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Ab- initio quantum chemical study of semicarbazide and 4-phenylsemicarbazide on mild steel surface as two anti corrosion inhibitors

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Abstract : Quantum chemical methods are becoming ever more prevalent for assessing surface interactions semicarbazid (SC) and 4-phenylsemicarbazide (4-PSC). The quantum chemical calculations have been performed by using DFT, *ab-initio* molecular orbital and semi-empirical methods for SC and 4-PSC being corrosion inhibitors and its comparison with that available experimental data. Interaction energies of these compounds on the surface or iron are calculated in hydrochloric acid medium by using quantum chemical calculations at DFT level. All calculations have been performed using the Gaussian 03W suite of programs. It was found that theoretical data support experimental results. The highest occupied molecular orbital energy (E_{HOMO}), low-

est unoccupied molecular orbital energy (E_{LUMO}), the energy gap between E_{HOMO} and E_{LUMO} ($\Delta E_{\text{HOMO-LUMO}}$), dipole moments (μ), charges on the O and N atoms, the total energies of the molecules. The results of quantum chemical calculations and experimental efficiencies of inhibitors were subjected to correlation analysis. We have reached the conclusion that the synthesis of better corrosion inhibitors can be achieved by controlling all electronic properties and parameters of a selected group of molecules. © Global Scientific Inc.

Keywords : DFT; Ab initio; Corrosion inhibitors; Semi-empirical calculation; Semicarbazide; 4-phenylsemicarbazid.

INTRODUCTION

Mild steel, also called plain-carbon steel, is the most common form of steel because its price is relatively low while it provides material properties that are acceptable for many applications, more so than iron.

Low carbon steel contains approximately 0.05–0.15% carbon and mild steel contains 0.16–0.29%^[1] carbon; making it malleable and ductile. Mild steel has a relatively low tensile strength, but it is cheap and malleable; surface hardness can be increased through carburizing^[1].

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Schiff bases, named after Hugo Schiff^[2], are formed when any primary amine reacts with an aldehyde or a ketone under specific conditions. Structurally, a Schiff base (also known as imine or azomethine) (Figure 1) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine group (Figure 1).

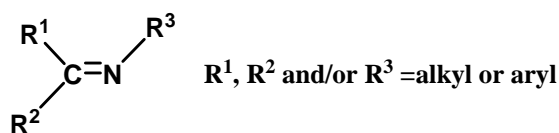


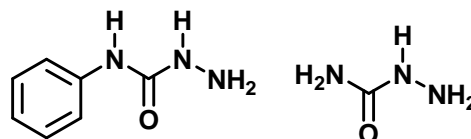
Figure 1 : General structure of a Schiff base compound

Schiff bases are some of the most widely used organic compounds. They are used as pigments and dyes, catalysts, intermediates in organic synthesis, and as polymer stabilizers^[3]. Schiff bases have also been shown to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties^[4-7].

In the other hand, organic substances have been used extensively as corrosion inhibitors during the last four decades. Of these, Schiff base compounds containing one or more N, O and S atoms can effect the inhibition of corrosion, in aqueous acid solutions, of metals^[8-14]. The effects of concentrations and functional groups on the corrosion of iron and steel have been studied^[14-17]. The inhibition efficiency of semicarbazid (SC) and 4-phenylsemicarbazide (4-PSC) on the corrosion inhibition of mild steel in acid media has been studied^[18]. The efficiency of an inhibitor does not only depend on its structure, but also on the characteristics of the environment in which it acts the nature of the metal and the other experimental conditions. Under certain condition, the electronic structure of the organic inhibitors has a key influence on the corrosion inhibition efficiency to the metal.

A lot of work on Schiff base inhibitors has been studied experimentally^[19-22]. However, its theoretical study is fewer relatively^[23-25]. Hence, it is necessary and significant to research corrosion mechanism and influence of the substituent on inhibition efficiency. Quantum chemical calculation has been widely used to study reaction mechanism and to interpret the experimental results as well as to resolve chemical ambiguities. Our

paper concerns the calculation of chemical adsorption energy between semicarbazid (SC) and 4-phenylsemicarbazide (4-PSC) and the Fe atom by quantum chemical methods, and the purpose of this paper is to provide information for the electron configuration of two Schiff base compounds by the quantum chemical calculation and to seek the relationship between molecular structures inhibition efficiency.

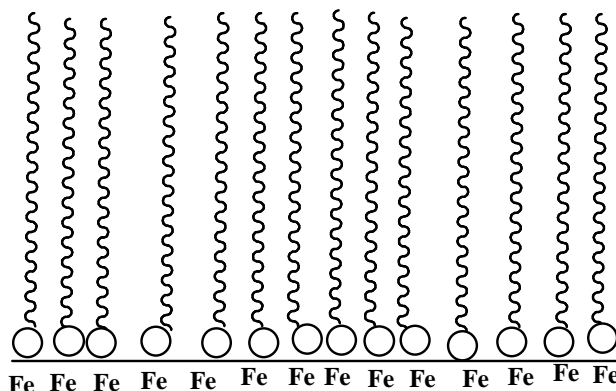


4-phenylsemicarbazide Semicarbazide

Scheme 1 : The structure of semicarbazide (SC) and 4-phenylsemicarbazide (4-PSC) compounds

COMPUTATIONAL MODEL AND METHODS

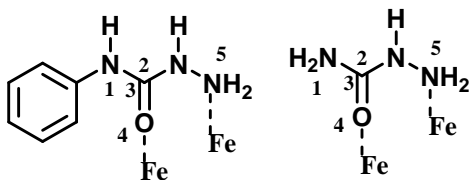
Theoretical calculations have become a powerful tool for clarifying the mechanism of selective capture and transportation of metal ions by ligands^[26,27]. In this model the view of film formulation mechanism, the adsorption model of the inhibitors on metal surface can be described in Scheme 2.



Scheme 2 : The adsorption model of the inhibitor on Fe surface

In this work we can only focus chemical adsorption of one single molecule on the Fe atom and therefore a model of chemical adsorption of SC or 4-PSC molecule on Fe atom can simulated as Scheme 3. The coordination sites for these compounds are N (5) and O (4).

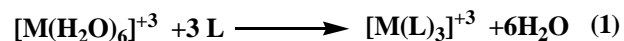
We have obtained molecular geometry, charge density, dipole moments and the other of structural



Scheme 3 : Model of chemical adsorption for SC or 4-PSC molecules on Fe surface

properties for SC and 4-PSC compounds by DFT calculation in gas phase. Density functional theory (DFT) calculations are performed to predict the host-guest interactions between the $[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$ and two Schiff bases. In the present work, to explicitly display the hydration of metal cation as six-coordination complex and ligands as the following equations are used to compute

the relative binding energies.



And ΔE or binding energy for this equation is:

$$E[\text{M}(\text{L})_3]^{+3} + 6E(\text{H}_2\text{O}) - E[\text{M}(\text{H}_2\text{O})_6]^{+3} - 3E[\text{L}] \quad (2)$$

TABLE 1 summarized the important calculated structural properties of SC and 4-PSC molecules. All the geometries including the reactions and products of the reaction are fully optimized using the B3LYP exchange correlation functional^[28,29]. All calculations were carried out with the GAUSSIAN 03 package^[30]. The geometry of both complexes were fully optimized in gas phase using 6-31 + G(d,p) basis set for H, C, N and O atoms and Lan12dz basis set for Fe without any symmetry constrain. TABLE 2 shows all energy calculations.

TABLE 1 : Some of DFT calculated structural properties for SC and 4-PSC compounds in the gas phase

Compound	M.W (g/mol)	Dipole moment (deby)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	Net atomic charge on two coordination sites	
						N(5)	O(4)
SC	75	4.6615	-0.2639	-0.0262	0.2377	-0.5030	-0.4051
4-PSC	151	5.1361	-0.3384	0.0710	0.2594	-0.8460	-0.7290

TABLE 2 : Energy calculations of $[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$, $[\text{Fe}(\text{L})_3]^{+3}$ and ΔE (calculated binding energy)

$E_{\text{SC(a.u.)}}$	$E_{\text{4-PSC(a.u.)}}$	$E_{[\text{Fe}(\text{H}_2\text{O})_6]^{+3}(\text{a.u.})}$	$E_{\text{H}_2\text{O}(\text{a.u.})}$	$E_{\text{A}(\text{a.u.})}$	$E_{\text{B}(\text{a.u.})}$	$\Delta E_1(\text{a.u.})$	$\Delta E_2(\text{a.u.})$
-280.6858	-505.7474	-1698.5243	-75.6193	-2104.5643	-2797.6824	-17.8084	-35.6317

$\text{A}=[\text{Fe}(\text{SC})_3]^{+3}$, $\text{B}=[\text{Fe}(\text{4-PSC})_3]^{+3}$ and ΔE_1 = binding energy calculated of (2) equation for SC ligand and ΔE_2 = binding energy calculated of (2) equation for 4-PSC ligand.

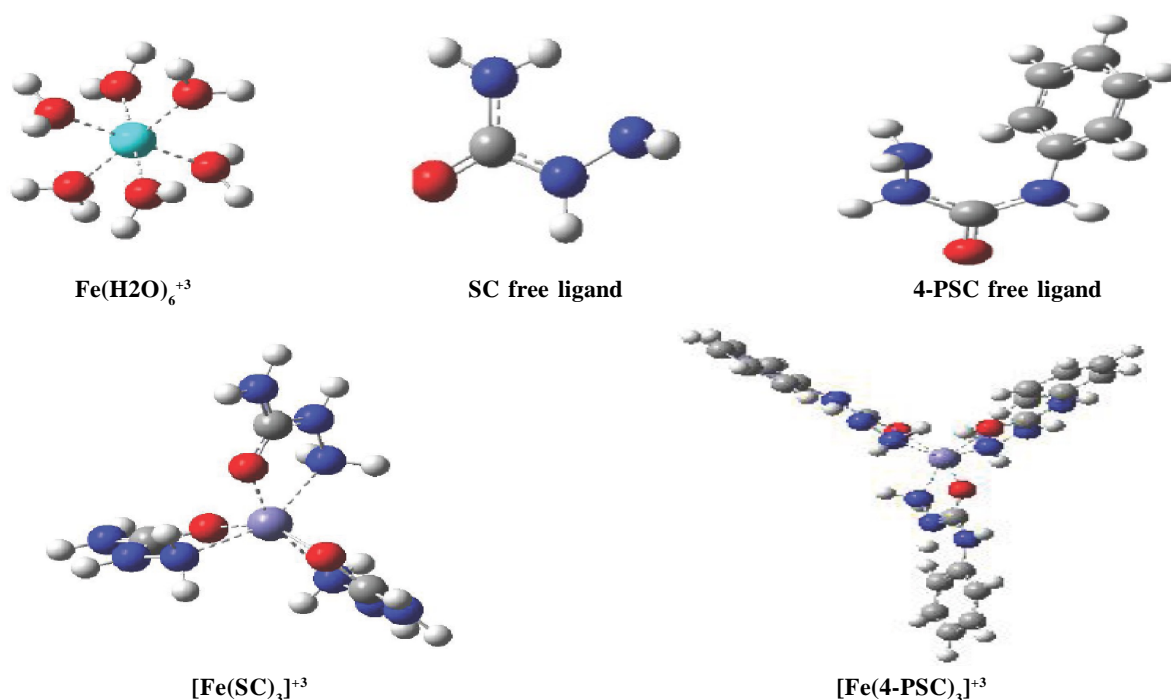


Figure 2 : Shows all optimized geometries for hydrated Fe cation, free two ligands SC and 4-PSC, two metal complex of Fe (III) with these ligands and Fe (III) ion is as a six-coordinated cation.

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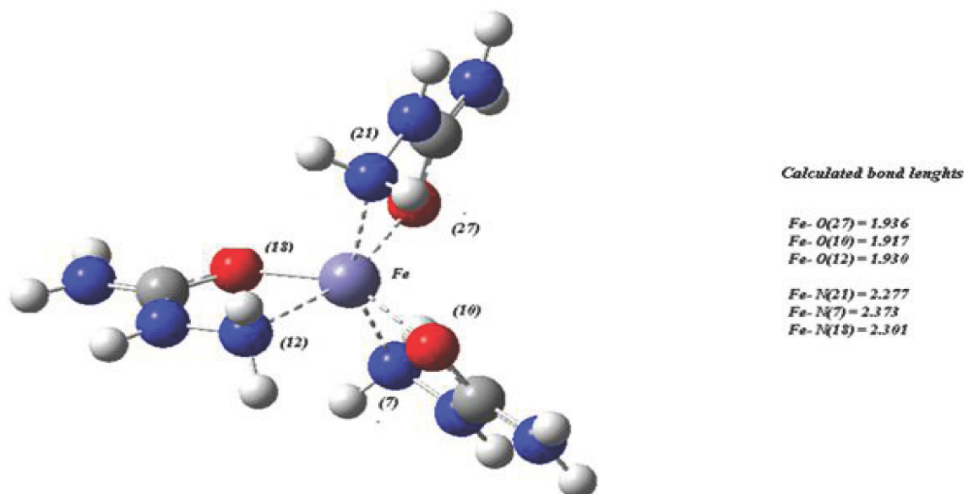


Figure 3 : The geometries optimized at the B3LYP/Lanel 2DZP level of theory of $[\text{Fe}(\text{SC})_3]^{+3}$ ion complex with some important bond lengths

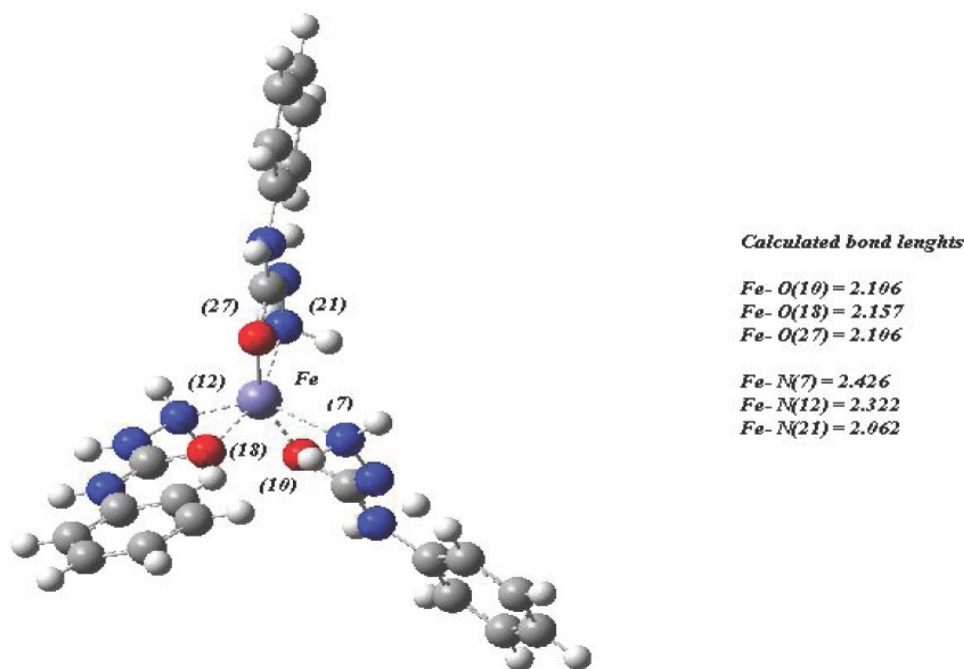


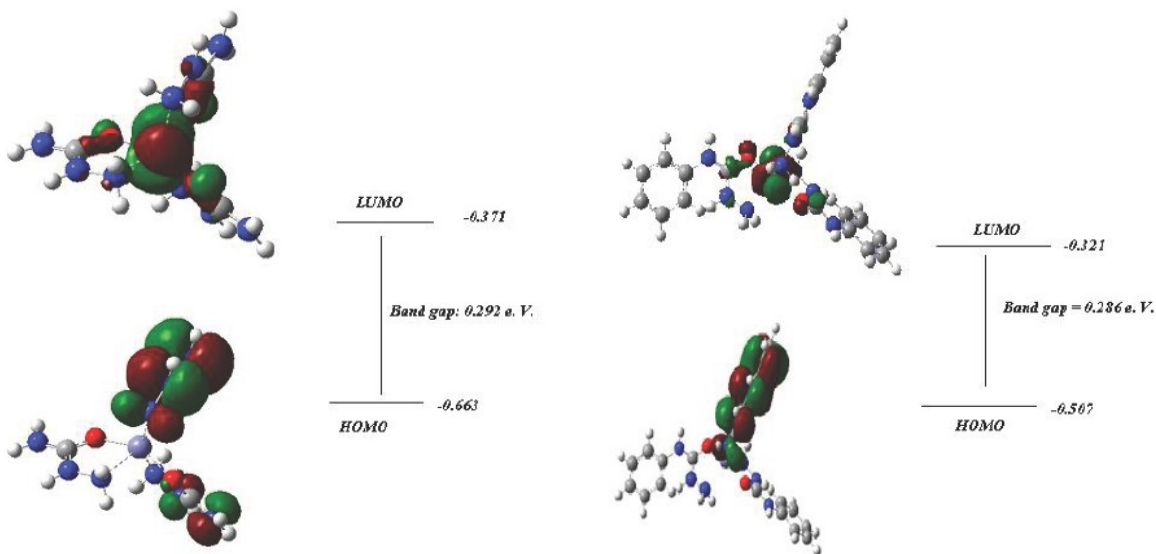
Figure 4 : The geometries optimized at the B3LYP/Lanel 2DZP level of theory of $[\text{Fe}(4\text{-PSC})_3]^{+3}$ ion complex with some important bond lengths

CONCLUSION AND RESULTS

TABLE 1 show the higher negative charge on coordination sites of SC and 4-PSC ($\text{N}5 = -0.5030$, $\text{O}4 = -0.4051$ for SC ligand and $\text{N}5 = -0.8460$, $\text{O}5 = -0.7290$ for 4-PSC ligand), the higher of the HOMO energy and the lower of the LUMO energy provide the higher inhibition efficiency of the inhibitor for metal surface. In the TABLE 1 and TABLE 2 the calculated values for binding energy for two inhibitors are represented. These

results suggest the following conclusions:

In the second inhibitor (4-PSC) the negative charge density on the coordination sites $\text{O}(4)$, -0.8460 eV and $\text{N}(5)$, -0.7290 eV are bigger than the other compound (-0.5030 eV and -0.4051 eV), so 4-PSC complex with Fe(III) cation $[\text{Fe}(4\text{-PSC})_3]^{+3}$ is more stable than the other complex $[\text{Fe}(\text{SC})_3]^{+3}$, TABLE 2 shows the $\text{Fe}(4\text{-PSC})_3$ complex is more stable than the other complex see ΔE_1 and ΔE_2 in this table. In general big negative charge on the adsorption's centers of 4-PSC molecule and big stabilization energy giving rise to an increase in

HOMO and LUMO molecular orbital levels for Fe(SC)₃ complex ionHOMO and LUMO molecular orbital levels for Fe(4-PSC)₃ complex ion**Figure 5 : HOMO, LUMO molecular orbitals and HOMO-LUMO gap for two Fe complexes**

the in The calculated binding energies of Fe (II) metal ion to the SC and 4-PSC ligands are given in TABLE 2. As expected, the Fe(III) cation with more positive charges have stronger interaction with the 4-PSC ligand in gas phase leading to higher values of binding energies (-35.6317). However, this cation has strong interactions with the other Sc ligand (-17.8084).

HOMO and LUMO energy gaps indicate the stability of the compound. The molecular orbital with the highest HOMO and lowest LUMO contours for complex are drawn in Figure 3. These figures show that the HOMO is located mainly on the ligand but the role of ligand orbitals in LUMO reduced and Fe metal center have a significant percentage for constructing the LUMO and higher MOs.

Generally in this study we saw a good agreement between theoretical and experimental data. 4-Phenylsemicarbazide (4PSC) and semicarbazide (SC) actually have very significant effects on the corrosion of mild steel in hydrochloric acid. 4PSC and SC tend to inhibit the corrosion of mild steel in hydrochloric acid to a remarkable extent, with 4PSC exhibiting a higher maximum inhibition efficiency (82%) than that of SC (66%)^[18].

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