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Research Article

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Quantum chemical studies on the inhibition potentials of thiophene derivatives for the corrosion inhibitors of carbon steel

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ABSTRACT

The Density functional theory (DFT) study was used to investigate the corrosion inhibition performance of two inhibitors namely: 2-thiophene carboxylic acid (TC) and 2-thiophene carboxylic acid hydrazide (TCH) on carbon steel using the B3LYP/6-311G(d,p) level of theory. The calculated quantum chemical parameters most relevant to their potential *action as corrosion inhibitors are:* E_{HOMO} *(highest occupied molecular orbital energy),* E_{LUMO} *(lowest unoccupied molecular orbital energy), energy gap* (ΔE)*, dipole moment* (μ)*, hardness* (η)*, softness (S), the absolute electronegativity* (χ)*, the electrophilicity index* (ω)*, the total energy(* E_{tot})*, the fractions of electrons transferred* (ΔN)*, back donation from the molecule* ($\Delta E_{backdonation}$)*.The local reactivity is analyzed through the Fukui function and condensed softness indices in order to compare the possible sites for nucleophilic and electrophilic attacks.The relationship between the inhibitory efficiency and quantum chemical parameters has been discussed in order to elucidate the inhibition mechanism.*

Keywords: Corrosion inhibitors, Thiophene derivatives, DFT, Fukui function, back donation

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INTRODUCTION

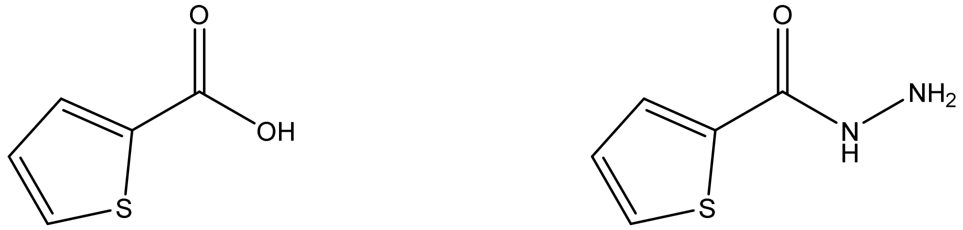
Corrosion of metals by chemical reaction with its environment, is a major industrial problem that has attracted many investigation and researches. Among numerous anticorrosion measures, corrosion inhibitors is widely used and act as one of the most economical effective ways [1]. It has been commonly recognized that organic inhibitor usually promotes formation of a chelate on the metal surface, which includes the transfer of electrons from the organic compounds to metal, forming coordinate covalent bond during such chemical adsorption process [2]. A number of heterocyclic compounds containing nitrogen, oxygen and sulphur either in the aromatic or long chain carbon system have been reported to be effective inhibitors [3]. Organic compounds, which can donate electrons to unoccupied d orbital of metal surface to form coordinate covalent bonds and can also accept free electrons from the metal surface by using their anti-bonding orbital to form feedback bonds, constitute excellent corrosion inhibitors [4].Their effectiveness as promising inhibitors is related to spatial molecular structural distribution, molecular electronic structure, chemical composition, surface charge density and of course to their affinity to the individual metal surface[5]. Density functional theory (DFT) has a potential application towards the design and development of organic corrosion inhibitors in corrosion field [6]. Substituted thiophene derivatives are important heterocycles found in numerous biologically active and natural compounds [7,8]. Thiophene moiety have attracted great attention in medicinal field due to its diversified biological activities such as anti-microbial activity [9], anti-fungal activity [10] and anti-tubercular activity [11]. They also have shown diverse pharmacological activities including anti-oxidant [12], anti cancer [13] and anti-convulsant activity [14]. The electronic properties exhibited by the thiophene and polythiophene derivatives have made them important in organic field effect transistors[15], organic light emitting diodes[16] and solar cells[17]. Dguigui *et al.,* have investigated the Ab-initio and dft study of polythiophene energy band gap and substitutions effects[18]. Raheem *et al.,* have investigated the electronic properties of thiophene compounds and their adducts[19]. Bishir Usman *et al.,* have investigated the QSAR Model of corrosion inhibition efficiency of thiophene derivatives on mild steel [20]. Recently Balachandran *et al.,* have studied the molecular structure, vibrational spectra, HOMO, LUMO, NBO analysis and hyperpolarizability calculations of thiophene-2-carbohydrazide with a different basis set [21].

Although experimental work of A. S. Fouda *et al.,* [22] provide valuable information on the corrosion inhibition efficiency of 2-thiophene carboxylic acid (TC) and 2-thiophene carboxylic acid hydrazide (TCH), a deep understanding of the inhibition property remain unclear. To date, however, no study has been performed to investigate the corrosion inhibition efficiency of TCH>TC by using quantum chemical calculations. The objective of the present paper is to extend the study of A. S. Fouda *et al.,* [22] by analyzing the inhibitive properties of TC and TCH using DFT calculations. These properties are: the molecular structure, the dipole moment, E_{HOMO}, E_{LUMO}, energy gap (ΔE), and those parameters that give valuable information about the reactive behavior: electronegativity (χ), global hardness (η) and the fraction of electrons transferred from the inhibitor molecule to the metallic atom (ΔN) and the back-donation(ΔE Back-donation). Total energy of the inhibitors also calculated. The local reactivity has been analyzed by means of the Fukui indices, since they indicate the reactive regions, in the form of the nucleophilic and electrophilic behavior of each atom in the molecule. Results obtained showed that the inhibition efficiency of TCH>TC. It is well correlated with the experimental results. From the calculations we have explained which adsorption site is favoured to bind to the metal surface.

EXPERIMENTAL SECTION

2.1 Quantum Chemical Calculation

Recently, the density functional theory (DFT) has been used to analyze the characteristics of the inhibitor/surface mechanism and to describe the structural nature of the inhibitor on the corrosion process [23]. It is also considered as a very useful technique to probe the inhibitor interaction as well as to analyze the experimental data. In the field of reaction chemistry, DFT study is emerging as a unique approach for the study of reaction mechanism [24]. The survey of theoretical corrosion literature presented by Gece [25] demonstrates that quantum chemistry is a powerful tool to study the fundamental, molecular-level processes related to corrosion inhibition. The present quantum chemical calculations have been performed with Gaussian-03 series of program package [26]. In our calculation we have used Becke's three parameter exchange functional [27] along with the Lee– Yang–Parr nonlocal correlation functional (B3LYP) [28] using 6-311G(d,p) basis set.



2-thiophene carboxylic acid (TC)

2-thiophene carboxylic acid hydrazide (TCH)

Figure 1. Names, molecular structure and the abbreviation of the inhibitors investigated

According to Koopman's theorem [29] the ionization potential (IE) and electron affinity (EA) of the inhibitors are calculated using the following equations.

$$IE = -E_{HOMO} \quad (1)$$

$$EA = -E_{LUMO} \quad (2)$$

Thus, the values of the electronegativity (χ) and the chemical hardness (η) according to Pearson, operational and approximate definitions can be evaluated using the following relations [30]:

$$\chi = \frac{I + A}{2} \tag{3}$$

$$\eta = \frac{I - A}{2} \tag{4}$$

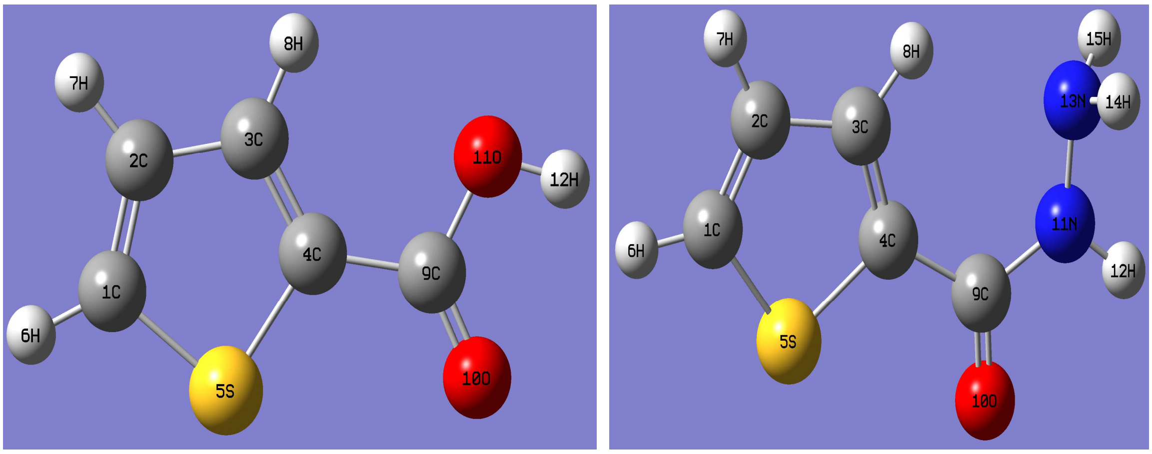


Figure 2. Optimized structure of TC and TCH calculated with the B3LYP/6-311G(d,p)

Electron polarizability, also called as chemical softness (σ) is the measure of the capacity of an atom or group of atoms to receive electrons [30], it is estimated by using the equation:

$$\sigma = \frac{1}{\eta} \tag{5}$$

When two systems, Fe and inhibitor are brought together, electrons will flow from lower electronegative (χ) inhibitor to higher electronegative (χ) Fe, until the chemical potentials become equal. Therefore the fraction of electrons transferred (ΔN) from the inhibitor molecule to the metallic atom was calculated according to Pearson electronegativity scale [31].

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{\left[2(\eta_{Fe} + \eta_{inh}\right]} \tag{6}$$

Where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule respectively η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of χ_{Fe}=7.0 eV/mol and η_{Fe} = 0 eV/mol for the computation of number of transferred electrons [31].

Recently, Parr et al. [32], have introduced an electrophilicity index (ω) defined as:

$$\omega = \frac{\chi 2}{2\eta} \tag{7}$$

This was proposed as a measure of the electrophilic power of a molecule. The higher the value of ω, the higher the capacity of the molecule to accept electrons. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment.

The local reactivity of the compounds under study, was analyzed through an evaluation of the Fukui indices [33]. Their values are used to identify which atoms in the inhibitors are more prone to undergo an electrophilic or a nucleophilic attack. The regions of a molecule where the Fukui function is large are chemically softer than the regions where the Fukui function is small. The change in electron density is the nucleophilic f^{+}(r) and electrophilic f^{-}(r) Fukui functions, which can be calculated using the finite difference approximation as follows [34].

$$f_k^{+} = q_{N+1} - q_N \qquad (8)$$

$$f_k^{-} = q_N - q_{N-1} \qquad (9)$$

where q_N, q_{N+1} and q_{N-1} are the electronic population of the atom k in neutral, anionic and cationic systems.

The local softness s, for an atom can be expressed as the product of the condensed Fukui function(f) and the global softness(S) as follows [35]

$$s^{+} = (f^{+})\, S \qquad (10)$$

$$s^{-} = (f^{-})\, S \qquad (11)$$

The local softness contains information as like those obtained from the condensed Fukui function also have the additional information about the total molecular softness, which is related to the global reactivity with respect to the reactive agents. A high value of s^{+} indicates high nucleophilicity and a high value of s^{-} high electrophilicity.

According to the simple charge transfer model for donation and back-donation of charges proposed recently by Gomez *et al*., [36] an electronic back-donation process might be occurring governing the interaction between the inhibitor molecule and the metal surface. The concept establishes that if both processes occur, namely charge transfer to the molecule and back-donation from the molecule, the energy change is directly related to the hardness of the molecule, as indicated in the following expression.

$$\Delta E_{\text{Back-donation}} = -\frac{\eta}{4} \qquad (12)$$

The $\Delta E_{Back\text{-}donation}$ implies that when $\eta > 0$ and $\Delta E_{Back\text{-}donation} < 0$ the charge transfer to a molecule, followed by a back-donation from the molecule, is energetically favored. In this context, hence, it is possible to compare the stabilization among inhibiting molecules, since there will be an interaction with the same metal, then it is expected that it will decrease as the hardness increases.

RESULTS AND DISCUSSION

According to the frontier molecular orbital (FMO) theory, of chemical reactivity, transition of electron is due to interaction between highest occupied molecular orbital and lowest unoccupied molecular orbital (LUMO) of reacting species [37]. Frontier molecular orbitals diagrams of TC and TCH is shown in figure 3. The energy of HOMO is often associated with the electron donating ability of a molecule Therefore, higher values of E_{HOMO} indicate better tendency towards the donation of electron, enhancing the adsorption of the inhibitor on carbon steel and therefore better inhibition efficiency. The calculated quantum chemical parameters for the inhibitors TC and TCH are given in Table.1

The inhibitor does not only donate electron to the unoccupied d orbital of the metal ion but can also accept electron from the d-orbital of the metal leading to the formation of a feedback bond. The highest value of E_{HOMO} -6.4966 (eV) of TCH indicates the better inhibition efficiency. The energy difference between the HOMO and the LUMO (ΔE) provides information about the overall reactivity of a molecule; the smaller the ΔE value is, the greater is the reactivity of a molecule [38]. The results presented in table.1 show that the inhibitor TCH have the lowest energy gap ie., 6.9464 (eV) than TC, Therefore, the higher reactivity of TCH allows it to be easily adsorbed onto the carbon steel surface leading to increase their inhibitive efficiency.

The dipole moment (μ in Debye) is another important electronic parameter used to describe the polarity of the molecule [39]. Molecules that have high dipole moment have a tendency to interact with other molecule through electrostatic interactions (e.g., dipole-dipole interactions). The high value of dipole moment probably increases the adsorption between chemical compound and metal surface [40]. The energy of the deformability increases with the increase in μ, making the molecule easier to adsorb at the steel surface. The volume of the inhibitor molecules also increases with the increase of μ. This increases the contact area between the molecule and surface of steel and increasing the corrosion inhibition ability of inhibitors [41]. In our present study the inhibitor TCH having the dipole moment value of 4.5413, which is greater than that of inhibitor TC, having higher inhibition efficiency.

Table 1. The calculated quantum chemical parameters for the investigated inhibitors TC and TCH obtained with B3LYP/6-311G(d,p) method

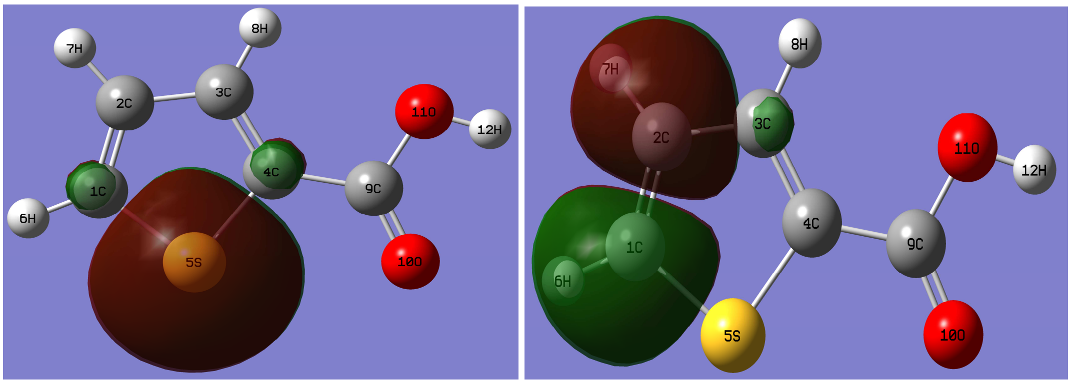
Parameters	TCH	TC
E_{HOMO} (eV)	-6.4966	-6.9573
E_{LUMO} (eV)	0.4498	0.050
Energy gap(ΔE)	6.9464	7.0073
Dipole moment (μ in Debye)	4.5413	2.4794
Ionization potential(I)	6.4966	6.9573
Electron affinity(A)	-0.4498	-0.050
Hardness(η)	3.4732	3.503
Electronegativity(χ)	3.0234	3.4537
Softness (S)	0.2879	0.285
Electrophilicity index(ω)	1.3159	1.7025
Fraction of electron transferred (ΔN)	0.5725	0.506
$\Delta E_{backdonation}$ (eV)	-0.8683	-0.8758
Total energy (E_{tot})	-777.15215	-741.70084

Global hardness and global softness are the basic chemical concepts, called global reactivity descriptors which has been theoretically justified within the framework of DFT. A hard molecule has a large energy gap and a soft molecule has a small energy gap [42]. It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation of the electron cloud of the atoms. Soft molecules are more reactive than the hard molecules because they could easily offer electrons to an acceptor. In accordance with the HSAB principle, normally the molecule with least value of global hardness is expected to have the highest inhibition efficiency [39]. In our present study, it is clear from the calculation that the compound TCH having the lowest hardness value and highest softness value is expected to be the best inhibitor.

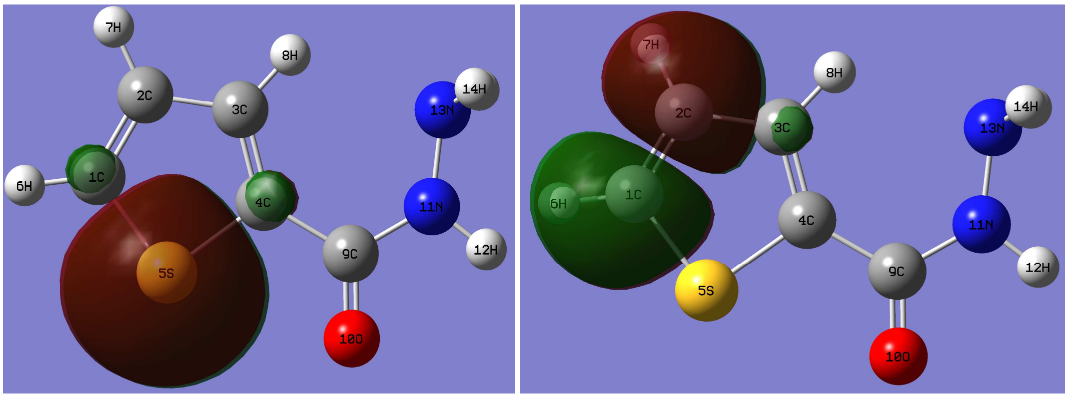
The calculation from the table 1. shows the order of electronegativity (χ) as TCH<TC. According to Sanderson's electronegativity equalization principle [43], the inhibitor TC with a high electronegativity and low difference of electronegativity quickly reaches equalization and hence low reactivity is expected.

In literature it has been reported that the values of ΔN show inhibition effect resulted from electrons donation [44]. The number of electrons transferred (ΔN) from the inhibitor to the iron was also calculated and tabulated in table.1. The values of ΔN show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study [45]. If $\Delta N < 3.6$, the inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface and it increases in the following order; TCH>TC. The results indicate that the ΔN value of TCH is greater which strongly correlates with the experimental inhibition efficiencies.

The total energy calculated by DFT methods is also a beneficial quantum chemical parameter. Hohenberg and Kohn [46] proved that the total energy of a system including that of the many body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. In our study the total energy of the inhibitor TCH is equal to -777.15215 au, this value is lower than that of the compound TC. The minimum value of the total energy functional is the ground state energy of the system. This result indicated that the inhibitor TCH is favourably adsorbed through active centres on the carbon steel.



HOMO of TC **LUMO of TC**



HOMO of TCH **LUMO of TCH**

Figure 3. HOMO and LUMO diagrams of TC and TCH using B3LYP/6-311G(d,p)

3.1 Local Selectivity

Fukui functions compute local reactivity indices that makes possible to rationalize the reactivity of individual molecular orbital contributions. The condensed Fukui function and local softness indices allow one distinguish each part of the molecule on the basis of its distinct chemical behaviour due to the different substituted functional group. The preferred site for nucleophilic attack is the atom in the molecule where the value of f_k^+ is maximum and it is associated with the LUMO energy while the site for electrophilic attack is controlled by the values of f_k^- which is associated with the HOMO energy.

Table 2. Fukui and local softness indices for nucleophilic and electrophilic attacks in TC atoms calculated from Mulliken atomic charges ; maxima in bold

Atom	f_k^+	f_k^-	S^+	S^-
1 C	0.06547	0.1199	0.03783	0.06929
2 C	0.004319	0.07869	0.00249	0.04547
3 C	0.05803	0.068131	0.03353	0.03937
4 C	0.027933	0.052995	0.01614	0.03062
5 S	**0.293284**	**0.167473**	**0.16950**	**0.09679**
6 H	0.081239	0.085364	0.04695	0.04933
7 H	0.07791	0.085967	0.04502	0.04968
8 H	0.073982	0.073093	0.04275	0.04224
9 C	0.07661	0.042619	0.04427	0.02463
10 O	0.129276	0.100486	0.07471	0.05807
11 O	0.036051	0.081633	0.02083	0.04717
12 H	0.075898	0.043648	0.04386	0.02522

The HOMO diagrams of both the inhibitors TC and TCH indicate that the S_5 atom in both the inhibitors are rich in electron density indicating the preferred site for electrophilic attack whereas the LUMO diagrams of both TC and

TCH indicate that the electron density away from S_5 atoms depicting nucleophilic attack in that site which is highly supported by Fukui indices which show that the S_5 atoms in both inhibitors to be the site for both electrophilic and nucleophilic attacks.

Table 3. Fukui and local softness indices for nucleophilic and electrophilic attacks in TCH atoms calculated from Mulliken atomic charges ; maxima in bold

Atom	f_k^+	f_k^-	S^+	S^-
1 C	0.07019	0.08918	0.04056	0.05154
2 C	0.01888	0.05687	0.01091	0.03287
3 C	0.05368	0.04265	0.03102	0.02465
4 C	0.07979	0.04778	0.04611	0.02761
5 S	**0.27339**	**0.12352**	**0.15800**	**0.07139**
6 H	0.09443	0.07489	0.05457	0.04328
7 H	0.08848	0.07319	0.05114	0.04230
8 H	0.08061	0.07911	0.04659	0.04572
9 C	0.00898	0.10765	0.00519	0.06221
10 O	0.14994	0.07378	0.08665	0.04264
11 N	0.01536	0.04369	0.00888	0.02525
12 H	0.04747	0.06642	0.02743	0.03838
13 N	-0.02778	0.01021	-0.01605	0.00590
14 H	0.03344	0.04439	0.01932	0.02566
15 H	0.01309	0.06660	0.00756	0.03849

CONCLUSION

The inhibition efficiency of thiophene derivatives namely TC and TCH has been investigated by using quantum chemical approaches utilizing DFT /B3LYP/6-311G(d,p) level of theory leading the following conclusions.

1. Through DFT calculations, a correlation between quantum chemical parameters related to the electronic and molecular structures of the inhibitors TC and TCH and their ability to inhibit the corrosion process could be established.
2. The inhibition efficiency of the investigated compounds are closely related to E_{HOMO}, energy gap ΔE , dipole moment (μ) and fraction of electron transferred ΔN. The inhibition efficiency increases with the increase in HOMO and decrease in energy gap.
3. From the calculation of quantum chemical parameters like E_{HOMO}, energy gap, the fraction of electron transfer, back donation and softness, it has been found that the order of inhibition efficiency of inhibitor is: TCH>TC, which agrees well with the experimental findings.
4. The total energy of the best inhibitor TCH is lower than that of the TC, thus, the TCH is favorably adsorbed through the active centre/s of adsorption on the carbon steel surface.
5. The Fukui function shows the nucleophilic and electrophilic attacking sites of the inhibitors.
6. Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of DFT method employed here.

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