



## Recent Progress in Benzimidazole-Based Corrosion Inhibition

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### ABSTRACT

Abstract: Corrosion remains a persistent challenge across industrial sectors, leading to significant economic losses and operational inefficiencies. Among the various strategies employed to mitigate corrosion, the use of inhibitors has proven particularly effective due to their ability to suppress electrochemical reactions at the metal–solution interface. Benzimidazole and its derivatives have emerged as a versatile class of organic inhibitors, owing to their structural adaptability, electronic properties, and strong affinity for metallic substrates. This review provides a comprehensive account of recent progress in benzimidazole-based corrosion inhibition, highlighting their performance in diverse corrosive environments, particularly hydrochloric acid media. The discussion encompasses mechanistic insights derived from electrochemical techniques such as polarization and impedance spectroscopy, as well as quantum chemical analyses that correlate molecular geometry and electronic distribution with inhibition efficiency. Studies on mild steel, carbon steel, iron, and aluminum demonstrate that benzimidazole derivatives act predominantly through adsorption, forming protective layers that suppress both anodic and cathodic reactions. The influence of substituents, especially nitrogen- and sulfur-containing groups, is emphasized as a key factor in enhancing adsorption strength and inhibition efficiency. By integrating structural, mechanistic, and computational perspectives, this review underscores the potential of benzimidazole frameworks as promising candidates for industrial corrosion control and advances the understanding of their role in modern corrosion science.

## 1. Introduction

Corrosion remains a pervasive and critical issue across a broad spectrum of industrial applications and manufactured products. Despite notable advances in corrosion science and technology, the phenomenon continues to pose significant challenges to industries worldwide. The deterioration of materials through corrosion is recognized as one of the foremost industrial problems, resulting in considerable economic losses. These losses manifest in various forms, including product contamination, diminished operational efficiency, increased maintenance demands, unscheduled plant shutdowns, and the necessity for costly overdesign. To mitigate such adverse impacts, several strategies have been employed, including the development of improved materials, enhanced process control, chemical inhibition, and the blending of production fluids. Among these approaches, the use of corrosion inhibitors has proven particularly effective. These substances, which may be synthetic or naturally derived, are capable of significantly reducing the rate of metal degradation when introduced in small concentrations into corrosive environments. Their role in extending the service life of industrial systems underscores their importance as a cornerstone of modern corrosion management practices.

A wide variety of organic and inorganic compounds have been extensively investigated for their ability to protect metals in diverse corrosive environments. Organic molecules, in particular, have attracted considerable attention due to their structural versatility and effectiveness as corrosion inhibitors. Compounds containing multiple bonds, heteroatoms such as nitrogen, phosphorus, sulfur, or oxygen, and specific functional groups including  $-\text{NH}_2$ ,  $-\text{COOH}$ , and  $-\text{OH}$  have been consistently reported in the literature as highly effective in mitigating corrosion. Representative examples include amines, carboxylic acids, alcohols, phenols, and amino acids, all of which exhibit strong inhibitory properties by interacting with metallic surfaces and reducing the rate of degradation. Their ability to form protective films or complexes highlights the importance of organic compounds as a central class of corrosion inhibitors in modern industrial applications.

Benzimidazole is a bicyclic aromatic organic compound characterized by the fusion of a benzene ring with a five-membered imidazole ring at the 4- and 5-positions. Its systematic IUPAC designation is 1H-benzimidazole, although it is also referred to in the literature as 1,3-benzodiazole, benzoglyoxaline, iminazole, and imidazole. Chemically, benzimidazole functions as a weak base, with sufficient NH-acidity to render it soluble in aqueous alkali solutions. The compound exhibits two dissociation constants, with pKa values of 5.3 and 12.3 corresponding to pKa<sub>1</sub> and pKa<sub>2</sub>, respectively. In its pure form, benzimidazole appears as white tabular crystals and possesses a molecular weight of

118.14 g mol<sup>-1</sup>. The benzimidazole nucleus has emerged as a highly versatile scaffold, notable for its broad spectrum of biological activities. Its significance was first highlighted when Woolley identified the structural resemblance of 2-aminobenzimidazole to purine, and later reinforced by the discovery of 5,6 dimethylbenzimidazole as a degradation product of vitamin B<sub>12</sub>. These findings established benzimidazole as a pivotal heterocyclic framework with wide-ranging applications in medicinal chemistry and material science.

Recent studies have highlighted the effectiveness of benzimidazole and its derivatives as corrosion inhibitors, with their performance closely linked to factors such as spatial molecular configuration, surface charge distribution, electronic properties, and their affinity for metallic substrates. The relevance of corrosion inhibitors is particularly pronounced in the petroleum industry, which represents the largest consumer of these compounds due to the severe corrosive environments encountered in oil and gas operations. Benzimidazoles, by virtue of their structural framework, exhibit strong coordination capabilities with metals, thereby enabling them to suppress corrosion in steel and other alloys. Numerous investigations have proposed mechanistic pathways wherein benzimidazoles adsorb onto the metal surface, forming protective layers that hinder corrosive attack. This adsorption-driven inhibition underscores the importance of benzimidazole derivatives as promising candidates for industrial corrosion control.

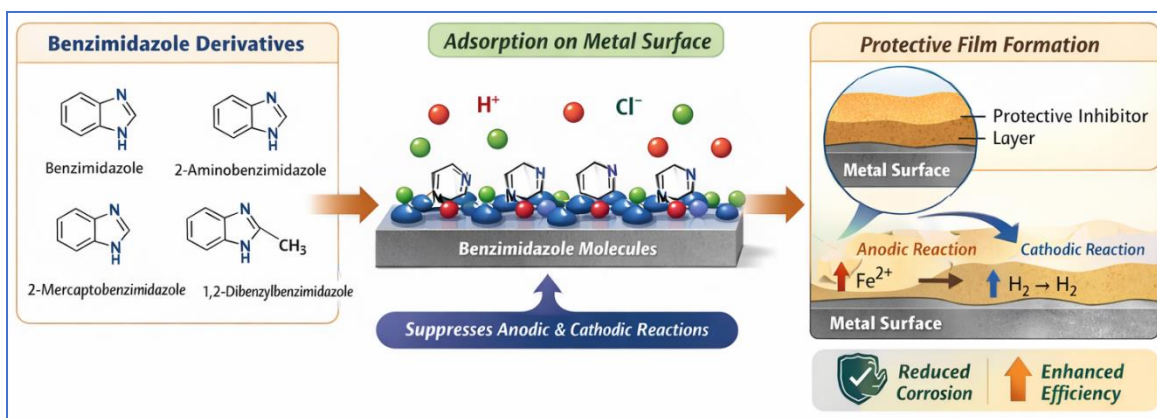


Figure 1. Representation of benzimidazole derivatives as corrosion inhibitors

In this review, we aim to provide a comprehensive account of benzimidazole derivatives that have been reported in the literature for their effectiveness as corrosion inhibitors for steels, metals, and alloys. Particular emphasis is placed on their methods of synthesis, alongside experimental investigations that have demonstrated their performance in corrosion testing. The discussion further encompasses the proposed inhibition mechanisms, the influence of acidic and basic media, and the quantum chemical parameters that have been correlated with their inhibitory properties. By integrating structural, mechanistic, and computational perspectives, this work seeks to highlight the multifaceted role of benzimidazole-based compounds in advancing corrosion science and technology.

### 1.1. Corrosion inhibitors in corrosive media

Corrosion inhibitors are chemical substances that, when introduced in small concentrations into a corrosive environment, are capable of reducing or preventing the rate of metal or alloy degradation. By interacting with the metallic surface or altering the corrosive medium, these compounds effectively suppress electrochemical reactions responsible for corrosion, thereby extending the service life of industrial materials and equipment.

Nitrogen-containing organic compounds such as amines, amides, nitriles, imines, and heterocyclic structures including triazoles, pyridines, and quinolines have long been recognized as effective corrosion inhibitors for steels, particularly during acidizing processes. Within this broad category, benzimidazoles have emerged over the past several decades as a distinct and valuable class of organic inhibitors. Functionally, benzimidazoles can be regarded as organic bases that undergo protonation in acidic environments, most prominently at the nitrogen atom located at the 3-position of the imidazole ring. The resulting cationic species exist in equilibrium with the neutral molecular form of benzimidazole, a balance that plays a critical role in their adsorption behaviour on metallic surfaces. This equilibrium, as illustrated in Figure 2, underpins the inhibitory mechanism by which benzimidazoles reduce corrosion rates, highlighting their relevance in both fundamental studies and industrial applications.

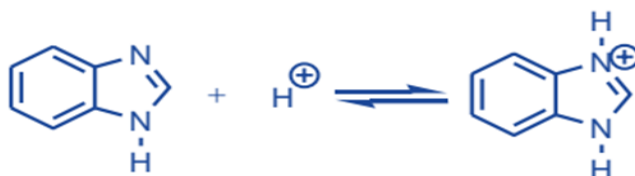


Figure 2. Ionization of benzimidazole in acidic medium

Benzimidazoles have been widely employed as corrosion inhibitors in various acidic environments, including hydrochloric acid (HCl), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and acetic acid (CH<sub>3</sub>COOH). Among these, hydrochloric acid is the most frequently utilized medium, typically in concentrations ranging from 0.1 M to 1 M. Table 1 provides a detailed overview of benzimidazole derivatives investigated as inhibitors, specifying the corrosive media employed, the metallic materials tested, inhibitor concentrations, experimental conditions, techniques applied, and the corresponding inhibition efficiencies ( $\eta$ ). The efficiency of inhibition (IE) is commonly determined using Equation (1), which quantitatively expresses the reduction in corrosion rate achieved by the presence of the inhibitor. where  $v_0$  and  $v$  are the corrosion rate in the absence and presence of inhibitor, respectively.

$$\eta\% = \frac{v_0 - v}{v_0} 100$$

### 1.2. Corrosion inhibitors for mild steel (ms)

Popova et al. reported that benzimidazole and its derivatives, including 2-aminobenzimidazole, 2-mercaptobenzimidazole, 1-benzylbenzimidazole, and 1,2-dibenzylbenzimidazole 1-4 (Figure 3), have demonstrated pronounced corrosion inhibition efficiencies across all tested temperatures for mild steel (MS) in deaerated 1 mol/L hydrochloric acid (HCl) solutions. these compounds exhibit strong adsorption behavior on the steel surface, forming protective layers that effectively suppress corrosive attack. Their performance under varying thermal conditions highlights the robustness of benzimidazole-based inhibitors and underscores their potential for practical application in acidizing and related industrial processes.

The inhibitory behaviour of benzimidazole derivatives can be attributed to their energetic interactions with the metallic surface and the blocking of active surface atoms. This process reduces the surface concentration of hydrogen ions and increases the overpotential for hydrogen evolution, thereby suppressing the overall corrosion rate. In particular, the effect of 2-mercaptobenzimidazole on the corrosion of mild steel (MS) in 1 M HCl solution has been extensively studied using polarization techniques and electrochemical impedance spectroscopy (EIS). Experimental results revealed that both anodic and cathodic current densities decreased progressively with increasing inhibitor concentration from 0.05 mM to 1 mM. This behavior indicates that 2-mercaptobenzimidazole effectively suppresses both anodic dissolution and cathodic hydrogen evolution through adsorption on the steel surface. Consequently, the compound can be classified as a mixed-type corrosion inhibitor, exerting its protective action by simultaneously influencing both anodic and cathodic processes.

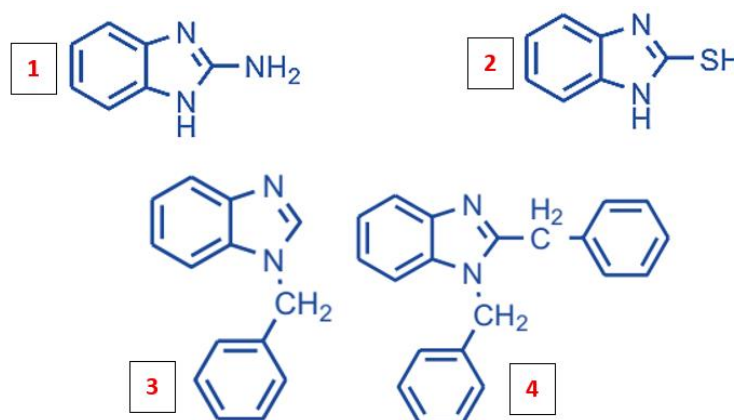


Figure 3. Chemical structures of the benzimidazoles 1-4.

Ramya et al. found that derivatives such as 2-methylbenzimidazole, 2-ethylbenzimidazole, and 2-propylbenzimidazole 5-7 (Figure 4), have been shown to be effective corrosion inhibitors for mild steel (MS) in 1 M hydrochloric acid (HCl) solutions. Their adsorption behaviour on the metallic surface does not conform strictly to either physisorption or chemisorption; rather, it represents a complex mixed-type mechanism. This conclusion is supported by the calculated values of the standard free energy of adsorption, which indicate contributions from both physical and

chemical interactions. Such dual adsorption characteristics enhance the stability of the protective layer formed on the steel surface, thereby improving inhibition efficiency across a range of experimental conditions.

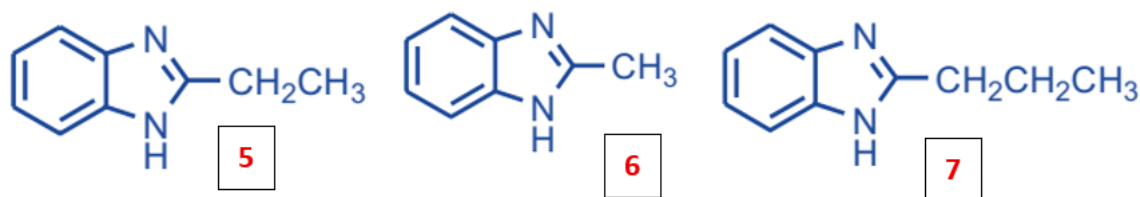


Figure 4. Chemical structures of the benzimidazoles 5-7.

Dutta et al. reveal that inhibition mechanism of benzimidazole derivatives has been elucidated through electrochemical impedance spectroscopy (EIS). Nyquist and Bode plots consistently reveal that these compounds adsorb physically onto the metallic surface, thereby blocking active sites and preventing electrochemical reactions at the metal–solution interface. Complementary quantum chemical studies, including optimized molecular geometries and frontier molecular orbital analyses, provide further insight into charge transfer processes during adsorption, reinforcing the mechanistic interpretation. Notably, the four bis-benzimidazole derivatives (Figure 5) exhibit significant inhibition efficiencies for mild steel in 1 M HCl, underscoring the role of structural modifications in enhancing adsorption and corrosion protection.



Figure 5. bis-benzimidazole derivatives

### 1.3. Corrosion inhibitors for carbon steel (cs)

Ochoa et al. studied the corrosion inhibition properties of compounds 8 and 9 for carbon steel (CS) in 0.5 M HCl medium have been investigated using both electrochemical and theoretical approaches. Corrosion rates were determined after 4.0 hours of exposure to the corrosive solution in the presence of varying concentrations of the inhibitors. The results demonstrated a continuous decrease in corrosion rate with increasing inhibitor concentration, while the corrosion potential remained largely unaffected. This behavior suggests that the inhibition mechanism is governed by adsorption of the inhibitor molecules onto the steel surface, thereby blocking active sites and suppressing both anodic dissolution and cathodic hydrogen evolution. Consequently, compounds 34 and 35 act as mixed-type inhibitors, providing effective protection through surface adsorption processes.

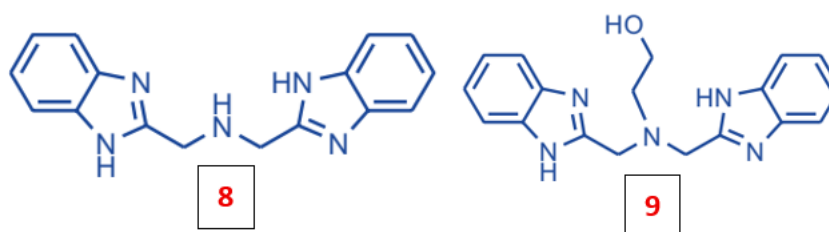


Figure 6. Chemical structures of the benzimidazoles 8, 9.

The compounds exhibited maximum inhibition at an inhibitor concentration of 0.15 mM. inhibitors adopt an upright orientation on the metal surface, which provides optimal protection, as illustrated in Figure 6. Adsorption occurs primarily through the sulfur atom and  $\pi$ - $\pi$  interactions between aromatic rings. Additionally, intermolecular hydrogen bonding via amide groups enhances the stability of the protective layer. Garcia Ochoa et al. observed increase in

inhibition with higher inhibitor concentrations suggests the possible formation of a secondary molecular bilayer, stabilized by hydrogen bonds and Van der Waals forces.

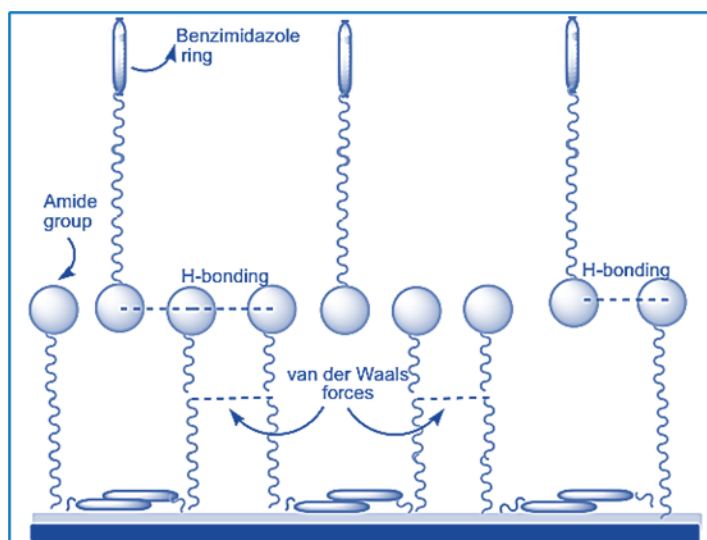


Figure 7. Schematic representation of the inhibitory effect by formation of the secondary molecular layer on the CS surface

#### 1.4. CORROSION INHIBITORS FOR OTHER METALS

- Benzimidazoles as corrosion inhibitors for iron

Khaled reported that several benzimidazole derivatives, including benzimidazole itself, 2-aminobenzimidazole 1, 2-hydroxybenzimidazole 10, 2-(2-pyridyl)benzimidazole 11, and 2-aminomethylbenzimidazole, exhibit significant corrosion inhibition for pure iron in 1 M HCl solution at 25 °C. These findings highlight the versatility of benzimidazole frameworks.

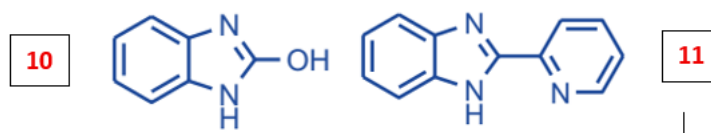


Figure 8. Chemical structures of the benzimidazoles 10, 11.

The nature of substituents on the benzimidazole ring plays a decisive role in determining inhibition efficiency. Substituents containing nitrogen atoms are particularly effective, with compound 10 exhibiting the highest efficiency. This enhanced performance is attributed to the electron-donating effect of the  $-NH_2$  group, which increases the availability of  $\pi$ -electrons within the benzimidazole ring. Such substituent effects highlight the importance of electronic contributions in modulating the inhibitory behaviour of benzimidazole derivatives.

- Benzimidazoles as corrosion inhibitors for aluminium and its alloys

Bereket and co workers investigated the inhibitory effects of 2 mercaptobenzimidazole (2), 5 methylbenzimidazole 2 thiol 12, and 5 chlorobenzimidazole 2 thiol 13, on the corrosion of aluminium in 0.1 M hydrochloric acid (HCl). Their study demonstrated that these sulfur containing benzimidazole derivatives exhibit significant protective action, attributed to their strong adsorption onto the aluminium surface. The presence of substituents such as methyl and chloro groups at the 5 position was found to influence the adsorption strength and inhibition efficiency, highlighting the role of structural modifications in tailoring benzimidazole derivatives for effective corrosion control in acidic environments.



Figure 9. Chemical structures of the benzimidazoles 10, 11.

As the concentrations of these organic compounds increased, the corrosion potentials shifted toward more negative values, while the corrosion current densities decreased. This trend confirms that the inhibitory action of the benzimidazole derivatives arises primarily from adsorption processes occurring at the cathodic sites of the metal surface. The authors concluded that the overall inhibition mechanism is governed by adsorption onto the metallic surface, a behaviour that correlates closely with the calculated total negative charge of each molecule. This parallelism underscores the importance of electronic structure in determining adsorption strength and inhibition efficiency.

## 2. Conclusion

Benzimidazole and its derivatives have demonstrated significant promise as corrosion inhibitors across a range of metallic substrates and acidic environments, particularly hydrochloric acid media. Their effectiveness is attributed to strong adsorption capabilities, structural adaptability, and favorable electronic properties that enable the formation of protective films on metal surfaces. Experimental studies supported by electrochemical techniques and quantum chemical analyses confirm that these compounds function predominantly through mixed-type inhibition mechanisms, suppressing both anodic and cathodic reactions. The influence of substituents—especially nitrogen and sulfur-containing groups—plays a critical role in modulating inhibition efficiency through enhanced electron donation and surface interaction. Overall, benzimidazole-based inhibitors offer a versatile and efficient approach to corrosion control, with potential for further optimization through molecular design and mechanistic refinement.

## Acknowledgement

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