

Quantum Mechanical Study of Some 2-Mercaptobenzimidazole Derivatives as Corrosion Inhibitors for Carbon/Mild Steel in Acidic Medium

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Abstract

In this work some of 2-mercaptobenzimidazole derivatives have been theoretically studied to prove their ability as corrosion inhibitors; Gaussian 09W program packages and its visualization interface program GaussView 5.0 have been used. Density Functional Theory (*DFT*) with basis set of 6-311G (d,p) / hybrid function of *B3LYP* has been used in all calculations. This work included simulation of these derivatives in three different mediums; gas phase, aqueous and acidic medium. Some parameters have been calculated such E_{HOMO} , E_{LUMO} , $\Delta E_{\text{L-H}}$, Electron Affinity (A), Ionization Potential (I), electronegativity (χ), Global Hardness (η), Total Negative Charges TNC, Dipole Moment (μ) and Fraction of Electron Transferred from Inhibitor Molecules to the Metallic Atoms (ΔN), all these parameters proved behaviors of these compounds as corrosion inhibitors for carbon steel, so these derivatives can be considered as corrosion inhibitors.

Introduction

The studied compounds have previously synthesized (Al-Jeilawi, 2013). One of important things is how to prevent of metals from corrosion (Obi-Egbedi *et al.*, 2011) because of the fact that corrosion means economic losses (Sayin and Karakaş, 2013). Corrosion that causes by acidic effects can be inhibited by heterocyclic compounds (El Adnani *et al.*, 2013) or aromatic systems (Mert *et al.*, 2011; Bahramia *et al.*, 2010) which containing nitrogen, oxygen and sulfur atoms (Mamosemh *et al.*, 2013; Khamis *et al.*, 2013; El Ashry *et al.*, 2006); This fact is due to interaction that done between these atoms and surface atoms of metals which based on donation of electrons such lone pairs (El Adnani *et al.*, 2013). The action of organic inhibitors is based on formation of a layer of inhibitor molecules that cover metal surface, this layer will adsorbed chemically or physically by metal surface atoms (Ebenso *et al.*, 2010), the adsorption is due to transfers of electrons from inhibitor molecules to atoms of metal (Eddy *et al.*, 2011), electrons transfer could done from p-orbitals of inhibitors to d-orbitals of metal atoms (Mert *et al.*, 2011).

Density functional theory (*DFT*) (Hohenberg and Kohn, 1964; Salahub and Zerner, 1989) is considered as an efficient quantum mechanical tool that used to obtain system electronic properties, large calculations for chemical systems can be done by *DFT* (Song *et al.*, 2011) with good agreements with experimental results (Hernández *et al.*, 2011), *DFT* can also study and explain corrosion and it has wide usages to estimate efficiency of corrosion inhibition (Gece and Bilgiç, 2010), the fact that *DFT* requires less computational requirements with less time of calculations made

this method more preferable than other methods (Obot and Obi-Egbedi, 2010); so, this method has used in all calculations of this work.

Computational method and theoretical parameters

GaussView 5.0.8 program package (Dennington II *et al.*, 2009) with Gaussian 09W Revision-A.02 (Frisch *et al.*, 2009) have used in all calculations, the calculations have included geometry optimization for compounds that shown in figure (1) by using DFT with basis set of 6-311G (d,p) (McLean and Chandler, 1980) and hybrid functional of Becke three-parameters Lee, Yang and Parr (B3LYP) (Becke,1993). Three calculations have been done for each molecule (I1-I5) ; for gas phase, aqueous and acidic medium. Several parameters have obtained for each calculation such E_{HOMO} (energy of highest occupied molecular orbital), E_{LUMO} (energy of lowest unoccupied molecular orbital) and $\Delta E_{\text{L-H}}$ (energy difference between them), electron donation can be represented by E_{HOMO} which indicate for donation of electrons for each molecules, the inhibitor molecule has good ability to make binds with metal surface when E_{HOMO} is high, this led to good electron donating. In the other hand; when E_{LUMO} is small this led to small energy gap ($\Delta E_{\text{L-H}}$); so, donation between orbitals of inhibitor molecules and metal surface orbitals will be easy, and high adsorption will be done (Mert *et al.*, 2011). Total negative charge (TNC) is another parameter have also obtained and calculated, TNC that calculated according to Mulliken (Mulliken, 1955) indicates for adsorption centers in inhibitor molecules, high adsorption of inhibitor on metal surface will be happened when high value of TNC.

Some other parameters such electron Affinity (A), ionization Potential (I), global hardness (η), electronegativity (χ), softness (ρ) and fraction of electron transferred from inhibitor molecules to the metallic atom (ΔN) which a parameter determine amounts of transferred electrons from molecules of inhibitor to metal atoms (Gece and Bilgiç, 2010). have been calculated by using equations (1) to (6) (Ebenso *et al.*, 2010; Musaa *et al.*, 2012).

$$A = -E_{\text{LUMO}} \quad \dots (1)$$

$$I = -E_{\text{HOMO}} \quad \dots (2)$$

$$\eta = (I-A)/2 \quad \dots (3)$$

$$\chi = (I+A)/2 \quad \dots (4)$$

$$\rho = 1/\eta \quad \dots (5)$$

$$\Delta N = [\chi_{\text{Fe}} - \chi_{\text{inh}}]/[2 (\eta_{\text{Fe}} + \eta_{\text{inh}})] \quad \dots (6)$$

Where χ_{Fe} and η_{Fe} are 7 and 0 respectively (Gece and Bilgiç, 2010).

Results and discussion

E_{HOMO} and E_{LUMO} have played a major role in electron transfers in any molecule. Energy gap $\Delta E_{\text{L-H}}$ is the deference in energy between E_{LUMO} and E_{HOMO} , from results (table (1)) $\Delta E_{\text{L-H}}$ for any compounds of I1-I5 has slightly increased when the medium changed from gas phase to aqueous medium; and decrease in energy gap has happened when the compound putted in acidic medium, so the minimum $\Delta E_{\text{L-H}}$

for any of compound I1-I5 can be found in acidic medium, this meant that electron transfers in these compounds have more easily to happened in acidic medium and efficiency of corrosion inhibition will increased, compound I2 has the minimum value of ΔE_{L-H} (2.634 eV), so it stronger than others in terms of ability of corrosion inhibition.

The fraction of electron transferred (ΔN) is an important factor that determine fraction of electrons that transferred from inhibitor molecule to atoms of metal surface. as the results; for each compound of I1-I5 the ΔN is $\approx$ (0.75, 0.7, 0.55) for gas phase, aqueous and acidic medium respectively, this decreasing in ΔN values is due to the decreasing of E_{HOMO} and fluctuating of E_{LUMO} for each compound in these three cases (table (1)), however, all values of ΔN for compounds I1-I5 is greater than zero and lower than 3.6, so all these compounds have a good ability to donate electrons to atoms of metal surface (El Adnani *et al.*, 2013).

According to hard soft acid base (HSAB), softness (ρ) and hardness (η) have a relationship with energy gap ΔE_{L-H} and they related with reactivity toward soft/hard acids and bases (Sayin and Karakaş, 2013), when ΔE_{L-H} is small the inhibitor could considered as soft base, therefor it have a tendency toward making coordination bindings with soft acid like atoms of bulky metal (Sayin and Karakaş, 2013), from table (1); softness for each compound increased in acidic medium by $\approx 0.1 \text{ eV}^{-1}$, this means that reactivity of corrosion inhibition for each compound increased, so, all these compounds I1-I5 are suitable to inhibit corrosion that happened by acidic effects, and the maximum value of softness is for compound I2 (0.759 eV^{-1}), so it has greatest ability to binding with metal surface and then corrosion prevention will done.

Total negative charges TNC is an indicator for centers of adsorptions in a molecule, when TNC is high this means the adsorption of inhibitor molecule on metal surface is high. From the results; the values of TNC for all calculations is not equal to zero; compound I2 has the greatest amounts of TNC in comparison with others, so I2 has the most ability toward adsorption on metal surface ($\approx -2.2 \text{ e}$).

Dipole moments (μ) which indicates for separation of charges in any molecule, when dipole moment has high value this means vary of distributions or separation of charges is high and this led to more adsorption of molecules on metal surface, also when μ is high value; interaction among inhibitor molecules themselves will be increased to make a good layer, as results in table (1); dipole moments increased slightly when compounds (I1-I5) have dissolved in water, and very sharp increasing have been happened in dipole moment values when these compounds putted in acidic medium, this because of solvent like water (polar solvent) can make more separation in charges of solute molecules, while very sharp increasing of dipole moments has happened for these compounds in acidic medium that due to protonation of these molecules by (H^+) and this let to changing in structure geometries and total charge will be (+1). All compounds I1-I5 undergone huge changing in dipole moment (≈ 50 Debye), this have supported reactivity toward corrosion inhibition in acidic medium.

According to results of table (2), the energies of compounds I1-I5 have is vary due to differences in their structures of these molecules. Although of these compounds have varied values of energy; the difference in energy $\Delta E_{\text{aqueous-Gas}}$ is (-

0.01 a.u) and $\Delta E_{\text{Acidic-Gas}}$ is (≈ -0.41 a.u) for all compounds I1-I5; this meant that a similarity in behaviors among these compounds toward changing of medium.

Finally, the visualized molecular orbitals (HOMO, LUMO) for compounds (I1-I5) in gas phase, aqueous and acidic medium have been shown in table (3).

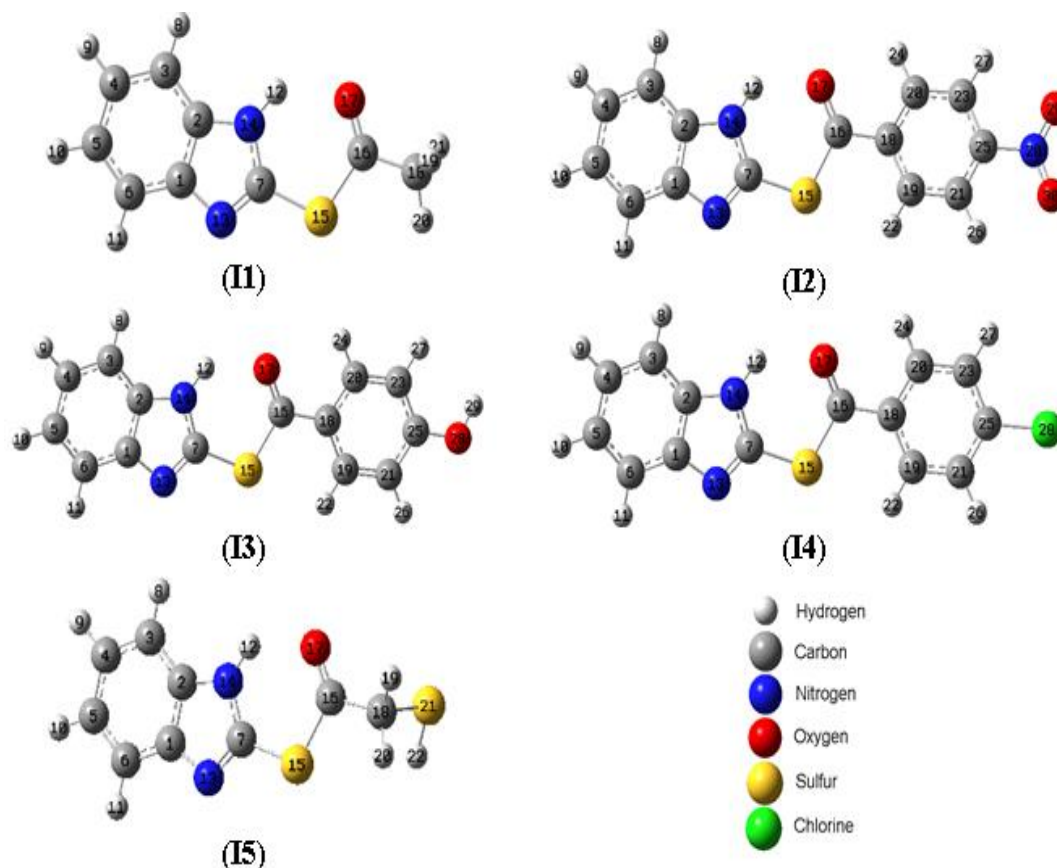


Figure (1): Optimized structures for compounds (I1-I5) in gas phase as resulted from *DFT B3LYP/6-311G (d, p)* calculations.

Table 1: Some quantum chemical parameters that have calculated by used *DFT B3LYP/6- 311G (d,p)* for inhibitors (I1-I5) in gas phase, aqueous medium and acidic medium.

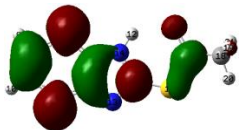
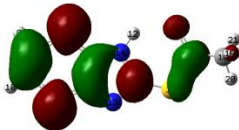
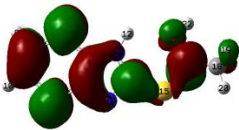
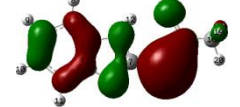
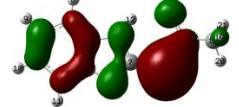
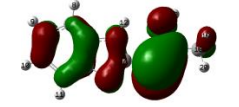
Compound Code		E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta E_{\text{L-H}}$ (eV)	I (eV)	A (eV)	χ (eV)	H (eV)	ρ (eV ⁻¹)	TNC (e)	ΔN	μ (Debye)
I1	Gas phase	-6.097	-1.518	4.578	6.097	1.518	3.808	2.289	0.436	-1.692	0.697	3.286
	Aqueous medium	-6.255	-1.432	4.822	6.255	1.432	3.844	2.411	0.414	-1.824	0.654	4.752
	Acidic medium	-6.848	-3.420	3.427	6.848	3.420	5.134	1.713	0.583	-1.596	0.544	49.645
I2	Gas phase	-6.288	-3.418	2.870	6.288	3.418	4.853	1.435	0.696	-2.211	0.747	2.411
	Aqueous	-6.311	-3.272	3.038	6.311	3.272	4.792	1.519	0.658	-2.372	0.726	3.147

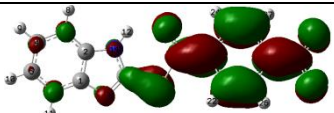
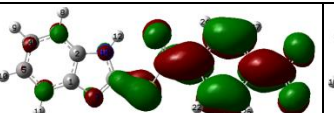
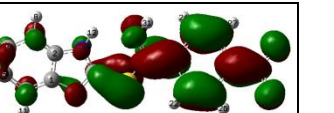
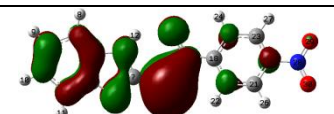
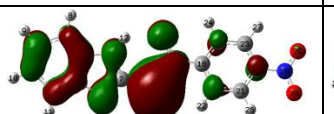
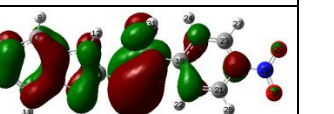
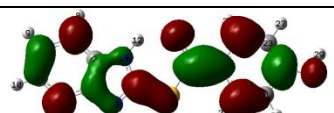
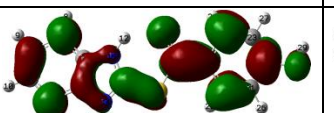
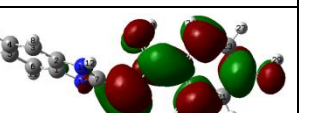
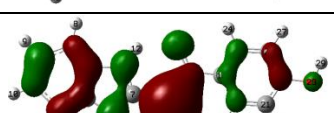
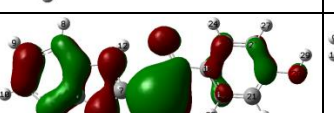
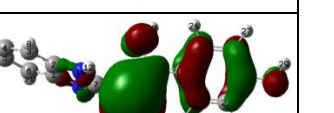
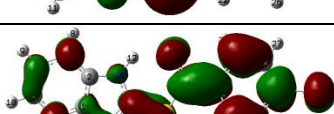
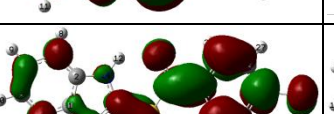
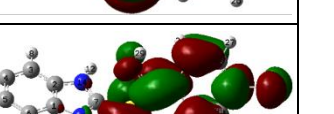
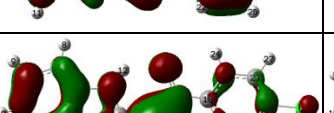
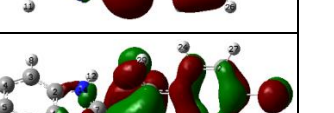
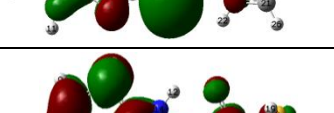
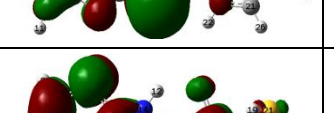
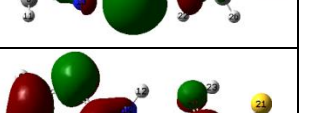
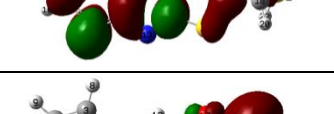
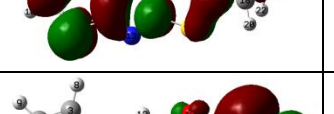
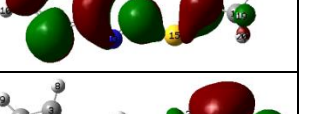
	medium											
	Acidic medium	-6.849	-4.215	2.634	6.849	4.215	5.532	1.317	0.759	-2.113	0.556	47.292
I3	Gas phase	-5.915	-2.126	3.789	5.915	2.126	4.021	1.894	0.527	-2.206	0.786	5.933
	Aqueous medium	-6.174	-2.090	4.084	6.174	2.090	4.132	2.042	0.489	-2.379	0.702	8.095
	Acidic medium	-6.786	-3.531	3.254	6.786	3.531	5.159	1.627	0.614	-1.976	0.565	53.170
I4	Gas phase	-6.104	-2.529	3.574	6.104	2.529	4.316	1.787	0.559	-1.882	0.750	2.745
	Aqueous medium	-6.258	-2.401	3.856	6.258	2.401	4.329	1.928	0.518	-2.024	0.692	3.980
	Acidic medium	-6.825	-3.841	2.984	6.825	3.841	5.333	1.492	0.670	-1.641	0.558	50.806
I5	Gas phase	-6.198	-1.956	4.241	6.198	1.956	4.077	2.120	0.471	-1.804	0.688	1.918
	Aqueous medium	-6.308	-1.824	4.484	6.308	1.824	4.066	2.242	0.445	-1.681	0.654	2.749
	Acidic medium	-6.836	-3.445	3.390	6.836	3.445	5.140	1.695	0.589	-1.944	0.548	52.747

Table 2: Calculated energy that resulted from *DFT B3LYP/6-311G* (d,p) calculations for compound I1-I5 in gas phase, aqueous and acidic medium with difference of energy between aqueous medium and gas phase, acidic medium and gas phase.

Compound code	E(a.u) Gas phase	E(a.u) Aqueous medium	E(a.u) Acidic medium	$\Delta E(a.u)$ Aqueous-gas	$\Delta E(a.u)$ Acidic-gas
I1	-930.87	-930.88	-931.27	-0.01	-0.41
I2	-1327.20	-1327.22	-1327.61	-0.01	-0.40
I3	-1197.90	-1197.91	-1198.31	-0.01	-0.42
I4	-1582.27	-1582.28	-1582.68	-0.01	-0.41
I5	-1329.08	-1329.09	-1329.48	-0.01	-0.41

Table (3): Visualization of molecular orbitals (HOMO and LUMO) for compounds (I1-I5) which have estimated by using *DFT B3LYP/6-311G* (d, p).

Comp. No.	M.O	Gas Phase	Aqueous Medium	Acidic Medium
I1	LUMO			
	HOMO			

I2	LUMO			
	HOMO			
I3	LUMO			
	HOMO			
I4	LUMO			
	HOMO			
I5	LUMO			
	HOMO			

Conclusions

In this research the ability of corrosion inhibition for some of 2-mercaptobenzimidazole derivatives have proved by using one of quantum mechanical tools; *DFT*. The prediction of properties and behaviors for compound have been done for compounds I1-I5, the results clearly shown that all these compounds have a good ability toward inhibition of corrosion, compound I2 slightly greater than others in term of ability of corrosion inhibition (due to its structure that contains aromatic rings with a number of nitrogen, oxygen and sulfur that is greater than what other compounds have. Finally, this work has been proved the ability of these compounds as inhibitors, moreover; these calculations can be done for other molecules in future for same aim.

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دراسة وفق ميكانيك الكم لبعض مشتقات 2-مركابتوبنزايميدازول كمثبطات للتآكل للفولاذ في الوسط الحامضي

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الخلاصة

في هذا البحث تم دراسة عدد من مشتقات 2-مركابتوبنزايميدازول نظرياً وفق ميكانيك الكم لاثبات قابليتها كمثبطات للتآكل؛ تم استخدام برنامج Gaussian 09W وبرنامج الواجهة الصورية له GaussView 5.0 لهذا الغرض. حيث طبقت نظرية دالة الكثافة (DFT) مع عناصر القاعدة 6-311G (d,p) والدالة الهجينة B3LYP في جميع الحسابات. وقد تضمن هذا العمل اجراء محاكاة لهذه المشتقات في ثلاث اوساط مختلفة وهي الطور الغازي والوسط المائي والوسط الحامضي.

بعض المعلومات قد تم حسابها في هذا البحث مثل E_{HOMO} , E_{LUMO} , ΔE_{L-H} ، جهد التأين (I)، اللفة الالكترونية (A)، الكهروسالبية (χ)، الصلابة (η)، عزم ثنائي القطب (μ) وكسر الالكترونات المنتقلة من جزيئات المثبط الى ذرات المعدن (ΔN)، جميع نتائج هذه المعلومات بينت بأن هذه المركبات تسلك كمثبطات لتآكل الفولاذ وبالتالي يمكن اعتبار هذه المشتقات مثبطات للتآكل.