ISSN: 0067-2904
GIF: 0.851

Quantum Mechanical Calculations for Some PINH C_s Symmetry Schiff Bases as Corrosion Inhibitors for Mild Steel

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Abstract

Density Functional Theory (DFT) at the B3LYP/6-311G basis set level was performed on six new substituted Schiff base derivatives of PINH [(phenylallylidene) isonicotinohydrazide], The calculated quantum chemical parameters correlated to the inhibition efficiency are E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), the energy gap [$\Delta E_{(HOMO-LUMO)}$], hardness (η), softness (S), dipole moment (μ), electron affinity (EA), ionization potential (IE), the absolute electronegativity (χ), Global electrophilicity index (ω) and the fraction of electron transferred (Δ**N**), all have discussed at their equilibrium geometry and their correct symmetry (Cs). Comparisons of the order of inhibition efficiency of the Schiff bases derivatives, and local reactivity were analyzed using Mulliken population analysis. The local reactivity has been studied through condensed softness indices in order to predict both the reactive centers and to know the possible sites of nucleophilic and electrophilic attacks. Also vibration frequencies and IR absorption intensities were carried out for the calculated Schiff bases molecules. Also some physical values were studied such as heat of formation and total energy.

Keywords: Corrosion inhibition, Schiff bases, Symmetry.

حسابات ميكانيك الكم لبعض قواعد شف المشتقة من المركب INHC ذات التماثل C_s كمثبطات تأكل للحديد المطاوع

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الخلاصة

تضمن البحث استخدام نظرية دوال الكثافة DFT الأساسية غير التقريبية لعناصر قاعدة 6-311G وباسلوب B3LYP وباستخدام برنامج Gaussian-03 في حساب الشكل الهندسي التوازني لستة من قواعد شف الجديدة المشتقة من المركب PINH [(phenylallylidene) isonicotinohydrazide], التي وجد امتلاك معظمها للتماثل Cs. وتم حساب ومناقشة معاملات اميكانيك الكم المرتبطة بدراسة كفاءة هذه المركبات كمثبطات تاكل مثل طاقة اعلى مدار محجوز بالالكترونات E_{HOMO}، وطاقة اوطأ مدار غير محجوز بالالكترونات E_{LUMO}، والفرق الطافي بينهما $\Delta E_{HOMO-LUMO}$، وتوزيع الكثافة الالكترونية والصلادة وعزم ثنائي القطب والالفة الالكترونية وجهد التأين والليونة وكسر الانتقال الالكتروني مع تعيين مواقع الامتزاز

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الفعالة، عند الشكل الهندسي التوازني وعند التماثل الصحيح لهذه الجزيئات. كما تم حساب وتصنيف ترددات اهتزاز طيف الأشعة تحت الحمراء وبعدد 3N-6 وادراج الاهم منها. كذلك تمت دراسة بعض القيم الفيزياوية كحرارة التكوين والطاقة الكلية.

Introduction

The protection of metal surfaces against corrosion is an important industrial and scientific topic. Many chemical phenomena cannot be explained by classical physics and need quantum mechanics for the complete analysis. In that case quantum chemical studies are used to analyze the inhibition efficiency of certain compounds on corrosion. A number of heterocyclic compounds containing nitrogen, oxygen and sulphur either in the aromatic or long chain carbon system have been reported to be effective inhibitors [1,2]. The planarity and the lone electron pairs in the heteroatoms are important features that determine the adsorption of molecules on the metallic surface [3]. The inhibition efficiency has been closely related to the inhibitor adsorption abilities and the molecular properties for different kinds of organic compounds. The strength of the inhibition depends on the molecular structure of the inhibitor. Organic compounds, which can donate electrons to unoccupied d orbital of metal surface to form coordinate covalent bonds and can also accept free electrons from the metal surface by using their antibonding orbital to form feedback bonds, constitute excellent corrosion inhibitors [4-9]. Reportedly, excellent corrosion inhibitors are usually organic compounds, which not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal [10]. The strength of the inhibition depends on the molecular structure of the inhibitor. Organic compounds, which can donate electrons to unoccupied d orbital of metal surface to form coordinate covalent bonds and can also accept free electrons from the metal surface by using their antibonding orbital to form feedback bonds, constitute excellent corrosion inhibitors. Quantum chemical calculations have been proved to be a very powerful tool for studying corrosion inhibition mechanism [11-14]. Density functional theory (DFT) [15,16] has provided a very useful framework for developing new criteria for rationalizing, predicting, and eventually understanding many aspects of chemical processes [17]. A variety of chemical concept, which are now widely used as descriptors of chemical reactivity, e.g., electronegativity [18] hardness or softness quantities etc., appear naturally within DFT. The objective of this study is to present theoretical study on the adsorption, electronic and molecular structures of six new Schiff bases molecules derivatives of PINH [(phenylallylidene) isonicotinohydrazide], which have prepared and studied experimentally and theoretically with three other Schiff bases compounds as a corrosion inhibitors for mild steel in acid solutions [19] PINH was shown to have the best inhibition efficiency in comparison to other three different Schiff bases compounds. (without mentioning the method of calculation and without any mention to the symmetry of the calculated molecules).

In the present work recalculated of the PINH Schiff base have done using DFT method taking into account the correct symmetry one time (Cs) and symmetry (C_1) in other time, comparison were done between them to find the better as an inhibitor [group I]. For finding a better corrosion inhibitor than PINH, groups of electron donors (o-OCH_3, p-OCH_3 and o,p-OCH_3) [group Π] and a groups of electron withdrawing (o-Br, p-Br and o,p-Br) [group Ш] were added, all had studied depending on the theoretical parameters to characterize the inhibition property of the new calculated substituted molecule, to establish correlations between inhibition efficiencies and some of the electronic properties of the studied molecules, In the right symmetry of molecules at equilibrium shape.

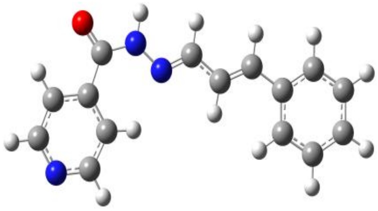
The molecules for [group Π] are (O-methoxy (phenylallylidene) isonicotinohydrazide (PINH o-OCH_3), (P-methoxy (phenylallylidene) isonicotinohydrazide (PINH p-OCH_3), (dimethoxy (phenylallylidene) isonicotinohydrazide (PINH o,p-OCH_3), and the molecules for [group Ш] are (O-bromo (phenylallylidene) isonicotinohydrazide (PINH o-Br) and (P- bromo (phenylallylidene) isonicotinohydrazide (PNHC p-Br), (di bromo (phenylallylidene) isonicotinohydrazide (PINH o,p-Br).

Computational details

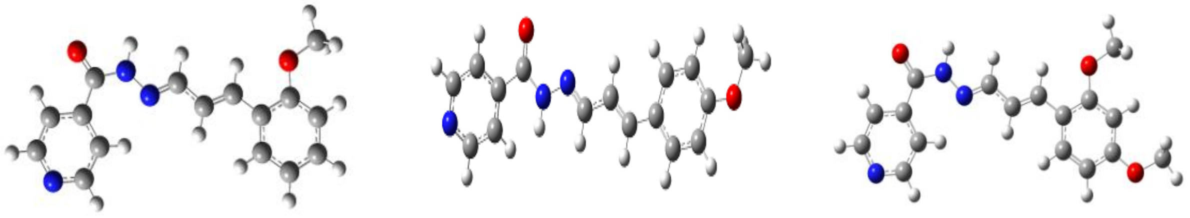
In computational chemistry tools, the DFT offers the fundamentals for interpreting multiple chemical concepts used in different branches of chemistry. In order to explore the theoreticalexperimental consistency, quantum chemical calculations were performed with complete geometry optimizations using Gaussian-03 software package [20]. Geometry optimization were carried out by B3LYP functional at the 6-311G (d,p) basis set and at the density functional theory

(DFT) level. Recently, Density functional theory (DFT) has been used to analyze the characteristics of the inhibitor/ surface mechanism and to describe the structural nature of the inhibitor in the corrosion process [21-22].

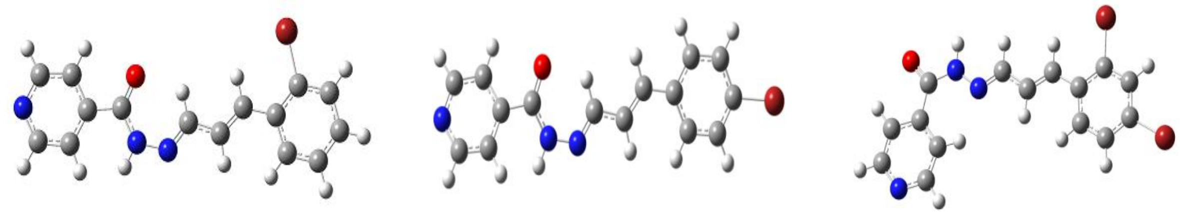
Figure 1 shows the equilibrium geometries of the calculated PINH Schiff bases molecule, with new six of its derivatives calculating by using DFT (B3LYP/ 6-311G) method.



PINH



PINH **(o–OCH$_3$)** PINH **(p-OCH$_3$)** PINH **(o,p-OCH$_3$)**



PINH **(o-Br)** PINH **(p-Br)** PINH **(o,p-Br)**

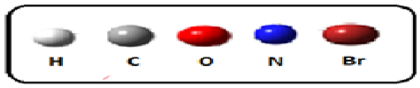


Figure 1-Optimized structures for derivatives of the PINH Schiff bases that calculated by DFT (B3LYP/ 6-311G) method.

Optimize geometries were shown that all the calculated molecules were planar with Cs symmetry, except PINH (p-OCH$_3$) were found to be C$_1$ symmetry with no plane of symmetry. The label of atoms for the optimized structures are shown in figure 2.

Table 1 has listed bond lengths that have resulted from optimized structures of PINH Schiff bases derivatives as calculated by DFT (6-311G/ B3LYP).

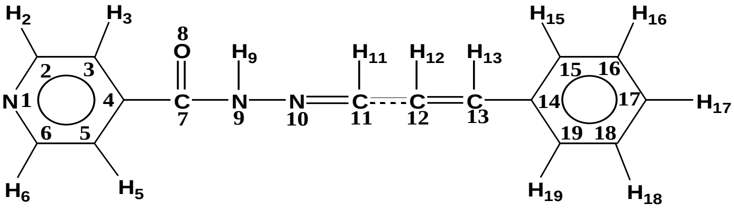


Figure 2.-Label of (phenylallylidene) isonicotinohydrazide (PINH).

Table 1.-DFT (6-311G/B3LYP) bond distances for the calculated PINH Schiff bases derivative molecules.

Bond	**Bond length (Å)**						
	PINH	PINH **o-OCH$_3$**	PINH **p-OCH$_3$**	PINH **o,p-OCH$_3$**	PINH **o-Br**	PINH **p-Br**	PINH **o,p-Br**
N1-C2	1.3532	1.3533	1.3532	1.3534	1.3531	1.3499	1.3531
N1-C6	1.3496	1.3498	1.3497	1.3497	1.3495	1.3522	1.3495
C2-H2	1.0808	1.0809	1.0806	1.0809	1.0807	1.0808	1.0806
C2- C3	1.3908	1.3907	1.3924	1.3907	1.3908	1.3949	1.3908
C3-H3	1.0791	1.0791	1.0797	1.0791	1.0791	1.0814	1.0791
C3-C4	1.4056	1.4054	1.4010	1.4055	1.4057	1.4033	1.4057
C4-C5	1.4032	1.4031	1.4025	1.4032	1.4032	1.4016	1.4032
C4-C7	1.4954	1.4958	1.4992	1.4960	1.4950	1.5014	1.4950
C5-H5	1.0753	1.0754	1.0816	1.0754	1.0751	1.0793	1.0751
C5-C6	1.3963	1.3962	1.3957	1.3963	1.3962	1.3924	1.3962
C6-H6	1.0812	1.0812	1.0811	1.0812	1.0811	1.0806	1.0811
C7-O8	1.2542	1.2550	1.2417	1.2557	1.2531	1.2541	1.2531
C7-N9	1.3850	1.3833	1.3852	1.3820	1.3875	1.3744	1.3875
N9-N10	1.3754	1.3780	1.3788	1.3792	1.3718	1.3901	1.3718
N9-H9	1.0185	1.0184	1.0148	1.0184	1.0186	1.0036	1.0186
N10-C11	1.3017	1.3022	1.3003	1.3027	1.3018	1.3063	1.3018
C11-H11	1.0937	1.0937	1.0956	1.0939	1.0928	1.0816	1.0928
C11-C12	1.4389	1.4383	1.4389	1.4370	1.4394	1.4434	1.4394
C12-H12	1.0828	1.0829	1.0827	1.0830	1.0828	1.0834	1.0828
C12-C13	1.3532	1.3544	1.3538	1.3559	1.3531	1.3523	1.3531
C13-H13	1.0872	1.0829	1.0877	1.0832	1.0824	1.0866	1.0824
C13-C14	1.4628	1.4596	1.4599	1.4555	1.4608	1.4628	1.4608
C14-C15	1.4101	1.4194	1.4084	1.4166	1.4108	1.4106	1.4108
C14-C19	1.4113	1.4076	1.4138	1.4115	1.4141	1.4092	1.4141
C15-H15	1.0830	--------	1.0813	--------	--------	1.0809	-------
C15-C16	1.3943	1.3969	1.3932	1.3989	1.3925	1.3917	1.3925
C15-OCH$_3$	--------	1.3929	--------	1.3922	--------	--------	--------
C15-Br	--------	--------	-------	--------	1.9599	--------	1.9599
C16-H16	1.0817	1.0792	1.0795	1.0768	1.0777	1.0796	1.0777
C16-C17	1.3968	1.3970	1.4014	1.3985	1.3901	1.3946	1.3901
C17-H17	1.0815	1.0816	--------	--------	1.0777	--------	--------
C17-C18	1.4001	1.3968	1.4007	1.4010	1.3937	1.3912	1.3937
C17-OCH$_3$	--------	--------	1.3886	1.3876	--------	--------	--------
C17-Br	--------	--------	--------	--------	--------	1.9512	1.9447
C18-H18	1.0817	1.0810	1.0800	1.0792	1.0792	1.0796	1.0792
C18-C19	1.3919	1.3926	1.3870	1.3852	1.3882	1.3944	1.3882
C19-H19	1.0813	1.0811	1.0829	1.0808	1.0803	1.0825	1.0803

From the calculation of bonds length of PINH derivatives Table 1, it was shown that:- For C4-C7 bond length in group Π the longest bond is (1.4992A°) due to PINH (p-OCH$_3$) molecule and the shortest bond (1.4954) belongs to PINH (o-OCH$_3$) molecule. For group Ш the longest C4-C7 bond (1.5014A°) belongs to PINH (o-Br)= PINH (p-Br) molecules and the shortest bond (1.4950A°) belongs to PINH (o,p-Br).

- For C=O bond length in group Π the longest one (1.2557A°) belongs to PINH (o,p-OCH$_3$) and the shortest (1.2417A°) belongs to PINH (p-OCH$_3$). For group Ш the longest C=O bond length (1.2541A°) due to PINH (p-Br) molecule and the shortest one (1.2531A°) belongs to PINH (o,p-Br) indicating possessing the greatest effect of electron donor.
- For C=N bond length in group Π the longest one is (1.3027A°) belongs to PINH (o,p-OCH$_3$) and the shortest bond (1.3003A°) belongs to PINH (p-OCH$_3$). For group Ш the longest the longest C=N bond

is (1.3063A°) belongs to PINH (o-Br) = PINH (p-Br) molecule and the shortest bond (1.3018A°) belongs to PINH (o,p-Br).

For C-O bond length in group Π the longest bond is C_{15}-OCH_3 (1.3929A°) belongs to PINH (o-OCH_3) molecule and the shortest bond (1.3876) belongs to PINH (o,p-OCH_3) (1.3876) at para position. For group Ш the longest C-Br bond is C_{15}-Br (1.9633A°) belongs to PINH (o-Br) molecule and the shortest bond (1.9447A°) belongs to PINH (o,p-Br), also at para position, at which the effect of electron withdrawing is greatest

Density functional theory (DFT) has been quite successful in providing theoretical basis for popular qualitative chemical concepts like electronegativity (χ), hardness (η), softness (S) and local softness S(r). For an N-electron system with total energy E, these reactivity indices are defined as the following first-order derivative [23].

χ (Electronegativity)□ **(IE + EA)/ 2**

Hardness (η) has been defined within the DFT as the second derivative of the E with respect to N as *v*(*r*) property which measures both the stability and reactivity of the molecule [24].

η (Hardness) **= (IE-EA)/ 2**

According to Koopman's theorem, the ionization potential energy (IE) and electron affinity (EA) of the inhibitors are calculated using the following equations and hence **χ** and η are calculated.

IE (Ionization potential**)= -E_{HOMO}**

EA (Electron affinity)**= -E_{LUMO}**

The higher HOMO energy corresponds to the more reactive molecule in the reactions with electrophiles, while lower LUMO energy is essential for molecular reactions with nucleophiles [25].

The global softness (S) is the inverse of the global hardness [26]

S (global softness) = 1/ η

Global electrophilicity index $(\omega) = -x^2/2\eta$

When two systems, Fe and inhibitor, are brought together, electrons will flow from lower χ (inhibitor) to higher χ (Fe), until the chemical potentials become equal. The fraction of transferred electrons (ΔN) was also calculated [26] by using the equation below.

ΔN (Electron transferred) = $(\chi_{Fe} - \chi_{inhib.}) / [2(\eta_{Fe} + \eta_{inhib.})]$

Where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule respectively η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of χ_{Fe}= 7.0 eV and η_{Fe} = 0 for the computation of number of transferred electrons [27]. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance [28].

Results and Discussion

According to Wang et al. [29], the frontier orbital (highest occupied molecular orbital-HOMO and lowest unoccupied molecular orbital-LUMO) of a chemical species play major role in defining its reactivity. As E_{HOMO} is often associated with the electron donating ability of a molecule, high value of E_{HOMO} is likely to indicate the tendency of the molecule to donate electrons to appropriate acceptor molecules with lower energy molecular orbital. Increasing values of E_{HOMO} facilitate adsorption of inhibition on metal surface and therefore enhance the inhibition efficiency, by influencing the transport process through the adsorbed layer. E_{LUMO} indicates the ability of the molecule to accept electrons. The binding ability of the inhibitor to the metal surface increases with increasing of the HOMO and decreasing of the LUMO energy values**,** because transition of electron is due to interaction between highest occupied molecular orbital HOMO and lowest unoccupied molecular orbital LUMO of reacting species. The higher values of E_{HOMO} indicate the greater its ability of offering electrons to unoccupied d-orbital of the metal and higher the corrosion inhibition efficiency through better adsorption. The inhibitor does not only donate electron to the unoccupied d orbital of the metal ion but can also accept electron from the d orbital of the metal leading to the formation of a feedback bond. For groups I, Π, and Ш the highest value of E_{HOMO} (-5.7020, -6.2470 and -6.2780eV), indicates the better inhibition efficiency of PINH (o,p-OCH_3), PINH (o,p-Br) and PINH respectively and the low value of E_{LUMO} for the three groups are (-2.8224, -2.8009 and -2.4994 eV), indicates the better inhibition efficiency of PINH (o,p-Br), PINH and PINH (o -OCH_3) respectively, table 2.

Table 2-Calculated energies of the PINH Schiff bases compounds by using DFT (6-311G/ B3LYP) method.

Inhibitor Molecule	P.G.	E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta E_{HOMO-LUMO}$ (eV)	μ (debye)
I					
PINH	**Cs**	**-6.2470**	**-2.4994**	**3.7476**	**6.2086**
	C_1	**-6.2473**	**-2.4988**	**3.7485**	**6.2089**
П					
PINH (o-OCH_3)	**Cs**	**-5.9841**	**-2.3655**	**3.6186**	**8.5343**
PINH (p-OCH_3)	**C_1**	**-5.8143**	**-2.2656**	**3.5487**	**5.1768**
PINH (o,p-OCH_3)	**Cs**	**-5.7020**	**-2.2150**	**3.4870**	**10.7386**
	C_1	**-5.7017**	**-2.2150**	**3.4867**	**10.7380**
Ш					
PINH (o-Br)	**Cs**	**-6.3175**	**-2.6455**	**3.6720**	**4.9835**
PINH (p-Br)	**Cs**	**-6.2780**	**-2.6535**	**3.6245**	**4.0197**
PINH (o,p-Br)	**Cs**	**-6.4027**	**-2.8009**	**3.6015**	**3.1560**

P.G: Point Group.

For E_{HOMO}, Table 2 shows the following correlations:
Group П: PINH (o,p -OCH_3) > PINH (p -OCH_3) > PINH (o -OCH_3)
Group Ш: PINH (p-Br) > PINH (o -Br) > PINH (o,p-Br)
As a whole:
PINH (o,p -OCH_3) > PINH (p-OCH_3) > PINH (o-OCH_3) > **PINH** > PINH (p-Br) > PINH (o-Br) > PINH (o,p-Br)
For E_{LUMO}, Table 2 shows the following correlations:
Group П: PINH (o -OCH_3) < PINH (p -OCH_3) < PINH (o,p -OCH_3)
Group Ш: PINH (o,p-Br) < PINH (p-Br) < PINH (o-Br)
As a whole:
PINH (o,p -Br) < PINH (p -Br) < PINH (o -Br) < **PINH** < PINH (o -OCH_3) < PINH (p -OCH_3) < PINH (o,p -OCH_3).

Energy gap $\Delta E = (E_{LUMO}–E_{HOMO})$ is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on the metallic surface. As ΔE decreases the reactivity of the molecule increases leading to increase inhibition efficiency. Lower values of the energy difference will render good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low [30]. A molecule with a low energy gap is more polarizable and is generally associated with the high chemical activity and low kinetic stability and is termed soft molecule [31].

The results as indicated in Table 2 show that the inhibitors PINH (o,p-OCH_3), PINH (o,p-Br) and PINH have the lowest energy gap (3.4870, 3.6015 and 3.7476 eV), this means that PINH (o,p-OCH_3), molecule could has the best performance as corrosion inhibitor. For $\Delta E_{HOMO–LUMO}$ Table 2 shows the following correlations:

Group П: PINH (o,p -OCH_3) < PINH (p -OCH_3) < PINH (o-OCH_3)

Group Ш: PINH (o,p-Br) < PINH (p-Br) < PINH (o-Br)

As a whole:

PINH (o,p-OCH_3) < PINH (p-OCH_3) < PINH (o,p-Br) < PINH (o-OCH_3) < PINH (p-Br) < PINH (o-Br) < P**INH**.

For Dipole moment (μ)

The dipole moment (μ in Debye) is another important electronic parameter that results from non uniform distribution of charges on the various atoms in the molecule. The high value of dipole moment probably increases the adsorption between chemical compound and metal surface [32].

The energy of the deformability increases with the increase in μ, making the molecule easier to adsorb at the Fe surface. The volume of the inhibitor molecules also increases with the increase of μ. This increases the contact area between the molecule and surface of iron and increasing the corrosion inhibition ability of inhibitors. In our study the values **(**10.7386, 6.2086 and 3.1560 eV), Debye of PINH (o,p-OCH_3), PINH and PINH (o-Br) according to groups П, I, and Ш, enumerates its better inhibition efficiency. For Dipole moment (μ) Table 2 shows the following correlations:

Group П: PINH (o,p-OCH_3) > PINH (o-OCH_3) > PINH (p-OCH_3)

Group Ш: PINH (o -Br) > PINH (p-Br) > PINH (o,p -Br)

As a whole:

PINH (o,p-OCH_3) > PINH (o-OCH_3) > PINH > PINH (p-OCH_3) > PINH (o -Br) > PINH (p -Br) > PINH (o,p-Br).

For IE (Ionization Energy)

Ionization energy is a fundamental descriptor of the chemical reactivity of atoms and molecules. High ionization energy indicates high stability and chemical inertness and small ionization energy indicates high reactivity of the atoms and molecules [33]. The lower ionization energy (5.7020, 6.2470 and 6.2780 eV) of PINH (o.p -OCH_3), PINH and PINH (p-Br). respectively, Table 3 indicates the high inhibition efficiency. Table 3 shows the following correlations:

Group П: PINH (o,p-OCH_3) < PINH (p-OCH_3) < PINH (o-OCH_3)

Group Ш: PINH (p-Br) < PINH (o-Br) < PINH (o,p-Br)

As a whole:

PINH (o,p-OCH_3) < PINH (p-OCH_3) < PINH (o-OCH_3)< PINH < PINH (p-Br) < PINH (o-Br) < PINH (o,p–Br) .

For EA (Electron Affinity)

The highest value of electron affinity (2.8009, 2.4994 and 2.3655eV), indicates the better inhibition efficiency of PINH (o,p-Br), PINH and PINH (o-OCH_3) respectively Table 3 shows the following correlations:

Group П: PINH (o-OCH_3) > PINH (p-OCH_3) > PINH (o,p-OCH_3)

Group Ш: PINH (o,p-Br) > PINH (p-Br) > PINH (o-Br)

As a whole:

PINH (o,p-Br) > PINH (p-Br) > PINH (o-Br) > **PINH** > PINH (o-OCH_3) > PINH (p-OCH_3) > PINH (o,p-OCH_3).

For η (Hardness)

Absolute hardness and softness are important properties to measure the molecular stability and reactivity. It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap [34]. In our present study PINH (o,p-OCH_3), PINH (o,p-Br) and PINH with lowest hardness value (1.7435, 1.8009 and 1.8738eV) in comparison each with other molecules in its group, have a low energy gap. Normally, the inhibitor with the least value of global hardness (hence the highest value of global softness) is expected to have the highest inhibition efficiency [35]. Table 3 shows the following correlations:

Group П: PINH (o,p-OCH_3) < PINH **(p-OCH_3) <** PINH **(o-OCH_3)**

Group Ш: PINH **(o,p-Br) <** PINH **(p-Br) <** PINH **(o-Br)**

As a whole:

PINH (o,p-OCH_3) < PINH (p-OCH_3) < PINH (o,p-Br) < PINH (o-OCH_3) < PINH (p-Br) < PINH (o-Br) < PINH.

For S (Global softness)

For the simplest transfer of electron, adsorption could occur at the part of the molecule where softness (S), which is a local property, has a highest value **[**35], PINH (o,p-OCH_3), PINH (o,p-Br), and PINH with the softness value of (0.5735, 0.5552, and 0.5336 eV), correlates the above statement. Table 3 shows the following correlations:

Group П: PINH **(o,p-OCH_3) >** PINH **(p-OCH_3) >** PINH **(o-OCH_3)**

Group Ш: PINH **(o,p -Br) >** PINH **(p -Br) >** PINH **(o -Br)**

As a whole:

PINH **(o,p-OCH_3)** > PINH (p-OCH_3) > PINH (o,p-Br) > PINH (p-Br) > PINH (o-OCH_3) > PINH (o-Br) > **PINH.**

For χ (Electronegativity)

According to Sanderson's electronegativity equalization principle [36], PINH (o,p-OCH_3), PINH and PINH (p-Br) has a lowest value (3.9585, 4.3732, and 4.4657eV) with a high electronegativity and low difference of electronegativity quickly reaches equalization and hence low reactivity is expected which in turn indicates low inhibition efficiency. Table 3 shows the following correlations:

Group П: PINH (o,p-OCH_3) < PINH **(o-OCH_3)** < PINH **(p-OCH_3)**

Group Ш: PINH **(p-Br)** < PINH **(o-Br)** < PINH **(o,p-Br)**

As a whole:

PINH (o,p-OCH_3) < PINH (p-OCH_3) < PINH (o-OCH_3) < **PINH** < PINH (p-Br) < PINH (o-Br) < PINH (o,p-Br).

For (ω) (Global electrophilicity index)

Global electrophilicity index (ω) introduced by Parr [37], calculated using the electronegativity and chemical hardness parameters through the equation: A high value of electrophilicity describes a good electrophile while a small value of electrophilicity describes a good nucleophile [38]. In Table 3 the highest value of (ω), PINH (o-Br), PINH (o-OCH_3) and PINH. The high value (5.8794, 4.8164 and 3.0362eV) indicates the better corrosion efficiency. Table 3 shows the following correlations:

Group П: PINH **(o-OCH_3) >** PINH **(p-OCH_3) >** PINH **(o,p-OCH_3)**

Group Ш: PINH **(o-Br) >** PINH **(p-Br) >** PINH **(o,p-Br)**

As a whole:

PINH (o -Br) > PINH (p-Br) > PINH (o,p -Br) > **PINH** > PINH (o-OCH_3) > PINH (p-OCH_3) > PINH (o,p-OCH_3) .

ForΔN(Eelectron transferred)

The values of **ΔN** in the table 3 represent the number of electronic charges that will be exchanged between the surface and the adsorbed species. The greater value of (0.8722, 0.7009 and 0.6992 eV) for PINH (o,p-OCH_3), PINH and PINH (p-Br) indicates the maximum transfer of electron and hence greater inhibition efficiency. Table 3 shows the following correlations:

Group П: PINH (o,p-OCH_3) > PINH **(p-OCH_3) >** PINH **(o-OCH_3)**

Group Ш: PINH **(p-Br) >** PINH **(o-Br) >** PINH **(o,p-Br)**

As a whole:

PINH (o,p-OCH_3) > PINH (p-OCH_3) > PINH (o-OCH_3) > **PINH** > PINH (p -Br) > PINH (o-Br) > PINH (o,p-Br).

Table 3-Some of the calculated quantum parameters for studied molecules that resulted by using DFT (6-311G/ B3LYP) method.

Inhibitor Molecule	**P.G.**	**IE (eV)**	**EA(eV)**	**η (eV)**	**□ (eV)**	**ω**	**S (eV)**	**□□**
I								
PINH	**Cs**	**6.2470**	**2.4994**	**1.8738**	**4.3732**	**5.1032**	**0.5336**	**0.7009**
	C_1	**6.2473**	**2.4988**	**1.6296**	**4.3730**	**5.8674**	**0.6136**	**0.8060**
Π								
PINH (o-OCH_3)	**Cs**	**5.9841**	**2.3655**	**1.8093**	**4.1748**	**4.8164**	**0.5526**	**0.7807**
PINH (p-OCH_3)	**C_1**	**5.8143**	**2.2656**	**1.7743**	**4.0399**	**4.5992**	**0.5636**	**0.8341**
PINH (o,p-OCH_3)	**Cs**	**5.7020**	**2.2150**	**1.7435**	**3.9585**	**4.4937**	**0.5735**	**0.8722**
	C_1	**5.7017**	**2.2150**	**1.7433**	**3.9583**	**4.4938**	**0.5736**	**0.8723**
Ш								
PINH (o-Br)	**Cs**	**6.3175**	**2.6455**	**1.8360**	**4.4815**	**5.8794**	**0.5446**	**0.6858**
PINH (p-Br)	**Cs**	**6.2780**	**2.6535**	**1.8122**	**4.4657**	**5.5022**	**0.5502**	**0.6992**
PINH (o,p-Br)	**Cs**	**6.4027**	**2.8009**	**1.8009**	**4.6018**	**5.4694**	**0.5552**	**0.6658**

P.G: Point Group.

Active sites:

For the purpose of establishing the active sites of the inhibitor calculated molecules, three influencing factors: natural atomic charge, distribution of frontier molecular orbital and indices. According to classical chemical theory, all chemical interactions are either by electrostatic or orbital interactions. Electrical charges in the molecule were obviously the driving force of electrostatic interactions. It is proven that local electric densities or charges are important in many chemical reactions and physicochemical properties of compound [39].

Table 4 shows that N1, C3, C6, O8, N9, N10, C12, C15, C16, C17, C18 and C19 carrying negative charges, while C7 carries positive charges (for all the calculated PINH Schiff bases derivatives). The negative charge centers could offer electrons to the Fe atoms to form coordinate bond. The positive charge centers can accept electrons from 3d orbital of the Fe atom to form feedback bond, thus further strengthening the interaction of inhibitor and Fe surface. For group Π, O atom (of OCH_3) belonging to PINH (o-OCH_3) is more negative (-0.538) than O atom (of OCH_3) belonging to PINH (p-OCH_3) (-0.518). For group Ш -Br belonging to PINH (o,p-Br) is more negative (-0.023) at ortho position than -Br (-0.045) at para position belonging to the same molecule PINH (o,p-Br), both are more positive than Br belonging to PINH (o-Br) or PINH (p-Br). The partial charges on the individual atoms in a molecule also indicate the reactive centers for a particular inhibitor. Atoms with the highest negative charge are considered to have an electron donor role when interacting with metal surfaces. The Mulliken atomic charges for the heteroatoms of the PINH derivatives are reported in Table (4) which showed that N1 has the highest negative charge with DFT/6-311G method. The negative charge on the N1 atom increases across the structures following the order;

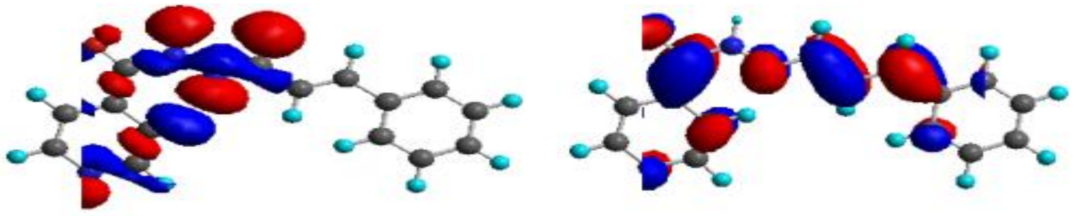
PINH (o,p-Br) > PINH (o -Br) = PINH (p-Br) > **PINH (o,p-OCH_3) =** PINH (o-OCH_3) > **PINH =** PINH (p-OCH_3)

Table 4-DFT (6-311G/ B3LYP) Mulliken charges population analysis for the calculated PINH Schiff bases molecules.

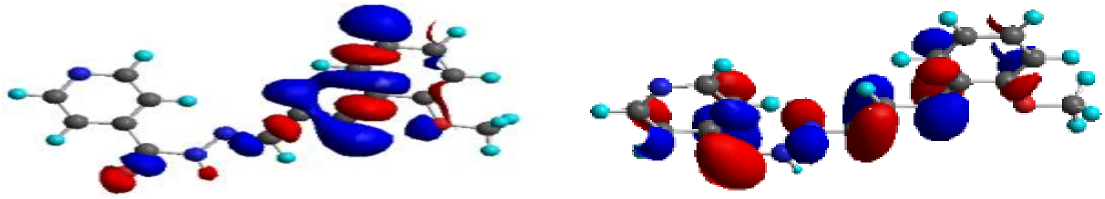
Atom	**Electronic charge**						
	PINH	**PINH o-OCH_3**	**PINH p-OCH_3**	**PINH o,p-OCH_3**	**PINH o -Br**	**PINH p -Br**	**PINH o,p-Br**
N1	-0.327	-0.328	-0.327	-0.328	-0.504	-0.504	-0.505
C2	0.004	0.004	0.000	0.003	-0.445	-0.446	-0.445
C3	-0.191	0.192	-0.160	-0.192	-0.139	-0.137	-0.138
C4	-0.112	-0.113	-0.109	-0.114	1.168	1.167	0.167
C5	-0.074	-0.074	-0.161	-0.074	0.020	0.022	0.022
C6	-0.029	-0.030	-0.014	-0.030	-0.496	-0.497	-0.496
C7	0.554	0.554	0.553	0.554	0.207	0.205	0.206
O8	-0.406	-0.409	-0.364	-0.412	-0.386	-0.386	-0.384
N9	-0.594	-0.594	-0.571	-0.594	-0.607	-0.606	-0.606
N10	-0.153	-0.156	-0.113	-0.161	-0.358	-0.359	-0.355
C11	0.011	0.012	0.003	0.012	-0.177	-0.167	-0.182
C12	-0.128	-0.125	-0.129	-0.131	-0.085	-0.102	-0.088
C13	-0.196	-0.138	-0.187	-0.134	0.292	0.338	0.295
C14	-0.023	-0.071	-0.016	-0.059	0.716	0.255	0.664
C15	-0.168	0.196	0.081	0.203	-0.360	-0.373	-0.481
C16	-0.163	-0.155	-0.180	-0.197	-0.120	-0.018	0.141
C17	-0.120	-0.123	0.261	0.271	-0.481	-0.513	-0.671
C18	-0.171	-0.153	-0.176	-0.166	-0.475	-0.029	-0.093
C19	-0.080	-0.090	-0.161	-0.080	-0.167	-0.196	-0.292
H2	0.175	0.174	0.181	0.173	0.197	0.197	0.198
H3	0.199	0.198	0.198	--------	0.192	0.192	0.193
H5	0.219	0.219	0.169	0.197	0.211	0.211	0.211
H6	0.172	-------	-------	0.220	0.191	0.192	0.192
H9	0.318	0.317	0.316	0.316	0.342	0.341	0.343
H11	0.150	0.150	0.134	0.147	0.169	0.165	0.169
H12	0.184	0.179	0.180	0.177	0.191	0.193	0.191
H13	0.158	0.184	0.152	0.180	0.202	0.178	0.203
H15	0.158	-------	0.165	-------	--------	0.178	---------
H16	0.156	0.175	0.174	0.204	0.189	0.190	0.196
H17	0.158	0.154	--------	-------	0.184	--------	--------
H18	0.155	0.154	0.172	0.173	0.189	0.191	0.194
H19	0.163	0.159	0.155	0.159	0.182	0.181	0.188
o-$\underline{OC}H_3$	-------	-0.538 -0.291	-------	-0.539 -0.290	--------	--------	--------
p-$\underline{OC}H_3$	-------	-------	-0.518 -0.293	-0.519 -0.293	---------	---------	--------
o-Br	-------	-------	-------	-------	-0.042	--------	-0.023
p-Br	-------	-------	-------	-------	---------	-0.063	-0.045

This result is consistent that the pyridine ring is higher effect as an electron withdrawing than Br atom, so it decreases the negative charge on the Br atom at the para or ortho position in (PINH –o,p Br), on the other hand the (-OCH_3) group is an electron donating role, so it increases the negative charge of N atom of pyridine ring in (PINH –OCH_3) molecule.

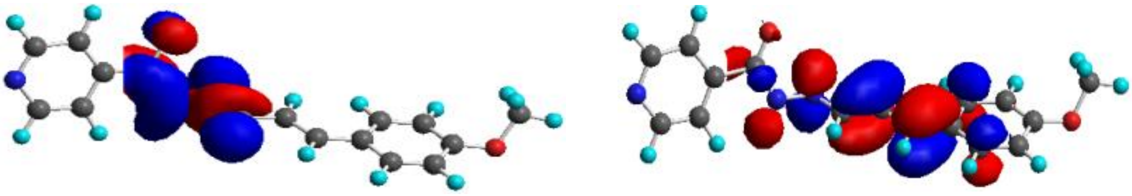
Figure 3 shows the frontier molecule orbital density distributions of (PINH) Schiff derivatives HOMO; LUMO.



HOMO **PINH** **LUMO**

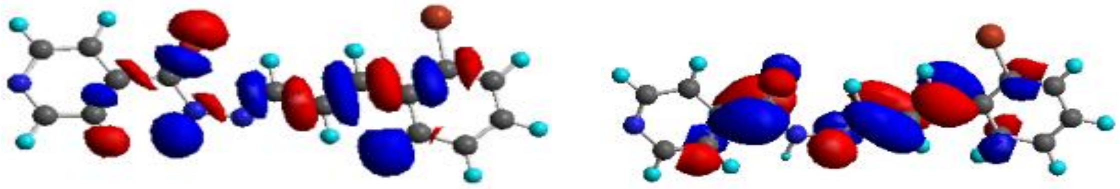


HOMO **PINH (o-OCH$_3$)** **LUMO**

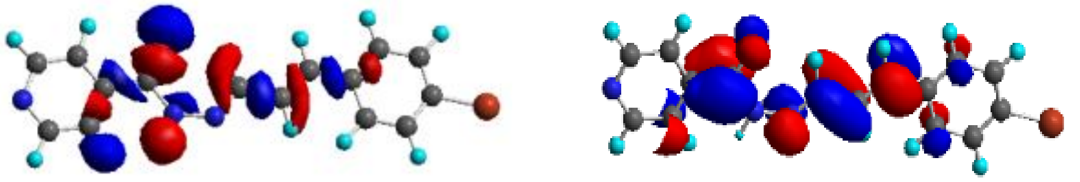


HOMO **PINH (p-OCH$_3$)** **LUMO**

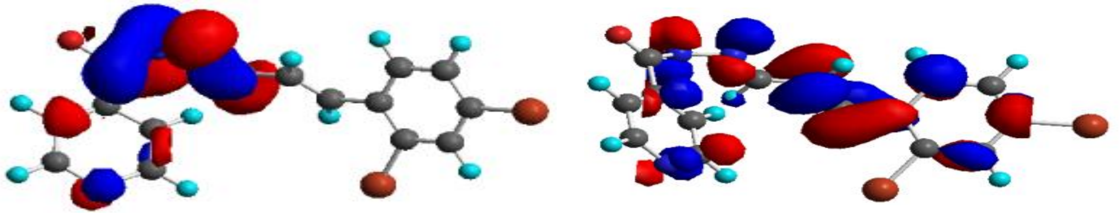
HOMO **PINH (o,p-OCH$_3$)** **LUMO**



HOMO **PINH (o-Br)** **LUMO**



HOMO **PINH (p-Br)** **LUMO**



HOMO **PINH (o,p-Br)** **LUMO**

Figure 3-The frontier molecule orbital density distributions of (**PINH**) derivatives HOMO; LUMO.

Infrared spectra (IR):

DFT (B3LYP/ 6-311G) calculations have carried out for the estimation of vibration frequencies, and normal coordinates for the calculated Schiff bases molecules, The results were compared with the experimental measured values [40 - 42]. The stretching vibration frequency of N-H bond due to amide group was found to have values range of (3456-3489 cm^{-1}), for aromatic C-H stretching (3209-3228 cm^{-1}), for aliphatic C-H stretching (2995-3184 cm^{-1}), for δCH scissoring (1215-1527 cm^{-1}), for amide C=O stretching, (1646-1669 cm^{-1}) for aliphatic C=C stretching (1670-1682 cm^{-1}), for aromatic C--C stretching (1608-1644 cm^{-1}), for C-C-C stretching vibration (phenyl ring) (1597-1641 cm^{-1}), for N-N stretching (1011-1167cm^{-1}).

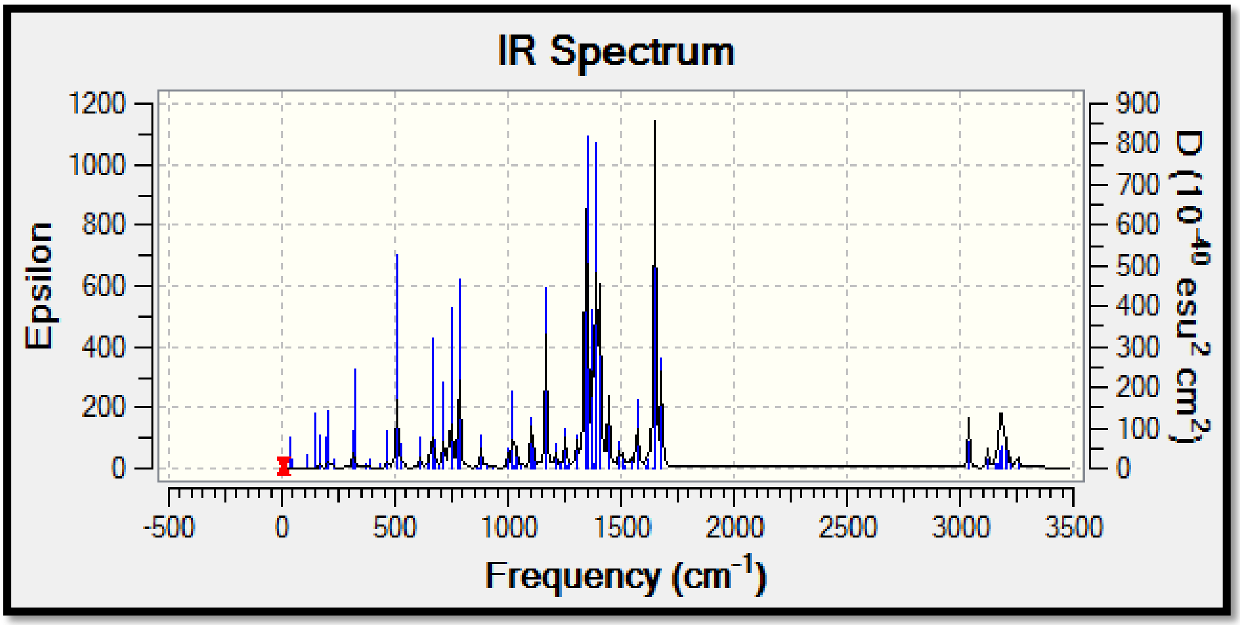
Table 5 shows values of some calculated vibration frequencies and IR absorption intensities for PINH molecule using DFT (B3LYP/ 6-311G) method, Scheme 1. shows the IR spectra for PINH molecule as calculated by DFT method, and figure 4. shows some modes of vibration frequencies for [(phenylallylidene) isonicotinohydrazide],using Gaussian 2005 view program.

Table 5-DFT vibration frequencies and IR absorption intensities for the studied **PINH** Schiff base molecule.

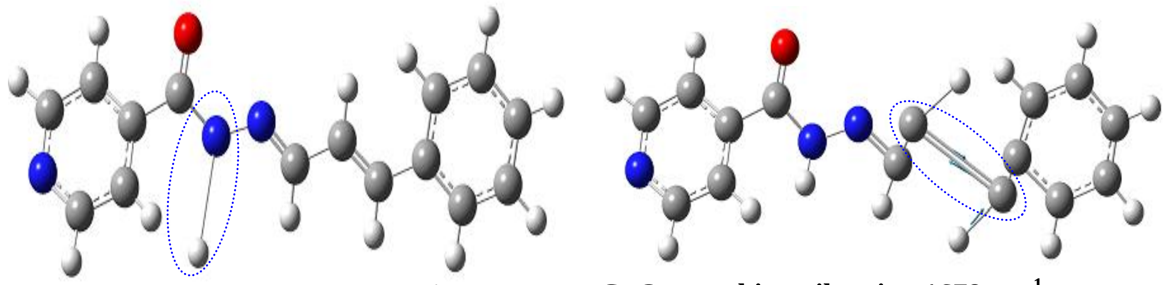
	Description	**PINH**		**Exp. [40-42]**
		Frequency cm^{-1}	**Intensity km/mol**	**Frequency cm^{-1}**
In plane of the molecule				
A_1'				
ν_1	N-H str. (amide)	3457	1.928	3450
ν_2	C-H sym. str. (pyridine ring)	3126	17.058	-------
ν_3	C-H asym. str.(pyridine ring)	3049-3093	6.904–36.173	-------
ν_4	CH sym str. (phenyl ring)	3073	35.304	3062
ν_5	C-H asym. str. (phenyl ring)	3034-3061	9.6925–41.518	-------
ν_6	CH asym. str. (phenyl ring)	3039-3044	6.5232–10.723	-------
ν_7	C9-H str.	2995	18.737	2975
ν_8	C_7-H str.	2915	48.824	2907
ν_9	C=C str.	1678	114.497	1610
ν_{10}	C=O str.	1648	329.388	1663
ν_{11}	C-C-C str.(phenyl ring)	1641	2.930	1645
ν_{12}	C-C str. (pyridine .ring) & C_7-N str.	1625	4.021	1627
ν_{13}	C_7-N str. + C-C str. (phenyl ring)	1608-1617	1.829–8.777	1600
ν_{14}	(C-C-N) str. (pyridine ring)	1570	16.840	1570
ν_{15}	δCH sym. (rocking ph. ring)	1392-1543	10.431–275.945	------
ν_{16}	δCH sym. (rocking pyridine ring)	1374-1521	1.441–135.128	------
ν_{17}	δCH scissoring	1511	14.798	------
ν_{18}	δCH asym. (rocking pyridine ring)	1494	24.598	------
ν_{19}	δCH sym. scissoring (pyridine ring)	1444	14.888	------
ν_{20}	δNH + δCH	1408	158.829	------
ν_{21}	C-N str. & δCH	1347	.275.945	------
ν_{22}	δCH scissoring	1307-1342	25.948–131.435	------
ν_{23}	C-C-N str. (pyridine ring str.)	1267	12.903	------
ν_{24}	δCH (pyridine ring)	698-1252	1.601–0.478	------
ν_{25}	δ(phenyl ring)	1262	2.451	------
ν_{26}	δC-H sym. scissoring (phenyl ring)	1213-1230	0.266-4.242	------
ν_{27}	δmolecule	34–1379	0.659–4.338	------
ν_{28}	N-N str. & δC-H (pyridine ring)	1167	130.162	------
ν_{29}	δC-H sym. scissoring (pyridine ring)	1119	4.227	------
ν_{30}	δC-H asym. rocking (phenyl ring)	1113	18.140	------
ν_{31}	δPyridine ring	1102	34.657	------
ν_{32}	δCH asym. rocking (phenyl ring)	1054	2.975	------

ν_{33}	δCCC (phenyl ring)	1028	0.564	------
ν_{34}	δC=O & δC-N	663	52.976	------
ν_{35}	δCH sym. rocking (phenyl ring) & δC=O	613	11.729	------
ν_{36}	δC=C--C=N-N & γCH (phenyl ring)	432	1.227	------
ν_{37}	δmolecule	228	1.330	------
Out of plane of the molecule				
A_1''				
ν_{38}	γCH asym. twisting (pyridine ring)	1031-1037	1.691–5.696	------
ν_{39}	γCH asym. twisting (phenyl ring)	1004-1035	0.073–4.692	------
ν_{40}	γCH sym. wagging γCH (phenyl ring)	1025	48.512	------
ν_{41}	γCH asym. twisting	972.98	0.271	------
ν_{42}	γCH (phenyl ring) & γCH (aliphatic)	957	0.013	925
ν_{43}	γCH asym. wagging (pyridine ring)	931	0.000	-------
ν_{44}	γCH sym. twisting (phenyl ring) & γCH	907	1.423	-------
ν_{45}	γCH sym.wagging (sym. pyridine ring)	780-879	18.415–24.381	840-880
ν_{46}	γCH wagging (phenyl ring)	716-785	37.752–91.403	-------
ν_{47}	γCH wagging asym. (phenyl ring)	869	0.056	-------
ν_{48}	γNH & γpyridine ring	676	2.519	660
ν_{49}	γCCC (phenyl ring)	532	7.859	-------
ν_{50}	γCCN (pyridine ring) + γC=O + γC-N	467	10.860	-------
ν_{51}	γCCN (pyridine ring)	396	0.004	------
ν_{52}	γC=C--C=N-N & γCH (phenyl ring)	367	1.227	------
ν_{53}	γmolecule	206	7.367	------
ν_{54}	γC--C-N (aliphatic)	144	4.974	------
ν_{55}	γC=C	90	0.015	------

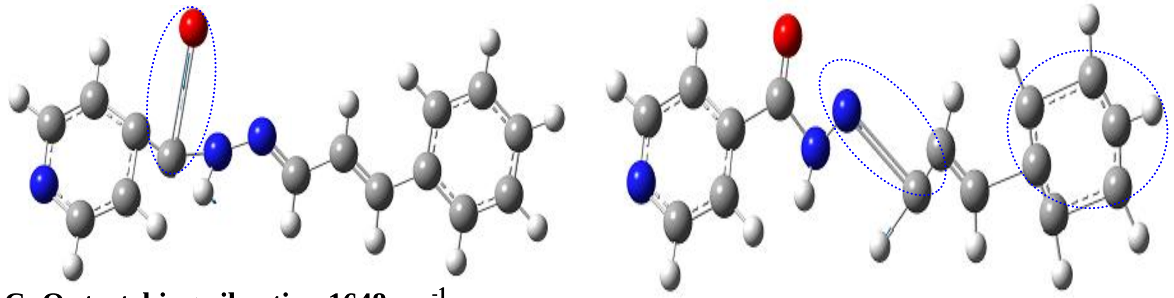
γ: out of plane bending vibration., δ:in-plane bending vibration.



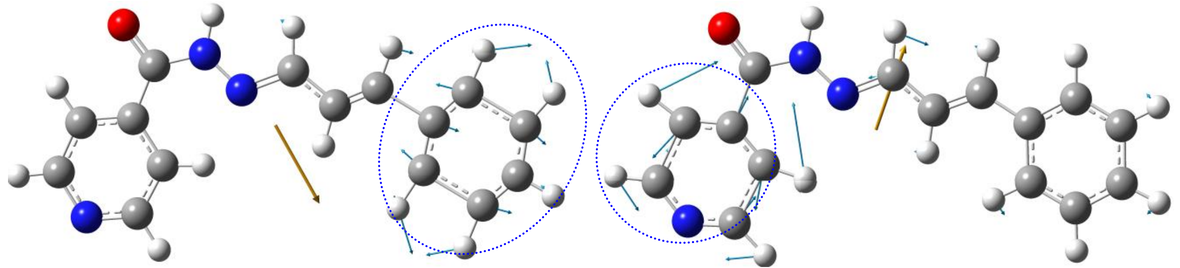
Scheme 1-IR spectra for PINH molecule as calculated by DFT method.



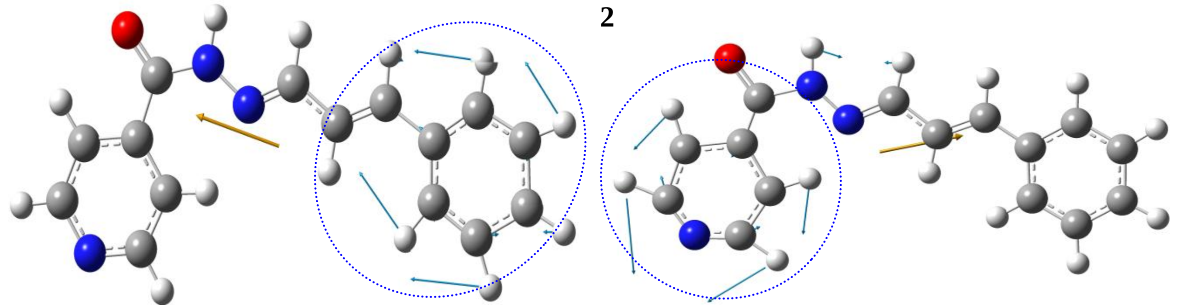
N-H stretching vibration 3457 cm^{-1} **C=O stretching vibration 1678 cm^{-1}**



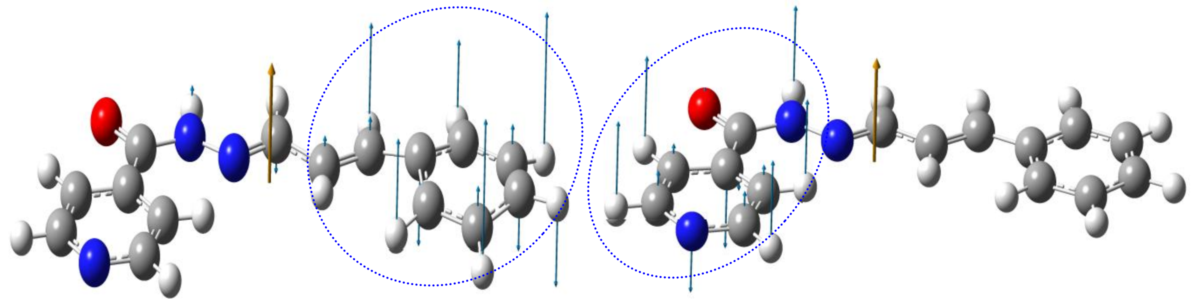
C=O stretching vibration 1648 cm^{-1} **C=N and C—C phenyl ring str. Vib. 1617 cm^{-1}**



C--C phenyl ring stret. vibration 1641 cm^{-1} **C--C pyridine ring stretching vib. 1625 cm^{-1} 2**



δC-H in plane phenyl ring 1543 cm^{-1} **δC-H in plane pyridine ring 1521 cm^{-1}**



γCCC phenyl ring bending vibration 532 cm^{-1} **γCCC pyridine ring bending vibration 467 cm^{-1}**

Figure 4. Some modes of vibration frequencies for **PINH** Schiff base molecule calculated by DFT method..

Conclusion.

1. The inhibition efficiency of the calculated INHC Schiff bases derivatives using DFT quantum mechanical method increase with increasing E_{HOMO}, μ, EA, **ω**, S, ΔN and with decrease in E_{LUMO}, energy gap ($\Delta E_{HOMO-LUMO}$), IE, η, and χ. For these efficiency parameters it was found that PINH (o,p-OCH_3) has the best inhibition efficiency parameters among group П, and PINH (p-Br) has the best inhibition efficiency parameters among group Ш, and both of them has the best inhibition efficiency parameters among group I (PINH), so for the inhibition efficiency parameters, the PINH Schiff bases derivatives may be confirms in the order of;

PINH (o,p-OCH_3) > PINH (o,p-Br) > PINH

2. Quantum chemical study for calculating the main positive and negative active sites (according to the charge type) which indicate the position of adsorption of PINH Schiff bases derivatives on the mineral surface shows that the positive active sites are located at (C2 and C7) atoms, whereas negative active sites are located at (C5, C6, O8, N9, N10, C12, C16 and C18) atoms.

3- Symmetry can be fixed as an additional important efficiency parameter. The calculated molecules with highest symmetry (Cs) gives better inhibition efficiency than that have lower symmetry (C_1), through increasing the planarity of adsorption on the metal surface.

4- DFT (B3LYP/ 6-311G) calculations of vibration frequencies and IR absorption intensities for PINH Schiff bases derivatives molecule gave a very good assignment values in comparison with experimental values.

References.

1. Eddy, N.O. and Odoemelam, S.A. **2008**. Ethanol Extract of Musa acuminate peel as an eco-friendly inhibitor for the corrosion of mild steel in $H_2 SO_4$. *Adv. Nat. & Appl. Sci.* 2, pp: 35-42.

2. Umoren, S.A. Obot, IB. Ebenso, EE. and Obi-Egbedi, NO. **2008**. Synergistic Inhibition between Naturally Occurring Exudate Gum and Halide Ions on the Corrosion of Mild Steel in Acidic Medium. Int. *J. Electrochem. Sci.* 3(9): pp: 1029-1043.

3. Abd El-Rehim, S.S. Ibrahimand M.A.M. and Khaled, F.F.J. **1999**. 4-Aminoantipyrine as an inhibitor of mild steel corrosion in HCl solution. *Appl. Electrochem.* 29, pp: 593-599.

4. Wang, H.L. Liu, R.B. and Xin, J. **2004**. Inhibiting effects of some mercapto-triazole derivatives on the corrosion of mild steel in 1.0 M HC1 medium. *Corros. Sci.* 46(10):pp: 2455–2466

5. Rengamati, S. Muralidharan, S. Anbu Kulamdainathan M. and Venkatakrishna Iyer, S. **1994**. Inhibiting and accelerating effects of aminophenols on the corrosion and permeation of hydrogen through mild steel in acidic solutions. *J. Appl. Electrochem.* 24, pp: 355-360.

6. Ebenso ,E.E. **2003**. Effect of halide on the corrosion inhibition of steel in H_2SO_4 using methyl red-Part 1. *Bull. Electrochem.* 19(5): pp: 209-216.

7. Khalil, N. **2003**, Quantum chemical approach of corrosion inhibition. *Electrochim. Acta.* 48(20): pp: 2635–2640.

8. Granese, S.L. **1988**. Study of the Inhibitory Action of Nitrogen-Containing Compounds. *Corrosion: June*. 44(6): pp: 322-327.

9. Wang, D. Li, S. ing, Y.Y Wang, M. Xiao, H. and Chen, Z. **1999**. Theoretical and experimental studies of structure and inhibition efficiency of imidazoline derivatives. *Corros. Sci.* 41, pp: 1911-1919.

10. Vosta, J. and Eliasek, J. **1971**. Study on corrosion inhibition from aspect of quantum chemistry. *Corros. Sci.* 11, pp: 223-229.

11. Choa, P. Liang, Q. and Li, Y. **2005**. Electrochemical, SEM/EDS and quantum chemical study of phthalocyanines as corrosion inhibitors for mild steel in 1 mol/l HCl. *Appl. Surf. Sci.* 252, pp: 1596-1607.

12. Xiao-Ci, Y. Hong, Z. Ming-Dao, L. Hong-Xuang R. and Lu-An, Y. **2000**. Quantum chemical study of the inhibition properties of pyridine and its derivatives at an aluminum surface *Corrosion Science.* 42, pp: 645-653.

13. Bentiss, F. Lebrini, M. and Lagrenée, M. **2005**. Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/2,5-bis(n-thienyl)-1,3,4-thiadiazoles/hydrochloric acid system. *Corrosion Science.* 47(12): pp: 2915–2931.

14. Issa, R. M. Awad, M. K. and Atlam, F. M. **2008**. Quantum chemical studies on the inhibition of corrosion of copper surface by substituted uracils. *Appl. Surf. Sci.* 255(5): pp: 2433–2441.

15. Hohenberg, P. and Kohn, W. **1964**. Inhomogeneous Electron Gas. *Phys. Rev.* 136, pp: B864-B871

16. Parr, R.G. and Yang, W. **1989**. *Density Functional Theory of Atoms and Molecules.* 1ST Ed., Oxford University Press: New York,

17. Cohen, M.H. Nalewajski R.F. **1996**. *In Topics in Current Chemistry*. Ed.; Springer-Verlag: Heidelberg, Germany. 183, pp: 143.

18. Sanderson, R.T. **1952**. An Interpretation of Bond Lengths in Alkali Halide Gas. *Molecules J. Am. Chem. Soc.* 74(1): pp: 272-274.

19. Ahamad, I. Prasad, R. and Quraishi, M.A. **2010**. Thermodynamic electrochemical and quantum chemical investigation of some Schiff bases as corrosion inhibitors for mild steel in hydrochloric acid solutions. *Corrosion Science.* 52 , pp:933–942

20. Frisch, M.J. Trucks, G.W. Schlegel, H.B. Scuseria, G.E. Robb,M.A. Cheeseman, J.R. Montgomery, J.A. Jr., Vreven, T. Kudin, K.N. Burant, J.C. Millam, J.M. Iyengar, S.S. Tomasi, J. Barone, V. Mennucci, B. Cossi, M. Scalmani, G. Rega, N. Petersson, G.A. Nakatsuji, H. Hada, M. Ehara, M. Toyota, K. Fukuda, R. Hasegawa, J. Ishida, M. Nakajima, T. Honda, Y. Kitao, O. Nakai, H. Klene, M. Li, X. Knox, J.E. Hratchian, H.P. Cross, J.B. Bakken, V. Adamo, C. Jaramillo,J. Gomperts, R. Stratmann,R. E. Yazyev, O.Austin, A.J. Cammi,R. Pomelli,C Ochterski, J.W. Ayala, P.Y. Morokuma, K. Voth, G.A. Salvador, P. Dannenberg, J.J. Zakrzewski, V.G. Dapprich, S. Daniels, A.D. Strain, M.C. Farkas, O. Malick, D.K. Rabuck, A. D. Raghavachari, K Foresman, J. B. Ortiz,J. V Cui, Q. Baboul, A. G. Clifford, S. Cioslowski, J. Stefanov, B.B. Liu, G. Liashenko, A. Piskorz, P. Komaromi, I. Martin, R.L. Fox, D.J. Keith, T. Al-Laham, M.A. Peng, C.Y. Nanayakkara, A. Challacombe, M. Gill, P.M. W. Johnson B. Chen, W. Wong, M.W. Gonzalez, C.and Pople, J.A. **2003.** *Gaussian 03,* Gaussian. Inc. Pittsburgh PA.

21. Rodriguez-Valdez L., Martinez-Villafane A., Glossman- Mitnik D., **2005** “CHIH-DFT theoretical study of isomeric thiatriazoles and their potential activity as corrosion inhibitors”, *J. Mol. Struct. (THEO CHEM).* 716: pp 61-65.

22. Lashkari M. and Arshadi, M.R.**2004** "DFT studies of pyridine corrosion inhibitors in electrical double layer; Solvent, substrate and electric field effects", *Chem. Phys.* 299: pp 131-138.

23. Parr,R.G. Donnelly,R.A. Levy,M. and Palke,W.E. **1978**. Empirical evaluation of chemical hardness. *J. Chem. Phys.* 68, pp: 3801-3807.

24. Parr, R.G. and Pearson, R.G. **1983**. Absolute hardness: companion parameter to absolute electronegativity. *J. Am. Chem. Soc.* 105, pp: 7512-7516.

25. Koopmans, T. **1933**. Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms. *Physica.* 1, pp: 104-113.

26. Rauk, A. **2001**. *Orbital interaction Theory of Organic Chemistry*. 2nd Ed, John Wiley & Sons:NewYork.

27. Pearson R.G., **1988**. Absolute electronegativity and hardness: application to inorganic chemistry. *Inorganic Chemistry*. 27(4): pp: 734–740.

28. Chermette, H. 1999. Chemical Reactivity Indexes in Density Functional Theory. *J. Comput. Chem.* 20, pp: 129-154.

29. Wang, H. Wang, X. Wang, H. Wang L. and Liu, A. **2007**. DFT Study of New Bipyrazole Derivatives and Their Potential Activity as Corrosion Inhibitors. *Journal of Molecular Modeling.* 13(1): pp: 147-153.

30. Obot, B. Obi-Egbedi N. O and Umoren S.A **2009**. Adsorption characteristics and corrosion inhibitive properties of clotrimazole for aluminium corrosion in hydrochloric acid. *Int. J. Electrochem. Sci.* 4, pp: 863-877.

31. Fleming, I. **1976**. *Frontier Orbitals and Organic Chemical Reactions.* John Wiley and Sons, NewYork.

32. Li, X. Deng, S. Fu,H. and Li, T. **2009**. Adsorption and inhibition effect of 6-benzylaminopurine on cold rolled steel in 1.0 M HCl. *Electrochimica Acta.* 54(16): pp: 4089–4098.

33. Sandip K. Rajak, Nazmul Islam and Dulal C.Ghosh, **2011**. Modeling of the Chemico-Physical Process of Protonation of Molecules Entailing Some Quantum Chemical Descriptors. *J. Quantum information Science,* 1, pp: 87-95.

34. Obi-Egbedi, N.O. Obot, I.B. El-Khaiary, M.I. Umoren S.A. and Ebenso, E.E. **2011**. Computational Simulation and Statistical Analysis on the Relationship between Corrosion

Inhibition Efficiency and Molecular Structure of Some Phenanthroline Derivatives on Mild Steel Surface. *Int. J. Electro Chem. Sci.*,6(11): pp: 5649-5675

35. Ebenso, E.E. Isabirye, D. A. and Eddy, N.O. **2010**. Adsorption and quantum chemical studies on the inhibition potentials of some thiosemicarbazides for the corrosion of mild steel in acidic medium. *Int. J. Mol. Sci*, 11(6): pp: 2473–2498.

36. Sanderson, R.T. **1988**. Principle of electronegativity. Part I. General nature. *J. Chem. Educ. Soc.* 65(2): pp: 112-118.

37. Parr, R.G. Szentpaly L.V. and Liu, S. **1999**. Electrophilicity Index. *J. Am. Chem. Soc*.121 (9): pp: 1922-1924.

38. Hasanov, R. Sadikglu, M. and Bilgic S. **2007**. Electrochemical and quantum chemical studies of some Schiff bases on the corrosion of steel in H_2SO_4 solution. *Appl. Surf. Sci.* 253(8): pp: 3913-3921.

39. Karelson, M. Lobanov, V.S. **1996**. Quantum descriptors in QSAR/QSPR studies, *Chemical Reviews.* . 96, PP: 1027-1043.

40. Silverstein, R.M. **1981** . *Spectrophotometric identification of organic compounds.* 4th Ed. John Wiley, New York

41. Scozzafava, A. Menabuoni , L. Mincione, F. Mincione,G. and Supuran ,C.T. **2001**. Carbonic anhydrase inhibitors: synthesis of sulfonamides incorporating dtpa tails and of their zinc complexes with powerful topical antiglaucoma properties. *Bioorganic and medicinal chemistry Letters*.11(4): pp -575-582

42. K. Nakamoto, **1978**. The *infrared spectra of inorganic and coord. Compounds,* 3rd Ed., New York, wiley interscience.