Synthesis, Characterization and Quantum Mechanical Study of Some New 2-benzylidenehydrazinecarbothioamide Derivatives as Corrosion Inhibitors for Carbon/mild Steel in Acidic Medium.

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Abstract:

In this work, some of new 2-benzylidenehydrazinecarbothioamide derivatives have been prepared by condensation of thiosemicarbazide and different substituted aromatic benzaldehydes in presence of glacial acetic acid to give compounds (1-6), these compounds have characterized by its physical properties and spectroscopic methods. This work also included theoretical study to prove the ability of these compounds as corrosion inhibitors; The program package of Gaussian 09W with its graphical user interface GaussView 5.0 had used for this purpose; the methods of Density Functional Theory (DFT) with basis set of 6-311G (d,p) / hybrid function of B3LYP and semiempirical method of PM3 have been used, the study included theoretical simulation to simulate the reactivity of these compounds as corrosion inhibitors for carbon steel in gas phase, aqueous medium and in acidic medium (acidic medium is a medium contains acid that able to protonate these compounds and change them to protonated form), some parameters have calculated in both previous methods such E_{HOMO}, E_{LUMO}, ΔE_{L-H}, Ionization Potential (I), Electron Affinity (A), electronegativity (χ), Global Hardness (η), Atomic Charges, Dipole Moment (μ) and Fraction of Electron Transferred from Inhibitor Molecules to the Metallic Atoms (ΔN), the resulted parameters showed that these compounds are behaving as inhibitors for corrosion of carbon steel.

Keywords: 2-benzylidenehydrazinecarbothioamide, corrosion inhibitors, DFT, PM3.

تحضير، تشخيص ودراسة نظرية وفق ميكانيك الكم لبعض المشتقات الجديدة لـ 2-بنزيليدين هايدرازين كاربوثايوايمايد كمثبطات لتآكل الفولاذ في الوسط الحامضي

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الخلاصة:

يتضمن البحث تحضير مشتقات جديدة لـ 2-بنزيليدين هايدرازين كاربوثايوايمايد (1-6) وذلك بتكاثف ثايوسيميكاربازايد مع الديهايدات اروماتية مختلفة التعويض بوجود حامض الخليك الثلجي، هذه المركبات شُخصّت من خلال الصفات الفيزيائية والطرق الطيفية مثل FT-IR, ^{1}H-NMR and ^{13}C-NMR، وتضمن هذا البحث دراسة نظرية لاثبات قابلية هذه المركبات كمثبطات للتآكل، وقد استخدم لهذا الغرض برنامج Gaussian 09W مع برنامج الواجهة الصورية له GaussView 5.0، تم استخدام نظرية دوال الكثافة (DFT) مع عناصر القاعدة 6-311G (d,p) واستخدام الدالة الهجينة B3LYP، كذلك تم استخدام طريقة

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من الطرق شبه التجريبية PM3، وقد تضمنت الدراسة النظرية محاكاة لهذه المركبات في الطور الغازي، الوسط المائي والوسط الحامضي للتوصل لفعالية هذه المركبات كمثبطات لتآكل الفولاذ، بعض المعلمّات في كلتا الطريقتين سابقتا الذكر مثل E_{HOMO}, E_{LUMO}, ΔE_{L-H}، جهد التأين (I)، الالفة الالكترونية (A)، الكهروسالبية (χ)، الصلادة (η)، الشحنات الذرية، عزم ثنائي القطب (μ) وكسر الالكترونات المنتقلة من جزيئات المثبط الى ذرات المعدن (ΔN)، المعلمات الناتجة بينت بأن هذه المركبات تسلك كمثبطات لتآكل الفولاذ.

Introduction:

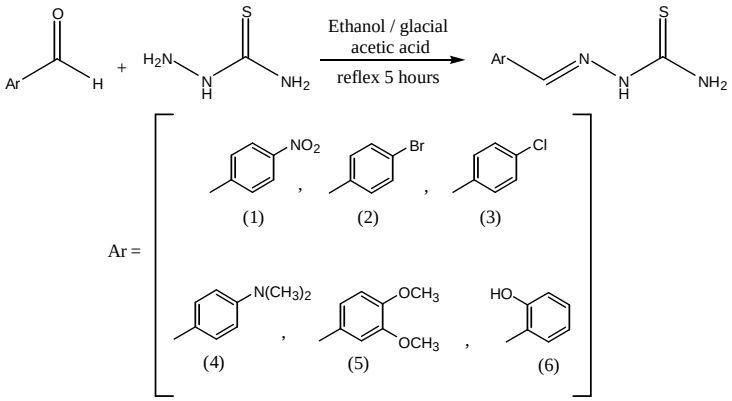
A problem that received a high attention is how to prevent metals from chemical corrosions [1] especially when the fact of how much loss of economy that caused by corrosion[2]. Acidic effect that causes corrosion could be inhibited by using inhibitors as organic compounds having atoms that can be making interactions with metal surface, these atoms such nitrogen, oxygen and sulfur [3-5]; this because of the effectiveness of inhibitors depended on the role of inhibitor ability toward donation of electrons that increasing when inhibitor molecule has properties such lone pairs and π orbitals which found in the mentioned atoms especially when these atoms found within in heterocyclic compounds [6] or aromatic systems [7]. Inhibitor molecules could prevent metal surface from corrosion by a layer of inhibitor molecules that formed and adsorbed on metal surface, the adsorption may be chemical or physical [8]; this adsorption is resulted from transfer of charge as electrons from inhibitor molecules to metal surface's atoms [9] this transfer of charge could be happened between p-orbitals of inhibitors with d-orbitals of metal surface's atoms [10].

PM3 [11] and DFT [12] are the methods that used in this work, DFT which considered an efficient tool used for obtained electronic properties for systems even when these systems involve large calculations [13], and results that obtained from DFT have a good agreement with experimental results [14], DFT can also study corrosion phenomena and it widely used by scientists to estimate corrosion inhibition efficiency [15], and it have been preferred and became more popular than other quantum mechanical methods because its calculations consumed less time with less computational requirements than other methods [16].

Experimental:

Preparation of 2-benzylidenehydrazinecarbothioamide Compounds (1-6):

preparation procedure that used to prepare the new compounds (1-6) was similar to procedure that mentioned in literatures [17], (0.01 mol. (0.9114 g.)) of thiosemicarbizied and (0.01 mol.) of different substituted aromatic aldehydes have reflexed with stirring for five hours in presence of absolute ethanol (20 ml) as solvent and (5 drops) glacial acetic acid. Reactants that used have analytical reagents chemicals (pure) and have used without further purification. After reflex completion; the mixture has cooled and poured over crushed ice, and then solid precipitate has filtered, washed with ice-cold distilled water and recrystallized by using ethanol, the preparation reactions have illustrated in scheme (1).



Scheme 1: preparation of compounds (1-6).

Instruments:

Shimadzu FTIR 8400 (Fourier Transform Infrared) spectrophotometer have performed, ^{1}H-NMR and ^{13}C-NMR spectra have recorded by Bruker spectro Spin ultra-shield magnets 300 MHz instrument with using DMSO-d_6 as a solvent and TMS as internal reference. Sharped melting points for compounds (1-6) have measured and determined by using Gallen kamp melting apparatus.

Computational method and theoretical details:

Firstly; the prepared molecules (1-6) have drew by using GaussView 5.0.8 program package [18], then these structures have submitted to Gaussian 09W Revision-A.02 [19] were the calculations such optimization of geometries and other calculations have been done. The first calculation was the optimization of geometry by using two methods; first is DFT with hybrid functional of Becke three-parameters Lee, Yang and Parr (B3LYP) [20] and basis set of 6-311G (d,p) [21], and second is semiempirical method as PM3. All these methods have done to the mentioned molecules in the gas phase, also in aqueous solution due to effect of solvation of H_2O; and acidic medium. The parameters that obtained are energy of highest occupied molecular orbital E_{HOMO}, energy of lowest unoccupied molecular orbital E_{LUMO} and the energy difference between them (Energy gap) ΔE_{L-H}, also by depending on frontier molecular orbital theory the Ionization Potential (I), Electron Affinity (A), electronegativity (χ), Global (absolute) Hardness (η), softness (ρ) and Fraction of electron transferred from inhibitor molecules to the metallic atom (ΔN) have been calculated by using equations (1) to (6) respectively [22] also Mulliken [23] total negative charge (TNC) and natural bond orbital populations have also obtained and reported.

$I = -E_{HOMO}$ … (1)

$A = -E_{LUMO}$ …(2)

$\chi = (I+A)/2$ …(3)

$\eta = (I-A)/2$ …(4)

$\rho = 1/\eta$ … (5)

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

Where χ_{Fe} and η_{Fe} are 7 and 0 respectively [15].

Results and discussion

Preparation of 2-benzylidenehydrazinecarbothioamide compounds have synthesized by one step synthesis as that shown previously in scheme (1), The prepared derivatives (1-6) have colors, solids and have sharp melting points, physical properties and FT-IR spectra for these purred compounds have listed in table 1. The percentages of yield is between (84-91)%. The structures of the 2-benzylidenehydrazinecarbothioamide derivatives have confirmed by FTIR, and some of these compounds confirmed by ^{1}H-NMR and ^{13}C-NMR spectroscopy. FT-IR (KBr) spectra showing strong υNH_2 and υN-H and absorptions at about (3151-3490) cm^{-1}, and displayed absorptions at about (1618-1640) cm^{-1} and (1224-1265) cm^{-1} that were assigned to υC=N and υC=S functions respectively. While the ^{13}C-NMR and ^{1}H-NMR spectra data [24] of some derivatives δ ppm in DMSO-d_6 solvent have listed in table 2. The signals in the range of 8.01-8.22 (s,1H,-CH=N-); 8.15-8.32 (s,2H, $-\overset{\overset{S}{\|}}{C}-NH_2$) and 9.70-9.65 (s,1H, $-HN-\overset{\overset{S}{\|}}{C}-$). ^{13}C-NMR spectral data have showed the peaks at about δ 145-62-140.22 and 179.64-177.91 for C=N and C=S (thioamide) respectively.

Table 1- Physical properties and FT-IR spectra for compounds (1-6)

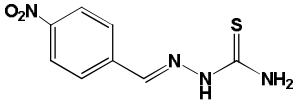
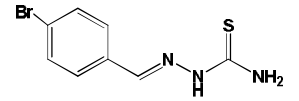
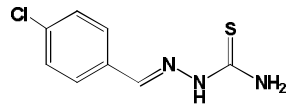
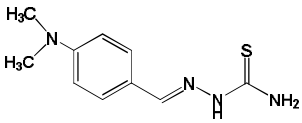
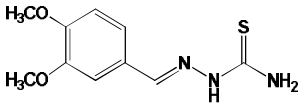
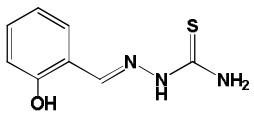
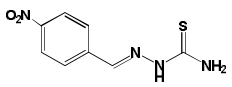
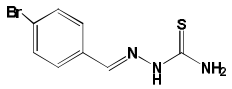
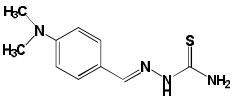
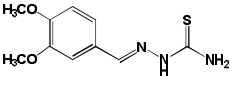
Comp. code	Compound structure	Molecular formula / Molecular weight	Melting point °C	Yield %	color	Major FTIR Absorptions cm^{-1}				
						νN-H_2 νN-H	νC-H arom.	νC=N	νC=S	Other bands
1		$C_8H_8N_4O_2S$ (224.24)	230-232 dec.	87	Deep yellow	3490, 3365 3145	3093	1620	1224	νN=O_2 Asym.1525; sym.1338 νpara-position 840
2		$C_8H_8BrN_3S$ (258.14)	209-211 dec.	85	Light white	3438, 3288 3190	3020	1618	1224	νC-Br 690 νp-position 842
3		$C_8H_8ClN_3S$ (213.69)	212-214 dec.	50	white	3438, 3282 3166	3095	1640	1230	ν(C-Cl)1091 δ (p-position) 852
4		$C_{10}H_{14}N_4S$ (222.31)	198-200 dec.	91	Light yellow	3406 3249, 3151	3010	1630	1228	νC-H aliph. 2997, 2890 δ (p-position) 877
5		$C_{10}H_{13}N_3O_2S$ (239.29)	207-209 dec.	84	off-white	3352, 3263 3184	3025	1618	1236	νC-H aliph. 2960, 2833 δ (m-position) 854 δ (p-position) 837
6		$C_8H_9N_3OS$ (195.24)	216-218 dec.	84	Pale yellow	3442, 3319 3174	3029	1616	1265	ν(O-H) overlap with ν NH

Table 2- ^{1}H-NMR and ^{13}C-NMR spectral data(ppm) for some of the prepared compounds.

Comp. Code	Compound structure	(^{1}H-NMR signals (ppm) δ-H) (^{13}C-NMR signals (ppm) δ-H)
1		7.11-7.49 (m,4H,Ar-H); 8.12 (s,1H,-CH=N-);8.32 (s, 2H, ); 9.65 (s,1H, ).
		122.59-127.34 (C-Aromatic); 142.67 (C=N); 179.64 (C=S).
2		7.11-7.49 (m,4H,Ar-H); 8.22 (s, 1H,-CH=N-);8.15 (s,2H, ); 9.34 (s,1H, ).
		120.01-129.22 (C-Aromatic); 140.22 (C=N); 177.92 (C=S).
4		2.80 (s,6H,CH_3); 6.52-7.50 (m, 4H, Ar-H); 8.01 (s, 1H,-CH=N-); 8.21 (s,1H , ); 9.70(s,1H,).
		40.45 (N-CH_3); 110.12-130.22 (C-Aromatic); 145.62 (C=N); 152.47 (-C-N-); 177.91 (C=S).
5		3.51 (s,3H,o-OCH_3); 3.82 (s,3H,p-OCH_3); 7.07-7.50(m, 3H, Ar-H); 8.15 (s,1H,-CH=N-); 8.40 (s,1H , ); 9.55(s,1H, ).
		52.55(O-CH_3); 108.11-112.25 (C-Aromatic); 144.56 (C=N); 148.08-150.65 (-C-OCH3); 178.03 (C=S).

Theoretically, some quantum parameters that obtained by using both of DFT and PM3 methods as that mentioned previously. The optimized structures calculations in ground state for inhibitors (1-6) in gas phase, aqueous medium and acidic medium, parameters of energy of highest occupied molecular

orbital (E_{HOMO}) which considered as an indicator for electrons donation for each molecules, also when E_{HOMO} is high amount this meant the inhibitor molecule has good ability to make binds with metal surface due to electron donating, while when energy of lowest unoccupied molecular orbital (E_{LUMO}) have small amount the energy gap will be small and the donation will be easer between orbitals of inhibitor molecules and metal surface this led to high adsorption between them [10]. Another important parameter that determines which inhibitor is the best in activity of inhibition is fraction of electron transferred ΔN, this parameter is a function of transferred or donated electrons from inhibitor molecules to metal atoms [23]. Also Mulliken total negative charge (TNC) calculated and discussed because the values of TNC indicate the adsorption center in inhibitor molecules, high value of TNC meant high adsorption of inhibitor on metal surface. The natural bond orbital have been used to determine which atom in inhibitor molecule skeleton will be attacked by protonium ion (in acidic medium) because atom of higher negative charge has more probability to binding with protonium ion. In the following; the three states have calculated and discussed.

Inhibitors in Gas Phase:

In this part; inhibitors have simulated as molecules in their gas phase (vacuum), the optimized structures gave results as that shown in table 3:

Table 3- Some quantum chemical parameters calculated for inhibitors (1-6) in gas phase.

DFT (B3LYP/6-311G (d,p))											
Inhibitor	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**ΔE_{L-H} (eV)**	**I (eV)**	**A (eV)**	**χ (eV)**	**η (eV)**	**ρ (eV^{-1})**	**ΔN**	**TNC (e)**	**E(a.u) Gas**
1	-6.0323	-2.9041	3.1282	6.0323	2.9041	4.4682	1.5641	0.6393	0.8093	-1.8877	-1077.39
2	-5.7931	-1.9737	3.8194	5.7931	1.9737	3.8834	1.9097	0.5236	0.8159	-1.5210	-3446.38
3	-5.7947	-1.9680	3.8267	5.7947	1.9680	3.8813	1.9133	0.5226	0.8149	-1.5754	-1332.46
4	-5.1756	-1.3027	3.8728	5.1756	1.3027	3.2391	1.9364	0.5164	0.9710	-2.0895	-1006.84
5	-5.6327	-1.6848	3.9479	5.6327	1.6848	3.6587	1.9739	0.5065	0.8463	-2.3281	-1101.94
6	-6.5045	-2.7113	3.7932	6.5045	2.7113	4.6079	1.8966	0.5272	0.6306	-1.8163	-948.07
Semiempirical (PM3)											
1	-8.9553	-1.6321	7.3232	8.9553	1.6321	5.2937	3.6616	0.2731	0.2329	-2.2949	0.1424
2	-8.8578	-1.2131	7.6447	8.8578	1.2131	5.0355	3.8223	0.2616	0.2569	-1.1309	0.1604
3	-8.8236	-1.1823	7.6412	8.8236	1.1823	5.0029	3.8206	0.2617	0.2613	-1.1843	0.1372
4	-8.3197	-1.0025	7.3172	8.3197	1.0025	4.6611	3.6586	0.2733	0.3196	-1.4054	0.1414
5	-8.7957	-1.1483	7.6474	8.7957	1.1483	4.9720	3.8237	0.2615	0.2651	-1.4127	0.0328
6	-8.6086	-0.9666	7.6420	8.6086	0.9666	4.7876	3.8210	0.2617	0.2894	-1.4089	0.0793

The optimized structures for compounds 1-6 in gas phase have been illustrated in figure 1, according to DFT results, fraction of transferred electrons ΔN has a range between (≈ 0.3 – 1) this meant that these compounds have ability to donate electrons to metal surface atoms, according to hard soft acid base (HSAB) softness (ρ) or hardness(η) related with reactivity toward soft/hard acids and bases, softness and hardness has a relationship with energy gap ΔE_{L-H}, when ΔE_{L-H} is small the inhibitor could considered as soft base and could have tendency toward make coordination bindings with soft acid like atoms of bulky metal[2]; so, compounds (1-6) can be considered as good soft bases especially when energy gap ΔE_{L-H} are small, the values of TNC in both of DFT and PM3 are between (≈ -1.15 – -2.3) that means high difference in population of atomic charges in these neutral molecules (more negative centers in these molecules have been found) and this leads to good adsorption on metal surface. When comparison among inhibitors done; the higher anticorrosion activity could be found in inhibitor 4 which has highest E_{HOMO} and lowest E_{LUMO} and have low energy gap, also has highest ΔN. There is an agreement between DFT and PM3 results (with differences in values of these parameters as differences in their calculations).

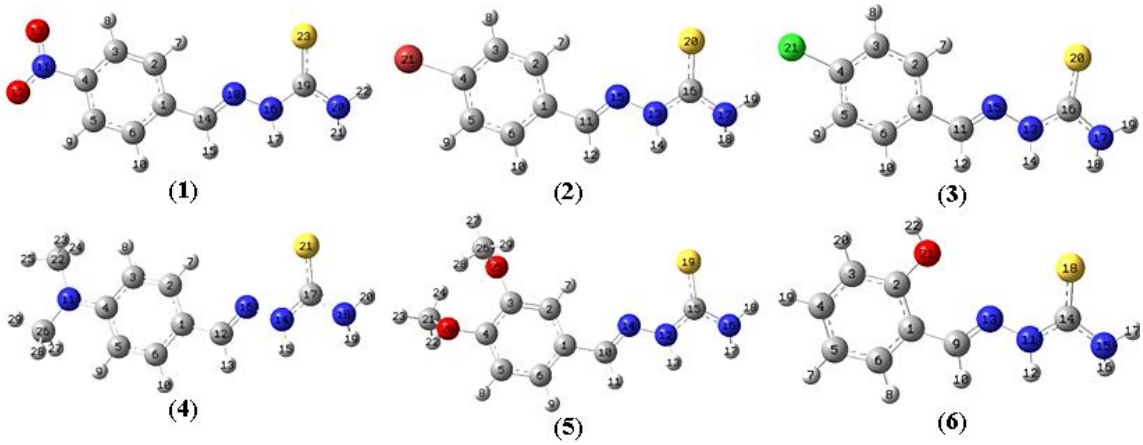


Figure 1- optimized structures for compounds (1-6) in gas phase as resulted from DFT B3LYP/6-311G (d,p).

Inhibitors in aqueous medium:

When calculations have included effectiveness of solvation (water) in additional to optimization of geometry for inhibitors 1-6; the reactivity of inhibition for these inhibitors in aqueous medium could be estimated. Table 4 included same parameters that found in table 3 with an additional parameter of difference of energy values between energy of molecules in aqueous medium and gas phase $\Delta E_{Aqueous-Gas}$ which indicates that molecules (1-6) have the same behavior toward solvation because the differences in energies $\Delta E_{Aqueous-Gas}$ seems same for these molecules (≈ -0.03 (DFT), ≈ -0.02 (PM3)) although of structure differences among these compounds and differences in molecular energies in each of gas and aqueous medium.

Table 4- Some quantum chemical parameters calculated for inhibitors (1-6) in aqueous medium.

DFT (B3LYP/6-311G (d,p)												
Inhibitor	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**ΔE_{L-H} (eV)**	**I (eV)**	**A (eV)**	**χ (eV)**	**η (eV)**	**ρ (eV^{-1})**	**ΔN**	**TNC (e)**	**E(a.u) Aqueous**	**ΔE(a.u) Aqueous-gas**
1	-6.2351	-3.0169	3.2181	6.2351	3.0169	4.6260	1.6090	0.6214	0.7376	-2.1152	-1077.42	-0.03
2	-6.1776	-1.9993	4.1782	6.1776	1.9993	4.0884	2.0891	0.4786	0.6968	-1.8348	-3446.40	-0.02
3	-6.1767	-1.9890	4.1877	6.1767	1.9890	4.0829	2.0938	0.4775	0.6965	-1.8788	-1332.48	-0.02
4	-5.2933	-1.5187	3.7746	5.2933	1.5187	3.4060	1.8873	0.5298	0.9521	-2.7949	-1006.87	-0.03
5	-6.1111	-1.8335	4.2776	6.1111	1.8335	3.9723	2.1388	0.4675	0.7077	-2.6692	-1101.96	-0.02
6	-6.0812	-1.7436	4.3375	6.0812	1.7436	3.9124	2.1687	0.4610	0.7118	-2.2074	-948.10	-0.03
Semiempirical (PM3)												
1	-9.2682	-1.4609	7.8073	9.2682	1.4609	5.3646	3.9036	0.2561	0.2094	-2.7287	0.1038	-0.04
2	-9.2480	-1.0222	8.2258	9.2480	1.0222	5.1351	4.1129	0.2431	0.2267	-1.3586	0.1379	-0.02
3	-9.1702	-1.0278	8.1423	9.1702	1.0278	5.0990	4.0711	0.2456	0.2334	-1.4059	0.1157	-0.02
4	-8.5514	-0.9636	7.5878	8.5514	0.9636	4.7575	3.7939	0.2635	0.2955	-1.6716	0.1180	-0.02
5	-9.0290	-0.9803	8.0487	9.0290	0.9803	5.0047	4.0243	0.2484	0.2479	-1.6585	0.0072	-0.03
6	-9.2180	-0.8683	8.3497	9.2180	0.8683	5.0431	4.1748	0.2395	0.2343	-1.6788	0.0557	-0.02

All molecules (1-6) can be considered as good inhibitors due to these calculation results, all E_{HOMO}, E_{LUMO} and ΔN have decreased in comparison with these values that resulted from gas phase; while TNC and ΔE_{L-H} increased (except the value of ΔE_{L-H} for compound 4); this because of solvation effects and behavior of molecule toward this effects that depended on molecular structure. According

to DFT and PM3; compound 4 has highest E_{HOMO} and lowest E_{LUMO} with highest ΔN and low ΔE_{L-H}, so it can be considered as best one in comparison with others in aqueous medium.

Inhibitors in acidic medium:

In acidic medium, the inhibitor molecules undergo protonation as a result of present of acid; first step of calculation is structure optimization for protonated conformation. For each compound (1-6) protonation location, have done by natural bond orbital calculations. table 5 shown charge distribution for each atom in inhibitors (1-6), from these results the most probable atom to binding with protonium ion for all these inhibitors is nitrogen atom of amine terminal, this atom in each compounds (1-6) is more negative than other atoms (≈ -0.7 e). After protonation locations have determined; the optimization calculations have been done for protonated inhibitors according to DFT and PM3 methods; table 6 shown the results that obtained from these calculations. According to DFT and PM3, all results of energy gap, E_{HOMO}, E_{LUMO} softness, TNC and ΔN indicated that these inhibitors have good corrosion inhibition reactivity, all ΔN are greater than zero and lower than 3.6 so it can be donate electrons to atoms of metal surface [6], also all TNC is greater than (-1 e) although of the positive charge (+1) of these inhibitors that due to protonation effects so a good charge separation has found which lead to good adsorption of these compounds on metal surface. The differences in energy values between acidic medium and gas phase for compound (1-6) $\Delta E_{Acidic-Gas}$ is (≈ -0.43 a.u (DFT), ≈ 0.15 a.u (PM3)) which indicates that molecules (1-6) have the same behavior toward acidic medium.

Table 5- natural bond orbital populations for inhibitors (1-6) calculated by using DFT B3LYP/6-311G (d,p)

Atom No.	Inhibitor					
	1	**2**	**3**	**4**	**5**	**6**
1	-0.0559	-0.0968	-0.0982	-0.1570	-0.1022	-0.1588
2	-0.1667	-0.1562	-0.1553	-0.1536	-0.2102	0.3688
3	-0.1741	-0.2256	-0.2252	-0.2646	0.2761	-0.2835
4	0.0622	-0.0774	-0.0123	0.2071	0.2877	-0.1668
5	-0.1722	-0.2286	-0.2282	-0.2772	-0.2330	-0.2392
6	-0.1723	-0.1608	-0.1601	-0.1556	-0.1800	-0.1579
7	0.2307	0.2267	0.2267	0.2157	0.2298	0.2144
8	0.2414	0.2288	0.2287	0.2160	0.2235	0.2115
9	0.2422	0.2296	0.2295	0.2166	0.2155	0.0764
10	0.2238	0.2199	0.2199	0.2091	0.0795	0.1692
11	0.5209	0.0754	0.0756	-0.4229	0.1756	-0.3961
12	-0.4077	0.1777	0.1776	0.0837	-0.3938	0.3852
13	-0.4071	-0.3923	-0.3924	0.1696	0.3879	-0.2559
14	0.0638	0.3890	0.3890	-0.3953	-0.2659	0.3185
15	0.1823	-0.2567	-0.2572	0.3855	0.3175	-0.7477
16	-0.3867	0.3165	0.3165	-0.2939	-0.7458	0.4036
17	0.3909	-0.7435	-0.7436	0.3191	0.4040	0.4159
18	-0.2373	0.4046	0.4046	-0.7522	0.4166	-0.4080
19	0.3132	0.4172	0.4172	0.4023	-0.4022	0.2133
20	-0.7389	-0.3947	-0.3950	0.4148	-0.5733	0.2165
21	0.4058	0.0472	-0.0179	-0.4231	-0.1913	-0.6625
22	0.4185	-	-	-0.3550	0.1673	0.4831
23	-0.3769	-	-	0.1910	0.1840	-
24	-	-	-	0.1874	0.1762	-
25	-	-	-	0.2046	-0.5774	-
26	-	-	-	-0.3549	-0.1909	-
27	-	-	-	0.1873	0.1840	-
28	-	-	-	0.1908	0.1735	-
29	-	-	-	0.2045	0.1670	-

Table 6- Some quantum chemical parameters calculated for inhibitors (1-6) in acidic medium.

DFT (B3LYP/6-311G (d,p))												
Inhibitor	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**ΔE_{L-H} (eV)**	**I (eV)**	**A (eV)**	**χ (eV)**	**η (eV)**	**$\rho_{(eV^{-1})}^{-1}$**	**ΔN**	**TNC (e)**	**E(a.u) Acidic**	**ΔE(a.u) Acidic-gas**
1	-7.1366	-3.3801	3.7565	7.1366	3.3801	5.2583	1.8782	0.5324	0.4636	-1.6934	-1077.83	-0.43
2	-6.7581	-2.8892	3.8688	6.7581	2.8892	4.8236	1.9344	0.5169	0.5625	-1.3102	-3446.81	-0.43
3	-6.7953	-2.8844	3.9109	6.7953	2.8844	4.8398	1.9554	0.5113	0.5523	-1.3627	-1332.89	-0.43
4	-5.5892	-2.5428	3.0464	5.5892	2.5428	4.0660	1.5232	0.6565	0.9630	-2.3061	-1007.28	-0.44
5	-6.5394	-2.7837	3.7557	6.5394	2.7837	4.6615	1.8778	0.5325	0.6226	-2.1706	-1102.37	-0.44
6	-6.5045	-2.7113	3.7932	6.5045	2.7113	4.6079	1.8966	0.5272	0.6306	-1.7063	-948.51	-0.44
Semiempirical (PM3)												
1	-9.6236	-2.3360	7.2875	9.6236	2.3360	5.9798	3.6437	0.2744	0.1399	-2.6080	0.2955	0.15
2	-9.4975	-2.2439	7.2535	9.4975	2.2437	5.8707	3.6267	0.2757	0.1556	-1.2953	0.3288	0.17
3	-9.3268	-2.2396	7.0872	9.3268	2.2396	5.7832	3.5436	0.2821	0.1716	-1.3542	0.3063	0.17
4	-8.6335	-2.1905	6.4430	8.6335	2.1905	5.4120	3.2215	0.3104	0.2464	-1.6690	0.3076	0.17
5	-9.0563	-2.2080	6.8482	9.0563	2.2080	5.6322	3.4241	0.2920	0.1997	-1.6569	0.1969	0.16
6	-9.3204	-2.1829	7.1374	9.3204	2.1829	5.7516	3.5687	0.2802	0.1748	-1.6597	0.2459	0.17

When a comparison has done among calculation results for compounds (1-6) in gas phase, aqueous medium and acidic medium E_{HOMO} and E_{LUMO} are lowest in gas phase and highest in acidic medium (with slightly changes in these values), while TNC and ΔN on the contrary (except the value of ΔE_{L-H} and ΔN for compound 4), DFT agreed with PM3 that inhibitor 4 in comparison with others can be considered as a most reactive compound toward corrosion inhibition.

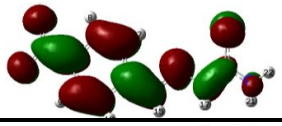
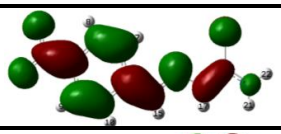
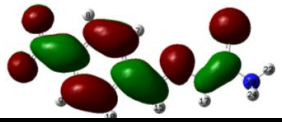
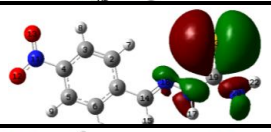
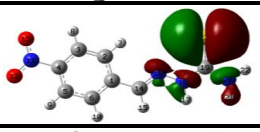
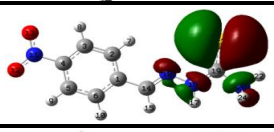
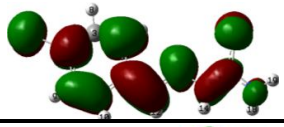
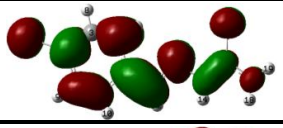
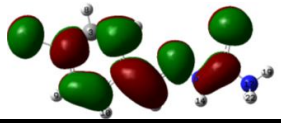
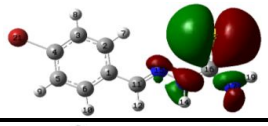
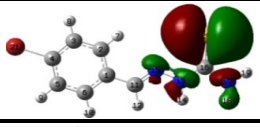
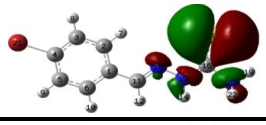
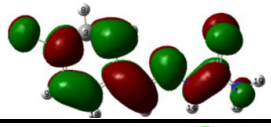
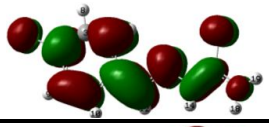
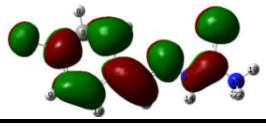
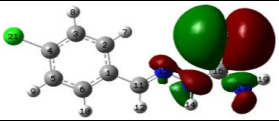
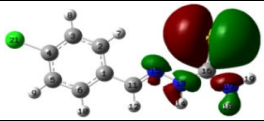
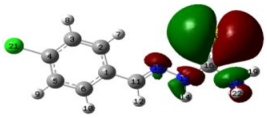
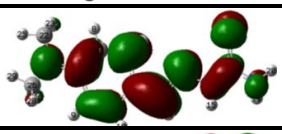
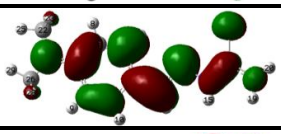
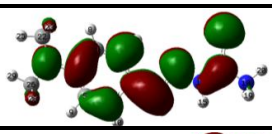
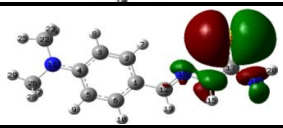
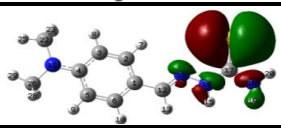
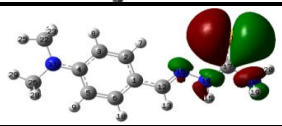
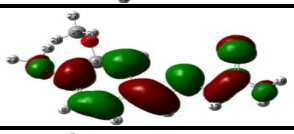
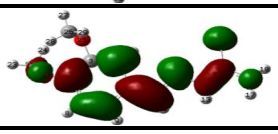
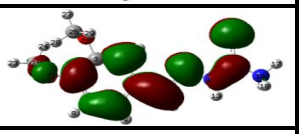
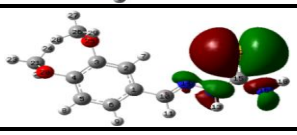
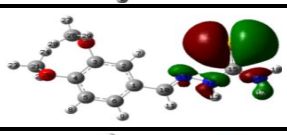
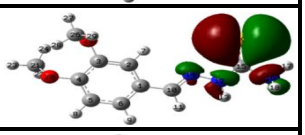
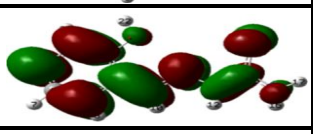
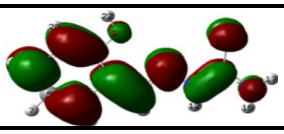
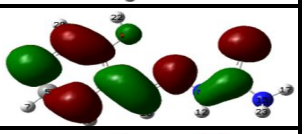
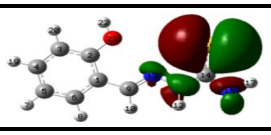
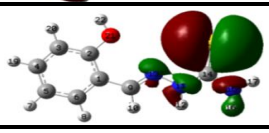
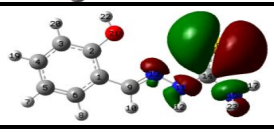
The calculations of dipole moments (μ) for compounds (1-6) in gas phase, aqueous medium and acidic medium have done table 7; the results shown that sharp changes in values of this parameter for each compound has been happened, dipole moment increased when these compound dissolved in water, and more increasing of these values when these compounds putted in acidic medium, this because of solvent like water (polar solvent) can separate charges of solute molecules, so dipole moment will be larger, while when same solvent of water included acid another effect of protonation of these compounds by acid will be effected on values of dipole moments of these compounds; also total charge will be increased by (+1) so the differences in charge distribution will be occurred in additional of effect of solvent and changes of structure geometries. All these increasing in dipole moment will support reactivity of these compounds toward corrosion inhibition; because more separation in charges in molecules lead to more adsorption of these molecules on metal surface and on the other hands more interaction among these molecules it selves to make a good layer that will adsorbed on metal surface and prevent metal from corrosion.

Table 7- Dipole moments for compounds (1-6) which resulted from both of DFT and PM3 calculations

Compound No.	**μ (gas) (Debye)**		**μ (aqueous)**		**μ (Acidic)**	
	DFT	**PM3**	**DFT**	**PM3**	**DFT**	**PM3**
1	8.6232	9.3638	12.8146	15.0930	39.4877	41.0253
2	6.2725	4.0017	10.2471	11.7969	35.5187	36.1605
3	6.3484	3.8160	10.3197	11.5775	35.6899	35.7696
4	6.6289	3.4170	10.5695	10.0613	28.4567	33.1616
5	5.3171	4.3343	9.1879	12.9874	32.9450	35.3773
6	4.9363	2.9145	8.6427	10.1110	31.6997	33.3861

Finally, for all previous calculations HOMO and LUMO for compounds 1-6 in three mentioned phases and mediums have visualized and listed in table 8.

Table 8- HOMO and LUMO molecular orbitals for compounds (1-6) obtained by using DFT B3LYP/6-311G

Comp. code	M.O	Gas Phase	Aqueous Medium	Acidic Medium
1	LUMO			
	HOMO			
2	LUMO			
	HOMO			
3	LUMO			
	HOMO			
4	LUMO			
	HOMO			
5	LUMO			
	HOMO			
6	LUMO			
	HOMO			

Conclusion:

The results of calculations of DFT B3LYP/63-11G(d,p) and PM3 semiemperical shown that the new 2-benzylidenehydrazinecarbothioamide derivatives (1-6) have good inhibition behavior toward corrosion, the parameters of E_{HOMO}, E_{LUMO}, ΔE_{L-H}, Mulliken atomic charges, dipole moment (μ) and fraction of electron transferred from inhibitor molecules to the metallic atoms (ΔN) helped to predict ability of corrosion inhibition, reactivity of each compound toward corrosion inhibition, mechanisms and behavior of these compounds in different mediums and prediction of protonation locations; for all these calculations, compound 4 has high ability toward inhibition of corrosion in comparison with other compounds.

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