



# Bipyrazole compounds as efficient corrosion inhibitors for metallic materials

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## Abstract

This review brings together predominant works on the use of bipyrazole compounds as corrosion inhibitors for the protection of metallic materials. Bipyrazoles, characterized by a structure with two pyrazole nuclei, have emerged as promising candidates in corrosion control due to their structural diversity and unique physicochemical properties. The article examines various methods of synthesizing these compounds and explores their inhibitory effectiveness against the corrosion of different metals. The studies presented show the ability of bipyrazole derivatives to form protective films on metal surfaces, thus delaying the corrosion process. Adsorption mechanisms, thermodynamic properties, and experimental results are discussed to provide a comprehensive overview of the inhibitory performance of bipyrazole compounds. This review offers a critical synthesis of recent advances in the field and highlights prospects for the development of new bipyrazole-based corrosion inhibitors.

**Keywords:** Corrosion; Adsorption; Inhibitor; Bipyrazole; Isotherm

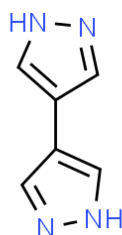
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## 1. Introduction

Corrosion causes enormous commercial losses at both the national and international levels, estimated by high costs and significant damage to materials and the environment (Messali *et al.* 2011; De Vuyst *et al.* 2008; Abdi *et al.* 2006). Industries suffer from various types of corrosion, including galvanic corrosion, uniform corrosion, corrosion of cracks, intergranular corrosion pitting, and erosion (Quraishi *et al.*, 2011; Hemme *et al.* 2004; Ogier *et al.* 2008). It is well documented that natural air humidity, aggressive metal polishing, water from oceans/seas, and chemical fluids are the most identified corrosion agents that contribute significantly to the initiation and propagation of corrosion reactions (Alabi *et al.* 2020).

Additional sources of corrosion have been reported, including oils/gases, basic salts, concentrated/diluted acids, ammonia, sulfur, and gaseous materials with acidic pH levels (De Vuyit *et al.* 2008). Various procedures enhance and accelerate the rate of corrosion reactions, such as electrochemical processes and chemical reactions occurring among resources in the surrounding environment (Messali *et al.* 2011; Zaidi *et al.*, 2023; Merimi *et al.*, 2023). This literature review on bipyrazoles highlights the numerous applications and properties of these organic compounds. Bipyrazoles, which are characterized by the presence of two pyrazole motifs, have attracted the attention of researchers owing to their structural diversity and unique physicochemical properties (Fig.1). Bipyrazoles are distinguished by their structure, with two linked pyrazole nuclei, providing a rich molecular platform for functional diversity (Secrieru *et al.*, 2020). These structures can be modified to produce compounds with specific properties. Various methods for synthesizing bipyrazoles have been described, including condensation reactions, cyclization reactions, and coupling strategies. These approaches yielded a wide variety of bipyrazole derivatives with specific substitutions. Bipyrazoles exhibit interesting physicochemical properties such as absorption properties in the UV-visible range, coordination capabilities with transition metals, and specific reactivities under defined conditions (Maissa *et al.* 2021).



**Figure 1.** Chemical structure of the bipyrazole compound.

Applications of bipyrazoles are vast, covering areas such as catalysis, medicinal chemistry, coordination chemistry, and nanotechnology. Their unique properties make them valuable in the development of functional materials and active compounds. Particular attention has been paid to the use of bipyrazoles as corrosion inhibitors. Their ability to form protective films on metal surfaces makes them promising candidates for preventing corrosion. This literature review highlights the recent progress in the field of bipyrazoles and emphasizes opportunities for future research. Perspectives include the development of new synthesis methods, exploration of new applications, and thorough understanding of their reaction mechanisms. Literature on bipyrazoles reflects the importance of these compounds in contemporary chemistry. Their structural diversity and unique properties render them versatile compounds with promising applications in various scientific and technological fields. The intrinsic properties of azoles, such as their ability to coordinate with metal ions and adsorb on metal surfaces, have been exploited to

enhance the efficiency of corrosion inhibition. In conclusion, the integration of azoles, especially within the context of ionic liquids, opens new perspectives for corrosion protection, offering an environmentally friendly and effective alternative to traditional organic solvents. Previous research has laid the groundwork for a thorough understanding of these systems, paving the way for future developments in the design of innovative and environmentally friendly corrosion-inhibitor compounds.

## 2. Literature Review

### 2.1 Preparation of Bipyrazoles

The preparation of bipyrazoles has garnered significant interest owing to the diversity of these compounds and their potential applications (Ihammi et al. 2021). The following is a general approach for synthesizing bipyrazoles, but it should be noted that the exact conditions may vary depending on the specific reactants and desired substituents.

#### General Synthesis of Bipyrazoles

*Condensation Reaction:* The synthesis of bipyrazoles often begins with a condensation reaction between two pyrazole molecules. Pyrazoles can be functionalized with various groups, such as alkyl, aryl, or heteroatomic groups, to introduce diversity (Semmar et al. 2007).

*Cyclization Reaction:* Condensation is followed by cyclization to form the bipyrazole core. Cyclization agents or catalysts may be necessary to promote bipyrazole motif formation.

*Selective Substitutions:* Selective substitutions can be performed to introduce specific functional groups into the bipyrazole core. The choice of the substitution reagent depends on the desired properties of the final compound.

*Purification:* The final product can be purified using chromatography, crystallization, or other methods.

*Characterization:* The synthesized product was characterized using analytical techniques such as infrared spectroscopy (IR), nuclear magnetic resonance (NMR) spectroscopy, and mass spectrometry to confirm its structure.

*General reaction of Bipyrazole:* A condensation reaction between two pyrazoles, followed by a cyclization reaction, might resemble the following:



This general synthesis can be adapted based on the specific substituents, nature of the pyrazoles, and chosen reaction conditions. It is important to note that the preparation of bipyrazoles can be complex because of the diverse structures and reactions involved. Specific methods are often selected based on the desired properties of the final compound. The scientific literature contains numerous specific approaches, depending on the research objectives.

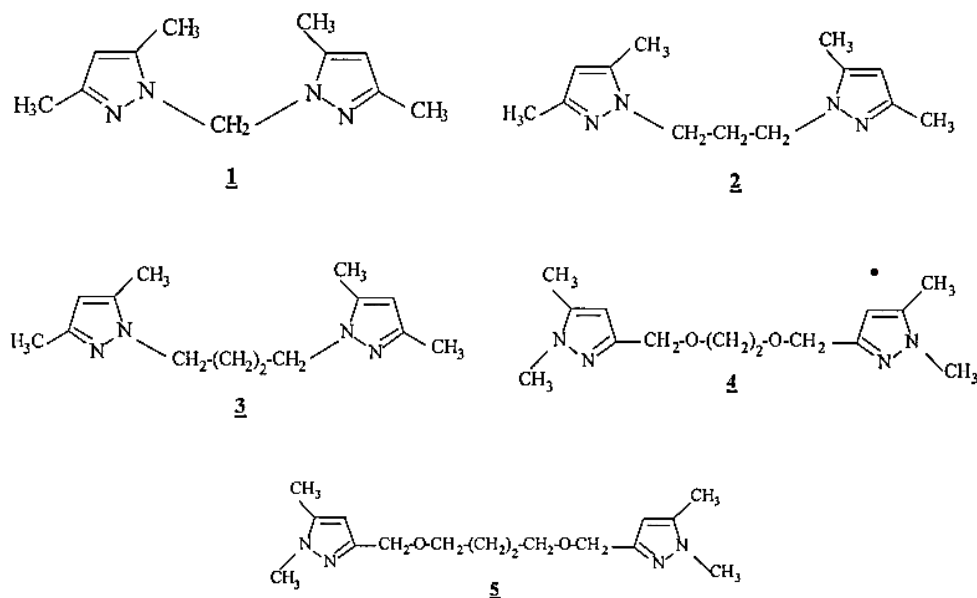
**In 1999**, F. Touhami and colleagues investigated the inhibitory effect of the newly synthesized compound, 1,3-Bis(3,5-dichloromethylpyrazolyl) propane (BDCMPP), on the corrosion of Armco iron in a 1M hydrochloric acid medium. They employed methods such as weight loss, electrochemical polarization, and impedance studies. The results revealed a maximum inhibition efficiency of approximately 90% at a concentration of  $10^{-3}$  M, which was attributed to the geometric blocking of the iron surface by adsorbed inhibitory molecules, according to an S-shaped adsorption isotherm. The cathodic curves exhibited a Tafel line shape, indicating a pure activation mechanism for the hydrogen evolution reaction on the iron surface. The inhibition efficiency of BDCMPP increased with increasing concentration, reaching 90% at  $10^{-3}$ M. Addition of the inhibitor did not affect the corrosion potential. The adsorption of BDCMPP on the iron surface followed an S-shaped adsorption model, and the transient results agreed with static measurements. In summary, this study provides a comprehensive understanding of the inhibitory effects of the synthesized compound on the corrosion of Armco iron in a specific acidic medium (Touhami *et al.* 1999).

**In 2000**, new bipyrazolic compounds were synthesized and tested as corrosion inhibitors for Armco steel in a 1M hydrochloric acid medium using methods such as weight loss, electrochemical polarization, and impedance measurements. The results demonstrated that 1,3-bis(3,5-dimethylpyrazolyl)propane (inh2) was the best inhibitor, achieving a maximum inhibition efficiency of 93% at  $10^{-3}$  M. It was observed that inh2 adsorbed onto the iron surface according to the Langmuir isotherm model. Additionally, the inhibition efficiency of inh2 increased with increasing temperature in the range 308–338 K. The authors also determined the apparent activation energy for iron corrosion (Fig.2) (Touhami *et al.* 2000).

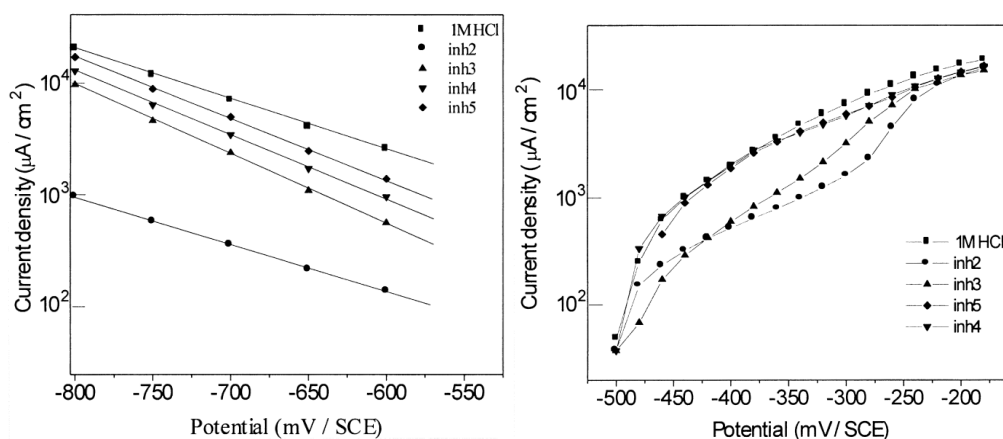
The synthesized and tested inhibitors were as follows: Bis(3,5-dimethylpyrazolyl)methane, 1,3-Bis(3,5-dimethylpyrazolyl)propane, 1,4-Bis(3,5-dimethyl pyrazolyl)butane, 1,6-[Bis(1,5-dimethylpyrazol-3-yl)]2,5-dioxahexane, 1,8-[Bis(1,5-dimethylpyrazol-3-yl)]2,7-dioxaoctane, the transient results were in good agreement with the stationary results. Additionally, it was observed that the inhibition efficiency of inh2 increased with temperature and the activation energy of corrosion decreased in the presence of the inhibitor. These observations contribute to a comprehensive understanding of the inhibitory properties of new bipyrazolic compounds on the corrosion of Armco steel in a hydrochloric acid medium.

In conclusion, all cathodic curves are presented in the Tafel plot, indicating that the hydrogen evolution reaction on the metal surface occurs through a pure activation mechanism. The inhibition efficiency of the compounds decreased with increasing length of the carbon chain connecting the pyrazole rings. Compound 2 proved to be the best inhibitor among the tested series, with an efficiency of 93% at a concentration of  $10^{-3}$  M. The corrosion potential values were only slightly affected by the addition of the

inhibitor. The adsorption of inh2 on the iron surface follows the Langmuir adsorption model. The transient results were in good agreement with the stationary results. The inhibition efficiency of inh2 increased with increasing temperature, and the activation energy of corrosion decreased in the presence of the inhibitor.



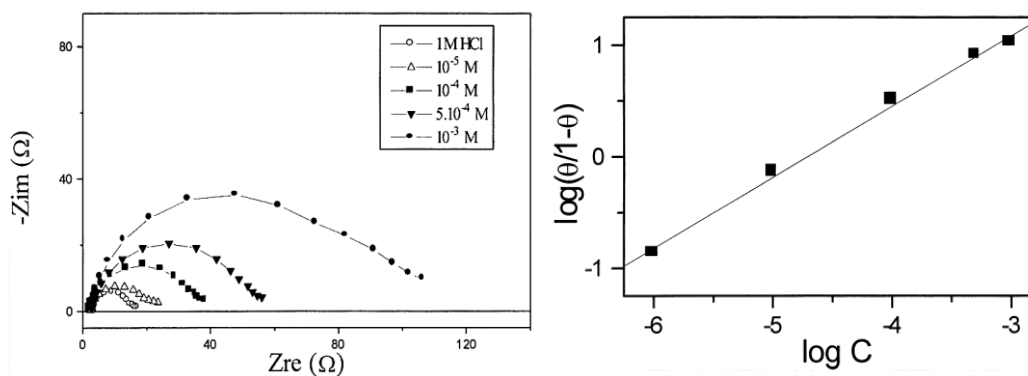
**Figure 2.** The molecular structures of the bipyrazole compounds studied by Touhami *et al.*, 1999.



**Figure 3.** Cathodic and Anodic curves of iron in 1 M HCl in presence of bipyrazoles studied at  $10^{-3}$  M.

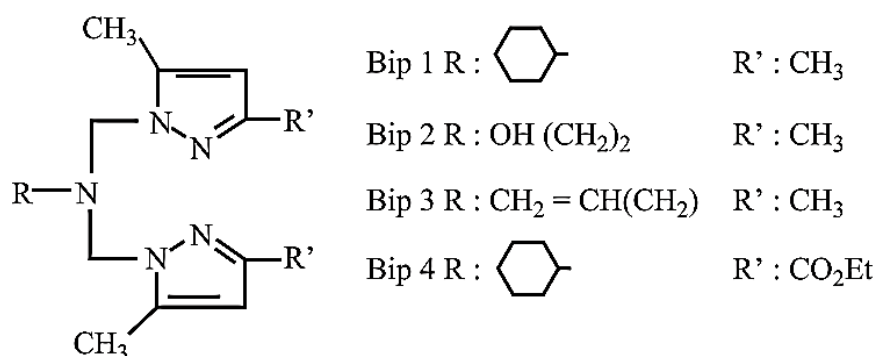
**Tableau 1.** Weight loss of Armco iron in 1 M HCl + different bipyrazolic products at  $10^{-3}$  M and the corresponding inhibition efficiency

| Inhibitors | $W$ (mg/cm <sup>2</sup> h) | $E\%$ |
|------------|----------------------------|-------|
| Blank      | 0.340                      | –     |
| inh1       | 0.042                      | 88    |
| inh2       | 0.031                      | 91    |
| inh3       | 0.064                      | 81    |
| inh4       | 0.089                      | 74    |
| inh5       | 0.143                      | 58    |

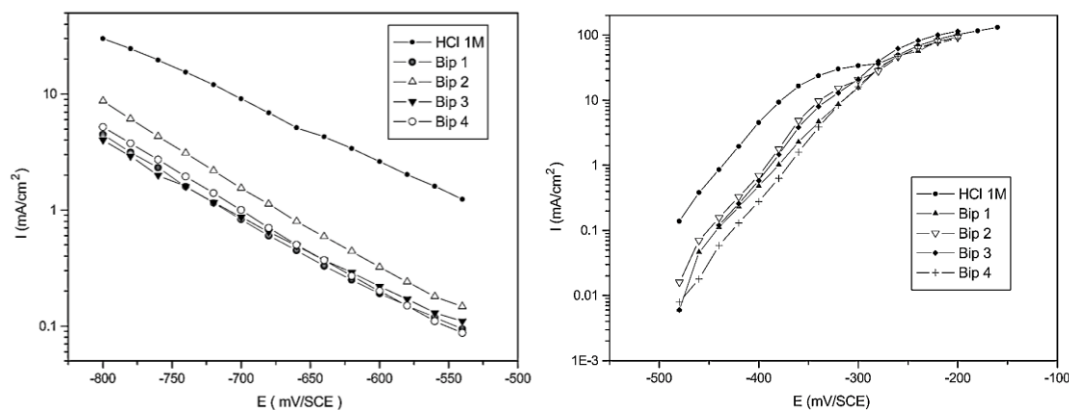


**Figure 4.** The impedance diagrams revealed  $E_{\text{corr}}$  after immersion for 30 min in the solution and the Langmuir-type isotherm model of inh2 on the iron surface.

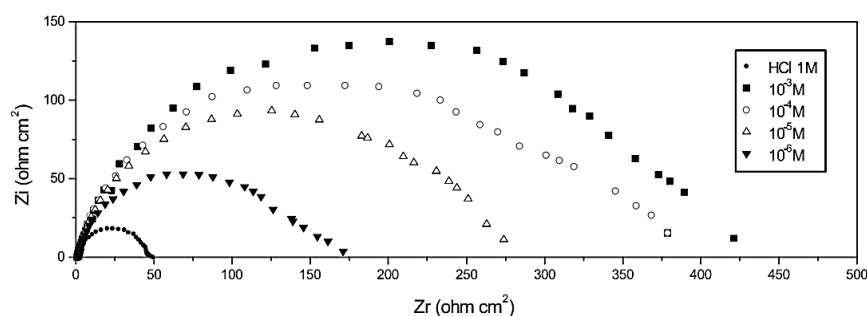
In 2002, El Ouafi and colleagues conducted a study on the corrosion inhibition of mild steel in a 1M hydrochloric acid solution using new bipyrazolic compounds, employing methods such as weight loss, electrochemical polarization, and electrochemical impedance spectroscopy (EIS). These results indicated that these compounds are highly effective inhibitors. The inhibition efficiency increased with increasing inhibitor concentration, reaching 94% at a concentration of  $10^{-3}$  M for the studied bipyrazoles. The molecules tested were N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-cyclohexylamine (Bip 1), N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-ethanolamine (Bip 2), N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)allylamine (Bip 3), and N,N-bis(3-carboethoxy-5-methylpyrazol-1-ylmethyl)-cyclohexylamine (Bip 4) (Fig.5). Potentiodynamic polarization studies clearly revealed that the presence of bipyrazoles does not alter the mechanism of the hydrogen evolution reaction, and they essentially act as cathodic inhibitors. Furthermore, the effect of temperature on the corrosion behavior of mild steel in the presence or absence of bipyrazoles at a concentration of  $10^{-3}$  M was examined in the temperature range of 298 K to 343 K. EIS measurements showed an increase in the transfer resistance with inhibitor concentration. These results provide valuable insights into the effectiveness of the new bipyrazolic compounds as corrosion inhibitors in acidic environments.



**Figure 5.** The molecular structure of bipyrazole compounds studied by El Ouafi et al.



**Figure 6:** Cathodic and Anodic curves of steel in 1M HCl in the presence of bipyrazoles studied at  $10^{-3}$  M



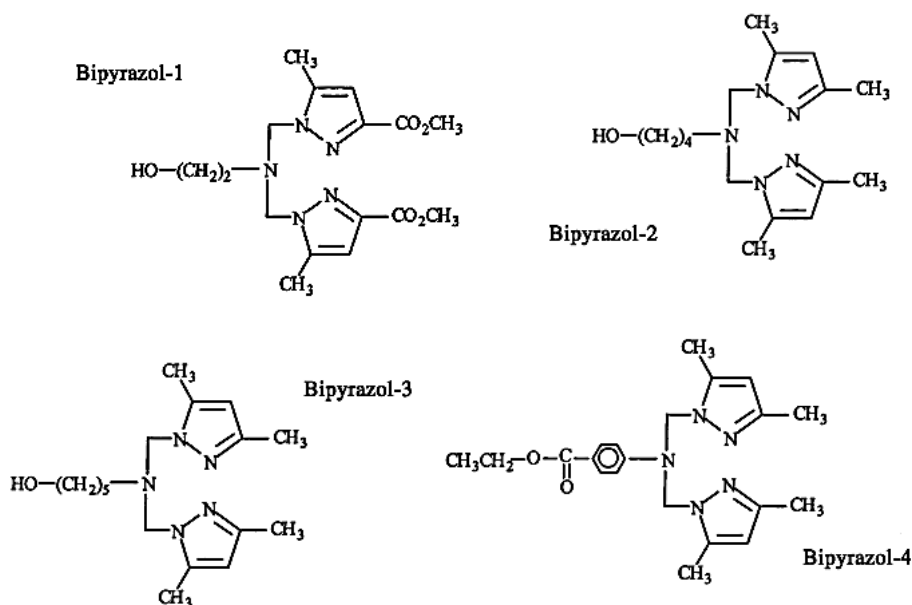
**Figure 7.** Nyquist diagrams of mild steel in 1M HCl containing different concentrations of Bip 3.

The results show significant trends. First, the inhibition efficiency of this group of inhibitors increases proportionally with concentration, reaching its maximum at  $10^{-3}$  M. Additionally, organic compounds of the bipyrazole type act as inhibitors without altering the mechanism of the cathodic reaction, as demonstrated by steady-state measurements. The consistency between data from different analytical techniques, such as weight loss, electrochemical impedance spectroscopy, and polarization curves, reinforces the reliability of our conclusions. Finally, the effect of temperature on inhibition efficiency highlights a thermodynamic dependence, with an increase observed for Bip 1 and Bip 4, but a decrease for Bip 2 and Bip 3. These results provide important insights into the inhibition mechanisms under varied conditions (Figs.6&7).

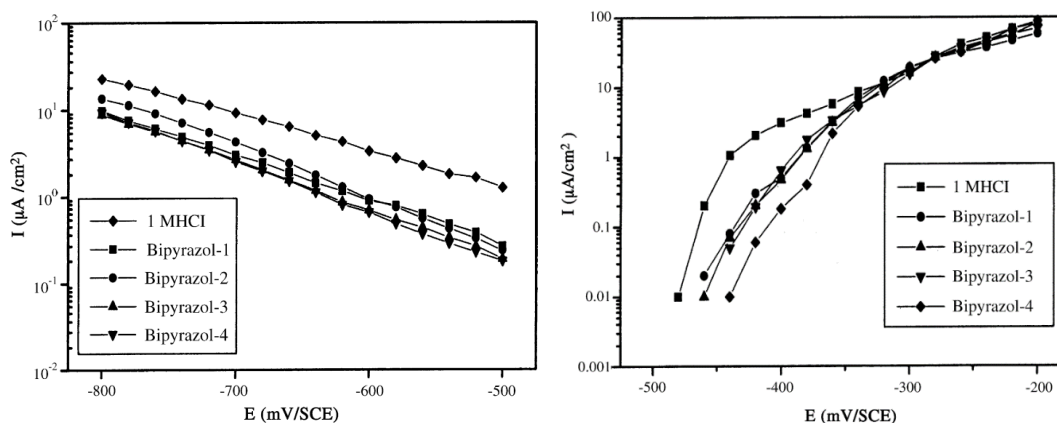
**In 2002**, A. Dafali and colleagues conducted a study on the corrosion inhibition of copper in a 3% sodium chloride aerated solution using electrochemical polarization, weight loss, and impedance measurements in the presence of different concentrations of synthesized bipyrazolic compounds. These compounds included N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)butylamine (bipy1); N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)allylamine (bipy2); N,N-bis(3,5-dimethylpyrazol-1-ylmethyl) ethanol amine (bipy3); N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)cyclohexylamine (bipy4); N,N-bis(3-carboethoxy-5-methylpyrazol-1-ylmethyl)cyclohexylamine (bipy5); N,N-bis(3-carboethoxy-5-methylpyrazol-1-ylmethyl)cyclohexylamine (bipy6). The inhibition efficiencies obtained from the cathodic

Tafel curves, polarization resistance, and weight loss were in good agreement with electrochemical impedance spectroscopy (EIS) measurements. All these additives proved to be excellent inhibitors of Cu corrosion. Although the difference in inhibition efficiencies of these inhibitors was not significant, the optimal concentration for maximum efficiency depended slightly on the substitution of each molecule. The studied molecules act as mixed-type inhibitors. A detailed study of bipy1 showed that a concentration of  $5 \times 10^{-4}$  M inhibitor achieved a maximum inhibition efficiency of approximately 99%. The latter was adsorbed on the copper surface according to the Frumkin isotherm model. The inhibition efficiency of bipy1 decreases with increasing temperature in the range 25–60 °C (Dafali et al. 2002).

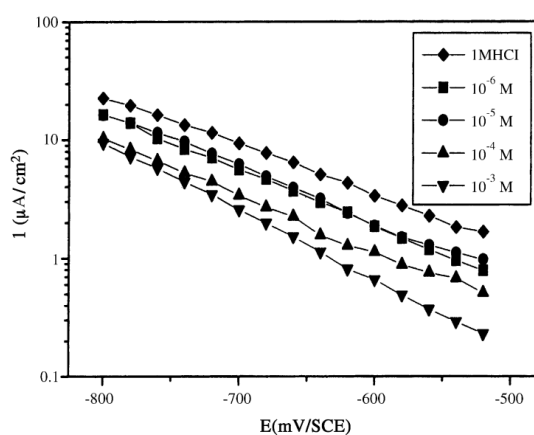
In 2005, M. Elayyachy and colleagues studied the influence of new bipyrazolic derivatives, synthesized in the laboratory, on the inhibition of mild steel corrosion in a 1M hydrochloric acid solution, using weight loss and electrochemical polarization techniques. The inhibition efficiency of all tested compounds increased with concentration. Polarization measurements indicated that the inhibition efficiency of bipyrazolic compounds depends on the electrode potential without altering the mechanism of the cathodic hydrogen evolution reaction. The results show that Ethyl 4-[bis(3,5-dimethyl-1H-pyrazol-1-yl)methyl]aminobenzoate (bipyrazole-4) was the best inhibitor among the tested compounds. The effect of temperature reveals that the inhibition efficiency of bipyrazole-4 decreases with increasing temperature in the range of 308 to 353 K. These observations contribute to understanding the inhibitory properties of bipyrazolic derivatives on steel corrosion in an acidic environment, with inhibitory efficiency reaching up to 93% at a concentration of  $10^{-3}$  M (Fig.8) (Elayyachy et al. 2005).



**Figure 8.** Molecular Structure of the bipyrazolic compounds used by Elayyachy et al., (2005)



**Figure 9.** Cathodic and anodic polarization curves of steel in 1 M HCl in the presence of Bipyrazoles

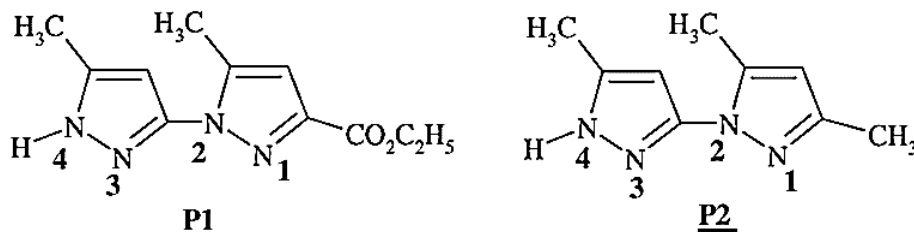


**Figure 10.** Cathodic polarization curves of steel at different concentrations of bipyrazol-4

The experimental results obtained from the weight loss and polarization measurements revealed consistency between the gravimetric and electrochemical methods. Cathodic polarization curves indicate that the hydrogen evolution reaction is activation-controlled, with modification of the proton reduction mechanism in the presence of bipyrazolic compounds. The structure of the amine chain between the pyrazole cycles influenced the inhibition efficiency of the studied compounds. However, the inhibition efficiency of bipyrazole-4 decreased with increasing temperature, and its performance at higher temperatures decreased. The adsorption of bipyrazole-4 on the metal surface followed the Langmuir isotherm model.

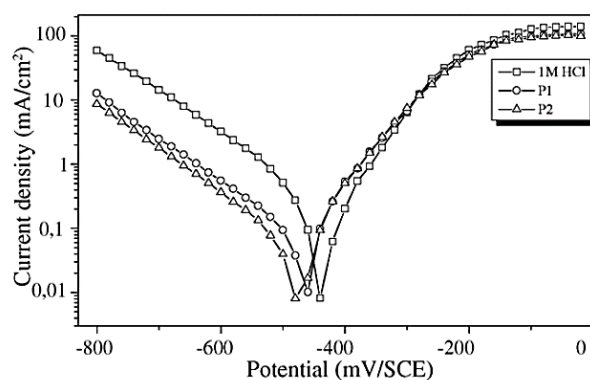
*Tebji et al.*, The authors studied the effect of two pyrazole-type organic compounds, namely ethyl 5,50-dimethyl-10H-1,30-bipyrazole-3 carboxylate (P1) and 3,5,50-trimethyl-10H-1,30-bipyrazole (P2), on the corrosion behaviour of steel in a 1 M hydrochloric acid solution at 308 K. They performed weight loss measurements, potentiodynamic polarizations, and electrochemical impedance spectroscopy (EIS). The results showed that compound P2 was the best inhibitor, reaching an efficiency of 84% at a concentration of  $10^{-3}$  M. Potentiodynamic polarization studies indicate that pyrazole derivatives are

cathodic-type inhibitors, acting on the cathodic reaction without changing the mechanism of the hydrogen evolution reaction. The inhibition efficiency of P2 depends on the temperature in the range 308–353 K, and the associated activation energy was determined.

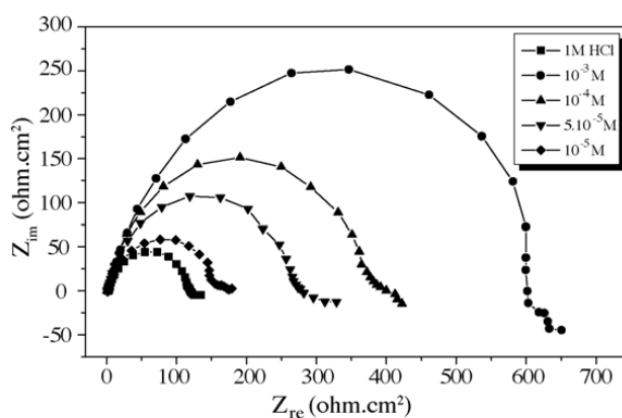


**Figure 11.** Molecular structure of bipyrzole derivatives synthesized by Elayyachy *et al.* 2005.

| Inhibitors | Concentration (M)  | $W$ ( $\text{mg cm}^{-2} \text{h}^{-1}$ ) | $E_w$ (%) |
|------------|--------------------|---|-----------|
| Blank      | 1                  | 1.06                                      | –         |
| P1         | $10^{-6}$          | 0.947                                     | 11        |
|            | $10^{-5}$          | 0.894                                     | 16        |
|            | $5 \times 10^{-5}$ | 0.664                                     | 37        |
|            | $10^{-4}$          | 0.526                                     | 50        |
|            | $5 \times 10^{-4}$ | 0.328                                     | 69        |
|            | $10^{-3}$          | 0.283                                     | 73        |
| P2         | $10^{-6}$          | 0.780                                     | 26        |
|            | $10^{-5}$          | 0.717                                     | 32        |
|            | $5 \times 10^{-5}$ | 0.462                                     | 56        |
|            | $10^{-4}$          | 0.352                                     | 67        |
|            | $5 \times 10^{-4}$ | 0.213                                     | 80        |
|            | $10^{-3}$          | 0.173                                     | 84        |



**Figure 12.** Polarization curves of steel in 1 M HCl for various compounds at  $10^{-3}$  M.



**Figure 13.** Nyquist plots of steel in 1 M HCl containing various concentrations of inhibitor P2.

This study concludes that inhibitor P2 is effective in protecting steel in 1 M hydrochloric acid solution. The inhibition efficiency reached a maximum of 84% at a concentration of  $10^{-3}$  M. Inhibitors P1 and P2 acted cathodically without altering the mechanism of hydrogen evolution. The results from the different measurement methods, including gravimetric, electrochemical, and impedance measurements, agree reasonably well. Additionally, the adsorption of P1 and P2 on the steel surface followed the Langmuir

model. These findings offer promising perspectives for the development of effective inhibitors for use in corrosive environments (Fig.12&13).

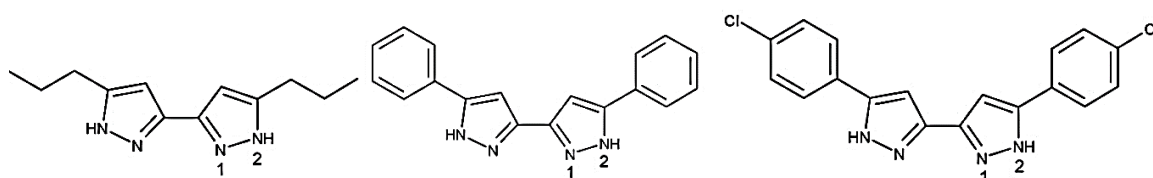
In another study by Tebbji, the inhibition of steel corrosion by two bipyrazolic compounds in a molar hydrochloric acid solution was investigated using weight loss and electrochemical polarization measurements. Both the methods yielded consistent results. The polarization curves indicate that bipyrazolic compounds act as mixed-type inhibitors. These compounds were found to be effective inhibitors, with inhibition efficiency increasing with inhibitor concentration, reaching 96% and 92% at  $5 \times 10^{-4}$  M for Bipyr 1 and Bipyr 2, respectively. The effect of temperature on the corrosion behavior of steel in 1 M HCl, with and without bipyrazolic compounds at  $5 \times 10^{-4}$  M, was studied in the temperature range 308–353 K. The adsorption of the inhibitors on the steel surface follows the Freundlich isotherm adsorption model. Thermodynamic data for the adsorption process ( $f$ ,  $K$ , and  $\Delta G_{\text{ads}}$ ) were calculated from the adsorption isotherm (Tebbjji *et al.* 2005).

Chetouani *et al.* conducted a study on the inhibitory effect of two newly synthesized bipyrazolic compounds, namely N,N-bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-N-(4-methylphenyl)amine (P1) and methyl-1-[(methylphenyl){[3-(methoxycarbonyl)-5-methyl-1H-pyrazol-1-yl]methyl}amino]-methyl-5-methyl-1H-pyrazole-3-carboxylate (P2), on the corrosion of pure iron in a 1 M HCl solution. Researchers have used chemical techniques, such as weight loss, and electrochemical techniques, such as potentiodynamic polarization, linear polarization, and impedance. The inhibition efficiencies obtained from different methods, including gravimetric curves, Tafel cathodic curves, linear polarization resistance, and electrochemical impedance spectroscopy (EIS), were in agreement, demonstrating the effectiveness of P1 and P2 as inhibitors. The inhibition efficiency increases with inhibitor concentration, reaching 93% for P1 at  $2.5 \times 10^{-4}$  M. Potentiodynamic polarization studies clearly reveal that P1 and P2 act as mixed-type inhibitors without modifying the mechanism of hydrogen evolution. The effect of temperature on the corrosion behavior of iron in the presence and absence of inhibitors at a concentration of  $2.5 \times 10^{-4}$  M was studied in the temperature range of 298–353 K. EIS measurements showed an increase in transfer resistance with inhibitor concentration. The inhibitors were adsorbed on the iron surface according to the Langmuir isotherm adsorption model. Thermodynamic data for the adsorption process ( $K$  and  $\Delta G_{\text{ads}}$ ) were calculated from the adsorption isotherm (Chetouani *et al.* 2005).

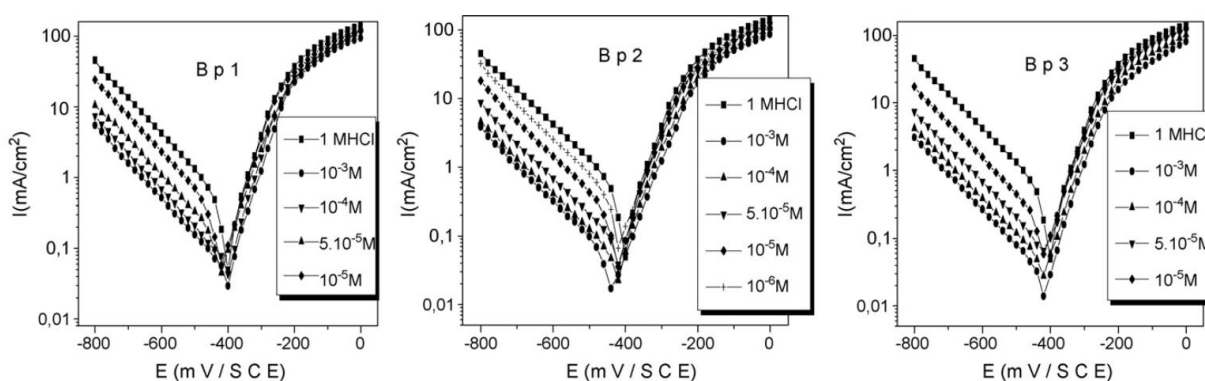
Bouklah *et al.* aimed to analyze the inhibition effect of new bipyrazolic derivatives on the corrosion of steel in hydrochloric acid (HCl) solutions at different temperatures. Innovative corrosion inhibitors, namely bipyrazoles, were synthesized and tested in 1 M hydrochloric acid solution. The degree of corrosion was measured using various techniques including weight loss, potentiodynamic polarization, linear polarization resistance ( $R_p$ ), and electrochemical impedance spectroscopy (EIS). The results

revealed that compound 1,5,50-trimethyl-1H,20H-3,30-bipyrazole (P1) exhibited the best inhibitory effect, with an inhibition efficiency of 79% at a concentration of  $10^{-2}$  M. The different methods showed good agreement. Polarization measurements also indicated that P1 acts as a cathodic inhibitor. The cathodic curves suggest that proton reduction on the steel surface is an activation mechanism. P1 was adsorbed onto the steel surface according to the Frumkin adsorption model. The limitations of this research lie in the fact that this synthetic route offers the opportunity to test other pyrazolic compounds in the future. Practically, the inhibitory efficiency of P1 increased with concentration and temperature (298–353 K), suggesting that P1 could be used in chemical cleaning and pickling processes (Bouklah *et al.* 2005).

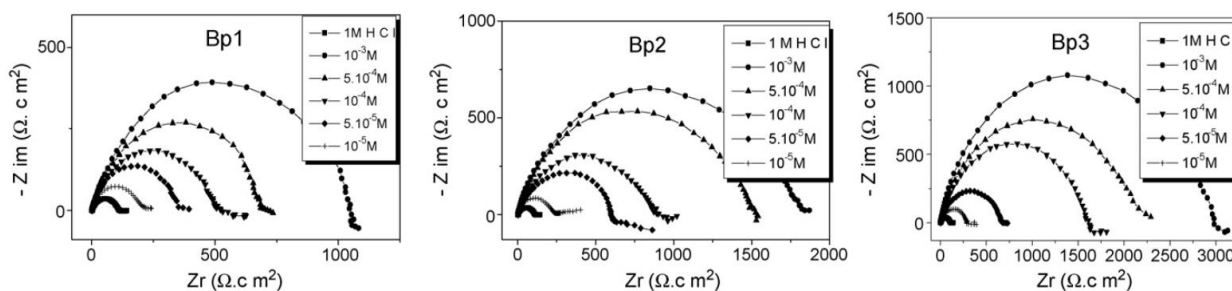
In 2007, Benabdellah *et al.* conducted studies involving potentiodynamic polarization, electrochemical impedance spectroscopy, and weight loss measurements on the inhibition of carbon steel in a 1 M hydrochloric acid solution using three bipyrazolic compounds. The examined inhibitors were 5,5'-dipropyl-1H,1'H-[3,3']bipyrazolyl (Bp1), 5,5'-diphenyl-1H,1'H-[3,3']bipyrazolyl (Bp2), and 5,5'-bis-(4-chlorophenyl)-1H,1'H-[3,3']bipyrazolyl (Bp3) (Fig.14). The results showed that the inhibition efficiency increased with the inhibitor concentration, and the variation in the inhibitory efficiency depended mainly on the type and nature of the substituents present in the inhibitor molecule, reaching 98% for the chlorinated derivative (Bp3) at  $10^{-3}$  M. This indicates that the inhibitory action of bipyrazolic compounds is primarily due to adsorption on the steel surface. The adsorption of these inhibitors followed a Langmuir adsorption isotherm (Tebbj *et al.* 2005).



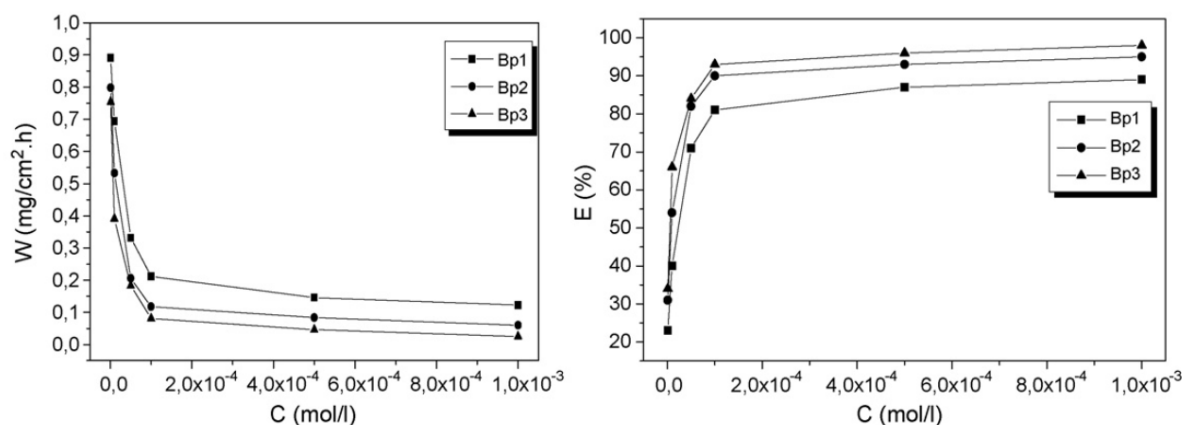
**Figure 14.** The molecular structures of bipyrazol compounds studied by Benabdellah *et al.* 2005.



**Figure 15.** Polarization curves for steel in 1 M HCl containing different concentrations of Bp1, Bp2, and Bp3 at 308 K.



**Figure 16.** Nyquist diagrams of steel in 1 M HCl containing different concentrations of Bp1, Bp2, and Bp3 at 308 K.



**Figure 17.** Variation of corrosion rate (W) and inhibition efficiency (E) with bipyrazolic compounds concentration for steel in 1 M HCl at 308 K

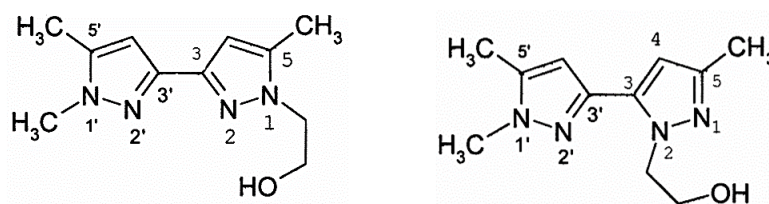
In conclusion, this study of bipyrazolic compounds as corrosion inhibitors revealed several key findings. First, these compounds mainly influence cathodic processes, and their inhibitory effects become more pronounced at higher inhibitor concentrations. Second, all studied molecules demonstrated effective corrosion inhibition in hydrochloric acid solutions, with the inhibition efficiency order of  $Bp3 > Bp2 > Bp1$  (Fig.15&16). Third, the results obtained from the three different methods (potentiodynamic polarization, EIS, and weight loss) show consistent agreement. Finally, the adsorption behavior of bipyrazolic molecules conforms to the Langmuir adsorption isotherm model, with negative values of the adsorption free energy ( $\Delta G^\circ_{ads}$ ), indicating spontaneous adsorption of these compounds on the steel surface. Overall, this study provides valuable insights into the corrosion-inhibition properties of bipyrazolic compounds in acidic environments.

Laarej *et al.* (2010) explored the correlation of the effectiveness of certain bipyrazoles, including N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-cyclohexylamine (Bip 1), N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-ethanolamine (Bip 2), N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-allylamine (Bip 3), and N,N-bis(3-carboethoxy-5-methylpyrazol-1-ylmethyl)-cyclohexylamine (Bip 4), to inhibit the corrosion

of mild steel in hydrochloric acid (HCl) using a density functional approach with B3LYP/6-31G(d) calculations. Bipyrazolic inhibitors exhibited the highest inhibition efficiency. The calculated quantum chemical parameters include the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), bandgap energy ( $\Delta E$ ), dipole moment ( $\mu$ ), softness ( $\sigma$ ), and total energy (TE). The obtained results provide valuable information on the inhibitory properties of bipyrazoles and their potential to mitigate mild steel corrosion in HCl (Laarej *et al.* 2010).

Researchers such as Zerga *et al.* investigated the corrosion inhibition of C38 steel in a molar hydrochloric acid solution using N,N-bis[2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyl] butylamine (P1) and 5-{N,N-bis[2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyl] amino}pentanol (P2). Electrochemical and weight loss measurements conducted at 308 K showed that these compounds acted as good inhibitors without altering the corrosion process mechanism. Additionally, the inhibition efficiency increased with increasing concentrations of the studied inhibitors. Compound P2 exhibited better protective properties, even at relatively high temperatures compared to P1. The activation energies of corrosion and the associated free adsorption were determined. The researchers concluded that P1 and P2 were adsorbed onto the surface of the C38 steel according to the Langmuir adsorption isotherm model (Zerga *et al.* 2010).

In 2011, K. Tebbji *et al.* investigated the inhibitory effect of two isomers, namely 2-(1',5,5'-trimethyl-1H,1'H-3,3'-bipyrazol-1-yl)ethanol (1-TBE) and 2-(1',5,5'-trimethyl-1H,2'H-3,3'-bipyrazol-2-yl)ethanol (2-TBE) (Fig.18), on the corrosion of mild steel in a 1.0 M hydrochloric acid solution at 308 K, using weight loss measurements and electrochemical techniques (impedance spectroscopy and polarization curves). The inhibition efficiency depended on the structure of the pyrazole, with 1-TBE acting as a better inhibitor than 2-TBE. The inhibition efficiency increased with increasing inhibitor concentration, reaching 93% at a concentration of  $10^{-3}$  M. Polarization curves indicated that 1-TBE and 2-TBE essentially acted as cathodic inhibitors. The percentage values of efficiency (E) obtained using the different methods were in reasonable agreement. Electrochemical impedance measurements showed an increase in the transfer resistance with increasing inhibitor concentration. The effect of temperature on the corrosion behavior of steel in 1.0 M HCl with and without the inhibitor at  $10^{-3}$  M was studied in the temperature range of 308 to 333 K (Tebbj *et al.* 2005).



**Figure 18.** The molecular structures of bipyrazol compounds studied by Tebbji *et al.*

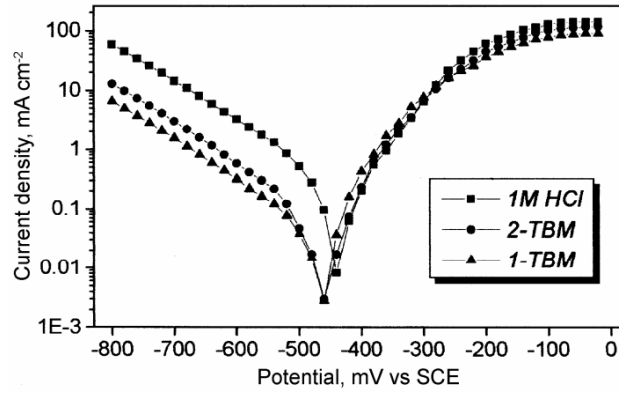


Figure 19. Polarization curves of steel in 1 M HCl without and with  $10^{-3}$  M of 1-TBE and 2-TBE

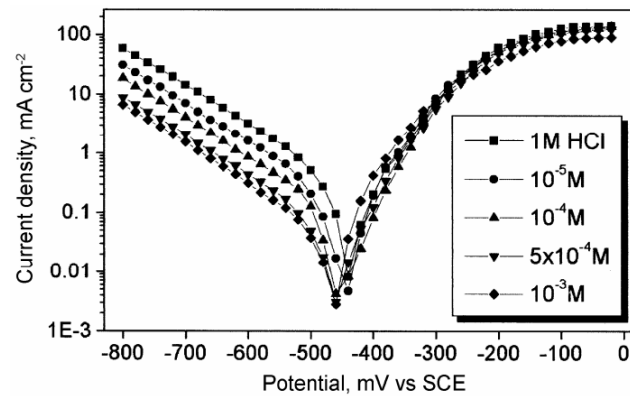


Figure 20. Polarization curves of steel in 1.0 M HCl containing various concentrations of 1-TBE

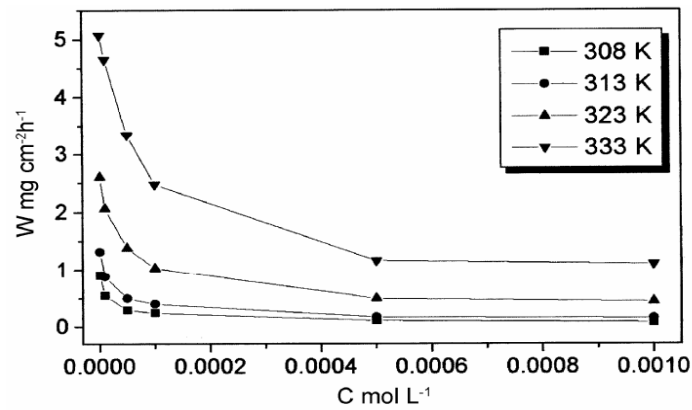


Figure 21. The relationship between corrosion rate and inhibitor concentration of 1-TBE

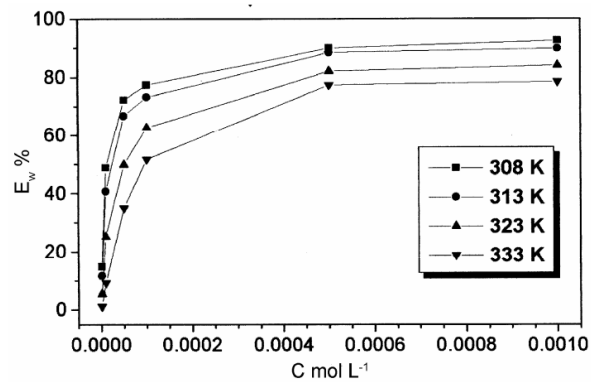
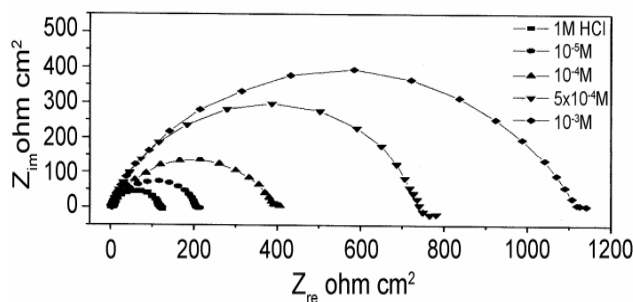


Figure 22. The relationship between inhibition efficiency ( $E_w$  %) and inhibitor concentration of 1-TBE in 1.0 M HCl



**Figure 23.** Nyquist diagrams for steel in 1M HCl containing different concentrations of 1-TBE.

In summary, this study highlighted several significant findings. First, both isomers demonstrate an inhibitory capacity against the corrosion of steel in a 1 M hydrochloric acid solution, with superior performance observed for 1-TBE. The inhibition efficiency increased proportionally with the inhibitor concentration, but decreased with increasing temperature. Both compounds acted as cathodic inhibitors. Furthermore, the adsorption of 1-TBE on the steel surface in an acidic solution follows a Langmuir adsorption isotherm, which is a spontaneous and exothermic process, resulting in a decrease in entropy. Interestingly, the inhibition efficiency of 1-TBE is temperature dependent, with a decrease in the adsorption equilibrium constant ( $K$ ) as the temperature increases. The results obtained using different methods, such as weight loss, potentiodynamic polarization, and impedance spectroscopy, show consistent agreement. These findings provided a thorough understanding of the inhibitory properties of 1-TBE in the context of steel corrosion in acidic environments (Fig.23).

**In 2012**, H. Zarrok et al. conducted a study on the corrosion inhibition of C38 steel in hydrochloric acid (HCl) solution by 1,1',5,5'-tetramethyl-1H,1'H-3,3'-bipyrazole (Bip) at temperatures ranging from 308 to 343 K. The key findings are as follows. The corrosion inhibition efficiency of Bip decreases with increasing temperature. Inhibition occurs through adsorption of Bip molecules onto the metal surface. Thermodynamic parameters, such as activation energy ( $E_a$ ), Arrhenius factor, enthalpy, and entropy, along with adsorption equilibrium constants ( $K_{ads}$ ), free energy of adsorption ( $\Delta G_{ads}$ ), heat of adsorption ( $\Delta H_{ads}$ ), and entropy of adsorption ( $\Delta S_{ads}$ ), were calculated and discussed. The adsorption of Bip on the surface of C38 steel in 1 M HCl follows the Langmuir adsorption isotherm model. Quantum chemical calculations using DFT at the B3LYP/6-31G\* theory level were also performed to evaluate certain electronic properties of the molecule, aiming to determine any correlation between the inhibitory effect and the molecular structure of 1,1',5,5'-tetramethyl-1H,1'H-3,3'-bipyrazole (Bip) (Zarrok et al. 2012).

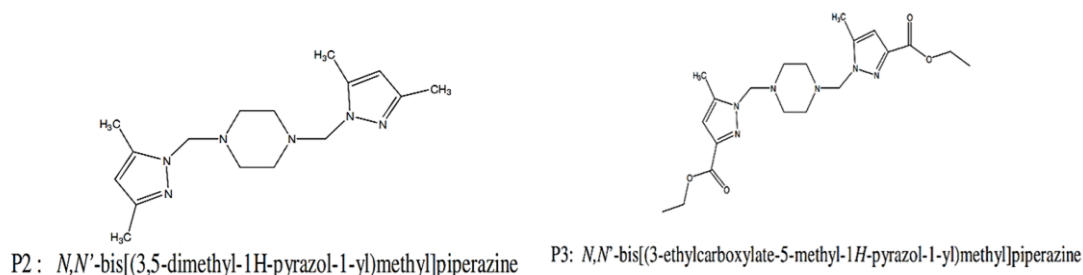
Hammouti et al. conducted experiments using a rotating electrode at different speeds to investigate oxygen reduction, following the Levich equation. The corrosion inhibition of copper in an aerated 3% NaCl solution was examined using potentiodynamic polarization and linear polarization resistance (LRP) in the presence of various concentrations of the bipyrazolic compound N,N-bis(3-carbomethoxy-

5-methylpyrazol-1-ylmethyl)cyclohexylamine (BiPyA). The presence of this compound in the solution reduced the corrosion current density and increased the linear polarization resistance. The inhibition efficiencies obtained from the Tafel cathodic curves and LRP methods were in good agreement. BiPyA was found to be an effective inhibitor of copper corrosion, acting as a mixed-type inhibitor, and adsorbing onto the copper surface according to the Langmuir isotherm model (Hammouti *et al.* 2012).

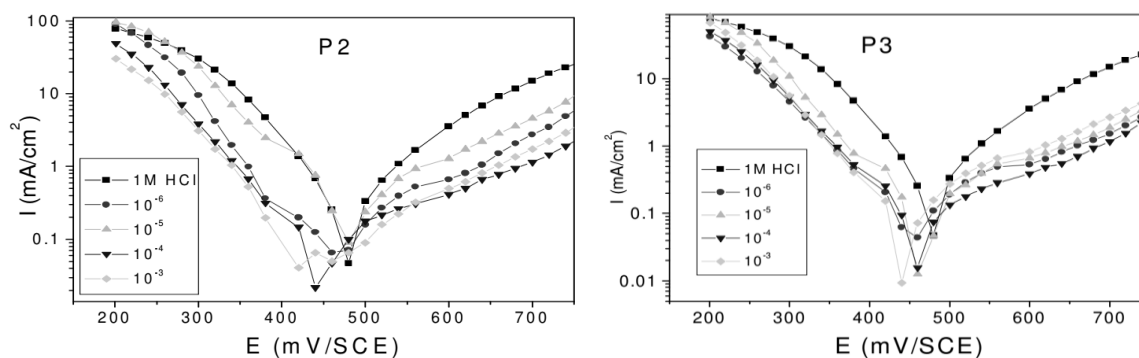
N. Boussalah *et al.* utilized density functional theory (DFT) to study six bipyrazolic compounds for their ability to inhibit copper corrosion. DFT calculations revealed that the inhibitory effect is strongly linked to the energies of the frontier orbitals, polarizability, electronic chemical potential, and global nucleophilicity. The theoretical results agree with the experimental data on corrosion inhibition efficiency, thus demonstrating the validity of the reactivity indices derived from DFT in predicting the inhibitory effect of bipyrazolic compounds on copper (Boussalah *et al.* 2009).

Zarrok *et al.* investigated three new derivatives of bipyrazole, namely ethyl 5,5'-dimethyl-10H-1,3'-bipyrazole-4-carboxylate (Bip1), 1,1',5,5'-tetramethyl-1H,1'H-3,3'-bipyrazole (Bip2), and 3-(bromomethyl)-5,5'-dimethyl-10H-1,3'-bipyrazole (Bip3), which were synthesized and used as additives to protect C38 steel from corrosion in aerated 1 M hydrochloric acid (HCl) solution. Various corrosion monitoring techniques, such as weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy, have been employed to study the inhibition efficiency. All techniques showed an increase in the inhibition efficiency and a decrease in the corrosion rate with increasing inhibitor concentration. Impedance measurements showed a decrease in double-layer capacitance and an increase in charge transfer resistance with increasing inhibitor concentration, leading to enhanced inhibition efficiency. A potentiodynamic polarization study revealed that all inhibitors acted in a mixed mode. The adsorption of bipyrazole derivatives followed the Langmuir adsorption isotherm, and the thermodynamic parameters were determined and discussed (Zarrok *et al.* 2012).

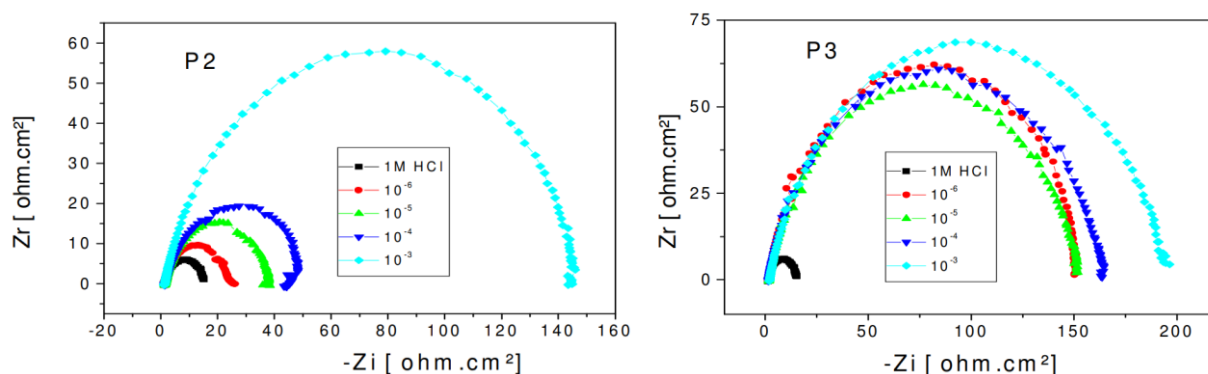
**In 2013**, M. Bouklah *et al.* investigated the corrosion inhibition of mild steel in 1M hydrochloric acid solutions using new derivatives of N,N'-bipyrazole piperazine, namely N,N'-bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]piperazine (P2) and N,N'-bis[(3-ethylcarboxylate-5-methyl-1H-pyrazol-1-yl)methyl]piperazine (P3) (Fig.24), using both chemical (weight loss) and electrochemical (potentiodynamic polarization and electrochemical impedance spectroscopy, EIS) measurements. These measurements revealed that the inhibition efficiency of these compounds increased with their concentration, reaching 91% for P2 and 92% for P3 at  $10^{-3}$ M concentration. The inhibition efficiency followed the order  $P3 > P2$ , with P2 increasing with temperature in the range 298–353 K. Polarization studies showed that these compounds act as mixed-type inhibitors in 1M hydrochloric acid solutions. These inhibitors operate through adsorption and follow the Langmuir isotherm (Bouklah *et al.* 2013).



**Figure 24.** The molecular structures of bipyrazol compounds studied by Bouklah *et al* 2013.



**Figure 25.** Typical polarization curves of steel in 1 M HCl for various P2 and P3 concentrations.



**Figure 26.** Nyquist diagrams for steel in 1M HCl with different concentrations of P2 and P3

The observations of this study underscore these crucial conclusions. Bipyrazole derivatives are excellent inhibitors that act as mixed-type inhibitors for mild steel in hydrochloric acid solutions, with inhibition efficiencies in the order  $P3 > P2 > P1$ . The increase in inhibitor concentration was correlated with an increase in inhibition efficiency, operating through adsorption on the surface of the steel, in accordance with the Langmuir adsorption isotherm. The decrease in double-layer capacity in the presence of these inhibitors suggests adsorption on the steel surface. The converging results from the electrochemical studies and weight loss measurements reinforce the reliability of the corrosion determination. In summary, this study demonstrates the promising relevance of bipyrazole derivatives as effective corrosion inhibitors, opening interesting prospects for their application in corrosive environments (Figs.25&26).

Guendouz et al. investigated the inhibitory activity of newly synthesized and characterized bipyrazole derivatives, namely methyl 2-(bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]amino)-4-methylpentanoate (BT39), methyl 2-(bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]amino)-3-methylbutanoate (BT40), and methyl 2-(bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]amino)propanoate (BT45), against the corrosion of C38 steel in molar hydrochloric acid solution. The investigation was conducted using weight-loss measurements and electrochemical techniques. These compounds proved to be highly effective inhibitors, with a protection percentage exceeding 88% for BT40 at concentrations as low as  $10^{-2}$  M. Cathodic inhibition from polarization and a charge transfer mechanism from impedance studies in the absence and presence of these compounds were observed. The Langmuir adsorption isotherms were obtained. The relationship between the inhibition efficiency and the molecular structures of BT36, BT43, and BT45 is discussed, considering quantum chemistry parameters. The study was complemented by calculations using B3LYP/6-31G density functional theory. The calculated quantum chemistry parameters showed good correlation with inhibition efficiency. The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), energy gap ( $\Delta E$ ), and dipole moment ( $\mu$ ) explain the experimental data well (Guendouz et al. 2013).

Missoum and colleagues synthesized two compounds, methyl 2-(bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino)acetate, also known as BT36, and methyl 2-(bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino)-3-(1H-indol-3-yl)propanoate, referred to as BT43. Their study revealed that these compounds are highly effective inhibitors of C38 steel corrosion in 1 M hydrochloric acid solutions. Specifically, BT43 showed a protection percentage exceeding 95% at concentrations as low as  $10^{-2}$  M. Analysis through weight loss and electrochemical techniques confirmed these findings. Furthermore, impedance studies demonstrated that the protective mechanism involved cathodic inhibition through polarization and charge transfer. The experimental data also indicated that the Langmuir adsorption isotherm was respected. By employing Density Functional Theory (DFT) with the B3LYP/6-31G\* level of theory, the researchers calculated quantum chemical data showing a satisfactory correlation between inhibition efficiency and the molecular structure of compounds BT36 and BT43. Parameters such as the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), energy separation ( $\Delta E$ ), and dipole moment ( $\mu$ ) of the compound relative to the metal surface were identified as influential factors in inhibition efficiency (Missoum et al. 2013).

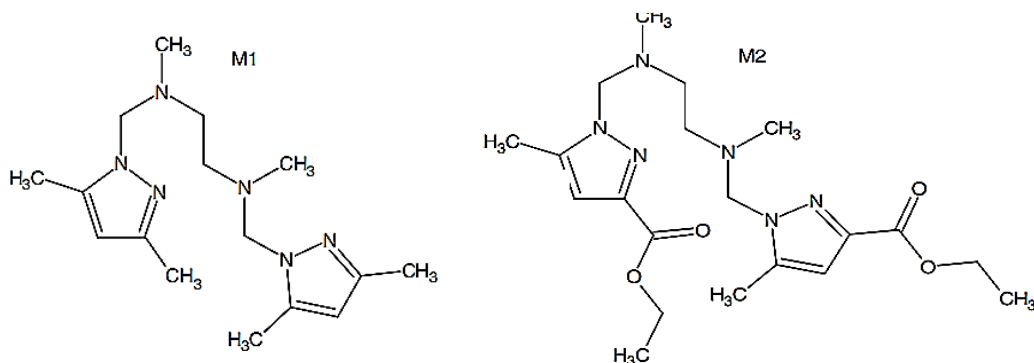
**In 2015**, Elmsellem and colleagues conducted a study on the corrosion inhibition of mild steel in a 1 M hydrochloric acid solution using two compounds: 1,1-bis(3-ethoxycarbonyl-5-methylpyrazolyl)methane (P1) and 1,4-bis(3-ethoxycarbonyl-5-methylpyrazolyl)butane (P2) at 308 K, employing electrochemical

measurements and weight loss techniques. Polarization curves revealed that both compounds acted as mixed-type inhibitors. The results demonstrated that the inhibition efficiency increased with the concentration of the inhibitor. A comparative study of the inhibitory performance of the two bipyrazolic derivatives showed that P2 was more effective than P1. The adsorption of P2 onto the steel surface followed the Langmuir adsorption isotherm. Kinetic and thermodynamic parameters of mild steel corrosion and inhibitor adsorption were determined and discussed. An evident correlation was found between corrosion inhibition efficiency and quantum chemical parameters using Density Functional Theory (DFT). The theoretical results obtained were compared with experimental outcomes (Elmsellem *et al.* 2015).

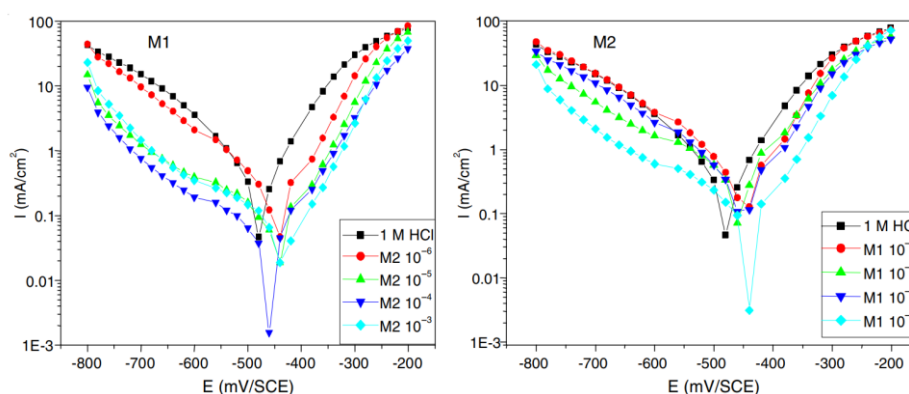
Ben Hmamou and colleagues conducted a study on the evaluation of 2-[Bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-amino]-4-[bis-(3,5-dimethyl-pyrazol-1-ylmethyl)carbonyl]-butyric acid (Pyr1-1) as a corrosion inhibitor for carbon steel using weight loss and electrochemical polarization (EIS) techniques. The study was also complemented by scanning electron microscopy (SEM) and quantum chemical calculations. The inhibition efficiency ( $\eta\%$ ) increased with the Pyr1-1 concentration, showing a maximum IE of 93.5% at 298 K at  $10^{-3}$  M, and decreased with increasing temperature. Electrochemical studies revealed that the Pyr1-1 inhibitor delayed both cathodic and anodic processes by adsorbing onto the metal surface and blocking active corrosion sites. The corrosion current density was around 165.8 mA/cm<sup>2</sup> for Pyr1-1 at the optimal concentration. EIS results showed that changes in impedance parameters ( $R_{ct}$  and  $C_{dl}$ ) with Pyr1-1 concentration indicated molecule adsorption leading to the formation of a protective layer on the carbon steel surface. A good fit to the Langmuir adsorption isotherm was obtained between the degree of surface coverage and inhibitor concentration. The weight loss measurement results were consistent with the electrochemical study findings. Quantum chemical approach was utilized to calculate the molecule's electronic properties to elucidate the relationship between the inhibitory effect and molecular structure. The equilibrium adsorption behavior of this molecule on the Fe (110) surface was studied using molecular dynamics simulations (Ben Hmamou *et al.* 2015).

**In 2017**, Bouklah and colleagues investigated the effect of certain bipyrazole derivatives, namely N,N'-bis-[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-N,N'-dimethylethane-1,2-diamine (M1) and N,N'-bis[(3-ethylcarboxylate-5-methyl-1H-pyrazol-1-yl)methyl]-N,N'-dimethylethane-1,2-diamine (M2) (Fig.27), as corrosion inhibitors for mild steel in a 1 M hydrochloric acid solution. They explored the influence of inhibitor concentration as well as temperature using chemical (weight loss) and electrochemical techniques. All employed methods yielded consistent results. The findings revealed that the protective efficiency increased with inhibitor concentration and temperature elevation. Weight loss data were

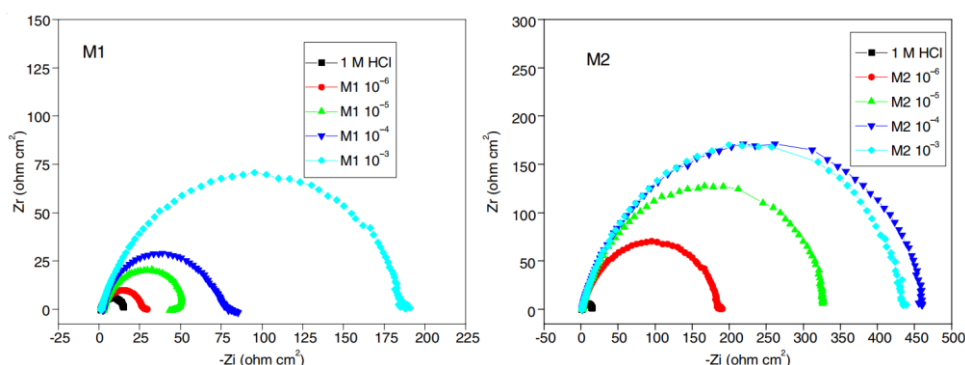
utilized to determine the thermodynamic parameters of dissolution and adsorption processes, with a detailed interpretation of the results. The inhibitor adsorption on the carbon steel surface followed the Langmuir adsorption isotherm (Figs. 28 & 29) (Bouklah et al. 2017).



**Figure 27.** Synthesis of bipyrazole derivatives by Bouklah et al 2017.



**Figure 28.** Typical polarization curves of steel in 1 M HCl for various concentrations of M1 and M2



**Figure 29.** Nyquist diagrams for steel in 1M HCl with different concentrations of M1 and M2

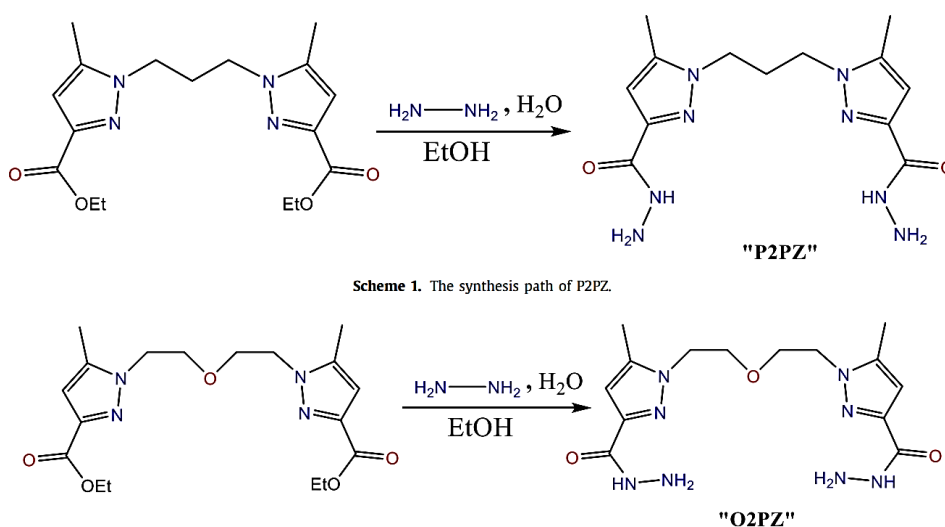
In summary, several studies have investigated the corrosion inhibition of mild steel in hydrochloric acid solutions using various bipyrazole derivatives.

**In 2017**, Bouklah and colleagues explored the effectiveness of bipyrazole derivatives M1 and M2 as mixed inhibitors for mild steel corrosion in 1 M HCl solution. Their study demonstrated that the protective efficiency increased with inhibitor concentration. Experimental results and DFT simulations

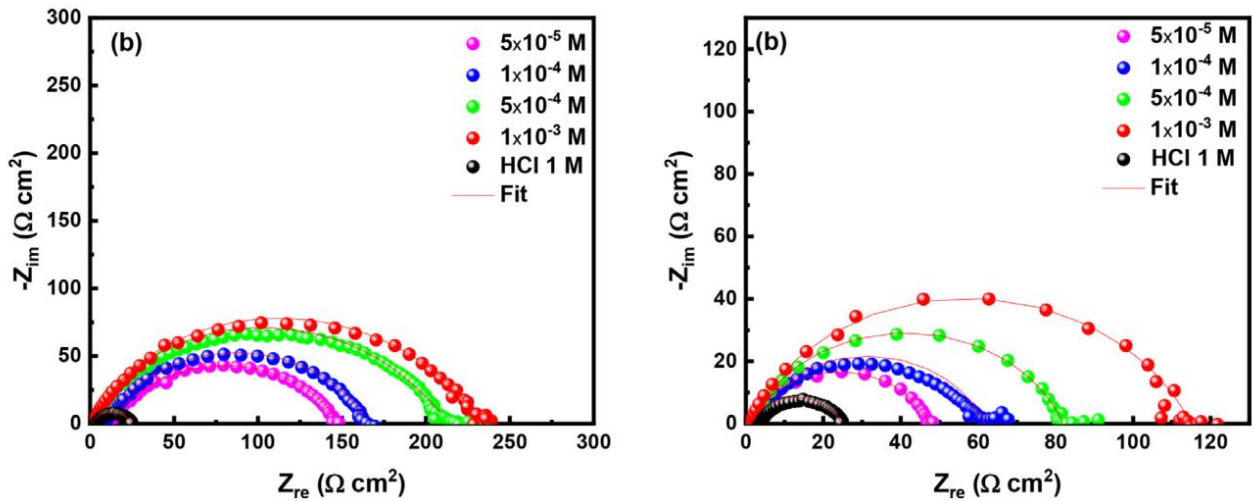
showed that M2 exhibited better inhibition performance than M1. The adsorption of bipyrazole derivatives on the steel surface followed the Langmuir adsorption isotherm, and potential active sites were identified. Overall, M1 and M2 were deemed effective inhibitors, acting through electron transfer mechanisms, highlighting the utility of quantum parameters in modeling their inhibitory effectiveness.

In 2020, another study by Bouklah *et al.* 2020 investigated the corrosion inhibition of mild steel in 1 M HCl by bipyrazole derivatives, including compounds 3a, 3b, and 3c. Their research indicated that the protection efficiency increased with both inhibitor concentration and temperature. Thermodynamic functions of dissolution and adsorption processes were calculated from weight loss measurements, with interpretations provided. The adsorption of the inhibitor on the carbon steel surface followed the Langmuir adsorption isotherm (Bouklah *et al.* 2020).

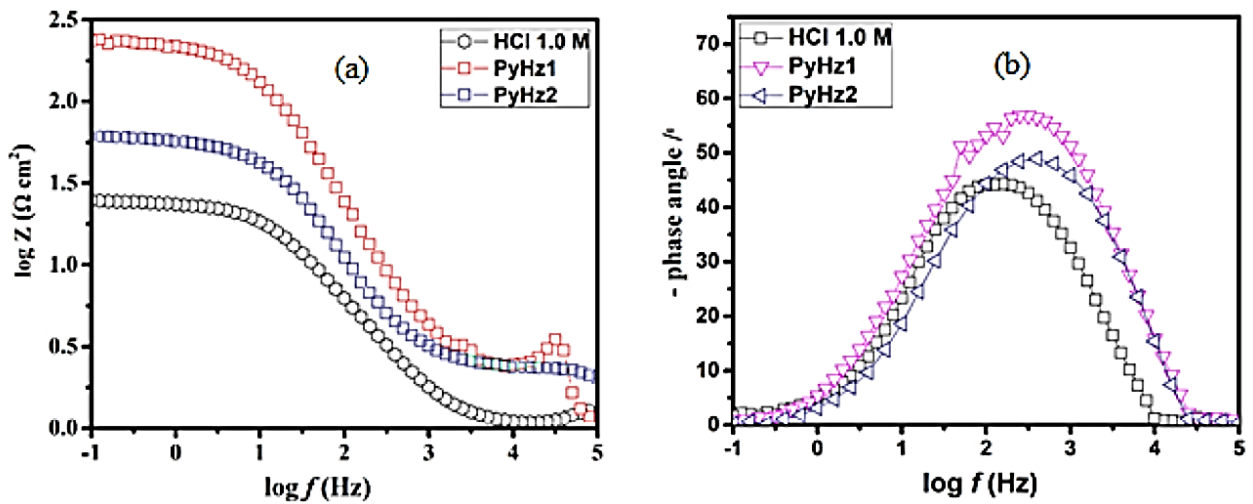
In 2022, Cherrak *et al.* evaluated two new bi-pyrazole-carbohydrazide derivatives, P2PZ and O2PZ, as corrosion inhibitors for mild steel in 1.0 M hydrochloric acid (Fig. 30). They found that P2PZ exhibited higher inhibition efficiency than O2PZ, with an inhibition efficiency of 95% at 308 K and  $10^{-3}$  mol/L. The inhibition efficiency increased with concentration and decreased with temperature. Electrochemical studies revealed a charge transfer process, confirmed by electrochemical impedance spectroscopy. Polarization curves suggested that P2PZ and O2PZ acted as mixed-type inhibitors following the Langmuir adsorption isotherm. The values of free adsorption energy confirmed a physicochemical adsorption process (Figs. 31-33). Electron microscope images showed the formation of a protective layer on the metal surface (Fig. 34). Theoretical studies (DFT and MD) corroborated the experimental results, confirming that the reactivity of inhibitors depended on their electron donor/acceptor capabilities. Overall, this research highlights the promising inhibitory properties of P2PZ and O2PZ for protecting mild steel against corrosion in acidic environments (Cherrak *et al.* 2022).



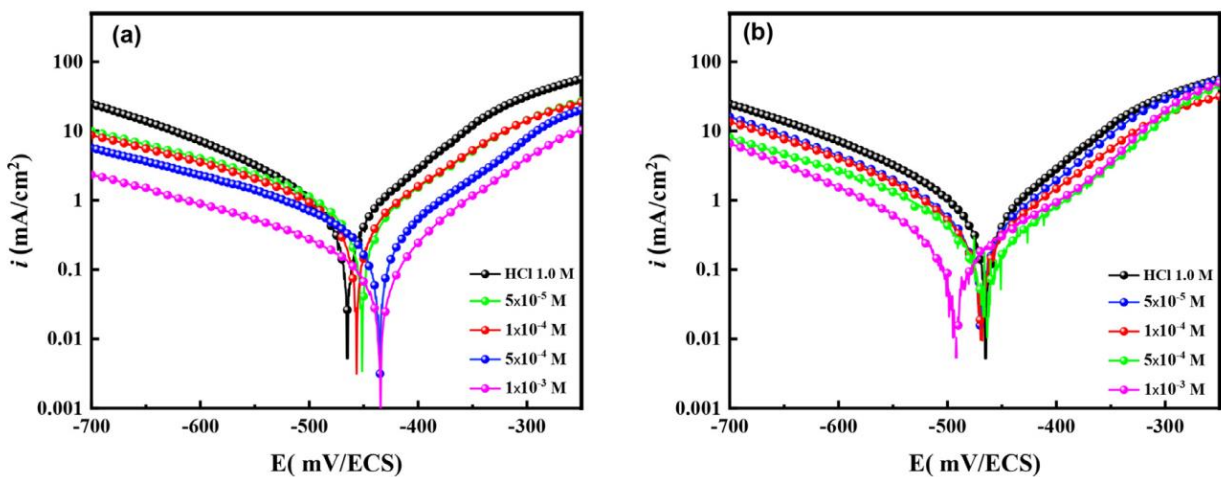
**Figure 30.** Synthesis of bipyrazole derivatives by Cherrak *et al.*



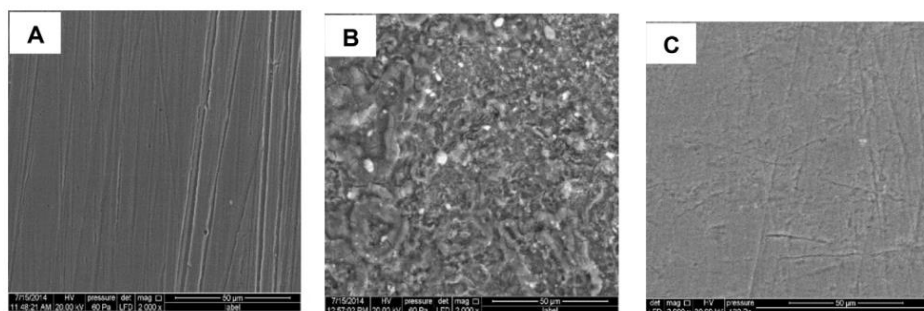
**Figure 31.** Nyquist plots representation of mild steel in 1.0 M HCl solution before and after the addition of different concentrations of (a) P2PZ and (b) O2PZ at 308 K



**Figure 32.** (a) Bode, and (b) phase angle recorded for mild steel in 1.0 M HCl without and with the optimum concentration of P2PZ and O2PZ at 308 K

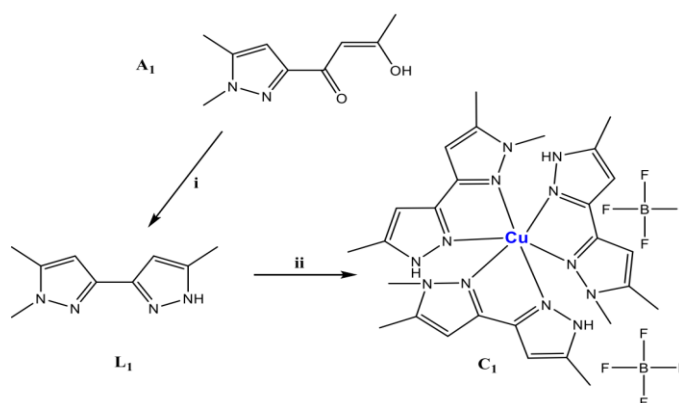


**Figure 33.** Potentiodynamic polarization curves obtained for mild steel in HCl solution in absence and presence of various concentrations of P2PZ and O2PZ at 308 K

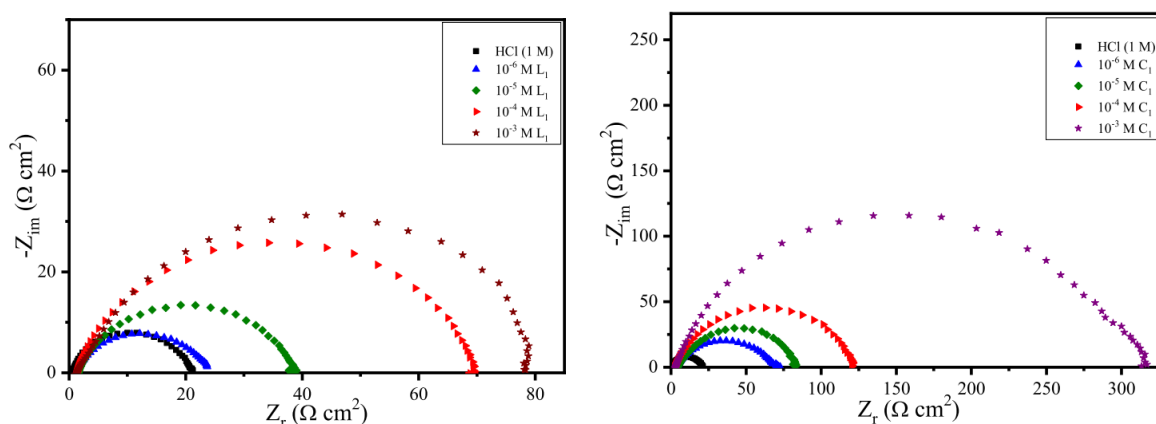


**Figure 34.** SEM/EDX analysis of polished, uninhibited, and inhibited samples of mild steel after 6h immersion time in HCl with and without inhibitor

Radi *et al.* conducted a comprehensive study on the corrosion inhibition capacity of a bipyrazole compound (L1) and its copper complex Cu (Hbpz) (C1) concerning mild steel (MS) (Figs. 35-37) corrosion in hydrochloric acid (HCl) solution at various concentrations and temperatures.



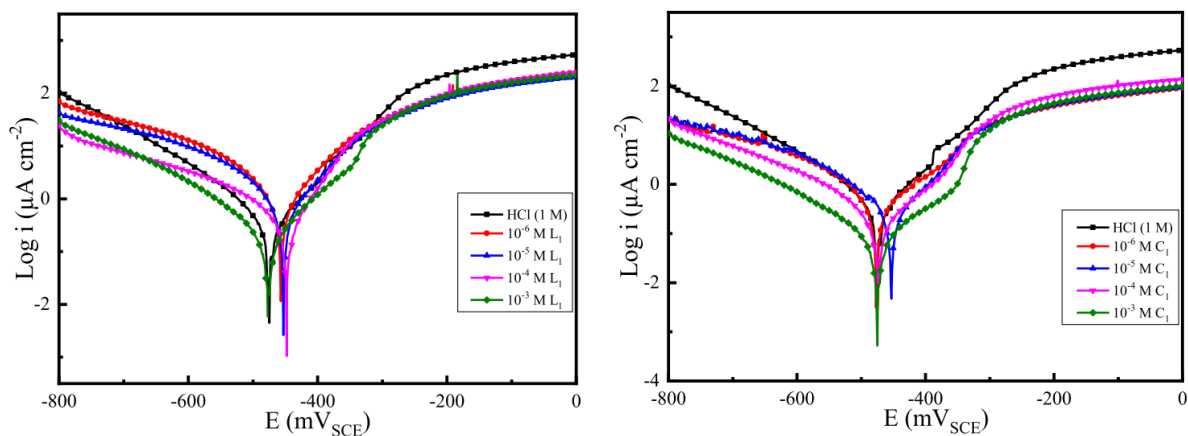
**Figure 35.** Synthetic route of Ligand L1 and coordination complex (C1). i)  $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ , MeCN ii)  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  by Radi *et al.*



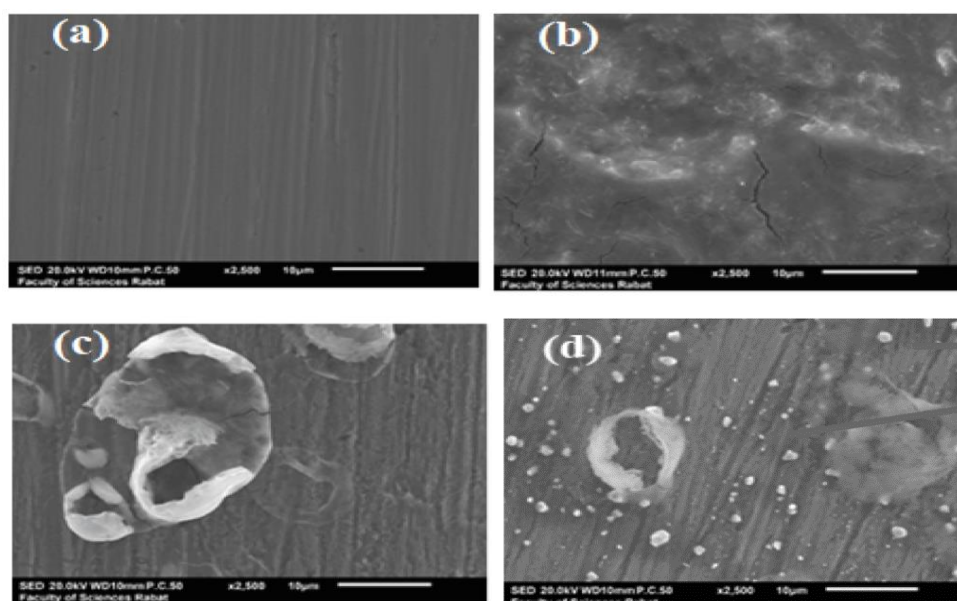
**Figure 36.** Nyquist spectra of MS samples for uninhibited and inhibited (L1 and C1) system.

They employed weight loss (WL) methods, potentiodynamic polarization curves (PPC), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) (Fig.38), energy-dispersive X-ray spectroscopy (EDS), UV-visible spectroscopy, and computational approaches. The polarization results revealed that both compounds exhibited mixed-type inhibition. The adsorption of both molecules on the

mild steel surface was confirmed by EDS, SEM, and UV-visible spectroscopy. Additionally, the adsorption of the two compounds followed the Langmuir adsorption isotherm. Density functional theory (DFT) and Monte Carlo (MC) simulation supported the experimental findings (Radi et al. 2022).



**Figure 37.** Mild steel Tafel plots in 1 M hydrochloric acid, with and without various concentrations of L1 and C1.



**Figure 38.** Surface morphology and EDS results of mild steel before (a) and after immersion in 1 M HCl in the absence (b) and presence of L1 (c) and C1 (d).

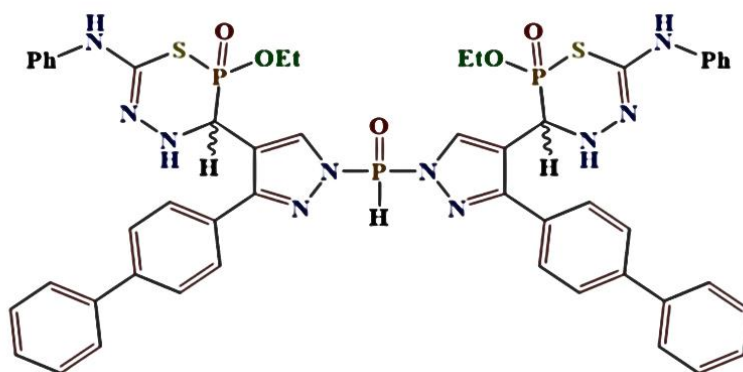
In summary, the conclusions of the two studies published in 2022 highlight the effectiveness of corrosion inhibitors in acidic environments, albeit with different compounds.

In the study by K. Cherrak and colleagues, the compounds P2PZ and O2PZ demonstrated effective corrosion inhibition, with P2PZ showing better performance (95.83%) compared to O2PZ (84.26%). Adsorption onto the mild steel surface followed the Langmuir adsorption isotherm, confirmed by SEM/EDX analyses. The experimental results were supported by theoretical simulations (DFT and MD).

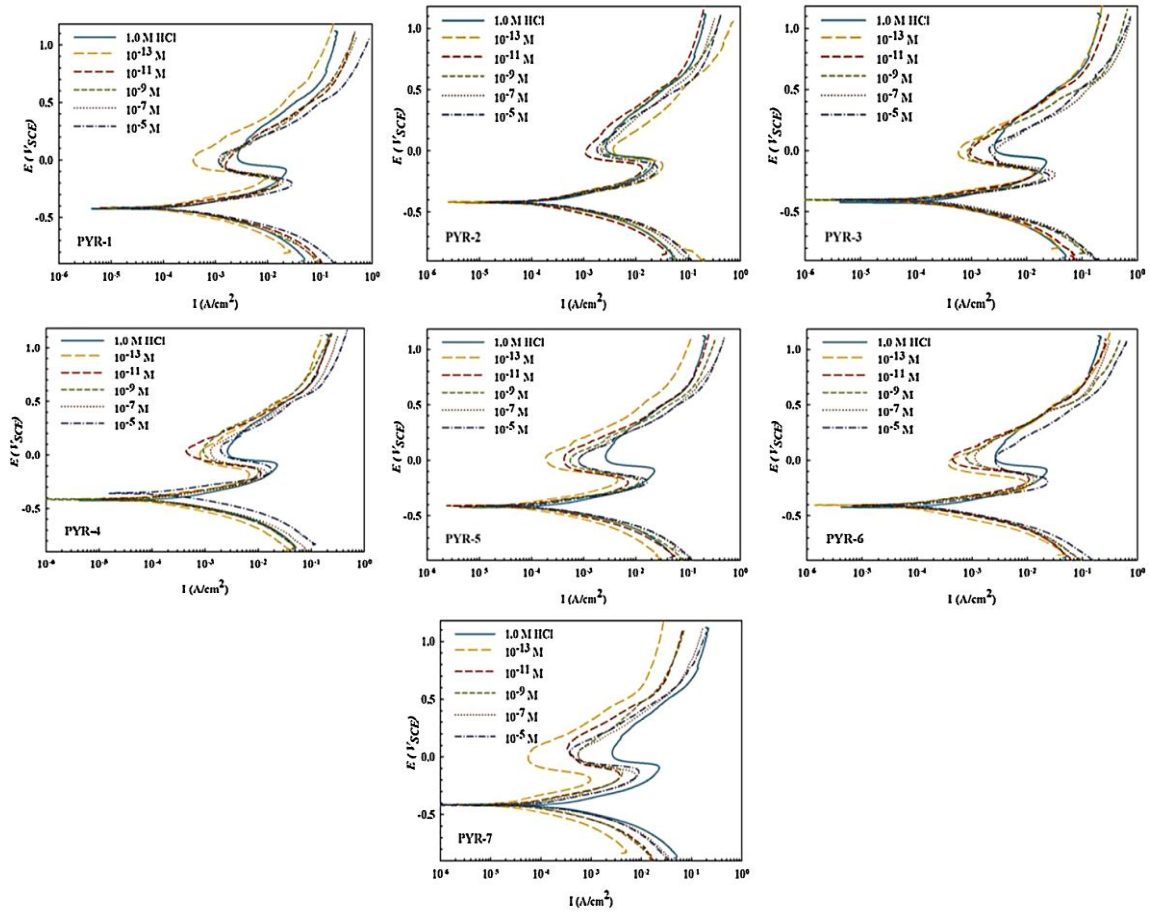
In the study by Radi et al., the mononuclear copper coordination complex C1 and its isolated ligand L1 also exhibited excellent corrosion inhibition, particularly for C1 (efficiency of 97.1% at  $10^{-3}$  M). Adsorption of the molecules onto the steel surface was described by the Langmuir adsorption model. Electrochemical studies revealed that L1 and C1 acted as mixed-type inhibitors. SEM and EDX analyses confirmed the presence of inhibitor molecules on the steel surface. DFT and MC simulations corroborated the adsorption mechanisms and the formation of a stable barrier, with adsorption efficiency in the order  $C1 > L1$ .

In synthesis, both studies demonstrate that the tested compounds act as excellent corrosion inhibitors, with varied adsorption mechanisms, confirming their potential for protecting mild steel in acidic environments.

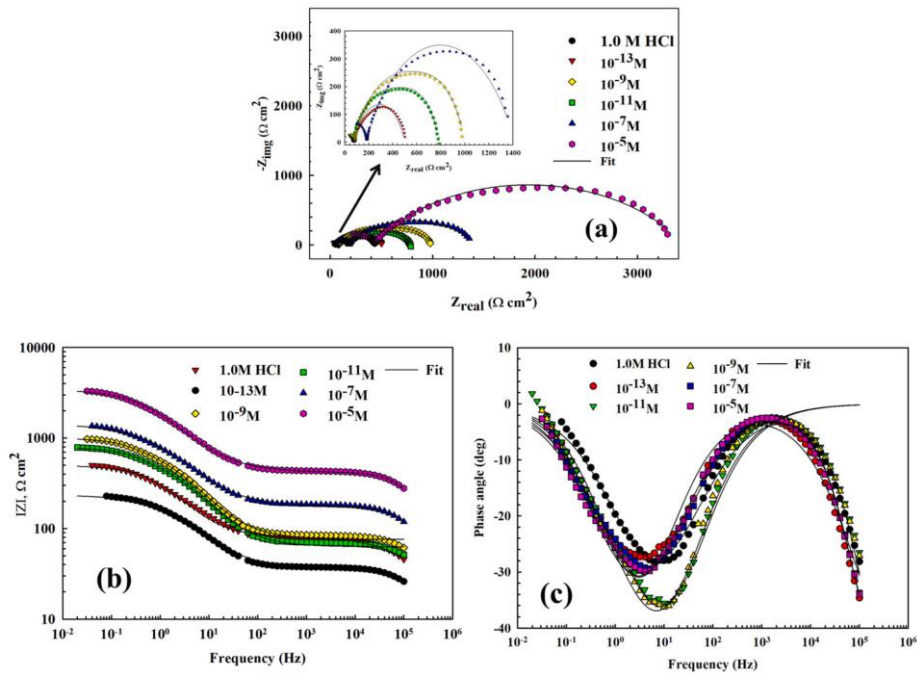
**In 2024**, A. Elsamman and his team investigated seven new bispyrazole derivatives (PYR-1 to PYR-7) as corrosion inhibitors for stainless steel 304 (304 SS) in 1.0 M hydrochloric acid solutions at various concentrations. Utilizing quantitative structure-activity relationship (QSAR) methodology, they developed a predictive model for the anticorrosion properties of another inhibitor (BPYR-P) from the same family. Experimental results were validated through various electrochemical techniques, confirming the predicted efficacy of BPYR-P as an excellent corrosion inhibitor for 304 SS, with an increase in inhibition efficiency with concentration (Fig.39). The adsorption of BPYR-P on the surface of 304 SS was characterized as mixed-type, following the Langmuir adsorption isotherm. AFM, SEM-EDX analyses, UV-visible spectra, contact angle measurement, X-ray diffraction (XRD), as well as quantum chemical calculations (DFT) and molecular dynamics (MD) simulations, all confirmed the agreement between experimental data and QSAR model predictions. In summary, this research offers a promising approach for predicting and validating the anticorrosion performance of inhibitors (Figs.40&41) (Elsamman *et al.* 2024).



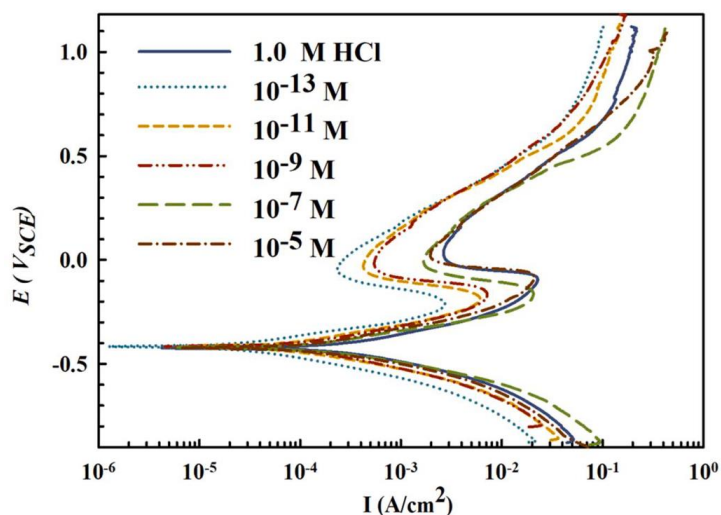
**Figure 39.** The chemical structure of the BPYR-P inhibitor synthesis by Elsamman et al 2024.



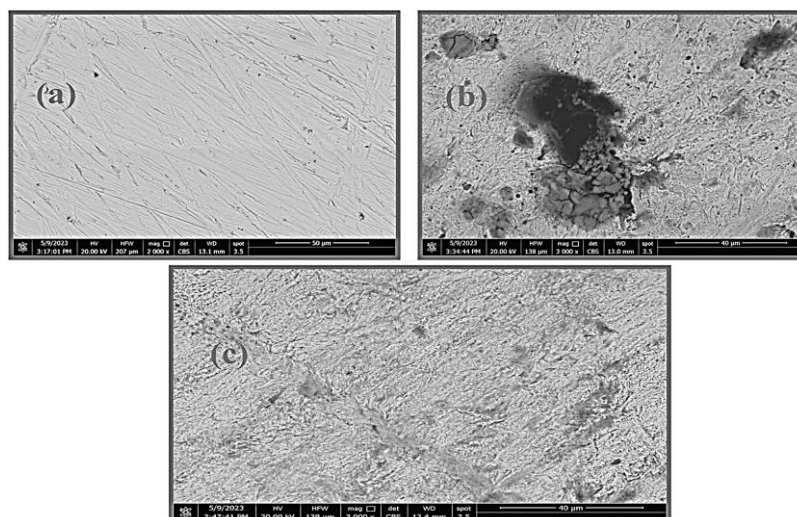
**Figure 40.** PDP spectra for 304 SS in a 1.0 M HCl solution in the absence and presence of  $10^{-5}$  M of PYR-s inhibitors at 298 K



**Figure 41.** (a) Nyquist, (b) Bode modulus, and (c) Bode phase plots of 304 SS in a 1.0 M HCl solution in the absence and presence of different concentrations of BPYR-P inhibitor at 298 K.



**Figure 42.** Potentiodynamic polarization curves of 304 SS in a 1.0 M HCl solution in the absence and presence of different concentrations of BPYR-P inhibitor at 298 K.



**Figure 43.** SEM images of (a) polished 304 SS surface, (b) polished 304 SS in a 1M HCl, and (c) polished 304 SS in a 1M HCl containing  $10^{-5}$  M of BPYR-P inhibitor after immersion for 24 h at 298 K

In summary, a study developed a QSAR model based on GFA to assess the effectiveness of bispyrazole corrosion inhibitors. The model predictions were validated by experimental measurements, demonstrating satisfactory agreement. The inhibitor BPYR-P proved to be effective, with increasing inhibition observed with concentration. Adsorption on the metal surface followed the Langmuir isotherm, confirming a physicochemical mechanism. EIS parameters revealed significant changes with inhibitor concentration, confirming its inhibitory effect. SEM/EDX and AFM analyses indicated the formation of a protective layer. Quantum calculations and molecular simulations corroborated the experimental data and results predicted by the QSAR model. In summary, this study provides a comprehensive approach to predict and confirm the effectiveness of specific corrosion inhibitors (Figs.43).

## Conclusion

In conclusion, this study highlights the promising properties of bipyrazole compounds as nitrogen derivatives, underscoring their effectiveness as corrosion inhibitors in aggressive environments for various metals. The ongoing exploration of nitrogen compounds and their derivatives is essential to optimize the performance of corrosion inhibitors, particularly for materials such as steel, copper, and aluminum. However, it is important to acknowledge the persistent challenges related to factors such as temperature, medium, economy, and environmental impact. Future research could also focus on the development of bio-based inhibitors, emphasizing the need for environmentally friendly and human-safe solutions. By expressing our pride as researchers and extending warm thanks to our collaborators, colleagues, students, and families for their continuous support, we are motivated to continue our efforts in the pursuit of sustainable chemical innovations.

**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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