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

M.E. Belghiti\textsuperscript{a,b,*}, M. Mihit\textsuperscript{a}, A. Mahsoune\textsuperscript{c}, A. Elmelouky\textsuperscript{d}, R. Mghaiouini\textsuperscript{e}, A. Barhoumi\textsuperscript{f}, A. Dafali\textsuperscript{b}, M. Bakasse\textsuperscript{g}, M.A. El Mhammedi\textsuperscript{h}, M. Abdennouri\textsuperscript{h}

\textsuperscript{a} Laboratory of Nernest Technology, 163 Willington Street, Sherbrook, J1H5C7, Quebec, Canada
\textsuperscript{b} Laboratory of Applied Analytical Chemistry, Materials & Environment (URAC 18), Faculty of Sciences, University M1er, B.P. 4808, Oujda, Morocco
\textsuperscript{c} Equipe of Molecular Modelling and Spectroscopy, Sciences Faculty, University of Chouai Doukkali, BP20, 24000 El Jadida, Morocco
\textsuperscript{d} Laboratory Physics of Condensed Matter, University Chouaib Doukkali, El-Jadida, Morocco
\textsuperscript{e} Department of chemistry, physical chemistry laboratory applied materials, Faculty of Sciences-Ben M’sik, Hassan II University, Morocco
\textsuperscript{f} Laboratoire de Chimie Organique, Bioorganique et Environnement, Département de Chimie, Faculté des Sciences, Université Chouaib Doukkali, BP 20, 24000 El Jadida, Morocco
\textsuperscript{g} Laboratory of Organic Chemistry, Biorganic & Environment (LCOBE), Faculty of Sciences, Chouaib Doukkali University, PO Box 20, M-24000 El-Jadida, Morocco
\textsuperscript{h} University Soultan Moulay Slimane, Laboratory of Chemistry, Modeling and Environmental Sciences, Polydisciplinary Faculty, Khouribga, Morocco

\begin{abstract}
Inhibition effect of ‘Cis and Trans’ conformations of three families of azines namely: [1,2-bis(pyrrrole-2-ylidenemethyl) hydrazine (HZ\textsubscript{1}), 1,2-bis(thiophene-2-idenemethyl) hydrazine (HZ\textsubscript{2}) and 1,2-Bis(furyl-2-idenemethyl) hydrazine (HZ\textsubscript{3})] 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 \(E_{exp} (%)\) 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, \(^1\text{H}\) & \(^13\text{C}\) 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 rigid adsorption energies of Trans-HZ\textsubscript{2}, was greater than Cis-HZ\textsubscript{2}, which agree with the trends of the experimental inhibition efficiencies.

\(©\ 2019\) The Author. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
\end{abstract}

* Corresponding author.
E-mail: eibelghiti10@gmail.com (M. Belghiti).
\url{https://doi.org/10.1016/j.jmrt.2019.09.051}
\url{2238-7854/© 2019 The Author. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/)}.
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 well 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=) 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-heteroatoms. The Azines has formally a single (=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 the two 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-yldienemethyl) hydrazine (HZ₁), 1,2-bis (thiophen-2-idemethyl) 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 1.8 (build 489) [23].

\[
\begin{align*}
    IE & : \quad \text{Ionization energy (eV)} \\
    EA & : \quad \text{Electron affinity (eV)} \\
    \Delta E_g & : \quad \text{Energy gap (eV)} \\
    \chi & : \quad \text{Absolute electronegativity (eV)} \\
    \eta & : \quad \text{Global hardness (eV)} \\
    S & : \quad \text{Global softness (eV)}^{-1} \\
    \Omega & : \quad \text{Global electrophilicity index (eV)} \\
    \Delta E_b-d & : \quad \text{Back donation (eV)} \\
    \Delta N & : \quad \text{Electron fraction transferred from HZ to the Fe-surface} \\
    \end{align*}
\]

Fig. 1 – 2D structures of the series of Azines compounds HZ (HZ₁, HZ₂ & HZ₃).
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 the 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 HZi 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-HZi and E-HZi conformational isomers is executed in a 3D periodic simulation box \( (L_x=L_y=0.35, L_z=0.40 \text{ nm}) \) 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 \((8 \times 8)\) 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 \( (\Delta E_{\text{int}}) \) or binding energy \( (\Delta E_{\text{bind}}) \) between the Fe substrate and inhibitor molecule could be calculated by:

\[
\Delta E_{\text{bind}} = -\Delta E_{\text{int}} = (E_{\text{sub}} + E_{\text{inh}}) - E_{\text{Total}}
\]

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

3. Molecular properties

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

3.1. Synthesis procedure of Azines HZi

A series of symmetrical Azines (HZi) 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 HZi.

3.2. Spectral measurements of Azines HZi

HZi : Yellow powder. Yield 85%. \( M_p=113^\circ \text{C} \). \( R_f=0.33 \) (silica/CH₂Cl₂) 1H NMR (300 MHz, CDCl₃) \( \delta ppm: 8.59 \) (s, 2H, Hmine); 7.62 (d, 2H, H9); 7.03 (d, 2H, H7); 6.63 (m, 2H, H8). 13C NMR (75 MHz, CDCl₃) \( \delta ppm: 150.76 \) (2C, Cmine); 148.14 (2C, furan-C9); 146.56 (2C, furanCQ); 101.18,20 (2C, furan-C7); 112.58 (2C, furan-C8). m/z (M+):189. IR (KBr, cm⁻¹): \( \nu(N-H)=3119, \nu(CH=N, imine)=1630, \nu(N-N)=1503, \nu(C-C)=1540, \nu(C=O, furan)=1309, \nu(C-H)=1071, 1008, 966, 869, 847.

HZZ: Yellow powder. Yield 64%. \( M_p=167^\circ \text{C} \). \( R_f=0.76 \) (silica/CH₂Cl₂) 1H NMR (300 MHz, DMSO) \( \delta ppm: 8.82 \) (s, 2H, Hmine); 7.76 (d, 2H, H8); 7.61 (d, 2H, H7); 7.18 (t, 2H, H6). 13C NMR (75 MHz, DMSO) \( \delta ppm: 156.26 \) (2C, Cmine); 138.87 (2C, thiophen-C9); 134.25 (2C, thiophen-CQ); 131.45 (2C, thiophen-C7); 128.75 (2C, thiophen-C8). m/z (M+): 121.02. IR (KBr, cm⁻¹): \( \nu(N-H)=3295, \nu(CH=N, imine)=1609, \nu(C=S, thiophene)=1321, \nu(C=O)=1540, \nu(C-H)=1040.

HZH: Yellow powder. Yield 62%. \( M_p=186^\circ \text{C} \). \( R_f=0.32 \) (silica/CH₂Cl₂) 1H NMR (300 MHz, DMSO) \( \delta ppm: 11.52 \) (s,
1H, pyrrole-NH); 8.36 (s, 2H, H_{mine}); 6.96 (d, 2H, H8); 6.59 (s, 2H, H6); 6.16 (m, 2H, H4). 13C NMR (75 MHz, DMSO) δ ppm: 151.03 (2C, C_{mine}); 127.81 (2C, pyrrole-C_{4}); 123.71 (2C, pyrrole-C_{2}) ; 115.25 (2C, pyrrole-C_{6}); 110.14 (2C, pyrrole-C_{6}). m/z (M+):187.08. IR (KBr, cm⁻¹): ν(N=H)=3212, ν(CH=N) = 1616, ν(C=O) = 1540, ν(N=N) = 1443, 1407, 1294, 1132, ν(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 H2 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 × n 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 EOCF at a disturbance sinusoidal signal of 10 mV amplitude within the frequency range (100 kHz — 1 Hz). The EIS data were analysed using ZView v. 0.0.2.2. The inhibition efficiencies IE_{imp}(%) obtained by the EIS test were calculated as follows:

$$IE_{imp} (%) = \frac{R_{ct}-R_{ct}^{0}}{R_{ct}^{0}} \times 100 \tag{11}$$

where R_{ct} and R_{ct}^{0} are the charge transfer resistant without and with different concentrations of HZ.

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.

Fig. 3 illustrates the relevant Nyquist diagrams for the mild steel electrode in (2.0 M / H3PO4) solution without and with the addition of HZ 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 HZ on mild steel/H3PO4, while the tailed line indicates steel dissolution controlled by diffusion mechanism and oxygen reduction [33,34]. Introducing HZ sharply increased the diameter of the capacitive loop, and the diameter continuously increased with increasing HZ 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 HZ 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 Eq. (11).

Table 1 shows the obtained EIS data. As seen that the C_{di} value decreased with the addition of HZ inhibitors. These values continuously decreased with increasing inhibitor concentration (from 10⁻⁶ to 10⁻³ M), 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 HZ 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 HZ on the mild steel/solution interface, leading to decreased extent of the mild steel dissolution [30]. The presence of HZ increased the R_{ct} values, and this effect was enhanced with increasing HZ concentration. This finding suggests the formation of a HZ adsorption film on the mild steel substrate, which retarded the charge transfer. Following these trends, IE_{imp}(%) values increased with increasing HZ inhibitors concentration. The classification of HZ according to its IE_{imp}(%) is: HZ₁(87.57%); HZ₂(84.6%); HZ₃(83.57%). The superior inhibition performance indicates that HZ 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.

5.1.2. Study of the imaginary part of the impedance

Fig. 5 illustrates the variation of the imaginary part(Z_{im}) of the impedance as a function of the frequency, in order to show the existence of the dielectric relaxation which does not appear in the representation of the dielectric permittivity. At very low frequencies, the polarization follows the alternating field, so that its contribution to the dielectric constant is max-
im 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 HZ1 and HZ3. The relaxation frequency does not change for inhibitor HZ2. This shows that the relaxation frequency for HZ2 due to a specific behavior of the HZ2 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 (Rs), charge-transfer resistance (Rct), and constant-phase angle element CPEdl, which are related to electrical double-layer capacitance (Cdl). During curve fitting, ideal capacitors (Cdl) were replaced by CPE because of the non-ideal capacitive behaviour of the inhomogeneous electrode. The impedance function of the CPE can be described as follows:

\[ Z_{\text{CPE}} = \frac{1}{j f \tau} \]

\[ f = \frac{1}{2 \pi R_C C} \]

\[ \tau = \frac{1}{2 \pi f_C} \]

5.1.4. Comparative study by Nyquist diagrams

This comparison is made to compare with that found by Nyquist diagram. We found that HZ1 has a very high ionic conductivity compared to other inhibitors such as HZ3 and HZ2. The relaxation frequency extracted from the imaginary conductivity measurement as a function of frequency has a lower frequency of HZ2 (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 mesomeric effects of positions of the active sites.

<table>
<thead>
<tr>
<th>Inhibitors Concentration</th>
<th>Rct (Ohm. cm²)</th>
<th>fmax (Hz)</th>
<th>Cdl (µF/cm²)</th>
<th>IEimp (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>2 M H3PO4</td>
<td>04.18</td>
<td>250.00</td>
<td>152.30</td>
</tr>
<tr>
<td></td>
<td>1 × 10⁻⁶ M</td>
<td>12.01</td>
<td>200.00</td>
<td>65.77</td>
</tr>
<tr>
<td></td>
<td>5 × 10⁻⁵ M</td>
<td>16.26</td>
<td>158.23</td>
<td>61.86</td>
</tr>
<tr>
<td>HZ1</td>
<td>1 × 10⁻⁴ M</td>
<td>17.00</td>
<td>158.23</td>
<td>59.67</td>
</tr>
<tr>
<td></td>
<td>5 × 10⁻⁴ M</td>
<td>19.88</td>
<td>158.23</td>
<td>50.60</td>
</tr>
<tr>
<td></td>
<td>1 × 10⁻³ M</td>
<td>25.44</td>
<td>158.23</td>
<td>49.21</td>
</tr>
<tr>
<td></td>
<td>5 × 10⁻³ M</td>
<td>18.88</td>
<td>125.00</td>
<td>67.44</td>
</tr>
<tr>
<td>Hz2</td>
<td>1 × 10⁻⁴ M</td>
<td>20.02</td>
<td>125.00</td>
<td>63.60</td>
</tr>
<tr>
<td></td>
<td>5 × 10⁻⁴ M</td>
<td>21.80</td>
<td>125.00</td>
<td>58.40</td>
</tr>
<tr>
<td></td>
<td>5 × 10⁻³ M</td>
<td>26.90</td>
<td>125.00</td>
<td>47.33</td>
</tr>
<tr>
<td>HZ3</td>
<td>1 × 10⁻⁴ M</td>
<td>33.74</td>
<td>125.00</td>
<td>44.93</td>
</tr>
<tr>
<td></td>
<td>1 × 10⁻³ M</td>
<td>11.38</td>
<td>125.00</td>
<td>55.94</td>
</tr>
<tr>
<td></td>
<td>5 × 10⁻⁵ M</td>
<td>15.50</td>
<td>125.00</td>
<td>82.14</td>
</tr>
<tr>
<td></td>
<td>1 × 10⁻⁴ M</td>
<td>17.74</td>
<td>125.00</td>
<td>71.77</td>
</tr>
<tr>
<td></td>
<td>5 × 10⁻⁴ M</td>
<td>24.06</td>
<td>100.00</td>
<td>64.80</td>
</tr>
<tr>
<td></td>
<td>1 × 10⁻³ M</td>
<td>27.15</td>
<td>100.00</td>
<td>58.62</td>
</tr>
</tbody>
</table>

Fig. 3 – Impedance spectra of mild steel in H3PO4 (2 M) of HZ1 at 308(±0.5 K).
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-$\equiv$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($\pm$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.
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 HZi inhibitors.

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

6. Gravimetric measurements

6.1. Effect of HZ; concentration

The effect of addition of Azines HZi at different concentrations in the range $10^{-3} - 10^{-6}$ M on the corrosion of steel in (C = 2.0 M /H3PO4) was studied by weight loss method at 308(±0.5) K after half hours of immersion period. From the weight loss results, the corrosion (Wcorr) rate, the inhibition efficiency IEW(%) of Azines HZi and the degree of surface coverage ($\theta$) were calculated by means of the following Eqs (12&13):

$$IE_W(\%) = \frac{W^0_{corr} - W_{corr}}{W^0_{corr}} \times 100$$ \hspace{1cm} (12)

$$\theta = \frac{W^0_{corr} - W_{corr}}{W^0_{corr}}$$ \hspace{1cm} (13)

Where $W_{corr}$ and $W^0_{corr}$ are the corrosion rate for (mild steel/ H3PO4) without and with HZi.

Table 3, summarizes the obtained values of $W_{corr}$ and $IEW(%)$. It is obvious from these results that this series of Azines HZi inhibits the corrosion of mild steel at all concentrations used in this study. From the Table 6, it can be observed that the $W_{corr}$ of mild steel decreases while the protection efficiency increases as the inhibitors concentration increases in (C = 2 M/H3PO4). This effect is hugely marked at higher concentration of inhibitors. The classification of these inhibitor molecules according to its $IEW(%)$ is: HZ2>HZ3>HZ1. It is predictable from the molecular structure of HZi that the inhibitor HZ2 will have the highest anti-corrosion performance ($IEW(%)$). It is due to the high electronegativity (electron...
Table 2 – Parameter obtained of conductivity.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>$\sigma_{eff} (S/cm^2)$</th>
<th>$\sigma_{eff} (S/cm^2)$</th>
<th>(CPE) ($F.S^2$)</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$_2$PO$_4$) without and with addition of HZ$_i$ at 308 (± 0.5) K.

<table>
<thead>
<tr>
<th>Inhs (M)</th>
<th>HZ$_i$</th>
<th>HZ$_j$</th>
<th>HZ$_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>W$_{corr}$ (mg/cm$^2$.h)</td>
<td>IE$_W$ (%)</td>
<td>W$_{corr}$ (mg/cm$^2$.h)</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$^{-4}$</td>
<td>1.1037 ± 0.003</td>
<td>73.29</td>
<td>0.8194 ± 0.003</td>
</tr>
<tr>
<td>1 × 10$^{-3}$</td>
<td>0.9940 ± 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 HZ$_1$, HZ$_2$ & HZ$_3$ at 308 K.

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 HZ$_i$ and the corresponding equation is as follows [41]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$  \hspace{1cm} (14)

Where $R$ is the gas constant (8.314/J/Kmol), $T$ is the absolute temperature (K), and the value 55.5 is the concentration of water in the solution expressed in M. The calculated values of $\Delta G_{ads}$, $K_{ads}$ and $R^2$ from gravimetric data for the HZ$_i$ are reported in Table 4.

Fig. 9 shows the plots of $C/\theta$– 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 HZ$_2$ 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 HZ$_3$, which has a highest efficiency, gives 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 $\Delta G_{ads}$ values for HZ$_1$, HZ$_2$, and HZ$_3$ are -39.38, -39.71 and -38.39 kJ/mol, respectively. The negative values of $\Delta G_{ads}$ indicates that the spontaneous adsorption of HZ$_2$, and the stability of the adsorbed layer on the metal surface; HZ$_2$ have always a highest value of $\Delta G_{ads}$ (in absolute value). According to the literature, the $\Delta G_{ads}$ 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 $\Delta G_{ads}$, values close to -40 kJ/mol, indicating that the adsorption mechanism of the HZ$_i$ 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 remind the effect of the temperature increase on the anti-corrosion property of HZ$_i$. The gravimetric experi-
ments were conducted in the range of 308–338(±0.5) K, without and with C = 10−3 M of HZ1. We also note that the inhibition efficiency decreased with increase in temperature from 308 to 338(±0.5) K, indicating 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 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]:

\[ W_{\text{corr}} = A \exp \left( \frac{-E_a}{RT} \right) \]  
(16)

\[ W_{\text{corr}} = \frac{RT}{N_h} \exp \left( \frac{\Delta S_a}{R} \right) \exp \left( -\frac{\Delta H_a}{RT} \right) \]  
(17)

Where \( E_a \) is the apparent activation energy, \( N \) is the Avogadro’s number, \( R \) is the universal gas constant and \( T(\text{K}) \) 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 \( \text{HZ}_1 \) 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 \( \text{HZ}_1, \text{HZ}_2 & \text{HZ}_3 \) are +47.75, +99.73 and +88.88 kJ/mol, respectively (Fig. 11).

The \( E_a \) values in the presence of the \( \text{HZ}_2 & \text{HZ}_3 \) 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 \( \text{HZ}_1 \) 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

---

**Table 4 – Adsorption parameters of HZi on mild steel in phosphoric acid (2M) at 308K.**

<table>
<thead>
<tr>
<th>Inhibitors HZn</th>
<th>( R^2 )</th>
<th>( K_{\text{ads}} ) (10^4 M⁻¹)</th>
<th>( \Delta G_{\text{ads}} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZ1</td>
<td>0.999</td>
<td>8.59</td>
<td>−39.38</td>
</tr>
<tr>
<td>HZ2</td>
<td>0.999</td>
<td>9.77</td>
<td>−39.71</td>
</tr>
<tr>
<td>HZ3</td>
<td>1</td>
<td>5.84</td>
<td>−38.39</td>
</tr>
</tbody>
</table>

**Table 5 – Temperature influence on the weight loss parameters for mild steel in (2 M/H3PO4) without and with 10⁻³ M of HZ1.**

<table>
<thead>
<tr>
<th>Inh</th>
<th>( W_{\text{corr}} ) (mg/cm² h)</th>
<th>( \Delta E_W ) (%)</th>
<th>( W_{\text{corr}} ) (mg/cm² h)</th>
<th>( \Delta E_W ) (%)</th>
<th>( W_{\text{corr}} ) (mg/cm² h)</th>
<th>( \Delta E_W ) (%)</th>
<th>( W_{\text{corr}} ) (mg/cm² h)</th>
<th>( \Delta E_W ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>4.132</td>
<td>****</td>
<td>9.077</td>
<td>****</td>
<td>15.392</td>
<td>****</td>
<td>22.792</td>
<td>****</td>
</tr>
<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
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 relationship 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), (0.086 & 0.1038 ppm) and (0.02756 & 0.020265 ppm) for HZ$_2$, HZ$_2$ and HZ$_3$, 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 to the =N−N = and −N=N in the HZ$_2$. The HOMO orbital is mainly derived from P$_{2z}$ orbitals thanks to the delocalized character of the electrons due to the presence of the heterocyclic rings together with several ($n$−$n$)-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 $=N_1−N_1$, and $C_5−C_4$ bond length increases in the order Cis>Trans while the $=C_1−X$ distance decreases in the order Trans>Cis. The strength of the intermolecular interaction increases with the shortening of the $=C−C−&−C=N=$ 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 $=N_1−N_1=$ and $=C_5−C_4=$ 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

| Table 6 – Activation descriptors $E_a$, $\Delta H_a$ and $\Delta S_a$ of the dissolution of steel in (C=2.0 M/H$_3$PO$_4$) at C=10$^{-3}$M of HZ$_2$. |
|-----------------|-----------------|-----------------|-----------------|
| $E_a$         | $\Delta H_a$   | $\Delta S_a$   | $E_a - \Delta H_a$ |
| Blank         | 55.362         | 52.718          | 62.091           | 2.644           |
| HZ$_1$        | 47.750         | 45.107          | 99.465           | 2.644           |
| HZ$_2$        | 99.732         | 97.086          | 68.190           | 2.645           |
| HZ$_3$        | 88.882         | 86.236          | 33.321           | 2.645           |
Table 7 – Simulated and Experimental $^1$H & $^{13}$C Chemical Shifts for the Trans-Form of HZ$_i$.

<table>
<thead>
<tr>
<th>$^1$H &amp; $^{13}$C Chemical Shift</th>
<th>HZ$_1$</th>
<th>HZ$_2$</th>
<th>HZ$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(4) and H(4')</td>
<td>Exp* 8.59</td>
<td>DFT 8.62</td>
<td>Exp* 8.82</td>
</tr>
<tr>
<td>H(5) and H(5')</td>
<td>7.62</td>
<td>7.71</td>
<td>7.76</td>
</tr>
<tr>
<td>H(6) and H(6')</td>
<td>7.03</td>
<td>7.18</td>
<td>7.61</td>
</tr>
<tr>
<td>H(7) and H(7')</td>
<td>6.63</td>
<td>6.72</td>
<td>7.18</td>
</tr>
<tr>
<td>C(5) and C(5')</td>
<td>150.76</td>
<td>150.80</td>
<td>156.26</td>
</tr>
<tr>
<td>C(4) and C(4')</td>
<td>148.14</td>
<td>148.79</td>
<td>138.87</td>
</tr>
<tr>
<td>C(3) and C(3')</td>
<td>146.56</td>
<td>146.88</td>
<td>134.25</td>
</tr>
<tr>
<td>C(2) and C(2')</td>
<td>118.20</td>
<td>118.13</td>
<td>131.45</td>
</tr>
<tr>
<td>C(1) and C(1')</td>
<td>122.53</td>
<td>128.75</td>
<td>132.13</td>
</tr>
</tbody>
</table>

* Exp in CDCl$_3$.

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 HZ$_i$ 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. Conversely, the standard deviation (SD) between the Cis conformers (calculated by DFT) and X-ray values of HZ$_i$ 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 HZ$_1$, HZ$_2$ and HZ$_3$, respectively. Hence, the crystal geometry of HZ$_i$ agrees more with the Trans than with the Cis geometric conformer. 

Fig. 12 – HOMO-LUMO plots for Cis- HZ$_i$.

Fig. 13 – HOMOs-LUMOs plots for Trans- HZ$_i$. 
7.4. Molecular electrostatic potential surface (MEPs)

3D-distribution of MEPs is highly useful in predicting the reactive sites behavior of the symmetrical Azines. The MEP surface of the geometric 'Cis & Trans' conformers of all HZ can be overlaid on 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 following table Azine (N=N=N=N) region of negative charges (red color) is seen around the electron-negative nitrogen N=N and N=N 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 (phosphine, furan and pyrrole) heterocyclic rings. The MEP surface picture of HZ for Cis / Trans-forms are shown in Fig. 14.

7.5. Mulliken atomic charges (MC)

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 heteroatom 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 HZ are presented in Fig. 15.

The Fig. 15 representing the effective atomic charges from Mulliken populations of HZ at different conformers (Cis & Trans), shows that the Trans-HZ, 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 -C=N=C- and =N=N= inducing a big difference in dipole moment, which would lead to very different intermolecular forces [44,45].

When HZ adsorbed on the mild steel in aqueous solution of ortho-phosphoric acid, the Cis-form geometric (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 HZ, Trans form have more potancy charges than Cis form. This is due to the tautomeric effect between the two heterocyclic rings and bond Azine (Fig. 16). This delocalisation character of electrons yields to a more stable planar structure of HZ. 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 IEQ (%) and some local quantum reactivity descriptors (μ, ΔEσ, σ & ΔEσ) 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 IEQ (%) of HZ, are exposed in Table 9 where R² stands for the correlation coefficient between IEQ (%) 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(ΔEg) 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 ΔEg [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 ΔEg 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 ΔEg decrease. The low value ΔEg (3.6196 eV) of Trans-HZ2 indicate the high (IEimp) than the same geometry conformers HZ2 & HZ3. This means that the molecule HZ2 of the geometric ‘Trans-form’ could have better performance as a corrosion inhibitor (there is excellent linearity between ΔEg 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 > HZ3 > HZ1 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 ΔEg value and a soft molecule has a small ΔEg value [56]. Table 9 show that the geometric ‘Trans’ conformers are energetically more stable than the geometric ‘Cis’ conform-
ers, whereas, in contrast, the parameter $\eta$ of the Cis isomer is greater than the Trans isomer. In the present study, the Trans-HZ2 has the lowest $\eta$ (+1.8098 eV) and the lowest $\Delta E_g$ (+3.6196 eV) when compared to the other Trans-conformers of HZ3 & HZ1. 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 HZ2 with the $S$ value of +0.553 eV has the highest $\mu_{\text{imp}}$. The high performance of geometric Trans-HZ2 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 $\mu_{\text{imp}}$, on the one hand, the $\eta$ (absolute hardness) and $S$ (softness) values and $\mu_{\text{imp}}$ 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. 16 – Schematic Representation of possible tautomeric forms of Trans-HZ_2 conformers.

literature [59]. Since the distance between the charges is larger in the Trans-forms than in the Cis-forms, the μ of the Cis-forms are expected to be higher than that on the Trans-forms for a given system. Indeed, the calculated μ are greater for the Cis-forms than for the Trans-forms for all inhibitors. A good linear correlation between μ values of geometric Trans-form and IE_{emp}(%) is obtained (R² = 0.904). This increases the contact area between the molecule and the Fe-surface increases the corrosion inhibition ability of HZ. The geometric Trans-HZ_2 may be adsorbed onto the Fe-surface by vertical or horizontal isomers, involving the displacement of water molecules form on the metal surface.

From the Table 9, it was found that the ΔE_{ads} values are favored for the geometric Trans-form than Cis-form. In Table 9, the order followed for Trans-form is HZ_2 > HZ_3 > HZ_1, which indicates that back-donation, is favored for the molecule Trans-HZ_2 which is the best inhibitor. The increase in inhibition efficiency of Trans-HZ_2 is due to the transfer of electron from HZ_2 to Fe^{2+} in mild steel or vice versa. This result, in turn, corroborate with the growth inhibition observed IE_{emp}(%) experimentally (R² = 0.96).

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 on the steel surface in vacuum. The experiments incorporating the theoretical calculation and MDs can provide an insight 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 and E-HZ conformations on Fe (111) surface in the gas phase. The final and lowest energy configuration results of the E-Z configuration of HZ obtained by forcite module simulation in vacuo at 308 K are depicted in Fig. 17.

The adsorption of the both conformers (Z-HZ and E-HZ) 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 and E-HZ 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 complex. 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 (ΔE_{ads}/dN), 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 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. Base of the adsorption energy values obtained by ‘Forcite’ module simulations, the adsorption strength of two E conformations of inhibitors HZ on Fe-surface in vacuo can follow the order: HZ_2 > 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) ~ r) Functions of the two possible conformational Z-HZ and E-HZ 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 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 heteratoms 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: HZ3-Trans < HZ2-Trans ≤ HZ3-Cis < HZ2-Cis < HZ1-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.
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 ($\text{IE}_{\text{exp}}(\%)$) increased with increasing HZ concentrations in the order HZ2 $>$ HZ1 $>$ HZ3.
- HZ showed superior inhibitive ability at relatively high temperatures, although the corrosion of mild steel /H3PO4 was accelerated by the increase in temperature. The thermodynamic parameter descriptors indicate that HZ is adsorbed on mild steel surface in 2 M H3PO4 solution by an endothermic process and reveal that the adsorption mechanism of HZ is mainly chemisorption.
- The Gaussian 09W/DFT/B3LYP/6–311 + +G* calculations on the HZ inhibitors were used to evaluate the conformational analysis of the two possible conformers (Cis and Tran)-HZ; to identify Trans- HZ 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 Trans conformers is HZ2 $>$ HZ1 $>$ HZ3, giving the best accordance with the $\text{IE}_{\text{exp}}(\%)$.
- The comparative study of the crystal structures of HZ, with DFT method shows a good correlation between geometric Trans-form and X-ray diffraction data. In fact, the standard deviation between the Trans conformers (calculated by DFT) and X-ray values of HZ are: (0.06 Å and 0.116 $^{\circ}$), (0.22 Å and 0.016 $^{\circ}$) and (0.05 Å and 0.13 $^{\circ}$) for bond lengths and bond angles of HZ1, HZ2 and HZ3 respectively.
- The theoretical computed $^{1}$H and $^{13}$C NMR chemical shift for Trans-form of all inhibitors; in turn, compare well with the experimental assignment, thus validating our results. Hence, the Trans- HZ should exist in solution only under normal conditions.

This statement is to certify that all Authors have seen and approved the manuscript being submitted. We warrant that the article is the Authors’ original work. We warrant that the article has not received prior publication and is not under consideration for publication elsewhere. On behalf of all Co-Authors, the corresponding Author shall bear full responsibility for the submission. This research has not been submitted for publication nor has it been published in whole or in part elsewhere. We attest to the fact that all Authors listed on the title page have contributed significantly to the work, have read the manuscript, attest to the validity and legitimacy of the data and its interpretation, and agree to its submission to the Journal of Materials Research and Technology.

All authors agree that author list is correct in its content and order and that no modification to the author list can be made without the formal approval of the Editor-in-Chief, and all authors accept that the Editor-in-Chief’s decisions over acceptance or rejection or in the event of any breach of the Principles of Ethical Publishing in the Journal of Materials Research and Technology being discovered of retraction are final.

Acknowledgments

Dr. M.E. Belghiti, would like to thank, Atika Lahbal, for the invaluable support. She has always been there for me to encourage me to get the best out of me.

References


Professor M. E. Belghiti is currently a member of the Laboratory of Nobel Technology, 163 Willington Street, Sherbrook, J1H5C7, Quebec, Canada. Born in 1977, he earned his Ph.D. in Materials Science and Corrosion at University M1er, B.P. 4808, Oujda, Morocco. His research activities focus on the electrochemical behavior of metals and alloys, corrosion and inhibition, the development of new surface modification processes and the fireproofing of materials. He has published more than 20 scientific research articles with h-index = 10 and presented about 10 papers at symposia with national / international meetings. In addition, he is a critic in several international journals.