

# A QUANTUM CHEMICAL CALCULATION (DFT) : 1-(4-NITRPHENYLO- IMINO) -1 (PHENYLHYDRAZONO) - PROPAN-2-ONE AS CORROSION INHIBITOR FOR MILD STEEL IN ACIDIC MEDIA

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## ABSTRACT

Quantum chemical calculations based on DFT method were performed on azomethine compound:  $\text{PhN}=\text{N}-\text{C}(\text{COCH}_3)=\text{NC}_6\text{H}_4\text{Y}$  { $\text{Y} = \text{NO}_2$  ( $\text{SB}_1$ )} used as corrosion inhibitor for mild steel in acid media to determine the relationship between the molecular structure of ( $\text{SB}_1$ ) and inhibition efficiency. The structural parameters, such as the frontier molecular orbital energy HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), the charge distribution of the studied inhibitor, the absolute electronegativity ( $\chi$ ) values, and the fraction of electrons ( $\Delta\text{N}$ ) transfer from inhibitor to iron, were also calculated and correlated with inhibition efficiencies. The results showed that the inhibition efficiency of ( $\text{SB}_1$ ) increased with the increase in  $E_{\text{LUMO}}$  and decrease in  $E_{\text{LUMO}} - E_{\text{HOMO}}$ ; and the areas containing N atoms are most possible sites for bonding the metal iron surface by donating electrons to the metal.

**Keywords:** *Quantum Chemical, DFT, Molecular Orbital, Azomethine.*

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## 1. INTRODUCTION

The use of corrosion inhibitor is one of the most effective measures for protecting metal surfaces against corrosion in acid environments [1]. Some organic compounds are found to be effective corrosion inhibitors for many metals and alloys. Generally, inhibitor molecules may physically or chemically adsorb on a corroding metal surface. In any case, adsorption is generally over the metal surface forming an adsorption layer that functions as a barrier protecting the metal from the corrosion [2, 3]. Schiff base compounds are a condensation product of an amine and a ketone/aldehyde. Recent publications show increased attention to these compounds as corrosion inhibitors in typically acidic environments for various metals like steel, aluminum and copper [4, 5]. Some azomethines compounds ( $\text{OCH}_3$ ,  $\text{CH}_3$ , H, Cl, Br and  $\text{NO}_2$ ) containing nitrogen have been found to be good inhibitors for mild steel in acidic medium [2].

Theoretical chemistry has been used recently to explain the mechanism of corrosion inhibition, such as quantum chemical calculations [1, 5]. Quantum chemical calculations have been proved to be a very powerful tool for studying the mechanism [2, 3]. The objective of this work is to present a theoretical study on electronic and molecular structure of ( $\text{SB}_1$ ) (Fig. 1) and to determine relationship between molecular structure of the compound and inhibition efficiency. The structural parameters, such as the frontier molecular orbital energy HOMO and LUMO, the charge distribution of the studied inhibitor, the absolute electronegativity ( $\chi$ ) values, and the fraction of electrons ( $\Delta\text{N}$ ) transfer from inhibitor to iron were calculated and correlated with inhibition efficiencies.

## 2. THEORY AND COMPUTATIONAL DETAILS

DFT (density functional theory) methods were used in this study. These methods have become very popular in recent years because they can reach exactitude similar to other methods in less time and less expensive from the computational point of view. In agreement with the DFT results, energy of the fundamental state of a polyelectronic system can be expressed through the total electronic density, and in fact, the use of electronic density instead of wave function for calculating the energy constitutes the fundamental base of DFT [6]. All the calculations were done by GAUSSIAN 03 W software [7], using the B3LYP functional [8, 9] and a 6-31G\* basis set [9]. The B3LYP, a version of DFT method, uses Beche's three-parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang, and Parr (LYP) [8, 9].

## 3. RESULTS

Table 1 presents the calculated energy levels of the HOMO and LUMO for the azomethine compound (SB<sub>1</sub>) (Fig. 1). The measured average inhibition efficiencies (%) of this compound were also listed in the table (these data were measured in 1 M HCl acid solution at 298 °K [2]). The relationship between corrosion inhibition efficiency and HOMO energy levels for the azomethine compound (SB<sub>1</sub>). As clearly, the inhibition efficiency increased with the  $E_{HOMO}$  level rising. The inhibition efficiency reduced with the  $E_{LUMO}$  level increase.

Quantiques paramètres	SB <sub>1</sub>
$E_{HOMO}$ (eV)	-5,73
$E_{LUMO}$ (eV)	-2,48
$\Delta E(E_{LUMO}- E_{HOMO})(eV)$	3,25
Inhibition efficiency [2] (%)	97,50

TABLE 1. Molecular property of SB<sub>1</sub> calculated with B3LYP/6-31G\*

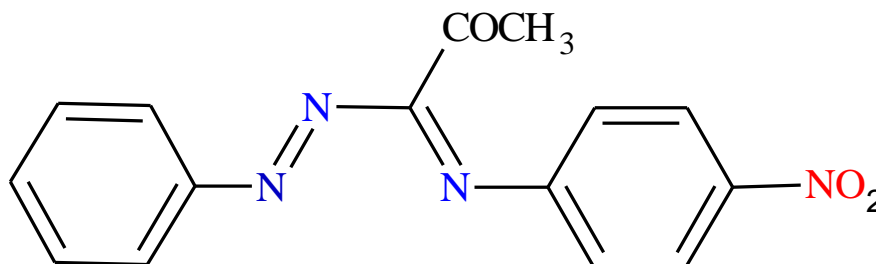


FIGURE 1. The chemical structure of the azomethine compound (SB<sub>1</sub>)

The relationship between the inhibition efficiency and the energy gap ( $E_{LUMO}-E_{HOMO}$ ) is negative. The frontier molecule orbital density distributions of the compound ( $SB_1$ ) were presented in Fig. 2. As seen from the figure, the populations the HOMO focused around the carbon chain containing nitro ( $-NO_2$ ). But the LUMO densities were mainly around the benzene cyclic. The Mulliken charge populations of the three azomethines were also calculated (Fig. 2). It can see that the area of carbon bone chain containing nitro ( $-NO_2$ ), charged a large electron density and might form adsorption active centers.

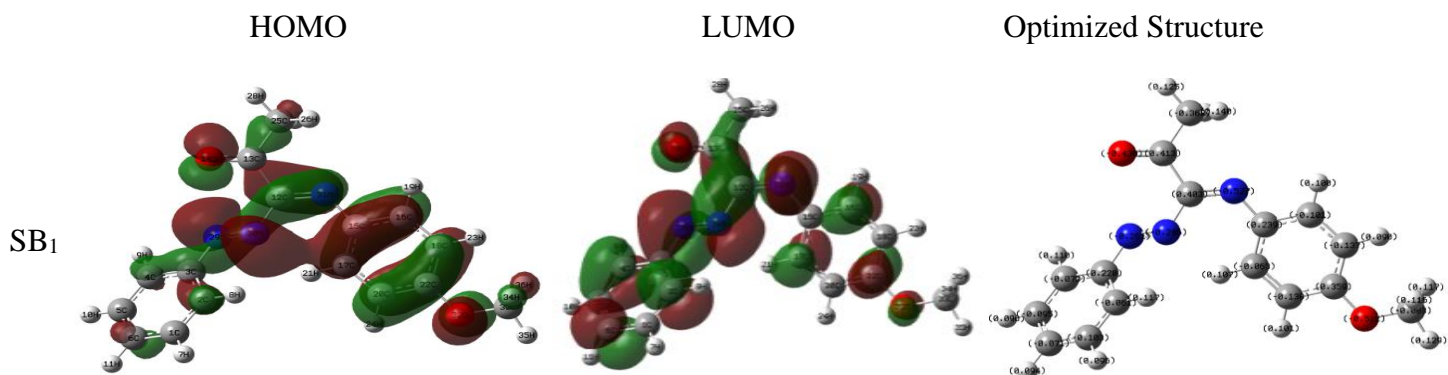


FIGURE2.The frontier molecule orbital density distributions of three compounds ( $SB_1$ ): HOMO; LUMO and Optimized Structure.

#### 4. Discussion (Correlation between MO energy level and inhibition efficiency)

Frontier orbital theory is useful in predicting adsorption centers of the inhibitor molecules responsible for the interaction with surface metal atoms [4, 7]. Terms involving the frontier MO could provide dominative contribution, because of the inverse dependence of stabilization energy on orbital energy difference [5]. Moreover, the gap between the HOMO and LUMO energy levels of the molecules was another important factor that should be considered. Reportedly, excellent corrosion inhibitors are usually those organic compounds who not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal [5, 8]. According to H.Hamani [2], when length of métoxy group -containing carbon increased, the corrosion inhibition efficiency increased significantly. The quantum chemistry calculation in this study revealed that as the length increases, the HOMO energy level boosted significantly while the energy gap dropped sharply. The linear correlation between MO energy level and the corrosion inhibition efficiency of the  $SB_1$  proved that the higher the HOMO energy of the inhibitor, the greater the trend of offering electrons to unoccupied d orbital of the metal, and the higher the corrosion inhibition efficiency for iron in HCl acid solutions; in addition, the lower the LUMO energy, the easier the acceptance of electrons from metal surface, as the HOMO-LUMO energy gap decreased and the efficiency of inhibitor improved. The number of transferred electrons ( $\Delta N$ ) was also calculated depending on the quantum chemical method [10, 11].

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

Where  $\chi_{Fe}$  and  $\chi_{inh}$  denote the absolute electronegativity of iron and the inhibitor molecule, respectively;  $\eta_{Fe}$  and  $\eta_{inh}$  denote the absolute hardness of iron and the inhibitor molecule, respectively. These quantities are related to electron affinity (A) and ionization potential (I)

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

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

I and A are related in turn to  $E_{LUMO}$  and  $E_{HOMO}$

$$I = -E_{HOMO}$$

$$A = -E_{LUMO}$$

Values of  $\chi$  and  $\eta$  were calculated by using the values of I and A obtained from quantum chemical calculation. Using a theoretical  $\chi$  value of 7 eV/mol and  $\eta$  value of 0 eV/mol for iron atom [10],  $\Delta N$ , the fraction of electrons transferred from inhibitor to the iron molecule, was calculated. And the plot of inhibition efficiency vs.  $\Delta N$  (Fig. 3) clearly shows that the inhibition efficiency increased with the  $\Delta N$  increase. According to other reports [10, 11], values of  $\Delta N$  showed inhibition effect resulted from electrons donation. Agreeing with Lukovits's study [11], if  $\Delta N < 3.6$ , the inhibition efficiency increased with increasing electron-donating ability at the metal surface. In this study, the three SB<sub>1</sub>, SB<sub>2</sub> and SB<sub>3</sub> were the donators of electrons, and the iron surface was the acceptor. The compounds were bound to the metal surface, and thus formed inhibition adsorption layer against corrosion. **SB<sub>1</sub>** had the highest inhibition efficiency because it had the highest HOMO energy and  $\Delta N$  values, and it had the greatest ability of offering electrons, and **SB<sub>1</sub>** had the lowest inhibition efficiency, for vice versa.

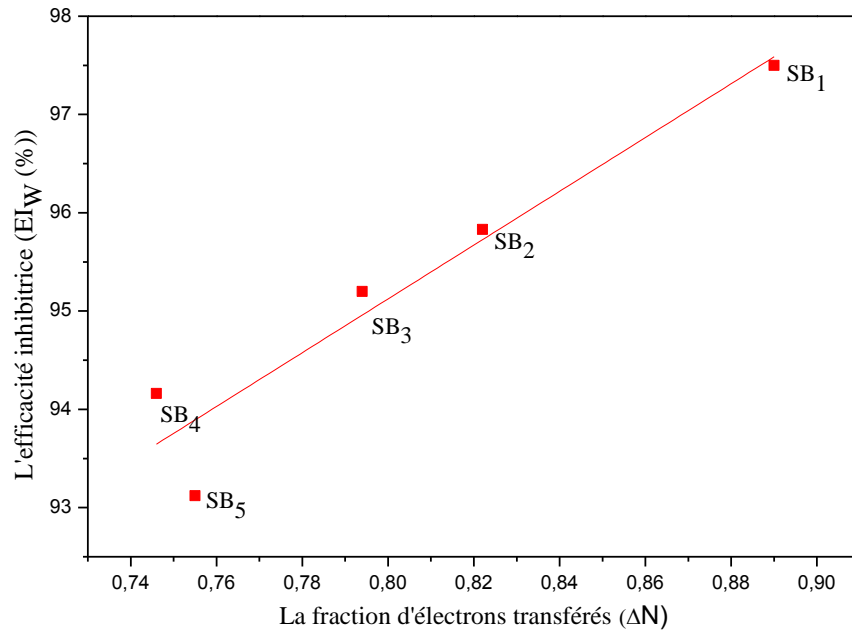


FIGURE3. Correlation of  $\Delta N$  with percent inhibition efficiency of SB<sub>1</sub>.

## 5. CONCLUSIONS

- The relationships between inhibition efficiency of iron in 1 M HCl and the  $E_{HOMO}$ ,  $E_{LUMO} - E_{HOMO}$  and  $\Delta N$  of SB<sub>1</sub> were calculated by DFT method. The inhibition efficiency increased with the increase in  $E_{HOMO}$  and decrease in  $E_{LUMO} - E_{HOMO}$ . SB<sub>1</sub> had the highest inhibition efficiency because it had the highest HOMO energy and  $\Delta N$  values, and it was most capable of offering electrons.
- The distribution of electronic density shows that the molecules of SB<sub>1</sub> had many negatively-charged active centers. The electron density was found to be positively correlated with length of nitro containing carbon, which was resulted in increasing in inhibition efficiency. The areas containing N atoms are most possible sites for bonding the metal iron surface by donating electrons to the metal.

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