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s as corrosion Inhibitor of Iron

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Abstract:
The corrosion inhibition characteristics of furan oligomers on Iron has been studied using density functional theory (DFT) at the B3LYP/6-31G (d, p), Quantum chemical parameters such as highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), and energy gap (ΔE) were calculated, quantum chemical parameters such as , the total amount of electronic charge transferred,(ΔN) from the inhibitor to metallic surface**,** electrophilicity index (ω) (electrons transfer from metals to the anti π- orbital's of the inhibitors), chemical softness (σ) and chemical hardness (η),The relationship between the inhibition efficiency and quantum chemical parameters has been discussed in order to elucidate the inhibition mechanism of these compounds. **Keywords**: Iron, DFT, Corrosion, Inhibitor, furan oligomers.

1-Introduction

Corrosion is the destructive attack of metal or alloy chemically or electrochemically against its environment which leads to loss of useful properties of materials[1].The protection of metals against corrosion can be achieved by adding inhibitors in small concentrations to its environment[2]. A survey of literature presents the applicability of organic compounds, particularly those containing O, S and/or N atoms in their long carbon chain/aromatic structure, as corrosion inhibitors for mild steel in acidic media[3]. Among these compounds, metal (N-methyl-p-aminophenol sulphate) has attracted much attention since it has been successfully used as a photographic developer,[4,5] analgesic-antipyretic agent,[6,7] and corrosion inhibitor [8] Although experimental work [9] provide valuable information on the corrosion inhibition efficiency of metal, a deep understanding of the inhibition property remains unclear. The advancements in computer simulation techniques hold promise that questions regarding the inhibitive properties of such compounds can be addressed at the atomic level. Hence, more corrosion studies contain substantial quantum chemical calculations in recent years[10] To date, how-ever, no study has been performed to investigate the corrosion inhibition efficiency of metal by using quantum chemical calculations. The objective of the present paper is to study the effect of structural parameters of metal on its inhibition efficiency of corrosion of steel by using density functional theory (DFT) methods. Molecular orbital calculations are performed looking for good theoretical parameters to characterize the inhibition property of inhibitor, which will be helpful to gain insight into the mechanism of the corrosion inhibition.

1.1 Ab initio and density functional theory (DFT) methods

Quantum mechanical methods (ab initio, density functional theory (DFT) and semiempirical) are all based on solving the time independent Schrodinger equation for the electrons of a molecular system as a function of the positions of the nuclei. The term ab initio indicates that the calculation is from first principles and that no empirical data is used. The simplest type of ab initio electronic structure calculation is the Hartree-Fock (HF), in which the instantaneous Columbic electron–electron repulsion is not specifically taken into account and only its average effect is included in the calculation. This is a variation procedure, and, therefore, the obtained approximate energies, expressed in terms of the system wave function, are always equal to or greater than the exact energy, and approach a limiting value called the Hartree–Fock limit as the size of the basis is increased [11]. Many types of calculations (Moller-plesset perturbation theory) begin with a Hartree–Fock calculation and subsequently correct for electron–electron repulsion, referred to also as electronic correlation, density functional theory (DFT) is used to investigate the electronic structure, principally the ground state of many-body systems, in particular atoms, molecules and the condensed phases. The main objective of DFT is to replace the many-body electronic wave function with the electronic density as the basic quantity [12]. Any exchange functional can be combined with any correlation functional in DFT calculations. For example, the notation BLYP/ 6-31G* denotes a density functional calculation done with the Becke 1988 exchange functional and the Lee-Yang-Parr correlation functional, with the orbital's expanded in a 6-31G* basis set [13]. density Functional Theory (DFT) [14, 15] which is an economic and efficient quantum chemistry computing method can provide accurate information about geometrical configuration and electron distribution. DFT is widely applied in the analysis of corrosion inhibition performance and the interaction of corrosion inhibitors and interfaces [16 - 17].

2- Results and discussion

The furan Oligomers under investigation and there structures are shown in Scheme.1. Frontier Molecular orbital's (HOMO and LUMO), energy gap (ΔE), hardness (η), softness (σ) the fraction of the electron transferred (ΔN), and electrophilicity index (ω), were calculated for furan oligomers. According to molecular orbital theory [18] the ionization potential (*I*) and electron affinity (*A*) are related in turn to E_{HOMO} and E_{LUMO} using the equations below [19]:

$$I = -E_{\text{HOMO}} \quad \ldots\ldots\ldots\ldots(1)$$

$$A = -E_{\text{LUMO}} \ldots\ldots\ldots\ldots..(2)$$

$$\chi = \frac{\mathrm{I+A}}{2} \quad ,,,,,,,,,,,,,,(3)$$

$$\eta = \frac{\mathrm{I-A}}{2} \quad \ldots\ldots\ldots\ldots(4)$$

Recently, a new global chemical reactivity parameter has been introduced and is called an electrophilicity index (*ω*) it is defined as [20]:

$$\omega = \frac{\mu^2}{2\eta} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

where μ represents the chemical potential,This was proposed as a measure of the electrophilicity power of a molecule. Global softness can also be defined as [21]:

$$\sigma = \frac{1}{\eta} \quad \ldots\ldots\ldots\ldots(6)$$

The number of transferred electrons (ΔN) from the inhibitor molecule to the metal surface can be calculated by using the following equation [22].

$$\Delta N = \frac{\chi_{\text{metal}} - \chi_{\text{inh}}}{2(\eta_{\text{metal}} + \eta_{\text{inh}})} \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

where χ_{metal} and χ_{inh} denote the absolute electronegativity of metal and the inhibitor molecule respectively , The difference in elecronegativity drives the electron transfer and the sum of hardness parameters acts as resistance [23].

Table1.Calculated HOMO – LUMO energies of inhibitor furan oligomers by DFT method.

Compounds	$E_{\text{HOMO (eV)}}$	$E_{\text{LUMO (eV)}}$
Fe	-7.9024 [a]	-0.151[a]
Furan1	-6.3645	0.2256
Furan2	-5.4848	-0.8729
Furan3	-5.1305	-1.3345
Furan4	-4.9459	-1.5854
Furan5	-4.8379	-1.7415
Furan6	-4.7688	-1.8460
Furan7	-4.7226	-1.9203
Furan8	-4.6902	-1.9750
Furan9	-4.6665	-2.0167
Furan10	-4.6491	-2.0490

[a]From ref [27]

According to the frontier molecular orbital theory, FMO, the chemical reactivity is a function of interaction between HOMO and LUMO levels of the reacting species [24]. E_{HOMO} is a quantum chemical parameter which is often associated with the electron donating ability of the molecule. High value of E_{HOMO} is likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy [25]. Therefore, the energy of the lowest unoccupied molecular orbital, E_{LUMO}, indicates the ability of the molecule to accept electrons [26]. So, the lower the value of E_{LUMO}, the more probable the molecule would accept electrons. Thus the binding ability of the inhibitor to the metal surface increases with increasing of the HOMO and decreasing of the LUMO energy values. The energies of HOMO and LUMO values for iron were taken from literature [27].

Table 2. shows the HOMO-LUMO gap for interaction of iron–inhibitor. Iron acts as a Lewis base while the inhibitor furan oligomers act a Lewis acid. So iron will

utilize the HOMO orbital to initiate the reaction with LUMO orbital of the furan oligomers. The interaction will have certain amount of ionic character because the values of $LUMO_{inhi}$ –

$HOMO_{Fe}$ gap fall between 6 and 4 eV. Strong

covalent bond can be expected only if $LUMO_{inh}$- $HOMO_{Fe}$ gap is approximately zero eV [28].

Table 2. HOMO –LUMO gap interactions of iron– inhibitor furan oligomers by DFT method.

Inhibitor	$LUMO_{inh}$ - $HOMO_{Fe\ (eV)}$	$LUMO_{Fe}$ - $HOMO_{inh(eV)}$
Furan1	8.1280	6.2135
Furan2	7.0295	5.3338
Furan3	6.5679	4.9795
Furan4	6.3170	4.7949
Furan5	6.1609	4.6869
Furan6	6.0564	4.6178
Furan7	5.9821	4.5716
Furan8	5.9274	4.5392
Furan9	5.8857	4.5155
Furan10	5.8534	4.4981

Furan oligomers will act as a Lewis bases while iron act as a Lewis acid (Table2)

Thus Furan oligomers act as anodic inhibitors. The electronegativity X, global chemical hardness η, global softness σ, the fraction of electrons transferred ΔN and electrophilicity ω, are involved in Table 3. The separation energy, $\Delta E = (E_{LUMO} - E_{HOMO})$, is an important parameter (Table 3) and it is a function of reactivity of the inhibitor molecule towards the adsorption on metallic surface. As ΔEgap decreases, the reactivity of the molecule increases leading to increase in the inhibition efficiency [29]. The

effectiveness of furan

oligomers as inhibitors under investigation has been further addressed by evaluating the global reactivity parameters.

All quantum chemical parameters are tabulated in Table 3.

Table 3. The calculated quantum chemical parameters for furan oligomers with iron by DFT method .

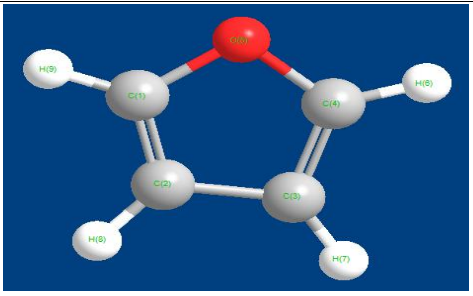
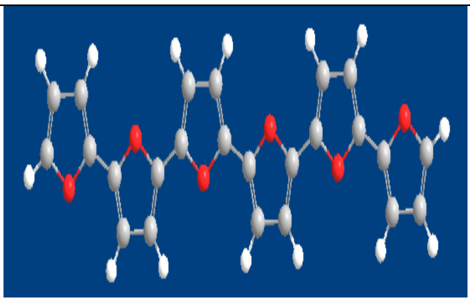
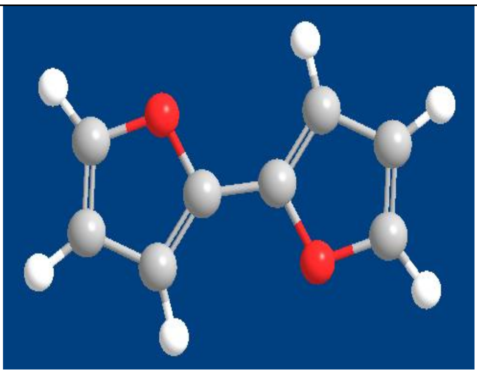
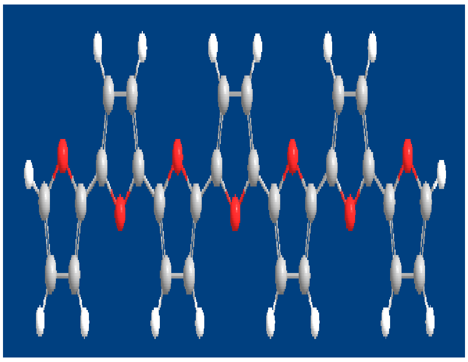
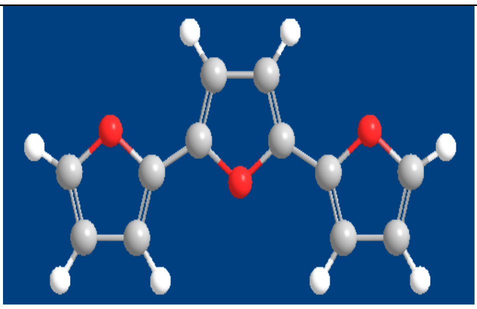
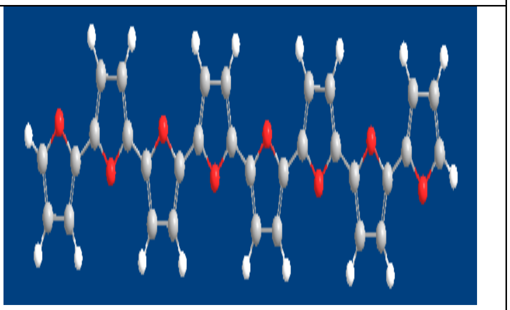
Quantum parameter	Fu1	Fu2	Fu3	Fu4	Fu5	Fu6	Fu7	Fu8	Fu9	Fu10
E_{HOMO}	-6.3645	-5.4848	-5.1305	-4.9459	-4.8379	-4.7688	-4.7226	-4.6902	-4.6665	-4.6491
E_{LUMO}	0.2256	-0.8729	-1.3345	-1.5854	-1.7415	-1.8460	-1.9203	-1.9750	-2.0167	-2.0490
ΔEgap	6.5901	4.6119	3.796	3.3605	3.0964	2.9228	2.8023	2.7152	2.6498	2.6001
I	6.3645	5.4848	5.1305	4.9459	4.8379	4.7688	4.72261	4.6902	4.6665	4.6491
A	-0.2256	0.8729	1.3345	1.5854	1.7415	1.8460	1.9203	1.9750	2.0167	2.0490
X	3.0695	3.1789	3.2325	3.2657	3.2897	3.3074	3.3215	3.3326	3.3416	3.3491
η	3.2951	2.3059	1.8980	1.6803	1.5482	1.4614	1.4012	1.3576	1.3249	1.3001
σ	0.3035	0.4337	0.5269	0.5951	0.6459	0.6843	0.7137	0.7366	0.7548	0.7692
N Δ	0.0667	0.0686	0.0688	0.0685	0.0679	0.0674	0.0668	0.0663	0.0659	0.0655
ω	1.4297	2.1912	2.7527	3.1735	3.4951	3.7426	3.9363	4.0904	4.2140	4.3137

The bonding tendencies of the inhibitors towards the metal atom can be discussed in terms of the HSAB (hard–soft-acid–base) and the frontier-controlled interaction concepts [30, 31]. General rule suggested by the principle of HSAB, is that hard acids prefer to co-ordinate to hard bases and soft acids prefer to co-ordinate to soft bases, On the other hand, metal atoms are known as soft acids. Hard molecules have a high HOMO–LUMO gap and soft molecules have a small HOMO–LUMO gap [32], and thus soft bases inhibitors are the most effective for metals [29]. So, furan oligomers which have the lowest energy gap and highest softness have the inhibition efficiency, The number of electrons transferred (Δ*N*) was also calculated and tabulated in Table 3. The inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface. It turns out that this donation of furan oligomers increases with increasing in number of furan molecules. Thus, the highest fraction of electrons transferred is associated with the best inhibitor. The electrophilicity index, ω, which shows the ability of inhibitor molecules accept electrons. Thus the increase in the values of ω, result from an

increase in the number of furan molecules (Table 3), which confirms its high capacity to accept electrons. Thus, unoccupied d orbital's of iron can accept electrons from the inhibitor to form a coordinate bond. Also the inhibitor can accept electron from Fe atom with its anti-bonding orbital's to from back-donating bond. These donation and back-donation processes strengthen the adsorption of furan oligomers [33].

CONCLUSIONS

It can be concluded that furan oligomers can be a good inhibitors for iron The adsorption of the inhibitor on the metal surface is spontaneous. This study, thus displays a good correlation between theoretical and experimental data which confirm the reliability of the DFT method to study the inhibition corrosion of metal surface.

inhibitor	Structure	inhibitor	Structure
Furan1		Furan6	
Furan4		Furan7	
Furan3		Furan8	

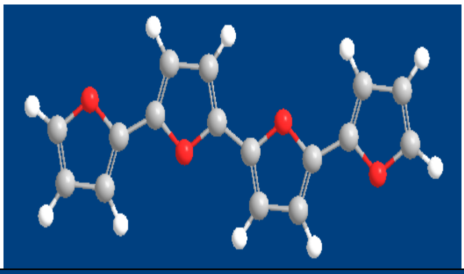
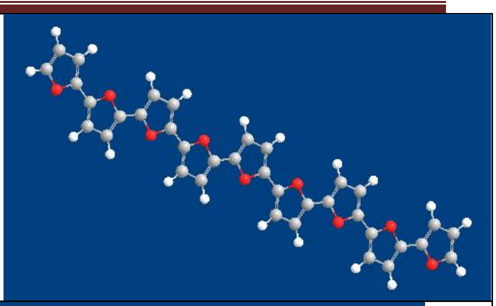
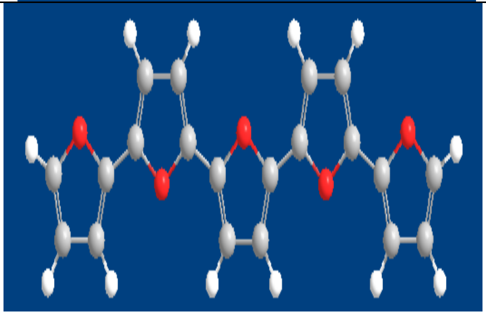
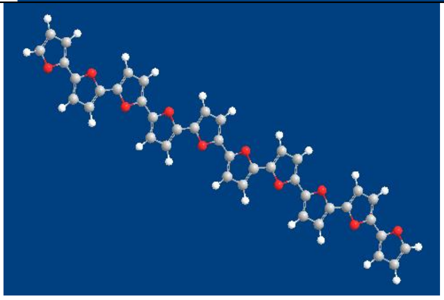
Furan4		Furan9	
Furan5		Furan10	

Figure 1 Optimized molecular structures of furan oligomers (1 to 10)

References

[1]Uhlig, H. H.; Revie, R. W. Corrosion and Corrosion Control; Wiley & Sons: New York, 1985.
[2] Jones, D. A. Principles and Prevention of Corrosion; Macmillan: New York, 1992.
[3] Sanyal, B. Prog. Org. Coat. **1981**, 9(2),165.
[4] Henney, K.; Dudley, B. Handbook of Photography; Whittlesey House: New York, 1939.
[5]Lunar, L.; Sicilia, D.; Rubio, S.; Pérez-Bendito, D.; Nickel, U. Water Res. **2000**, 34, 1791.
[6] Cekic, S. D.; Filik, H.; Apak, R. J. Analytical Chem. **2005**, 60, 1019.
[7] Chu, Q.; Jiang, L.; Tian, X.; Ye, J. Anal. Chim. Acta **2008**, 606, 246.
[8] Kirk, R.; Othmer, D. Encyclopedia of Chemical Technology; Wiley & Sons: New York, 1994.
[9] Praveen, B. M.; Venkatesha, T. V. Int. J. Electrochem. Sci. **2009**, 4, 267.
[10] Gece, G. *Corros. Sci.* **2008**, *50*, 2981.

[11] R.G. Parr, D.P. Craig, I.G. Ross, Molecular orbital calculations of the lower excited electronic levels of benzene, configuration interaction included, J. Chem. Phys.**18**, 1561 (1950).
[12] F. Jensen, Introduction to Computational Chemistry, John Wiley & Sons, Chichester, (2007).
[13] I.N. Levine, Quantum Chemistry, Prentice Hall, New Jersey, 1991.

[14] P. Hohenberg, W. Kohn, Phys. Rev. **136**, 864(1964).
[15] W. Kohn, L. J. Sham, Phys. Rev. **140**, 1133 (1965).

[16] G.Gece, S.Bilgiç, Corros. Sci. 52, 3435 (2010).
[17] J. Zhang, G. M. Qiao, S. Q. Hu, Y. G. Yan, Z. J. Ren, L. J. Yu, Corros. Sci. **53**, 147(2011).
[18] K. F. Khaled, S. A. Fadl-Allah, B. Hammoutic,Mater. Chem. Phys. **117**, 148(2009).
[19] K. Fukui, Angew. Chem. Int. Ed. Engl. **21**, 801 (1982).
[19] M. J. S. Dewar, W. Thiel, Chem. Soc. **85**, 3533 (1963).

[20] P.K. Chattaraj, U. Sarkar, D.R. Roy. Chem. Rev. **106**, 2065 (2006).

[21] A. Lesar, I. Milosev, Chem. Phys. **483**, 198 (2009).

[22] I. Lukovits, E. Kalman, F. Zucchi, Corrosion (NACE), **57,** 3 (2001).

[23] A. Y. Musa, A. H. Kadhum, A. B. Mohamad, A. B. Rohoma, H. Mesmari, J. Mol. Struct, **969**, 233 (2010). [24] G. Gece, S. Bilgic. Corrosion. Sci, **51**, 1876 (2009).

[25] I. Ahamad, R. Prasad, M. A. Quraishi, Corrosion. Sci, **52**, 1472 (2010).

[26] D. R. Lide, CRC Handbok of Chemistry and Physics, 88th ed, 2007-2008.

[27] G. Klopman, J. Am. Chem. Soc. 90, 233 (1968). W. B. Jenswn, chem. Rev. 78, 1 (1978).

[28] M. K. Awad, M. R. Mustafa, M. M. Abo Elnga, J. Mol. Struct. (Theochem), **959**, 66 (2010).

[29] R. G. Pearson Inorg. Chem, **27**, 734 (1988).

[30] E. Koch Propellants, Explos, Pyrotech. **30**, 5 (2005).

[32] X. Li, S. Deng, H. Fu, T. Li, Electrochim. Acta, **54**, 4089(2009).
[33] T. Arslan, F. Kandemirli, E. E. Ebenso, I. Love, H. Alemu, Corrosion, **51**,35(2009).