

Quantum Chemical Calculations on Some Substituted Benzothiazole Derivatives as Corrosion Inhibitors for Brass in Acidic Media

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Abstract: Gas phase and aqueous phase quantum chemical calculations for the inhibition efficiency of some substituted Benzothiazole (BTH) and its 2-methyl (MeBTH), 2-amino (ABTH), 2-mercapto (MBTH) and 2-phenyl (PhBTH) as corrosion inhibitors for brass in HClO₄ were investigated by means of the AM1, PM6, MNDO and RM1 semi-empirical SCF molecular orbital methods. The calculated quantum chemical parameters correlated to the inhibition efficiency are, E_{HOMO}, E_{LUMO}, energy of the gap (ΔE) and other parameters. The calculated results are in agreement with the experimental data.

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1. Introduction

The use of inhibitors is one of the most practical methods to protect metals against corrosion, especially in acidic media [1]. Most efficient inhibitors are organic compounds containing electronegative functional groups and π -electrons in triple or conjugated double bonds. The remarkable inhibitory effect is reinforced by the presence of heteroatom such as sulphur, nitrogen and oxygen in the ring which facilitates its adsorption on the metal surface following the sequence O < N < S [2]. Researchers conclude that the adsorption on the metal surface depends mainly on the physicochemical properties of the inhibitor group, such as the functional group, molecular electronic structure, electronic density at the donor atom, π orbital character and the molecular size [3-5]. The reaction mechanism includes the transfer of one pair of electrons from the organic compound, and the formation of the coordinate covalent bond with metal or an alloy [6]. Under such conditions, for a given metal, the efficiency of the inhibitor depends on the stability of the formed chelate and the inhibitor molecule should have centers, which are capable of forming bonds with metal surface via the electron transfer. In this way the metal acts as an electrophile, whereas the inhibitor molecule acts as a Lewis base, whose nucleophile centers are normally hetero atoms with free electron pairs which are readily available for the sharing to form a bond.

Quantum chemical calculations have been widely used to study reaction mechanisms. They have also proved to be a very powerful tool for studying corrosion inhibition mechanisms [7].

Recently, theoretical prediction of the efficiency of corrosion inhibitors has become very popular in parallel with the progress in computational hardware and the development of efficient algorithms which assisted the routine development of molecular quantum mechanical calculations [8]. The semi-empirical methods of calculation have been used in most successfully completed studies in which the calculated quantum chemical properties are used enables the correlation of the obtained data with inhibitor efficiency [9] and [10]. The electronic properties of the inhibitors, the effect of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, the difference between highest occupied molecular orbital and lowest unoccupied molecular orbital energies (E_{LUMO}-E_{HOMO}), charge on the reactive center, dipole moments had to be investigated to achieve the appropriate correlation [9] and [10].

Benzothiazoles have been used as corrosion inhibitors for steel [11],[12] and [13] copper[14] and [15] and brass[16], but the studies on corrosion of zinc are sparse. Chia and Lin [17] used benzothiazole and mercaptobenzthiazole to copper corrosion inhibitor. Thiazole derivatives proved to be effective in protecting copper corrosion in acidic sulfate containing medium [18].

The aim of this work is to investigate the applicability of quantum chemical calculations, to predict inhibition efficiencies of some benzothiazole derivatives for the inhibition of brass in perchloric acid in gas phase and in aqueous phase from the data presented by Taha K. K. and co-workers [19] to predict the mechanism of the corrosion process.

2. Method of calculations

Theoretical calculations were carried out by using AM1, PM6, MNDO and RM1 semi-empirical methods in MOPAC2007 program, implemented on an Intel Pentium (R) 1.86 GB personal computer. Initial estimates for the geometries of all the structures were obtained by molecular mechanics program (ACD11) for Widows, followed by full optimization of all geometrical variables (bond lengths, bond angles and dihedral angles), without

any symmetry constraint, using the above mention semi-empirical methods in gas phase and in aqueous phase.

3. Results and Discussion

The chemical structures of the compounds under investigation are presented in figure 1. The optimized molecular structures of the studied molecules using semi-empirical methods are shown in Figure 2.

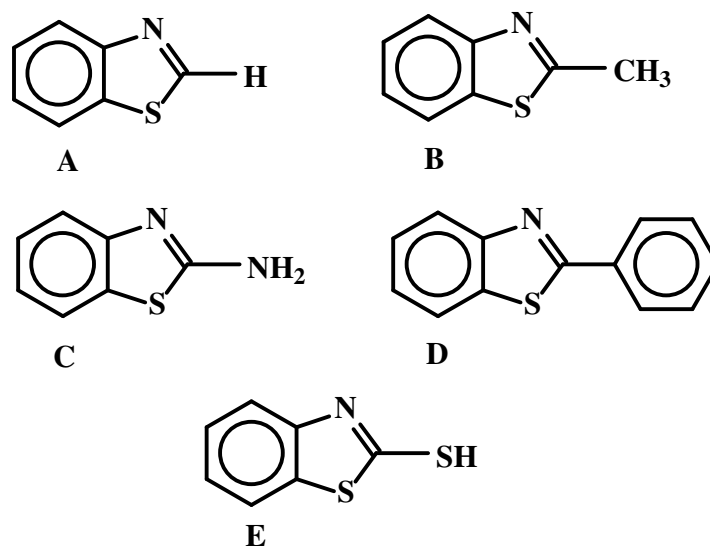


Figure 1. Chemical Structure of Studied Benzothiazoles Derivatives: Benzothiazole (BTH) (A), 2-methyl-benzothiazole (MeBTH) (B), 2-amino-benzothiazole (ABTH) (C), 2-phenyl-benzothiazole (PhBTH) (D), 2-mercapto-benzothiazole (MBTH) (E).

The calculated quantum chemical indices E_{HOMO} , E_{LUMO} , $E_{\text{L}}-E_{\text{H}}$, charge on nitrogen atoms, dipole moment, ionization potential in aqueous phase and in gaseous phase and inhibition efficiencies obtained from the experimental measurements are given in Table 1 and Table 2. It has been proven that local electron densities or charges are important in many chemical reaction and physicochemical properties of compounds [20]. Inhibition action of organic molecules can be explained by the adsorption on metal surface. Since the surface of the brass is positively charged in acidic solution [19], Table 1 and Table 2 show that all nitrogen atoms of benzothiazole derivatives carry the negative charges, this indicate that these atoms are the negative charge centers which could offer electrons to the brass surface to form a coordination type of bond. Another important point to be considered in the energy level terms is gap between the HOMO and LUMO energies for the studies molecules (1-5). Cherry *et al.* [21] have used the concept of LUMO-HOMO energy gap in developing theoretical models which capable of explaining the structure and conformation barriers in many molecular

systems qualitatively. Low absolute values of the energy band gap (ΔE) gives good inhibition efficiencies, because the energy to remove an electron from the last occupied orbital will be low [22]. According to the data in Table 1, AM1 method give good correlation in LUMO- HOMO energy gap in aqueous phase, it can be seen that 2-mercapto-benzothiazole (MBTH) is best inhibitor and has smallest LUMO- HOMO gap (i.e 7.987 eV) but the benzothiazole (BTH) which is least inhibitor and has highest LUMO- HOMO gap (i.e 8.478 eV). Thus the difference between the LUMO- HOMO of the MBTH and LUMO- HOMO of BTH of 0.491 eV caused an inhibition increase to 33.1%. As can be seen from Table 1 for AM1 calculations, the inhibition efficiencies increases as the $E_{\text{L}}-E_{\text{H}}$ values decrease, which indicates the stability of formed complexes between benzothiazole derivatives and brass in perchloric acid media, i.e the order of inhibition efficiencies as follows: MBTH> PhBTH> ABTH> MeBTH> BTH as can be obtained from experimental data [19]. This indicates that the best correlations between experimental and inhibition efficiencies were obtained using AM1 for both

aqueous phase and gaseous phase calculations for benzothiazole derivatives, correlations are almost in the same order (Figure 3). Correlation coefficient greater than 60% were well accepted in quantum chemical calculations of corrosion studies [23]. The high inhibition efficiency in MBTH is due to the presence of other hetero-atom S which has excess free lone pair of electrons able to bond with brass.

MBTH is known to form a thin polymeric film [24] on Cu forming a complex of the type $[\text{Cu}(\text{I})\text{MBTH}]_n$, thus yielding high inhibitor efficiency, the high inhibition efficiency of MBTH may also be attributed to a similar type of a thin polymeric complex film formed with MBTH and Cu(I) and Zn(I) species.

High inhibition efficiency of PhBTH is due to the presence of phenyl ring which has sites susceptible to the electrophilic attack as well as high HOMO energy and low ΔE . In the case of ABTH the lone pair of electrons of the "N" atom of the amino group attached

to the thiazole ring provides an additional anchoring site for the inhibitor to bind with the metal surface thereby increasing the strength of adsorption and hence the inhibition. The introduction of methyl group in MeBTH relatively enhanced inhibitor efficiency when compared with BTH due to the inductive effect of the methyl group [25] in position 2 in the thiazole ring.

High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbital. Increasing values of the E_{HOMO} facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer [22]. The results obtained by AM1 method in gas phase [table 2] show that MBTH has highest HOMO energy ($E_{\text{HOMO}} = -8.694$ eV), lower dipole moment (0.92 D), lower ionization potential (8.643 eV) among the studied molecules, and BTH has low HOMO energy ($E_{\text{HOMO}} = -8.980$ eV) and higher ionization potential (8.980 eV).

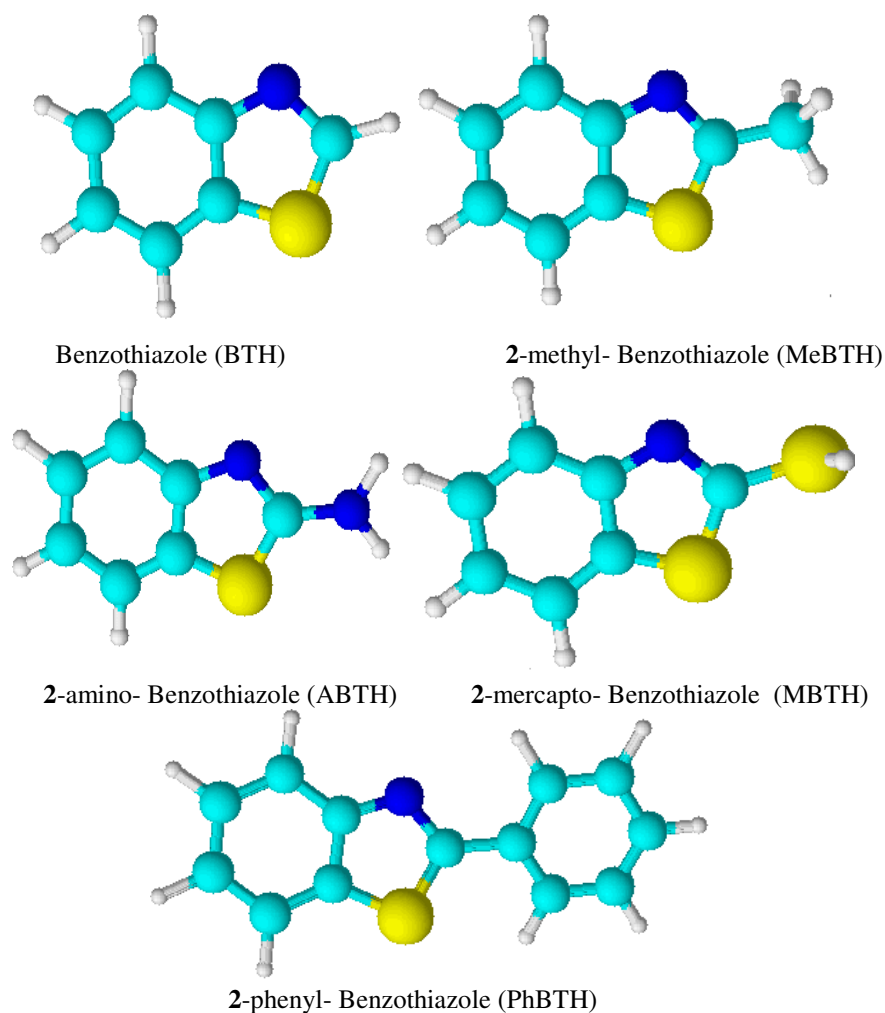


Figure 2. The Optimized Structure of Benzothiazole and its Derivatives

Table 1. Aqueous Phase AM1, PM6, MNDO and RM1 Data for Benzothiazole Derivatives (1-5)

Inhibitor	E_{LUMO} (eV)	E_{HOMO} (eV)	E_L-E_H (eV)	Charge on nitrogen	Dipole Moment (D)	Ionization Potential (eV)	% Inhibition in 0.1M HClO ₄
AM1							
1 BTH	-0.603	-9.081	8.478	-0.1713	2.501	9.080	64.8
2 MeBTH	-0.658	-9.086	8.428	-0.1776	2.276	9.086	84.7
3 ABTH	-0.330	-8.692	8.362	-0.3096	3.518	8.692	86.0
4 PhBTH	-0.997	-9.105	8.108	-0.1595	2.282	9.104	94.8
5 MBTH	-0.846	-8.833	7.987	-0.1776	1.359	8.633	97.9
RM1							
1 BTH	-0.483	-9.129	8.646	-0.2834	2.218	9.129	64.8
2 MeBTH	-0.495	-9.143	8.648	-0.3038	1.964	9.143	84.7
3 ABTH	-0.155	-8.661	8.506	-0.4395	2.068	8.661	86.0
4 PhBTH	-0.766	-9.156	8.390	-0.2880	1.897	9.156	94.8
5 MBTH	-0.679	-9.078	8.399	-0.2857	1.874	9.077	97.9
PM6							
1 BTH	-0.890	-9.365	8.475	-0.3492	1.964	9.365	64.8
2 MeBTH	-0.813	-9.398	8.585	-0.4234	1.118	9.398	84.7
3 ABTH	-0.687	-8.995	8.308	-0.5583	2.880	8.995	86.0
4 PhBTH	-1.228	-9.394	8.166	-0.3748	1.030	9.393	94.8
5 MBTH	-1.200	-9.398	8.198	-0.3208	2.972	9.397	97.9
MNDO							
1 BTH	-0.658	-9.226	8.568	-0.2526	1.924	9.226	64.8
2 MeBTH	-0.755	-9.225	8.470	-0.2403	1.841	9.225	84.7
3 ABTH	-0.365	-8.701	8.336	-0.3864	2.969	8.701	86.0
4 PhBTH	-0.980	-9.079	8.099	-0.2453	1.442	9.079	94.8
5 MBTH	-0.863	-9.122	8.259	-0.2482	1.686	9.122	97.9

% Inhibition are taken from reference [19]

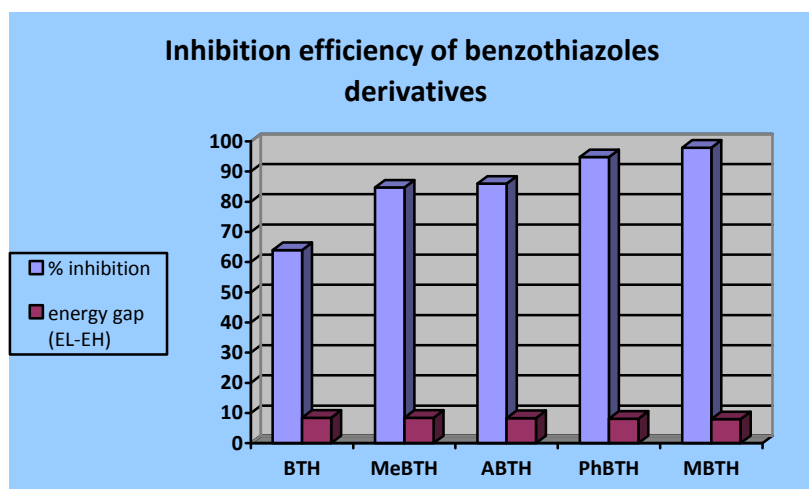


Figure 3. The Relation Between The Energy of The Gap and The Inhibition Efficiency of Benzothiazoles Derivatives.

Table 2. Gas Phase AM1, PM6, MNDO and RM1 Data for Benzothiazole Derivatives (1-5)

Inhibitor	E _{LUMO} (eV)	E _{HOMO} (eV)	E _L -E _H (eV)	Charge on nitrogen	Dipole Moment (D)	Ionization Potential (eV)	% Inhibition in 0.1M HClO ₄
AM1							
1 BTH	-0.482	-8.980	8.498	-0.0897	1.557	8.980	64.8
2 MeBTH	-0.453	-8.911	8.458	-0.0999	1.299	8.910	84.7
3 ABTH	-0.338	-8.830	8.492	-0.1677	1.728	8.830	86.0
4 PhBTH	-0.809	-8.908	8.099	-0.0975	1.179	8.908	94.8
5 MBTH	-0.665	-8.694	8.029	-0.1193	0.920	8.643	97.9
RM1							
1 BTH	-0.380	-9.062	8.682	-0.2100	1.458	9.061	64.8
2 MeBTH	-0.311	-9.002	8.691	-0.2295	1.156	9.001	84.7
3 ABTH	-0.034	-8.532	8.498	-0.3334	2.047	8.532	86.0
4 PhBTH	-0.579	-8.984	8.405	-0.2287	1.028	8.983	94.8
5 MBTH	-0.577	-8.958	8.441	-0.2287	1.278	8.957	97.9
PM6							
1 BTH	-0.788	-9.161	8.373	-0.2617	1.551	9.160	64.8
2 MeBTH	-0.590	-9.058	8.468	-0.3301	0.976	9.058	84.7
3 ABTH	-0.497	-8.873	8.376	-0.4190	1.794	8.873	86.0
4 PhBTH	-0.947	-9.074	8.127	-0.3003	0.966	9.043	94.8
5 MBTH	-0.918	-9.031	8.113	-0.3096	1.210	9.030	97.9
MNDO							
1 BTH	-0.627	-9.201	8.574	-0.1739	1.335	9.201	64.8
2 MeBTH	-0.663	-9.166	8.503	-0.1675	1.163	9.163	84.7
3 ABTH	-0.556	-8.980	8.424	-0.2294	1.557	8.980	86.0
4 PhBTH	-0.614	-9.138	8.519	-0.1627	0.997	9.137	94.8
5 MBTH	-0.799	-9.070	8.271	-0.1946	1.292	9.069	97.9

% Inhibition are taken from reference [19]

4. Conclusions

Through semi-empirical calculations a correlation between parameters related to structure of some benzothiazoles derivatives and their ability to inhibit the corrosion process could be established. The highest occupied molecular orbital energy levels and energy gaps calculated by AM1 and RM1 in aqueous phase and in gas phase show reasonably good correlation as compared to the other calculated data. Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the method employed here.

Supplementary Information

Supplementary information (output results of semi-empirical calculations) is available free of charge, on correspondence to the author on request.

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