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Theoretical studies on corrosion inhibition efficiency of pyridine carbonyl derivatives using DFT method

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ABSTRACT

A theoretical study for two organic corrosion inhibitor, namely 4-(4-methoxyphenyl)-6-(thiophen-2-yl)-2-thioxo-1,2-dihydropyridine-3-carbonitrile (PYCARS) and 4-(4-methoxyphenyl)-6-thioxo-1,6-dihydro-2,3'-bihydro-2,3'-bipyridine-5-carbonitrile (PYCAR) was investigated using density functional theory (DFT) at the B3LYP/6-31G(d,p) basis set level through the relationship between their molecular and electronic structure. The calculated quantum chemical parameters correlated to the inhibition efficiency such as E_{HOMO} *(highest occupied molecular orbital energy),* E_{LUMO} *(lowest unoccupied molecular orbital energy), energy gap (*ΔE*), dipole moment (*μ*), absolute hardness (*η*), the absolute electronegativity (*χ*), the fractions of electrons transferred from the inhibitor molecule to the metallic iron atom (*ΔN*) and the electrophilicity index (*ω*) were calculated. The theoretical results are in well accordance with the experimental data, reported earlier.*

Keywords: DFT, corrosion inhibition, pyridine carbonitrile, G09

INTRODUCTION

The corrosion of steel has received a considerable amount of attention as a result of its industrial relevance. The use of corrosion inhibitors is probably more attractive from the point of view of economics and ease of application [1]. Review of the most commonly used corrosion inhibitor types and the various possible mechanisms of inhibition have been recently published [2-4]. The corrosion inhibition efficiency of organic compounds is related to their adsorption properties. Adsorption depends on the nature and the state of the metal surface, on the type of corrosive medium and on the chemical structure of the inhibitor [5]. The use of corrosion inhibitors is one of the most effective methods to protect metal surfaces against corrosion, especially in acid media [6,7]. A number of heterocyclic compounds containing nitrogen, oxygen and sulphur either in the aromatic or long chain carbon system have been reported as effective inhibitors of metal corrosion [8]. Quantum chemical methods

have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity [9]. Density functional theory (DFT) has proven to be an important tool in modern quantum chemistry because of its ability to include some effects of electron correlation at a greatly reduced computation cost [10,11]. It also have provided a very useful framework for developing new criteria for rationalizing, predicting, and eventually understanding many aspects of chemical processes [12-16].

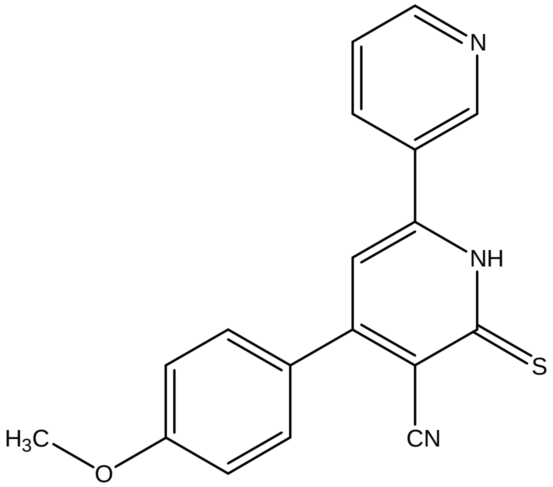
The quantum chemical calculations have been widely used to study the reaction mechanisms and to interpret the experimental results as well as to solve chemical ambiguities. This is a useful approach to investigate the mechanisms of reaction in the molecule and its electronic structure level and electronic parameters can be obtained by means of theoretical calculations using the computational methodologies of quantum chemistry [17]. The advancement in methodology and implementations has reached a point where predicted properties of reasonable accuracy can be obtained from density functional theory (DFT) calculations [18]. The geometry of the inhibitor in its ground state, as well as the nature of their molecular orbitals, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are involved in the properties of activity of inhibitors. The inhibition efficiency of the present study compounds PYCARS and PYCAR was experimentally studied previously [19].

The molecules which having nitrogen and sulfur in their structures are of particular importance, since these provide an excellent inhibition compared with the compounds that contain only sulfur or nitrogen [20]. The property of inhibition of the corrosion of these compounds is attributed to their molecular structure. The planarity (p) and the lonely electron pairs in the heteroatoms, are important features that determine the adsorption of these molecules on the metallic surface [21]. The effect of the molecular structure on the chemical reactivity has been object of great interest in several disciplines of chemistry [22].

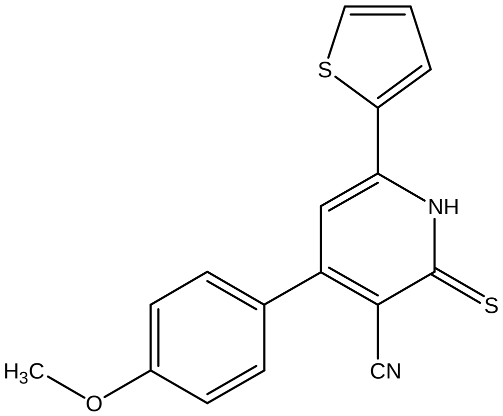
The objective of this paper is to investigate the dependence of inhibition efficiency of these compounds on theoretical chemical parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and the total energy (E_{tot}). The chemical structures of the compounds studied are given in **Figure 1.**

MATERIALS AND METHODS

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-09 software package. Geometry optimization were carried out by B3LYP functional at the 6-31G (d,p) basis set and at the density functional theory (DFT) level. Furthermore, DFT is considered a very useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data. The results of the geometry optimization of the compounds PYCARS and PYCAR are presented in **Figure 2.**

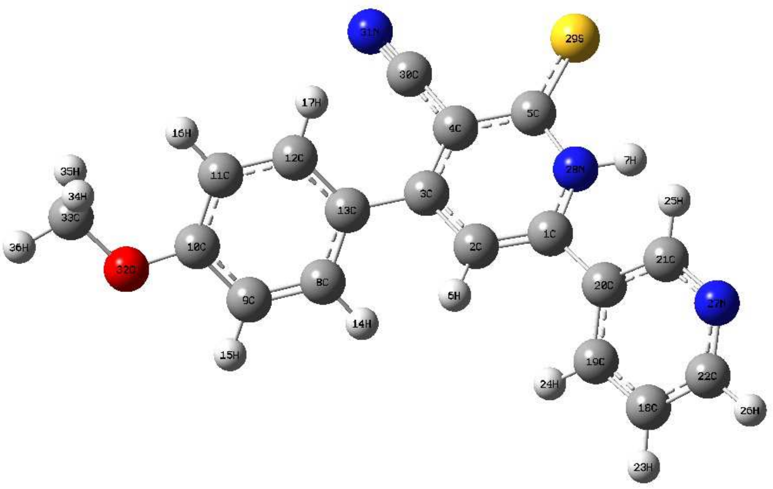


4-(4-methoxyphenyl)-6-thioxo-1,6-dihydro-2,3’-bihydro-2,3’-bipyridine-5-carbonitrile (PYCAR)

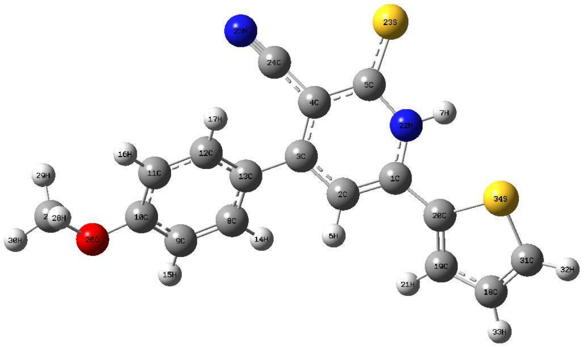


4-(4-methoxyphenyl)-6-(thiophen-2-yl)-2-thioxo-1,2-dihydropyridine-3-carbonitrile (PYCARS)

Figure 1: Chemical structure of pyridine carbonitrile derivatives



PYCAR



PYCARS

Figure 2: Optimized structures of pyridine carbonitrile derivatives

3. Theory and computational details

3.1. Theoretical calculations

The quantum chemical calculations have been widely used to study the reaction mechanisms and to interpret the experimental results as well as to solve chemical ambiguities [23]. The recent progress in DFT has provided a very useful tool for understanding molecular properties and for describing the behavior of atoms in molecules [24]. The basic relationship of the density functional theory of chemical reactivity is precisely, the one established by Parr, Donnelly, Levy and Palke, that links the electronic chemical potential μ with the first derivative of the energy with respect to the number of electrons, which in a finite difference version is given as the average of the ionization potential (I) and electron affinity (A), and therefore with the negative of the electronegativity (χ) [24].

$$-\mu = \chi = \partial E/ \partial N_{elec} \approx (I + A)/2 \qquad 1.$$

Electronegativity has also been expressed in terms of orbital energies [25]. According to Koopman's theorem, E_{HOMO} and E_{LUMO} of the inhibitor molecule are related to the ionization potential (I) and the electron affinity (A), respectively, i.e. by taking I as the negative of the HOMO energy and A as the negative of the LUMO energy [23, 26]. This gives

$$\chi = -(E_{HOMO} + E_{LUMO})/2 \qquad 2.$$

The second derivative of the energy with respect to the number of electrons is the hardness η [27], which again can be approximated in terms of ionization potential (I) and the electron affinity (A) of the inhibitor molecule.

$\eta = 1/2\ \partial^2 E/\ \partial N^2_{elec}\ = (I - A)/2$ 3.

Global softness (σ) is the reciprocal of global hardness [28]. From Eq. (3) it becomes:

$\sigma = 1/\ \eta = 2/(I\text{-}A)$ 4.

The electrophilicity index measures the electrophilic power of a molecule [29]. This parameter, is defined as

$\omega = \chi^2/2\eta \approx (I+A)^2/4(I\text{-}A)$ 5.

According to Pearson theory [30], the number of electrons transferred (ΔN) can be calculated depending on the quantum chemical method. The values of ΔN show inhibition effect resulted from electrons donation

$\Delta N = \chi_{Fe} - \chi_{inh} / 2\sum \eta_{Fe} + \eta_{inh}$ 6.

where χ_{Fe} and χ_{inh} denotes the absolute electronegativity of iron and the inhibitor molecule, respectively; η_{Fe} and η_{inh} denotes the absolute hardness of iron and the inhibitor molecule, the absolute electronegativity, χ and absolute hardness, η is a chemical property that describes the ability of a molecule to attract electron towards itself in a covalent bond [31]. In this study, we use the theoretical value of $\chi_{Fe} = 7.0$ eV [32] and $\eta_{Fe} = 0$ by assuming that for a metallic bulk I = A [33] because they are softer than the metallic atoms. Therefore, the difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance.

According to the simple charge transfer model for donation and back-donation of charges proposed recently by Gomez et al., [34] an electronic back-donation process might be occurring governing the interaction between the inhibitor molecule and the metal surface. The concept establishes that if both processes occur, namely charge transfer to the molecule and back-donation from the molecule, the energy change is directly proportional to the hardness of the molecule, as indicated in the following expression.

$\Delta E_{Back\text{-}donation} = -\ \eta/4$ 7.

The $\Delta E_{Back\text{-}donation}$ implies that when $\eta > 0$ and $\Delta E_{Back\text{-}donation} < 0$ the charge transfer to a molecule, followed by a back-donation from the molecule, is energetically favoured. In this context, hence, it is possible to compare the stabilization among inhibiting molecules, since there will be an interaction with the same metal, it is expected that it will decrease as hardness increases.

The electron donating (ω^-) and electron accepting (ω^+) powers have been defined as [35]

$\omega^- = (3I + A)^2/16(I - A)$ 8.

and

$\omega^+ = (I + 3A)^2/16(I - A)$ 9.

It follows that a large ω^+ value corresponds to better capability of accepting charge, whereas a smaller value of ω^- value of a system makes it a better electron donor. In order to compare ω^+ with ω^- , the following definition of net electrophilicity has been proposed [36]

$\Delta\omega^{\pm} = \omega^+ - (-\ \omega^-) =\ \omega^+ + \ \omega^-$ 10.

That is the electron accepting power relative to the electron donating power.

RESULTS AND DISCUSSION

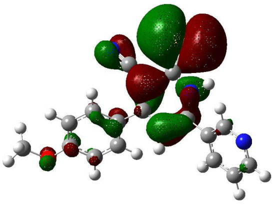
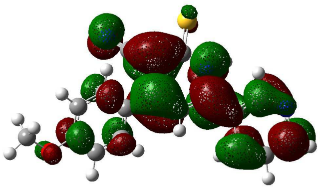
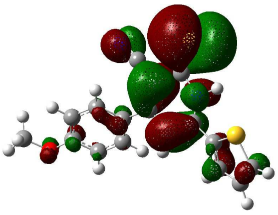
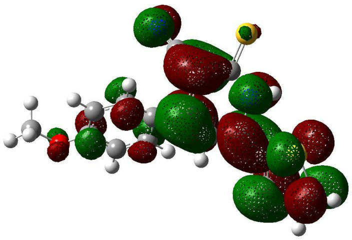
Density functional theory (DFT) has become an attractive theoretical method because it gives exact basic vital parameters for even huge complex molecules at low cost. According to the Frontier Molecular Orbital Theory (FMO) of chemical reactivity, transition of electrons is due to interaction between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of reacting species [37].

4.1 Mulliken atomic charges

The HOMO and LUMO diagrams **(figure 3)** of the corrosion inhibitors, reflects that the electron densities were distributed homogeneously throughout the molecules. Therefore, the mulliken atomic charges **(Table 1)** were examined to explain the inhibition approach of the molecules under investigation.

The more negative the atomic charges of the adsorbed inhibitors, the more easily the atom donates its electrons to the unoccupied orbital of the metal and adsorb preferentially on the metal surface. It is clear from **table 1** that Nitrogen and Sulphur atoms carrying negative charges could offer electrons to the metal surface to form a coordinate type bonds. Pyridine carbonitrile derivative (PYCAR) has three negatively charged N-donor atoms and one S atom. The negatively charged N-donor atoms may prefer adsorption of soft iron ion. However, Pyridine carbonitrile derivative (PYCARS) has two N donor atoms and two S atoms, and one six membered ring modified to five membered ring, the charges on the N and S atom of the Pyridine carbonitrile derivative have negative charges. PYCARS have one S atom outside the ring have negative charge, but the S in the five membered ring gets positive charge is due to the delocalization of electron current in the ring. The charges on the N and S atoms of PYCARS are more negative than PYCAR. Hence the order of inhibition is higher for PYCARS than PYCAR. The reason for this order of corrosion inhibition is clearly observed from the electron density map**.** The charges on the S and N atoms have a correlation with the corrosion inhibition efficiency investigated through the DFT method. Hence, it is understood that 4-(4-methoxyphenyl)-6-(thiophen-2-yl)-2-thioxo-1,2-dihydropyridine-3-carbonitrile (PYCARS) has the highest order of corrosion inhibition efficiency than 4-(4-methoxyphenyl)-6-thioxo-1,6-dihydro-2,3'-bihydro-2,3'-bipyridine-5-carbonitrile (PYCAR).

Figure 3: Frontier molecular orbital diagram of PYCAR and PYCARS using B3LYP/6-31G(d,p) basis set

Compounds	HOMO	LUMO
PYCAR		
PYCARS		

4.2 Frontier molecular orbital (FMO)

The energy of the HOMO provides information about the electron donating ability of the molecule. The molecule with the highest E_{HOMO} value often has the highest tendency to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy [38]. The inhibitor does not only donate electron to the unoccupied d orbital of the metal ion but can also accept electron from the d-orbtial of the metal leading to the formation of a feedback bond. The highest value of E_{HOMO} -5.57009 eV of PYCARS indicates the better inhibition efficiency than the inhibitor PYCAR (E_{HOMO} = -5.68574 eV). The energy gap

Table 1: Mulliken atomic charges on pyridine carbonitrile derivatives

PYCAR

1	C	0.340124
2	C	-0.21216
3	C	0.148441
4	C	0.003711
5	C	0.15032
6	H	0.115154
7	H	0.28607
8	C	-0.10606
9	C	-0.12118
10	C	0.362521
11	C	-0.14044
12	C	-0.09833
13	C	0.039746
14	H	0.090091
15	H	0.102878
16	H	0.100941
17	H	0.119198
18	C	-0.10305
19	C	-0.06519
20	C	0.040952
21	C	0.069511
22	C	0.106668
23	H	0.109795
24	H	0.114
25	H	0.12049
26	H	0.117035
27	N	-0.42608
28	N	-0.57727
29	S	-0.24292
30	C	0.270969
31	N	-0.49077
32	O	-0.51222
33	C	-0.08663
34	H	0.117935
35	H	0.124126
36	H	0.131596

PYCARS

1	C	0.42087
2	C	-0.21106
3	C	0.147189
4	C	0.002868
5	C	0.152025
6	H	0.114649
7	H	0.290778
8	C	-0.1063
9	C	-0.1213
10	C	0.361761
11	C	-0.14054
12	C	-0.09845
13	C	0.04003
14	H	0.090941
15	H	0.102002
16	H	0.100002
17	H	0.118827
18	C	-0.05723
19	C	-0.04678
20	C	-0.24336
21	H	0.11217
22	N	-0.59533
23	S	-0.24796
24	C	0.269369
25	N	-0.49289
26	O	-0.51271
27	C	-0.08608
28	H	0.117366
29	H	0.123694
30	H	0.130775
31	C	-0.28444
32	H	0.145606
33	H	0.114326
34	S	0.289168

Table 2: Quantum chemical parameters for inhibitor PYCAR and PYCARS calculated using B3LYP/6-31G(d,p) basis set

Parameters	PYCAR	PYCARS
Enthalpy of formation (au)	-1331.41308449	-1636.13211125
Dipole moment (Debye)	9.4932	9.8027
HOMO (eV)	-5.68574	-5.57009
LUMO (eV)	-2.55566	-2.52980
Ionization Potential (I) eV	5.68574	5.57009
Electron affinity (A) eV	2.55566	2.52980
Energy gap (ΔE)	3.13008	3.04029
Hardness (η) eV	1.56504	1.52105
Global Softness (σ) eV	0.63896	0.65744
Electrophilic index ω eV	5.42484	5.39172
Electronegativity χ eV	4.12070	4.04995
Chemical Potential μ eV	-4.12070	-4.04995

($\Delta E_{L-H} = E_{LUMO} - E_{HOMO}$) is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on the metal surface. Low values of the ΔE_{L-H} gap will render good inhibition efficiencies since the energy to remove an electron from the last occupied orbital will be minimized [39]. 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. **Table 2** shows that PYCARS has the lowest energy gap 3.04029 eV compared to of PYCAR inhibitor 3.13008 eV. It indicates that PYCARS could have better performance as corrosion inhibitor than PYCAR.

4.3 Ionization energy

Table 2 summarized the important global chemical parameters. Ionization energy is a fundamental descriptor of the chemical reactivity of atoms and molecules. High ionization energy indicates high stability and chemical inertness and vice versa [40]. The low ionization energy 5.57009 eV of PYCARS indicates its high inhibition efficiency compared to 5.68574 eV of PYCAR.

4.4 Electronegativity

The absolute electronegativity is the chemical property that describes the ability of a molecule to attract electrons towards itself in a covalent bond. According to Sanderson's electronegativity equalization principle, the molecule PYCAR with a high electronegativity quickly reaches equalization and hence low reactivity is expected which in turn indicates low inhibition efficiency [41]. The table 2 shows the order of electronegativity as PYCAR > PYCARS. Hence the increase in the difference of electronegativity between the metal and the inhibitior is observed in the order PYCARS > PYCAR.

4.5 Hardness and softness

Absolute hardness (η) is 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 reaction. A hard molecule has a large energy gap (large ΔE_{L-H} value) and a soft molecule has a small energy gap [42]. In our investigation PYCARS have low hardness value $\eta = 1.52105$ eV compared to that of the PYCAR ($\eta = 1.56504$ eV). The inhibitor with the least value of absolute hardness is expected to have the highest inhibition efficiency [43].

4.6 Number of electrons transferred

The number of electrons transferred (ΔN) and $\Delta E_{\text{Back-donation}}$ was also calculated and tabulated in **table 3**. Values of ΔN show that the inhibition efficiency resulting from electron donation agrees with Lukovit's study [44]. 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 PYCARS > PYCAR. Thus, the highest fraction of electrons transferred is associated with the best inhibitor PYCARS (0.96974 eV), while the least fraction is associated with the inhibitor that has the least inhibition efficiency PYCAR (0.91987 eV).

Table 3: The number of electron transferred (ΔN) and ΔE Back donation (eV) calculated for inhibitor PYCAR and PYCARS.

Parameters	PYCAR	PYCARS
transferred electron fraction (ΔN)	0.91987	0.96974
$\Delta E_{\text{Back donation}}$ (eV)	-0.39126	-0.38026

4.7 Back-donation

In **table 3.** $\Delta E_{\text{Back-donation}}$ values calculated for the inhibitors PYCARS and PYCAR are listed. According to Gomeze et al [45], during the presence of charge transfer the back-donation of charges is the negative of hardness ($-\eta/4$) which governing the interaction between the inhibitor molecule and metal surface. $\Delta E_{\text{Back-donation}}$ implies that $\eta > 0$ and $\Delta E_{\text{Back-donation}} < 0$ the charge transfer to a molecule, followed by a back-donation from a molecule is energetically favoured [46]. The order back-donation is followed as: PYCARS (-0.38026 eV) > PYCAR (-0.39126 eV), which indicates that back-donation is fovoured for the PYCARS, which is the best inhibitor.

There is general consensus by several authors that the more negatively charged a heteroatom is the more it can be adsorbed on the metal surface through the donor acceptor type reaction [47]. 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 one.

4.8 Electrophilicity index

The electron donating (ω^-) and electron accepting (ω^+) powers and net electrophilicity ($\omega^\pm$) of the inhibitor molecules calculated with B3LYP/6-31G(d,p) basis set, are presented in **table-4**. It follows that a larger ω^+ value corresponds to a better capability of accepting charge, whereas a smaller value of ω^- value of a system makes it a better electron donor. Based on the electron donating and accepting powers of PYCARS and PYCAR presented in the **table 4**, the order of corrosion inhibition is in the order cited below PYCARS > PYCAR.

Table – 4 Electron donating (ω^-) and electron accepting (ω^+) powers and net electrophilicity $\Delta\omega^\pm$ of inhibitor calculated with B3LYP/6-31G(d,p) basis set

Property	PYCAR	PYCARS
ω^- (eV)	7.68082	7.60988
ω^+ (eV)	3.56012	3.55994
$\Delta\omega^\pm$ (eV)	11.24094	11.16982

CONCLUSION

The inhibitory properties of two pyridine carbonitrile derivatives has been elucidated using quantum chemical calculations based on density functional theory at B3LYP/6-31G(d,p) basis set level. The calculated electronic parameters involved in the activity of the inhibitors confirmed that the order of inhibition efficiency. The inhibition efficiency increase with the increase in E_{HOMO}, and decrease in energy gap (ΔE). PYCARS has the highest inhibition efficiency because it had the highest HOMO energy and ΔN values and lowest energy gap it was most capable of offering electrons and it could have a better performance as corrosion inhibitor.

The parameters like hardness(η), Softness (S), electron affinity (EA) ionization potential (IE), electronegativity (χ), $\Delta E_{Back\text{-}donation,}$ ω^{+}, ω^{-}, $\omega^{\pm}$ and the fraction of electron transferred (ΔN) confirm the inhibition efficiency in the order of PYCARS > PYCAR. Finally, this study displays a good correlation between the theoretical and experimental data (earlier published data) which confirm the reliability of the quantum mechanical methods to study the inhibition of corrosion of metal surfaces.

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