Recent advances in the use of benzimidazoles as corrosion inhibitors

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Abstract

Background: Benzimidazole, a key heterocycle in therapeutic chemistry, and its derivatives, are recently mentioned in the literature as corrosion inhibitors for steels (CS, MS), pure metals (Fe, Al, Cu, Zn) and alloys. Benzimidazoles are good corrosion inhibitors for extremely aggressive, corrosive acidic media such as 1 M HCl, 1 M HNO₃, 1.5 M H₂SO₄, basic media, 0.1 M NaOH or salt solutions. Benzimidazole derivatives act as mixed type inhibitors, exhibiting stronger inhibitive effect on the cathodic reaction than on the anodic one.

Conclusion: These review highlights recent research in the field of benzimidazole compounds that their role as corrosion inhibitors, the structure of the compounds, electrochemical studies, the experimental conditions, the proposed mechanisms as well as the quantum theoretical studies that predict the structure of the compounds with inhibition properties.

Keywords: Corrosion science, Organic synthesis, Nanomaterials, Electrochemical impedance spectroscopy, Inhibition efficiency

Background

Corrosion is a serious problem, of great relevance in a wide range of industrial applications and products [1, 2]. Despite breakthrough in the field of corrosion science and technology, the unwanted corrosion process remains a major obstacle for industries all over the world. Corrosion of materials is one of the main problems in industry that is associated to significant economic losses, such as: loss or contamination of the product, reduction in efficiency, increase of maintenance needs, plant shutdowns and expensive overdesign [2]. Upgrading materials, process control, chemical inhibition and blending of production fluids are different ways for preventing corrosion damage. Corrosion inhibitors are synthetic or natural substances which, added in small amounts to a corrosive solution, decrease the rate of attack by the environment on metals [3, 4].

Several authors reported the effectiveness of organic inhibitors which generally protect the metal from corrosion by forming a film on the metal surface [4]. There are many classes of organic and inorganic compounds investigated for their properties of protection of metal in different corrosive media. Organic compounds with multiple bonds, compounds which contain heteroatoms (such as N, P, S, O) or those possessing certain functional groups such as –NH₂, –COOH or –OH (amines, acids, alcohols, phenols, aminoacids, etc.) are mentioned in literature to be effective corrosion inhibitors [3].

Although organic compounds preferred to be corrosion inhibitors are "green", such as amino acids, drugs, surfactants, biopolymers, or ionic liquids, there is a pronounced preference for heterocyclic organic compounds, especially those containing nitrogen, sulfur or oxygen, such as imidazoles, triazoles, thiazoles, benzimidazoles, benzotriazoles, purine or adenine [5].

Benzimidazole 1 (Fig. 1), a heterocyclic aromatic compound discovered by Hoebrecker, part of vitamin B₁₂, is one of the most prominent heterocycles, very known for...
the therapeutic properties of its compounds [6, 7], but very used in many others fields, like electronics, dyes, pigments, aeronautic industry, optical sensing, catalysts, electrolyte for fuel cells, fungicides, herbicides, etc. [8–11]. Recent literature reported benzimidazole and its derivatives as corrosion inhibitors (CIs) in relation to spatial molecular structure, surface charge density, the electronic parameters and their affinity for the metal surface [2, 12]. Also, the subject of CIs, becomes very important if we mention that the petroleum industry is the largest consumer of CIs. Benzimidazoles possess appropriate structures to coordinate metals; therefore they have ability to control the corrosion of steel or metals. Several papers propose various mechanisms of action in which benzimidazoles are adsorbed on the metal surface [2, 13].

In this paper we propose to present most of the benzimidazole derivatives which are mentioned in literature for their properties of corrosion inhibitors for steels, metals and alloys, their synthesis, as well as experimental results that have highlighted these materials used for corrosion tests, the proposed mechanisms, acidic or basic media used, and the quantum chemical parameters that are correlated with their properties.

**Synthesis of the benzimidazoles with corrosion inhibition properties**

Today, there are many classical benzimidazoles syntheses that have improved over the classic synthesis initially used by Hoebrecker. An extensive review of the synthesized benzimidazoles was carried out by Wright [14] and Preston [15]. Mainly, there are two methods used for synthesis of benzimidazoles: a. The reaction of 1,2-diaminobenzene (PDA) with carboxylic acids—Phillips–Ladenburg method in presence of 4 N HCl as catalyst; b. reaction of 1,2-diaminobenzenes with aldehydes or ketones—Weidenhagen method (Fig. 2). In the Phillips-Ladenburg reaction, also can be used: esters, acid anhydrides, acid chlorides and lactones instead of acids. Also, 2-nitroaniline in presence of a reductive agent can be used as substrate instead of PDA [14, 15].

Several syntheses mentioned in the literature for benzimidazoles with corrosion inhibitor properties will be given below.

**Synthesis of benzimidazoles by Phillips–Ladenburg method**

Dutta et al. synthesized five benzimidazoles 1a–e by refluxing PDA with aromatic carboxylic acids, for 3 h in presence of 2 M sulfuric acid as catalyst (Fig. 3) [16]. Yadav et al. synthesized three benzimidazole Mannich bases 3a–c in two steps: i. synthesis of 2-(1H-benzo[d]imidazol-2-yl)phenol 2 by refluxing PDA with salicylic acid for 3 h with 4 N HCl and ii. synthesis of Mannich bases by reaction between 2, formaldehyde and one secondary amine, morpholine, piperazine or piperidine under reflux in methanol for 180 min (Fig. 4) [17].

Yildirim et al. synthesized a series of 2-substituted benzimidazoles 5a–e in two steps: synthesis of 1H-Benzo[d]imidazol-2-yl)ethanol 4 by Phillips reaction; and final compounds by refluxing 4 with 11-Bromo-N-aryl decanamide in acetone along with potassium carbonate and a catalytic amount of sodium iodide under nitrogen atmosphere (Fig. 5) [18].

**Synthesis of benzimidazoles by Weidenhagen method**

Singh et al. reported synthesis of benzimidazoles 6a–c, starting from PDA and three aldehydes, in presence of boric acid as catalyst in water, at room temperature for 15–30 min (Fig. 6) [19].

**Synthesis of poli-benzimidazoles by Phillips–Ladenburg method**

Dutta et al. reported synthesis of four bis-benzimidazoles 8a–d by microwave irradiation method, at 180 W, starting by PDA and four dicarboxylic acids 7a–d in presence of methanesulfonic acid and alumina (Fig. 7) [20].

Ibrahim et al. synthesized tris(2-benzimidazolylmethyl)amine TBIA by microwave heating (500 W),
at 120 °C from PDA and 2,2',2''-nitrilotriacetic acid (Fig. 8) [21].

**Benzimidazoles as corrosion inhibitors in corrosive media**

The chemical substances which will prevent or decrease the corrosion rate of the metal or alloy, by adding them in small quantities, in the corrosive environment, are called corrosion inhibitors [1]. It is known that the nitrogen-containing organic compounds, like amines, amides, nitriles, imines, heterocycles (triazoles, pyridines, quinolines) have been noted as corrosion inhibitors for steels during the acidizing procedure [21]. Benzimidazoles also are one of the classes of organic compounds used as corrosion inhibitors in the last decades. Benzimidazoles used as inhibitors can be considered as organic bases which are protonated in an acidic medium, predominantly at the nitrogen atom at the 3-position in the imidazole ring [22]. The cations formed are in equilibrium with the benzimidazole molecular form as show in Fig. 9.

Literature mentions various techniques used to assess the corrosion inhibition efficiency and to characterize the protective film formed on the metal surface for benzimidazoles, such as, weight loss (WL); electrochemical measurements, like electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSW), polarization curve method or Tafel plot measurements; thermometric method; hydrogen evolution measurements; microscopy techniques, like scanning electron
Benzimidazoles as corrosion inhibitors for mild steel (MS)

For hydrochloric acid (HCl) medium

Popova et al. reported that benzimidazole, 2-aminobenzimidazole, 2-mercaptobenzimidazole, 1-benzylbenzimidazol and 1,2-dibenzylbenzimidazol 10–13 (Fig. 10) have pronounced corrosion inhibition properties at all temperatures for MS in deaerated 1 mol/L HCl solution [22] (Table 1). The inhibiting behaviour appears as consequence of energetic effect and blocking of the active surface atoms, leading to the decrease of the surface concentration of the hydrogen ions and the increase of hydrogen evolution overpotential. Mahdavian et al. studied the effect of 2-mercaptobenzimidazole 11 on the corrosion of MS in 1 M HCl solution by polarization and electrochemical impedance spectroscopy (EIS) [23]. Both anodic and cathodic current densities were decreased with increasing concentration from 0.05 mM to 1 mM, indicating that 11 suppressed both the anodic and cathodic reactions through adsorption on the MS surface, suggesting that 11 act as mixed type corrosion inhibitor. The results of SEM–EDX showed presence of sulfur on the MS surface confirming the adsorption of 11 on the MS surface as showed by the EIS measurements. Wang et al. shows that 1,8-bis(1-chlorobenzylbenzimidazolyl)octane 14 (Fig. 10) acted as an excellent inhibitor via strongly chemical adsorption onto MS surface to suppress simultaneously both anodic and cathodic processes according to the Langmuir adsorption isotherm [24]. They found that increasing concentration of inhibitor and HCl lead to increasing of inhibition efficiencies (IEs) and proposed an inhibition mechanism. Wang et al. found that 4-bis-benzimidazolyl-butane 15 inhibits both anodic and cathodic processes of mild steel in 0.5 M HCl solution and IE enhances with the increase of concentration of inhibitor. AFM images show the mean roughness of the.

The protective film formation of inhibitor 15 protects MS from corrosion. Thus, in experimental conditions, as consequence of the 0.5 M HCl solution attack, MS surface is 42.18 nm, in uninhibited solution, while the roughness of 12.69 nm is obtained in the presence of benzimidazole 15. The adsorption of 15 on MS surface obeys Langmuir adsorption isotherm. Dutta et al. applied electrochemical techniques and found that four benzimidazoles 16–19 act as mixed type inhibitors in 1 M HCl solution on mild steel [26]. From Temkin adsorption isotherm studies, it may be argued that inhibitors adsorb spontaneously on the MS surface. It was proposed that inhibitors are adsorbed parallel to the metal surface through the benzimidazole moiety, considering electron density in the HOMO level mostly distributed over this planar moiety. Zhang et al. found that 2-(4-pyridyl)benzimidazole 20 acts as a mixed-type inhibitor with predominant cathodic effectiveness, being a good inhibitor for MS corrosion in 1.0 M HCl [27]. Presence of compound 20 inhibits the reduction of $\text{H}^+$ ions, by immobilization of the reactive centers from the MS surface, without changing the process mechanism, as can be seen by the Tafel lines. Inhibition efficiency (IE) depends on the temperature and the concentration of the acid solution, and also increases with increasing inhibitor concentration. Tang et al. reported the inhibition properties for the corrosion of MS in 1 M HCl of 2-aminomethylbenzimidazole 21, bis(2-benzimidazolylmethyl) amine 22 and tris(2-benzimidazolyl methyl) amine 9 [28]. The IEs of the three compounds decreasing the order: $9 > 22 > 21$, for the same concentration, showing that the IE increases with the increase in the number of benzimidazole scaffold in the molecules. From the potentiodynamic polarization (PP) curves (Fig. 11), all these inhibitors exhibit stronger inhibitive effect on the cathodic reaction than on the anodic one, indicating that the compounds act as mixed type inhibitors for reaction of mild steel in 1.0 M HCl. SEM images (Fig. 12) confirm the effectiveness of these inhibitors as the surface of MS in the uninhibited solution is seriously damaged in comparison with that before immersion. In the presence of the inhibitors, the damage of the steel surfaces is significantly reduced.

Ramya et al. found that 2-methylbenzimidazole 23, 2-ethylbenzimidazole 24 and 2-propyl-benzimidazole 25
Table 1 The inhibition efficiencies, η, of different benzimidazoles\textsuperscript{a} as corrosion inhibitors on the different materials in various solutions

| Inhibitor (I) | Medium | Material | $I_{\text{conc}}$ (mmol/L) | Techniques | η (%) | Refs. |
|---------------|--------|----------|-----------------------------|------------|-------|-------|
| Benzimidazole 1 | Deaerated 1 mol/L HCl | MS | 20 | EIS; TE at T = 20–60 °C | 29.5–60% | [22] |
| 2-Aminobenzimidazole 10 | | | 20 | | 84.0–86.8% | |
| 2-Mercapto benzimidazole 11 | | | 1 | | 93.9–97.0% | |
| 1-Benzyl benzimidazole 12 | | | 5 | | 97.2–97.8% | |
| 1,2-Dibenzyl benzimidazole 13 | | | 1 | | 97.4–98.2% | |
| 2-Mercapto benzimidazole 11 | 1 M HCl | MS | 50–1000 | TE at 30 °C; SEM–EDX; EIS | 82.6–96.5 | [23] |
| 1,8-Bis(1-chlorobenzyl benzimidazolyl)-octane 14 | | | 0.0017–0.13 | TE at 30 °C, WL; EIS, SEM | 54.3–97.6% | [24] |
| 1,4-Bis-benzimidazolyl-butane 15 | | | 0.017–0.68 | EIS, TE at 30 °C, Al; WL; AFM | 64.2–98.1% | [25] |
| N-(2-(1H-benzo[d]imidazol-2-yl)ethyl) benzamide 16 | 1 M HCl | MS | 0.1–1 | EIS, TE at 25 °C, Al; DFT | 72–97% | [26] |
| N-(2-(1H-benzo[d]imidazol-2-yl)ethyl)benzenesulfonamide 17 | | | | | 67–96% | |
| N-((1H-benzo[d]imidazol-2-yl)methyl)benzamide 18 | | | | | 56–95% | |
| N-((1H-benzo[d]imidazol-2-yl)methyl)benzenesulfonamide 19 | | | | | 40–93% | |
| 2-(4-Pyridil) benzimidazole 20 | 1 M HCl | MS | 0.1–2 | EIS, WL at 25, 35 and 45 °C; Al, MD, DFT | 72.4–94.05% | [27] |
| 2-Aminomethyl benzimidazole 21 | 1 M HCl | MS | 0.5–0.1 | TE at 25 °C, WL; Al, SEM; XPS | 77.4–84.0% | [28] |
| Bis(2-Benzimidazolylmethyl) amine 22 | | | | | 88.1–88.8% | |
| Tri(2-Benzimidazolylmethyl) amine 9 | | | | | 91.4–93.4% | |
| 2-Methyl benzimidazole 23 | 1 M HCl | MS | 0.05–0.2 | WL and El at 30, 35 and 45 °C | 88.3–91.01% | [29] |
| 2-Ethyl benzimidazole 24 | | | | | 88.3–91.3% | |
| 2-Propyl benzimidazole 25 | | | | | 88.3–91.4% | |
| 2-(2-Pyridyl) benzimidazole 26 | | | | | 91.33–97.18% | [30] |
| 2-Chlorobenzimidazole 27 | 1 M HCl | MS | 0.5–5 | TE at 30 °C, WL, EIS, Al | 88.55–95.43% | |
| 2-Bromobenzimidazole 28 | | | | | 87.16–93.78% | |
| 6-(Dodecyloxy)-1H-benzo[d] imidazole 29 | | | 0.1–0.001 | WL at 25 ± 1 °C, DFT | 74.2–95.0% | [31] |
| 2-(4-Nitrophenyl) benzimidazole 1a | 1 M HCl | MS | 0.1–1 | TE at 25 °C, WL at 30 °C; EIS; SEM; DFT; MD | 90.3–95.9% | [16] |
| 2-(4-aminophenyl) benzimidazole 1b | | | | | 86.1–93.9% | |
| 2-(4-nitrophenoxy) benzimidazole 1c | | | | | 82.8–90.9 | |
| 2-(2-aminophenyl) benzimidazole 1d | | | | | 79.1–89.3% | |
| Bis-benzimidazole 8a | 1 M HCl | MS | 0.1–1 | TE at 25 °C, WL at 25 °C, MD | 84.0–97.0% | [20] |
| Bis-benzimidazole 8b | | | | | 73.0–94.5 | |
| Bis-benzimidazole 8c | | | | | 62.0–94.0 | |
| Bis-benzimidazole 8d | | | | | 62.0–94.0 | [20] |
| 1-Butyl-3-methyl-1H-benzimidazolium iodide 30 | 0.5 M H_2SO_4 | MS | 0.25–5 | TE at 25 °C, WL, EIS, Al, SEM; AFM, DFT | 90.6–98.7% | [32] |
| Inhibitor (I)          | Medium          | Material | \( I_{\text{corr}} \) (mmol/L) | Techniques | \( \eta \) (%) | Refs. |
|-----------------------|-----------------|----------|-------------------------------|------------|----------------|-------|
| Benzimidazole 1       | 1 M HCl         | CS       | 0.05–0.25                     | TE at 25 °C; AI | 35.5–52.0%    | [33]  |
| 2-Methylbenzimidazole 23 |                |          |                               |            |                |       |
| 2-Mercaptobenzimidazole 11 | 0.5 M H₂SO₄ |          |                               |            |                |       |
| Benzimidazole 1       | 0.5 M H₂SO₄+ 0.02 mM NaBr |          |                               |            |                |       |
| 2-Methylbenzimidazole 23 |                |          |                               |            |                |       |
| 2-Mercaptobenzimidazole 11 |              |          |                               |            |                |       |
| 1-H-Benzimidazol-5-amine 21 |        |          |                               |            |                |       |
| 1-H-Benzimidazol-5-yl-methanol 33 |              |          |                               |            |                |       |
| N,N'-bis(benzimidazole-2-yl-methyl) hydroxyethyamine 34 |              |          |                               |            |                |       |
| N,N'-bis(benzimidazole-2-yl-methyl) hydroxyethyamine 35 |              |          |                               |            |                |       |
| 2-(2-Pyridyl)benzimidazole 26 | NACE brine ID196 | API X60 steel | 2.56, 7.68 | TE at 30 °C FTIR; EIS | 46.0–67.3 | [40]  |
| 3-(4-Methoxyphenyl)-1H-Benzo[d]Imidazole 6a | 3.5 wt % NaCl+CO₂ | J55 steel | 0.176–1.407 | TE at 25 °C; WL at 60 °C; EIS; XPS | 56.8–94.7% | [19]  |
| 2-(3,4,5-Trimethoxyphenyl)-1H-Benzo[d]Imidazole 6c | 32% NaCl | AIS 316 | 0.025–1 | TE at 24 °C | 40.42–71.44% | [39]  |
| 2-(2-Pyridyl)benzimidazole 26 | NACE brine ID196 | API X60 steel | 2.56, 7.68 | TE at 30 °C FTIR; EIS | 46.0–67.3 | [40]  |
| 2-Aminobenzimidazole 10 | 1 M HCl         | Pure Fe  | 1–50                          | TE at 25 °C; EIS, AI | 47.58–51.07% | [41]  |
| 2-Hydroxybenzimidazole 40 |              |          |                               |            |                |       |
| 2-(2-Pyridyl)benzimidazole 26 | 0.1 M HCl | Pure Fe | 1–100                         | TE at 20-60 °C, AI | 60.1–80.9% | [42]  |
| 2-Mercaptobenzimidazole 11 | 0.1 M HCl | Al      | 0.01–1                        |            |                | [41]  |
| 5-Methylbenzimidazole-2-thiol 41 |              |          |                               |            |                |       |
| 5-Chlorobenzimidazole-2-thiol 42 |              |          |                               |            |                |       |
Table 1 (continued)

| Inhibitor (I) | Medium | Material | \( I_{\text{conc}} \) (mmol/L) | Techniques | \( \eta \) (%) |
|--------------|--------|----------|-------------------------------|------------|--------------|
| Benzimidazole 1 | 10% AcOH | Al-SiCp | 0.05–0.2 | TE at 30–50 °C | 13.29–58.56% |
| | 20% AcOH | | | | 17.05–64.58 |
| | 30% AcOH | | | | 10.29–58.90 |
| 2-Mercaptobenzimidazole 11 | Aerated 0.5 M HCl | Cu | 0.5 | TE at 40 °C, WL at 40 °C; EIS | 91.6% |
| 2-Mercaptobenzimidazole 11 | 1 M HNO3 | Cu | 0.005–1 | WL at 25, 35, and 45 °C | 27.5–91.5% |
| 2-(methylthio)benzimidazole 43 | 0.4 M NaCl + 0.1 M NaOH | Cu, brass | 1 | TE at 25 °C, EIS | 91.0, 97.4 |
| 2-Mercaptobenzimidazole 11 | 0.1 M HCl | Zn | 0.063–0.5 | TE at 30 °C; WL; Al; SEM | 68.5–89.7% |
| 2-Hydroxybenzimidazole 40 | 0.063–0.5 | | | | 75.2–93.0% |
| 2-Hydroxy-5-nitro-benzimidazole 46 | 0.05–0.2 | | | | 55.6–82.5% |

**Table 1** Techniques: TE Tafel extrapolation, WL weight loss, EIS electrochemical impedance spectroscopy, MS mild steel, CS carbon steel, SS stainless steel, \( \eta \) inhibition effectiveness, EIS electrochemical impedance spectroscopy, CR corrosion rate, AI adsorption isotherm, SEM scanning electron microscopy, AFM atomic force microscopy, FTIR Fourier transform infrared, OP optical profilometry, XPS X-ray Photoelectron Spectroscopy (XPS), MD molecular dynamics simulation, EDX energy-dispersive X-ray spectroscopy, DFT Density Functional Theory.

* The structures of the benzimidazoles are found in Figs. 2, 3, 4, 5, 6, 7, 8, 9, 10, 11.

(Fig. 10) are effective CIIs for the corrosion of MS in 1 M HCl [29]. The adsorption of inhibitors is neither typical physisorption, nor chemisorption but it is complex mixed type, as resulted from the values of standard free energy of adsorption \( \Delta G^0_{\text{ads}} \). Lgaz et al. reported the inhibition effects on MS in 1 M HCl of 2-(2-pyridyl)benzimidazole 26, 2-chlorobenzimidazole 27 and 2-bromobenzimidazole 28 [30]. These compounds have good IE, which increases with the inhibitor concentration and follows the order: 26 > 28 > 27. Langmuir adsorption isotherm suggest that these derivatives are strongly adsorbed on the mild steel surface and PP study shows that the studied compounds are mixed type inhibitors. Zhang et al. reported that 6-(dodecylxoxy)-1H-benzo[d]imidazole 29 (Fig. 13) exhibits effective inhibition for corrosion of MS in 1 M HCl medium [31]. Table 2 depicts the corrosion rate of MS and inhibition efficiency from weight loss measurements in the absence and presence of benzimidazole 29. It is obviously that the corrosion rate of MS decreases significantly and the inhibition efficiency increases with increasing inhibitor concentration.

Following the theoretical study performed on compound 29 (Fig. 14), it was determined that its structural “key” is the non-polar long chain, which blocks the action of the erosive solution, and is absorbed on MS by electron donation to the vacant d-orbital. Therefore, the non-protonated benzimidazole 29 (DBI), less polar, is a much more effective inhibitor against erosive species on the iron surface, compared to its protonated species (DBIH), surrounded by a thick layer of water. Dutta et al. studied the inhibition properties of five benzimidazoles 1a–e (Fig. 3) towards MS in 1 M HCl [16]. A strong decrease in corrosion rate is determined by the inhibitors 1a–e in acidic solution, as can be seen in polarization curves. Studies show that para-substituted derivatives are more potent anticorrosive agents than ortho-substituted compounds, and nitro-derivatives are better inhibitors than amine homologues. The mechanism of action of the benzimidazoles as inhibitors was determined by electrochemical impedance spectroscopy (EIS). Nyquist and Bode impedance plots indicate the physical adsorption of benzimidazoles on the metal surface, which prevents reactions at the metal-solution interface. Also, optimized molecular geometry and electron distribution in the frontier molecular orbitals provided valuable information on charge transfer during adsorption. Dutta et al. reveal that four bis-benzimidazoles derivatives 8a–d (Fig. 7) possess good inhibition efficiency for mild steel in 1 M HCl [20]. The inhibition efficiencies of the benzimidazoles towards prevention of corrosion of mild steel in 1 M HCl follow the order 8a > 8b > 8c > 8d, and, more important, their effectiveness is maintained for an exposure time of as long as 96 h. EIS study indicates that the extent of adsorption increases with concentration of the inhibitors and thus provides better barrier towards
charge transfer reactions at the metal–solution interface. Quantum mechanical studies show a series of factors, like stereochemistry of the molecule, presence of heteroatoms, π electron density and charge on individual atom important for corrosion inhibitors.

For sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) medium
Zheng et al. revealed that 30 is a good inhibitor for mild steel in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution and IE increases with the increasing concentration of 30 (Fig. 13) [32]. Addition of inhibitor 30, at different concentrations, at a temperature of 298 K, to a solution of 0.5 M H\textsubscript{2}SO\textsubscript{4}, led to a relatively small inhibition of the corrosion effect on MS, which is shown in the Nyquist (a) and Bode (b) plots (Fig. 15). The only exception to visible improvement of corrosion inhibition is visualized on the diameter of high frequencies capacitive loop which markedly increases with enhancing inhibitor concentration. In this case, the gradual disappearance of the low-frequency loop is observed, that is, a “degradation” phenomenon of impedance spectroscopy. A strong interaction between inhibitor 30 and the MS surface in 0.5 M H\textsubscript{2}SO\textsubscript{4} is revealed by the positive values of $\Delta G_{\text{ads}}^0$, negative values of $\Delta G_{\text{ads}}^0$ and high values of adsorption constants $K_{\text{ads}}$, as seen in Table 3.

Compound 30 proved to be a mixed type corrosion inhibitor because polarization measurements inhibit both the anodic and cathodic processes of the corrosion of MS in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution. DFT data show that cation 30 is adsorbed on the MS surface by benzimidazole ring using a flat mode.
**Fig. 11**  Bode plots for mild steel in 1.0 M HCl without and with different concentrations of inhibitors at 25 °C for compounds: a 21, b 22, and c 9  
(Reproduced with permission from Elsevier, Ref. [28])

**Fig. 12**  SEM images for mild steel surface: a before immersion, b blank, c 21, d 22, and e 9  
(Reproduced with permission from Elsevier, Ref. [28])
Benzimidazoles as corrosion inhibitors for carbon steel (CS)

Aljourani et al. studied the inhibition characteristics of benzimidazole 1, 2-methylbenzimidazole 23 and 2-mercaptobenzimidazole 11 for CS in HCl solution.

**Table 2** Corrosion rate and inhibition efficiency in the absence and presence of 6-(dodecyloxy)-1H-benzo[d]imidazole 29 as inhibitor in 1 M HCl solution.

| C(M)  | ν (gm⁻² h⁻¹) | η(%) | θ   |
|-------|--------------|------|-----|
| 0     | 4.8±0.02     | –    | –   |
| 10⁻⁶  | 1.24±0.16    | 74.2 | 0.742|
| 2 10⁻⁶| 1.06±0.23    | 77.9 | 0.779|
| 4 10⁻⁶| 0.81±0.04    | 83.1 | 0.831|
| 8 10⁻⁶| 0.39±0.03    | 91.9 | 0.919|
| 10⁻⁵ | 0.35±0.01    | 92.7 | 0.927|
| 10⁻⁴ | 0.24±0.01    | 95.0 | 0.950|

**Fig. 13** Chemical structures of the benzimidazoles 29–47

**Fig. 14** Equilibrium configurations of 29 (DBI) and its protonated form (DBIH) in aqueous solution. Top: topview, bottom: sideview (Reproduced with permission from Elsevier, Ref. [31])
and H$_2$SO$_4$ solutions using PP measurements [33]. The straight line of Langmuir absorption isotherms (Fig. 16) shows that the inhibition of CS in acid solutions by benzimidazoles is an adsorptive process. This isotherm assumes that the adsorbed molecules occupy only one site and there are no interactions between the adsorbed species [33]. Also, synergistic effects of bromine ion on the sulfuric acid and the comparing with the behaviour in hydrochloric acid and sulfuric acid elucidated the dominant active form of the inhibitors (molecular or ionic) during the adsorption process. It was found that the order of IE is $11 > 23 > 1$ in all solutions. The corrosion inhibition of 1 and 23 in both acidic media is due to the physisorption (adsorption of cationic forms), while corrosion inhibitions of 11 is due to the chemisorption of the molecular form. Gutierrez et al. studied five benzimidazoles as potential corrosion inhibitors of CS in 1 M HCl, 2-chlorobenzimidazole 27, 6-bromo-1H-benzimidazole 31, 1H-benzimidazole-5-amine 32, 2-amino-methyl benzimidazole 21 and 1H-Benzimidazol-5-yl-methanol 33 [2]. From the Nyquist plots, it is clear that the presence of the substituents in the structure of the molecule has an effect on the inhibition properties (Fig. 17). The authors concluded that differences in inhibition properties were certainly a consequence of presence of substituents and their position have a significant effect on the protection on steel. According to the mathematical model proposed the properties as electronegativity, aromaticity, volume and the charge of nitrogen atoms are associated with the corrosion inhibition efficiency. Yildirim et al. investigated the inhibition properties of five long-chain benzimidazoles 5a–5e for CS in H$_2$SO$_4$ (Fig. 5). The 3D optical profilometer images of the metal to acidic medium without inhibitor show corrosion damages on the metal surface, while the treatment of the metal with inhibitor prevents the corrosion of the surface [18]. The compounds exhibited the highest inhibition at 0.15 mM inhibitor concentration. Authors proposed an upright position of the inhibitor in the metal surface which provides maximum protection as is shown in Fig. 18. The inhibitor is absorbed on the metal surface through the sulfur atom and π–π interactions between aromatic rings. Intermolecular hydrogen bonds formed via amide groups, increase the protective layer. Increasing the inhibitory effect due to increased in inhibitor concentrations may indicate that secondary molecular bi-layer may occur via hydrogen bonds and Van der Waals forces. Garcia-Ochoa et al. studied the corrosion inhibition properties of 34 and 35 (Fig. 18) on CS in 0.5 M HCl medium by electrochemical and theoretical methods. Here, the corrosion rates (Table 4) were measured after the metal surface exposure to corrosive medium for 4.0 h in the presence of compounds 34 and 35 at different concentrations. It is observed that, as the concentration of inhibitors increases, the corrosion rate decreases continuously, while the corrosion potential does not suffer significantly. This indicates that the corrosion inhibition mechanism on the metal surface...
is an adsorption process that prevents both anodic and cathodic reactions. The data show that ligands form an adsorption layer over an iron surface, obeying the Langmuir isotherm ($\Delta G_{ads}^{\text{f}}$ of $-32.96$ kJ mol$^{-1}$); the value is in the range $-20$ to $-40$ kJ mol$^{-1}$, belonging to a conversion stage of physical adsorption to chemical adsorption or a comprehensive adsorption [34]. The efficiency of inhibitors increases with increasing their concentration in the corrosion medium.

El-Hajjaji et al. observed that both cathodic and anodic current densities decrease in presence of $36$ [35], in the acidic solution, which indicate the adsorption of the inhibitor molecules onto the active sites of the CS surface [36], and suggests the inhibitor influence in the anodic metal dissolution reaction, as well as on the cathodic reaction of hydrogen evolution [37]. The successive increase in the inhibitor concentration resulted in a more pronounced inhibition behavior. The inhibitory behavior was attributed to the nitrogen atoms of the imidazole ring and the sulphur atom present in the alkyl chain of the inhibitor molecule.
Benzimidazoles as corrosion inhibitors for other steels

Benzimidazoles as corrosion inhibitors for acidic media

1-(2-Pyridinyl)-2-(o-, m-, p-hydroxyphenyl) benzimidazoles 37–39 were studied as corrosion inhibitors in API 5L X52 steel/HCl 1 M corrosion system by Rodriguez-Clemente et al. [38]. It is proved that the inhibitory action depends on the concentration of the compound, double-layer capacitance and resistance to charge transfer. The protective, stable and uniform efficiency of the inhibitor was experimentally proved by SEM micrograph, in the presence of the inhibitor at an optimum concentration. Yadav et al. synthesized and assessed for the corrosion inhibition potentials on N80 steel in 15% HCl solution compounds 3a–c (Fig. 4). Basic information on the interaction between the organic inhibitors and the N80 steel surface were obtained from various adsorption isotherms. Large values of $K_{\text{ads}}$ obtained for all the three inhibitors indicate more efficient adsorption and hence better corrosion inhibition efficiency. All compounds show good inhibition efficiencies and the IE increases on increasing concentration of the inhibitors and decreases with increasing temperature. IE decreases in the order: 3c > 3a > 3b [17]. SEM and AFM images confirmed the adsorption of the inhibitors on the steel surface while FTIR and UV–VIS spectra established the interactions between the inhibitors and N80 steel.

Benzimidazoles as corrosion inhibitors for salt media

Moreira et al. reported that benzimidazole 1 possess best corrosion inhibition result for AISI 316 steel and AISI 1010 steel in 3% aqueous solution NaCl using inhibitor concentration of 0.1 mM, and the IE values were ~71% and ~51%, respectively [39]. Electrochemical studies have shown that in the presence of an inhibitor at concentration of 0.025 ÷ 1 mM, there was an increase of the polarisation resistance of both steels, indicating that there was an increase in corrosion resistance. Onyechu et al. assessed the performance of 2-(2-pyridyl)benzimidazole 26 (Fig. 10) as inhibitor for the CO$_2$ corrosion of X60 steel in NACE brine ID196 (contained 3.5 wt % NaCl, 0.305 wt% CaCl$_2$·2H$_2$O and 0.186 wt% MgCl$_2$·6H$_2$O prepared with double distilled water) with electrochemical methods [40]. The extended Nyquist semicircle plots (Fig. 19) shows the molecules of the compound 26 adsorbed on the steel surface lead to a barrier that isolates against the brine solution. Under static and hydrodynamic conditions, inhibitor 26 behaves very well during CO$_2$ corrosion, but not so well at high rotation speed, when the inhibition efficiency is decreased. The best adsorption of the inhibitor 26 is realized by the formation of the pyridinium ion after the protonation of 2-pyridyl nitrogen. The proposed mechanism for this interaction is shown in Fig. 20. Singh et al. reported that benzimidazoles 6a–6c (Fig. 6) are good inhibitors in 3.5% NaCl solution saturated with carbon dioxide at 60 °C for J55 steel [19]. The potentiodynamic polarization measurement supports the mixed mode of inhibitors with predominantly cathodic effects. Both experimental and theoretical investigations suggest that increasing the number of methoxy groups improve corrosion protection ability of the inhibitors, therefore, 6c with three methoxy groups is the best inhibitor. The DFT study confirms that the imine nitrogen is the most preferred site for protonation.

### Table 4 Electrochemical polarization data of the inhibitors. Reproduced with permission from Elsevier, Ref. [34]

| Conc (mM) | $\beta_a$ (mV dec$^{-1}$) | $\beta_c$ (mV dec$^{-1}$) | $E_{\text{corr}}$ (V) | $I_{\text{corr}}$ (A/cm$^2$) | $\theta$ | %E |
|-----------|-----------------|-----------------|-----------------|-----------------|--------|-----|
| **Compound 34** |                   |                   |                 |                 |        |     |
| 0.0       | 194             | 133             | −0.5340         | $5.89 \times 10^{-4}$ | –      | –   |
| 0.01      | 211             | 135             | −0.5284         | $5.194 \times 10^{-4}$ | 0.1183 | 11.83 |
| 0.03      | 241             | 133             | −0.5470         | $3.977 \times 10^{-4}$ | 0.3249 | 32.49 |
| 0.07      | 229             | 115             | −0.5472         | $3.577 \times 10^{-4}$ | 0.3928 | 39.28 |
| 0.2       | 176             | 91              | −0.5433         | $2.399 \times 10^{-4}$ | 0.5927 | 59.27 |
| **Compound 35** |                   |                   |                 |                 |        |     |
| 0.0       | 194             | 133             | −0.5340         | $5.89 \times 10^{-4}$ | –      | –   |
| 0.01      | 151             | 117             | −0.5184         | $3.46 \times 10^{-4}$ | 0.4126 | 41.26 |
| 0.03      | 153             | 112             | −0.5309         | $3.29 \times 10^{-4}$ | 0.4415 | 44.15 |
| 0.07      | 171             | 119             | −0.5332         | $2.881 \times 10^{-4}$ | 0.5109 | 51.09 |
| 0.2       | 166             | 95              | −0.5296         | $1.813 \times 10^{-4}$ | 0.6922 | 69.22 |
Benzimidazoles as corrosion inhibitors for other metals

**Benzimidazoles as corrosion inhibitors for iron**

Khaled found that benzimidazole 1, 2-aminobenzimidazole 10, 2-hydroxybenzimidazole 40, 2-(2-pyridil) benzimidazole 26 and 2-aminomethylbenzimidazole 21 (Figs. 10, 13) inhibit the corrosion of pure iron in 1 M HCl solutions at 25 °C. He found that the IE increases with increasing electron donating ability of these molecules according to the order, 10 > 26 > 21 > 40 > 1 [41]. Results obtained from potentiodynamic polarization indicated that the benzimidazole inhibitors are mixed-type inhibitors. This order can be explained by the nature of substituents on benzimidazole ring, namely, the most effective are those containing nitrogen, and among them, 10 most efficiently because the electron donating effect of the –NH2 group which contributes to increasing the availability of the electrons π in benzimidazole ring and attachment on the iron surface by the free amino group.

**Benzimidazoles as corrosion inhibitors for aluminum and its alloys**

Bereket et al. investigated the effect of 2-mercaptobenzimidazole 11, 5-methyl-benzimidazole-2-thiol 41 and 5-chlorobenzimidazole-2-thiol 42 on the corrosion of aluminum in 0.1 M HCl by a PP technique at 20–60 °C [42]. It was reported that the IE of these compounds has the following order: 11 > 41 > 42. Corrosion potentials shifted to more negative values and corrosion currents decreased as the concentrations of these organic compounds was increased. These results show that the inhibitive action of all compounds was due to adsorption on the cathodic sides. Authors found that the inhibitive action of benzimidazoles was mainly due to adsorption on the metal surfaces, which show parallelism with the calculated total negative charge of each molecule. Chacko et al. used benzimidazole 1 at different concentrations as corrosion inhibitor for the 6061 Al–SiCp composite on 10–30% concentrations of acetic acid and at different temperatures [43]. The maximum efficiency of inhibition obtained using 1 as inhibitor was 64.58%. IE increases with temperature and Ea (activation energy) values obtained for inhibited solutions are smaller than that obtained in the uninhibited solution which suggested that 1 is adsorbed on the composite surface by mixed adsorption, where chemisorption is predominant.

**Benzimidazoles as corrosion inhibitors for copper and its alloys**

Zhang et al. reported that 2-mercaptobenzimidazole 11 has inhibitory effects on anodic dissolution of copper in 0.5 mol/L HCl solution and that the introduction of a mercapto group to a heterocyclic compound improves
its inhibitory effect [44]. Potentiodynamic polarization results revealed that 11 acted as anodic inhibitor and quantum chemical calculation shows higher energy levels of HOMO and LUMO and a larger π-electron density. Niemien et al. studied corrosion behaviour of copper in 1 M nitric acid in the presence of two Cls, 2-mercaptopbenzimidazole 11 and 2-(methylthio)benzimidazole 43 (Fig. 11) via WL method and quantum chemical approaches. It was found that the inhibition efficiencies increase with increasing concentration and increasing temperature [45]. It has been found that the compounds adsorb onto copper according to the modified Langmuir adsorption isotherm and the kinetic/thermodynamic isotherm of El-Awady. Ozbay et al. reported good corrosion efficiencies for two Schiff bases 2-[(6-nitro-1H-benzimidazol-5-yl)imino][methyl]phenol 44 and 1-[(6-nitro-1H-benzimidazol-5-yl)imino][methyl] naphthalene-2-ol 45 on copper and brass (Cu40Zn60) in alkaline media, of 92.0% and 97.4% respectively [46]. The effect of benzimidazole derivatives on the impedance behaviour of copper and brass in alkaline media at 25 °C shows a semicircle response. Electrochemical parameters calculated from polarization measurements on copper and brass in solution of (0.4 M NaCl + 0.1 M NaOH) without and with 10^{-3} M of benzimidazole derivatives at 25 °C are given in Table 5. Polarization curves for copper in 0.4 M NaCl + 0.1 M NaOH solution of benzimidazoles 44 and 45 are given in Fig. 21.

Benzimidazoles as corrosion inhibitors for zinc
Shanbhag et al. found that benzimidazoles 2-mercapto-benzimidazole 11, 2-hydroxy-benzimidazole 40, 2-hydroxy-5-nitro-benzimidazole 46 and ethyl 2-(benzimidazol-2-thio) acetate 47 reduced the rate of corrosion of zinc considerably in 0.1 M HCl [47] by electrochemical method. The maximum inhibition efficiency of 93% was observed in the presence of 47 at 0.5 mM. Scanning electron microscopy (SEM) images reveal the existence of organic film on metal surface in presence of inhibitors.

Quantum chemical assessment of benzimidazoles as corrosion inhibitors
A number of articles only refer to the theoretical prediction of the use of benzimidazoles as Cls [48–52]. Quantum chemical calculations, density functional theory (DFT) molecular dynamics simulations and QSAR analyses, were used to research the abilities for being a corrosion inhibitor of a benzimidazole. Roque et al. show that applying the DFT theory reveals the formation of an adsorption layer over the metallic surface, due passing of the π density from delocalization region (N1=−C3=−N3) through its HOMO orbital to the metal LUMO orbital [50]. Density functional theory (DFT) was successfully applied to describe the structural importance of corrosion inhibitor and its adsorption efficiency on metal surfaces [52].

Polar functional groups grafted on the benzimidazole nucleus
The efficiency of the benzimidazole inhibitors strongly depends on their ability to form complexes with the metal because they act by adsorption on the metal surface. The polar functional groups containing sulfur, oxygen and nitrogen and the π electrons serve as the chelating centre for chemical adsorption. The inhibition efficiency of organic compounds containing different donor atoms is in the sequence S>N>O [53]. Several quantum-chemistry studies have been performed that relate inhibition efficiency to the molecular properties of benzimidazoles. Obayes et al. demonstrated that presence of nitro group (NO2) on corrosion inhibitor molecules decreases the IE (79.21% for 5-nitro-benzimidazole-2-thiol), while presence of the amino group (NH2) led to an increase in IE (101.38 for 5- amino-benzimidazole-2-thiol) [48]. Li et al. indicated that benzimidazole molecules with a dimethyl amino (N(CH3)2) group in positions “4” or “5” and a hydrazine (NH–NH2) group in position “2” are promising corrosion inhibitors [52]. Rodriguez-Clemente et al. show that the inhibition capacities of 1-(2-pyridinyl)-2-(o, m, p-hydroxyphenyl)benzimidazole indicate that presence of “OH” group at the ortho position, confers the best inhibition properties [38].

| Table 5 Electrochemical parameters calculated from polarization measurements on copper and brass in 0.4 M NaCl + 0.1 M NaOH without and with 10^{-3} M of benzimidazole derivatives at 25 °C. Reproduced with permission from Elsevier, Ref. [46] |
|----------------|----------------|----------------|----------------|----------------|----------------|
|               | E_{corr} (V)  | β_{c} (mV dec^{-1}) | β_{dec} (mV dec^{-1}) | I_{corr} (μA cm^{-2}) | IE (%)            |
| Copper        |               |                |                |                 |                  |
| Blank         | −0.194        | 324            | 286            | 41.0            | −               |
| 44            | −0.153        | 206            | 196            | 3.67            | 91.0            |
| 45            | −0.168        | 219            | 291            | 12.0            | 71.0            |
| Brass         |               |                |                |                 |                  |
| Blank         | −0.437        | 483            | 136            | 118.0           | −               |
| 44            | −0.225        | 187            | 144            | 2.97            | 97.4            |
| 45            | −0.200        | 232            | 116            | 9.1             | 92.0            |

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Quantum chemical indices

The effects of the molecular structure on chemical reactivity have been studied extensively [53–57]. Quantum chemical indices calculated to predict that a compound is fitted to be a corrosion inhibitor are: energy of the highest occupied molecular orbital (EHOMO), energy of the lowest unoccupied molecular orbital (ELUMO), dipole moment (μ), polarizability (α), total natural charges (Qtotal), total Mulliken charges (Ztotal), adiabatic ionization potential (Ia), adiabatic electron affinity (Aa), Molar volume (Vi), aromaticity-magnetism based on Nuclear Independent Chemical Shift (NICS), the number of electrons transferred (ΔN) and electrophilicity index (ωa) [52, 58–71].

The radial distribution function (RDF) study confirmed that both the neutral and protonated form of the inhibitor show significant interaction with the steel surface. Various interaction patterns are proposed to explain the corrosion efficiency of several benzimidazoles using the quantum chemical parameters mentioned above [16, 19, 20, 33, 43, 46].

Aromaticity-magnetism based on Nuclear Independent Chemical Shift (ΛNICS)

The inhibitory activity depends on the aromaticity of the benzimidazole systems. Thus, the delocalization of the π-electrons in the aromatic systems plays a central role in the adsorption of the compounds on the metal surface. The delocalized π-electrons are transferred to the vacant orbitals of the metal atoms, establishing stable coordination bonds [20, 21, 32, 52].

Frontier orbitals (HOMO, LUMO) and inhibition efficiency

The energy of HOMO (EHOMO) is associated with the electronic donating ability of a molecule. Therefore, an increase in the values of EHOMO facilitates the adsorption, thus the inhibition efficiency, and indicates the availability of the molecule to donate electrons to an appropriate acceptor with empty molecular orbitals. The energy of LUMO (ELUMO) indicates the ability of the molecule to accept electrons. The parameter that determines chemical reactivity and kinetic stability of the molecule is the frontier orbital gap. A small frontier orbital gap defines a molecule with high chemical reactivity, low kinetic stability and more polarisable [72, 73]. The lower the value of ELUMO, the more probable it is that the molecule accepts electrons. A molecule with low energy gap ΔE = ELUMO − EHOMO will possess good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low [53]. These correlations are made also considering the terms of ionization potential (I) —the ability of a species to donate electrons; and the electronic affinity (A) —the ability of a species to accept electrons.

The number of electrons transferred (ΔN)

The number of electrons transferred (ΔN) from the inhibitor molecule (donor) to the metallic atom (acceptor) indicates the tendency of a molecule to donate electrons. A higher value of ΔN indicates the greater tendency of a molecule to donate electrons [52]. According to Dibetsoe et al. negative values of ΔNa suggest that the inhibition of metal corrosion is predominantly controlled by retro-donation from the metal to the inhibitor molecule [68]. According to Lukovits et al. [69] and to other recent studies [64, 70], a value of ΔN less than 3.6 indicates that the inhibition efficiencies of an inhibitor tend to increase by increasing the electron-donating ability to the metal surface.

Dipole moment (μ) and inhibition efficiency

Several authors stated that inhibition efficiency increases with increasing values of the dipole moments, by influencing the transport process through the adsorbed layer [20, 53]. However, Zhang et al. reported that the low
polarity species, such as 29, are more efficient corrosion inhibitors than higher polarity species, like the protonated form of 29, since the last is surrounded by a denser water layer compared to 29 [31].

**Total charge \((Q_{\text{total}})\) or Mulliken population analysis \((Z_{\text{total}})\)**

The total negative charge represents the amount of charge carried by all non-hydrogen atoms of the benzimidazole. A larger total charge indicates a greater tendency for the molecule to be adsorbed on a metal surface [12, 52]. Therefore, the efficiency of an organic inhibitor depends on the many factors, such as chemical structure; size of the organic molecule; aromaticity and/or conjugated bonding; type and number of bonding atoms or groups in the molecule; and the charges of the metal surface of adsorption, such as mode like bonding strength to metal substrate; ability for a layer to become compact or cross-linked; capability to form a complex with the atom as a solid in the metal lattice; and the type of the electrolyte solution like adequate solubility in the environment [58–63, 74–76]. El-Hajjaji selected 1-octyl-2-(octylthio)-1H-benzimidazole because it can readily adsorb onto the steel surface, due to a positively charged nitrogen atom; also, the long hydrocarbon chain is likely to form a hydrophobic network which can further reduce the interaction between the metal and the corrosive environment [35].

Shi et al. found that the Mulliken atomic charges indicate that the adsorption of CIs occurs mostly through benzene ring and the lone pair electrons of the “nitro” atoms [77]. Similar results were reported by Baskar group for a series of benzimidazoles [78]. Sun et al. show two types of adsorption by calculating charges on the atoms: parallel adsorption, when the molecule is chemosorbed on the metal surface and perpendicular adsorption, in the case of dehydrogenated molecules chemosorbed [79]. The inhibition efficiencies are explained in theoretical terms by chain length, relative effects of amido and sulphonamido groups, spatial orientations, structural factors, energy gap between the frontier orbitals and charges on atoms for a series of benzimidazoles [26, 80].

**Substitution in the “2” position at benzimidazoles**

Substitution in the “2” position at benzimidazoles, respectively 2-substituted benzimidazoles, have a better inhibitory activity than the unsubstituted benzimidazoles at position “2”, as can be seen from several studies [1, 16, 35], both experimental [16, 23, 27, 38, 40, 49] and theoretical [19, 26, 50, 72]. The superior inhibitory activity of the 2-substituted benzimidazoles compared to the unsubstituted benzimidazoles in position “2” can be concluded from the comparative inhibitory efficiency data mentioned in Table 2. Thus, if for benzimidazole 1, not substituted in the “2” position, the maximum inhibitory efficiency is 60%, for 2-Aminobenzimidazole 10 and 2-Mercaptobenzimidazole 11, the maximum inhibitory efficiency is much higher, of 86.8% and respectively 97.0% [22].

**Mechanisms of corrosion inhibition for benzimidazole compounds**

There are many mechanisms proposed for the inhibition of metal corrosion by benzimidazole inhibitors. The first stage in the action mechanism of the inhibitor in the aggressive acid media is its adsorption on the metal surface [81]. The parameters implied in the adsorption of the organic inhibitors on the metal surface are: (1) the structure of the inhibitor which confers specific charges on the atoms and some type of interaction between metallic surface and organic substance; (2) the corrosive electrolyte (acid or basic); (3) nature of metal surface [82, 83]. The formation of donor–acceptor surface complexes between π-electrons of an inhibitor and the vacant d-orbital of metal was formulated in many inhibition studies [80, 84, 85]. Thus, the adsorption of the bis(benzimidazole) as neutral molecules on the metal surface can occur by displacement of water molecules from the metal surface and sharing of electrons between the nitrogen atoms and the metal surface. A schematic representation of the adsorption behaviour of bis(benzimidazole) on mild steel in 1 M

![Fig. 22 Schematic representation of adsorption behaviour of bis(benzimidazole) on mild steel in 1 M HCl solution: a mild steel surface with positive charge, b mild steel surface with negative charge and c mild steel surface at potential of zero charge](Reproduced with permission from Elsevier, Ref. [81])
HCl solution is shown in Fig. 22. Three kinds of species can be adsorbed on a mild steel surface when is immersed in dilute solution of HCl containing bis(benzimidazole): (a) the chloride ions will first be adsorbed on the metal surface, if the metal surface is positively charged and a close packed triple layer will form on the metal surface which inhibit the entry of iron ions to the solution (Fig. 22a); (b) the benzimidazole compound is directly adsorbed on the metal surface if the metal surface is negatively charged (Fig. 22b); (c) when the metal surface has the potential surface charge zero, none of the ions (neither cations nor anions) adsorb on the surface through their ionic centre (Fig. 22c). Another proposed scheme of the inhibition mechanism in acidic is shown in Fig. 23. The inhibitor molecules move quickly to the damaged regions to form strong coordination bonds with Fe atoms, by adding a certain concentration of corrosion inhibitors to the corrosive media. Consequently a protective barrier is formed to prevent the attack corrosive particles (such as Cl\textsuperscript{−}, H\textsubscript{3}O\textsuperscript{+}) on Fe surface.

Conclusion
In this paper we presented the syntheses of the tested benzimidazoles as corrosion inhibitors, the experimental conditions, the proposals of mechanisms of interaction between the inhibitor and the protected surface, as well as the theoretical approaches of these molecules. It has been shown that benzimidazoles are good and very good corrosion inhibitors for extremely aggressive, corrosive acidic media such as 1 M HCl, 1 M HNO\textsubscript{3}, 1.5 M H\textsubscript{2}SO\textsubscript{4}, 30% acetic acid, basic, as 0.1 M NaOH or solutions of salts such as 3% NaCl and NACE brine ID196. Also the metals tested are diverse, from the most searching, steels, mild steel and carbon steel, pure metals like Fe, Al, Cu, Zn, and alloys. EIS measurements suggest the adsorptive property of the benzimidazoles, that form a physical barrier on the metal surface hindering charge transfer reactions at the metal-solution interface. Generally, all these benzimidazole derivatives act as mixed type inhibitors, exhibit stronger inhibitive effect on the cathodic reaction than on the anodic one. SEM and AFM images confirm the adsorption of the inhibitors on the metal surface, therefore the protection of metals. Benzimidazoles can have very good inhibition efficiencies of up to 97–99% for concentrated acidic solutions of hydrochloric acid or sulfuric acid. Experimental methods for investigating corrosion processes and benzimidazole inhibitors have been presented. Polar groups, quantum parameters like, the energy of the HOMO and LUMO orbitals, aromaticity-magnetism based on Nuclear Independent Chemical Shift, dipole moment and total charge, are important parameters that define the anti-corrosion capacity of an inhibitor. We hope this study will open new horizons in the science of organic corrosion inhibitors to be applied even at industrial level.

Abbreviations
CIs: corrosion inhibitors; PDA: 1,2-diaminobenzene; WL: weight loss; EIS: electrochemical impedance spectroscopy; LSW: linear sweep voltammetry; SEM: scanning electron microscopy; AFM: atomic force microscopy; IE: inhibition efficiency; HOMO: high occupied molecular orbital; LUMO: low unoccupied molecular orbital; PP: potentiodynamic polarization; CS: carbon steel; MS: mild steel; FTIR: Fourier Transform infrared; UV–VIS: ultraviolet–visible; DFT: density functional theory; RDF: radial distribution function.

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Author MM designed and prepared the manuscript. The author read and approved the final manuscript.

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