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Inhibitory effect of some benzoxazole derivatives on corrosion of mild steel: a computational study

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Abstract

Inhibitory effect of five benzoxazole derivatives (Benzoxazole [BZ], 2-methylbenzoxazole [MBZ], 6-Nitro-1,3-benzoxazole [NBZ], 2-benzoxazolethiol [BZT] and 2-phenylbenzoxazole [PBZ]) on corrosion of mild steel were theoretically evaluated using Density Functional Theory (DFT) method in gas phase. Quantum chemical parameters such as highest occupied molecular orbital energy ($E_{(HOMO)}$), lowest unoccupied molecular orbital energy ($E_{(LUMO)}$), energy gap (ΔE), global hardness (η), global softness (σ), polarizability (α), dipole moment (μ), ionization potential (I), electron affirnity (A), electronegativity (χ), and fraction of electron transferred (ΔN), were calculated at the B3LYP level of theory with 6-31G* basis set. PBZ showed the highest inhibitory effect among the five molecules having close agreement with experimental results. The Mullikan charges of the atoms of these molecules were also computed. They revealed that the possible sites of electrophilic attack were on the nitrogen and oxygen atoms, which had greater negative charges. The electronic structures as well as reactivity of these molecules and other parameters could be used in designing novel, high-efficient, cheap, and eco-friendly inhibitors.

Key word: Benzoxazole, Density Functional Theory, corrosion inhibitors, mild steel

Introduction

Benzoxazoles are derivatives of oxazoles, they are aromatic organic compounds having a benzene-fused oxazole ring structure. It is an important heterocyclic ring system, which can be isolated from natural products or by total synthesis. Its aromaticity makes It relatively stable but as a heterocycle, it has reactive sites that allow for functionalization [1]. They have remarkable biological activities such as antimicrobial, anti-inflammatory, anti-viral, anti-histaminic, herbicidal, anti-culvulsant, anti-cancer and diuretic properties [1-2]. Benzoxazoles also have remarkable industrial applications such as pesticides, dyes, fluorescent brightening agents, synthetic heat resistant fibres; optical bleaching agents and as corrosion inhibitors [3].

Corrosion refers to the conversion into another insoluble compound of the surface layers of a solid in contact with a fluid. Owing to the tremendous economic damage it can cause, corrosion has continued to be the subject of extensive study especially with a view to its minimization at acceptable expense both economically and environmentally [4]. Among the methods to avoid or prevent destruction or degradation of metal surface, the corrosion inhibitor is one of the best-known methods of corrosion protection and the most useful in the industry due to its low cost and practice method [5]. The most efficient inhibitors are organic compounds that contain electronegative functional groups such as P, O, N, or S and having π bonds or π e^- s in triple or conjugated double bonds [6]. Most of the commercial inhibitors are toxic hence the need to replace them with new non-toxic, ecofriendly inhibitors.

Quantum chemical calculations have been widely used to study reaction mechanism. They have been proven to be a powerful tool for studying corrosion inhibition mechanism [6-11]. Density functional theory

(DFT) has provided a very useful framework for developing new criteria for rationalizing, predicting, and understanding different aspects of chemical processes. A variety of chemical concepts, which are now widely, used as descriptors of chemical reactivity, appear naturally within DFT [8]. Quantum chemical studies have been successfully used to link the corrosion inhibition efficiency with molecular orbital (MO) energy levels for heterocyclic organic compounds.

This study reports the theoretical investigation carried out on the electronic and molecular structural properties of non-toxic, ecofriendly benzoxazole and its derivatives and the effect of these properties on their inhibition efficiency on corrosion of mild steel using the quantum chemically calculated parameters.

Computational methods

Quantum chemical calculations were performed for benzoxazole and its derivatives as corrosion inhibitors using the density functional theory (DFT) method at the hybrid functional B3LYP level of theory with 6-31G* basis set implemented in Spartan 14 version 1.2.0 software [12]. All quantum chemical calculations were carried out in gas phase.

Results and discussion

Global reactivity descriptors

Quantum chemical calculations were performed to investigate the structural parameters that affect the inhibition efficiency of inhibitors. Geometric and electronic structures of the inhibitors were calculated by the optimization of their bond length. The optimized molecular structures with minimum energies obtained from the DFT calculations are illustrated in Fig. 2.

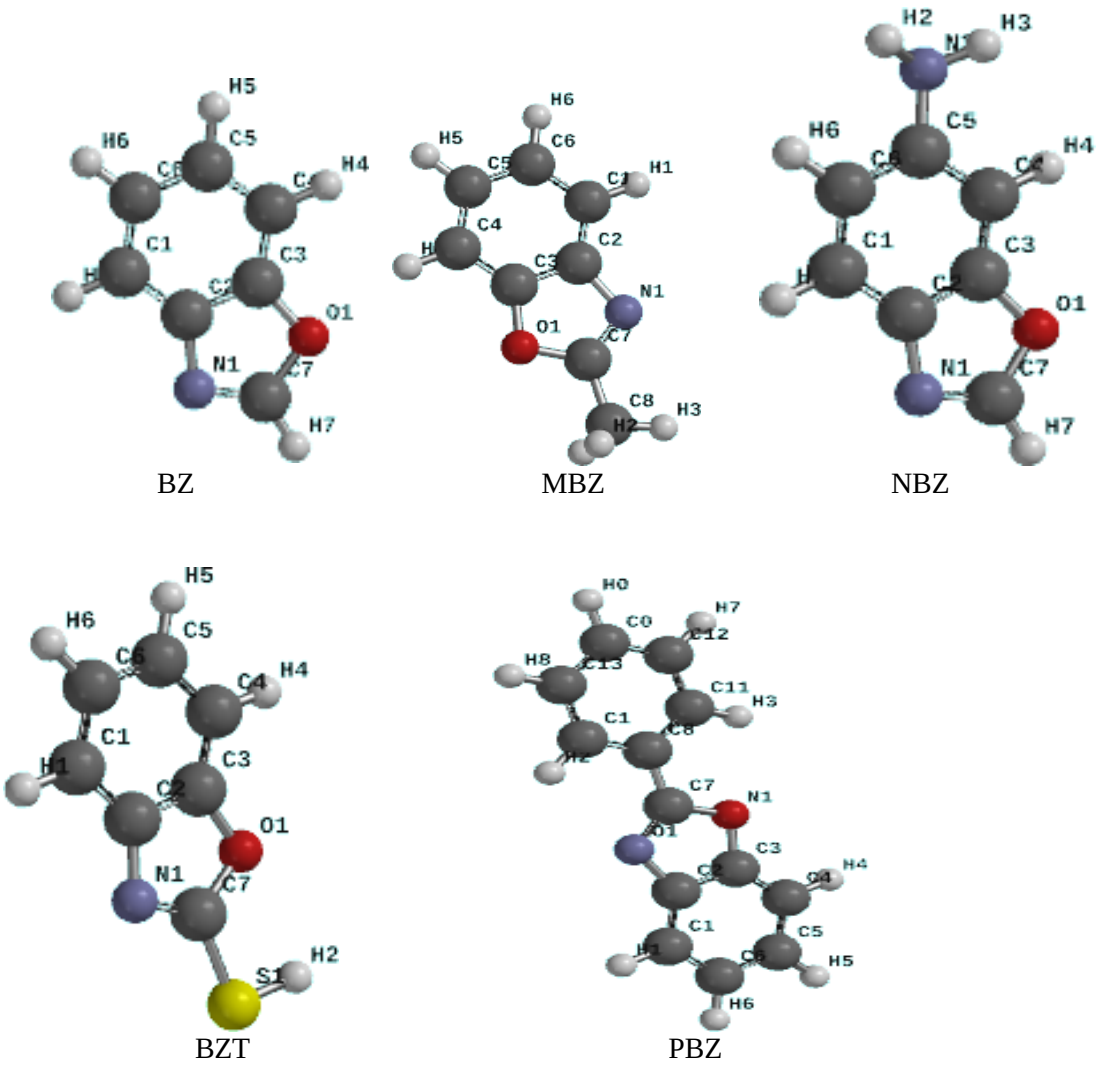

Figure 1. Labeled structures of the Compounds

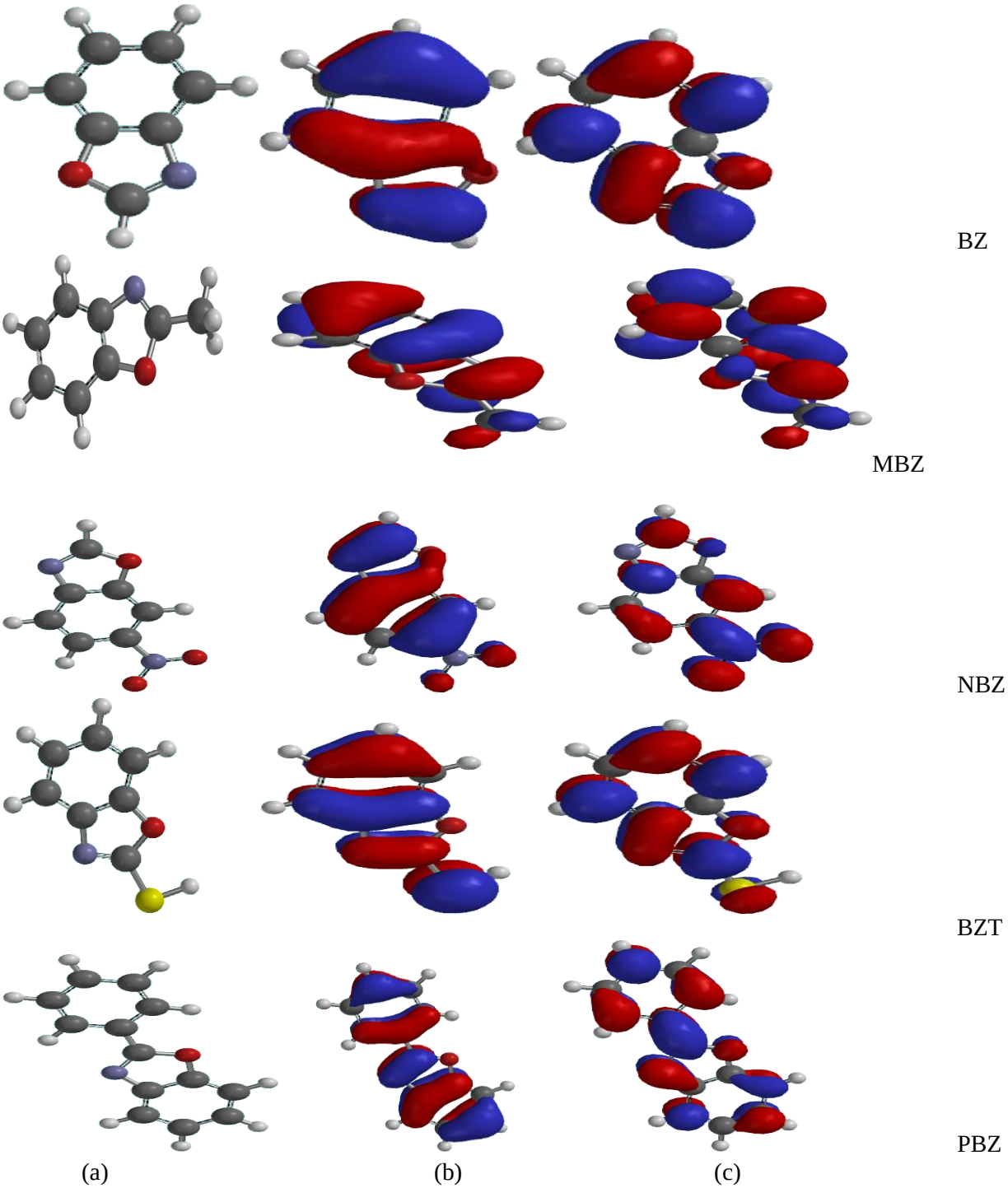

Figure 2. (a) Optimized structure, (b) HOMO and (c) LUMO of Benzoxazole and its derivatives

The effectiveness of a molecule as an inhibitor can be related not only to its spatial molecular structure but also with their molecular electronic structure. According to frontier orbital theory, the reaction of molecules mainly occurred on the HOMO and LUMO and the properties of these molecules are determined by the frontier orbitals. As shown in Fig. 2, all five inhibitor molecules have similar HOMO and LUMO distribution that is they are distributed over the entire molecule and are not localized over some parts of the molecule. This kind of distribution favored the preferential adsorption of inhibitors on the metal surface either by the Fe atom accepting electrons donated by the inhibitor molecule with its unoccupied d orbital forming coordinate bond or that the inhibitor molecule accepts electrons from the Fe atom with its anti-bonding orbitals to form back-donating bond. [9].

Inhibition efficiency increases with increasing E_{HOMO} values. High E_{HOMO} value indicates that the molecule tends to donate electrons to the appropriate acceptor molecules with a low energy molecular

orbital while a lower E_{LUMO} value suggests the molecule easily accepts electrons from the donor molecule [11]. Table 1 depicts the calculated value of E_{HOMO} and E_{LUMO} for the molecules under study. Based on the increasing value of E_{HOMO}, the order of inhibition efficiencies of the inhibitors under study follows the trend PBZ > BZT > MBZ > BZ > NBZ. This trend confirms the fact that nitro groups are strong acceptors indicated by its lowest E_{HOMO} value. Table 1 also shows the calculated HOMO-LUMO gap (ΔE). It is an established fact that low ΔE value depicts good inhibition efficiency because the energy of removing an electron from the last occupied orbital will be low. The value of ΔE for the studied inhibitors decreases in the order: PBZ < NBZ < BZT < MBZ < BZ. PBZ has the highest E_{HOMO} and the lowest ΔE among the five - benzoxazole molecules. Therefore, PBZ has the strongest interaction with the iron surface and the best inhibition effect in theory.

Table 1. Electronic parameters [orbital energies for HOMO and LUMO, HOMO–LUMO energy gap (ΔE), total energy] and dipole moment (μ) for BZ, MBZ, NBZ, BZT and PBZ

Inhibitor	E_{HOMO}/eV	E_{LUMO}/eV	ΔE /eV	μ
BZ	- 6.57	- 0.77	5.80	1.32
MBZ	- 6.32	- 0.60	5.72	1.17
NBZ	- 7.35	- 3.03	4.32	5.58
BZT	- 6.20	- 0.72	5.48	2.22
PBZ	- 6.01	- 1.43	4.58	1.14

The effectiveness of the BZ and its derivatives were further addressed by calculating the global reactivity parameter which includes global softness (σ), global chemical hardness (*η*), electronegativity (χ), global electrophilicity index (φ), number of electrons transferred (ΔN), and initial molecule-metal interaction energy (Δψ). The corresponding results are shown in Table 2.

Table 2. Some quantum chemical descriptors for BZ, MBZ, NBZ, BZT and PBZ

Inhibitors	I	A	χ	η	σ	α	ΔN
BZ	6.56	0.77	3.67	2.90	0.17	49.92	0.57
MBZ	6.32	0.60	3.46	2.96	0.17	51.42	0.59
NBZ	7.44	2.63	5.04	2.41	0.21	51.90	0.40
BZT	6.20	0.72	3.46	2.74	0.18	51.40	0.64
PBZ	6.01	1.43	3.72	2.29	0.22	57.02	0.71

I is ionization potential, A is electron affinity, χ is electronegativity, η is global hardness, σ is global softness α is polarizability and ΔN is fraction of electron transferred

Global hardness and softness are very important parameters when describing molecular reactivity and stability. Soft molecules are more reactive than hard molecules because they can easily offer electrons. Therefore inhibitors with the least values of global hardness are expected to be good corrosion inhibitors for bulk metals in acidic medium. Wang et al. 2007 [13] reported that adsorption of inhibitors onto a metallic surface occurs at the part of a molecule which has the greatest softness and lowest hardness. From the calculated values the softness of the inhibitors follows the trend PBZ>NBZ>BZT>MBZ=BZ.

Polarizability (α) indicates the polarity of a molecule, which is a good reactivity indicator [8]. It is the ease of distortion of the electron cloud of a molecule by electric field. The larger the value of polarizability, the greater the possibility of the molecule to change its original shape and the better the tendency of the molecule to be adsorbed on the metal surface. Eddy et al 2009 [16] reported that induced dipole moment is proportional to polarizability. Various attempts have been made to relate the polarizability of some corrosion inhibitors to their inhibition efficiency. Arslan et al. [14] reported that the minimum polarizability principle (MPP) expects that the natural direction of evolution of any system be toward a state of minimum polarizability. The obtained polarizability values for benzoxazole and its derivatives as shown in Table 2 suggest that increasing inhibition efficiencies of the inhibitors corresponds to increasing polarizability. PBZ has the highest polarizability value and from all parameters so far analyzed stands out as the most efficient inhibitor.

The number of electrons transferred (ΔN)) was also calculated and tabulated in Table 2. It was observed from Table 2 that the entire molecules studied have values of $\Delta N < 3.6$. Lukovits et al. [15] in their study proposed that if $\Delta N < 3.6$, the inhibition efficiency increases along with the increasing electron donating ability of the inhibitor at the metal surface. Also it was observed that the higher the value of ΔN, the greater the tendency of a molecule to donate electrons to the electron poor species. In the case of corrosion inhibitors, a higher ΔN implies a greater tendency to interact with the metal surface (i.e., a greater tendency to adsorb on the metal surface). Values of ΔN for the inhibitors

show that PBZ has the highest. This value correlates strongly with experimental inhibition efficiencies. Thus, the highest fraction of electrons transferred is associated with the most efficient inhibitor being PBZ in this case.

Selectivity descriptor

Selectivity descriptors indicate the regions of a molecule that are likely to interact with the metal surface. Some of these parameters include the Mulliken atomic charges, the condensed Fukui functions, and the local softness indices. The atom with the highest negative partial atomic charge interacts strongly with the metal surface through a donor-acceptor type of interaction since it represents the site with the highest electron density. Table 3 shows the Mulliken atomic charges on the atoms of the studied compounds. In all the compounds, the highest negative charge is on the heteroatoms mainly because these atoms have lone pair of electrons. These lone pair of electrons could be donated to the vacant s or partially filled d orbitals of the metal and thereby facilitate the adsorption of the inhibitor on the metal surface. The result shows that N and O atoms (especially N1 and O1) have the highest negative charge; the S atom in NBZ is electron deficient and the benzene rings in all the compounds have delocalization of slightly negative charge on its atoms. This result suggests that the N and O atoms in all the structures are possible sites for adsorption by the inhibitor on the metal surface [17].

Table 3. The Mulliken atomic charges on the atoms of the studied molecules

Compounds	Atom numbering and corresponding Mulliken atomic charges[a]									
	O1	N1	S1	C1	C2	C3	C4	C5	C6	C7
BZ	-0.465	-0.463	-	-0.165	0.228	0.324	-0.178	-0.144	-0.144	0.361
MBZ	-0.501	-0.505	-	-0.111	0.215	0.311	-0.123	-0.101	-0.100	0.488
NBZ	-0.459	-0.460	-	-0.169	0.254	0.328	-0.207	0.263	-0.169	0.269
BZT	-0.486	-0.484	0.048	-0.167	0.233	0.319	-0.178	-0.145	-0.143	0.311
PBZ	-0.529	-0.542	-	-0.173	0.251	0.336	-0.186	-0.145	-0.143	0.486

[a]Atomic numbering for individual molecules shown in Fig. 1

Conclusion

From the results and findings of this study, the following conclusions were made, BZ, MBZ, NBZ, BZT and PBZ are excellent corrosion inhibitors for the corrosion of mild steel in acidic medium.

The experimental inhibition efficiencies are closely related to the quantum chemical parameters such as $E_{\mathbf{HOMO}}$, η, ΔN, α and ΔE .

Comparing the PBZ with the other inhibitors, it exhibits a better electrophilic character; the highest $E_{\mathbf{HOMO}}$, hence its good ability as an electron-donor. The MBZ has the largest hardness and therefore a favorable back-donation charge.

Quantum chemical calculations on the Fe-inhibitor complex also reveal that PBZ tends to form the most stable complex and therefore as an inhibitor has the highest tendency to adsorb strongly onto the metal surface. The frontier orbitals electron density distributions, together with the Mulikan charge distribution , predict that all species studied possess more than one attack center which enables multicenter adsorption of the inhibitor molecules on a metal surface.

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