

## Quantum chemical study on the corrosion inhibition of N-benzylpiperidine-4-one oxime

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### ABSTRACT

A theoretical study of N-benzyl piperidine -4-one oxime, an organic corrosion inhibitor for mild steel in 1 M HCl medium, was undertaken by means of the Semi empirical quantum chemical PM6 method. The calculated quantum chemical parameters correlated to the inhibition efficiency are the highest occupied molecular orbital ( $E_{HOMO}$ ) and the lowest unoccupied molecular orbital ( $E_{LUMO}$ ), the energy difference ( $\Delta E$ ) between  $E_{HOMO}$  and  $E_{LUMO}$ , dipole moment ( $\mu$ ), electronegativity ( $\chi$ ), electron affinity (A), global hardness ( $\eta$ ), global softness ( $\sigma$ ), ionization potential (I) and the fraction of electrons transferred ( $\Delta N$ ). It is an attempt to find the correlation between the molecular structure of the compound and possible behaviour like corrosion inhibitor. The agreement with the experimental data was also found to be satisfactory.

**Keywords:** N-benzylpiperidin-4-one oxime, Semi empirical quantum chemical PM6, electro negativity, electron affinity, ionization potential,  $E_{HOMO}$ ,  $E_{LUMO}$ , and corrosion inhibition.

### INTRODUCTION

Corrosion inhibitors are widely used in acid solutions for protection of metal surfaces from corrosion. Several organic compounds with hetero atoms like O, N, S, P and having multiple bonds are useful and are widely used as effective corrosion inhibitors [1-2]. In different acid solutions the corrosion inhibition of metals generally depends on how the metals are interacting with the concerned organic molecule [3]. The organic molecules should have centres which are capable of forming coordination bonds with metal surfaces [4, 5]. Stronger is the coordination bond, better is the inhibition efficiency. 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 [6-8]. In this present paper, quantum chemical calculations have been performed to investigate the reaction mechanism of corrosion inhibition behaviour of N-benzyl piperidine -4-one oxime. It strengthens the fact that this type of calculations are proving to be a very important and cost effective tool for corrosion inhibition mechanism even without doing each and every wet chemical studies [9,10]. Many researchers report that the inhibition effect mainly depends on some physico-chemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons, and so on [11,12]. The damages by corrosion generate not only high costs for inspection, repairing and replacement, but in addition these constitute a public risk. Thus the necessity of developing novel substances that behaves like corrosion inhibitors. In general, the organic compounds have demonstrated a great effectiveness in inhibiting the watery corrosion of many metals and alloys. It has been demonstrated that the compounds that have nitrogen and sulfur in their structure provide a greater inhibition. The concept of assessing the efficiency of a corrosion inhibitor with the help of computational chemistry is to search for compounds with desired properties using chemical intuition and experience into a mathematically quantified and computerized form.

The aim of this particular work is to extend this investigation to ascertain whether the experimental results are fully supported by theoretical predictions by finding a clear relationship between calculated quantum chemical and

experimentally determined inhibition efficiency of inhibitor. This is achieved by calculating relevant molecular properties of inhibitor and there by explaining the mechanism of inhibition of the inhibitor with the steel surface.

## MATERIALS AND METHODS

### 2.1 Preparation N-benzyl piperidine-4-one oxime

To the boiling solution N-benzyl piperidine -4-one (0.01mol) in methanol (45ml) and few sodium acetate , hydroxylamine hydrochloride (0.01 mol) and the methanol solution were added by stirring .The reaction was refluxed for 3 hours on a water bath . After cooling, the solid product was filtered and recrystallized from methanol to get the corresponding oxime .

### 2.2. Characterisation of 1-benzyl piperidin-4-one oxime

Table-1

Compound Name	Yield(%)	Melting point(°C)	Elemental analysis
N-benzyl piperidin-4-one oxime	96	160-162	C(%) <b>70.53</b> H(%) <b>7.60</b> N(%) <b>13.79</b>

### 2.3 Spectral analysis (1-benzyl piperidin-4-one oxime)

Yield: 96% ; IR (cm<sup>-1</sup>): 3114 (O-H stretching); 1635 (C=N stretching); <sup>1</sup>H NMR (δ ppm) : 3.17 (t, 2H, H-2, J = 5.2 Hz); 3.02 (t, 2H, H-6, J = 5.4 Hz); 2.74 (t, 2H, H-3, J = 5.3 Hz); 2.49 (t, 2H, H-5, J = 5.4 Hz); 4.30 (s, 2H, -N-CH<sub>2</sub>-Ph); 10.78 (s, 1H, OH proton); 7.64-7.42 (m, 5H, aryl protons); <sup>13</sup>C NMR (δ ppm) : 50.69 (C-2); 49.41 (C-6); 27.17 (C-3); 20.63 (C-5); 149.53 (C=N); 58.24 (-N-CH<sub>2</sub>-Ph); 129.32, 131.25, 128.67 (aromatic carbons).

### 2.4 Quantum Chemical Calculations

All the calculations were done by means of Semi empirical quantum chemical PM6 method [13-17]. These methods can reach exactitude similar to other methods in less time and with a smaller investment from the computational point of view . This approach is shown to yield favourable geometries for a wide variety of systems. This basis set gives good geometry optimizations. The geometry structure was optimized under no constraint. The following quantum chemical parameters were calculated from the obtained optimized structure: The highest occupied molecular orbital (E<sub>HOMO</sub>) and the lowest unoccupied molecular orbital (E<sub>LUMO</sub>), the energy difference (ΔE) between E<sub>HOMO</sub> and E<sub>LUMO</sub>, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), global softness (σ), ionization potential (I) and the fraction of electrons transferred (ΔN) . According to Koopman's theorem [13], the ionization potential (E) and electron affinity (A) of the inhibitor are calculated using the following equations.

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

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

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 [14]:

$$\chi = \frac{E+A}{2} \quad (3)$$

$$\eta = \frac{E-A}{2} \quad (4)$$

Global chemical softness (σ), which describes the capacity of an atom or group of atoms to receive electrons [15], was estimated by using the equation:

$$\sigma = \frac{1}{\eta} = \frac{2}{E_{\text{HOMO}} - E_{\text{LUMO}}} \quad (5)$$

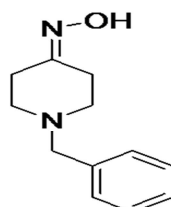
The number of transferred electrons (ΔN) was also calculated depending on the quantum chemical method [16, 17], by according to the equation:

$$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})} \quad (6)$$

Where  $\chi_{\text{Fe}}$  and  $\chi_{\text{inh}}$  denote the absolute electronegativity of iron and inhibitor molecule,  $\eta_{\text{Fe}}$  and  $\eta_{\text{inh}}$  denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of  $\chi_{\text{Fe}} = 7.0$  eV and  $\chi_{\text{inh}} = 0$ , for calculating the number of electrons transferred.

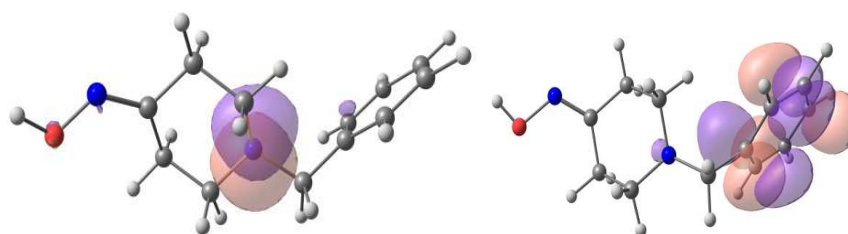
## RESULTS AND DISCUSSION

The optimized molecular structure and HOMO-LUMO of the N-benzyl piperidine -4-one oxime are shown in fig1,2 and 3 . From figures 2,3 it can be seen that the electronic density in HOMO and LUMO on the entire area of each molecule are quite uniform which is due to its  $\pi$ -electron cloud density. The analysis of orbital HOMO and LUMO (Figures 2,3), implies that the preferential area of nucleophilic attack to the inhibitor is the 1-benzyl ring.



**1-Benzyl-piperidin-4-one oxime**

Figure:1



1\_HOMO

1\_LUMO

Figure:2

Figure:3

**Table 1: Calculated quantum chemical parameters of the studied inhibitor**

Quantum parameters	N-benzyl piperidine -4-one oxime (BPOX)
$E_{\text{HOMO}}$ (eV)	-9.2377
$E_{\text{LUMO}}$ (eV)	0.2569
$\Delta E$ gap (eV)	9.4946
$\mu$ (debye)	2.387
$I = -E_{\text{HOMO}}$ (eV)	9.2377
$A = -E_{\text{LUMO}}$ (eV)	-0.2569
$\chi = \frac{I + A}{2}$	4.4904
$\eta = \frac{I - A}{2}$	4.7473
$\sigma = \frac{1}{\eta}$	0.2106
$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})}$	0.26432

Highest occupied molecular orbital energy ( $E_{\text{HOMO}}$ ) and lowest unoccupied molecular orbital energy ( $E_{\text{LUMO}}$ ) are very popular quantum chemical parameters. These orbitals, also called the frontier orbitals, determine the way the molecule interacts with other species. According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between the frontier orbitals (HOMO and LUMO) of reactants [18].  $E_{\text{HOMO}}$  is often associated with the electron donating ability of the molecule. High  $E_{\text{HOMO}}$  values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbital. Increasing values of the  $E_{\text{HOMO}}$  facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer [19,20].  $E_{\text{LUMO}}$  indicates the ability of the molecules to accept electrons. The lower values of the  $E_{\text{LUMO}}$ , the more probable it is that the molecule would accept electrons. A low value of the energy band gap ( $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ ) gives good inhibition efficiencies, because the energy to remove an electron from the last occupied orbital will be low [21]. From table-1 it is evident that  $E_{\text{LUMO-HOMO}}$  (energy gap) was also found to decrease hence the percentage of corrosion inhibition is high.

Literature reveals that a larger value of the energy gap indicates low reactivity to a chemical species because the energy gap is related to the softness or hardness of a molecule. A soft molecule is more reactive than a hard molecule because a hard molecule has a larger energy gap [22]. The dipole moment ( $\mu$ ) is an index that can also be used for the prediction of the direction of a corrosion inhibition process. Dipole moment is the measure of polarity in a bond and is related to the distribution of electrons in a molecule [23]. Although literature is inconsistent on the use of ' $\mu$ ' as a predictor for the direction of a corrosion inhibition reaction, it is generally agreed that the adsorption of polar compounds possessing high dipole moments on the metal surface should lead to better inhibition efficiency. Comparison of the results obtained from quantum chemical calculations with experimental inhibition efficiency indicated that the % inhibition efficiencies of the inhibitor increase with increasing value of the dipole moment.

Absolute hardness and softness are important properties to measure the molecular stability and reactivity. It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap [24]. Normally, the inhibitor with the least value of global hardness (hence the highest value of global softness) is expected to have the highest inhibition efficiency which is in agreement with our result [25].

According to Sanderson's electro negativity equalization principle N-benzyl piperidine -4-one oxime with a high electro negativity and low difference of electronegativity quickly reaches equalization and hence low reactivity is expected which in turn indicates low inhibition efficiency. The calculated fraction of electrons transferred,  $\Delta N$  for N-benzyl piperidine -4-one oxime was carried out using Eq. (6) by using the theoretical  $\chi$  value of 7 eV/mol and  $\eta$  value of 0 eV/mol for iron. The values of  $\Delta N$  showed inhibition effect resulting from electrons donation which agrees with Lukovits *et al.*'s study. If  $\Delta N < 3.6$  (as obtained in this study), the inhibition efficiency increased with the increasing electron-donating ability at the metal surface.

## CONCLUSION

Quantum chemical parameters such as  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , energy gap ( $\Delta E$ ), hardness ( $\eta$ ), Softness ( $\sigma$ ), electron affinity (A), ionization potential (E), the absolute electronegativity ( $\chi$ ) and the fraction of electron transferred ( $\Delta N$ ). were calculated using Semiempirical quantum chemical PM6 method. The inhibition efficiency of N-benzyl piperidine -4-one oxime has been investigated by utilizing quantum chemical approaches using the Density Functional Theory method. The inhibitor efficiency of N-benzyl piperidine -4-one oxime on mild steel in 1M HCl was measured by weight loss technique. Obvious correlations were found between corrosion inhibition efficiency and some quantum chemical parameters. The agreement with the experimental data was also found to be satisfactory.

## REFERENCES

- [1] Naik U.J., Panchal V.A., Patel A.S., Shah N.K., *J. Mater. Environ. Sci.* 3 (2012) 935.
- [2] Al Hamzi A.H., Zarrok H., Zarrouk A., Salghi R., Hammouti B., Al-Deyab S.S., Bouachrine M., Amine A., Guenoun F. *Int. J. Electrochem. Sci.* 8 (2013) 2586.
- [3] Khaled K.F., *Electrochim Acta.* 55 (2010) 6523.
- [4] Ansari K. R., Quraishi M. A., *Corros. Sci.* 79 (2014) 5.
- [5] Zhang F., Tang Y., Cao Z., Jing W., Wua Z., Chen Y., *Corros. Sci.* 61 (2012) 1.
- [6] Umoren S. A., Obot I.B., *Surf. Rev. Lett.* 15 (3) (2008) 277.
- [7] Ergun U., Yuzer D., Emregul C., *Mater. Chem. Phys.* 109 (2008) 492.
- [8] Ebenso E. E., Alemu H., Umoren S. A., Obot I.B., *Int. J. Electrochem. Sci.* 3 (2008) 1325.
- [9] Bereket G., Öğretir C., Özşahin Ç., *J. Mol. Struct. (THEOCHEM)* 633 (2003) 39.
- [10] Awad M.K., Mustafa M.R., Abo Elnga M.M., *J. Mol. Struct. (THEOCHEM)*. 959 (2010) 66.
- [11] M. Bouayed, H. Rabaa, A. Srhiri, J.Y. Saillard and A. Ben Bachir, *Corros. Sci.*, 41, 501 (1999).
- [12] M.A. Quraishi and R. Sardar, *Mater. Chem. Phys.*, 78, 425(2002).
- [13] Dewar M.J.S., Thiel, W., *J. Am. Chem. Soc.*, 99 (1977) 4899.
- [14] Pearson R.G., *Inorg. Chem.*, 27 (1988) 734.
- [15] Henríquez-Román J.H., Padilla-Campos L., Páez M.A., Zagal J.H., María Rubio A., Rangel C.M., Costamagna J., Cárdenas-Jirón G., *J. Mol. Struct. (THEOCHEM)* 757 (2005) 1.
- [16] Sastri V.S., Perumareddi J.R., *Corrosion (NACE)* 53 (1997) 617.
- [17] Lukovits I., Kalman E., Zucchi F., *Corrosion(NACE)* 57 (2001) 3.
- [18] Fukui K., Theory of Orientation and Stereoselection, Springer-Verlag, New York, 1975.
- [19] Ashassi-Sorkhabi H., Shaabani B., Seifzadeh D., *Electrochim. Acta* 50 (2005) 3446.
- [20] Ozcan M., Dehri I. Erbil M., *Appl. Surf. Sci.* 236 (2004) 155.
- [21] Khalil N., *Electrochim. Acta.* 48 (2003) 2635.

[22] Ebenso E.E., Arslan T., Kandemirli F., Caner N., Love I., *Int. J. Quantum Chem.* 110 (2010) 1003.

[23] Gece G., *Corros. Sci.* 50 (2008) 2981.

[24] Obi-Egbedi NO., Obot IB., El-Khaiary MI., Umoren SA., Ebenso EE., *Int. J. Electrochem. Sci.* 6 (2011) 5649.

[25] Ebenso EE, Isabirye DA., Eddy NO., *Int. J. Mol. Sci.* 11 (2010) 2473.