Studies of Inhibition effect “E & Z” Configurations of hydrazine Derivatives on Mild Steel Surface in phosphoric acid

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\textbf{A B S T R A C T}

Inhibition effect of ‘Cis and Trans’ conformations of three families of azines namely: [1.2-bis(pyrrrole-2-ylidenemethyl) hydrazine (HZ\textsubscript{2})], 1.2-bis(thiophene-2-idenemethyl) hydrazine (HZ\textsubscript{3}) and 1.2-Bis(furly-2-idenemethyl) hydrazine (HZ\textsubscript{4})] on mild steel corrosion in 2.0M H\textsubscript{3}PO\textsubscript{4}, were investigated through electrochemical impedance spectroscopy, Weight loss measurements and X-ray diffraction. A compact HZ\textsubscript{2} inhibitor film was fabricated on the steel surface, and the film showed high inhibition efficiency, also, a reduction of the inhibition efficiency IE\textsubscript{exp}(\%) as the solution temperature. The isomers of Cis and Trans- HZ\textsubscript{2} were studied on the basis of their degree of planarity, their local and global electronic properties as well as their deformation capacity to adhere to the Fe-surface, using DFT and molecular dynamic simulations. A comparative study by standard deviation (SD) of Cis- and Trans-HZ\textsubscript{2}, with DFT method shows the higher correlation between X-ray diffraction, \(^1\text{H} & \(^1\text{C} \text{NMR Chemical Shifts and Trans geometric form. The adsorption behaviour of the both forms (Cis & Trans)-HZ\textsubscript{2} onto the Fe (111) face were investigated by Molecular Dynamics simulations in vacuo to verify their anti-corrosive efficiency. The results indicate that the adsorption energies, deformation energies and rigidity adsorption energies of Trans-HZ\textsubscript{2}, was greater than Cis-HZ\textsubscript{2}, which agree with the trends of the experimental inhibition efficiencies.

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1. Introduction

The use of mild steel or carbon steel is foremost in several construction works, possibly due to its superb mechanical properties and comparatively cheaper cost. Like other metals, however, its degradation, when in contact with corrosion agents like acids, is a considerable issue for its extensive use [1]. For instance, essential processes like pickling, descaling and oil wash acidizing employ acids such as hydrochloric (HCl), sulfuric (H₂SO₄) and phosphoric (H₃PO₄) acid mediums, with the disadvantage of corroding metal components [2]. NACE (National Association of Corrosion Engineers) reportedly projected the global cost of corrosion to be US$2.5 trillion to emphasize the cost management of the corrosion effects, not limited to environmental damage and safety, in global society. Meanwhile, proper implementation of corrosion control measures can save about $875 billion annually [1,3]. This can be well achieved with the use of effective corrosion inhibitors. Thus, research attention is geared towards both exploring existing materials and developing new materials that are capable of inhibiting metal corrosion in presence of acid.

The Family of heterocyclic (HZ) Azines is an important class with broad applications in organic synthesis [4]. The anti-corrosion efficiency of organic heterocyclic compounds containing different donor atoms facilitates the adsorption on the Fe-surface obeys the following order: -S- > -N- > -O- [5]. The Azines, (N = N), have achieved great significance in organic synthesis of heterocyclic compounds [6,7]. The Azine bond (N-N-N) play an important role as a corrosion inhibitor in heating systems for the isolation, the water or metal-surface treatment, the strong reduction ability and pharmacological activity [8–12]. The inhibitory effects are reinforced by the existence of the X-heteratoms. The Azines has formally a single (N=N=N) bond and can adopt nearly planar; Cis, Trans or twisted conformations, depending upon the co-ligands bonded to the Fe²⁺ and their preference for different coordination geometries [13]. Several theoretical analyzes have been carried out for two the isomeric forms of Hetero-cyclic Azines [14,15].

In resumption of previous works on the acid corrosion inhibitors [16,17], the family of azine compounds: [1,2-bis (pyrrole-2-ylidenemethyl) hydrazine (HZ₁), 1,2-bis (thiophen) 2-idenemethyl) hydrazine (HZ₂) and 1,2-bis (furyl-2-lidemethyl) hydrazine (HZ₃) were studied as corrosion inhibitors in (C = 2.0 M/H₃PO₄). The choice of ortho-phosphoric acid is justified by its wide use in the industry for example ‘Phosphate coatings’, very few publications have been published on corrosion inhibitors for mild steel/H₃PO₄. In addition, no studies on the relationship between structural parameters (Cis & Trans) and anti-corrosion efficiency of these molecules have been reported.

In order to continue the works already realized on the classification of anti-corrosion efficiency via quantum modeling and Molecular Dynamics simulations [16,17], we propose a new family of Azines (HZ₁, HZ₂ & HZ₃). Fig. 1 shows their respective molecular structures that were determined by spectroscopic analyses and confirmed by theoretical modeling. Thus, the present work focused on theoretical investigation of geometric Cis- & Trans- HZ, on mild steel surface in ortho-

phosphoric acid by analyzing the interaction between these inhibitors and crystal (111) face.

2. Computational methodology

2.1. Quantum chemical descriptors and parameters definition

DFT simulations were performed using Lee–Yang–Parr correlation functional (B3LYP) and 6–311+G(2d,2p) basis set by means of the Gaussian 09 W package [18]. The structural geometry of each of the heterocyclic Azines was firstly minimized, followed by the vibrational frequency analysis, prior to other quantum chemical calculations whose outputs were used to estimate some useful derived parameters such as EA(electron affinity), IP (ionization potential), η (global hardness), χ (electronegativity), ω (global electrophilicity index), ΔN (quantity of electron transferred to Fe atom from inhibitor molecule), μ (Dipole moment) and TE (Total Energy) were used to explain the electron transfer mechanism between the neutral form of the both geometric ‘Cis & Trans’ isomerism inhibitor molecules (HZ₁) and the Fe-surface in vacuo [19–21]. Visual inspections were performed using the GaussView program (version 5.0.8) [22] and Chemcraft program version 1.6 (build 489) [23].

\[
\begin{align*}
IE & : \text{Ionization energy (eV)} \\
IA & = -E_{\text{HOMO}} \\
EA & : \text{Electron affinity (eV)} \\
IE & = -E_{\text{LUMO}} \\
\Delta E_g & : \text{Energy gap (eV)} \\
\Delta E_g & = E_{\text{LUMO}} - E_{\text{HOMO}} \\
\eta & : \text{Global hardness (eV)} \\
\eta & = -\frac{1}{2} \Delta E_g \\
S & : \text{Global softness(eV)}^{-1} \\
S & = \frac{2}{\Delta E_g} \\
\Omega & : \text{Global electronegativity index(eV)} \\
\omega & = \frac{(E_{\text{HOMO}} + E_{\text{LUMO}})}{2} \\
\Delta E_{\text{back}} & : \text{Back donation(eV)} \\
\Delta E_{\text{back}} & = -\frac{\Delta E_g}{\Omega} \\
\Delta N & : \text{Electron fraction transferred from HZ to the Fe-surface} \\
\Delta N & = -\frac{\mu_{\text{HZ}} - \mu_{\text{Fe}}}{\mu_{\text{HZ}} - \mu_{\text{Fe}}} 
\end{align*}
\]
2.2. Molecular Dynamics simulation (MDs)

The MDs were conducted out to further gain insight into the interaction between the adsorbate and the iron sorbent. Metropolis Molecular Dynamics simulation methodology [24] using ‘Forcite’ module in Biovia Material Studio v 8.0 software [25], was used to model the surface—inhibitor molecules interactions. The ‘Forcite’ geometry minimization of two-possible conformational Cis(Z) and Trans(E) isomers of HZ₂ in neutral form before putting them on the Fe-face were performed by B3LYP/DNP + basis sets. Herein, the interaction between the Fe (111) crystal face and Z-HZ₂ and E-HZ₂ conformational isomers is executed in a 3D periodic simulation box (Lₓ=Lᵧ=0.35, L₂=0.40 nm) with periodic boundary conditions. The crystal (111) face was chosen for this simulation because it is among the thermodynamically stable miller indices faces as reported in the literature [26]. The simulation system was carried out with a slab thickness of 0.05 nm, a supercell of (8 × 8) and a vacuum of 0.3 nm along the C-direction (Oz-axis) with periodic boundary conditions in order to simulate the representative part of an interface devoid of any arbitrary boundary effects. The COMPASS force field is an ab initio force field that provides correct predictions of gas phase properties like conformational, structural, vibrational as well as the condensed phase properties such as cohesive energies and interaction energies for a wide range of organic molecules, inorganic molecules and metals [27]. MDs were run in microcanonical (NVT) ensemble at 308 K. Interaction energy (ΔE₁) or binding energy (ΔE₂) between the Fe substrate and inhibitor molecule could be calculated by:

$$\Delta E_{bind} = -\Delta E_{int} = (E_{sub} + E_{inh}) - E_{Total}$$

Where $E_{sub}$ is the energy of the Fe-substrate, $E_{inh}$ is the energy of the free inhibitor, and $E_{Total}$ is the total energy of the system.

3. Molecular properties

The geometries and electronic structures for Cis and Trans isomers of HZ₁ in vacuo were calculated by the minimization of equilibrium geometries and are gathered in Fig. 2.

3.1. Synthesis procedure of Azines HZ₁

A series of symmetrical Azines (HZ₁) has been synthesized in one-step, yields. Indeed, to a solution of each heterocycle-2-carboxaldehyde (31.24 mmol) in dry ether (20 ml), Azines was added (0.5 g, 15.62 mmol) with a few drops of glacial acetic acid as a catalyst. The mixture was stirred at room temperature for 72 h, the formed product was filtered and washed with dry ether. (FT-IR, 1H-NMR and 13C-NMR, XRD and MS) identified structures of HZ₁.

3.2. Spectral measurements of Azines HZ₁

HZ₁: Yellow powder. Yield 85%. Mp = 113 °C. Rf = 0.33 (silica/CH₂Cl₂) 1H NMR (300 MHz, CDCl₃) δ ppm: 8.59 (s, 2H, Hₙmine); 7.62 (d, 2H, H9); 7.03 (d, 2H, H7); 6.63 (m, 2H, H8). 13C NMR (75 MHz, CDCl₃) δ ppm: 150.76 (2C, Cₙmine); 148.14 (2C, furan-Cₙ); 146.56 (2C, furan-Cₙ); 151.80 (2C, furan-Cₙ). m/z (M⁺): 189. IR (KBr, cm⁻¹): ν(N-H) = 3119, ν(CHₙN, imine) = 1630, ν(N-N) = 1503, ν(C-C) = 1540, ν(C=O, furan) = 1309, ν(C-H) = 1071, 1008, 966, 869, 847.

HZ₂: Yellow powder. Yield 64%. Mp = 167 °C. Rf = 0.76 (silica/CH₂Cl₂) 1H NMR (300 MHz, DMSO) δ ppm: 8.82 (s, 2H, Hₙmine); 7.76 (d, 2H, H8), 7.61 (d, 2H, H7); 7.18 (t, 2H, Hₙ). 13C NMR (75 MHz, DMSO) δ ppm: 156.26 (2C, Cₙmine); 138.87 (2C, thiophen-Cₙ); 134.25 (2C, thiophen-Cₙ); 131.45 (2C, thiophen-Cₙ); 128.75 (2C, thiophen-Cₙ). m/z (M⁺): 121.02. IR (KBr, cm⁻¹): ν(N-H) = 3295, ν(CHₙN, imine) = 1609, ν(C=S, thiophene) = 1321, ν(C=O) = 1540, ν(C-H) = 1040.

HZ₃: Yellow powder. Yield 62%. Mp = 186 °C. Rf = 0.32 (silica/CH₂Cl₂). 1H NMR (300 MHz, DMSO) δ ppm: 11,52 (s,
1H, pyrrole-NH); 8.36 (s, 2H, H_{mine}); 6.96 (d, 2H, H8); 6.59 (s, 2H, H5); 6.16 (m, 2H, H9). 13C NMR (75 MHz, DMSO) δ ppm: 151.03 (2C, C_{mine}); 127.81 (2C, pyrrole-CI); 123.71 (2C, pyrrole-C2); 115.25 (2C, pyrrole-C9); 110.14 (2C, pyrrole-C7). m/z (M+):187.08. IR (KBr, cm⁻¹): v(N-H)=3212, v(CH=N, pyrrol)=1616, v(C=C)=1540, v(N-N)=1443, 1407, 1294, 1132, v(C-H)=1028, 953, 881, 810.

4. Experimental method

4.1. Weight loss(WL) measurements

Before all measurements, the steel samples (0.09% - P, 0.01% - Al, 0.38% - Si, 0.05% - Mn, 0.21% - C, 0.05% - S and remainder iron) were abraded with a series of emery boards papers from 400 to 1200 grids. The samples were thoroughly washed ultrasonically with ultrapure water and acetone, and finally dried under cold air flow. Gravimetric experiments were performed according to standard methods [28-32]. The WL measurements were performed in a double-walled glass cell. The volume of the solution was 100 cm³. The temperature of the solution was 308 (± 0.5) K controlled by thermostatically. The WL of steel in (C=2.0 M) aggressive solutions without and with addition of HZ3 inhibitors was determined after immersion in H3PO4 for 4 h. The steel specimens used for these examinations had a rectangular shape (1.5 cm × 1.5 cm × 0.2 cm).

4.2. Electrochemical measurements (EIS)

Electrochemical measurement(EIS) was conducted on a Tacussel electrochemical workstation (Tacussel-Radiometre PGZ-100) equipped with a standard three-electrode cell system under non stirred condition. The steel specimen was served as WE (working electrode), a 4 cm² platinum sheet was utilized as CE(counter electrode), and a saturated calomel electrode used as RE (reference electrode). All the potentials were in reference to the RE. The exposed surface area of disk S = (0.5)² × r cm² was fixed. All the tests were carried out in a temperature-controlled water bath at 308(±0.5) K.

EIS analysis was then performed on stable EOCP at a disturbance sinusoidal signal of 10 mV amplitude within the frequency range (100 kHz—1 Hz). The EIS data were analysed using ZViewer v. 0.0.2.2. The inhibition efficiencies IE_{imp}(%) obtained by the EIS test were calculated as follows:

\[ IE_{imp}(\%) = \frac{R_t - R_{ct}}{R_{ct}} \times 100 \]

where \( R_t \) and \( R_{ct} \) are the charge transfer resistant without and with different concentrations of HZ3.

Fig. 3 illustrates the relevant Nyquist diagrams for the mild steel electrode in (2.0 M/ H3PO4) solution without and with the addition of HZ3 concentration at 308 (± 0.5) K.

The capacitive loops in the Nyquist diagrams (Fig. 3) presents a depressed semi-circle at high frequencies. These depressed circles might be due to the frequency dispersion of the interfacial impedance and the in-homogeneity of the HZ3 on mild steel/H3PO4, while the tilted line indicates steel dissolution controlled by diffusion mechanism and oxygen reduction [33,34]. Introducing HZ3 sharply increased the diameter of the capacitive loop, and the diameter continuously increased with increasing HZ3 concentration. This finding implies the formation of an adsorbed film and the protective ability for mild steel. Moreover, the shapes of the curves for the inhibited samples are the same as the uninhibited ones, indicating the addition of HZ3 increased the impedance but did not alter the other electrochemical characteristics of this system. The different values obtained Table 1 show the representative parameter values of the best fit to experimental data and allow describing the overall impedance through Equ (11).

Table 1 shows the obtained EIS data. As seen that the C_{di} value decreased with the addition of HZ3 inhibitors. These values continuously decreased with increasing inhibitor concentration(from10⁻⁸ to 10⁻³M), which could be attributed to a decrease in local dielectric constant and the exposed steel surface and/or an increase in the electrical double-layer thickness [31]. Accordingly, it could be inferred that the HZ3 interacted with mild steel surface by adsorption action, and thus the reduction in the C_{di} value was due to the gradual displacement of H2O molecules by HZ3 on the mild steel/solution interface, leading to decreased extent of the mild steel dissolution [30]. The presence of HZ3 increased the R_{ct} values, and this effect was enhanced with increasing HZ3 concentration. This finding suggests the formation of a HZ3 adsorption film on the mild steel substrate, which retarded the charge transfer. Following these trend, IE_{imp}(%) values increased with increasing HZ3 inhibitors concentration. The classification of HZ3 according to its IE_{imp}(%) is: HZ3(87.57%); HZ3(84.6%) HZ3(83.57%). The superior inhibition performance indicates that HZ3 confer effective protection against mild steel corrosion in (C=2.0 M/ H3PO4).

The actual part of the impedance conduction to the grain boundaries. The chemical composition of the intermetallic compounds is identical at low frequency because one conduction DC is dominated. Only their size varies according to their location in the material: Microns for surface apparent phases and nanometric for grain boundary phases such that water molecules and H⁺ protons present in the medium.

In order to progress in the quantification of phenomena shows in Fig. 4, we first propose to decompose the cooperative electrical and chemical phenomena, indicated by the representation of the imaginary part of the complex impedance.

5. Results and discussion

5.1. Impedance measurement

5.1.1. Nyquist and Bode plots

EIS is widely used to explore the adsorption of corrosion inhibitors because it provides a convenient and rapid method for evaluation of the surface properties of metal materials.
imal and the losses do not appear. At very high frequencies, the field alternates too fast for the polarization to increase and there is no contribution to the dielectric constant - no energy is lost in the medium [33]. But somewhere between these two extremes, polarization begins to lag behind the electric field from which dissipation of energy at the same time the relaxation time. So, we can say at the lowest frequencies.

It is found that the relaxation frequency changes for some concentrations for HZ$_1$ and HZ$_3$. The relaxation frequency does not change for inhibitor HZ$_2$. This shows that the relaxation frequency for HZ$_2$ due to a specific behavior of the HZ$_2$ molecule.

5.1.3. Equivalent electrical circuit and modeling of mechanism of conduction

The EIS data were fitted using an classical equivalent circuit (Fig. 6) composed of solution resistance ($R_s$), charge-transfer resistance ($R_{ct}$), and constant-phase angle element $CPE_{dl}$, which are related to electrical double-layer capacitance ($C_{dl}$). During curve fitting, ideal capacitors ($C_{dl}$) were replaced by $CPE_{dl}$ because of the non-ideal capacitive behaviour of the inhomogeneous electrode. The impedance function of the CPE can be described as follows:

5.1.4. Comparative study by Nyquist diagrams

This comparison is made to compare with that found by Nyquist diagram. We found that HZ$_1$ has a very high ionic conductivity compared to other inhibitors such as HZ$_2$ and HZ$_3$. The relaxation frequency extracted from the imaginary conductivity measurement as a function of frequency has a lower frequency of HZ$_2$ (125 Hz) equivalent to a relaxation frequency in the Bode representation of value (125 Hz), in frequency results in a majority contribution to the level of the ionic conductivity at high frequency thanks to the mesomorphic effects of positions of the active sites.

![Impedance spectra of mild steel in H$_3$PO$_4$ (2 M) of HZ$_1$ at 308(±0.5 K).](image-url)
Based on Fig. 7, the increase in resistance can be detected significantly with increasing effect of the mesomeric inhibitor. Greater mesomeric effect at HZ₁, then HZ₃ and finally HZ₂ in descending order of the mesomeric effect.

5.1.5. Modeling Analysis
Fig. 8 shows the variation of the electrical hopping conductivity $\sigma_{ho}$. The mesomeric effect arises due to the substituents of the heteroatoms (-O-, -S- & =N-) in the both heterocyclic rings attached to azine bond (=N-N=). This effect favors a better conduction by jumping under the influence of the electric field applied to the sample. For example, Fig. 8 shows that the best $\sigma_{ho}$ is that of HZ₁ for the concentration $C = 10^{-3}$ M at 308(±0.5 K). This behavior has been discussed by Wang et al. [34], which reflects the aggregation of inhibitors particles due to compression of the electrical double layer, which favors the release of adsorbed water.
Fig. 6 – Corresponding equivalent circuit used to fit the EIS experimental data.

Fig. 7 – Nyquist diagram of HZ$_i$ ($i = 1, 2, 3$) for $10^{-3}$ M at 308±0.5 K.

In order to determine the mechanisms responsible for the very high conductivity, impedance spectroscopic investigations have been carried out. The electrical behaviour has been summarized in this figure at different HZ$_i$ inhibitors.

The values of the fitted equivalent electrical circuit, modeled of the conductivity at of all inhibitor molecules are listed in the Table 2.

6. Gravimetric measurements

6.1. Effect of HZ$_i$ concentration

The effect of addition of Azines HZ$_i$ at different concentrations in the range $10^{-3}$-$10^{-6}$M on the corrosion of steel in ($C=2.0$ M/H$_3$PO$_4$) was studied by weight loss method at 308±0.5 K after half hours of immersion period. From the weight loss results, the corrosion ($W_{\text{corr}}$) rate, the inhibition efficiency $I_{E_w}$(%) of Azines HZ$_i$ and the degree of surface coverage ($\theta$) were calculated by means of the following Eqs (12&13):

$$I_{E_w}(\%) = \frac{W_{\text{corr}}^0 - W_{\text{corr}}}{W_{\text{corr}}^0} \times 100 \quad (12)$$

$$\theta = \frac{W_{\text{corr}}^0 - W_{\text{corr}}}{W_{\text{corr}}^0} \quad (13)$$

Where $W_{\text{corr}}$ and $W_{\text{corr}}^0$ are the corrosion rate for (mild steel/H$_3$PO$_4$) without and with HZ$_i$.

Table 3, summarizes the obtained values of $W_{\text{corr}}$ and $I_{E_w}$(%). It is obvious from these results that this series of Azines HZ$_i$ inhibits the corrosion of mild steel at all concentrations used in this study. From the Table 6, it can be observed that the $W_{\text{corr}}$ of mild steel decreases while the protection efficiency increases as the inhibitors concentration increases in ($C=2.0$ M/H$_3$PO$_4$). This effect is hugely marked at higher concentration of inhibitors. The classification of these inhibitor molecules according to its $I_{E_w}$(%) is: HZ$_2$/HZ$_3$/HZ$_1$. It is predictable from the molecular structure of HZ$_i$ that the inhibitor HZ$_2$ will have the highest anti-corrosion performance ($I_{E_w}$(%)). It is due to the high electronegativity (electron
donating groups) of both heterocyclic rings (thiophene (HZ2) than pyrrol (HZ3) and furan (HZ1)) linked to bond azine (N1-N2) can give and share electrons to the empty orbital of iron on the steel surface, substituting aggressive substances on the Fe-surface and forming coordination links. The corrosion inhibition can be attributed to the interaction for (HZ3/mild steel/H3PO4) interfaces [34].

6.1.1. Adsorption Isotherm

The adsorption phenomenon of the organic inhibitors on the surface of metal is considered one of the most important factors of the inhibitor action in acidic media [16]. It is always possible to trace them back to adsorption mechanisms while determining the surface coverage (θ). In this study, the adsorption isotherms known in this scientific area were evaluated. Based on results obtained through gravimetric method, it has been found that the Langmuir isotherm is most suitable for the three compounds HZ3, and the corresponding equation is as follows [41]:

\[
\frac{C}{θ} = \frac{1}{K_{ads}} + C
\]

\[K_{ads}\] is the constant of adsorption; the \( K_{ads}\) value was calculated from the intercepts of the straight lines \( C/θ\) – axis and related to the standard free energy of adsorption (\( ΔG_{ads}\)) according this equation:

\[
ΔG_{ads}^0 = -RT \ln(K_{ads} \times 55.55)
\]

Where \( R \) is the gas constant (8.314/J/Kmol), \( T \) is the absolute temperature (K), and the value

55.55 is the concentration of water in the solution expressed in M. The calculated values of \( ΔG_{ads}^0 \), \( K_{ads} \) and \( R^2 \) from gravimetric data for the HZ3 are reported in Table 4.

Fig. 9 shows the plots of \( C/θ \) – axis against \( C \). A very good fit is observed with the regression coefficients up to 1 and the slopes of the obtained lines are near unity (that of HZ1 is close to 1.2), meaning that each inhibitor molecules occupies one active site on the metal surface and that the experimental data are well described by Langmuir isotherm and exhibit single layer adsorption characteristic [16]. In fact, the obtained \( K_{ads} \) values are considered as a measure of the adsorption strengths at the interface inhibitor/ metal [19,41]. From Table 4, we remark that the HZ3, which have a highest efficiency, give a most high value of \( K_{ads} \) leading in the strongest interaction between the double layer existing at the phase boundary and the adsorbed molecules. The calculated \( ΔG_{ads}^0 \) values for HZ1, HZ2 and HZ3 are -39.38, -39.71 and -38.39 kJ/mol, respectively. The negative values of \( ΔG_{ads}^0 \) indicates that the spontaneous adsorption of HZ3 and the stability of the adsorbed layer on the metal surface; HZ2 have always a highest value of \( ΔG_{ads}^0 \) (in absolute value). According to the literature, the \( ΔG_{ads}^0 \) values of -20 kJ/mol or less negative are associated to physical adsorption; those of -40 kJ/mol or more negative involves chemical adsorption. [16,41]. The obtained values of \( ΔG_{ads}^0 \) values close to -40 kJ/mol, indicating that the adsorption mechanism of the HZ3 molecules on mild steel in phosphoric acid solution (2 M) is more chemical than physical adsorption (a chemisorption).

6.1.2. Influence of temperature

In Table 5, we remark the effect of the temperature increase on the anti-corrosion property of HZ3. The gravimetric experi-

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**Table 2 – Parameter obtained of conductivity.**

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>( \sigma_{eff} ) (S/cm²)</th>
<th>( \sigma_{eff} ) (S/cm²)</th>
<th>(CPE) ( (F \cdot S^0) )</th>
<th>( n ) coefficient dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZ3</td>
<td>0.2044 ± 0.29</td>
<td>0.0443 ± 0.29</td>
<td>0.0001491 ± 1.93</td>
<td>0.8834 ± 0.29</td>
</tr>
<tr>
<td>HZ1</td>
<td>0.2041 ± 0.26</td>
<td>0.0492 ± 0.28</td>
<td>0.00020917 ± 1.70</td>
<td>0.87212 ± 0.28</td>
</tr>
<tr>
<td>HZ2</td>
<td>0.1933 ± 0.26</td>
<td>0.0354 ± 0.26</td>
<td>0.00012619 ± 1.62</td>
<td>0.85819 ± 0.25</td>
</tr>
</tbody>
</table>

**Table 3 – Gravimetric results of mild steel in \( C = 2 M/H_3PO_4 \) without and with addition of HZ3 at 308 (±0.5) K.**

<table>
<thead>
<tr>
<th>( \text{Inhibs} )</th>
<th>HZ1</th>
<th>HZ2</th>
<th>HZ3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C ) (M)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>4.1322 ± 0.024</td>
<td>------</td>
<td>4.1322 ± 0.024</td>
</tr>
<tr>
<td>1 × 10⁻⁵</td>
<td>1.5508 ± 0.055</td>
<td>62.47</td>
<td>1.3752 ± 0.016</td>
</tr>
<tr>
<td>5 × 10⁻⁵</td>
<td>1.3136 ± 0.001</td>
<td>68.21</td>
<td>1.1876 ± 0.008</td>
</tr>
<tr>
<td>1 × 10⁻⁴</td>
<td>1.1764 ± 0.013</td>
<td>71.53</td>
<td>1.0492 ± 0.001</td>
</tr>
<tr>
<td>5 × 10⁻⁵</td>
<td>1.0137 ± 0.003</td>
<td>73.29</td>
<td>0.8194 ± 0.003</td>
</tr>
<tr>
<td>1 × 10⁻³</td>
<td>0.9340 ± 0.008</td>
<td>77.40</td>
<td>0.7235 ± 0.002</td>
</tr>
</tbody>
</table>

**Fig. 9 – Langmuir adsorption isotherm for mild steel in phosphoric acid (2 M) containing HZ1, HZ2 & HZ3 at 308 K.**
Table 4 – Adsorption parameters of HZ₄ on mild steel in phosphoric acid (2 M) at 308 K.

<table>
<thead>
<tr>
<th>Inhibitors HZᵢ</th>
<th>R²</th>
<th>Kₑₒₑ (10⁻⁵ M⁻¹)</th>
<th>ΔGᵢₑₒₑ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZ₁</td>
<td>0.999</td>
<td>8.59</td>
<td>−39.38</td>
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<tr>
<td>HZ₂</td>
<td>0.999</td>
<td>9.77</td>
<td>−39.71</td>
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<tr>
<td>HZ₃</td>
<td>1</td>
<td>5.84</td>
<td>−38.39</td>
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</table>

Table 5 – Temperature influence on the weight loss parameters for mild steel in (2 M/H₂PO₄) without and with 10⁻³ M of HZᵢ.

<table>
<thead>
<tr>
<th>Inhs</th>
<th>Wₑₒₑ (mg/cm²·h)</th>
<th>IEₑ</th>
<th>Wₑₒₑ (mg/cm²·h)</th>
<th>IEₑ</th>
<th>Wₑₒₑ (mg/cm²·h)</th>
<th>IEₑ</th>
<th>Wₑₒₑ (mg/cm²·h)</th>
<th>IEₑ</th>
</tr>
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<tr>
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<td>9.077</td>
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<td>15.392</td>
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<td>22.792</td>
<td>****</td>
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<tr>
<td>HZ₁</td>
<td>0.934</td>
<td>77.4</td>
<td>1.680</td>
<td>70.79</td>
<td>2.909</td>
<td>65.1</td>
<td>10.170</td>
<td>55.37</td>
</tr>
<tr>
<td>HZ₂</td>
<td>0.723</td>
<td>82.49</td>
<td>3.579</td>
<td>81.49</td>
<td>7.702</td>
<td>81.1</td>
<td>12.170</td>
<td>46.60</td>
</tr>
<tr>
<td>HZ₃</td>
<td>0.769</td>
<td>81.37</td>
<td>3.140</td>
<td>65.41</td>
<td>6.338</td>
<td>58.8</td>
<td>11.209</td>
<td>50.82</td>
</tr>
</tbody>
</table>

CPE: Pseudo capacitance

ments were conducted in the range of 308–338(±0.5)K, without and with C = 10⁻³M of HZᵢ. We also note that the inhibition efficiency decreased with increase in temperature from 308 to 338(±0.5) K, indicates that high temperature dissolution of steel predominates over adsorption at the iron surface. This can be explicated by the decrease of the strength of the adsorption process at high temperature, and can suggesting that physisorption occurs.

The thermodynamic parameter descriptors of Fe-HZᵢ complexes on can provide valuable information about the mechanism of corrosion inhibition. In order to determine these activation thermodynamic descriptors, the Arrhenius equation Eq. (16) and its alternative formulation called transition state equation Eq. (17) were used [33]:

\[
Wₑₒₑ = A \exp \left( \frac{-E_a}{RT} \right) \tag{16}
\]

\[
Wₑₒₑ = \frac{RT}{N_k} \exp \left( \frac{-\Delta S_a}{R} \right) \exp \left( -\frac{\Delta H_a}{RT} \right) \tag{17}
\]

Where \(E_a\) is the apparent activation energy, \(N\) is the Avogadro's number, \(R\) is the universal gas constant and \(T(K)\) is the absolute temperature, \(h\) is the Planck's constant, \(\Delta H_a\) the enthalpy of activation and \(\Delta S_a\) entropy of activation (Fig. 10).

The calculated \(E_a\) without HZᵢ in acidic medium (+55.36 kJ/mol) is approximately in the same order of magnitude as that previously described [34]. The obtained \(E_a\) values with inhibitors HZ₁, HZ₂&HZ₃ are +47.75, +99.73 and +88.88 kJ/mol, respectively (Fig. 11).

The \(E_a\) values in the presence of the HZ₂&HZ₃ inhibitors are higher than those of the uninhibited acidic solution. This increase in \(E_a\) value may be interpreted as physisorption [35]. Moreover, Szauer et al. [36] explained that the increase in \(E_a\) value can be attributed to an appreciable decrease in the adsorption of the inhibitor on the Fe-surface with increase in temperature. The \(E_a\) value in the presence of HZᵢ is lower than that of the uninhibited acid solution, indicating that chemisorption may be the type of adsorption of the inhibitor on the Fe-surface [37]. On the other hand, the thermodynamic parameter descriptors, \(\Delta H_a\&\Delta S_a\), were calculated and

---

Fig. 10 – Arrhenius plots for (mild steel/2M/H₂PO₄) without and with 10⁻³ M of HZᵢ.

Fig. 11 – Transition state plots for (mild steel/2M/H₂PO₄) without and with 10⁻³ M of HZᵢ.
depicted in Table 6. The $\Delta H_a$ values are positive in the absence and presence of Azines HZ$_2$, and the maximum $\Delta H_a$ value was noted for HZ$_2$ best inhibitors of this series. The positive $\Delta H_a$ value reflect the endothermic nature of mild steel dissolution process suggesting that its dissolution is slow in the presence of these compounds [38]. The high $\Delta H_a$ value in the case of HZ$_2$ indicated that this last is more strongly adsorbed onto the Fe-surface. One can notice that $E_a$ and $\Delta H_a$ values vary in the same way permitting to verify the known thermodynamic equation between the $E_a$ and $\Delta H_a$: $E_a - \Delta H_a = RT$ as exposed in Table 6 [39].

The positive $\Delta S_a$ value of HZ$_2$ than other inhibitors reflects the fact that the adsorption process is accompanied by an increase of the entropy, which is the driving force for the adsorption of the inhibitor onto the Fe-surface [40]. The increase of $\Delta S_a$ value is generally interpreted as an increase in disorder as the reactants are converted to the activated complexes. The large negative $\Delta S_a$ value of HZ$_2$ implies that the activated complex is the rate determining step, rather than the dissociation step.

7. MD simulation

7.1. Simulated and Experimental 1H & 13C NMR spectral analysis

The $^1$H & $^{13}$C NMR chemical shifts were also determined for HZ$_2$ using the B$_3$LYP/6-311+G(2d,2p) level of theory and SCRF with chloroform as solvent. The experimental $^1$H & $^{13}$C chemical shifts are closer to the theoretical values and a linear relationships between experimental and theoretical $^1$H & $^{13}$C values was found (Table 7). The higher correlation between $^1$H & $^{13}$C NMR chemical shifts values of Trans-form between DFT method and experimental NMR are provided by standard deviation (SD). In fact, SD’s between the Trans-conformer and experimental NMR of $^1$H & $^{13}$C chemical shift values are: (0.0102 & 0.2159 ppm), (0.86 & 0.1038 ppm) and (0.2756 & 0.20265 ppm) for HZ$_2$, HZ$_2$ and HZ$_2$, respectively. The $^1$H & $^{13}$C NMR values of geometric Trans-forms of HZ$_2$ are listed in Table 7.

7.2. Frontier molecular orbitals

The employed DFT(B3LYP) method is suitable for rationalizing the frontier molecular orbitals for the assessment of inhibitor-metal interaction [42]. The $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ are directly obtainable, alongside with the $\Delta E_g (E_{\text{HOMO}} − E_{\text{LUMO}})$ from the computational output. Quantum reactive descriptors are accomplished to study the influence of structural parameters on the inhibition efficiency of HZ$_2$ and to unravel their adsorption mechanisms on the Fe-surface. Zhang et al [43], reported a convincing argument against the accuracy of quantitative values for $E_{\text{HOMO}}$ & $\Delta E_g$ without necessary correction factors, especially for small molecules. Therein, depending on the DFT functional, equations were given to obtain corrected values from uncorrected values, with experimental validations [43]. With respect to the functional employed in this study, Eqs (18 & 19) were used to obtain corrected values for both $E_{\text{HOMO}}$ & $\Delta E_g$.

$$E_{\text{HOMO}}^\text{corrected} = 1.42 + (1.2 \times E_{\text{HOMO}}^\text{uncorrected})$$

$$\Delta E_g^\text{corrected} = -1.02 + (0.93 \times \Delta E_g^\text{uncorrected})$$

Frontier molecular orbital diagrams of Geometric ‘Cis’ and ‘Trans’ Isomerism of HZ$_2$ are calculated by DFT at [B$_3$LYP/6-311+G(2d,2p), Gas] level and are summarized in Figs. 12 and 13.

From the charge density distribution of the frontier molecular orbitals for Cis/Trans geometric forms of Azines HZ$_2$, as presented in Figs. 12 and 13, it could be seen that the Cis conformation has high HOMOs and low density LUMOs distributions than Trans which were mainly located around the $\equiv N-N \equiv$ and $\equiv N-C \equiv$ moiety in the HZ$_2$. The HOMO orbital is mainly derived from $P_{2z}$ orbitals than to the delocalized character of the electrons due to the presence of the heterocyclic rings together with several ($\pi$-$\pi$)-electrons in the entire inhibitor molecule. Conversely, the formation of density LUMOs orbital does not involve the participation of the former $P_{2z}$ orbitals. Thus; unoccupied (3d)-orbitals of mild steel can accept electrons from the inhibitors and forming a feed-back bonds between these inhibitor molecules and Fe$^{2+}$ ions.

7.3. Calculated geometric parameters

The link lengths, link angles and torsional angles of the conformations of HZ$_2$ were determined theoretically, at the [B$_3$LYP/6-311+G(2d,2p), gas] level, and experimentally (X-ray diffraction) and gathered in Table 8.

Comparison of bond lengths listed in Table 8, for Cis & Trans isomers shows that, for any given substrate, the $\equiv N_1-N_1$ and $C_5-C_4$ bond length increases in the order Cis > Trans while the $\equiv C_1-X$ distance decreases in the order Trans > Cis. The strength of the intermolecular interaction increases with the shortening of the $\equiv C-C \equiv$ bond. As well for all inhibitors, the minimized geometric forms easily interconvert from Cis conformation to a Trans conformation (stable form) and reveal rotation around the $\equiv N_1-N_1 \equiv$ and $\equiv C_5-C_4 \equiv$ bond. Overall, the Cis $\rightarrow$ Trans isomerization energy barriers are found to be influenced by the size, electronic character of substituted halogens and temperature [44].

Survey of Table 8 shown that, the Cis & Trans- HZ$_2$ fully planar by means of X-ray and our DFT calculations at the B$_3$LYP/6-311+G(2d,2p) level in vacuo. We have already used
the standard deviation (SD) as part of comparative studies between the data of X-ray and those derived from the quantum mechanics calculations [41]. In the present work, a comparative study of conformations of the Azine substituents with DFT method shows a good correlation between Trans-Form and X-ray diffraction data. Indeed, the standard deviation (SD) between the Trans conformers (calculated by DFT) and X-ray values of HZi are: (0.06 Å and 0.116 °), (0.22 Å and 0.016 °) and (0.05 Å and 0.13 °) for bond lengths and bond angles of HZ1, HZ2 and HZ3, respectively. Conversely, the standard deviation (SD) between the Trans conformers (calculated by DFT) and X-ray values of HZi are: (0.07 Å and 0.05 °), (0.0011 Å and 0.012 °) and (0.003 Å and 0.114 °) for bond lengths and bond angles of HZ1, HZ2 and HZ3, respectively. Hence, the crystal geometry of HZi agrees more with the Trans than with the Cis geometric conformer.
3D-distribution of MEPs is highly useful in predicting the reactive site behavior of the symmetrical Azines. The MEP surface of the geometric ‘Cis & Trans’ conformers of all HZ2 are on overlaying of the electrostatic potential on to the isoelectronic density surfaces. This is a valuable tool for describing overall molecule charge distribution as well as anticipating sites of electrophilic addition. In the link Azine (≡N1-N2 ≡ region of negative charges (red color) is seen around the electronegative nitrogen≡N1, and ≡N2 are susceptible for electrophilic attack. Blue color represents strongly positive region (electrophile region) and the predominant green region in the MEP surfaces corresponds to a potential halfway between the two extremes red and blue region in (thiophene, furan and pyrrole) heterocyclic rings. The MEP surface picture of HZ2 for Cis/Trans-forms are shown in Fig. 14.

### 7.4. Molecular electrostatic potential surface (MEPs)

By extension, DFT Mulliken population analysis can be used to determine the active sites of single inhibitor molecules and its function entails using local descriptors to theoretically justify the HSAB principle [42]. This gives information about the most probable site for electrophilic or nucleophilic attack on the molecule. It is confirmed that the more negatively charged het erotatom is, the more is its ability to adsorb on the Fe-surface through a donor-acceptor type reaction [43]. The DFT-Mulliken charge distributions for the structures Cis- and Trans-forms of HZ2 are presented in Fig. 15.

The Fig. 15 representing the effective atomic charges from Mulliken populations of HZ2 at different conformers (Cis &Trans), shows that the Trans- HZ2, have high negative charge densities trough to the active’s sites specially the nitrogen atoms. This is due to the existence of possible rotations around the links -C1-C4 - and ≡N1-N2= inducing a big difference in dipole moment, which would lead to very different intermolecular forces [44,45].

When HZ2 adsorbed on the mild steel in aqueous solution of ortho-phosphoric acid, the Cis-form geometry (highest-energy structure) change to a planar geometry (lowest-energy structure) Trans form; thus, the theoretical study predicts the favored configuration as Trans only [46]. Experimentally, the Trans geometric conformer is synthesized and stable in water (not Cis) [47,48]. The molecules of HZ2, Trans form have more potency charges than Cis form. This is due to the tautomeric effect between the two heterocyclic rings and bond Azine (Fig. 16). This delocalization character of electrons yields to a more stable planar structure of HZ2. Thus, the minimized structure is in accordance with the fact that corrosion inhibitors efficiency.

### 7.6. General Quantum descriptors

The reactivity of Cis &Trans-forms of Azines, on mild steel corrosion in aqueous solutions of phosphoric acid has been explained based on electron-donor properties related to the structure and the mode of adsorption. Preliminary study of inhibitor as isolated molecule, found that the solvent does not affect the molecular activity. So, this is an important argument to study the species reactivity only in vacuo [49].

High correlation coefficients between IE_{exp} (%) and some local quantum reactivity descriptors (μ, ∆ E_b, σ & ∆E_b,a) were found for both forms Trans and Cis (Table 9). Indeed, as electronic properties, these parameters play a main role in the corrosion inhibition mechanism [16]. The effect of the structural parameters on the inhibition efficiency of the both geometric forms, their relative stability and their adsorption mechanisms on the Fe-surface. The quantum reactivity descriptors of Geometric ‘Cis & Trans’ forms and inhibition efficiency IE_{exp} (%) of HZ2, are exposed in Table 9 where R2 is stands for the correlation coefficient between IE_{exp} (%) and the considered local quantum reactivity indices.

The difference in the stability between geometric Cis- & Trans-Forms can be estimated from the corresponding total energy (TE) reported in Table 9. In Trans-Form, the two heterocyclic moieties are opposite to each, whereas, in Cis the two heterocyclic moieties are on the same sides. The possibility existing in the conformation Cis-Form of all HZ is ruled out because severe steric crowding exists between the two
heterocyclic, the geometric Trans-form was found to be more stable than the Cis-form [49]. Thus, the Azines adopt a 'Trans' configuration slightly more stable than the geometric Cis conformers. In the totally symmetric structures where μ (deby) values tend to 0, there is no μ (deby) to interact with water and hence, we have a lower energy of solvation. Conversely, the structures of the Cis isomer are slightly deviated out of the plane due to the steric hindrance between the heterocyclic rings (thiophen, furan and pyrrol) attached to the chain linked in hydrazine.

The energy gap (ΔE₀) is an important parameter as a function of reactivity of the inhibitor molecule towards an understanding the adsorption process on the Fe-surface. High chemical reactivity and low kinetic stability are general features of a molecule with low ΔE₀ [50]. Reportedly, excellent corrosion inhibitors are usually organic compounds, which not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal [51]. A molecule with a low ΔE₀ is more polarizable, is generally associated with the high chemical activity and low kinetic stability, and is termed soft molecule [52]. The inhibition efficiency of Trans conformer increases when ΔE₀ decrease. The low value ΔE₀ (~3.6196 eV) of Trans-HZ₂ indicate the high (IEₘp) than the same geometry conformers HZ₃ & HZ₁. This means that the molecule HZ₂ of the geometric ‘Trans-form’ could have better performance as a corrosion inhibitor (there is excellent linearity between ΔE₀ values and experimental data with a correlation coefficient R² which tend to → 1)).

It is clear from Table 9, that HZ₁, HZ₂ & HZ₃, have higher IP (ionization potential) with low AP(electron affinity). In fact, under DFT minimization, the vertical electron affinities show positive values indicating that these inhibitors are extremely stable and may not undergo any reaction easily. The low IP of geometric ‘Trans-form’ indicates the high inhibition efficiency than geometric Cis-form [55]. The calculated ionization potential (I) follows the order HZ₂ > HZ₁ > HZ₃ which does not support the order obtained for the inhibition efficiencies (value of R² tends to → 0).

The both descriptors η (hardness) and S (softness) are important properties to measure the molecular reactivity and stability. It is apparent that the parameter η signifies the resistance towards the polarization or deformation of the electron cloud of the ions, atoms or inhibitor molecules under small perturbation of chemical reaction. A hard molecule has a large ΔE₀ value and a soft molecule has a small ΔE₀ value [56]. Table 9 show that the geometric ‘Trans’ conformers are energetically more stable than the geometric ‘Cis’ conformers.

---

### Table 9 - Quantum reactivity descriptors for the geometric Cis and Trans-Form of HZ₁

<table>
<thead>
<tr>
<th>R² (Cis)</th>
<th>R² (Trans)</th>
<th>HZ₁(Cis)</th>
<th>HZ₁(Trans)</th>
<th>HZ₂(Cis)</th>
<th>HZ₂(Trans)</th>
<th>HZ₃(Cis)</th>
<th>HZ₃(Trans)</th>
<th>T.E (au)</th>
<th>Eₜ (eV)</th>
<th>μ (deby)</th>
<th>σ(eV)¹</th>
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<th>χ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.39</td>
<td>+0.39</td>
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<td>-605.226</td>
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<td>-645.930</td>
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<td></td>
</tr>
<tr>
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<td>-5.878</td>
<td>-5.8718</td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>-1.8155</td>
<td>-2.3641</td>
<td>-2.3333</td>
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<tr>
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<td>+0.97</td>
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<td>0.548</td>
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<td>-0.4561</td>
<td>-0.4524</td>
<td>-0.4677</td>
<td>-0.4628</td>
<td>1.3877</td>
<td>0.000008</td>
<td>-Δb(d(eV))</td>
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<td></td>
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</tr>
<tr>
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<td>+0.805</td>
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<td>83.57</td>
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<td>+0.99</td>
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<td>+3.6487</td>
<td>+3.6484</td>
<td>+3.6196</td>
<td>+3.7418</td>
<td>+3.7023</td>
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<td>87.61</td>
<td>83.57</td>
<td></td>
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</table>
ers, whereas, in contrast, the parameter $\eta$ of the Cis isomer is greater than the Trans isomer. In the present study, the Trans-HZ$_2$ has the lowest $\eta$ (+1.8098 eV) and the lowest $\Delta E_g$ (+3.6196 eV) when compared to the other Trans-conformers of HZ$_3$ & HZ$_1$. Normally, the inhibitors with the least value of $\eta$ (hence the highest value of global softness) are expected to have the highest inhibition efficiency [57]. For the simplest transfer of electron, adsorption could occur at the part of the molecule where $S$, which is a local property, has a highest value [58]. Trans-form of HZ$_2$ with the S value of +0.553 eV has the highest IE$_{imp}$. The high performance of geometric Trans-HZ$_2$ is attributed to the size of the molecule covering the surface and thereby inhibits corrosion of metal. Hence, we have a good linear correlation between geometric properties and IE$_{imp}$, on the one hand, the $\eta$ (absolute hardness) and S (softness) values and IE$_{imp}$ values, on the other hand with good regression coefficients (with a correlation coefficient $R^2$ of +0.97).

The $\mu$ (Dipole moment) is another crucial descriptor that is well correlated with inhibition efficiency of a molecule in the

Fig. 15 – DFT Mulliken charge distributions for Cis- and Trans- HZ$_i$.  

<table>
<thead>
<tr>
<th>Cis-Forms</th>
<th>Trans-Forms</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZ$_1$</td>
<td></td>
</tr>
<tr>
<td>HZ$_2$</td>
<td></td>
</tr>
<tr>
<td>HZ$_3$</td>
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</tr>
</tbody>
</table>
8. Molecular Dynamics simulation (MDs)

MDs was implemented to inspect the experimental data and elucidate the adsorption behavior and inhibition mechanism of the two-possible conformational Cis(Z) and Trans(E) isomers of HZ$_i$ on the steel surface in vacuum. The experiments incorporating the theoretical calculation and MDs can provide insights into the understanding of interactions between the adsorbate and substrate. The Atomistic MDs can reasonably predict the lowest-energy adsorption and most favorable configuration of the both forms Z-HZ$_i$ and E-HZ$_i$ conformations on Fe (111) surface in the gas phase. The Final and lowest energy configuration results of the E-Z configuration of HZ$_i$, obtained by forcite module simulation in vacuo at 308 K are depicted in Fig. 17.

The adsorption of the both conformers (Z-HZ$_i$ & E-HZ$_i$) on Fe (111) surface takes nearly parallel to the surface so as to maximize its contact with the Fe-surface, as shown as the MDs (Fig. 17). Several outputs and descriptors derived Z-HZ$_i$ & E-HZ$_i$ configurational isomers in vacuo at 308 K by “forcite” module simulation is listed in Table 10.

In this work, the $E_{ads}$ (adsorption energy) is defined as the sum of the R.A.E (rigid adsorption energy) and the $E_{def}$ (deformation energy) for the complexe. The R.A.E reports the energy released (or required) when the unrelaxed adsorbate before the geometry optimization step are adsorbed on the Fe (111) face in the gas phase. The $E_{def}$ reports the energy released when the adsorbed component inhibitor molecule is relaxed on the Fe- surface. Table 12, also shows (dE$_{ads}$/dN$_i$), which defines the energy of the substrate–adsorbate configurations where one of the adsorbate components has been removed.

From the Table 10, it’s quite clear that the large negative values of adsorption energies for Z and E configurational isomers of HZ$_i$ suggest that all inhibitor molecule conformation can be adsorbed onto the Fe (111) surface strongly. We can see also that the E conformations has higher interaction energy compared with E conformations of HZ$_i$. Base of the adsorption energy values obtained by ‘Forcite’ module simulations, the adsorption strength of two E conformations of inhibitors HZ$_i$ on Fe-surface in vacuo can follow the order: HZ$_2$-Trans > HZ$_1$-Trans > HZ$_3$-Trans. This same trend is observed with respect to quantum chemical parameters that are well correlated with corrosion inhibition performance. Altogether, results from this computational studies are in good agreement with the inhibition efficiencies reported experimentally.

The Radial Distribution ($g(r)$) Functions of the two-possible conformational Z-HZ$_i$ & E-HZ$_i$ are obtained by “Forcite” module simulations (Fig. 18). As shown in Fig. 18, the distance between the active centers in both conformers (Cis and Trans)-HZ$_i$ and Fe (111) surface in vacuo are in the range 2.91-3.20 Å, less than 3.55 Å, which designated that chemical bonds have formed between E & Z geometry corrosion inhibitors and Fe atoms and that outside 3.55 by Van der Waals and Coulomb interactions [60,61].

The distance between Fe atom and heteroatoms of azines indicates the strength for the metal-inhibitor complex; a
shorter distance indicates stronger interactions while a longer distance indicates feebler interactions. As can be seen in Fig. 18, that the trend follows the order: \( \text{HZ}_2\text{-Trans} < \text{HZ}_3\text{-Trans} \leq \text{HZ}_3\text{-Cis} < \text{HZ}_2\text{-Cis} < \text{HZ}_1\text{-Cis} \), which confirms that the E-conformers has the strongest interaction with the Fe-surface than Z-conformers. This is consistent with our observed experimental trend of inhibitory efficacy of E-conformers inhibitors.

**Table 10 – Energy parameters (kJ/mol) for (Fe(111)/Z & E-(HZ)) complexes**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>( E_{\text{Total}} )</th>
<th>( E_{\text{ads}} )</th>
<th>R.A.E</th>
<th>( E_{\text{Def}} )</th>
<th>( dE_{\text{ads}}/dN )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZ(_1)-Z</td>
<td>–74.849</td>
<td>–74.845</td>
<td>–72.67</td>
<td>–162.03</td>
<td>–234.70</td>
</tr>
</tbody>
</table>

**Fig. 17 – Side and top views of most stable adsorption configurations for (Fe (111) / (E&Z)-HZ\(_i\)/Gas phase) systems at 308 K.**

**Fig. 18 – Radial Distribution \( g(r) \sim r \) Functions for (Fe (111) / (E&Z)-HZ\(_i\)/Gas phase) systems at 308 K.**
9. Conclusion

On the basis of the systematic experimental and theoretical investigation of HZ as a corrosion inhibitor of mild steel in this work, the following points can be drawn:

- EIS results were in good agreement with those obtained from Weight loss measurements, and the calculate of inhibition efficiency ($I_{\text{exp}}(\%)$) increased with increasing HZ concentrations in the order HZ$_2$/HZ$_3$/HZ$_1$.
- HZ$_1$ showed superior inhibiting ability at relatively high temperatures, although the corrosion of mild steel /H$_2$PO$_4$ was accelerated by the increase in temperature. The thermodynamic parameter descriptors indicate that HZ$_2$ is adsorbed on mild steel surface in 2 M H$_2$PO$_4$ solution by an endothermic process and reveal that the adsorption mechanism of HZ$_1$ is mainly chemisorption.
- The Gaussian 09W/DFT/B3LYP/6 – 311 ++G** calculations on the HZ$_2$ inhibitors were used to evaluate the conformational analysis of the two possible conformers(Cis and Tran)-HZ$_2$ to identify Tran- HZ$_2$ conformation (the most stable conformation); and to determine the HOMO-LUMO energies, bond lengths, bond angles and torsional angles, MEPs surface and MC, which were theoretically derived. The Trend of The quantum chemical parameters and Molecular Dynamics simulations of Tran conformers is HZ$_2$ > HZ$_1$ > HZ$_3$, giving the best accordance with the $I_{\text{exp}}(\%)$.
- The comparative study of the crystal structures of HZ$_2$ with DFT method shows a good correlation between geometric forms and X-ray diffraction data. In fact, the standard deviation between the Tran conformers (calculated by DFT) and X-ray values of HZ$_2$ are: (0.06 Å and 0.116 °), (0.22 Å and 0.016 °) and (0.05 Å and 0.13 °) for bond lengths and bond angles of HZ$_1$, HZ$_2$ and HZ$_3$, respectively.
- The theoretical computed $^1$H and $^{13}$C NMR chemical shift for Tran-form of all inhibitors; in turn, compare well with the experimental assignment, thus validating our results. Hence, the Tran- HZ$_2$ should exist in solution only under normal conditions.

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References


Zhurko G, Zhurko D. Chemcraft, Version 1.7 (build 365); 2013.


Materials Studio version 8.0., Accelrys Inc. USA, 2017.


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