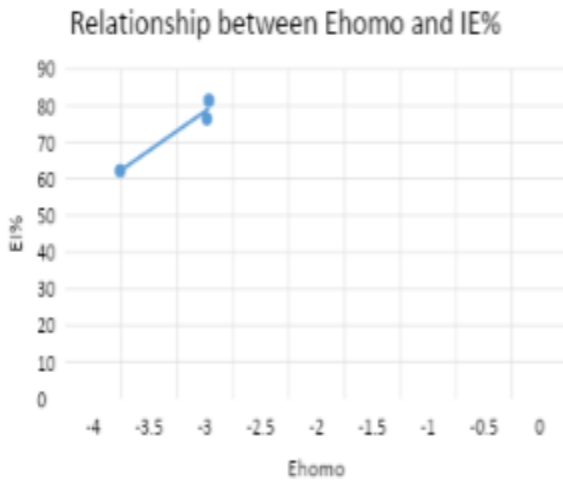
$$-0.06181 * 27.2114 = -1.6819 \text{ eV}$$

- Table(3.2) presents the calculated parameters for the three selected compounds. The measured average inhibition efficiencies (%) of these three heterocyclic compounds were also listed in the **table(3.2)**[38].

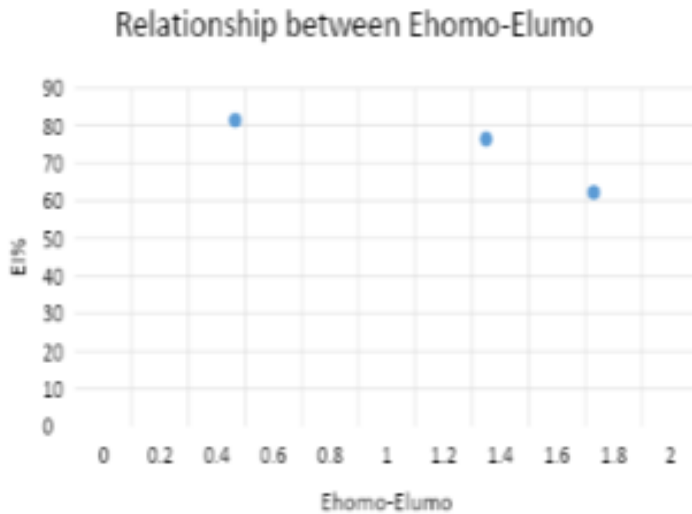
Inhibitor	E_{HOMO} {eV}	E_{LUMO} {eV}	$E_{\text{LUMO}} - E_{\text{HOMO}}$ {eV}	DIPOLE MOMENT {Deby}	Inhibition efficiency D%
1-pox	-2.733	-1.2827	1.4503	0.433	76.4
2-pox	-2.715	-2.15	0.565	0.463	81.4
3-pox	-3.51	-1.68	1.83	0.292	62.2

Table(3.2): Molecular property and inhibition efficiency of n-POXs calculated with B3LYP/6-31G*.

The relationship between corrosion inhibition efficiency and E_{HOMO} energy levels for these three compounds is plotted in Figure (3.13). As clearly seen in the figure, the inhibition efficiency is increased with the Level rising. In Figure (3.14), inhibition efficiency as a function of E_{LUMO} , As shown the inhibition efficiency reduced with the E_{LUMO} level increase. The relationship between the inhibition efficiency and the energy gap ($E_{\text{LUMO}} - E_{\text{HOMO}}$) is negative.

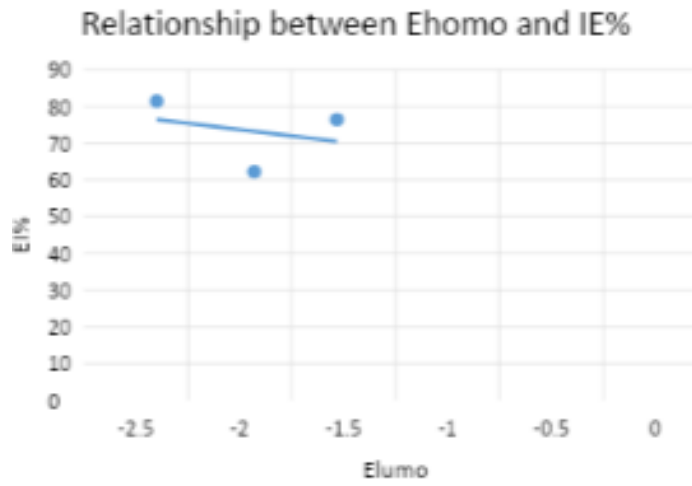


• figure (3.13). The relations between corrosion IE and "EHOMO" of n-POX showed



w

figure (3.14).The relations between corrosion IE and "ELUMO" of n-POX showed



- figure(3.15) The relation between E homo-Elumo and IE% showed

3.3 Discussion

- 3.3.1 Correlation between MO Energy Level and Inhibition Efficiency:

Frontier orbital theory is useful in predicting adsorption centers of the inhibitor molecules responsible for the interaction with surface metal atoms[33]. Terms involving the frontier MO could provide dominative contribution, because of the inverse dependence of stabilization energy on orbital energy difference. Moreover, the gap between the HOMO and LUMO energy levels of the molecules was another important factor that should be considered. Reportedly, excellent corrosion inhibitors are usually those organic compounds which not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal[29].

when the position of N atoms was changing, the corrosion inhibition efficiency changed. The quantum chemistry calculation in this study revealed that the HOMO energy level of 2-POX was boosted significantly while the energy gap dropped sharply. The linear correlation between MO energy level and the corrosion inhibition efficiency of the n-POXs (Figures 1, 2, and 3) proved that the higher the HOMO energy of the inhibitor, the greater the trend of offering electrons to unoccupied d orbital of the metal and the higher the corrosion inhibition efficiency for iron in HCl acid solutions; in addition, the lower the LUMO energy, the easier the acceptance of electrons from metal surface[38],

As the HOMO-LUMO energy gap decreased and the efficiency of inhibitor improved.

The number of transferred electrons (ΔN) was also calculated depending on the quantum chemical method[39][40].

$$\Delta N = \frac{X_{Fe} - X_{inh}}{\{2(\eta_{Fe} + \eta_{inh})\}}$$

where X_{Fe} and X_{inh} denote the absolute electronegativity of iron and the inhibitor molecule, respectively; η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule, respectively.

These quantities are related to electron affinity (A) and ionization potential (I):

$$X = \frac{(I+A)}{2}$$

$$\eta = \frac{(I-A)}{2}$$

where I and A are related in turn to E_{HOMO} and E_{LUMO}

$$I = -E_{\text{HOMO}}$$

Values of X and η were calculated by using the values I of A and obtained from quantum chemical calculation. Using a theoretical X value of 7 eV/mol and η value of 0 eV/mol for iron atom, ΔN , the fraction of electrons transferred from inhibitor to the iron molecule, was calculated. And the plot of inhibition efficiency versus ΔN (Figure) clearly shows that the inhibition efficiency increased with the ΔN increase. According to other reports, values of ΔN showed that inhibition effect resulted from electrons donation. Agreeing with Lukovits's study[40], if $\Delta N \leq 3.6$, the inhibition efficiency increased with increasing electron-donating ability at the metal surface. In this study, the three n-POXs were the donators of electrons, and the iron surface was the acceptor. The compounds were bound to the metal surface and thus formed inhibition adsorption layer against corrosion. 2-POX had the highest inhibition efficiency because it had the highest HOMO energy and ΔN values, and it had the greatest ability of offering electrons, and 3-POX had the lowest inhibition efficiency, for vice versa.

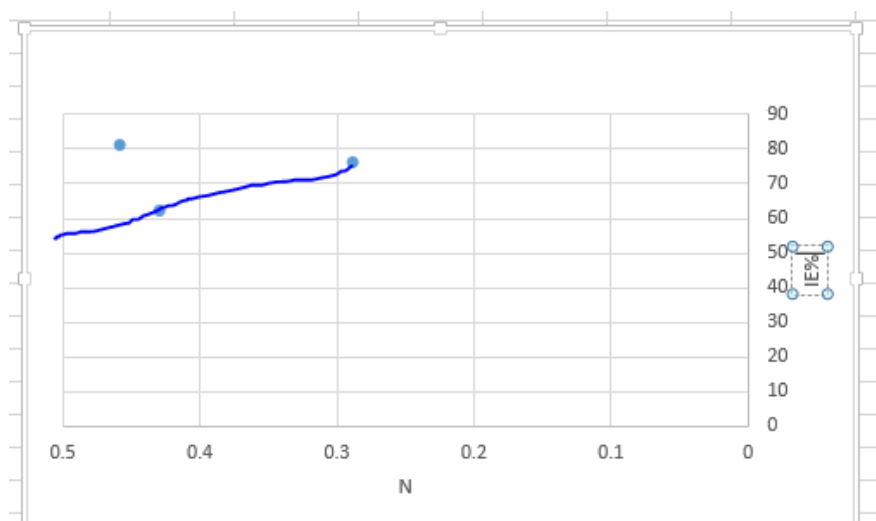


Figure (3.16) showed relationship between IE% and ΔN

3.3.2 Correlation between Electronic Density and Inhibition Efficiency:

Frontier orbital energy level indicates the tendency of bonding to the metal surface. Further study on formation of chelating centers in an inhibitor requires the information of spatial distribution of electronic density of the compound molecules.

The structure of the molecules can affect the adsorption by influencing the electron density at the functional group. Generally, electrophiles attack the molecules at negative charged sites., the electron density focused on N atoms. The regions of highest electron density are generally the sites which electrophiles attacked. So N and O atoms were the active center, which had the strongest ability of bonding to the metal surface. On the other side, HOMO was mainly distributed on the areas containing nitrogen and oxygen atoms. Thus, the areas containing N and O atoms were probably the primary sites of the bonding. And inhibition efficiency was enhanced by increase in HOMO energy and electron density. It is concluded that the region of active centers transforming electrons from N atoms to iron surface. The electron configuration of iron is [Ar] 4s²3d⁶; the 3d orbitals are not fully filled with electrons. N and O atoms have lonely electron pairs that are important for bonding unfilled 3d orbitals of iron atom and determining the adsorption of the molecules on the metal surface. 2-POX had the highest inhibition efficiency among the n-POX, which resulted from the geometry change that led to HOMO energy increase and electron density distribution in the molecule. On the contrary, 3-POX had the lowest inhibition efficiency because of the lowest and the most uneven population density of HOMO[41].

Based on the discussion above, it can be concluded that the 2-POX molecules have many active centers of negative charge. In addition, the areas containing N and O atoms are the most possible sites of bonding metal surface by donating electrons to the metal iron. According to these results, we could calculate the quantum chemical parameters before the experiment to forecast the inhibitor effectiveness. This can help improve accuracy and save time.

At present, more and more researchers are engaged in the calculation of the quantum chemistry of the organic heterocyclic inhibitors, especially the nitrogen-heterocyclic inhibitors[42].

- **3.4 Conclusions**

The relationships between inhibition efficiency of iron in hydrochloric acid solution and E_{HOMO} , $E_{\text{LUMO}}-E_{\text{HOMO}}$, and ΔN of n-POXs were calculated by DFT method. The inhibition efficiency increased with the increase in E_{HOMO} and decrease in $E_{\text{LUMO}}-E_{\text{HOMO}}$. 2-POX had the highest inhibition efficiency because it had the highest HOMO energy and ΔN values, and it was most capable of offering electrons. The distribution of electronic density shows that the molecules of n-POXs had many negatively charged active centers. The electron density was found to be positively correlated with nitrogen and oxygen atoms, which resulted in increasing inhibition efficiency. The areas containing N and O atoms are most possible sites for bonding the metal iron surface by donating electrons to the metal.

Quantum chemical calculations indicated that considering only one parameter is not convenient; hence several parameters or a composite index of more than two or more quantum chemical parameters were taken into consideration to characterize the inhibition activity of the molecules. Quantum chemical calculation approach is adequately sufficient to also forecast the inhibitor effectiveness using the theoretical approach. Moreover, it may be used to find the optimal group of parameters that might predict the structure and molecule suitability to be an inhibitor.

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