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A Theoretical Investigation on the Inhibition Efficiencies of Some Schiff bases as Corrosion Inhibitors of Steel in Hydrochloric Acid

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The corrosion inhibition characteristics of three Schiff bases used as inhibitors have been studied by quantum chemistry method at the level of DFT/B3LYP with the 6-31+G (d, p) base sets. Quantum chemical parameters such as highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), the charge distributions, the absolute electro-negativity values (χ) , electron affinity (A), global hardness (η), softness (σ), ionization potential (I) and the fraction of electrons transferred from inhibitors to iron (ΔN) have been calculated. The relationships between the corrosion inhibitor efficiency (IE) and these quantum chemical parameters are discussed using linear regression analysis to determine the most effective parameter on inhibition efficiency, and the regression equations showed that the corrosion inhibition performances of these inhibitors have a good linear relationship to E_{HOMO}, χ and Q_{N1}. The theoretical data were well accorded with reported experimental results. Finally, this research may provide a theoretical inhibition performance prediction approach for new homologous inhibitors.

Keywords: quantum calculation; corrosion inhibitor; Schiff base; inhibition performance prediction

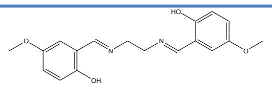
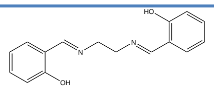
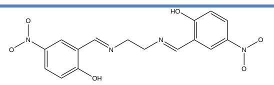
1. INTRODUCTION

The use of corrosion inhibitors is a good way to keep metal and metal alloy away from corrosion in environmental medium [1-2]. As a protection technique, the addition of corrosion inhibitors are widely used in many industries, such as petroleum, chemical industry, construction, etc. And it is also one of the most economical ways to protect the metal [3-4-5].

However, most of the corrosion inhibitors, which are often toxic to the environment [6], should replaced by new compounds with environmentally acceptable chemicals [7-8]. Recent studies showed that some Schiff bases compounds as corrosion inhibitors were environmental-friendly inhibitors[9] which could be applied in various acidic solution for protection of metals, such as copper, aluminum and mild steel [10-15]. Because some of these Schiff bases compounds often have a special structural –CH=N- which may provide electrons from inhibitor to metal.

Quantum chemical calculation is a good research tool applied in the structure and performance research of corrosion inhibitors to make faster design and evaluation [16]. This method, which is an effective way to make research on complex systems at molecule, atom and even electron level, can provide specific information about molecular structure, electron distribution and adsorbent process of corrosion inhibitors. It is also beneficial for deeply discussing the relationship between the structure and performance of corrosion inhibitors and studying corrosion inhibition at the micro level. This method will set new trend for the molecular design of corrosion inhibitors [17-19]. The objective of this paper is to present an investigation on the properties of three Schiff bases inhibitors namely, N,N'-bis (5-methoxysalicylidene) -1,2-ethylenediamine (M1), N,N'-bis (salicylidene) -1,2-ethylenediamine (M2) and N,N'-bis (5-nitrosalicylidene) -1,2-ethylenediamine (M3) (Table1), and explore the relationship between molecular structural parameters and their inhibition efficiency. These quantum chemical parameters such as highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), the charge distributions, the absolute electro-negativity values (χ) , electron affinity (A=- E_{LUMO}), ionization potential (I=- E_{HOMO}),global hardness (η), softness (σ), ionization potential (I) and the fraction of electrons transferred from inhibitors to iron (ΔN) have been calculated. Meanwhile, according to theoretical study, through structural parameters such as frontier orbital energy level, charge distribution and their interaction with metal surface, we could study on the corrosion inhibition mechanism of these corrosion inhibitors, which will provide theoretical information for design and discover new homologous Schiff bases inhibitors with better inhibition efficiency.

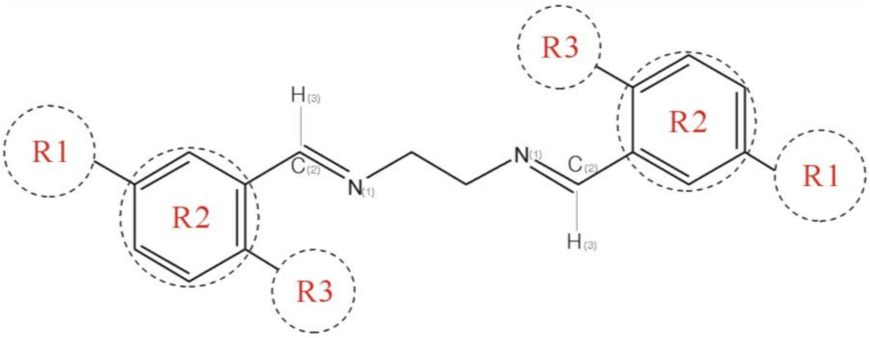
Table 1. The chemical structures and abbreviations the investigated Schiff bases compounds.

Inhibitor	Conformation	Abbreviation
N,N'-bis (5-methoxysalicylidene) -1,2-ethylenediamine		M1
N,N'-bis (salicylidene) -1,2-ethylenediamine		M2
N,N'-bis (5-nitrosalicylidene) -1,2-ethylenediamine		M3

2. CALCULATION METHOD

Density Functional Theory (DFT) [20-21], an economic and efficient quantum chemistry computing method, can provide accurate information of geometrical configuration and electron distribution. It is widely applied in the analysis of corrosion inhibition performance and the interaction of corrosion inhibitors and interfaces. Adopting DFT/B3LYP in Gaussian03W [22], this method conduct geometry optimization and frequency analysis on the objects on the basis set of 6-31+G (d, p) [23-24]. Making sure that all the structures are minimal points on potential energy surface, we calculate molecular parameters, such as frontier orbital distribution, mulliken charge population, etc.

3. RESULTS AND DISCUSSION



R_1 =-OCH_3(M1)、-H (M2)、-NO_2 (M3), R_2=-Ph, R_3= -OH

Figure 1. The molecular schematic of inhibitor

Table 2. Quantum chemical parameters of the studied inhibitors calculated at B3LYP/6-31+G (d, p) level.

Phase [a]	Inhibitor	E_{HOMO} (ev)	E_{LUMO} (ev)	ΔE [b] (ev)	x	η	σ	ΔN	Q_{N1}	Q_{C2}	Q_{H3}	Q_{R1}	Q_{R2}	Q_{R3}	IE[b]
G	M1	-5.757	-1.441	4.316	3.599	2.158	0.463	3.670	-0.040	0.203	0.123	-0.056	-0.681	-0.174	87.0
	M2	-6.268	-1.490	4.778	3.879	2.389	0.419	3.728	-0.213	-0.047	0.121	0.126	-0.349	-0.163	82.0
	M3	-7.112	-2.765	4.347	4.939	2.174	0.460	2.240	-0.028	0.194	0.128	-0.385	-0.432	-0.139	76.0
A	M1	-5.851	-1.650	4.201	3.750	2.100	0.476	3.413	-0.150	0.344	0.146	-0.082	-0.835	-0.189	87.0
	M2	-6.298	-1.598	4.700	3.948	2.350	0.426	3.586	-0.166	-0.212	0.145	0.161	-0.376	-0.176	82.0
	M3	-6.789	-3.027	3.762	4.908	1.881	0.532	1.968	-0.130	0.334	0.154	-0.497	-0.588	-0.123	76.0

[a] G, gas phase (dielectric constant ε = 1.0); A, aqueous phase (dielectric constant ε= 78.5). [b] Exp. value from Ref. [15], containing 1.0mol/L HCl, 10^{-3} M inhibitor at 298K.

The structure of these Schiff bases molecular is shown in Fig.1. After DFT B3LYP/6-31+G (d, p) optimization, structural parameters are shown in Table 2. E_{HOMO} and E_{LUMO} are energy of HOMO and LUMO orbitals, and the energy gap $\Delta E=E_{HOMO}-E_{LUMO}$. According to Koopman's theorem [25], ionization potential (I) and electron affinity (A) are related to the energy of HOMO and LUMO orbitals where: I=- E_{HOMO} and A=- E_{LUMO}. The concept of absolute electro-negativity values (χ) and global hardness (η) [26]are calculated as: $\chi=(I+A)/2$, $\eta=(I-A)/2$, and the reverse of global hardness is defined as softness: $\sigma=1/\eta$. *The obtained values of* absolute electro-negativity values (χ) and global hardness (η) are used to calculate the fractions of the electrons transferred from inhibitors to metallic surface, such as Fe surface, it has the following format[27-32]: $\Delta N=(\chi_{Fe}-\chi_{inh})/2(\eta_{Fe}+\eta_{inh})$, where we use a theoretical value, χ_{Fe}=7.0ev/mol and η_{Fe}=0 ev/mol for iron according to assumption that as for a metallic bul*k*, *I*=*A*, because they are softer than neutral metallic atoms [26]. Q_{N1}、Q_{C2} and Q_{H3} refer to average net charge of N、C and H on –CH=N- group respectively. Q_{R2} refers to average net charge of R1. Q_{R2} refers to average C atom's net charge on benzene ring R2. Q_{R3} refers to average net charge of R3.

3.1 Relationship between frontier molecular orbital and inhibition efficiency

From the theory of quantum chemistry [33-34], we know that the interaction between reactants only happens in frontier molecular orbital and the theory is often used to explain the adsorption centers of the inhibitor molecules when considering the adsorption on a metal surface [33,35]. The relationships between the frontier molecular orbital energy of three Schiff bases inhibitors and their inhibition efficiency are plotted in Fig.2. From Fig.2 it is very clear that the inhibition efficiency has a good correlation with E_{HOMO}, no matter in gas phase or aqueous phase. And the square correlation coefficient R^2 is close to 0.99. With the energy of HOMO increasing, the molecule becomes active and it can provide more electrons for its adsorption on a metallic surface and the inhibition efficiency increases too. It can be found that HOMO may play a main role in corrosion inhibition efficiency.

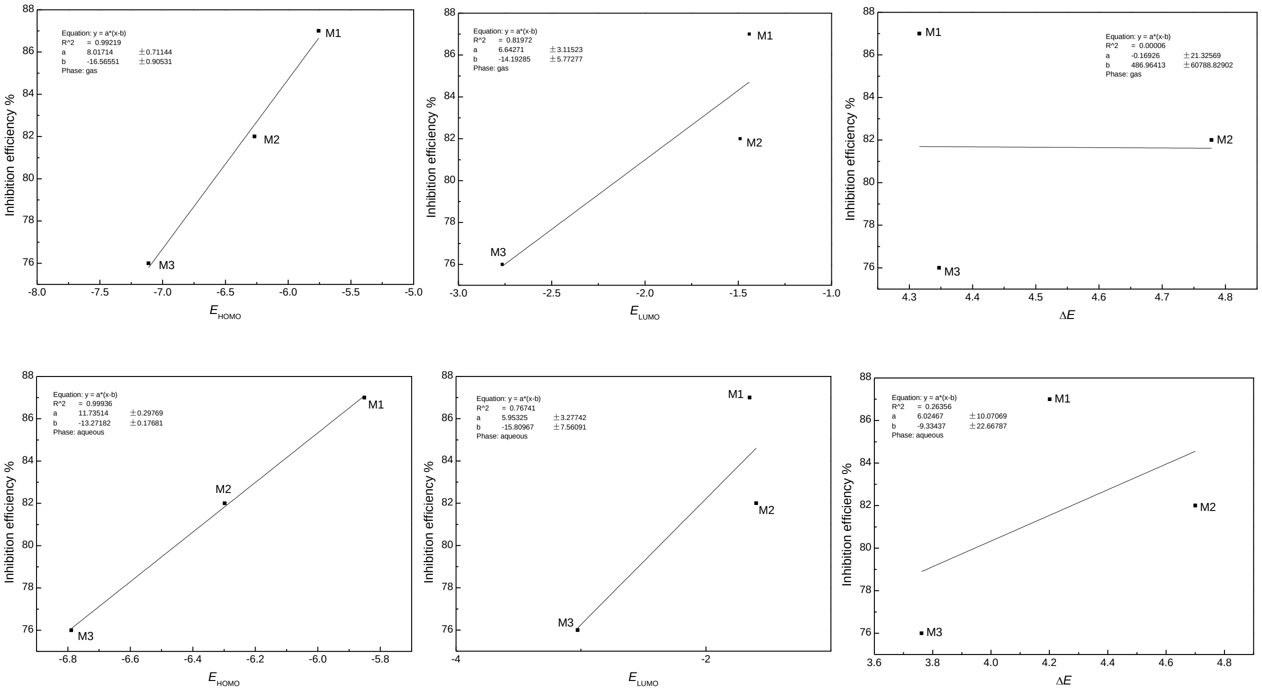


Figure 2. Correlation between frontier molecular orbital energies and inhibition efficiency

To analyze the adsorption process of corrosion inhibitor we should take HOMO and LUMO of inhibitor molecules into consideration; therein, E_{HOMO} is the measurement of electron donating ability.

The smaller E_{HOMO} is, the more stable the electrons are and smaller the electron donating ability is. E_{LUMO} is closely related to molecular electron affinity. E_{LUMO} is small means the electron's system energy decreases much when it enters into this orbital. It also indicates that the molecule can accept electrons easily. $\Delta E= (E_{\mathrm{HOMO}}-E_{\mathrm{LUMO}})$, the orbital energy difference of HOMO and LUMO, is an important stability indicator. The bigger ΔE is, the better the stability is and the worse the activity in chemical reaction. The charge in molecule is the main factor leading to the interaction of electrons. With the charge of atom, it decides many chemical reactions and physical properties [31]. The charge density of atom frontier orbital is of great significance for the study of donor-receptor interaction, as chemical reaction is the charge migration between HOMO and LUMO [34]. But how the orbit plays the role during the adsorption process? The frontier molecule orbital density distributions of HOMO and LUMO for these three inhibitor molecules were shown in Fig.3. As see from the Fig.3, the HOMO seemed focused on the same sting R2 while the LUMO distributions had a little bit different cause for C1 whose LUMO focused on only one R3.

Hence, from the previous analysis, we could reach the following conclusion that the efficiency of these three Schiff bases inhibitors were mainly decided by the electrons on HOMO because when they adsorbed on a metallic surface, the inhibitor could provide electrons to the LUMO orbit of metal atom and then form a coordination bond. If the energy of HOMO is more negative, the electrons will be more attractive with strong activation and the inhibition efficiency will be higher.

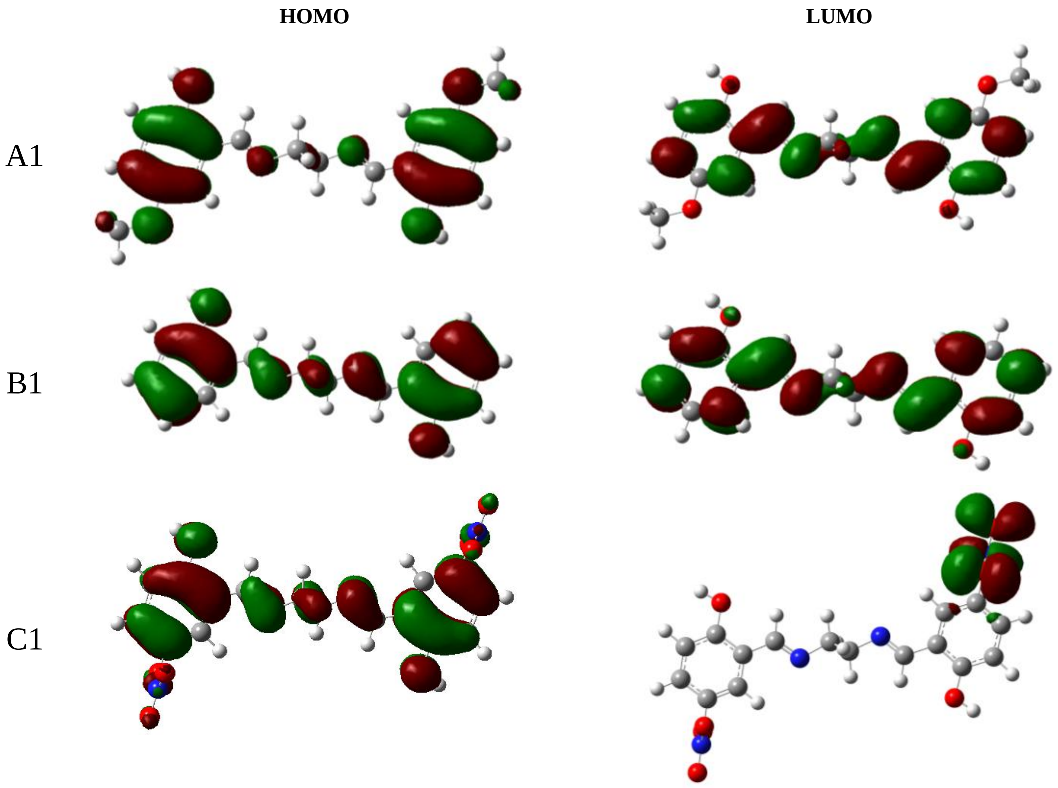


Figure 3. The orbital density distributions for inhibitors A1, B1, C1, isosurfaces with a value of 0.02a.u.

The electro-negativity values (χ), global hardness (η), softness (σ) and the number of transferred electrons (ΔN) were also calculated. The relationships between these parameters and corrosion inhibition efficiency were plotted in Fig.4. As clearly seen from the Fig.4, the inhibition efficiency has a good relationship with electro-negativity values (χ) and they are well correlated. The multiple correlation coefficient square R^2 can reach about 0.90 whatever in gas or aqueous phase. Other parameters have less significant correlation with inhibition efficiency. From Table 2, we can find that with the increase of electro-negativity values, the inhibition efficiencies decrease. This shows that when the electron-negativity increases, distribution of electrons in the molecule will become uneven. Hence, once the molecules adsorb on metallic surface, it will provide uniform electrons to the surface, leading to decline inhibition efficiency.

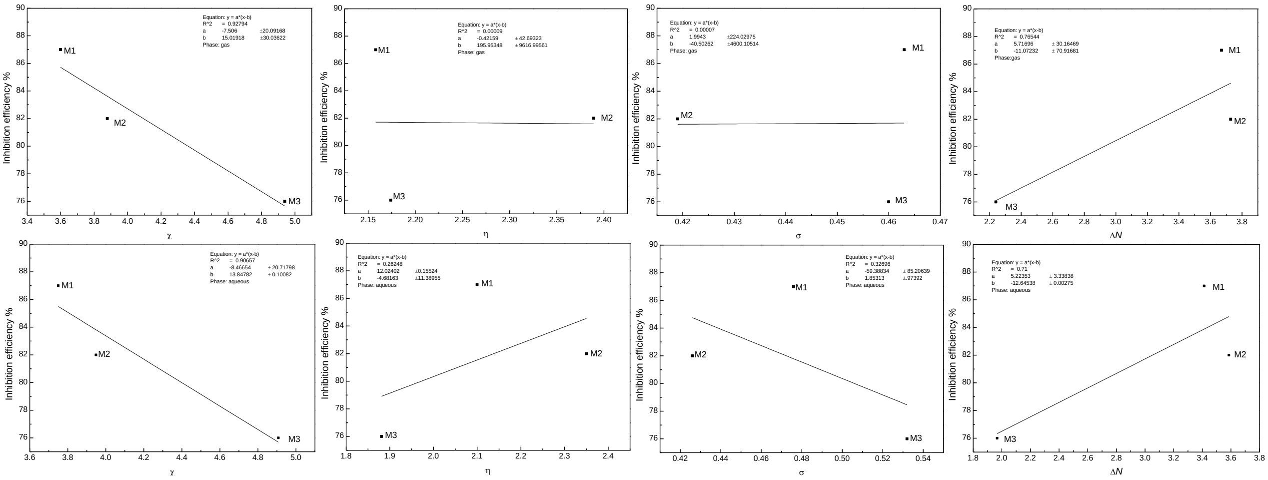


Figure 4. Correlation between electro-negativity values (χ), global hardness (η), softness (σ), the number of transferred electrons (ΔN) and inhibition efficiency

3.2 Correlation between charge and inhibition performance

Generally the charge of the inhibitor could affect the adsorption through influencing the charge distribution at some functional atoms or groups. In most case, if the molecule has more negative charge site or centre, the better inhibition efficiency it will have. We make some analysis on linear regression of net charges, such as Q_{N1}、Q_{C2}、Q_{H3}、Q_{N1+C2}、$Q_{N1+C2+H3}$、Q_{R1}、Q_{R2} and Q_{R3}, etc. After the linear regression, we find that inhibition efficiency shows positively correlation with net charges of atom N1 and string R3 no matter how the phase is gas or aqueous (Fig.5.). The reason is that atom N has lone pair of electrons and can act as electron donor. As for R3 (-OH), O is similar as N and could provide electrons. So they have more negative charges and affect the inhibition efficiency a lot. Why M1 has better inhibition efficiency? Because R1 of M1 is $-OCH_3$, which has strong electron donor ability, and finally affect its R3 and N1 and they have more negative charges too. But as for R1 of M3 is $-NO_2$, which has strong electron-withdrawing ability, and finally its R3 and N1 have less negative charges, so as has less inhibition efficiency.

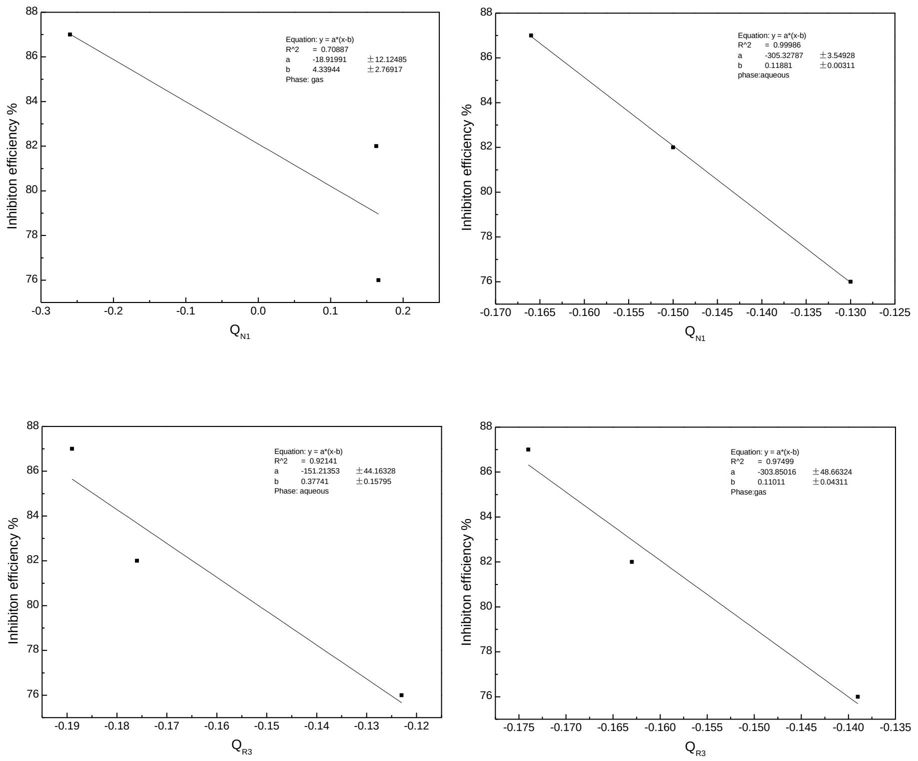
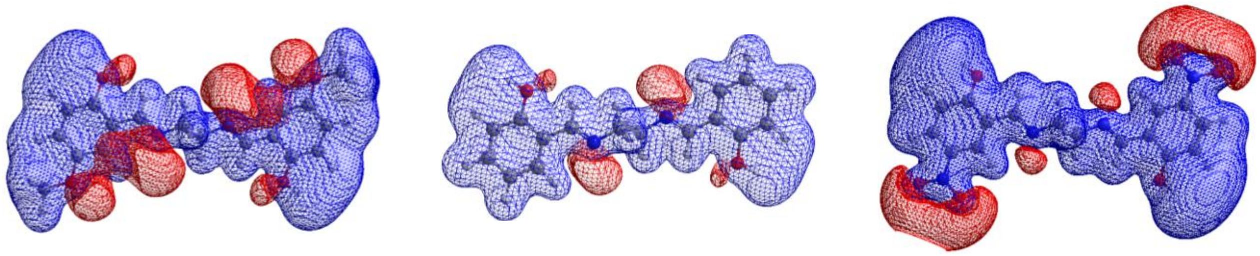


Figure 5. Correlation between charge Q_{N1}, Q_{R3} and inhibition efficiency

In order to further illustrate which part of the inhibitor plays an important role, molecular electrostatic potential surfaces for each molecular are calculated. It can be obviously seen from Fig.6 that for M1 most of negative potential concentrate on –OH, N, and –OCH_3. For inhibitor M2, negative potential concentrate on N and –OH. As for inhibitor M3, there is a little negative charge on N, almost no charge on –OH, and most of negative charges locate on –NO_2. From the negative charge distribution we could also find that uniform negative charge distribution was as follows: M1>M2>M3. This also explains why the M1 has the best corrosion inhibition efficiency and this is consistent with the previous analysis results of electro-negativity values



M1 M2 M3

Figure 6. The molecular electrostatic potential surfaces for inhibitors with isopotential value of 1.2 a.u. * Red: negative, Blue: positive

3.3 Prediction of new inhibitors' efficiency

Table 3. Structures of other homologous inhibitors

Inhibitor	R1	R2	R3
M4	-OC_2H_5	-Ph	-OC_2H_5
M5	-OCH_3	-Ph	-OC_2H_5
M6	-OH	-Ph	-OC_2H_5
M7	-SH	-Ph	-OC_2H_5
M8	-OC_2H_5	-Ph	-OCH_3
M9	-OCH_3	-Ph	-OCH_3
M10	-OH	-Ph	-OCH_3
M11	-SH	-Ph	-OCH_3
M12	-OC_2H_5	-Ph	-OH
M13	-OH	-Ph	-OH
M14	-SH	-Ph	-OH
M15	-OC_2H_5	-Ph	-SH
M16	-OCH_3	-Ph	-SH
M17	-OH	-Ph	-SH
M18	-SH	-Ph	-SH

Table 4. Quantum chemical parameters and prediction of inhibition efficiency for homologous inhibitors

Inhibitor	HOMO/ev	LUMO/ev	x	Q_{N1}	Prediction of inhibition efficiency [a]			Average
					IE=11.735*(E_{HOMO}+13.27182)	IE=-8.466*(x-13.848)	IE=-305.328*(Q_{N1}-0.119)	
M4	-5.745	-1.601	3.673	-0.186	88.333	86.146	93.152	89.210
M5	-5.756	-1.634	3.695	-0.156	88.199	85.958	83.966	86.041
M6	-5.800	-1.650	3.725	-0.169	87.682	85.707	87.952	87.113
M7	-5.761	-1.683	3.722	-0.164	88.145	85.733	86.354	86.744
M8	-5.777	-1.644	3.710	-0.158	87.953	85.829	84.555	86.112
M9	-5.792	-1.633	3.712	-0.191	87.774	85.812	94.568	89.385
M10	-5.832	-1.660	3.746	-0.174	87.308	85.527	89.503	87.446
M11	-5.788	-1.696	3.742	-0.167	87.822	85.562	87.385	86.923
M12	-5.843	-1.663	3.753	-0.175	87.180	85.469	89.586	87.412
M13	-5.910	-1.704	3.807	-0.154	86.391	85.011	83.330	84.911
M14	-5.850	-1.717	3.784	-0.162	87.091	85.209	85.662	85.987
M15	-5.833	-1.726	3.780	-0.165	87.292	85.244	86.649	86.395
M16	-5.849	-1.733	3.791	-0.168	87.113	85.148	87.468	86.576
M17	-5.896	-1.755	3.826	-0.165	86.551	84.853	86.523	85.976
M18	-5.867	-1.808	3.837	-0.167	86.902	84.756	87.160	86.273

[a] formula presented in Fig.2 , Fig.4 and Fig.5.

Through theoretical study, not only we can understand the mechanism of corrosion and inhibitor adsorption on metal surfaces, determine the merits of corrosion inhibitors, but also the results can help to predict the performance of some homologous corrosion inhibitors and to provide useful information for the synthesis of these new homologous corrosion inhibitors. According to the quantum properties of the correlation between the chemical parameters and performances of inhibitors, to play a better inhibition performance, for these three Schiff bases inhibitors we can try to replace R1 and R3 by some electron donor group. So, we design other groups of homologous corrosion inhibitors just change R1 and R3 (Table 3, Inhibitor M4~M18), obtain their quantum chemical parameters using B3LYP/6-31+G(d,p) method and predict their inhibition efficiency by using their HOMO energies, electro-negativity values and Q_{N1} Mulliken charge (using the formula presented in Fig.2 , Fig.4 and Fig.5).

From Table 4 we can find inhibitor M4 and M9 have a better performance than M1~M3. It is easy to draw the conclusion that if R1 and R3 have more tendencies to provide electrons, and the center of the inhibitor will get more negative potential which could benefit for the inhibitor to adsorb on the iron surface and then achieve a better inhibition effect. Because $–OCH_3$ and $–OC_2H_5$ have more tendencies to provide electrons, the mulliken charges of N1 for M4 and M9 also get more negative potential than other inhibitors. This also explains why they have better corrosion performance.

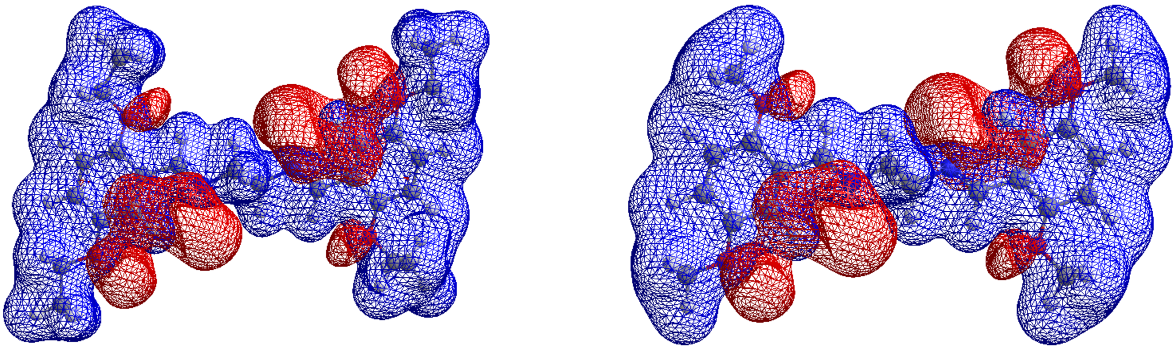

M4 M9

Figure 6. The molecular electrostatic potential surfaces for M4 and M9 with isopotential value of 0.65 a.u.(* Red: negative, Blue: positive)

It can be seen from Fig.6 that after optimization, N atoms and O atoms of R1 and R3 have more negative charges. Particularly, electrostatic potential surfaces O (R3) and N link into one part. This factor may help these inhibitors to adsorb on metal surface, improving its inhibition effect.

4. CONCLUSIONS

Using quantum chemistry theoretical calculation, we have studied the relationship between three benzimidazoles inhibitors’ corrosion inhibition performance and their quantum chemical structure parameters at the level of DFT/B3LYP with the 6-31+G (d, p) base sets. Quantum chemical parameters such as highest occupied molecular orbital energy, lowest unoccupied molecular orbital energy, energy gap, the charge distributions, the absolute electro-negativity values, electron affinity, global hardness, softness, ionization potential and the fraction of electrons transferred from inhibitors to iron have been calculated. The relationships between the corrosion inhibitor efficiency and these quantum chemical parameters are discussed using linear regression analysis to determine the most effective parameter on inhibition efficiency, and the results show that the corrosion inhibition performances of these inhibitors have a good linear relationship to E_{HOMO}, χ and Q_{N1}. The theoretical data were also well accorded with reported experimental results. So, we can theoretically find that HOMO orbital, χ and Q_{N1} play important roles for these inhibitors.

We can design some homologous corrosion inhibitors from this study: just keep the main structure -R2-CH=N-CH_2-CH_2-N=CH-R2- and then change other part of molecular (R1 and R3) to design the new homologous corrosion inhibitors. After that, we calculate the quantum chemical structure parameters and use structure-activity relationships (regression formula) to predict the performance of these inhibitors and then we may find which corrosion inhibitors have good performance. Hence, the study may give a theoretical prediction for new homologous inhibitors and point a direction for laboratory studies and chemical synthesis.

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