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Research Article

Computational Investigations on the Corrosion Inhibition efficiency of some Pyridine based alkaloids

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ABSTRACT

The adsorption mechanism and inhibition performance of two pyridine based derivatives 4-methoxy-1-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile(C1) and 4-methoxy-2-oxo-1,2-dihydropyridine-3 carbonitrile (C2) were investigated using Density functional theory (DFT) at the B3LYP/6-31G(d,p) basis set level in order to elucidate the different inhibition efficiencies and reactive sites of these compounds as corrosion inhibitors. The calculated results are in agreement with the experimental data. 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(ΔE), hardness(η), Softness(S), dipole moment(μ), electron affinity(EA), ionization potential(IE), the absolute electronegativity (χ) and the fraction of electron transferred (ΔN). The local reactivity has been studied through the Fukui and condensed softness indices in order to predict both the reactive centres and to know the possible sites of nucleophilic and electrophilic attacks.

Keywords: Pyridine, corrosion inhibitors, reactivity, DFT, Fukui function, softness indices

INTRODUCTION

An important method of protecting metallic materials against deterioration due to corrosion is by the use of inhibitors. There has been a growing interest in the use of organic compounds as inhibitors for the aqueous corrosion of metals. Among efficient corrosion inhibitors used to prevent the deterioration of mild steel are heterocyclic organic compounds consisting of a π -system and / or O, N, or S hetero atoms¹⁻⁵. The planarity and the lone electron pairs in the hetero atoms are important features that determine the adsorption of molecules on the metallic surface⁶.

The inhibition efficiency has been closely related to the inhibitor adsorption abilities and the molecular properties for different kinds of organic compounds⁷⁻¹¹. The power 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 anti bonding orbital to form feedback bonds, constitute excellent corrosion inhibitors. Free electron pairs

on heteroatoms or π electrons are readily available for sharing to form a bond and act as nucleophile centers of inhibitor molecules and greatly facilitate the adsorption process over the metal surface, whose atoms act as electrophiles¹². Recently the effectiveness of an inhibitor molecule has been related to its spatial as well as electronic structure^{13, 14}. Quantum chemical methods have proved to be a very powerful tool for studying corrosion inhibition mechanism¹⁵⁻¹⁸.

Density functional theory (DFT)^{19,20} has provided a very useful framework for developing new criteria for rationalizing, predicting, and eventually understanding many aspects of chemical processes²¹⁻²⁵. A variety of chemical concepts which are now widely used as descriptors of chemical reactivity, e.g., electronegativity²² hardness or softness quantities etc., appear naturally within DFT¹⁹. The Fukui function²⁴ 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^{26,27}.

P. P. Singh *et al.* have studied the DFT based study of charge transfer and interaction energy between phenyl tin (IV) chlorides and derivatives of pyridine²⁸. DFT study of proton transfer, cooperativity, and tautomerization in 2-pyridineselenol and 2-pyridinethiol ammonia and water clusters was investigated by M. Nsangou *et al.*²⁹.

The pyridine derivatives investigated in the present work are:

- (i) 4-methoxy-1-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile(C1)
- (ii) 4-methoxy-2-oxo-1, 2-dihydropyridine-3-carbonitrile (C2)

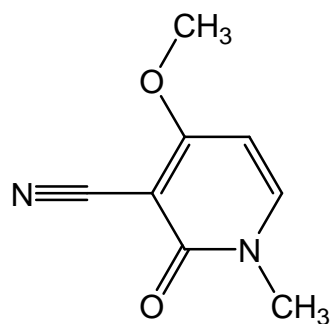
The objective of the present paper is to extend the study of Rinki Goel *et al.*³⁰ by analyzing the inhibitive properties of C1 and C2 using DFT calculations. Molecular orbital calculations are performed looking for good theoretical parameters to characterize the inhibition property of inhibitor, which will be helpful to gain insight into the mechanism of the corrosion inhibition. Results obtained showed that the inhibition efficiency of C1>C2. It is well correlated with the experimental results. From the calculations we have explained which adsorption site is favoured to bind to the metal surface.

Computational calculations were obtained by means of B3LYP/6-31G (d,p) method. Parameters like E_{HOMO} , E_{LUMO} , energy gap(ΔE), dipole moment(μ), global hardness(η), softness(S), the fraction of electron transferred (ΔN) and total energy change (ΔE) were calculated. The local reactivity has been analyzed by means of the Fukui indices, since they indicate the reactive regions, in the form of the nucleophilic and electrophilic behaviour of each atom in the molecule.

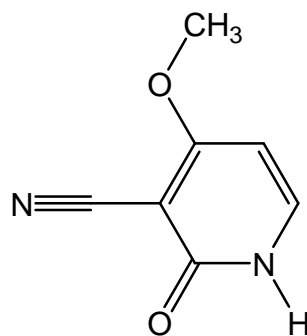
Materials and Methods

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 theoretical-experimental consistency, quantum chemical calculations were performed with complete geometry optimizations using standard Gaussian-03 software package³¹.

Geometry optimization were carried out by B3LYP functional at the 6-31G (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^{32,33}. Furthermore, DFT is considered a very useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data.

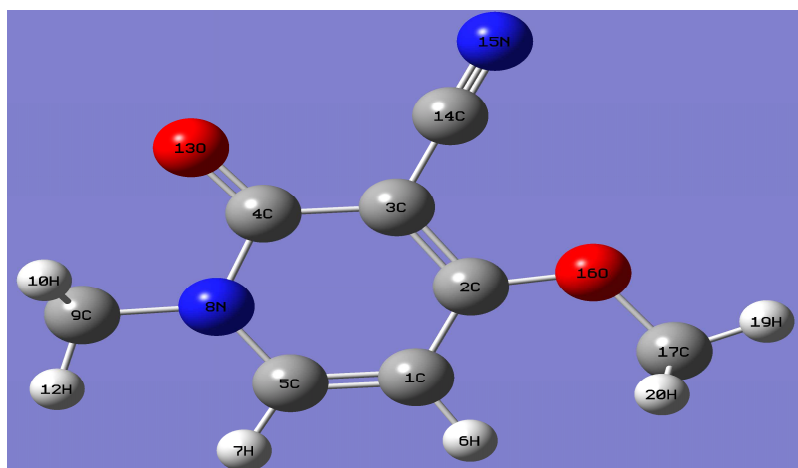


4-methoxy-1-methyl-2-oxo-
1,2-dihydropyridine-3-carbonitrile
(C1)

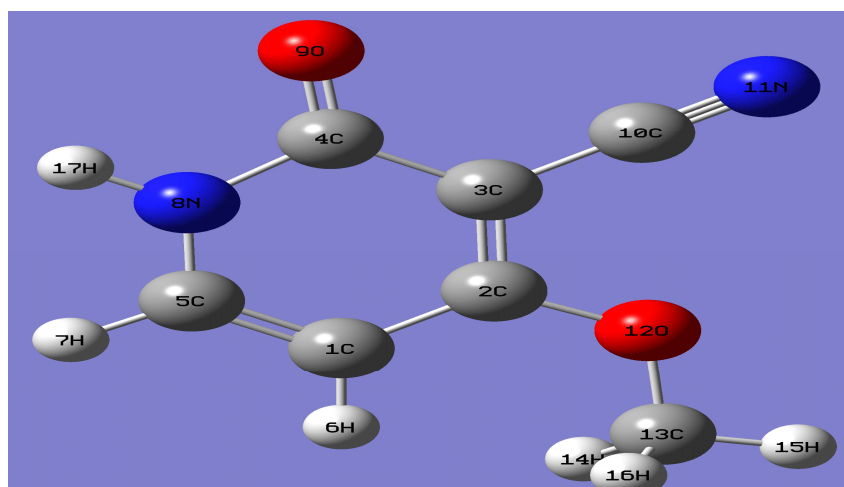


4-methoxy-2-oxo-
1,2-dihydropyridine-3-carbonitrile
(C2)

Fig. 1: Names, molecular structure and the abbreviation of the inhibitors investigated



C1



C2

Fig. 2: Optimized structure of C1 and C2 calculated with the B3LYP/6-31G(d,p)

Density functional theory (DFT)¹⁹ 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, $s(r)$. The basic relationship of the density functional theory of chemical reactivity is precisely, the one established by Parr, Donnelly, Levy and Palke³⁴, that links the chemical potential of DFT with the first derivative of the energy with respect to the number of electrons, and therefore with the negative of the electronegativity χ .

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(r)} = -\chi$$

Where μ is the chemical potential, E is the total energy, N is the number of electrons, and $v(r)$ is the external potential of the system.

Hardness (η) has been defined within the DFT as the second derivative of the E with respect to N at $v(r)$ property which measures both the stability and reactivity of the molecule³⁵.

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)}$$

Where $v(r)$ and μ are, respectively, the external and electronic chemical potentials.

From the value of the total electronic energy, the ionization potential (IE) and electron affinity (EA) of the inhibitors are calculated using the following equations and hence χ and η are calculated.

$$IE = E_{(N-1)} - E_{(N)}$$

$$EA = E_{(N)} - E_{(N+1)}$$

Where E is the total electronic energy, N is the number of electrons, and $v(r)$ is the external electrostatic potential that the electrons feel due to the nuclei.

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 nucleophiles³⁶.

$$\chi = \frac{IE + EA}{2}$$

$$\eta = \frac{IE - EA}{2}$$

The global softness (S) is the inverse of the global hardness³⁷.

$$S = \frac{1}{\eta}$$

Electronegativity, hardness and softness have proved to be very useful quantities in the chemical reactivity theory. When two systems, Fe and inhibitor, are brought together, electrons will flow from lower $\chi(\text{inhibitor})$ to higher $\chi(\text{Fe})$, until the chemical potentials become equal. The number of transferred electrons (ΔN) was also calculated³⁶ by using the equation below.

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

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 $\chi_{\text{Fe}}=7.0$ eV and $\eta_{\text{Fe}} = 0$ for the computation of number of transferred electrons³⁷. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance³⁸. The local selectivity of a corrosion inhibitor is best analyzed by means of condensed Fukui function.

The global electrophilicity index was introduced by Parr³⁹ and is given by $\omega = \mu^2/2\eta$. According to the definition, this index measures the propensity of chemical species to accept electrons. A good, more reactive, nucleophile is characterized by lower value of μ , ω ; and conversely a good electrophile is characterized by a high value of μ , ω . This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment.

The change in electron density is the nucleophilic $f^+(r)$ and electrophilic $f^-(r)$ Fukui functions, which can be calculated using the finite difference approximation as follows⁴⁰.

$$f_k^+ = q_{N+1} - q_N$$

$$f_k^- = q_N - q_{N-1}$$

Where q_N , q_{N+1} and q_{N-1} are the electronic population of the atom k in neutral, anionic and cationic systems.

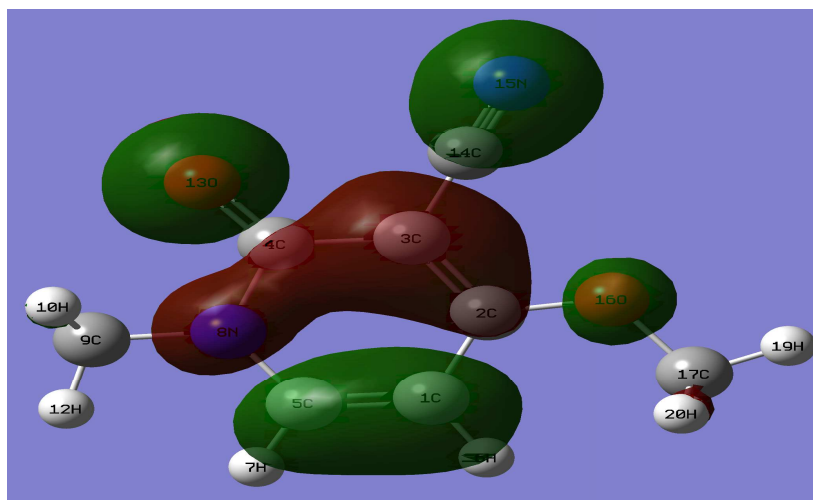
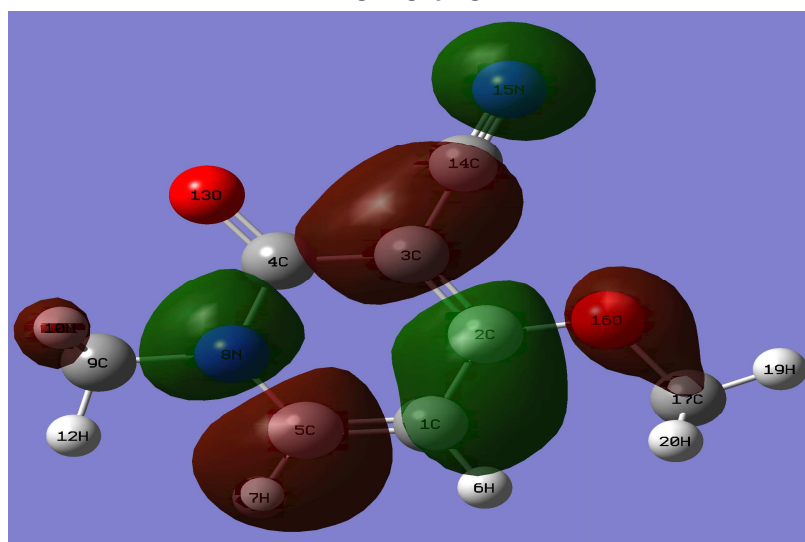
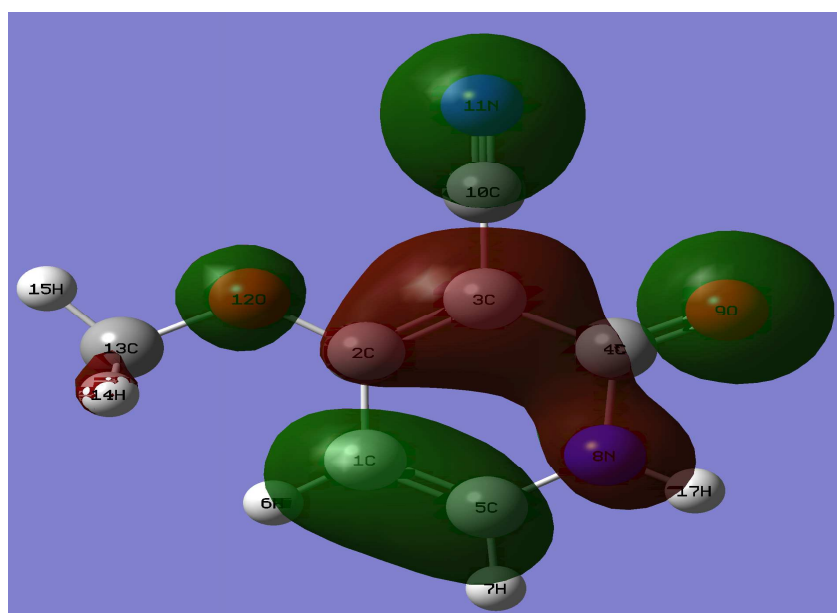
Condensed softness indices allowing the comparison of reactivity between similar atoms of different molecules can be calculated easily starting from the relation between the Fukui function $f(r)$ and the local softness $s(r)$ ⁴¹.

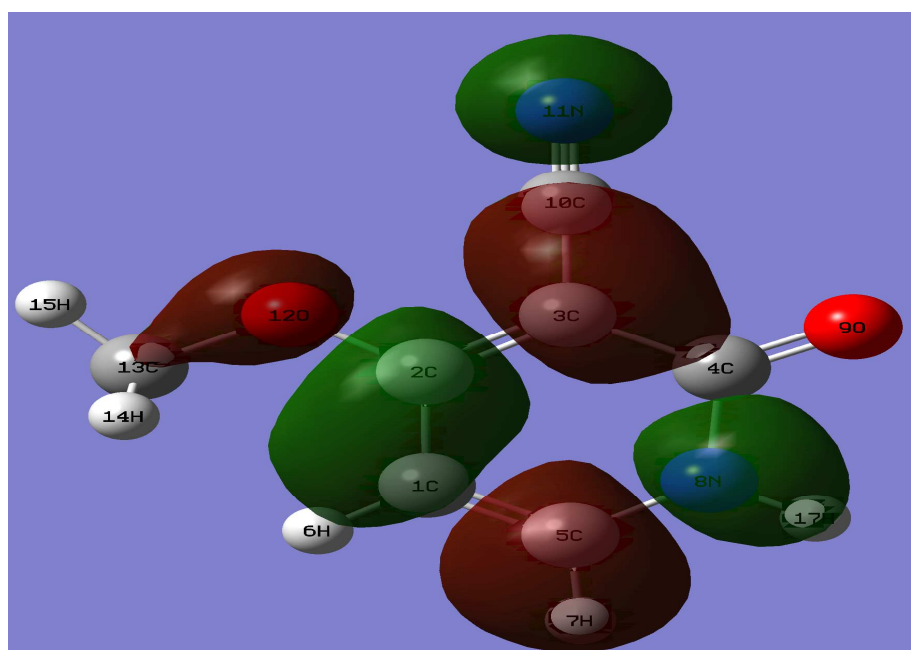
$$s(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)} \left(\frac{\partial N}{\partial \mu} \right)_{v(r)} = f(r)S$$

From this relation, one can infer that local softness and Fukui function are closely related, and they should play an important role in the field of chemical reactivity.

RESULTS AND DISCUSSION

The inhibition effect of inhibitor compound is usually ascribed to adsorption of the molecule on metal surface. There can be physical adsorption (physisorption) and chemical adsorption (chemisorption) depending on the adsorption strength. When chemisorption takes place, one of the reacting species acts as an electron pair donor and the other one acts as an electron pair acceptor. The energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency towards the donation of electron by a molecule⁴². High values of E_{HOMO} have a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy, empty molecular orbital. Increasing values of E_{HOMO} facilitate adsorption and therefore enhance the inhibition efficiency, by influencing the transport process through the adsorbed layer. Therefore, higher values of E_{HOMO} indicate better tendency towards the donation of electron, enhancing the adsorption of the inhibitor on mild steel and therefore better inhibition efficiency. 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. Frontier molecular orbital diagrams of C1 and C2 is represented in **figure 3**.

**HOMO of C1****LUMO of C1****HOMO of C2**



LUMO of C2

Fig. 3: Frontier molecular orbital diagrams of C1 and C2 by B3LYP/6-31G(d,p)**Table- 1:** Quantum chemical parameters for C1 and C2 calculated using B3LYP/6-31G(d,p).

Parameters	C1	C2
E_{HOMO} (eV)	-6.13834	-6.25154
E_{LUMO} (eV)	-1.74275	-1.78697
Energy gap(ΔE) (eV)	4.39559	4.46457
Dipole moment (Debye)	9.5475	9.6643

According to the frontier molecular orbital theory (FMO) of chemical reactivity, transition of electron is due to interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting species⁴³. E_{HOMO} is a quantum chemical parameter which is often associated with the electron donating ability of the molecule. High value of E_{HOMO} is likely to a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy⁴⁴. 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 feed back bond. The highest value of E_{HOMO} -6.138346 (eV) of C1 indicates the better inhibition efficiency.

The energy gap, ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) 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 low⁴⁵. 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 metal¹⁵. 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 molecule⁴⁶. The results as indicated in table 1 shows that inhibitor C1 has the lowest energy gap, this means that the molecule could have better performance as corrosion inhibitor.

It is shown from the calculation that there was no obvious correlation between the values of dipole moment with the trend of inhibition efficiency obtained experimentally. In the literature there is a lack

of agreement on the correlation between the dipole moment and inhibition efficiency^{47,48}. 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 molecules⁴⁹. The low ionization energy 7.916787 (eV) of C1 indicates the high inhibition efficiency.

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 gap⁵⁰. In our present study C1 with low hardness value 3.909684(eV) compared with other compound 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 efficiency⁵¹. 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 value⁵². C1 with the softness value of 0.255775 has the highest inhibition efficiency.

The **Table 2** shows the order of electronegativity as C2>C1. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order C1>C2. According to Sanderson's electronegativity equalization principle⁵³, C2 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 -2: Quantum chemical parameters for C1 and C2 calculated using B3LYP/6-31G (d,p).

Parameters	C1	C2
E_N (au)	-569.60802	-530.29463
E_{N-1} (au)	-569.31709	-529.99744
E_{N+1} (au)	-569.61160	-530.29883
IE(eV)	7.916787	8.087134
EA(eV)	0.097419	0.114290
η (eV)	3.909684	3.986422
S (eV)	0.255775	0.250852
χ (eV)	4.007103	4.100712
ω	2.053475	2.109139
ΔN	0.382754	0.363645

The number of electrons transferred (ΔN) was also calculated and tabulated in **Table 2**. Values of ΔN show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study⁵⁴. If $\Delta N < 3.6$, the inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface and it increases in the following order: C1>C2. The results indicate that ΔN values correlates strongly with experimental inhibition efficiencies. Thus, the highest fraction of electrons transferred is associated with the best inhibitor (C1), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (C2).

Table- 3: Fukui and local softness indices for nucleophilic and electrophilic attacks on C1 atoms calculated from Mulliken atomic charges.

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
C 1	-0.003139	0.024742	-0.0008028	0.0063286
C 2	0.081476	0.058747	0.0208395	0.0150265
C 3	0.044924	0.086936	0.0114904	0.0222368
C 4	0.027394	0.046638	0.0070067	0.0119293
C 5	0.131306	0.047519	0.0335847	0.0121546
H 6	0.079043	0.07212	0.0202172	0.0184471
H 7	0.098082	0.074498	0.0250869	0.0190554
N 8	0.000101	0.009223	0.0000258	0.0023591
C 9	-0.009449	-0.028239	-0.0024168	-0.007223
H 10	0.088596	0.042267	0.0226606	0.0108112
H 11	0.02062	0.042208	0.0052740	0.0107961
H 12	0.045184	0.051509	0.0115569	0.0131752
O 13	0.084965	0.152228	0.0217319	0.0389375
C 14	0.073958	0.080348	0.0189166	0.0205517
N 15	0.105985	0.109482	0.0271083	0.0280037
O 16	0.024945	0.034872	0.0063803	0.0089197
C 17	-0.04836	-0.036447	-0.0123692	-0.009323
H 18	0.046859	0.040334	0.0119853	0.0103168
H 19	0.060969	0.050813	0.0155943	0.0129972
H 20	0.046541	0.040202	0.0119040	0.0102830

The use of Mulliken population analysis to estimate the adsorption centres of inhibitors has been widely reported and it is mostly used for the calculation of the charge distribution over the whole skeleton of the molecule⁵⁵. There is a general consensus by several authors that the more negatively charged an heteroatom, is the more it can be adsorbed on the metal surface through the donor-acceptor type reaction¹⁵. It is important to consider the situation corresponding to a molecule that is going to receive a certain amount of charge at some centre and is going to back donate a certain amount of charge through the same centre or another one⁵⁶. Parr and Yang proposed that larger value of Fukui function indicate more reactivity²⁶. Hence greater the value of condensed Fukui function, the more reactive is the particular atomic centre in the molecule. The f_k^+ measures the changes of density when the molecules gains electrons and it corresponds to reactivity with respect to nucleophilic attack. On the other hand, f_k^- corresponds to reactivity with respect to electrophilic attack or when the molecule

loss electrons. The FMO diagram of C1 and C2 indicates that the dense electron cloud around O13 and O9 respectively showing the electrophilic attack at the particular site as confirmed by the Fukui function f_k^- . The nucleophilic attack at the site C5 in both the compounds, calculated by Fukui function f_k^+ is confirmed by the LUMO of the FMO diagram.

Table- 4: Fukui and local softness indices for nucleophilic and electrophilic attacks in C2 atoms calculated from Mulliken atomic charges

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
C 1	-0.00561	0.021403	-0.0014072	0.0053690
C 2	0.08837	0.061124	0.0221677	0.0153331
C 3	0.045716	0.08722	0.0114679	0.0218793
C 4	0.038696	0.054592	0.0097069	0.0136945
C 5	0.131524	0.052318	0.0329930	0.0131241
H 6	0.083402	0.073573	0.0209215	0.0184559
H 7	0.105738	0.080982	0.0265245	0.0203145
N 8	0.012901	0.018606	0.0032362	0.0046674
O 9	0.100405	0.152596	0.0251867	0.0382790
C 10	0.08214	0.084268	0.0206049	0.0211388
N 11	0.111638	0.113076	0.0280046	0.0283653
O 12	0.026495	0.040139	0.0066463	0.0100689
C 13	-0.051072	-0.03771	-0.0128115	-0.009460
H 14	0.049586	0.043402	0.0124387	0.0108875
H 15	0.063765	0.053008	0.0159955	0.0132972
H 16	0.049728	0.043439	0.0124743	0.0108968
H 17	0.066577	0.057965	0.0167009	0.0145406

CONCLUSION

The following conclusions can be deduced from the present study:

1. Through DFT calculations a correlation between parameters related to the electronic and molecular structures of some Pyridine base alkaloids and their ability to inhibit the corrosion process could be established.
2. The inhibition efficiency of pyridine derivatives obtained Quantum chemically increase with the increase in E_{HOMO} , and decrease in energy gap (ΔE). C1 has the highest inhibition efficiency because it had the highest HOMO energy and ΔN values and it was most capable of offering Electrons.
3. The parameters like hardness(η), Softness(S), dipole moment(μ), electron affinity(EA) ionization potential(IE), electronegativity(χ) and the fraction of electron transferred (ΔN) confirms the inhibition efficiency in the order of C1>C2.
4. Fukui function shows the nucleophilic and electrophilic attacking sites in the pyridine derivatives.
5. Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the method employed here.

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