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Alkylphenyl-substituted imidazolines as corrosion inhibitors: experimental and DFT study

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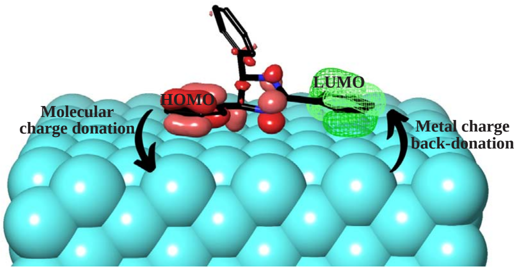
A series of steel corrosion inhibitors based on poly(alkylphenyl)-2-imidazolines was synthesized from available reagents. Electronic parameters that influence binding to a metal surface have been determined, and the influence of substituents on the geometry of binding to the surface has been studied. The resulting compounds have a degree of protection of steel in hydrochloric acid solutions in individual form above 98% at 60 °C and in a mixture with urotropine more than 99% at 95 °C.



Keywords: 2-imidazolines, corrosion inhibitors, metal protection, DFT designing corrosion inhibitors, hydrochloric corrosion, metal surface adsorption.

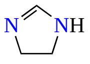
An effective method of anticorrosive protection of metals is the use of corrosion inhibitors (CIs). According to Standard ISO 8044–1989, these are individual compounds or compositions that reduce the rate of corrosion without significantly changing the concentration of any aggressive reagent. Hydrochloric acid solutions are distinguished among the corrosive industrial environments. Such solutions in contact with steel technological equipment cause serious destruction without the use of inhibitory protection.[1] A promising group of steel corrosion inhibitors in hydrochloric acid solutions are substituted imidazolines of various structures[2–13] (some of them are shown in Online Supplementary Materials, Figure S1).

In this work, we paid attention to six imidazolines **1–6**. Representatives **1–3** are the common stock compounds while derivatives **4–6** were herein synthesized. Recently we have shown that modified triarylimidazolines have the ability to activate the p53 protein,[14–16] possess antioxidant,[17] anticorrosion[7] properties, and their hydroxy derivatives can be used as dichloroacetate delivery molecules.[18]

In our previous work, we studied in detail the anti-corrosion effect of 2,4,5-tri(*p*-tolyl)imidazoline **5** by various methods,[7] and this compound showed an inhibition efficiency of more than 90%. In this work, we explored the inhibitory properties of 2,4,5-tris(*p*-alkylphenyl)imidazolines *in silico* using the electron density functional (DFT) and molecular dynamics (MD) method and employed gravimetry method for confirmation.

An important factor for the corrosion inhibitor to be practically applied is its simple large-scale adaptive synthetic accessibility in combination with cheap raw materials. In this regard, the reaction of aldehydes with ammonia is a simple and easily scalable method for the synthesis of symmetric triarylimidazolines.[19] In the present study, benzaldehyde, *p*-tolylaldehyde and cuminaldehyde were used for the two-step preparation of symmetric 2,4,5-triarylimidazolines **4–6** (Scheme 1).

First, we studied the effect of phenyl substituents on the imidazoline ring using the DFT method. The calculation of energy values, geometry optimization and visualization of orbitals were carried out in the Schrödinger 2023.1 program (B3LYP, QM Basic 6-31g**, solvent model PBF, water). The main primary molecular electronic parameter is the gap between the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO). The latest analysis of calculated HOMO–LUMO gaps indicates $\Delta\varepsilon = 5.0–5.4$ eV as range of ‘good’ $\Delta\varepsilon$



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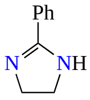

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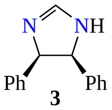

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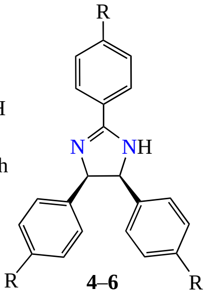
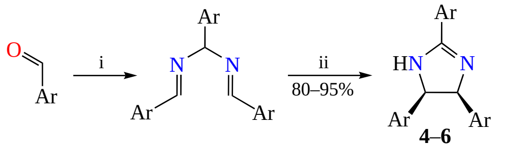


4–6

4 R = H
5 R = Me
6 R = Pr^i



4–6

4 Ar = Ph
5 Ar = 4-MeC_6H_4
6 Ar = 4-$Pr^iC_6H_4$

Scheme 1 *Reagents and conditions*: i, NH_3 (25% aq.), room temperature, 24 h; ii, Bu^tOK, THF or 1,3-dioxolane, 0–5 °C, 1 min.

values for inhibitors of iron and steel corrosion in acidic media.[20] It should be noted that in an acidic solution, imidazoline inhibitors are present in a protonated form. Therefore, molecular orbital energies were calculated for both neutral molecules and their protonated form [Figure 1(*a*)]. We calculated the energy differences both for the substances under study **4–6** and for imidazoline **1**, 2-phenylimidazoline **2** and 3,4-diphenylimidazoline **3** for structure–activity relationships. Unsubstituted imidazoline **1** has a high $\Delta\varepsilon$ equal to 6.0 eV and the protonation increases $\Delta\varepsilon$ significantly to 6.4 eV. The introduction of a phenyl substituent into the second position of the imidazoline fragment (**2**) decreases $\Delta\varepsilon$ to 4.9 eV, and protonation in this case increases $\Delta\varepsilon$ to 5.4 eV. The introduction of two phenyl substituents into positions 4 and 5 (**3**) decreases $\Delta\varepsilon$ compared to unsubstituted imidazoline to 5.7 eV, but protonation in this case changes $\Delta\varepsilon$ insignificantly to 5.6 eV. In the presence of three phenyl substituents at positions 2, 4 and 5 (**4**) $\Delta\varepsilon$ decreases to 4.8 eV, and protonation reduces $\Delta\varepsilon$ to 4.7 eV. The summarized data are presented in Table 1 and Figure 1.

According to the $\Delta\varepsilon$ values, 2-phenylimidazoline **2** should be the most effective inhibitor. It should be noted that in the work[20] that studies the dependence of the inhibition efficiency on energy differences, the protonation factor is not taken into account. It is especially interesting to note the effect of alkyl substituents on the energy value. For the phenyl derivative **2**, protonation does not significantly affect the energy value, while alkyl substituents reduce the energy value by about 10%. These observations are in good agreement with the traditional view of increasing the HOMO energy by electron-donating substituents.[21,22] In the present example, this is particularly evident in the protonated forms: the positive inductive effect of the alkyl substituents on the phenyl groups stabilizes the positive charge on the imidazoline core. All data obtained suggest that the compounds under study may be effective in protecting steel, especially triphenyl derivative **4**. At the same time, their protonation in HCl solution should not lead to a loss of inhibitory properties of compounds **4–6**.

Table 1 Calculated $\Delta\varepsilon = (E_{\text{LUMO}} - E_{\text{HOMO}})$ for imidazoline derivatives **1–6** and their protonated forms. B3LYP, QM Basis 6-31g**, solvent model PBF (water).

Imidazoline	$\Delta\varepsilon$/eV	
	non-protonated	protonated
1	6.0	6.4
2	4.9	5.4
3	5.7	5.6
4	4.8	4.7
5	4.8	4.4
6	4.8	4.4

The molecular dynamics method makes it possible to estimate the geometry of binding (adsorption) of the molecules under study in an aqueous solution on a metal surface.[23–25] This method allows one to take into account the influence of the steric factor, which is especially important when moving from phenyl to isopropylphenyl. For the study, we simulated a cell (BIOVIA Materials Studio 2023) containing a six-layer iron surface (–1 0 0), an organic molecule surrounded by 200 water molecules, and a vacuum layer to prevent the water layer from interacting with the repeating metal surface on top.[26] Dynamics was performed in Forcite module of BIOVIA Materials Studio 2023 (NVT ensemble, 95 °C, Andersen thermostat, timestep 1 fs, time 100 ps, COMPASSIII forcefield). Based on the results, the following conclusions may be drawn: the phenyl derivative **2** can occupy a position in which the aromatic fragments in positions 2 and 4, as well as the imidazoline core, are parallel to the iron surface and protonation does not significantly change the binding geometry [Figure 2(*a*),(*b*)]. This fact is noteworthy in that the phenyl substituent in position 2 is responsible for the LUMO, and the substituent in position 4 is responsible for the HOMO [see Figure 1(*d*)]. This ensures the possibility of molecular charge donation (HOMO) and metal charge back-donation (LUMO) with the metal surface.[27] The binding geometry is slightly distorted when moving to the *p*-tolyl derivative **5**. The presence of an isopropyl group prevents the aromatic substituents in positions 4 or 5 from interacting with the metal surface. As a result, in all cases, the aromatic substituent in position 2 and the imidazoline ring are parallel to the metal surface, which indicates a good adsorption possibility. However, the introduction of bulky substituents reduces the probability of interaction of aryl fragments at position 4 or 5 and, as a consequence, the interaction of the HOMO of the inhibitor molecule with the iron surface.

The study of the corrosion inhibition ability of compounds **4–6** was performed in 2 M hydrochloric acid at different temperatures by gravimetric method. The corrosion rate was determined for 08PS low-carbon steel (composition, mass %: C, 0.08; Mn, 0.5; Si, 0.11; P, 0.035; S, 0.04; Cr, 0.1; Ni, 0.25; Cu, 0.25; As, 0.08). The corrosion rate was calculated from the mass loss of the metal samples:

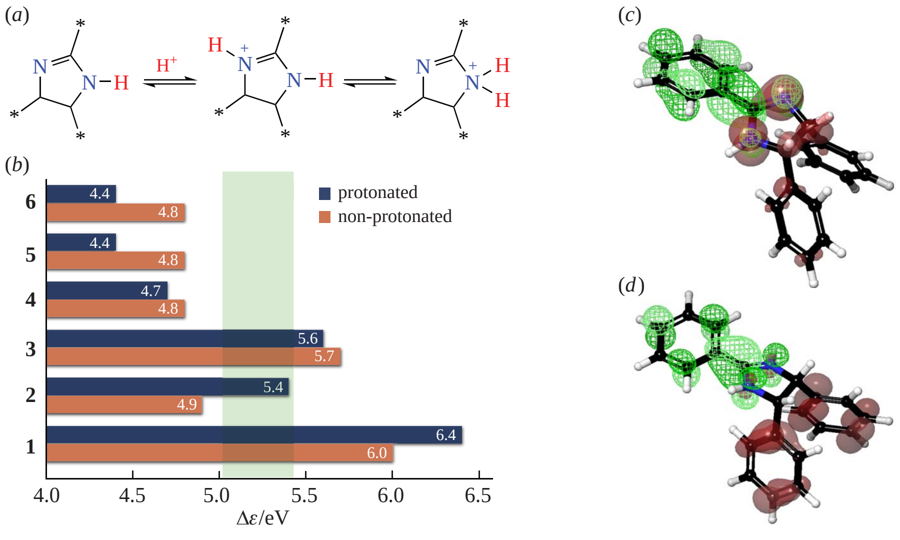


Figure 1 (*a*) Protonated forms of imidazoline derivatives. (*b*) Visualization of $\Delta\varepsilon$ gaps. Green region indicates ‘good’ values. Visualization of (*c*) HOMO (red, solid) and (*d*) LUMO (green, mesh) molecular orbitals for non-protonated and protonated form of **4**, respectively (isovalue: –0.05).

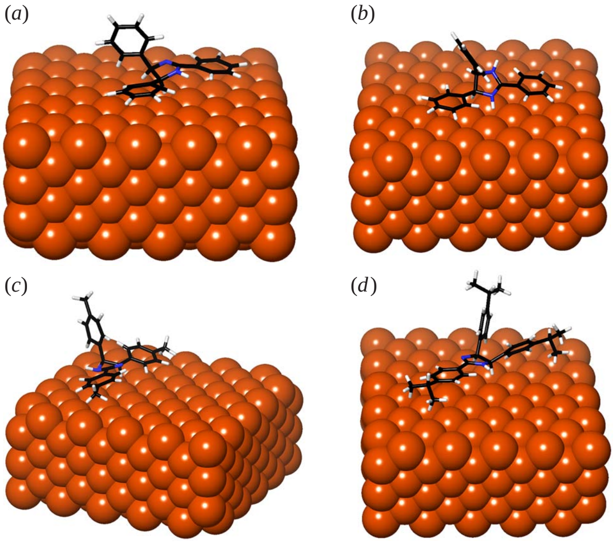


Figure 2 Conformations obtained by molecular dynamics. Water is omitted for clarity. The orange is iron surface. (*a*) Non-protonated form of compound **4**. (*b*) Protonated form of compound **4**. (*c*) Non-protonated form of compound **5**. (*d*) Non-protonated form of compound **6**.

$$k = (m_0 - m_\tau)S^{-1}\tau^{-1},$$

where m_0 is the mass of a metal sample before the corrosion test; m_τ is the same after the test; S is the area of the metal sample; and τ is the time of corrosion test (τ = 2 h). The efficiency of the CIs was evaluated from the corrosion inhibition factors $\gamma = k_0(k_\mathrm{in})^{-1}$ and degree of protection $Z = (k_0 - k_\mathrm{in})k_0^{-1} \times 100\%$, where k_0 is the corrosion rate in control solution and k_in is the same in a solution with an addition.

Corrosion studies showed that all synthesized compounds effectively slowed down the corrosion of steel in HCl solution at temperatures up to 60 °C. Under these conditions, in the presence of 5 mM compound **4** and 5 mM compound **5**, the corrosion rate does not exceed 1.4 g m^{-2} h^{-1}, and in the presence of 5 mM compound **6** – 2.4 g m^{-2} h^{-1}. Degree of protection at 60 °C for **4** and **5** is 98.7% and for **6** 97.7%. At temperatures higher than 60 °C the corrosion rate of steel increases significantly, which makes inhibitory protection with compounds **4–6** less effective, especially for **6** [Figure 3(*a*) and Table S1 of Online Supplementary Materials]. The data obtained correlate well with the results of the MD study; for example, the *p*-isopropylphenyl derivative **6** demonstrates worse anticorrosion activity and according to MD studies is worse adsorbed by metal surface.

The temperature range of use of CIs can be expanded by using them in the form of mixtures with other substances. To enhance the protective effect of the studied compounds at $T > 60$ °C, a cheap and accessible additive of urotropine was used.[28–30] Urotropine is a weak inhibitor of steel corrosion in hot 2 M HCl. For example, at T = 60–100 °C in the presence of 30 mM urotropine, the value of k = 7.8–200 g m^{-2} h^{-1} (γ = 7–14). The mixture of 5 mM triarylimidazoline **4–6** + 25 mM urotropine significantly reduces steel corrosion at T = 60–95 °C, which is an important practical result. The mechanism of inhibition with the addition of urotropine apparently changes, and the differences between imidazoline derivatives **4–6** become insignificant [Table S1 and Figure 5(*b*)]. Degrees of protection at 95 °C are above 99% for all imidazoline derivatives **4–6**.

To conclude, based on available raw materials, a simple synthesis of effective low-carbon steel corrosion inhibitors for hydrochloric acid solutions has been proposed. The synthesized triarylimidazolines reduce steel corrosion at 60 °C with degree of protection 98%. The introduction of bulky substituents reduces the inhibition efficiency and is in accordance with molecular dynamics data. The mixture of corrosion inhibitors containing synthesized triarylimidazolines **4–6** and urotropine can protect steel in hydrochloric acid solutions at temperatures up to 95 °C, providing the temperature range necessary for industrial operations.

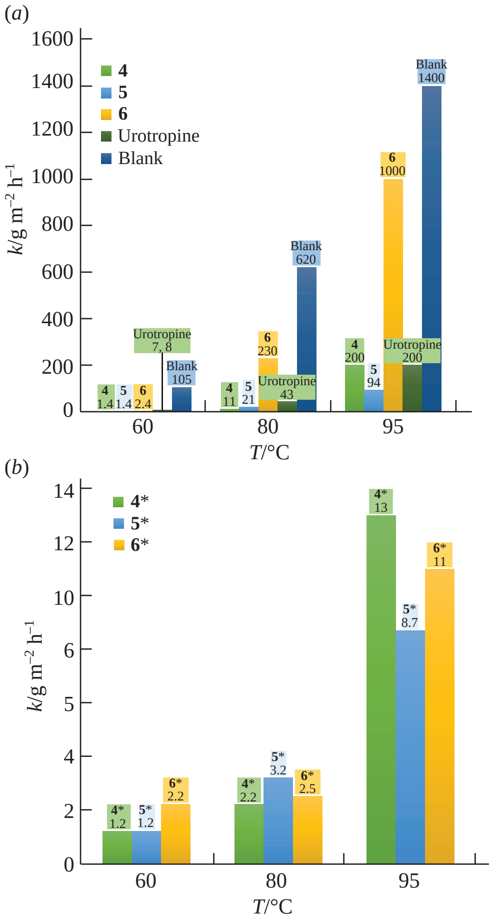


Figure 3 Corrosion rate dependence on temperature of imidazoline derivatives and urotropine. (*a*) Individual forms of compounds **4**, **5** and **6** (5 mM) and urotropine (30 mM) in 2 M hydrochloric acid at 60, 80 and 95 °C. (*b*) Mixtures of compounds **4–6** (5 mM) and urotropine (25 mM).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.09.041.

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