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A theoretical evaluation on quinoxaline derivatives as corrosion inhibitors on mild steel

P. Udhayakala

Department of Chemistry, Dr. M. G. R. Educational and Research Institute, Chennai, India

ABSTRACT

Quantum chemical calculations using Density Functional Theory (DFT) method at B3LYP functional was used to study the inhibition performance of two quinoxaline derivatives namely 3,7-dimethylquinoxalin-2(1H)-thione (DQT) and 3,7-dimethylquinoxalin-2(1H)-one (DQO) which were recently used as corrosion inhibitors for mild steel corrosion. The quantum chemical properties such as E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), energy gap (ΔE), dipole moment (μ), hardness (η), softness (σ), the absolute electronegativity (χ), the fractions of electrons transferred (ΔN) and the electrophilicity index (ω) were calculated. The molecular electrostatic potential map (MEP) is used to predict the electron rich and electron deficient centres of the studied inhibitors. The local reactivity has been analyzed through the Fukui function and local softness indices in order to compare the possible sites for nucleophilic and electrophilic attacks. The theoretical results are in consistent with the experimental outcomes.

Keywords: Quinoxaline, corrosion inhibitors, DFT, Fukui function, molecular electrostatic potential (MEP).

INTRODUCTION

Corrosion of mild steel is an inevitable process and corrosion inhibition of iron and its alloys, steel have received a great attention in different media [1,2]. When mild steel is used in the field of metallurgy, marine applications, chemical and oil industries it suffers severe corrosion. Several research methods on inhibition of mild steel corrosion have been reported and it has been established that the use of organic inhibitors is one of the best method for the prevention of the corrosion of mild steel in acidic medium [3]. Organic compounds containing sulphur, nitrogen, oxygen, polar functional groups and conjugated double bonds are proven as potential corrosion inhibitors [4]. Quinoxaline and its derivatives are having various biologically interesting properties with several pharmaceutical applications. Quantum chemical calculations have been widely used to study the reaction mechanism of the inhibitors molecules and the metal surface, density functional theory (DFT) has shown significant promise and appears to be adequate for pointing out the changes in electronic structure responsible for inhibitory action [5]. Kabanda et al., have studied the DFT calculation of some quinoxaline derivatives as potential corrosion inhibitors [6]. Saranya et al., have studied chemical, electrochemical and theoretical inhibition efficiency of some quinoxaline derivatives [7]. The objective of this paper is to extend the experimental observation of Adardour et al., [8] to investigate the dependence of inhibition efficiency of the inhibitors DQT and DQO on theoretical chemical parameters such as the energies of highest occupied molecular orbital (EHOMO) and the lowest unoccupied molecular orbital (ELUMO), the energy difference (ΔE) between EHOMO and ELUMO, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (S), ionization potential (I), the global electrophilicity (ω) and the fraction of electrons transferred (Δ N).

MATERIALS AND METHODS

2.1 Quantum Chemical Calculation

Quantum chemical methods also have been proved to be a very useful in determining the molecular structure as well as elucidating the electronic structure, reactivity [9] and also a powerful tool for studying inhibition of corrosion of the metals [10]. The Complete geometrical optimizations of the investigated molecules are performed using DFT (density functional theory) with the Beck's three parameter exchange functional along with the Lee– Yang–Parr nonlocal correlation functional (B3LYP)[11,12] with 6-311G(d,p) basis set. All calculations were done by GAUSSIAN 09 W software [13]. The geometry of all species under investigation was determined by optimizing all geometrical variables without any symmetry constraints. The chemical and optimized structures of the compounds studied are given in Fig 1 and 2.



3,7-dimethylquinoxaline-2(1*H*)thione(DQT)



3,7-dimethylquinoxalin-2(1*H*)-one (DQO)

Figure 1. Molecular structure and the abbreviation of the studied compounds



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

The basic relationship of the density functional theory of chemical reactivity is precisely, the one established by *Parr et al.*, [14] to the number of electrons, and therefore with the negative of the electronegativity χ .

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\nu(r)} = -\chi \tag{1}$$

Where μ is the electronic chemical potential, E is the total electronic energy, N is the number of electrons, and v(r) is the external potential of the system. The global chemical hardness (η) has been defined as following[15],

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu(r)} \tag{2}$$

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where v(r) and μ are, respectively, the external and electronic chemical potentials.

Molecular properties related to the reactivity and selectivity of the inhibitors like ionization potential (I), electron affinity (A), the electronegativity(χ), global hardness(η) and softness (σ), were estimated according to Koopman's theorem[16] which relates to the energy of the HOMO and the LUMO.

Ionization potential (I) is related to the energy of the E_{HOMO} through the equation:

$I = -E_{HOMO}$	(3)
Electron affinity (A) is related to E_{LUMO} through the equation:	

$$\mathbf{A} = -E_{LUMO} \tag{4}$$

When the values of I and A are known, one can determine the electronegativity χ and the global hardness (η).

The absolute electronegativity (χ) and absolute chemical hardness (η) of the inhibitor molecule are given [15]

$$\chi = \frac{I+A}{2}$$
(5)
$$\eta = \frac{I-A}{2}$$
(6)

Electron polarizability, also called as chemical softness (σ) is the measure of the capacity of an atom or group of atoms to receive electrons [17], it is estimated by using the equation:

$$\sigma = \frac{1}{\eta} \tag{7}$$

When two systems, Fe and inhibitor are brought together, electrons will flow from lower (χ) inhibitor to higher (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 [18].

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{\left[2(\eta_{Fe} + \eta_{inh}\right]} \tag{8}$$

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[19].

The electrophilicity index (ω)[20] which was proposed by Parr *et al.* was calculated by the equation

$$\omega = \frac{\mu^2}{2\eta} \tag{9}$$

According to the definition, this index measures the propensity of chemical species to accept electrons. A high value of electrophilicity index describes a good electrophile while a small value of electrophilicity index describes a good nucleophile. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment.

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According to the simple charge transfer model for donation and back-donation of charges proposed recently by Gomez *et al.*,[21] 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.

$$\Delta E_{\text{Back-donation}} = -\frac{\eta}{4} \tag{10}$$

The $\Delta E_{Back-donation}$ implies that when $\eta > 0$ and $\Delta E_{Back-donation} < 0$ 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, the adsorption ability of the molecule over metal surface is related to interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting species [22]. The 3D plots of the frontier orbitals HOMO and LUMO figures are shown in Fig. 3. The energy of HOMO is often associated with the electron donating ability of a molecule with the metal with low energy empty orbital. Therefore, higher values of E_{HOMO} indicate better tendency towards the donation of electron, enhancing the adsorption of the inhibitor on mild steel and therefore better inhibition efficiency. In the present study, from the table1 it has been observed that the inhibitor DQT has the highest HOMO energy -6.0239 eV, implies the highest tendency to donate electrons. The various quantum chemical parameters are collected and reported in Table 1.

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

Parameters	DQT	DQO
E _{HOMO} (eV)	-6.0239	-6.2939
E _{LUMO} (eV)	-2.421	-1.8553
Energy gap(ΔE)	3.6029	4.4386
Dipole moment(µ)	5.0350	3.6961
Ionization potential(I)	6.0239	6.2939
Electron affinity(A)	2.421	1.8553
Hardness(η)	1.8015	2.2193
Electronegativity(χ)	4.222	4.0746
Softness (σ)	0.5551	0.4506
Electrophilicity index(ω)	4.947	3.7404
Fraction of electron transferred (ΔN)	0.7710	0.6591
$\Delta E_{\text{backdonation}}$ (eV)	-0.4504	-0.5548

The energy of LUMO represents the tendency of inhibitors to accept electrons from the metal surface. A greater adsorption ability and better corrosion inhibition efficiency can be expected from the lower value of E_{LUMO} [23]. The lowest E_{LUMO} value -2.421 eV of the inhibitor DQT would preferentially accept more electrons from metal surfaces than the other inhibitor DQO. The trend in the E_{LUMO} correlates well with the experimentally determined inhibition efficiency.

The energy gap ΔE , is an important parameter as a function of static chemical reactivity of the inhibitor molecule. The energy gap between HOMO and LUMO determines the kinetic stability, chemical reactivity, optical polarizability and chemical hardness–softness of a compound [24]. A molecule with a low energy gap is more polarizable and is generally associated with the high chemical activity and low kinetic stability and is termed soft molecule [25]. It has been observed from the table1, the inhibitor DQT has the lowest energy gap 3.6029 eV compared to the inhibitor DQO which has the energy gap value of 4.4386 eV. The result is in total agreement with the experimental data.

The dipole moment (μ) is the most widely used quantity to describe the polarity of a covalent bond that results from non-uniform distribution of charges on the various atoms in the molecule. The high value of dipole moment probably increases the adsorption between the inhibitor and the metal surface [26]. The volume of the inhibitor molecules increases with the increase of μ , this increase the contact area between the molecule and the surface of

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iron and increasing the corrosion inhibition ability of the inhibitor. In our study, the value 5.0350 (Debye) of DQT enumerates its better inhibition efficiency compared to 3.6961 (Debye) of DQO which agrees well with the experimental findings.

The global hardness η and global softness σ are the very important basic chemical concepts that describe the molecular reactivity. Hard molecules (atoms or ions) are more resistant to eventual deformation or polarization of the electronic cloud caused by a relatively small perturbation of molecular reactions [27]. 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 [28]. The result presented in Table1 shows that the inhibitor DQT has the lowest hardness value 1.8015 eV and the highest softness value 0.5551 is expected to be the best inhibitor.

The number of electrons transferred (ΔN) from the inhibitor to the iron was also calculated and tabulated in table.1. According to Lukovits's study [29] the fraction of electrons transferred describes the trend of electrons donation within a set of inhibitor. Generally, if the ΔN values less than 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; DQT>DQO. The results indicate that the ΔN value of DQT is greater which strongly correlates with the experimental inhibition efficiencies.



Figure 3.HOMO and LUMO diagrams of the inhibitors DQT and DQO using B3LYP/6-311G(d,p)

3.1 Molecular electrostatic potential (MEP)

Molecular electrostatic potential (MEP) is a plot of static potential mapped on to the constant electron density surface and is a very useful descriptor in understanding the reactive sites of a molecule [30,31]. In the present study the MEP was calculated at the B3LYP/6-311G(d,p) optimized geometry. The MEP also displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of colour grading and is very useful in research of molecular structure with its physiochemical property relationship [32,33]. Different values of

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the electrostatic potential are represented by different colours. In most of the MEP, the maximum negative region which is the preferred site for electrophilic attack indicated as red color, while the maximum positive region indicted by blue colour which is the preferred site for nucleophilic attack. Potential increases in the order red < orange < yellow < green < blue. As can be seen from the MEP of the title inhibitors, in the inhibitor DQT the negative potential are over the electronegative sulphur atom (S23) and the regions having the most positive potential are over the hydrogen atom(H12). In the inhibitor DQO the negative potential are over the electronegative oxygen atom (O23) and the regions having the most positive potential are over the hydrogen atom (H12). The electrostatic potential surface mapped on isodensity surface (MEP) of the studied compounds are given in Fig.4.



Figure 4. Molecular electrostatic potential map of (a) DQT (b) DQO $\,$

3.2 Local molecular reactivity

The Hard and Soft Acids and Base principle (HSAB) has been useful to predict the reactivity of chemical systems [34-36]. Thus, from HSAB principle in combination with the Density Functional Theory, it has been possible to identify many useful and important reactivity concepts such as the Fukui Function [37]. Their values are used to identify which atoms in the inhibitors are more prone to undergo an electrophilic or a nucleophilic attack. The change in electron density is the nucleophilic $f^+(\mathbf{r})$ and electrophilic $f(\mathbf{r})$ Fukui functions, which can be calculated using the finite difference approximation as follows[38].

$f_k^+ = q_{N+1} - q_N$	for nucleophilic attack	(11)	
$f_k = q_N - q_{N-1}$	for electrophilic attack	(12)	

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 σ^+ and σ^- for an atom can be expressed as the product of the condensed Fukui function (f) and the global softness (σ), as follows [39].

$\sigma^+ = (\mathrm{f}^+). \ \sigma$	(13)
$\sigma = (f). \sigma$	(14)

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 f_k^+ measures reactivity with respect to nucleophilic attack or the characteristic of the molecule to accept electrons while the f_k^- measures reactivity with respect to electrophilic attack or the characteristic of the molecule to donate electrons. 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. The value of Fukui function and softness values of the

studied inhibitors are listed in Table 2 and 3. Fukui function depicted in table 2, implies that in the inhibitor DQT the atom S23 is the preferred site for both electrophilic and nucleophilic attack. On the other hand, the most susceptible site for both electrophilic attack in the inhibitor DQO is in the O23 atom. In the present study, both the inhibitors DQT and DQO differ only by the substitution of S and O in the atom number 23. The higher value of f_{k}^{+} and f_{k}^{-} in the Fukui function also indicates that the inhibitor DQT is more reactive than DQO.

Atom	f_k^+	f_k	σ^{+}	σ
1 C	0.0103	0.0326	0.0059	0.0188
2 C	0.0653	0.0283	0.0377	0.0163
3 C	-0.0277	0.0307	-0.0160	0.0177
4 C	0.0204	-0.0095	0.0117	-0.0055
5 C	0.0636	0.0321	0.0367	0.0186
6 C	-0.0024	-0.0053	-0.0014	-0.0030
7 H	0.0530	0.0428	0.0306	0.0248
8 H	0.0543	0.0389	0.0314	0.0225
9 H	0.0472	0.0307	0.0273	0.0178
10 C	-0.0137	0.0384	-0.0079	0.0222
11 C	0.0447	0.0313	0.0258	0.0181
12 H	0.0334	0.0224	0.0193	0.0129
13 C	0.0067	0.0065	0.0039	0.0037
14 H	0.0479	0.0278	0.0277	0.0161
15 H	0.0349	0.0275	0.0202	0.0159
16 H	0.0141	0.0195	0.0081	0.0113
17 C	0.0001	-0.0488	0.0001	-0.0282
18 H	0.0347	0.0241	0.0200	0.0139
19 H	0.0348	0.0244	0.0201	0.0141
20 H	0.0443	0.0503	0.0256	0.0290
21 N	0.0878	0.0424	0.0507	0.0245
22 N	0.0340	0.0126	0.0196	0.0071
23 S	0.3117	0.4997	0.1801	0.2888
		1		

 Table. 2 Fukui and local softness indices for nucleophilic and electrophilic attacks in DQT atoms calculated from Mulliken atomic charges ; maxima in bold calculated with B3LYP/6-311G(d,p)

 $Table. \ 3 \ Fukui \ and \ local \ softness \ indices \ for \ nucleophilic \ and \ electrophilic \ attacks \ in \ DQO \ atoms \ calculated \ from \ Mulliken \ atomic \ charges; \ maxima \ in \ bold \ calculated \ with \ B3LYP/6-311G(d,p)$

Atom	f_k^+	f_k	$\sigma^{\!\!\!+}$	σ
1 C	0.0075	0.0700	0.0043	0.0404
2 C	0.0728	0.0321	0.0421	0.0185
3 C	-0.0318	0.0935	-0.0183	0.0540
4 C	0.0399	-0.0105	0.0231	-0.0060
5 C	0.0634	0.0464	0.0366	0.0268
6 C	0.0059	-0.0181	0.0034	-0.0104
7 H	0.0583	0.0645	0.0336	0.0373
8 H	0.0616	0.0587	0.0356	0.0339
9 H	0.0548	0.0488	0.0317	0.0282
10 C	0.0347	0.0444	0.0200	0.0256
11 C	0.0831	0.0567	0.0480	0.0327
12 H	0.0499	0.0769	0.0288	0.0444
13 C	0.0051	0.0199	0.0029	0.0114
14 H	0.0466	0.0327	0.0269	0.0189
15 H	0.0446	0.0395	0.0258	0.0228
16 H	0.0223	0.0291	0.0129	0.0167
17 C	-0.0043	0.0269	-0.0024	0.0155
18 H	0.0363	0.0365	0.0209	0.0211
19 H	0.0594	0.0414	0.0343	0.0239
20 H	0.0536	0.0390	0.0309	0.0225
21 N	0.0963	0.0121	0.0556	0.0069
22 N	0.0196	0.0525	0.0114	0.0304
23 O	0.1200	0.1069	0.0693	0.0617

The local softness contains the information similar to those condensed Fukui function plus additional information about the total molecular softness, which is related to the biological reactivity. A high value of σ^{\dagger} indicates high nucleophilicity and the high value of σ^{\dagger} indicates high electrophilicity.

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CONCLUSION

A theoretical study of the inhibition efficiency of the two inhibitors, DQT and DQO was carried out at the density functional theory (DFT) calculation level. The inhibition efficiency of the studied inhibitors obtained theoretically increased with increase in HOMO and decrease in LUMO and energy gap. DQT has the highest inhibition efficiency than DQO because it has the highest HOMO and lowest LUMO and energy gap. Parameters like hardness (η), electronegativity (χ), softness (σ), chemical potential (μ), the fractions of electrons transferred (ΔN) and the electrophilicity index (ω) confirm the order of inhibition efficiencies : DQT > DQO. The theoretically obtained inhibitor order gives good correlation with experimentally determined inhibition efficiency. The presented MEP surface, an overlaying of the electrostatic potential (the attraction or repulsion of a molecule) is valuable for describing overall molecular charge distribution. The condensed Fukui functions predicts the electrophilic and nucleophilic attacking sites of the inhibitors providing the information about the reactivity of the molecules.

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