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DFT, PM3, AM1, and MINDO/3 Quantum Mechanical Calculations for Some INHC 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 and semiemperical methods (PM3, AM1, and MINDO/3) were performed on six new substituted Schiff bases derivatives of INHC (N-(3-(phenylidene-allylidene) isonicotinohydrazide) using Gaussian-03 program. The calculated quantum chemical parameters correlated to the inhibition efficiency were studied and discussed at their equilibrium geometry and their correct symmetry (Cs). Comparisons of the order of inhibition efficiency of the Schiff bases derivatives, and local electrophilic and nucleophilic reactivity have analyzed. Some physical properties also were studied such as heat of formation, total energy and dipole moment...etc. Also vibration frequencies and IR absorption intensities were carried out for the calculated Schiff bases molecules.

Keywords: Corrosion inhibition, Schiff bases, Vibrational frequencies.

حسابات ميكانيك الكم DFT وPM3 و AM1 و MINDO/3 لبعض قواعد شف المشتقة من المركب INHC ذات التماثل C_s كمثبطات تأكل للحديد المطاوع

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الخلاصة

تم استخدام حسابات ميكانيك الكم العائدة لنظرية دوال الكثافة DFT الأساسية عند عناصر قاعدة-6 311G وباسلوب B3LYP وللحسابات التقريبية (PM3 و AM1 وMINDO/3)، وباستخدام برنامج Gaussian-03 لست من قواعد شف الجديدة المشتقة من المركب INHC (N-(3-(phenylidene-allylidene) isonicotinohydrazide). وتم حساب ومناقشة معاملات ميكانيك الكم المرتبطة بدراسة كفاءة هذه المركبات كمثبطات تاكل عند الشكل الهندسي التوازني وعند التماثل الصحيح لهذه الجزيئات (Cs). كذلك تمت مقارنة كفاءة التبيط لمشتقات قواعد شف مع تعيين مواقع الامتزاز الفعالة الباحثة عن الالكترونات والباحثة عن النواة مع دراسة بعض الصفات الفيزياوية كحرارة التكوين والطاقة الكلية وعزم ثنائي القطبين...الخ. كما تم حساب وتصنيف ترددات اهتزاز طيف الأشعة تحت الحمراء لقواعد شف المحسوبة.

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Introduction

Corrosion of metals is a major industrial problem that has attracted many investigation and researches [1,2]. The use of inhibitors is one of the most practical methods to protect metals against corrosion, especially in acidic media [3]. Most efficient inhibitors are organic compounds containing electronegative functional groups and π-electrons in triple or conjugated double bonds. Researchers conclude that the adsorption on the metal surface depends mainly on the physicochemical properties of the inhibitor group, such as the functional group, molecular electronic structure, electronic density at the donor atom, p orbital character and the molecular size [4-6]. 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 [7,8].

Quantum chemical methods have proved to be a very powerful tool for studying corrosion inhibition mechanism [9-12]. Density functional theory (DFT) [13,14] has provided a very useful framework for developing new criteria for rationalizing, predicting, and eventually understanding many aspects of chemical processes [15-19]. A variety of chemical concepts which are now widely used as descriptors of chemical reactivity, e.g., electronegativity hardness or softness quantities etc., appear naturally within DFT. The Fukui function [18] represents the relative local softness of the electron gas, measures the local electron density/population displacements corresponding to the inflow of a single electron. The reactive ability of the inhibitor is closely linked to their frontier molecular orbital (FMO), including highest occupied molecular orbital, HOMO, and lowest unoccupied molecular orbital, LUMO, and the other parameters such as hardness and softness. Quantum chemical studies have been successfully performed to link the corrosion inhibition efficiency with molecular orbital (MO) energy levels for some kinds of organic compounds [20,21].

The objective of this study is to present theoretical study on the adsorption, electronic and molecular structures of nine new Schiff bases molecules derivatives of INHC (N-(3-(phenylidene-allylidene) isonicotinohydrazide), which have prepared and studied experimentally and theoretically with three other Schiff bases compounds as corrosion inhibitors for mild steel in acid solutions [22], INHC was shown to have the best inhibition efficiency in comparison to others three different Schiff bases compounds, (without mentioning the method of calculation and without any mention to the symmetry of the calculated molecules).

Recalculated of the INHC Schiff base were done using DFT method taking into account the correct symmetry one time (Cs) and without symmetry (C1) in other time, comparison were done between them finding that the better as an inhibitor is of Cs symmetry [group **I**]. For finding a better corrosion inhibitor than INHC, a groups of electron donor (o-CH_3 , p-CH_3 and o,p-CH_3) [group Π] and a groups of electron withdrawing (o-Cl , p-CL and o,p-Cl) [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 using DFT at the B3LYP/ 6-311G method, taking in to account the correct symmetry of molecules. The molecules for [group **Π**] are N-(3-(2-methyl phenylidene-allylidene) isonicotinohydrazide (INHC o-CH_3), N-(3-(4-methyl phenylidene-allylidene) isonicotinohydrazide (INHC p-CH_3), N-(3-(2,4-dimethyl phenylidene-allylidene) isonicotinohydrazide (INHC o,p-CH_3), and the molecules for [group Ш] are N-(3-(2- chloro phenylidene-allylidene) isonicotinohydrazide (INHC o-Cl) and N-(3-(4- chloro phenylidene-allylidene) isonicotinohydrazide -chloro (INHC p-Cl), N-(3-(2,4-di chloro phenylidene-allylidene) isonicotinohydrazide (INHC o,p-Cl), Figure-1 shows the structures of the calculated INHC Schiff bases molecule, and new six of its derivatives drawing by using the Mopac (Ultra Chem. Draw 2003).

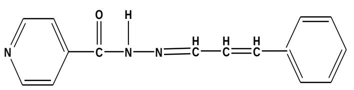
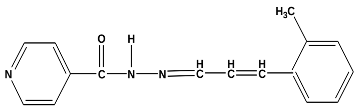
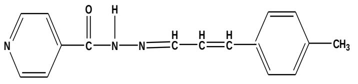
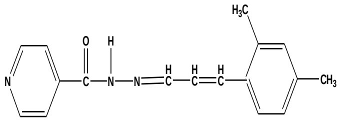
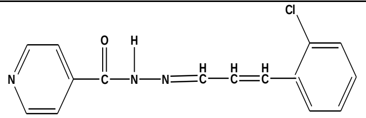
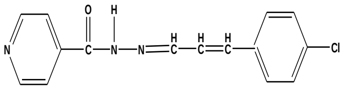
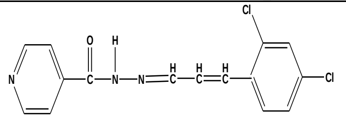
		
	INHC	
		
INHC (o-CH_3)	**INHC (p-CH_3)**	**INHC (o,p–CH_3)**
		
INHC (o-Cl)	**INHC (p-Cl)**	**INHC (o,p-Cl)**

Figure 1-Chemical structures of the calculated derivatives of the INHC Schiff bases molecule.

Computational Details

All the quantum chemical calculations were performed with complete geometry optimizations using Gaussian-03 software package [23]. Geometry optimization were carried out by B3LYP functional at the 6-311G basis set and at the density functional theory (DFT) method B3LYP functional is obtained by adding gradient corrections to the LDA method specifically the exchange correction of Becke [24] and the correlation function of Lee et al. [25].

In order to make computation less cumbersome, solvent and charge effects were neglected. This is because when being compared, they are subjected to identical conditions and the overall effect will be the same and virtually cancel out. 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 ones such as Fukui function F(r) 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 [26].

x (Electronegativity)**= $-\mu= -(\partial E/N)\nu(r)= (IE + EA)/ 2$** (1)

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 [27].

η (Hardness) = **(Hardness) = $(\partial^2E/\partial N^2)\nu(r)$ η = (IE - EA)/2** (2)

According to Koopman's theorem [28] the ionization potential (IE) and electron affinity (EA) of the inhibitors are calculated using the following equations and hence x and η are calculated.

IE (Ionization potential**) = $-E_{HOMO}$** (3)

EA (Electron affinity) **= $-E_{LUMO}$** (4)

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 [29].

x = (IE + EA)/ 2 (5)

η = (IE - EA)/ 2 (6)

The global softness (S) is the inverse of the global hardness [27]

S (global softness) = 1/ η (7)

Global electrophilicity index **(ω) = $-x^2/2\eta = \mu^2/2\eta$** (8)

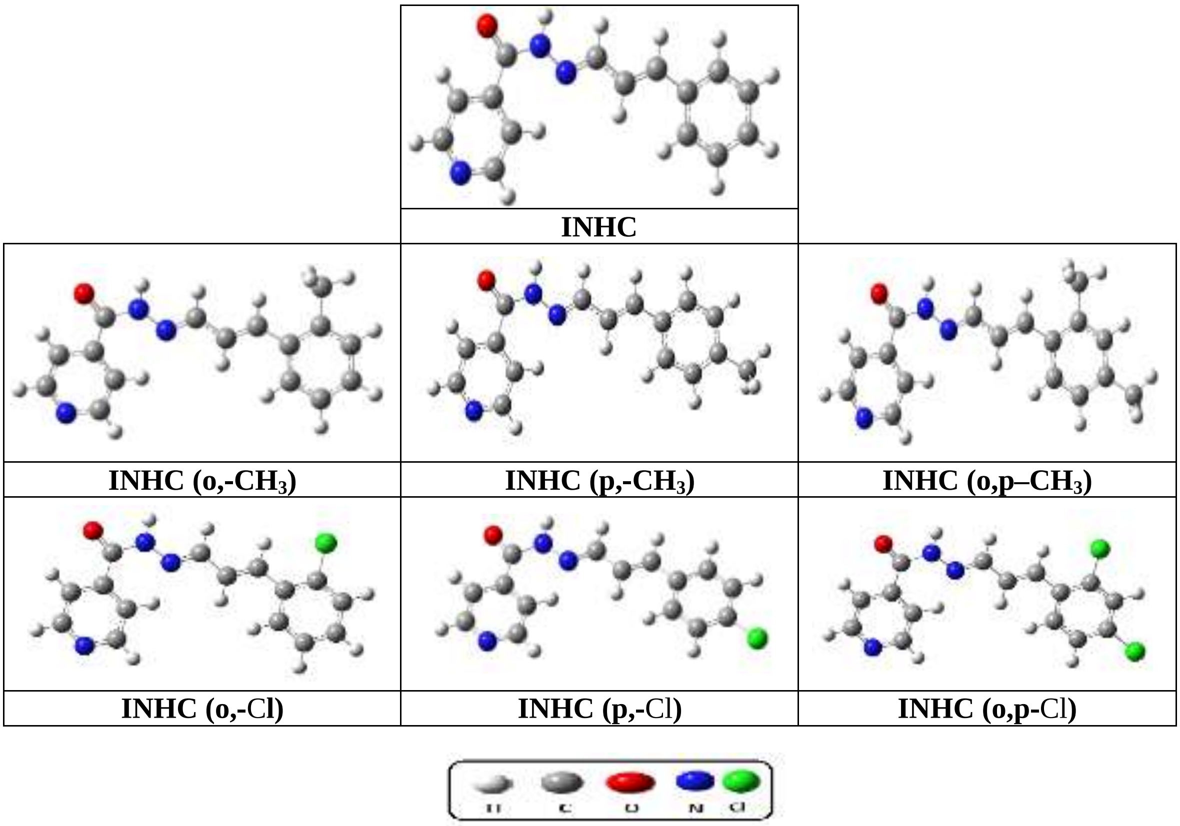
When two systems, Fe and inhibitor, are brought together, electrons will flow from lower x (inhibitor) to higher x (Fe), until the chemical potentials become equal. The number of transferred electrons (ΔN) was also calculated [29] by using the equation below.

ΔN (Electron transferred) = $(\chi_{Fe} - \chi_{inhib.})/[2(\eta_{Fe} + \eta_{inhib.})]$ (9)

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[30]. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance [31].

Results and Discussion

Figures-2 shows the equilibrium geometries of these Schiff bases molecules calculating by using DFT (B3LYP/ 6-311G) method.



INHC

INHC (o,-CH$_3$) **INHC (p,-CH$_3$)** **INHC (o,p–CH$_3$)**

INHC (o,-Cl) **INHC (p,-Cl)** **INHC (o,p-Cl)**

Figure 2-Optimize structure of the calculated derivatives of the INHC Schiff bases molecule calculated by DFT (6-311G/ B3LYP) method using Gaussian 05 program.

Optimize geometries were shown that all the calculated molecules were planar with Cs symmetry, Table-1 has listed bond lengths that have resulted from optimized structures of INHC Schiff bases derivatives as calculated by DFT (6-311G/ B3LYP). The label of atoms for the optimized structures are shown in Figure-3.

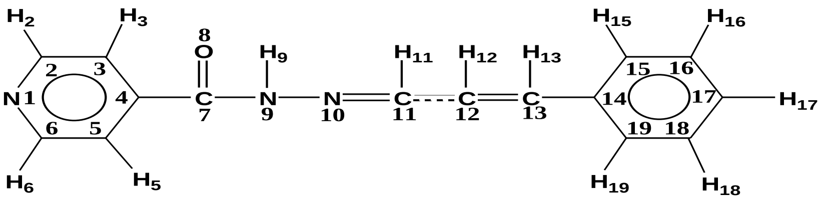


Figure 3-label of N-(3-phenyl-allylidene) isonicotinohydrazide (INHC).

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

Bond	**Bond length (Å)**						
	INHC [41]	**INHC (o-CH_3)**	**INHC (p-CH_3)**	**INHC (o,p-CH_3)**	**INHC (o-Cl)**	**INHC (p-Cl)**	**INHC (o,p-Cl)**
N1-C2	1.3532	1.3532	1.3533	1.3533	1.3532	1.3532	1.3531
N1-C6	1.3496	1.3496	1.3497	1.3497	1.3495	1.3495	1.3494
C2-H2	1.0808	1.0808	1.0808	1.0808	1.0807	1.0807	1.0807
C2- C3	1.3908	1.3908	1.3908	1.3907	1.3907	1.3908	1.3909
C3-H3	1.0791	1.0791	1.0791	1.0791	1.0791	1.0791	1.0791
C3-C4	1.4056	1.4057	1.4056	1.4056	1.4057	1.4057	1.4056
C4-C5	1.4032	1.4032	1.4032	1.4032	1.4030	1.4032	1.4032
C4-C7	1.4954	1.4956	1.4955	1.4956	1.4950	1.4952	1.4946
C5-H5	1.0753	1.0752	1.0753	1.0753	1.0752	1.0751	1.0751
C5-C6	1.3963	1.3963	1.3963	1.3963	1.3964	1.3962	1.3962
C6-H6	1.0812	1.0811	1.0812	1.0812	1.0811	1.0811	1.0811
C7-O8	1.2542	1.2544	1.2547	1.2548	1.2533	1.2535	1.2528
C7-N9	1.3850	1.3849	1.3842	1.3840	1.3867	1.3867	1.3882
N9-N10	1.3754	1.3755	1.3765	1.3766	1.3733	1.3730	1.3711
N9-H9	1.0185	1.0184	1.0184	1.0184	1.0184	1.0186	1.0186
N10-C11	1.3017	1.3020	1.3019	1.3023	1.3016	1.3016	1.3018
C11-H11	1.0937	1.0938	1.0939	1.0940	1.0930	1.0934	1.0928
C11-C12	1.4389	1.4386	1.4384	1.4380	1.4396	1.4393	1.4395
C12-H12	1.0828	1.0826	1.0829	1.0825	1.0827	1.0829	1.0828
C12-C13	1.3532	1.3548	1.3539	1.3555	1.3529	1.3528	1.3529
C13-H13	1.0872	1.0841	1.0874	1.0843	1.0823	1.0868	1.0821
C13-C14	1.4628	1.4644	1.4610	1.4624	1.4619	1.4624	1.4613
C14-C15	1.4101	1.4229	1.4081	1.4209	1.4084	1.4098	1.4090
C14-C19	1.4113	1.4116	1.4119	1.4122	1.4150	1.4111	1.4144
C15-H15	1.0830	--------	1.0832	--------	--------	1.0823	-------
C15-C16	1.3943	1.4014	1.3940	1.4011	1.3891	1.3944	1.3901
C15-CH_3	--------	1.5144	--------	1.5146	---------	--------	--------
C15-Cl	--------	-------	--------	--------	1.8397	--------	1.8332
C16-H16	1.0817	1.0825	1.0826	1.0835	1.0792	1.0794	1.0776
C16-C17	1.3968	1.3946	1.4010	1.3990	1.3951	1.3890	1.3881
C17-H17	1.0815	1.0817	--------	--------	1.0809	--------	-----
C17-C18	1.4001	1.3976	1.4076	1.4049	1.3988	1.3925	1.3918
C17-CH_3	--------	--------	1.5102	1.5103	--------	--------	-------
C17-Cl	--------	--------	--------	--------	--------	1.8263	1.8205
C18-H18	1.0817	1.0816	1.0832	1.0829	1.0811	1.0794	1.0789
C18-C19	1.3919	1.3899	1.3890	1.3872	1.3895	1.3919	1.3893
C19-H19	1.0813	1.0812	1.0816	1.0814	1.0806	1.0808	1.0801

From the calculation of bonds length of INHC derivatives Table-1, it was shown that:

- For group Π the longest C4-C7 bond is (1.٤٩٥٦A°) due to INHC (o-CH_3) = INHC (o,p-CH_3) molecule and the shortest bond (stronger one) is belongs to INHC (o.p-CH_3) (1.4956) molecule. For group Ш the longest C4-C7 bond is (1.4952A°) due to INHC (p-Cl) = INHC (p-Br) molecule and the shortest bond is (1.4946A°) belongs to INHC (o,p-Cl).
- For group Π the longest C=O bond is (1.2548A°) belongs to INHC (o,p-CH_3) and the shortest bond belongs to INHC (o-OCH_3) (1.2544A°) molecule. For group Ш the longest C=O bond (1.2535A°) belongs to INHC (p-Cl) and the shortest bond (1.2528A°) belongs to INHC (o,p-Cl).

- For group П the longest C=N bond (1.3023A°) belongs to INHC (o,p-CH_3) and the shortest bond (1.3019A°) belongs to INHC (p-CH_3). For group Ш the longest C=N bond (1.3018A°) belongs to INHC (o,p-Cl) and the shortest bond (1.3016A°) belongs to INHC (o-Cl)= INHC (p-Cl).

- For group П the longest C_{15}-CH_3 bond (1.5144A°) belongs to INHC (o-CH_3) and the shortest one (1.5146) belongs to INHC (o,p-CH_3) at ortho position. For group Ш the longest C_{15}-Cl bond (1.8397A°) belongs to INHC (o-Cl) molecule and the shortest (1.8332A°) belongs to INHC (o,p-Cl) at ortho position too.

- For group П the longest C_{17}-CH_3 bond (1.5103A°) belongs to INHC (o,p-CH_3 at para position. and the shortest (1.5102) belongs to INHC (p-CH_3).

- For group Ш the longest C_{17}-Cl bond (1.8397A°) belongs to INHC (o-Cl) molecule and the shortest one (1.8305A°) belongs to INHC (o,p-Cl) at para position too.

For the calculation of geometrical structure of all INHC derivatives molecule, it was shown that the shortest bonds are N1-C6 and C7=O8 with bonds length of (1.3494-1.3497A°) and (1.2548-1.2528A°) respectively, which can facilitate the adsorption of INHC molecule on the metal surface through the C-N (pyridine ring) and C=O bonds. This is confirmed from the calculation of their bond order, 0.986 and 1.796, which show weak bond character, and accordingly, the adsorption of the inhibitor on the metal surface becomes easier.

According to Wang et al. [32], the frontier orbital's HOMO and 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 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.

For groups I, П, and Ш the highest value of E_{HOMO} (-6.0410, -6.2470 and -6.4252eV), indicates the better inhibition efficiency of INHC (o.p -CH_3), INHC and INHC (p-Cl) respectively Table-2a. and the low value of E_{LUMO} for the three groups (-2.8972, -2.4994 and -2.4953 eV), indicates the better inhibition efficiency of INHC (o,p -Cl), INHC and INHC (o -CH_3) respectively Table-2a. The results show the following correlations:

For E_{HOMO}

Group П: INHC (o.p-CH_3) > INHC (p-CH_3) > INHC (o-CH_3)

Group Ш: INHC (p-Cl) > INHC (o-Cl) > INHC (o,p-Cl)

As a whole:

INHC (o,p-CH_3) > INHC (p-CH_3) > INHC (o-CH_3) > **INHC** > INHC (p-Cl) > INHC (o-Cl) > INHC (o,p -Cl)

For E_{LUMO}

Group П: INHC (o-CH_3) < INHC (o.p -CH_3) < INHC (p-CH_3)

Group Ш: INHC (o,p-Cl) < INHC (o -Cl) < INHC (p-Cl)

As a whole:

INHC (o,p-Cl) < INHC (o-Cl) < INHC (p-Cl) < **INHC** < INHC (o-CH_3) < INHC (p-CH_3) < INHC (o,p-CH_3)

Energy gap $\underline{\Delta}E$ = (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 in the %IE of the molecule. 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 [33]. 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 [34]. The results as indicated in Table-2a show that the inhibitors INHC (o,p-CH_3), INHC (o-Cl) and INHC have the lowest energy gap (3.6167, 3.7430 and 3.7476 eV), this means that INHC (o,p-CH_3), molecule could has the best performance as corrosion inhibitor. Table-2a shows the following correlations:

Group П: INHC (o,p-CH_3) < INHC (o-CH_3) < INHC (p-CH_3)
Group Ш: INHC (o,p-Cl) < INHC (p-Cl) < INHC (o-Cl)
As a whole:
INHC (o,p-CH_3) < INHC (o-CH_3) < INHC (p-CH_3) < INHC (o-Cl) < INHC (p-Cl) < INHC (o,p-Cl) < **INHC**

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 [35].
The energy of the deformability increases with the increase in μ, making the molecule easier to adsorb at the Fe surface. In our study the values (7.0391, 6.2086 and 5.2636eV), debye of INHC (o,p-CH_3), INHC and INHC (o-Cl), according to groups П, I, and Ш**,** enumerates its better inhibition efficiency. Table-2a shows the following correlations:

Group П: INHC (o,p-CH_3) > INHC (p-CH_3) > INHC (o-CH_3)
Group Ш: INHC (o-Cl) > INHC (p-Cl) > INHC (o,p-Cl).
As a whole:
INHC(o,p-CH_3) > INHC (p-CH_3) > INHC (o-CH_3) > INHC (o -Cl) > INHC (p-Cl) > INHC (o.p-Cl) > **INHC.**

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 [36]. The lower ionization energy (6.0410, 6.2470 and 6.4252eV) of INHC (o.p-CH_3), INHC and INHC (p-Cl). respectively, indicates the high inhibition efficiency. Table-2b shows the following correlations:

Group П: INHC (o.p-CH_3) < INHC (p-CH_3) < INHC (o-CH_3)
Group Ш: INHC (p-Cl) < INHC (o-Cl) < INHC (o,p-Cl)
As a whole:
INHC (p-CH_3) < INHC (o-CH_3) < INHC (o,p-CH_3) < **INHC** < INHC (p-Cl) < INHC (o-Cl) < INHC (o,p-Cl)

The highest value of electron affinity (2.8972, 2.4994 and 2.4953 eV), indicates the better inhibition efficiency of INHC (o,p-Cl),INHC and INHC (o-CH_3) respectively Table-2b. Which shows the following correlations:

Group П: INHC (o-CH_3) > INHC (p-CH_3) > INHC (o,p-CH_3)
Group Ш: INHC (o,p-Cl) > INHC (o-Cl) > INHC (p-Cl)
As a whole:
INHC (o,p -Cl) > INHC (o -Cl) > INHC (p-Cl) > **INHC** > INHC (o-CH_3) >INHC (p-CH_3) > INHC (o.p-CH_3) .

For absolute hardness 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 [37]. In our present study (INHC o,p-CH_3), INHC and (INHC o,p-Cl) with lowest hardness value (1.8083, 1.8738 and 1.8972eV) 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 [38].
Table-2b shows the following correlations:

Group II: INHC (o,p-CH_3) < INHC (o-CH_3) < INHC (p-CH_3)
Group III: INHC (o,p-Cl) < INHC (p-Cl) < INHC (o-Cl)
As a whole:
INHC(o,p-CH_3) < IINHC (o-CH_3) < INHC (p-CH_3) < INHC (o,p-Cl) < INHC (p-Cl) < INHC (o-Cl) < INHC

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 [39], INHC (o, p-CH_3), INHC (o.p-Cl), and INHC with the softness value of (0.5529, 0.5402 and 0.5336eV), correlates the above statement. Table-2b shows the following correlations:

Group II: INHC (o,p-CH_3) > INHC (o-CH_3) > INHC (p-CH_3)
Group III: INHC (o,p-Cl) > INHC (p-Cl) > INHC (o-Cl)
As a whole:
INHC (o.p-CH_3) > INHC (o-CH_3) > INHC (p-CH_3) > INHC (o,p- Cl) > INHC (p-Cl) > INHC (o-Cl) > INHC

According to Sanderson's electronegativity equalization principle [40], (INHC o,p-CH_3), INHC and (INHC p-Cl) has a lowest value (4.2326, 4.3732, and 4.5629eV) 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-2b shows the following correlations:

Group II: INHC (o,p-CH_3) < INHC (p-CH_3) < INHC (o-CH_3
Group III: INHC (p-Cl) < INHC (o-Cl) < INHC (o,p-Cl)
As a whole:
INHC (o,p-CH_3) < INHC(p-CH_3) < INHC (o-CH_3) < INHC < INHC (p-Cl) < INHC (o-Cl) < INHC (o,p-Cl)

Global electrophilicity index (ω) introduced by Parr [41], calculated using the electronegativity and chemical hardness parameters through the equation: $(\omega) = -x^2/2\eta = \mu^2/2\eta$
A high value of electrophilicity describes a good electrophile while a small value of electrophilicity describes a good nucleophile .In Table-3 the highest value of (ω), INHC (o,p-Cl), INHC (o-CH_3) and INHC. The high value (6.0901, 5.1074 and 3.0362eV) indicates the better corrosion efficiency, Table-2b shows the following correlations: Table-3a, 3b

Group II: INHC (o-CH_3)> INHC (o,p-CH_3) >INHC (p-CH_3)
Group III: INHC (o,p- Cl) >INHC (o-Cl) > INHC (p-Cl)
As a whole:
INHC (o,p-Cl) > INHC (o-Cl) > INHC (p-Cl) > INHC (o-CH_3)> INHC (o,p-CH_3) >INHC (p-CH_3) > INHC

The values of ΔN in the Table-3 represents the number of electronic charges that will be exchanged between the surface and the adsorbed species. The greater value of (0.7009, 0.7201 and 0.6543 eV) for INHC (o,p-CH_3), INHC and INHC (p-Cl) indicates the maximum transfer of electron and hence greater inhibition efficiency Table-2b.

Group II: INHC (o.p-CH_3) > INHC (p-CH_3) > INHC (o-CH_3)
Group III: INHC (p-Cl) > INHC (o-Cl) > INHC (o,p-Cl)
As a whole:
INHC (o.p-CH_3) > INHC (p-CH_3) > INHC (o-CH_3) > INHC > INHC (p-Cl) > INHC (o-Cl) > INHC (o,p-Cl)

On comparison semiemperical methods (PM3, AM1, and MINDO/3) with DFT calculations method, PM3 is agree completely with DFT calculations for indicating that [INHC (o.p -CH_3)] has the best inhibition efficiency coefficients among the seven calculating Schiff bases molecule, Table-3a, 3b. On the other side AM1 calculations result differ from DFT and PM3 only in χ value at which ((INHC o-Cl) has the lowest value instead of INHC (p-Cl)), and ω at which INHC (o,p-CH_3) has the highest value instead of INHC (o-CH_3), and as a final result also agree with DFT and PM3 on indicating that INHC (o.p -CH_3) has the best inhibition efficiency among the seven calculating Schiff bases molecule, Table -4a,4b.

Mindo/3 calculation method. differs than DFT and PM3 calculations at E_{LUMO} [INHC (o.p-CH_3)], μ [INHC (o-CH_3)], EA [INHC (o-CH_3)], and χ [INHC (o.p-CH_3)], have the best inhibition coefficient values, and the final result also agree with DFT and PM3 on indicating that INHC (o.p -CH_3) has the best inhibition efficiency among the seven calculating Schiff bases molecule, Table-5a,5b.

Table 2a- DFT (6-311G/ B3LYP) calculated for the energies and electronic properties of INHCs Schiff bases compounds.

Inhibitor Molecule	**P.G.***	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**$\Delta E_{HOMO-LUMO}$ (eV)**	**μ (debye)**
I					
INHC*	**Cs**	**-6.2470**	**-2.4994**	**3.7476**	**6.2086**
	C_1	**-6.2473**	**-2.4988**	**3.7485**	**6.2089**
II					
INHC (o-CH_3)	**Cs**	**-6.1746**	**-2.4953**	**3.6793**	**6.4050**
INHC (p- CH_3)	**Cs**	**-6.1145**	**-2.4259**	**3.6886**	**6.8904**
INHC(o.p-CH_3)	**Cs**	**-6.0410**	**-2.4243**	**3.6167**	**7.0391**
	C1	**-6.1948**	**-2.4830**	**3.7118**	**6.3658**
III					
INHC (o-Cl)	**Cs**	**-6.4478**	**-2.7048**	**3.7430**	**5.2636**
INHC (p-Cl)	**Cs**	**-6.4252**	**-2.7007**	**3.7245**	**4.1645**
INHC (o,p-Cl)	**Cs**	**-6.5991**	**-2.8972**	**3.7019**	**2.7455**
	C1	**-6.5959**	**-2.8548**	**3.7411**	**2.6524**

*****: P.G: Point Group.

Table 2b- Quantum chemical parameters for the calculated inhibitor Schiff bases molecules using by DFT (6-311G/ B3LYP) method.

Inhibitor Molecule	**P.G.***	**IE (eV)**	**EA(eV)**	**η (eV)**	**χ (eV)**	**ω**	**S (eV)**	**ΔN**
I								
INHC*	**Cs**	**6.2470**	**2.4994**	**1.8738**	**4.3732**	**3.0362**	**0.5336**	**0.7009**
	C_1	**6.2473**	**2.4988**	**1.6296**	**4.3730**	**5.8674**	**0.6136**	**0.8060**
II								
INHC (o-CH_3)	**Cs**	**6.1746**	**2.4953**	**1.8396**	**4.3349**	**5.1074**	**0.5435**	**0.7243**
INHC (p- CH_3)	**Cs**	**6.1145**	**2.4259**	**1.8443**	**4.2702**	**4.9435**	**0.5422**	**0.7400**
INHC(o.p-CH_3)	**Cs**	**6.0410**	**2.4243**	**1.8083**	**4.2326**	**4.9535**	**0.5529**	**0.7651**
	C_1	**6.1948**	**2.4830**	**1.8559**	**4.3389**	**5.0719**	**0.5388**	**0.7169**
III								
INHC (o-Cl)	**Cs**	**6.4478**	**2.7048**	**1.8715**	**4.5763**	**5.5951**	**0.5343**	**0.6475**
INHC (p-Cl)	**Cs**	**6.4252**	**2.7007**	**1.8622**	**4.5629**	**5.5889**	**0.5369**	**0.6543**
INHC (o,p-Cl)	**Cs**	**6.5991**	**2.8972**	**1.8509**	**4.7481**	**6.0901**	**0.5402**	**0.6083**
	C_1	**6.5959**	**2.8548**	**1.8705**	**4.7253**	**5.9685**	**0.5346**	**0.6080**

*****:P.G: Point Group.

Table 3a- PM3 calculated for the energies and electronic properties of INHCs Schiff bases compounds.

Inhibitor Molecule	**P.G.***	**ΔH_f (kcal /mol)**	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**$\Delta E_{HOMO-LUMO}$ (eV)**	**μ (debye)**
I						
INHC	**Cs**	**76.1296**	**-8.8795**	**-1.0305**	**7.8490**	**3.9596**
	C_1	**66.8312**	**-8.9380**	**-0.9034**	**8.0346**	**3.7529**
II						
INHC (o-CH_3)	**Cs**	**68.2978**	**-8.8294**	**-1.0209**	**7.8085**	**4.1513**
INHC (p- CH_3)	**Cs**	**66.6469**	**-8.7851**	**-1.0120**	**7.7731**	**4.2245**
INHC(o.p-CH_3)	**Cs**	**58.8467**	**-8.7358**	**-1.0035**	**7.7323**	**4.3973**
	C_1	**59.7247**	**-8.6509**	**-0.6637**	**7.9872**	**4.2453**
III						
INHC (o-Cl)	**Cs**	**70.2648**	**-8.9089**	**-1.1328**	**7.7761**	**3.4328**
INHC (p-Cl)	**Cs**	**69.4925**	**-8.8697**	**-1.1524**	**7.7173**	**3.3412**
INHC (o,p-Cl)	**Cs**	**63.8950**	**-8.9059**	**-1.2576**	**7.6483**	**2.7567**
	C_1	**66.0214**	**-8.9492**	**-1.1679**	**7.7813**	**2.5974**

*****:P.G: Point Group.

Table 3b-Quantum chemical parameters for the calculated inhibitor Schiff bases molecules using by PM3 method.

Inhibitor Molecule	**P.G.***	**IE (eV)**	**EA(eV)**	**η (eV)**	**x (eV)**	**ω**	**S (eV)**	**ΔN**
I								
INHC	**Cs**	**8.8795**	**1.0305**	**3.9245**	**4.9550**	**3.1280**	**0.2548**	**0.2605**
	C_1	**8.9380**	**0.9034**	**4.0173**	**4.9207**	**3.0136**	**0.2489**	**0.2587**
II								
INHC (o-CH_3)	**Cs**	**8.8294**	**1.0209**	**3.9042**	**4.9251**	**3.1064**	**0.2561**	**0.2657**
INHC (p- CH_3)	**Cs**	**8.7851**	**1.0120**	**3.8865**	**4.8985**	**3.0870**	**0.2573**	**0.2703**
INHC(o.p-CH_3)	**Cs**	**8.7358**	**1.0035**	**3.8661**	**4.8689**	**3.0659**	**0.2586**	**0.2756**
	C_1	**8.6509**	**0.6637**	**3.9936**	**4.6573**	**2.7156**	**0.2504**	**0.2933**
III								
INHC (o-Cl)	**Cs**	**8.9089**	**1.1328**	**3.8880**	**5.0208**	**3.2418**	**0.2572**	**0.2545**
INHC (p-Cl)	**Cs**	**8.8697**	**1.1524**	**3.8586**	**5.0110**	**3.2537**	**0.2591**	**0.2577**
INHC (o,p-Cl)	**Cs**	**8.9059**	**1.2576**	**3.8241**	**5.0817**	**3.3764**	**0.2614**	**0.2508**
	C_1	**8.9492**	**1.1679**	**3.8906**	**5.0585**	**3.2884**	**0.2570**	**0.2495**

*****:P.G: Point Group.

Table 4a-AM1 calculated for the energies and electronic properties of INHCs Schiff bases compounds.

Inhibitor Molecule	**P.G.***	**ΔH_f (kcal /mol)**	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**$\Delta E_{HOMO-LUMO}$ (eV)**	**μ (debye)**
I						
INHC	**Cs**	**84.6578**	**-8.8120**	**-0.8473**	**7.9647**	**3.6979**
	C_1	**68.5085**	**-8.9941**	**-0.6305**	**8.3636**	**3.5791**
II						
INHC (o-CH_3)	**Cs**	**78.4409**	**-8.7524**	**-0.8375**	**7.9149**	**3.8291**
INHC (p- CH_3)	**Cs**	**78.0499**	**-8.7007**	**-0.8321**	**7.8686**	**4.0237**
INHC(o.p-CH_3)	**Cs**	**70.7041**	**-8.6428**	**-0.8228**	**7.8200**	**4.1247**
	C_1	**66.1592**	**-8.6057**	**-0.6792**	**7.9265**	**3.8536**
III						
INHC (o-Cl)	**Cs**	**79.2684**	**-8.8939**	**-0.9671**	**7.9268**	**3.3541**
INHC (p-Cl)	**C_1**	**77.6625**	**-8.8749**	**-1.0014**	**7.8735**	**2.6034**
INHC (o,p-Cl)	**Cs**	**72.8339**	**-8.9543**	**-1.1385**	**7.8158**	**2.0461**
	C_1	**70.3551**	**-8.9541**	**-1.1385**	**7.8156**	**2.0456**

*****:P.G: Point Group.

Table 4b-Quantum chemical parameters for the calculated inhibitor Schiff bases molecules using by AM1 method.

Inhibitor Molecule	**P.G. ***	**IE (eV)**	**EA(eV)**	**η (eV)**	***x* (eV)**	**ω**	**S (eV)**	**Δ*N***
I								
INHC	**Cs**	**8.8120**	**0.8473**	**3.9823**	**4.8296**	**2.9285**	**0.2511**	**0.2725**
	C_1	**8.9941**	**0.6305**	**4.1818**	**4.8123**	**2.7689**	**0.2391**	**0.2615**
II								
INHC (o-CH_3)	**Cs**	**8.7524**	**0.8375**	**3.9574**	**4.7949**	**2.9048**	**0.2526**	**0.2786**
INHC (p- CH_3)	**Cs**	**8.7007**	**0.8321**	**3.9343**	**4.7664**	**2.8872**	**0.2541**	**0.2838**
INHC(o.p-CH_3)	**Cs**	**8.6428**	**0.8228**	**3.9100**	**4.7328**	**2.8643**	**0.2557**	**0.2899**
	C_1	**8.6057**	**0.6792**	**3.9632**	**4.6424**	**2.7189**	**0.2523**	**0.2974**
III								
INHC (o-Cl)	**Cs**	**8.8939**	**0.9671**	**3.9634**	**4.9305**	**3.0667**	**0.2523**	**0.2610**
INHC (p-Cl)	**Cs**	**8.8749**	**1.0014**	**3.9367**	**4.9381**	**3.0875**	**0.2540**	**0.2618**
INHC (o,p-Cl)	**Cs**	**8.9543**	**1.1385**	**3.9079**	**5.0464**	**3.2583**	**0.2559**	**0.2499**
	C_1	**8.9541**	**1.1385**	**3.9078**	**5.0463**	**3.2582**	**0.2558**	**0.2499**

*****:P.G: Point Group.

Table 5a- Mindo/3 calculated for the energies and electronic properties of INHCs Schiff bases **compounds.**

Inhibitor Molecule	**P.G.***	**ΔH_f (kcal /mol)**	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**ΔE HOMO-LUMO (eV)**	**μ (debye)**
I						
INHC	**Cs**	**48.4712**	**-7.9635**	**0.0585**	**8.0220**	**3.4181**
	C_1	**36.1408**	**-8.2582**	**0.0546**	**8.8051**	**4.1301**
II						
INHC (o-CH_3)	**Cs**	**36.6859**	**-7.9472**	**0.0220**	**7.9692**	**3.3836**
INHC (p- CH_3)	**Cs**	**31.2845**	**-7.9293**	**-0.0065**	**7.9228**	**3.3502**
INHC(o.p-CH_3)	**Cs**	**48.4712**	**-7.9113**	**-0.0421**	**7.8692**	**3.3190**
	C_1	**66.8497**	**-8.2640**	**0.5594**	**8.8234**	**4.1360**
III						
INHC (o-Cl)	**Cs**	**50.8576**	**-8.0561**	**-0.0917**	**7.9644**	**3.6187**
INHC (p-Cl)	**C_1**	**44.7797**	**-8.0474**	**-0.0895**	**7.9579**	**1.4421**
INHC (o,p-Cl)	**Cs**	**47.4456**	**-8.1363**	**-0.3447**	**7.7916**	**1.6837**
	C_1	**38.9959**	**-8.2988**	**-0.3817**	**7.9171**	**1.9834**

*****:P.G: Point Group.

Table 5b-Quantum chemical parameters for the calculated inhibitor Schiff bases molecules using by Mindo/3 method.

Inhibitor Molecule	**P.G.***	**IE (eV)**	**EA(eV)**	**η (eV)**	***x* (eV)**	**ω**	**S (eV)**	**Δ*N***
I								
INHC	**Cs**	**7.9635**	**-0.0585**	**4.0110**	**3.9525**	**1.9474**	**0.2493**	**0.3798**
	C_1	**8.2582**	**-0.5469**	**4.4025**	**3.8556**	**1.6883**	**0.2271**	**0.3889**
II								
INHC (o-CH_3)	**Cs**	**7.9472**	**-0.0220**	**3.9846**	**3.9626**	**1.9703**	**0.2509**	**0.3811**
INHC (p- CH_3)	**Cs**	**7.9293**	**0.0065**	**3.9614**	**3.9679**	**1.9872**	**0.2524**	**0.3827**
INHC(o.p-CH_3)	**Cs**	**7.9113**	**0.0421**	**3.9346**	**3.9767**	**2.0096**	**0.2541**	**0.3841**
	C_1	**8.2640**	**-0.5594**	**4.4117**	**3.8523**	**1.6819**	**0.2266**	**0.3567**
III								
INHC (o-Cl)	**Cs**	**8.0561**	**0.0917**	**3.9822**	**4.0739**	**2.0838**	**0.2511**	**0.3673**
INHC (p-Cl)	**Cs**	**8.0474**	**0.0895**	**3.9789**	**4.0684**	**2.0799**	**0.2513**	**0.3683**
INHC (o,p-Cl)	**Cs**	**8.1363**	**0.3447**	**3.8958**	**4.2405**	**2.3078**	**0.2566**	**0.3541**
	C_1	**8.2988**	**0.3817**	**3.9585**	**4.3402**	**2.3793**	**0.2526**	**0.3359**

*****:P.G: Point Group.

Active sites:

The local reactivity has been studied through the Fukui and condensed softness indices in order to predict both the reactive centers and to know the possible sites of nucleophilic and electrophilic attacks. 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. 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 [42]. Table-6 shows that N_1, C3. C4, C5, C6 , O8, N9, N10, C12, C13, C14, C15, C16, C17, C18 and C19 carry negative charges, C2 (0.004-0.006) and C_7 (0.554) carries positive charges in (all Schiff bases molecules). This indicated that N1 (-0.327-(-0.325)), O8 (-0.406-(-0.399)), N9 (-0.594-(-0.594)), N10 (-0.153-(-0.149)) are the negative charges centers which could offer electrons to the Fe atoms to form coordinate bond while 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.

Table-6 shows that N_1, C3, C4, C5, C6, O8, N9, N10, C12, C13, C14, C15, C16, C17, C18 and C19 are negative charges, C2 and C7 are positive charges in (all Schiff bases molecules). The negative charges centers could offer electrons to the Fe atoms to form coordinate bond, while 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, C atom (of CH_3) belonging to INHC (o-CH_3) is more negative (-0.645) than C atom (-0.612) belonging to INHC (p-CH_3). For group Ш -Cl atom belonging to INHC (o,p-Cl) is more negative (-0.008) at ortho position than Cl (-0.005) at para position belonging to the same molecule, -Cl atom belonging to INHC (p-Cl) is negative charge (-0.011) and mor negative than –Cl (-0.006) atom belonging to INHC (o-Cl), indicating the effect of Cl electron withdrawing is greatest at para position with ortho substitution. So the preferred sites for attack by nucleophilic agent is near (C5, O8 and C12) atom due to the π-electron density which is slightly shifted towards C7, and at the approach of a reagent the electromeric shift results in complete transfer of this π-electron pair to N. The powerfully activating dialkyl group makes C7 to be the site for the nucleophilic attack and (C5, O8 and C12) to be the sites for electrophilic attack in INHC Schiff bases compound.

The partial charges on the individual atoms in a molecule also indicate the reactive centres 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 INHC derivatives are reported in Table-6 which shows that N1, N9 and O8 havethe highest negative charge.

This result is consistent with the fact that the electron withdrawing effect of the (Cl) group in (INHC –Cl) decreases the negative charge on N1 atom in pyridine ring while the electron donating role of the (-CH_3) group increases the negative charge on N1 atom in (INHC –CH_3) molecules. So N-(3-(2,4-di methyl phenylidene-allylidene) isonicotinohydrazide INHC (o,p-CH_3), has the greatest tendency to adsorb on the metal surface among other calculated groups (I, Π, and Ш) because it has the highly negative charge centers while INHC (o,p-Cl) is preferentially the molecule with the lowest adsorption tendency. Figure-4, shows the frontier molecule orbital density distributions of INHC derivatives HOMO; LUMO.

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

Atom	**Electronic charge**						
	INHC	**INHC o-CH_3**	**INHC p-CH_3**	**INHC o,p-CH_3**	**INHC o -Cl**	**INHC p-Cl**	**INHC o,p-Cl**
N1	-0.327	-0.327	-0.327	-0.327	-0.326	-0.325	-0.325
C2	0.004	0.004	0.004	0.004	0.005	0.005	0.006
C3	-0.191	-0.191	-0.191	-0.191	-0.191	-0.191	-0.189
C4	-0.112	-0.112	-0.112	-0.113	-0.111	-0.111	-0.111
C5	-0.074	-0.074	-0.074	-0.074	-0.073	-0.074	-0.074
C6	-0.029	-0.029	-0.030	-0.030	-0.029	-0.029	-0.028
C7	0.554	0.554	0.554	0.554	0.555	0.554	0.554
O8	-0.406	-0.406	-0.407	-0.408	-0.402	-0. 402	-0.399
N9	-0.594	-0.594	-0.594	-0.594	-0.594	-0.594	-0.594
N10	-0.153	-0.153	-0.154	-0.155	-0.150	-0.150	-0.149
C11	0.011	0.008	0.011	0.007	0.011	0.012	0.012
C12	-0.128	-0.109	-0.130	-0.110	-0.127	-0.129	-0.129
C13	-0.196	-0.179	-0.193	-0.176	-0.191	-0.191	-0.186
C14	-0.023	-0.026	0.000	-0.011	0.107	0.010	0.124
C15	-0.168	0.047	-0.182	0.044	-0.371	-0.170	-0.382
C16	-0.163	-0.179	-0.153	-0.184	-0.068	0.058	0.047
C17	-0.120	-0.115	0.052	0.070	-0.114	-0.287	-0.292
C18	-0.171	-0.154	-0.148	-0.137	-0.149	-0.064	-0.041
C19	-0.080	-0.121	-0.094	-0.129	-0.095	-0.080	-0.099
H2	0.175	0.175	0.175	0.175	0.177	0.177	0.178
H3	0.199	0.199	0.198	0.198	0.200	0.200	0.200
H5	0.219	0.219	0.219	0.219	0.218	0.218	0.218
H6	0.172	0.172	0.172	0.172	0.172	0.173	0.173
H9	0.318	0.318	0.318	0.317	0.321	0.320	0.322
H11	0.150	0.147	0.149	0.146	0.157	0.152	0.159
H12	0.184	0.184	0.182	0.183	0.185	0.185	0.186
H13	0.158	0.173	0.158	0.172	0.204	0.161	0.205
H15	0.158	--------	0.154	--------	--------	0.167	--------
H16	0.156	0.154	0.155	0.157	0.190	0.191	0.222
H17	0.158	0.153	--------	0.150	0.167	--------	--------
H18	0.155	0.152	0.153	0.157	0.162	0.190	0.195
H19	0.163	0.160	0.160	--------	0.168	0.171	0.176
o-$\underline{C}H_3$	--------	-0.645	--------	-0.649	--------	--------	--------
p-$\underline{C}H_3$	--------	--------	-0.612	-0.617	--------	--------	--------
o-Cl	--------	--------	--------	--------	-0.006	--------	-0.008
p-Cl	--------	--------	--------	--------	--------	-0.011	-0.005

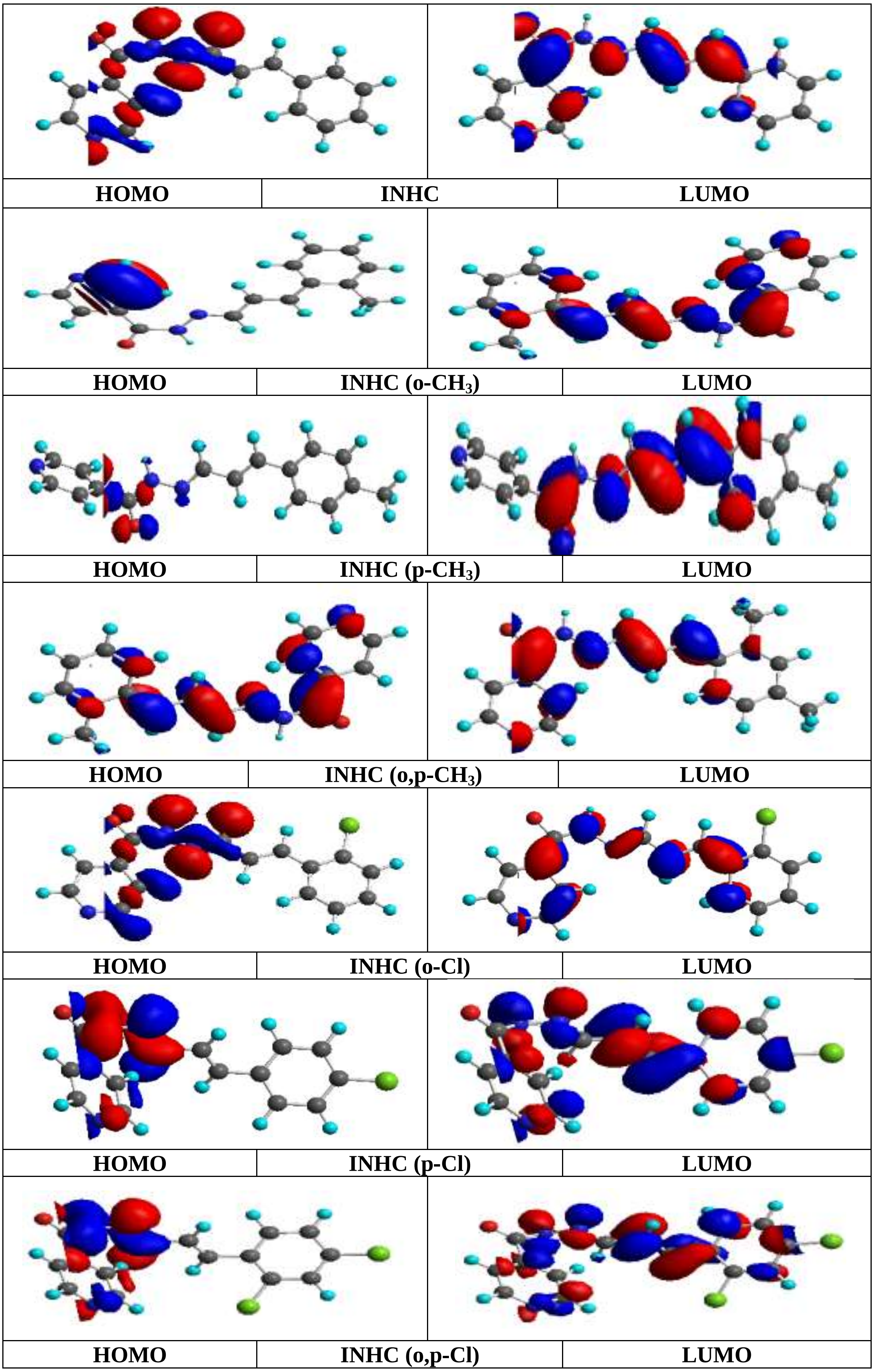


Figure 4-The frontier molecule orbital density distributions of INHC derivatives HOMO; LUMO.

Infrared spectra (IR):

DFT (B3LYP/ 6-311G) calculations were carried out for the estimation of vibration frequencies, and normal coordinates for the calculated Schiff bases molecule derivatives, by using Gaussian-03 program. The results were compared with the experimental measured values [43 - 45].

The stretching vibration of N-H bond due to amide group was found to have values of (3457cm^{-1}) for group **I** (INHC), for group **Π** (INHC–CH_3), it was found to have values range of (3454-3458cm^{-1}) and for group **Ш** (INHC-Cl), it was found to have values range of (3456-3457 cm^{-1}).

-for aromatic C-H stretching, it was found to have values of (3001 cm^{-1}) for group **I** (INHC), for group **Π** (INHC–CH_3), it was found to have values range of (3061-3060 cm^{-1}) and for group **Ш** (INHC-Cl), it was found to have values range of (3093-3101cm^{-1}).

-for aliphatic C-H stretching, it was found to have values of (2995 cm^{-1}) for group I (INHC), for group **Π** (INHC–CH_3), it was found to have values range of (2915-3047 cm^{-1}) and for group **Ш** (INHC-Cl), it was found to have values range of (3040-3042 cm^{-1}).

-for C=O amide group stretching vibration, it was found to have values of (1648 cm^{-1}) for group **I** (INHC), for group **Π** (INHC –CH_3) have values range of (1647-1648 cm^{-1}) and for group **Ш** (INHC-Cl) have values range of (1650-1674 cm^{-1}).

-for stretching vibration frequency of C=C, it was found to have values of (1678 cm^{-1}) for group **I** (INHC), for group **Π** (INHC –CH_3), it was found have values range of (1673-1679 cm^{-1}) and for group **Ш** (INHC-Cl) have values range of (1675-3046 cm^{-1}).

-for stretching vibration frequency of C--C aromatic, it was found to have values of (1608 cm^{-1}) for group **I** (INHC), for group **Π** (INHC–CH_3), it was found to have values range of (1596-1641 cm^{-1}) and for group **Ш** (INHC-Cl), it was found to have values range of (1585-1623 cm^{-1}).

-for stretching vibration frequency of C-C-C (phenyl ring), it was found to have values of (1641cm^{-1}) for group I (INHC), for group **Π** (INHC–CH_3), it was found to have values range of (1598-1641cm^{-1}) and for group **Ш** (INHC-Cl), it was found to have values range of (1585-1601cm^{-1}).

- for C-Cl stretching, it was found to have values of (353-708cm^{-1})

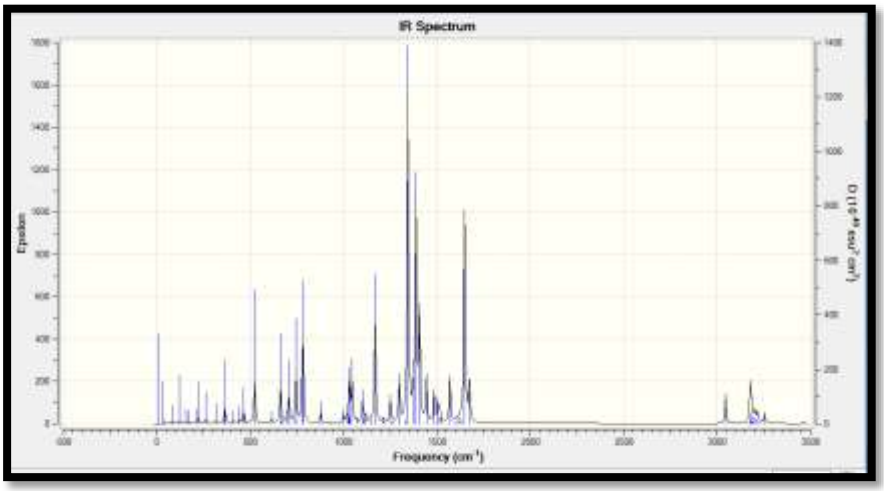
Table-7 shows values of some calculated vibration frequencies and IR absorption intensities for INHC molecule using DFT (B3LYP/ 6-311G) method, Scheme-1. Shows the IR spectra for INHC (o-Cl) molecule as calculated by DFT method, and Figure-5. shows some modes of vibration frequencies for N-(3-phenyl-allylidene) using Gaussian 2005 view program.

Table 7-DFT vibration frequencies and IR absorption intensities for INHC (o-Cl) molecule.

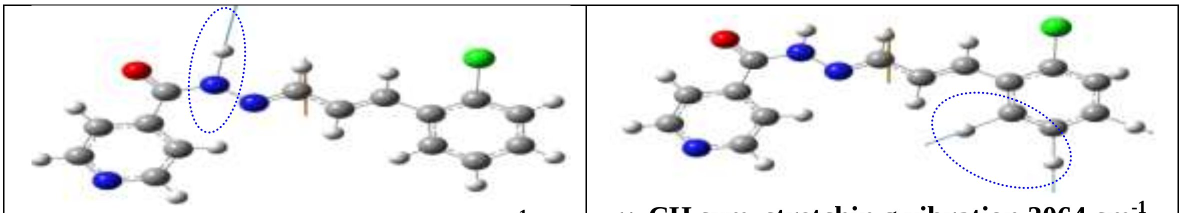
	Description	**Frequency cm^{-1}**	**Intensity km/mol**	**Exp. Freq. cm^{-1} [43-45]**
In plane of the molecule				
A_1'				
ν_1	NH str.	3458	2.020	3452
ν_2	C-H sym. str. (pyridine ring)	3094	15.952	-------
ν_3	C-H sym. str. (phenyl ring)	3087	14.683	-------
ν_4	C-H sym. str. (phenyl ring)	3074-3064	18.187-5.529	3062
ν_5	CH asym. str. (pyridine ring)	3057-3051	22.037-32.682	-------
ν_6	CH asym. str. (CH=CH)	3052-3050	15.077-9.331	-------
ν_7	CH sym. str. (CH=CH)	3169	1.795	2975
ν_8	CH str. (N=CH)	3046	41.802	2907
ν_9	C=C str.	1675	62.600	1612
ν_{10}	C=O str.	1649	4.586	1663
ν_{11}	C--C str. (phenyl ring)	1634	324.978	1645
ν_{12}	C--C str. (pyridine ring)	1624	4.165	1627
ν_{13}	C=N str.	1610	9.425	1600
ν_{14}	CCC str. (phenyl ring)	1597	2.969	1600
ν_{15}	C—C--N str. (pyridine ring)	1570	68.202	1570
ν_{16}	δCH sym. rocking	1521-1517	8.668-8.682	------

ν_{17}	δNH + δCH scissoring + δCH rocking (phenyl ring)	1507	29.589	------
ν_{18}	δCH rocking (phenyl ring)	1486	44.659	------
ν_{19}	δCH rocking (pyridine ring)	1444	66.620	------
ν_{20}	δCH (CH-- & =CH)	1346	467.866	------
ν_{21}	δCH (C-- CH=C)	1389	321.968	------
ν_{22}	δCH rocking (sym. phenyl ring)	1339	0.781	------
ν_{23}	δCH (pyridine ring)	1332	4.481	------
ν_{24}	δCH (C-- CH=C)+ (phenyl ring) str.	1299	60.163	------
ν_{25}	(pyridine ring) str.	1267	2.915	------
ν_{26}	δCH scissoring (phenyl ring)	1259	1.292	------
ν_{27}	δCH scissoring (pyridine ring)	1119	11.290	------
ν_{28}	δ(pyridine ring)	1102-1111	34.267-5.687	------
ν_{29}	δC-C-C str. (phenyl ring) + C-Cl str.	1047	62.964	1085
ν_{30}	C-Cl str.	708	41.675	727
ν_{31}	δmolecule	411	4.870	------
ν_{32}	δC-Cl	369	2.937	-----
ν_{33}	δmolecule	365	21.229	------
Out of plane of the molecule				
A_1''				
ν_{34}	γCH twisting (pyridine ring)	1035	4.874	------
ν_{35}	γ CH wagging (CH--CH=CH)	1032-1029	53.248-6.798	------
ν_{36}	γ CH twisting (phenyl ring)	1021	9.333	------
ν_{37}	γCH wagging asym. (pyridine ring)	974	0.000	------
ν_{38}	γCH wagging sym. (pyridine ring)	889	0.209	840-880
ν_{39}	γCH wagging (pyridine ring)	879	18.001	------
ν_{40}	γCH wagging (phenyl ring)	784	102.917	------
ν_{41}	γNH	747- 676	71.954- 2.162	660
ν_{42}	γ(phenyl ring) wagging	736	4.180	------
ν_{43}	γ(pyridine ring) wagging	466	15.641	------
ν_{44}	γ(pyridine ring) twisting	395	0.002	------
ν_{45}	γCH twisting asym.	368	1.845	------

γ: out of plane bending vibration., δ:in-plane bending vibration.
0.96: is scalling factor for C-H stretching vibration.

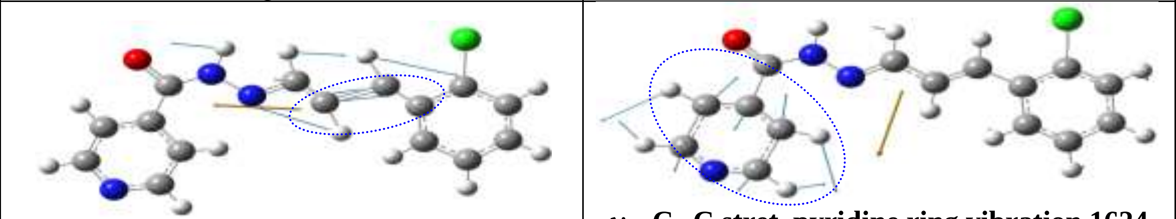


Scheme 1-IR spectra for INHC (o-Cl) molecule as calculated by DFT method.



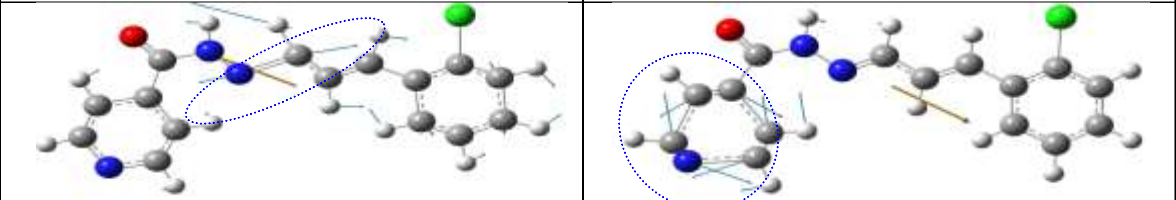
ν_1 N-H stretching vibration 3458 cm^{-1}

ν_4 CH sym. stretchin g vibration 3064 cm^{-1}



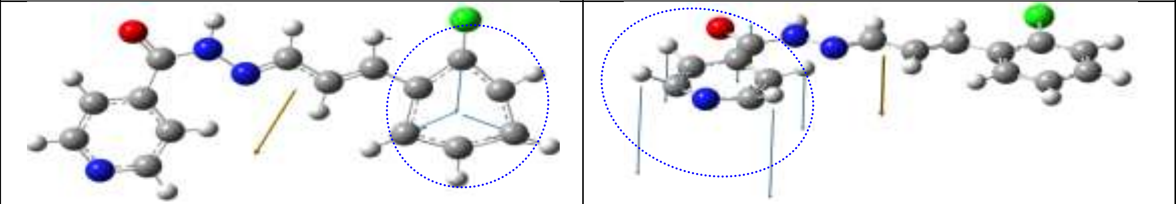
ν_9 C=C stretching vibration 1675 cm^{-1}

ν_{12} C--C stret. pyridine ring vibration 1624 cm^{-1}



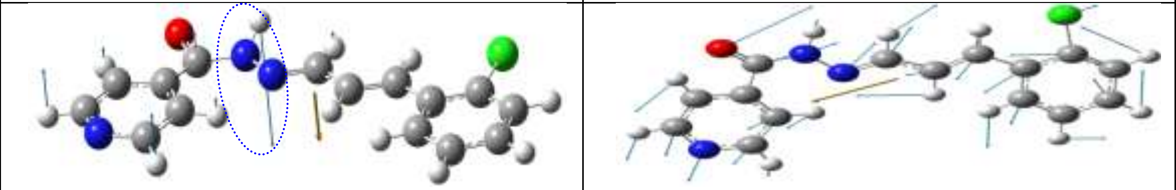
ν_{13} C=N stret. vibration 1610 cm^{-1}

ν_{25} pyridine ring stretching vibration 1267 cm^{-1}



ν_{29} δphenyl ring in plane 1047 cm^{-1}

ν_{39}γCH wagging (pyridine ring) 879 cm^{-1}



ν_{41}γNH vibration 676 cm^{-1}

ν_{33} δmolecule in- plane bend. vib. 365 cm^{-1}

Figure 5-Some modes of vibration frequencies for INHC (o-Cl) molecule.

Conclusion.

1. The calculated of inhibition efficiency parameters for the INHC Schiff bases derivatives using DFT, semiemperical methods (PM3, AM1, and MINDO/3) showing that **INHC (o,p-CH_3)** Schiff base derivative (electron donors) has the best inhibition efficiency parameters among groups **П** and **INHC (o,p-Cl)** (electron withdrawing) has the best inhibition efficiency parameters among group **Ш**, and both of them has the best inhibition efficiency parameters among group **I** (INHC).
2. For the inhibition efficiency parameters **(η)**, (**S**), (**µ**), **(EA)** (**IE**), **(χ), (ω)** and (**ΔN**), the inhibition efficiency confirms the order of;

   INHC (o,p-CH_3) > INHC (o,p- Cl) > INHC
3. Quantum chemical study for calculating the main positive and negative active sites (according to the charge type) which indicate the position of adsorption of INHC 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.

4. 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 (C1), through increasing the planarity of adsorption on the metal surface.
5. DFT (B3LYP/ 6-311G) calculations of vibration frequencies and IR absorption intensities for INHC Schiff bases derivative molecules gave a very good assignment values in comparison with experimental values.

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