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Theoretical confirmation of benzothiazole derivatives as corrosion inhibitors for carbon steel in hydrochloric acid

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Abstract

This study presents an in-depth theoretical approach based on density functional theory (DFT) to elucidate the mechanisms of corrosion inhibition of benzothiazole derivatives 2-mercaptobenzothiazole (MBT) and 2-aminobenzothiazole (ABT) on carbon steel in a 1 M HCl solution. Quantum chemistry parameters, including Frontier molecular orbitals energies, electrostatic potential maps (MEP), and Fukui indices were calculated in order to evaluate the inhibition mechanisms of these two drifts.

The results indicate that MBT has a higher HOMO energy and greater electron donor capacity than ABT, thus promoting stronger chemisorption on the steel surface. In addition, MBT's tendency to protonate enhances its physisorption due to electrostatic forces acting on the metal surface in an acidic environment. These theoretical results are consistent with experimental observations from electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM), confirming the superior inhibitory performance of MBT compared to ABT, especially after prolonged immersion time. This study highlights the essential role of molecular electronic properties in determining inhibitor efficacy and supports the rational design of high-performance benzothiazole-based corrosion inhibitors.

1. Introduction

The destruction of metals by corrosion is a major phenomenon that causes considerable economic losses[1]. In order to limit the effects of this process, one of the most effective methods is to use corrosion inhibitors. Organic compounds, in particular, are characterized by their strong affinity for metal surfaces, onto which they adsorb to form a protective layer capable of slowing down the electrochemical reactions responsible for material degradation[2].

In this context, benzothiazole derivatives represent a particularly promising class of compounds. Their heterocyclic structure, containing both a nitrogen atom and a sulfur atom, as well as a conjugated system, gives them multiple potential active sites for adsorption with the metal substrate[3]. To evaluate the inhibitory potential of these compounds and better understand their mode of action at the molecular level, a theoretical chemistry approach based on density functional theory (DFT)[4].

This quantum calculation method is widely used to evaluate inhibitory efficacy and confirm experimental results. Indeed, studying the electronic properties of inhibitors provides very precise information about their molecular reactivity. The DFT study is based on the fundamental principle that the electronic properties of a multi-electron system can be determined from its electron density. Among its applications is the prediction of inhibitory performance, i.e., the capacity of inhibitor molecules to interact with metal surfaces, through the analysis of fundamental parameters such as energies (EHOMO, ELUMO) and electron density. These predictions help analyze the adsorption process and contribute to the development of more effective inhibitors.

The objective of this study is to evaluate and compare, using a DFT computational approach, the inhibitory potential of two benzothiazole derivatives: 2-mercaptobenzothiazole (MBT) and 2-aminobenzothiazole (ABT)[5]. Our objective is to analyze their frontier orbitals (HOMO and LUMO) and their electrostatic potential maps,to identify interaction sites. This comparative analysis will provide insight into the influence of molecular structure on the adsorption process and predict which of these two compounds is most likely to act as an effective corrosion inhibitor for carbon steel in acidic environments.

2. Materials and Methods

Quantum studies are performed using Gaussian 09W software. This method, recognized as an essential tool for studying many chemical phenomena, allows for in-depth analysis of the electronic properties of the molecules studied as well as adsorption processes[6].

The calculations were performed using the following bases: B3LYP/6-311G(d,p) and B3LYP/6-311G++(d,p), which enable an in-depth study to be carried out in order to obtain as much information as possible about the molecule, in particular electronic parameters such as :

- Electronegativity (χ), energy gap (ΔEg), softness (S), and fraction of electrons transferred (ΔN).

These parameters were calculated using the following relationships :

$$\chi = -\mu = \frac{E_{LUMO} \pm E_{HOMO}}{2} \qquad (1)$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \qquad (2)$$

$$S = \frac{1}{\eta} \qquad (3)$$

$$\omega = \frac{\mu^2}{2\eta} \qquad (4)$$

$$E_{gap} = E_{LUMO} - E_{HOMO} \qquad (5)$$

$$\Delta N = \frac{z_{métal} - z_{mol}}{2(\eta_{métal} + \eta_{mol})} \qquad (6)$$

$$\Delta E = \frac{(z_{métal} - z_{mol})2}{4(\eta_{métal} + \eta_{mol})} \qquad (7)$$

With χ_metal = 7.00 eV·mol^{-1} and η_metal = 0 eV·mol^{-1} [8]

Analysis of these quantum chemistry parameters therefore confirms the high anti-corrosion performance of MBT and ABT inhibitors, in agreement with experimental results.

3. Results and discussions

3.1 Geometry optimization

The optimization of the structures of the two benzothiazole-derived molecules (ABT and MBT) that are the subject of our comparative study was performed by DFT, using Gaussian 09 software. Applying B3LYP and the 6-31G(d, p) basis set.

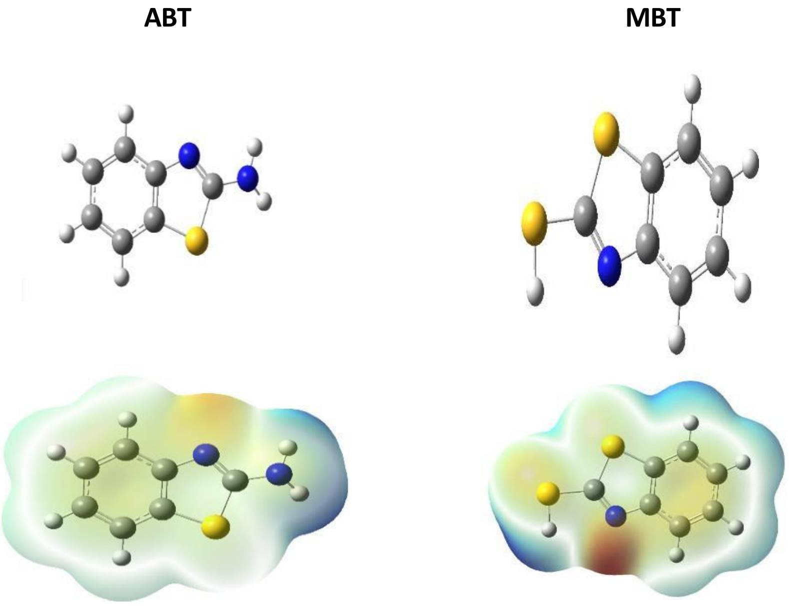

Fig. 1. Optimized geometries and molecular electrostatic potential (MEP) maps of the inhibitors MBT and ABT.

3.2 The ESP map

The electrostatic potential (ESP) map of benzothiazole derivatives, ABT and MBT, highlights important information about charge distribution and molecular reactivity. The red areas correspond to nucleophilic regions (negatively charged), capable of donating electrons, while the blue areas indicate electrophilic regions (positively charged), susceptible to nucleophilic attack[3] . The green areas represent regions of neutral charge.

For the ABT molecule, the ESP map shows red areas concentrated around the nitrogen and sulfur atoms. These electron-rich atoms act as electron donor sites, promoting adsorption onto the metal surface[7]. The blue areas are mainly located around the hydrogen atoms, indicating the electrophilic zone. This balanced distribution of electrostatic potential reflects good electronic stability of the molecule, which enhances its ability to interact with the metal through chemisorption[8].

Analysis of the MBT ESP map indicates a pronounced concentration of red areas around the sulfur and nitrogen atoms, with a higher electron density compared to ABT . This reflects a greater electron donor capacity, attributed to its molecular structure. Specifically, the substitution of the amino group (-NH_2) in ABT with a thiol group (-SH) in MBT increases its reactivity, thus promoting more effective adsorption on the metal surface. Conversely, the blue areas on the hydrogen atoms and certain regions of the aromatic ring indicate positively charged zones that can interact with metal surface ions, contributing to the formation of a stable protective layer[9].

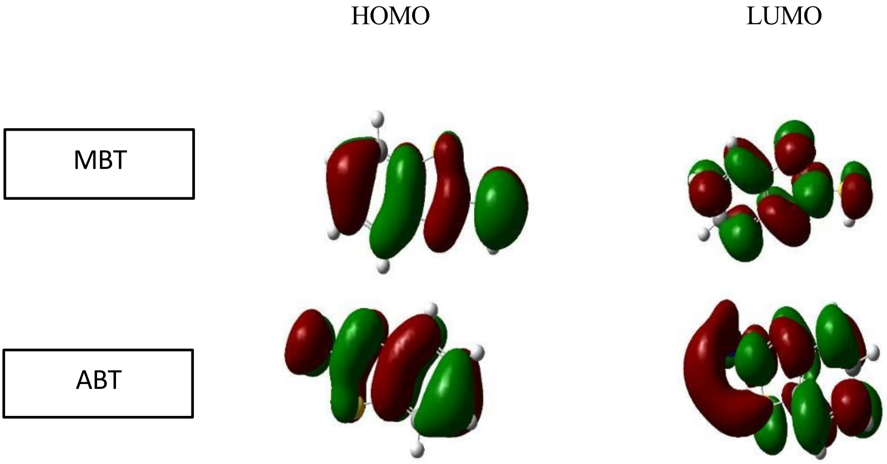

Fig. 2. Representation of the frontier molecular orbitals (HOMO and LUMO) for the inhibitors MBT and ABT

3.4 Analysis of the Frontier Molecular Orbitals of ABT and MBT Molecules

Analysis of the molecular frontier orbitals, namely (HOMO) and (LUMO), indicates fundamental differences in the electronic properties and chemical reactivity of MBT and ABT. For the MBT molecule, the HOMO orbital is mainly localized around the sulfur atom (S) of the thiol group (-SH) and also extends over the aromatic system of the thiazole ring. This spatial distribution highlights sulfur as a preferred site for electron donation[4] . As for the LUMO, its electron density is mainly distributed over the aromatic system, indicating that these aromatic rings are electron acceptance sites.

The presence of the thiol group and the conjugated system gives MBT a strong ability to form electronic bonds with metal through electron transfer.

For the ABT compound, the HOMO orbital is located at the nitrogen atom (N) of the amine group (-NH2) as well as on the benzothiazole system. This concentration on nitrogen is due to the presence of a non-bonding doublet. As for LUMO, it is mainly located on the benzene ring, indicating that this region is the main site for electron acceptance.

3.5 Molecular and electronic parameters of inhibitors

Table 1. Molecular and electronic parameters of inhibitors MBT and ABT

Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	μ	I	A	χ	μ	η	S	ΔE	ΔN
ABT	-0,24	-0,03	0,20	1,195	0,24	0,03	0,124	-0,124	0,097	10,22	-0,52	0,22
MBT	-0,22	-0,05	0,19	0,913	0,22	0,05	0,142	-0,142	0,094	10,62	-0,54	0,23

According to the literature, high HOMO energy indicates that the compound is likely to donate electrons, while low LUMO means that the molecule has a high capacity to accept electrons. The energy gap (ΔEg) is an essential parameter for evaluating molecular reactivity and stability[10]. A low ΔEg value indicates greater molecular reactivity, resulting from the ease of interaction between the HOMO and LUMO frontier orbitals. This property is a key indicator of stability: a low ΔE corresponds to a more stable complex[3].

Table 1 shows that the substitution of the amino group (-NH2) of the ABT inhibitor by the thiol group (-SH) of the MBT inhibitor results in significant changes in electronic properties. There is a slight increase in HOMO energy, from -0.24 eV (ABT) to -0.22 eV (MBT), and a marked decrease in LUMO energy, from -0.03 eV to -0.05 eV. This leads to a reduction in the energy gap from 0.20 eV to 0.19 eV. This decrease in ΔE indicates high reactivity of the thiol (-SH) group of the MBT inhibitor. Chemical hardness (η) decreases, while softness (σ) increases. This can be explained by the fact that the electron cloud is easily deformable, which therefore enhances the reactivity of the molecule and facilitates its adsorption on the surface of the metal.

Electronegativity (χ) also increases, rising from 0.124 eV to 0.142 eV. This increase demonstrates the molecule's greater ability to attract electrons, thereby promoting its interaction with the metal surface. At the same time, the chemical potential decreases, resulting in electronic stability. This increase in electronegativity and decrease in chemical potential both give the MBT molecule a more polar and reactive character compared to ABT, which explains its high inhibitory performance. The dipole moment **μ**, which is a key parameter in assessing molecular polarity, increases with the substitution of the amino group (-NH2) of the ABT inhibitor by the thiol group (-SH) of the MBT inhibitor, from 0.913 Debye to 1.96 Debye. This indicates an increase in the polarity of the molecule[6]. In order to understand the adsorption mechanism of our inhibitor, we calculated the electron transfer fraction (ΔN), a key parameter used to determine whether the molecule under study will donate or accept electrons at the steel surface.

According to the literature, inhibitory efficiency increases with ΔN when its value is less than 3.6, indicating a strong ability to donate electrons. Conversely, negative ΔN values indicate electrophilic behavior, i.e., the molecule's ability to accept electrons from the metal. Analysis of ΔN shows a slight increase from ABT to MBT due to the substitution of the amino group (-NH2) with thiol (-SH), rising from 0.22 to 0.23. This increase, although small, indicates that MBT has a slightly greater ability to transfer electrons to the steel surface, thereby enhancing its adsorption power and inhibitory efficiency[11]. Finally, the substitution of the amino group (-NH2) of the ABT inhibitor by the thiol group (-SH) of the MBT inhibitor leads to a decrease in the binding energy difference (ΔE_e), from -0.52 eV to -0.54 eV. This reduction indicates that the MBT inhibitor forms weaker interactions with the corrosive environment, thereby promoting optimal adsorption of the inhibitor onto the steel surface. Theoretical studies (DFT) and experimental results show that the MBT inhibitor adsorbs effectively onto metal surfaces, contributing to the formation of a compact protective barrier that prevents corrosion compared to ABT[5].

3.6 Charges Mulliken

Mulliken's atomic charge tends to produce qualitative results at best; it is very useful for estimating the partial atomic charges of molecular systems. The distribution of charges on the atoms of ABT and MBT is given in Tables (2) and (3).

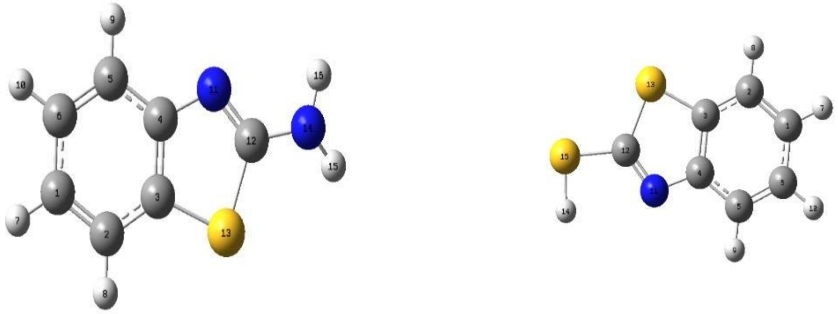

Fig. 3. structure and Mulliken's charges of inhibitors ABT et MBT

Table 2. Mulliken atomic charges of inhibitor ABT

Atomes	Charge	Atomes	Charge
C1	0.001	H9	0.133
C2	-0.031	H10	0.125
C3	0.756	N11	-0.246
C4	-0.711	C12	0.190
C5	-0.635	S13	0.187
C6	-0.136	N14	-0.494
H7	0.124	H15	0 .293
H8	0.131	H16	0.313

Table 3. Mulliken atomic charges of inhibitor MBT

Atomes	Charge	Atomes	Charge
C1	-0.032	H9	0.137
C2	-0.033	H10	0.129
C3	0.934	N11	-0.070
C4	-0.855	C12	-0.005
C5	-0.696	S13	0.159
C6	-0.171	H14	0.098
H7	0.128	S15	0.139
H8	0.136		

Among the parameters obtained from DFT calculations, Mulliken charges provide a comprehensive view of the electronic distribution within ABT and MBT molecules, thereby identifying areas favorable for interaction with the metal surface. According to the literature, a more negative charge on an atom indicates a greater ability to donate electrons to the metal, while a more positive charge reflects an ability to accept electrons[8].

Analysis of the figure shows that nitrogen atoms N14 (−0.494) and N11 (−0.246) are the most negatively charged, indicating that they are the main electron donor sites. These atoms can therefore actively participate in the formation of bonds with the metal surface.[12] In addition, the carbons of the aromatic ring, particularly C4 (−0.711) and C5 (−0.635), also have significant negative charges, indicating their potential contribution to adsorption following the electronic delocalization of the conjugated π system. While the sulfur atom S13, despite having a slightly positive charge (+0.187), retains non-bonding doublets that can participate in the association with the metal. These results suggest that the ABT molecule interacts with the metal surface mainly through its nitrogen and sulfur atoms, rather than through its aromatic ring, which promotes stable chemisorption.

With regard to the MBT molecule, Mulliken charges reveal that carbons C4 (−0.855) and C5 (−0.696) are the most negative, thus constituting the main electron donor sites likely to participate in the bond with the metal surface [15]. Nitrogen N11 (−0.070) has a slightly negative charge, also indicating its contribution to adsorption. Thus, the adsorption of the MBT molecule appears to occur mainly via the carbons of the aromatic ring (C4, C5) and the heteroatoms S and N, giving the molecule a good ability to form a protective layer on the metal surface,which consequently slows down the electrochemical reactions responsible for corrosion. Mulliken charge analysis indicates that both inhibitors, ABT and MBT, have several potential active sites (aromatic N, S, and C) that promote their interaction with the metal surface[11].

3.7 Comparison of Theoretical and Experimental Results

This study aims to compare the results obtained by the DFT method with the experimental observations reported by Hojat Jafari, Kazem Akbarzade, and Iman Danaee in their study entitled “Corrosion inhibition of carbon steel immersed in a 1 M HCl solution using benzothiazole derivatives.”[5]. In this research, the authors evaluated the effect of benzothiazole derivatives such as 2-mercaptobenzothiazole (MBT) and 2-aminobenzothiazole (ABT) as corrosion inhibitors on ST-37 carbon steel in an acidic medium (1 M HCl) using electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM).

The experimental results indicate that both compounds exert a significant inhibitory effect and that corrosion resistance increases with immersion time, from 15 to 300 minutes. At equal immersion times, MBT exhibited greater inhibitory efficiency than ABT. AFM observations confirmed the formation of a more homogeneous and dense protective layer film on the metal surface in the presence of MBT, reflecting better adsorption of the inhibitor on the metal surface[5]. This high performance of MBT compared to ABT can be attributed to their structural differences. Indeed, replacing the amino group (-NH2) of the ABT inhibitor with a thiol group (-SH) in the MBT inhibitor significantly alters the electronic distribution. This substitution promotes stronger adsorption and the formation of a stable protective barrier, which explains the high inhibitory performance observed for MBT.

The consistency between the experimental results and the theoretical parameters confirms the reliability of the DFT approach for predicting the anticorrosion behavior of benzothiazole derivatives, in particular the high performance of MBT compared to ABT.

4. Conclusion

Computational modeling is an effective and reliable tool for predicting and explaining the performance of corrosion inhibitors. Our theoretical study predicted that MBT is a more effective inhibitor than ABT due to its molecular properties that promote strong adsorption.This prediction is confirmed by experimental data, which show superior efficacy and protective resistance for MBT. This work demonstrates that computational evaluation is a powerful and reliable tool for predicting and understanding the performance of corrosion inhibitors. It not only validates experimental observations, but also guides the future design of even more effective inhibitor molecules.

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