*Int. J. New. Chem.*, 2025, Vol. 12, Issue 4, pp. 502-518.

**International Journal of New Chemistry**

**Published online 2024 in http://www.ijnc.ir/.**

Open Access

**Print ISSN: 2645-7236**

**Online ISSN: 2383-188x**

**Original Research Article**

# Multiple heteroatom additions effect on the empirical rule for organic corrosion inhibitors with nitrogen, oxygen, and sulfur atoms, a DFT approach.

**Osi Valentine [1*], Orie Kingsley John [1], Sorbari Keerabana [1]**

[1]Department of Chemistry, Ignatius Ajuru University of Education, P.M.B. 5047 Rumuolumeni, Port Harcourt, Rivers State, Nigeria

***Received: 2024-10-13*** ***Accepted: 2024-12-17*** ***Published: 2024-12-18***

## ABSTRACT

The purpose of this study was to investigate using density functional theory (DFT) whether the general trend of inhibition efficiency, which is in the order of O<N<S, and increased inhibition as the number of heteroatoms increases, holds true under all conditions. Sixteen organic compounds which consisted of N, O, and S atoms in different combinatory ratios were used and were studied using B3LYP level of theory and 6-31G(d,p) basic set with iron being the metal of consideration. It was found that the order O<N<S only applies to single heteroatom configurations, increasing the number of heteroatoms does not always result in increased inhibition, and O played a significant role in improving a compound's inhibition efficiencies. The multiple heteroatom configuration was in the order of O and N < N and S < O and S, resulting in an order trend of inhibition efficiencies of N<O< S. Therefore, a compound with more O or S and less N atoms would thus be a better corrosion inhibitor.

**Keywords:** electrophilic, inhibition efficiencies, molecular descriptors

*Corresponding author email address: osivalentine02@gmail.com

## Introduction

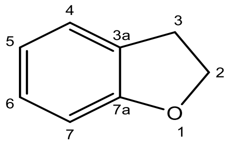
Despite being natural, the corrosion process of metals especially steel has been observed to be minimized by employing various methods, one of which is the use of chemical inhibitors [1-7]. Their practicability as well as their economic and environmental implications has increased the popularity of chemical inhibitors as corrosion combatant agent [8-11]. Chemical inhibitors are chemical substances that reduces drastically the rate of metal corrosions when added in small quantities and they can be either organic or inorganic with organic inhibitors surpassing inorganic inhibitors in popularity [12,13]. Organic compounds containing heteroatoms such as Nitrogen, (N), Oxygen, (O), and Sulphur, (S), have recently aroused the interest of researchers because they have been reported to be effective corrosion combatant agents. Furthermore, complex molecules with more than one heteroatom in their structure are said to be the more effective corrosion inhibitors [14-17], this has led to a surge of investigations into molecules with more than one heteroatom in their structure [18-50]. The use of theoretical and computational chemistry has enabled experts to make sense of why most compounds act the way they do. These strategies are often used as a guide to finding solutions to important human challenges, and have been employed effectively in drug discovery and materials science. Each structure bears information that discloses its reactivity; using this data can help with the design of inhibitors. Recently, density functional theory (DFT), a dependable and inexpensive method, has been used to examine the molecular activity and interaction of adsorbates with metal surfaces. The advantage of this approach is that it provides relatively simple information about the interactions between corrosion inhibitors and metal surfaces. It is efficient and cost-effective in developing novel corrosion in1hibitor molecules for use in a variety of corrosion systems for domestic and industrial applications, and it is effective in revealing the impact of minor structural changes in compounds on their inhibition efficiency [14]. It is hypothesized that N, O and S heteroatoms possess a decreasing inhibitory potential in the order of S>N>O, and that two of these heteroatoms combined are more potent inhibitors than just one [14,51-53]. These ideas have resulted in a significant amount of research into the synthesis of compounds containing larger numbers of heteroatoms being done by the scientific community. So, does the level of inhibition necessarily increase with a greater amount of heteroatoms? This inquiry is what initiated the necessity for this study, whose purpose is to use Density Function Theory (DFT) to answer this question and also see if the empirical rule of organic inhibitors with heteroatoms N, O and S holds true in all instances. This should then be a guide for finding chemical inhibitors for corrosion prevention.

## Methodology

### Presentation of molecules used

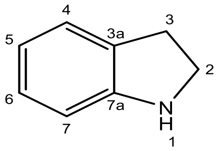
The experiment used sixteen molecules to investigate the effect of multiple heteroatoms on the efficacy of inhibition. Three molecules had one heteroatom, three had two heteroatoms, seven had three heteroatoms, and three had more than three heteroatoms. These molecules were drawn using the chemdraw software and obtained from the pubchem database (https://pubchem.ncbi.nlm.nih.gov) (Figure 1).

**1**



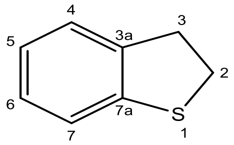
2,3-dihydrobenzofuran

**2**



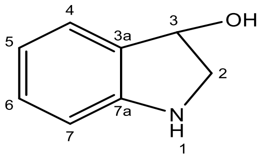
indoline

**3**



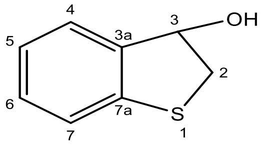
2,3-dihydrobenzo[*b*]thiophene

**4**



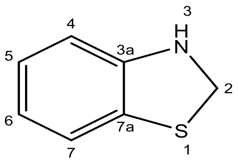
indolin-3-ol

**5**



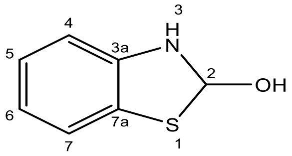
2,3-dihydrobenzo[*b*]thiophen-3-ol

**6**



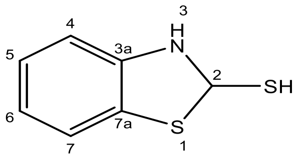
2,3-dihydrobenzo[*d*]thiazole

**7**



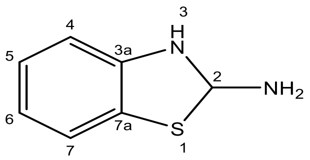
2,3-dihydrobenzo[*d*]thiazol-2-ol

**8**



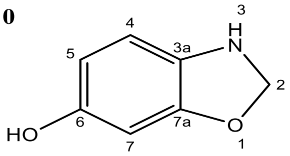
2,3-dihydrobenzo[*d*]thiazole-2-thiol

**9**



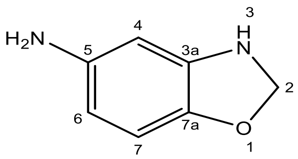
2,3-dihydrobenzo[*d*]thiazol-2-amine

**10**



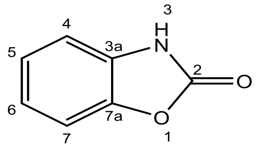
2,3-dihydrobenzo[*d*]oxazol-6-ol

**11**



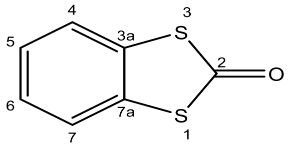
2,3-dihydrobenzo[*d*]oxazol-5-amine

**12**



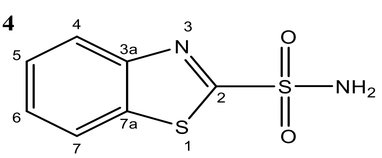
benzo[*d*]oxazol-2(3*H*)-one

**13**



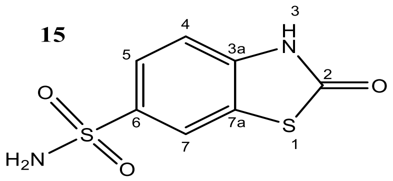
benzo[*d*][1,3]dithiol-2-one

**14**



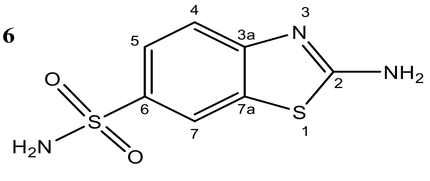
2-methylbenzo[*d*]thiazole

**15**



2-oxo-2,3-dihydrobenzo[*d*]thiazole-6-sulfonamide

**16**



2-aminobenzo[*d*]thiazole-6-sulfonamide

**Figure 1:** Organic compound structures containing heteroatoms N, O, and S in various combinations

## Computational Methodology

Density functional theory has been demonstrated to be an effective technique when assessing the capability of compounds as possible efficient corrosion inhibitors. The computation was conducted by utilizing the hybrid functional B3LYP/6-31G(d,p) level of theory with the aid of the Gaussian 09w software [54].

The optimization resulted in the acquisition of the frontier molecular orbitals values: the energy of the highest occupied molecular orbital ($E_{HOMO}$) and the energy of the lowest unoccupied molecular orbital ($E_{LUMO}$) which were then used to calculate other parameters.

The global parameters that were used were the ionization potential (I), electron affinity (A), electronegativity (χ), chemical potential (μ), global hardness (η), global softness (σ), electrophilicity index (ω), the amount of electron transferred (ΔN) and the energy of back donation ($\Delta E_{b-d}$). From the Koopmans' theorem, these parameters are related to the values of the energies of the frontier molecular orbital and the equations that display these connections are given as follows:

$\Delta E_{gap} = E_{LUMO} - E_{HOMO}$ 1

Electron affinity (A) = $- E_{LUMO}$ 2

Ionization potential (I) = $- E_{HOMO}$ 3

Electronegativity (χ) = $-\mu = \frac{I + A}{2}$ 4

Hardness (η ) = $= \frac{I - A}{2}$ 5

Softness (σ) $= \frac{1}{\eta}$ 6

Electrophilicity (ω) = $\frac{\chi^2}{2\eta}$ 7

Energy of back donation ($\Delta E_{b-d}$) = $-\frac{\eta}{4}$ 8

Furthermore, charge transfer between the corrosion inhibitor and the metal is driven by the difference in their electronegativities (and chemical potentials) when in contact until a chemical potential balance is achieved [55].

The number of electrons transferred (ΔN) is determined by

$$\Delta N = \frac{\chi_{Fe} - \chi_{inb}}{2(\eta_{Fe} + \eta_{inb})} \qquad 9$$

Where $\chi_{Fe} = 7$ ev and $\eta_{Fe} = 0$ ev

Analyzing local reactivity of compounds can be assisted by calculating local parameters, which is based on the Fukui function and condensed local softness suggested by Yang and Parr [56], in addition to Yang and Mortier [57]. The condensed Fukui function was estimated by employing the atomic charges of the atoms in the compounds and a finite difference approximation was implemented as illustrated below:

$$f^{+} = [q(N+1) - q(N)] \quad \text{for nucleophilic attack} \qquad 10$$

$$f^{-} = [q(N) - q(N-1)] \quad \text{for electrophilic attack} \qquad 11$$

Where q was used to represent the charges of an atomic site in the neutral (N), anionic (N + 1), when a molecule accepts electron, and cationic (N – 1), when it loses an electron.

The dual descriptor ($\Delta f$) now better explains which site is preferable for electrophilic or nucleophilic attack. This descriptor specifies the type of attack that each atom in a compound is highly susceptible to and it is given as

$$\Delta f = f^{+} - f^{-} \qquad 12$$

## Results and Discussion

The frontier molecular orbital (FMO) theory is an important theory always considered when studying chemical reactivity of compounds. The FMO which is made of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) gives an insight into how electrons interact with various orbitals. [51]. A major assumption made was the fact that an increase in the number of heteroatoms would lead to an increase in the FMO distribution, this was not the case as presence of multiple heteroatoms had no effect on the FMO distribution (Figure 2)

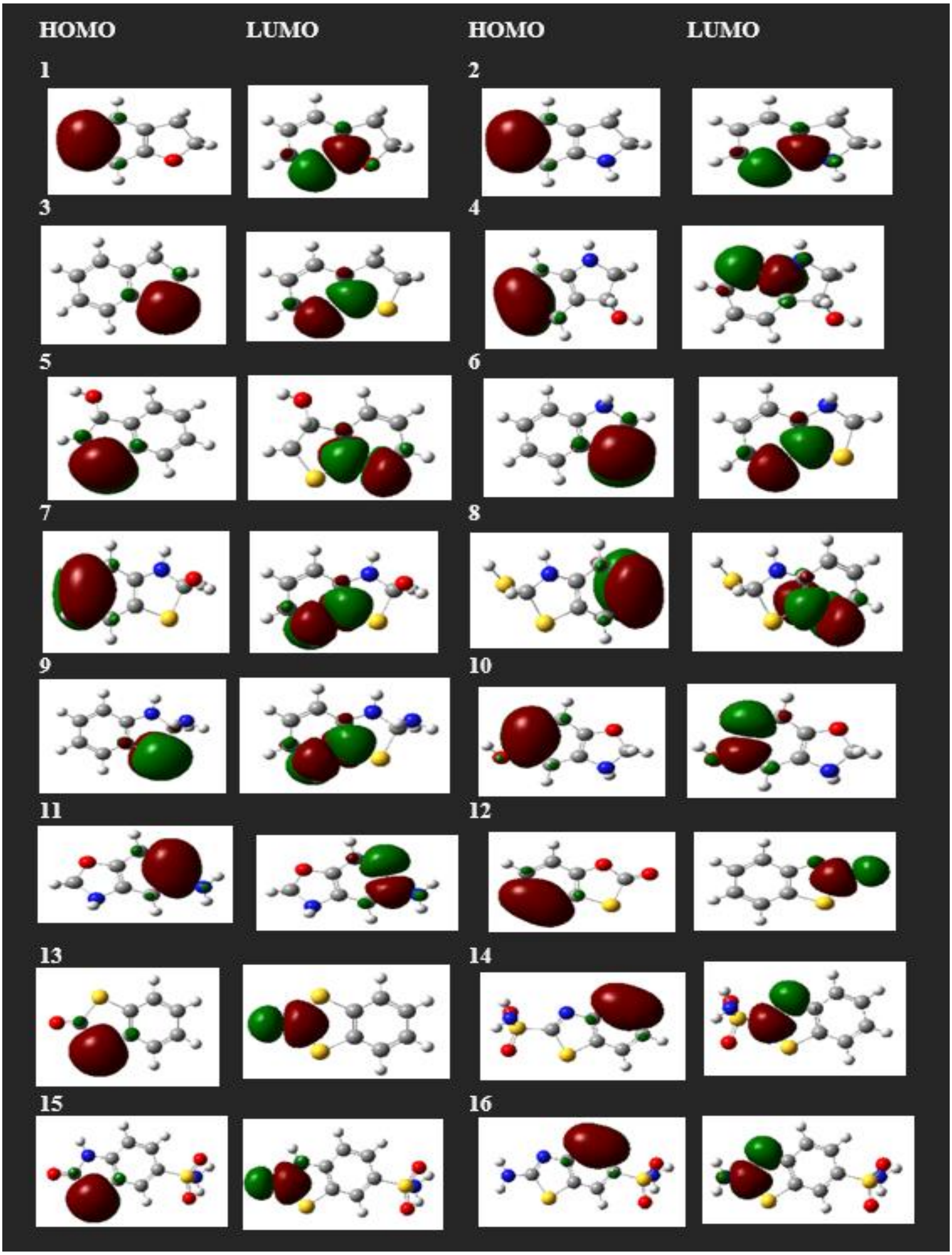


**Figure 2:** HOMO and LUMO distribution of compounds

The HOMO is related to charge transfer, while the LUMO is related to charge acceptance [47,49]. High values of the HOMO energy implies that a molecule can donate electrons with ease to congruent molecules of low energy vacant molecular orbitals which have been said to increase adsorption and inhibition efficiency [20,48]. The values of $E_{HOMO}$ for the compounds are shown in Table 1**.** Compounds with the presence of single heteroatom had $E_{HOMO}$ values that were in the order of 2 > 3 > 1, while compounds that consisted of double heteroatoms had $E_{HOMO}$ values that were observed to be in the order of 4 > 6 > 5 while compounds that possessed triple heteroatoms had $E_{HOMO}$ values that were in the order of 9 > 11 > 7 > 8 > 10 > 12 > 13, with compounds composed of more than three heteroatoms being in the order of 14 > 15 > 16. Lower LUMO energy ($E_{LUMO}$) implies better electron acceptance potential. Compounds with the presence of single heteroatom had $E_{LUMO}$ values that were in the order of 3 < 1 < 2, while compounds that consisted of double heteroatoms had $E_{LUMO}$ values that were observed to be in the order of 6 < 5 < 4 while compounds that possessed triple heteroatoms had $E_{LUMO}$ values that were in the order of 13 < 12 < 10 < 8 < 7 < 9 < 11, with compounds of more than three heteroatoms being in the order of 14 < 15 < 16.

**Table 1:** $E_{HOMO}$, $E_{LUMO}$, $\Delta E_{Gap}$, I and A quantum chemical descriptors in gas phase

| | $E_{HOMO}$(eV) | $E_{LUMO}$(eV) | $\Delta E_{Gap}$(eV) | I(eV) | A(eV) |
|---|---|---|---|---|---|
| **1** | -6.35657 | 1.210904 | 7.567469 | 6.356565 | -1.2109 |
| **2** | -6.0469 | 1.508324 | 7.555224 | 6.046901 | -1.50832 |
| **3** | -6.24609 | 0.862055 | 7.108142 | 6.246087 | -0.86205 |
| **4** | -6.20718 | 1.361927 | 7.569102 | 6.207175 | -1.36193 |
| **5** | -6.38133 | 0.823687 | 7.205015 | 6.381328 | -0.82369 |
| **6** | -6.34677 | 0.81117 | 7.157939 | 6.346769 | -0.81117 |
| **7** | -6.38813 | 0.926273 | 7.314404 | 6.388131 | -0.92627 |
| **8** | -6.54786 | 0.742869 | 7.29073 | 6.547861 | -0.74287 |
| **9** | -6.33507 | 0.955117 | 7.290186 | 6.335068 | -0.95512 |
| **10** | -7.08773 | 0.620146 | 7.70788 | 7.087734 | -0.62015 |
| **11** | -6.36827 | 1.285191 | 7.653457 | 6.368266 | -1.28519 |
| **12** | -7.19086 | -0.6011 | 6.589766 | 7.190865 | 0.601098 |
| **13** | -7.18052 | -0.91838 | 6.262142 | 7.180524 | 0.918382 |
| **14** | -7.10569 | -0.74994 | 6.355749 | 7.105693 | 0.749944 |
| **15** | -7.21508 | -0.58287 | 6.632216 | 7.215083 | 0.582867 |
| **16** | -6.98052 | -0.33688 | 6.643645 | 6.980521 | 0.336876 |

The ionization potential (I) and electron affinity (A) for molecules are quantum descriptors that are determined from orbital energies of optimized molecules using the Koopmans theorem. This theorem equates I as the negative of the $E_{HOMO}$ and A as the negative of the $E_{LUMO}$. Higher value of ionization potential is said to be associated with high stability and chemical inertness making lower values preferred for good inhibitors [58], making 2, 4, 9 and 16 compounds of probable best inhibition efficiency for single, double, triple and more than three heteroatoms containing compounds. Higher values of electron affinity imply better inhibition, because this parameter provide information on a molecules ability to accept electrons. Based on electron affinity compounds 3, 6, 13 and 14 are better inhibitors for single, double, triple and more than three heteroatoms containing compounds. Chemical potential (μ) and electronegativity (χ) are of equal and opposite magnitudes (negatives of each other). Compounds with low chemical potential and high electronegativity values quickly reaches quantization [58]. Higher values of chemical potential and lower values of electronegativity are suggested for inhibitors, giving an order of 3<1<2, 5<6<4, 13<12<10<8<7<9<11 and 14<15<16 for single, double, triple and more than three heteroatoms containing compounds. Hardness (η) and softness (σ) are descriptors that provide information about the likelihood of a molecule to interact with a metal surface. These descriptors have an inverse relationship with one another. Generally, more reactivity is anticipated from softer molecules which increase their potential as effective corrosion inhibitors [19,20]. The classification of compounds under study based on global hardness and softness as related to inhibition efficiency is in the order of 3>2>1, 6> 5> 4, 13>12>10>8>7>9>11 and 14>16>15 for one, two, three and above three heteroatom containing compounds (Table 2).

**Table 2:** $\chi$, $\mu$, $\eta$, $\sigma$, $\omega$, $\Delta E_{b-d}$ and $\Delta N$ quantum chemical descriptors in gas phase

| | **χ(eV)** | **μ(eV)** | **η(eV)** | **σ(eV)** | **ω(eV)** | **ΔE$_{b-d}$(eV)** | **ΔN** |
|---|---|---|---|---|---|---|---|
| **1** | 2.572831 | -2.57283 | 3.783735 | 0.264289 | 0.874725 | 0.945934 | 0.585026 |
| **2** | 2.269288 | -2.26929 | 3.777612 | 0.264717 | 0.681604 | 0.944403 | 0.626151 |
| **3** | 2.692016 | -2.69202 | 3.554071 | 0.281367 | 1.019528 | 0.888518 | 0.606063 |
| **4** | 2.422624 | -2.42262 | 3.784551 | 0.264232 | 0.775403 | 0.946138 | 0.604745 |
| **5** | 2.77882 | -2.77882 | 3.602507 | 0.277584 | 1.071732 | 0.900627 | 0.585867 |
| **6** | 2.7678 | -2.7678 | 3.578969 | 0.27941 | 1.070241 | 0.894742 | 0.59126 |
| **7** | 2.730929 | -2.73093 | 3.657202 | 0.273433 | 1.019628 | 0.914301 | 0.583653 |
| **8** | 2.902496 | -2.9025 | 3.645365 | 0.274321 | 1.155506 | 0.911341 | 0.562016 |
| **9** | 2.689975 | -2.68998 | 3.645093 | 0.274341 | 0.992563 | 0.911273 | 0.591209 |
| **10** | 3.233794 | -3.23379 | 3.85394 | 0.259475 | 1.356718 | 0.963485 | 0.488618 |
| **11** | 2.541538 | -2.54154 | 3.826729 | 0.26132 | 0.843986 | 0.956682 | 0.582542 |
| **12** | 3.895981 | -3.89598 | 3.294883 | 0.303501 | 2.30337 | 0.823721 | 0.471036 |
| **13** | 4.049453 | -4.04945 | 3.131071 | 0.31938 | 2.618604 | 0.782768 | 0.471172 |
| **14** | 3.927819 | -3.92782 | 3.177875 | 0.314676 | 2.427371 | 0.794469 | 0.48337 |
| **15** | 3.898975 | -3.89897 | 3.316108 | 0.301558 | 2.292145 | 0.829027 | 0.46757 |
| **16** | 3.658699 | -3.6587 | 3.321822 | 0.30104 | 2.014869 | 0.830456 | 0.502932 |

Fraction of electron transferred (ΔN), energy of back donation ($\Delta E_{b-d}$) and electrophilicity (ω) are now becoming important parameters in describing chemical reactivity of molecules [59]. This is because of their relationship with other important parameters of chemical reactivity like hardness/softness and chemical potential/electronegativity [31,43]. The fraction of electron transferred provides useful information on the potential of adsorption of an inhibitor. It also gives an insight on molecules ability to donate and bind to metal surfaces. Higher values of ΔN implies higher probability of interaction of molecules with metal surfaces, which in turn leads to better adsorption and inhibition [55]. Based on fraction of electron transferred, the chemical reactivity of the compounds under study are expected to be in the order of 2>3>1, 4>6>5, 9>7>11>8>10>12=13 and 16>14>15 for single, double, triple and more than three heteroatoms containing compounds. The energy of back donation ($\Delta E_{b\text{-}d}$) on the other hand provides information about the energy that is required to cause an electron transfer from the metal surface back to the inhibitor. Lesser values are encouraged as they imply better inhibition and the order of probable inhibition efficiency is in the order of 3>2>1, 6>5>4, 13>12>9=8>7>11>10 and 14>15>16 for single, double, triple and more than three heteroatoms containing compounds. While the electrophilicity (ω) is now becoming a preferred parameter for prediction and description of chemical reactivity than other parameters because it takes into consideration the electronegativity/chemical potential and softness of the compound [20]. Having high electrophilicity index values implies having a high tendency to act as an electrophile and signifies better inhibition [55], thus having an order of 3>1>2, 5=6>4, 13>12>10>8>7>9>11 and 15>14>16 for single, double, triple and more than three heteroatoms containing compounds. Because inhibitors are expected to be constantly exposed to the environment, the geometry of the compounds were also optimized in solution. Solvation had no effect on the geometry of the compounds because the bond lengths of the compounds were not altered however, solvation had a significant impact on the FMO distribution of the compounds. This is not surprising given that the corrosion process has nothing to do with a compound's physical properties and everything to do with its chemical and electronic properties.

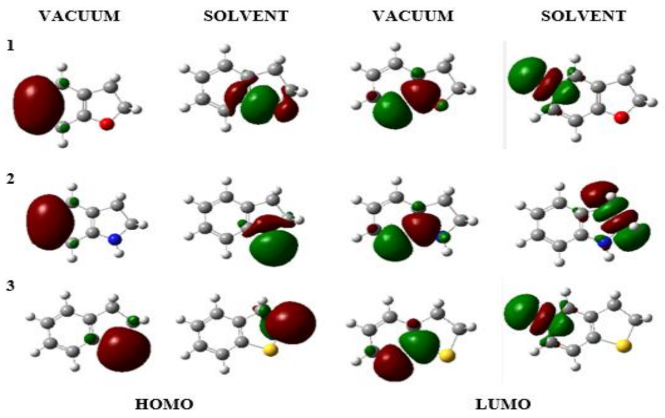


**Figure 3:** Distribution of HOMO and LUMO in single heteroatom compounds in vacuum and solvent

The FMO distribution in solution differed from the corresponding vacuum FMOs. Figure 3, which depicted the FMO distribution of 1, 2 and 3, showed the HOMO orbitals shifting to the heteroatoms in 1 and 2, with 3 shifting away from its heteroatom S. This shifting of the FMO from S to other atoms was observed to be consistent in all compounds that had their FMOs on S in vacuum.

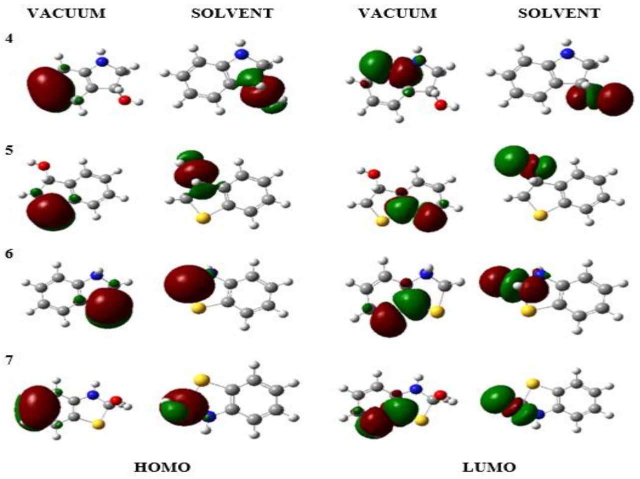


**Figure 4:** Distribution of HOMO and LUMO in vacuum and solvent in double heteroatom compounds (4,5 and 6) and a triple heteroatom compound (7)

The two heteroatom configurations revealed which heteroatom possessed the FMOs. In solution, the FMOs had a greater tendency of shifting towards O if the compound contained only N and O heteroatoms and O or N, but definitely away from S for compounds in which S was present (Figure 4**)**. Similarly, in compounds containing all three heteroatoms, the FMOs were found to shift away from S and towards O or N (Figure 5**)**.

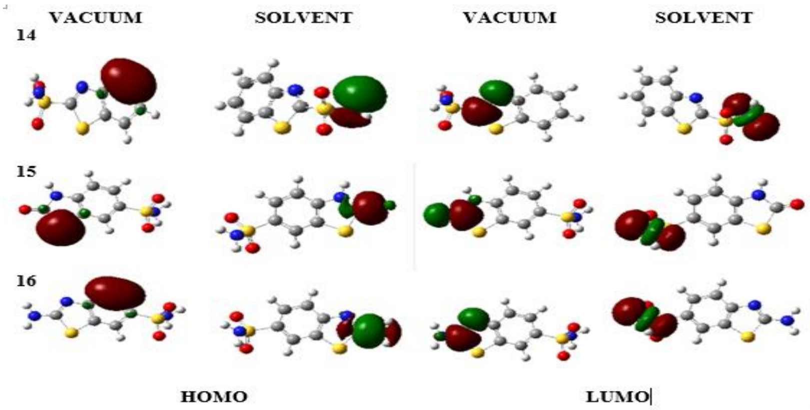


**Figure 5:** HOMO and LUMO distribution in more than three heteroatom compounds in vacuum and solvent

With the exception of 10, 12-16, the HOMO values of the compounds shifted to more negative values in solution, indicating that inhibitors either increase or decrease in electron donating ability in solution. This implies that most inhibitors in solution may or may not be capable of donating electrons to metallic surfaces, as evidenced by the decrease in fraction of electron transferred in 1-9 and 11, and increase in fraction of electron transferred in 10,12-16 (Table 3). The LUMO values of the compounds in solution, on the other hand, showed a general shift to lower negative values, implying that in solution inhibitors are more prone to accepting electrons, which is supported by the increased electronegativity of compounds in solution over those in vacuum.

**Table 3:** $E_{HOMO}$, $E_{LUMO}$, $\Delta E_{Gap}$, I and A quantum chemical descriptors in solution

| | **$E_{HOMO(}$(eV)** | **$E_{LUMO}$(eV)** | **$\Delta E_{Gap}$(eV)** | **I(eV)** | **A(eV)** |
|---|---|---|---|---|---|
| **1** | -6.54133 | 1.004914 | 7.546245 | 6.54133 | -1.00491 |
| **2** | -6.18894 | 1.26315 | 7.452093 | 6.188944 | -1.26315 |
| **3** | -6.50895 | 0.684365 | 7.193314 | 6.508949 | -0.68436 |
| **4** | -6.46623 | 1.129542 | 7.595769 | 6.466227 | -1.12954 |
| **5** | -6.62705 | 0.639738 | 7.266784 | 6.627046 | -0.63974 |
| **6** | -6.56881 | 0.666405 | 7.235219 | 6.568814 | -0.66641 |
| **7** | -6.56881 | 0.712937 | 7.28175 | 6.568814 | -0.71294 |
| **8** | -6.64473 | 0.609534 | 7.254267 | 6.644733 | -0.60953 |
| **9** | -6.53072 | 0.759468 | 7.290186 | 6.530718 | -0.75947 |
| **10** | -5.6254 | -0.65498 | 4.970421 | 5.625397 | 0.654977 |
| **11** | -6.54677 | 1.096888 | 7.643661 | 6.546773 | -1.09689 |
| **12** | -6.9993 | -0.85961 | 6.139691 | 6.999297 | 0.859606 |
| **13** | -6.44364 | -0.89525 | 5.548389 | 6.443642 | 0.895253 |
| **14** | -7.03903 | -0.93253 | 6.106493 | 7.039025 | 0.932532 |
| **15** | -7.16256 | -0.64763 | 6.514935 | 7.162565 | 0.64763 |
| **16** | -7.10352 | -0.41225 | 6.691265 | 7.103516 | 0.412252 |

The order of reactivity prediction based on these quantum descriptors in vacuum were not identical to that observed in solvent, particularly for the three heteroatom compounds 7-13(Table 4). The most notable effects of solvation were found to be on compounds with a higher degree of O, particularly 10, making it one of the compounds with good inhibitory potential. This suggests that a key component to take into account when creating organic corrosion inhibitors is oxygen, as a higher proportion may result in better inhibition.

**Table 4:** χ, μ, η, σ, ω, $\Delta E_{b-d}$ and ΔN quantum chemical descriptors in solution

| | **χ(eV)** | **μ(eV)** | **η(eV)** | **σ(eV)** | **ω(eV)** | **$\Delta E_{b-d}$(eV)** | **ΔN** |
|---|---|---|---|---|---|---|---|
| **1** | 2.768208 | -2.76821 | 3.773122 | 0.265032 | 1.015469 | 0.943281 | 0.560781 |
| **2** | 2.462897 | -2.4629 | 3.726047 | 0.268381 | 0.813981 | 0.931512 | 0.608836 |
| **3** | 2.912292 | -2.91229 | 3.596657 | 0.278036 | 1.179073 | 0.899164 | 0.568265 |
| **4** | 2.668342 | -2.66834 | 3.797885 | 0.263304 | 0.937371 | 0.949471 | 0.570272 |
| **5** | 2.993654 | -2.99365 | 3.633392 | 0.275225 | 1.233278 | 0.908348 | 0.551323 |
| **6** | 2.951204 | -2.9512 | 3.61761 | 0.276426 | 1.203779 | 0.904402 | 0.559595 |
| **7** | 2.927939 | -2.92794 | 3.640875 | 0.274659 | 1.177303 | 0.910219 | 0.559215 |
| **8** | 3.0176 | -3.0176 | 3.627134 | 0.2757 | 1.255249 | 0.906783 | 0.548973 |
| **9** | 2.885625 | -2.88562 | 3.645093 | 0.274341 | 1.142197 | 0.911273 | 0.564372 |
| **10** | 3.140187 | -3.14019 | 2.48521 | 0.40238 | 1.983891 | 0.621303 | 0.776557 |
| **11** | 2.724942 | -2.72494 | 3.821831 | 0.261655 | 0.971434 | 0.955458 | 0.559295 |
| **12** | 3.929451 | -3.92945 | 3.069846 | 0.325749 | 2.51488 | 0.767461 | 0.500115 |
| **13** | 3.669447 | -3.66945 | 2.774195 | 0.360465 | 2.426802 | 0.693549 | 0.600274 |
| **14** | 3.985779 | -3.98578 | 3.053247 | 0.32752 | 2.601564 | 0.763312 | 0.493609 |
| **15** | 3.905097 | -3.9051 | 3.257468 | 0.306987 | 2.340742 | 0.814367 | 0.475047 |
| **16** | 3.757884 | -3.75788 | 3.345632 | 0.298897 | 2.110467 | 0.836408 | 0.48453 |

The Local reactivity parameters was used to further investigate this impact because it would give a clearer insight on how these atoms affected their chemical environment and reactivity of surrounding atoms which was achieved using fukui function. The condensed fukui function provides information about site specific reactions, it describes which type of reaction (nucleophilic or electrophilic), an atom in a molecule susceptible to. $f^+$ and $f^-$ are used to represent sites for nucleophilic and electrophilic attack respectively (see supplementary information), while $\Delta f$ represented the dual descriptor [60]. The dual descriptor was used to further classify each atom as either electrophilic or nucleophilic attack susceptible. While positive dual descriptor values signify electrophilicity, negative dual descriptor values signify nucleophilicity. It was observed that the compounds whose atoms were highly electrophilic favours increased inhibition. 13 which was observed to be the most efficient inhibitor had $\Delta f$ values that were mostly electrophilic and weakly nucleophilic. This was also observed for 12, 14, 15, and 16, as they all had high electrophilicity values (Table 5). Oxygen (O) was also observed to have a much more electrophilic effect on surrounding atoms than Sulphur (S): 1 and 3, 8 and 10, and 12 and 13.

**Table 5:** Dual descriptors (Δ*f*) of compounds

| **1** | | **2** | | **3** | | **4** | | **5** | |
|---|---|---|---|---|---|---|---|---|---|
| C1 | -0.00311 | C1 | -0.00013 | C1 | 0.001387 | C1 | 0.016336 | C1 | 0.082731 |
| C2 | 0.009927 | C2 | -0.03089 | C2 | -0.03061 | C2 | -0.03674 | C2 | -0.1615 |
| C3 | -0.03418 | C3 | -0.01673 | C3 | -0.00247 | C3 | 0.001902 | C3 | 0.014883 |
| C4 | -0.06451 | C4 | -0.08765 | C4 | -0.08559 | C4 | -0.07891 | C4 | -0.06999 |
| C5 | 0.062256 | C5 | 0.059022 | C5 | 0.067677 | C5 | 0.06588 | C5 | 0.093057 |
| C6 | -0.07453 | C6 | -0.07883 | C6 | -0.07482 | C6 | -0.06243 | C6 | -0.05474 |
| C11 | 0.031774 | C11 | 0.032387 | C11 | 0.002263 | C11 | 0.020155 | C11 | -0.11598 |
| C14 | -0.02965 | C14 | -0.03996 | C14 | -0.05144 | C14 | -0.04942 | C14 | -0.00808 |
| O17 | 0.102022 | N17 | 0.162781 | S17 | 0.173608 | N16 | 0.172768 | O16 | -0.04695 |
| | | | | | | O18 | -0.04954 | S18 | 0.266547 |
| **6** | | **7** | | **8** | | **9** | | **10** | |
| C1 | -0.02741 | C1 | -0.04817 | C1 | -0.00216 | C1 | -0.05868 | C1 | 2.052802 |
| C2 | -0.00892 | C2 | -0.00651 | C2 | -0.04941 | C2 | -0.04552 | C2 | -0.42732 |
| C3 | -0.0175 | C3 | -0.02776 | C3 | 0.031421 | C3 | 0.02977 | C3 | -0.01655 |
| C4 | -0.07223 | C4 | -0.08506 | C4 | -0.0189 | C4 | -0.09478 | C4 | -0.83405 |
| C5 | 0.059996 | C5 | 0.057391 | C5 | -0.00834 | C5 | 0.010459 | C5 | 1.737641 |
| C6 | -0.06574 | C6 | -0.07193 | C6 | 0.012844 | C6 | -0.01797 | C6 | -1.95239 |
| C11 | 0.027606 | C11 | 0.01844 | C11 | -0.00236 | C11 | 0.004583 | C10 | 0.467422 |
| S14 | 0.129554 | S13 | 0.131814 | S13 | 0.139182 | S13 | 0.130066 | N12 | -0.60994 |
| N15 | -0.02535 | N14 | 0.008025 | N14 | 0.016275 | N14 | 0.020435 | O15 | 0.091571 |
| | | O16 | 0.023764 | S16 | -0.11855 | N16 | 0.021646 | O16 | -0.50919 |
| **11** | | **12** | | **13** | | **14** | | **15** | |
| C1 | -0.06003 | C1 | 0.007594 | C1 | 0.017493 | C1 | 0.006872 | C1 | 0.008757 |
| C2 | 0.018262 | C2 | 0.015253 | C2 | 0.017338 | C2 | 0.012726 | C2 | 0.012587 |
| C3 | -0.04013 | C3 | -0.02118 | C3 | -0.02406 | C3 | -0.03538 | C3 | -0.04688 |
| C4 | -0.06145 | C4 | -3.5E-05 | C4 | -0.005 | C4 | -0.02099 | C4 | 0.010905 |
| C5 | 0.024173 | C5 | 0.003443 | C5 | -0.00505 | C5 | -0.02143 | C5 | -0.00293 |
| C6 | -0.03859 | C6 | -0.01849 | C6 | -0.02423 | C6 | -0.03962 | C6 | -0.02744 |
| C10 | 0.056273 | C10 | -0.05962 | C10 | -0.01336 | C10 | -0.05332 | C9 | -0.05026 |
| N12 | 0.048972 | O11 | -0.01593 | O11 | 0.197924 | S12 | -0.08311 | S11 | -0.03652 |
| O15 | 0.063171 | O12 | 0.113763 | S12 | -0.08064 | S13 | 0.063943 | N12 | -0.02197 |
| N16 | -0.01066 | S13 | -0.0248 | S14 | -0.0804 | N14 | -0.06707 | O14 | 0.168066 |
| | | | | | | O15 | 0.129817 | S15 | -0.01347 |
| | | | | | | O16 | 0.08816 | N16 | -0.0024 |
| | | | | | | N17 | 0.019403 | O19 | 0.000575 |
| | | | | | | | | O20 | 0.000979 |
| **16** | | | | | | | | | |
| C1 | 0.101934 | | | | | | | | |
| C2 | -0.04912 | | | | | | | | |
| C3 | -0.083 | | | | | | | | |
| C4 | -0.02446 | | | | | | | | |
| C5 | -0.00887 | | | | | | | | |
| C6 | -0.05851 | | | | | | | | |
| C9 | 0.13728 | | | | | | | | |
| S11 | -0.03017 | | | | | | | | |
| N12 | -0.10852 | | | | | | | | |
| S13 | 0.076101 | | | | | | | | |
| N14 | -0.03402 | | | | | | | | |
| O17 | 0.015553 | | | | | | | | |
| O18 | 0.025076 | | | | | | | | |
| N19 | 0.040725 | | | | | | | | |

An important assumption made in the course of this study was that, the presence of more heteroatoms would significantly improve a molecule's inhibition efficiency which was not entirely true.  Random additions of heteroatoms because of its informed increased reactivity may not yield the desired results, as seen in 4 which consisted of two heteroatoms, and 9 and 11 which consisted of three heteroatoms having lower chemical reactivity tendencies than 3 which consisted of a single heteroatom, S. However, there seems to be a set of favoured atom configuration that do result in greater chemical reactivity, making the empirical rule of organic inhibitors with heteroatoms N, O and S questionable when considering multiple heteroatoms systems causing the empirical rule to shift from O<N<S to N<O<S when moving from single heteroatom systems to multiple heteroatoms system.

## Conclusion

Density functional theory was used to assess the reactivity characteristics of organic compounds containing the heteroatoms S, N, and O. The goal of the study was to provide information that will inform future research aimed at addressing the corrosion threat and to address questions about how these heteroatoms affect inhibition. The following finding was made in response to questions raised in the context of this study,

1. An increase in the number of heteroatoms does not always imply an increase in inhibition efficiency

2.The best heteroatoms configuration is in the order of O and N < S and N < S and O, giving rise to an inhibition efficiency trend is of N<O<S, as opposed to O<N<S, which holds true for only single heteroatom compounds.

3. Oxygen has a significant impact on improving the inhibition efficiency of organic inhibitors.

## Conflict of Interest

The authors wish to state that there is no conflict of interest.

## References

[1] J. R. Davis, *ASM International.*, Materials Park (2000).

[2] R. Javaherdashti. Anti-Corros Method M., 47, 30 (2000)

[3] M.B. Kermani, D. Harrop, *SPE Prod. Oper*., 11, 186 (1996).

[4] A.P.L. Popoola, O.E. Olorunniwo, O.O. Ige, *InTech, London.*, (2014).

[5] E.S. Ibrahim, Electr. Power Compon. Syst., 27, 795 (1999)

[6] S.L. Chawla, *ASM international,* Materials park (1993).

[7] E. Ghali, V.S. Sastri. M. *Wiley, NJ,* (2007)

[8] N. Hossain, M Asaduzzaman Chowdhury, M. Kchaou, *J Adhes Sci Technoly*., 35, 671 (2021)

[9] M. Mobin, I. Ahmad, M. Basik, M. Murmu, P. Banerjee, *Sustain. Chem. Pharm,* 18, 100377 (2020).

[10] J. Tan, L. Guo, H. Yang, F. Zhang, Y. El Bakri, *RSC Adv.*, 10, 15163 (2020).

[11] B. E.l. Ibrahimi, A. Jmiai, L. Bazzi, S. El Issami, *Arab. J. Chem.*, 13, 740 (2020).

[12] G. Serdaroğlu, S. Kaya, *Wiley*, NJ (2021).

[13] P. Rajeev, A.O. Surendranathan, C.S. Murthy, *J. Mater. Environ. Sci*., 3, 856 (2012).

[14] L. Guo, I.B. Obot, X. Zheng, X. Shen, Y. Qiang, S. Kaya, d C. Kaya, *Appl Surf Sci*., 406,301 (2017).

[15] S. Gao, L. Li, K. Geng, X. Wei, S. Zhang. *Nano Energy*., 16, 408 (2015).

[16] W. Yang, W. Yang, A. Song, L. Gao, L. Su, G. Shao, *J Power Sources.*, 359, 556 (2017).

[17] S.K. Saha, A. Dutta, P. Ghosh, D. Sukul, P. Banerjee, *Phys Chem Chem Phys*., 18, 17898 (2016).

[18] F. Chioma, O.W. Nnenna, O. Moses, *Prot Met Phys Chem Surf*., 56, 651 (2020)

[19] F. Chioma, N.W. Odozi, M.M. Moses, M.A. Olatunde, *Global Journal of Pure and Applied Sciences,* 28, 39 (2022).

[20] N. Odozi, C. Festus and K. Sorbari, *Fudma J Sci*., 6, 144 (2022).

[21] K. Zhang, W. Yang, B. Xu, X. Yin, Y. Chen, Y. Liu, *Chemistry Select*, 3, 12486 (2018).

[22] P. Sılku, S. Özkınalı, Z. Öztürk, A. Asan, D.A. Köse, *J Mol Struct*., 1116, 72 (2016).

[23] A. Pandey, B. Singh, C. Verma, E.E. Ebenso. *RSC Adv.*, 7, 47148 (2017).

[24] A.M. Jassim. *J.Thi-Qar Sci*., 3, 64, (2012).

[25] N.A. Negm, F.M. Ghuiba, S.M. Tawfik. *Corros Sci.*, 53, 3566 (2011).

[26] S. Issaadi, T. Douadi, A. Zouaoui, S. Chafaa, M.A. Khan, G. Bouet, *Corros Sci*., 53, 1484 (2011).

[27] N.A. Negm, M.F. Zaki, M.A. Salem, *J Surfactants Deterg.*, 12, 321 (2009).

[28] M.A Hegazy, A.M. Badawi, S.S. Abd El Rehim, W.M. Kamel, *Corros sci.*, 69, 110 (2013).

[29] D. Daoud, T. Douadi, S. Issaadi and S. Chafaa. *Corros sci.*, 79, 50 (2014)

[30] A. Paul, K.J. Thomas, V.P. Raphael, K.S. Shaju, *Orient J Chem.*, 28 1501 -1507 (2012).

[31] A.A Al-Amiery, A.A.H. Kadhum, A.B. Mohamad, S. *Junaedi, Materials*, 6, 1420 (2013).

[32] A.A. Al-Amiery, A.A.H. Kadhum, A.H.M Alobaidy, A.B. Mohamad, *P.S. Hoon. Materials.*, 7, 662 (2014).

[33] N.A. Negm, M.F. Zaki, *J Dispers Sci Technol*., 30, 649 (2009).

[34] W.A.G.A. Arafa, N.H. El-Sayed. *Eur J Chem*., 5, 563 (2014).

[35] Y.B. Zemede, A. Kumar, *Synthesis,* 7, 279 (2014).

[36] Y. Tang, F. Zhang, S. Hu, Z. Cao, Z. Wu, *W. Jing, Corros Sci.*, 74, 271 (2013).

[37] C.P. Kumar, K.N. Mohana. *J Taiwan Inst Chem Eng*., 45, 1031 (2014).

[38] H.M. Abd El-Lateef, M. Ismael, I.M. Mohamed, *Corros.*, 33, 77 (2015).

[39] U. Nazir, Z. Akhter, N.Z. Ali, F.U. Shah. *RSC Adv.*, 9, 36455 (2019).

[40] J.N. Asegbeloyin, P.M. Ejikeme, L.O. Olasunkanmi, A.S. Adekunle, *E.E Ebenso, Materials.*, 8, 2918 (2015).

[41] S. Alaoui Mrani, E. Ech-chihbi, N. Arrousse, Z. Rais, F. El Hajjaji, C. El Abiad, S. Jodeh. *Arab J Sci Eng.*, 46, 5691 (2021).

[42] S.K. Saha, M. Murmu, N.C. Murmu, P. Banerjee. *J Mol Struct.*, 1245, 131098 (2021).

[43] P. Dohare, M.A. Quraishi, I.B. Obot, *J Chem Sci.*, 130,1 (2018).

[44] Q.A. Jawad, D.S. Zinad, R.A. Dawood Salim, A.A. Al-Amiery, T. Sumer Gaaz, M.S. Takriff, A.A.H. Kadhum. *Coatings*, 9, 729, (2019).

[45] S. Boukazoula, D. Haffar, R. Bourzami, L. Toukal, V. Dorcet, *J Mol Struct*., 1261, 132852, (2022).

[46] M.M. Abdelsalam, M.A. Bedair, A.M. Hassan, B.H. Heakal, A. Younis, Z.I. Elbialy, S.A. Fareed. *Arab J Chem.*, 15, 103491 (2021).

[47] P. Singh, M.A. Quraishi, *Measurement*, 86, 114 (2016).

[48] H.M. Abd El-Lateef, *Corros Sci.*, 92, 104 (2015).

[49] F. Tezcan, G. Yerlikaya, A. Mahmood, G. Kardaş, *J Mol Liq.*, 269, 398 (2018).

[50] A.J.M. Eltmimi, A. Alamiery, A.J. Allami, R.M. Yusop, A.H. Kadhum, T Allami, *Int J Corros Scale Inhib*., 10, 634 (2021).

[51] N.O. Obi-Egbedi, I.B. Obot, M.I. El-Khaiary, *J. Mol. Struct.* 1002, 86 (2011).

[52] B. Cui, T. Chen, D. Wang, *L.J. Wan, Langmuir* 27, 7614 (2011).

[53] F. Bentiss, M. Traisnel, L. Gengembre, M. Lagrenée, *Appl. Surf. Sci*. 152, 237 (1999).

[54] F. Chioma, I.B. Nwoke and O. Valentine, *J Anal Pharm Res*, 11, 45 (2022).

[55] H. Chermette. *J Comput Chem*., 20, 129 (1999).

[56] W. Yang, R.G. Parr, *Proc Natl Acad Sci.*, 82, 6723 (1985).

[57] W. Yang, W.J. Mortier, *J Am Chem Soc.*, 108, 5708 (1986).

[58] I.B. Obot, N.O Obi-Egbedi, *Corros Sci.*, 52, 198 (2010).

[59] C. Morell, A. Grand, A. Toro-Labbé. *J. Phys. Chem. A.*, 109, 205 (2005).

[60] J.I. Martínez-Araya JOMC, 5, 451(2015).

HOW TO CITE THIS ARTICLE

Valentine Osi; Kingsley John Orie; Keerabana Sorbari. **"Multiple heteroatom additions effect on the empirical rule for organic corrosion inhibitors with nitrogen, oxygen, and sulfur atoms, a DFT approach.",** International Journal of New Chemistry, 2025; 12(4), 502-518. doi: 10.22034/ijnc.2023.1995885.1344.