Theoretical Study of the Efficiency of Benzo-Phenoxazinone Derivatives in Aqueous Medium to Serve as Effective Organic Corrosion Inhibitors of Mild Steel

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ABSTRACT

The use of inhibitors is one of the most practical methods to protect metals against corrosion, especially in acidic media. Quantum chemical calculations using Austin Model 1 (AM1) semi-empirical method were performed to find the relation between the molecular structure of the inhibitor and the inhibition efficiency and it also compared the inhibition efficiency of benzo-phenoxazinone derivatives with other known organic inhibitor compounds. The following quantum chemical indices were considered: The energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest occupied molecular orbital (E_{LUMO}), separation energy (E_{LUMO}-E_{HOMO}), dipole moment (μ), Log P, and polarizability of the various benzo-phenoxazinone derivatives. The calculated quantum chemical indices confirm that the benzo-phenoxazinone derivatives are potentially effective corrosion inhibitors. The calculated quantum chemical indices also confirm that the benzo-phenoxazinone derivatives actually possess inhibiting properties which are generally more efficient than those of the other known organic inhibitors used in oil and gas systems.

Keywords: AM1, corrosion inhibitors, benzo-phenoxazinone derivatives, quantum chemical indices

INTRODUCTION

Corrosion of metals is a major industrial (Olawale et al, 2019) problem that has attracted many investigations and researches. The use of inhibitors is one of the most practical methods to protect metals against corrosion, especially in acidic media. Acids are widely used in industries for different purposes such as pickling, cleaning, descaling etc. (Popoola, 2019 and Tarab, 2006).

It has been noted that organic compounds containing nitrogen, sulphur and oxygen are confirmed to be excellent inhibitors. The ability of an organic compound to get adsorbed on a metal surface which entails the replacement of a water molecule at a corroding interface determines its efficiency as an inhibitor. The adsorption of these compounds is influenced by the electronic structure of inhibiting molecules, steric factor, aromatic and electron density at donor site, presence of functional group such as –CHO, –N=N, R–OH etc., molecular area and molecular weight of the inhibitor molecule (Ojo et al, 2022 and Ambrish et al, 2010).

The adsorbed inhibitors can affect the corrosion reaction, either by the blocking effects of corrosion on the metal surface or by the effect attributed to the change in the activation barriers of the anodic and cathodic reaction of the corrosion process.

Experimental means are useful in explaining the inhibition mechanism but they are often expensive and time-consuming. Advances in computer hardware and software and in theoretical chemistry have brought high-

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performance computing and graphic tools within the reach of many academic and industrial laboratories. Recently, more corrosion publications contain substantial quantum chemical calculations. Such calculations are usually used to explore the relationship between the inhibitor molecular properties and their corrosion inhibition efficiencies (Ojo et al, 2023 and Blajiev et al, 2012).

Corrosion inhibitors are widely used in industries to reduce the corrosion rate of metals in contact with aggressive environments (Mohd, 2010). Most of the inhibitors used in the industries are chemicals which are very toxic to humans. This has a very detrimental effect on the human health and in severe cases can lead to death. Hence, the need for further research on a more effective group of green corrosion inhibitors is required.

Also, the theoretical prediction of the efficiency of corrosion inhibitors in selecting excellent corrosion inhibitors has continuously gained popularity especially with the significant progress in the building of sophisticated software packages which has been employed in quantum mechanical calculations.

However, no report has been made on the studies of benzo-phenoxazinone derivatives in aqueous medium to serve as effective organic corrosion inhibitors of mild steel. Therefore, in this study, the efficiency of two of such organic compounds as corrosion inhibitors will be considered.

THEORETICAL METHOD

All quantum chemical calculations were performed with SPARTAN'14. The full optimization was initially achieved by using molecular mechanics force fields (MMFF). The results from MMFF were further selected as input and re-optimized using semi empirical AM1.

It represents an excellent compromise between completeness and economy. The molecular geometry was fully optimized without any constraint, using analytical gradient procedure implemented within the program package (Gokham, 2008).

The following quantum chemical indices were considered: The energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest occupied molecular orbital (E_{LUMO}), separation energy (E_{LUMO}-E_{HOMO}), dipole moment (μ), Log P, and polarizability of the various benzo-phenoxazinone derivatives. The chemical structures and optimized geometry of the benzo-phenoxazinone derivatives being considered in this study are shown in Fig 1 and 2.

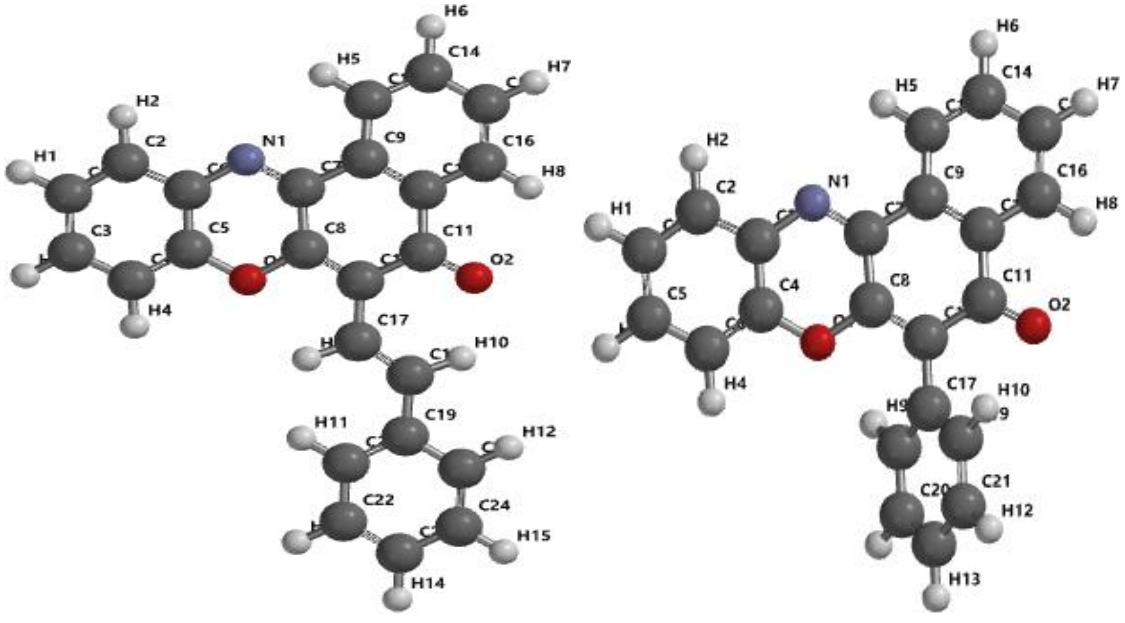

Fig 1: Optimized structure of 6-styryl-5H-benzo[α]phenoxazin-5-one and 6-phenyl-5H-benzo[α]phenoxazin-5-one

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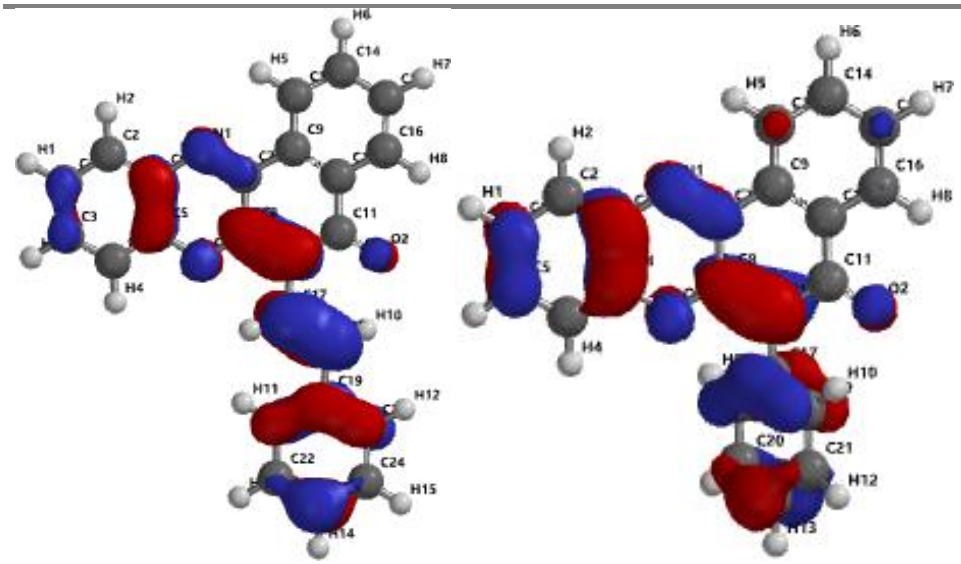

Fig 2: HOMO plot of optimized structure of 6-styryl-5H-benzo[α]phenoxazin-5-one and 6-phenyl-5H-benzo[α]phenoxazin-5-one

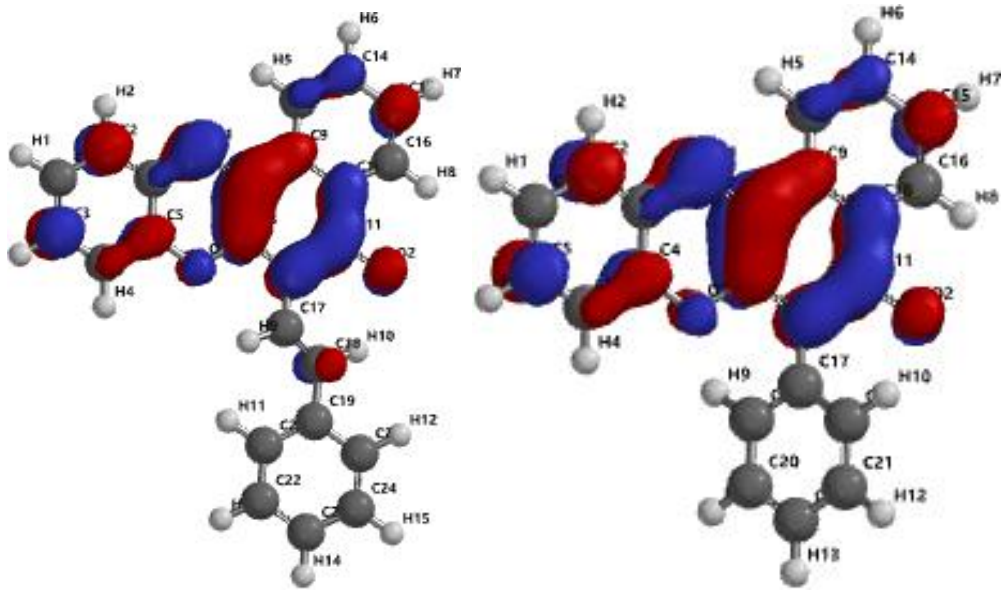

Fig 3: LUMO plot of optimized structure of 6-styryl-5H-benzo[α]phenoxazin-5-one and 6-phenyl-5H-benzo[α]phenoxazin-5-one

RESULTS AND DISCUSSION

From the molecular structure of the benzo-phenoxazinone compounds being considered, it is apparent that due to the presence of the O and N atoms, they can serve as organic corrosion inhibitors when they transfer their electrons to the metals and become adsorbed to the metal surface.

The efficiency of inhibition of the two benzo-phenoxazinone compounds being considered was measured based on the calculations obtained from SPARTAN'14. It was then compared with the results obtained when the same calculations were made using other known organic inhibitors that have been used extensively in oil and gas systems and have a range of inhibition efficiency that falls between 72-92%.

The quantum chemical parameters obtained from the calculations which are responsible for the inhibition efficiency of inhibitors such as the energies of frontier molecular orbitals (E_{HOMO} and E_{LUMO}), separation energy (E_{LUMO} - E_{HOMO}), dipole moment, substituent constant (log p), polarizability and molecular volumes are tabulated in Table 1.

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Table 1: Quantum chemical parameters of benzo-phenoxazinone derivatives and other known organic inhibitors using AM1 method

	E_{HOMO} (eV)	E_{LUMO} (eV)	E_L-E_H	Dipole moment (Debye)	Log P	Polarizability	Volume
***Molecule 1**	**-8.32**	**-1.64**	**6.68**	**3.49**	**1.64**	**69.15**	**361.88**
***Molecule 2**	**-8.62**	**-1.59**	**7.03**	**3.58**	**1.12**	**66.42**	**329.22**
Molecule 3	-9.45	-1.40	8.05	3.14	-0.07	55.61	198.98
Molecule 4	-8.57	-1.21	7.36	2.59	-1.73	58.45	231.96
Molecule 5	-9.19	-0.71	8.48	2.26	0.36	53.64	200.57
Molecule 6	-8.75	-1.20	7.55	4.55	-1.68	64.83	311.18
Molecule 7	-8.38	-0.97	7.41	4.95	-3.73	66.83	335.40
Molecule 8	-9.02	2.90	11.92	0.88	1.26	49.58	139.42
Molecule 9	-8.40	0.30	8.7	1.88	0.14	50.10	132.83
Molecule 10	-9.35	-1.97	7.38	5.05	-1.10	50.65	135.82

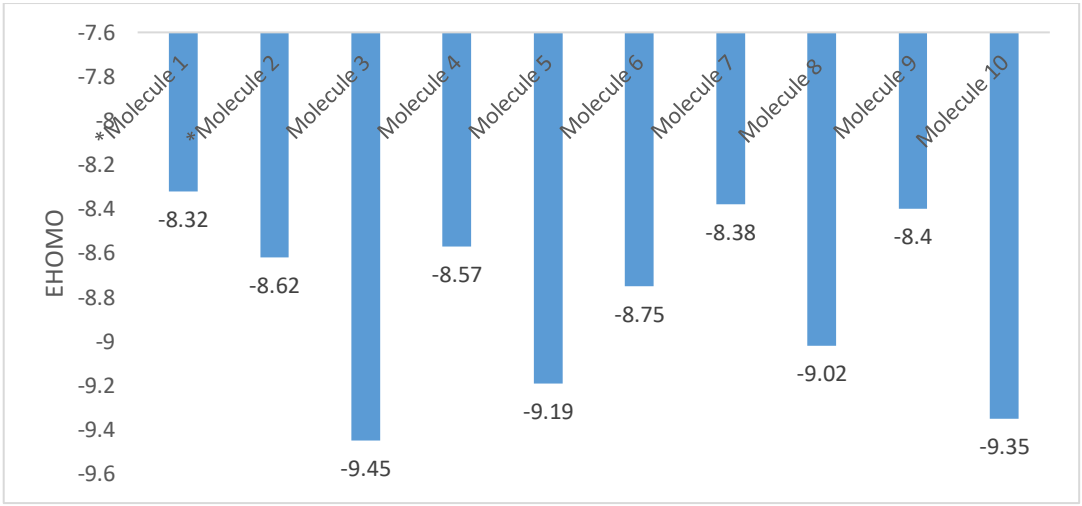

Fig 4: EHOMO vs Molecule

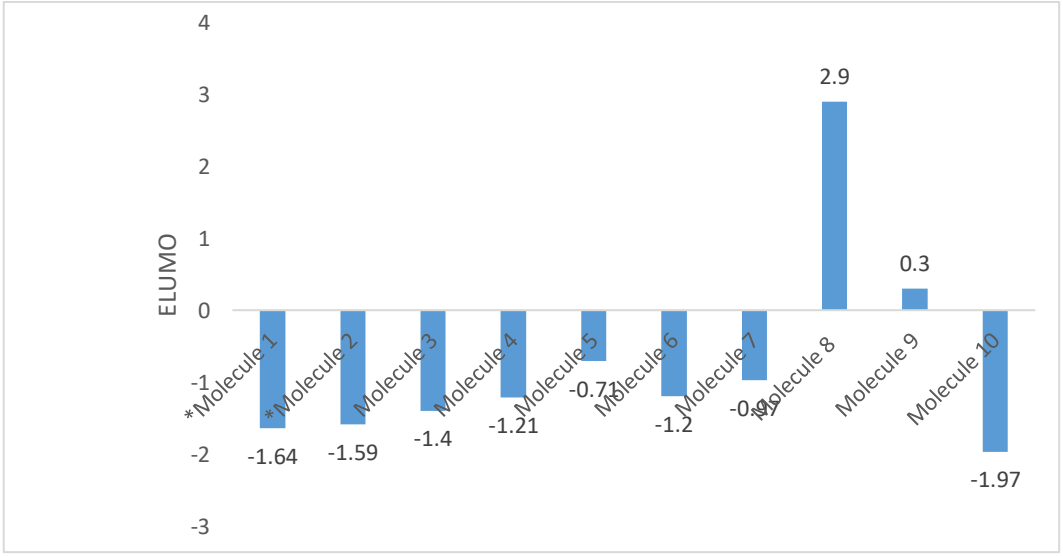

Fig 5: ELUMO vs Molecule

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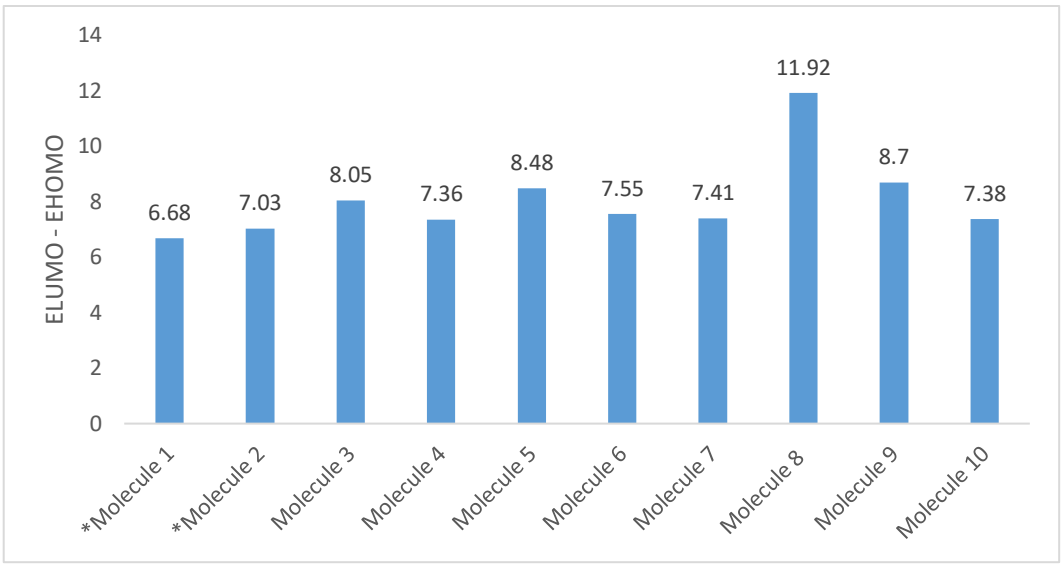

Fig 6: ELUMO-EHOMO vs Molecule

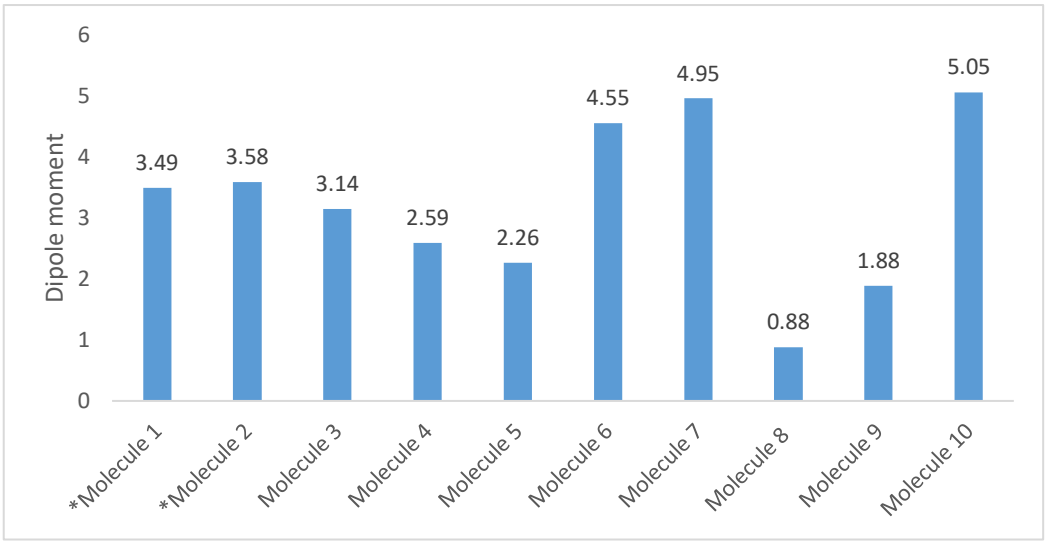

Fig 7: Dipole moment vs Molecule

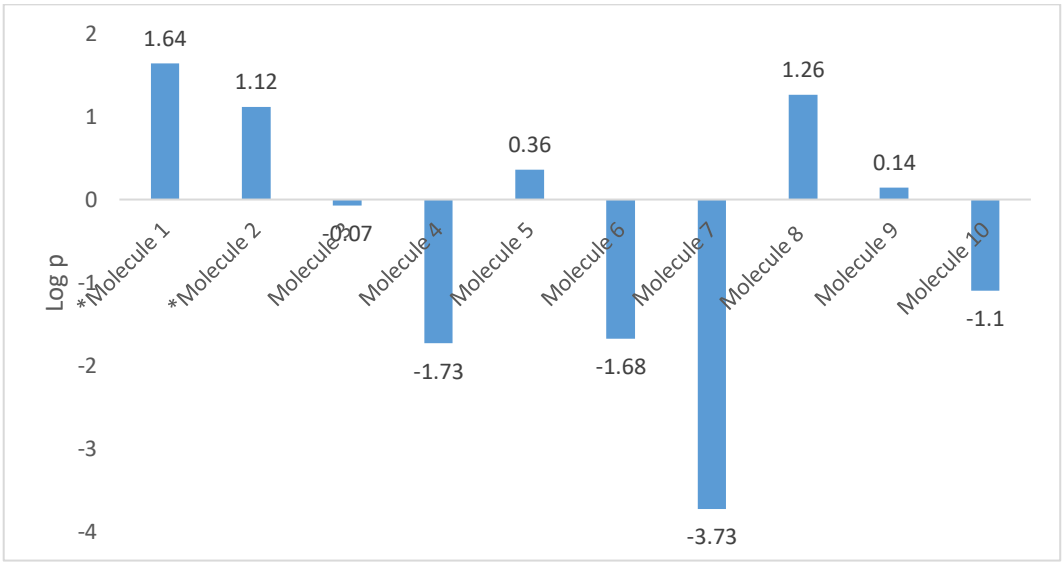

Fig 8: Log p vs Molecule

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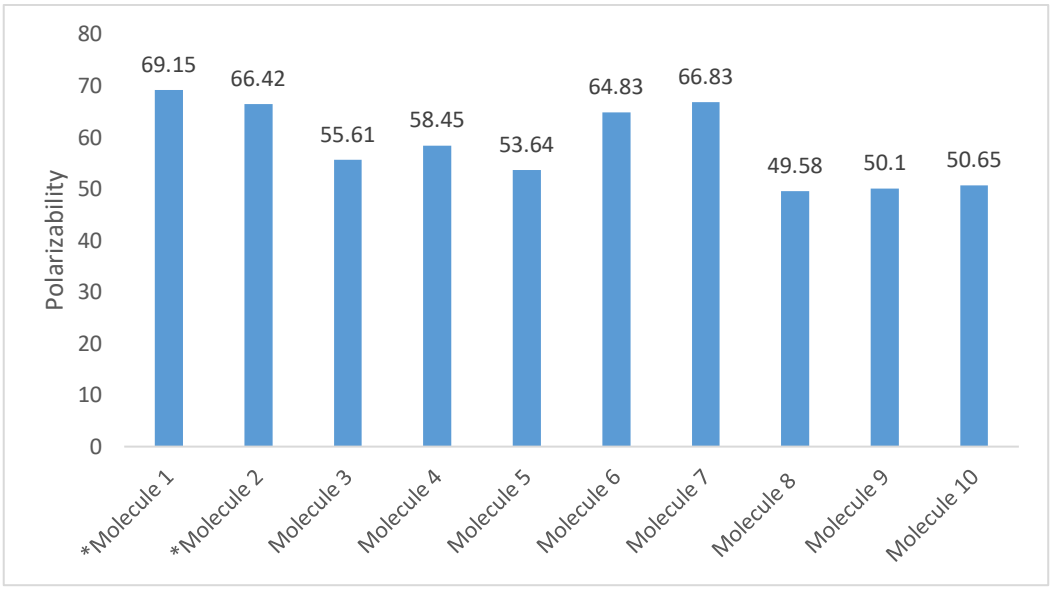

Fig 9: Polarizability vs Molecule

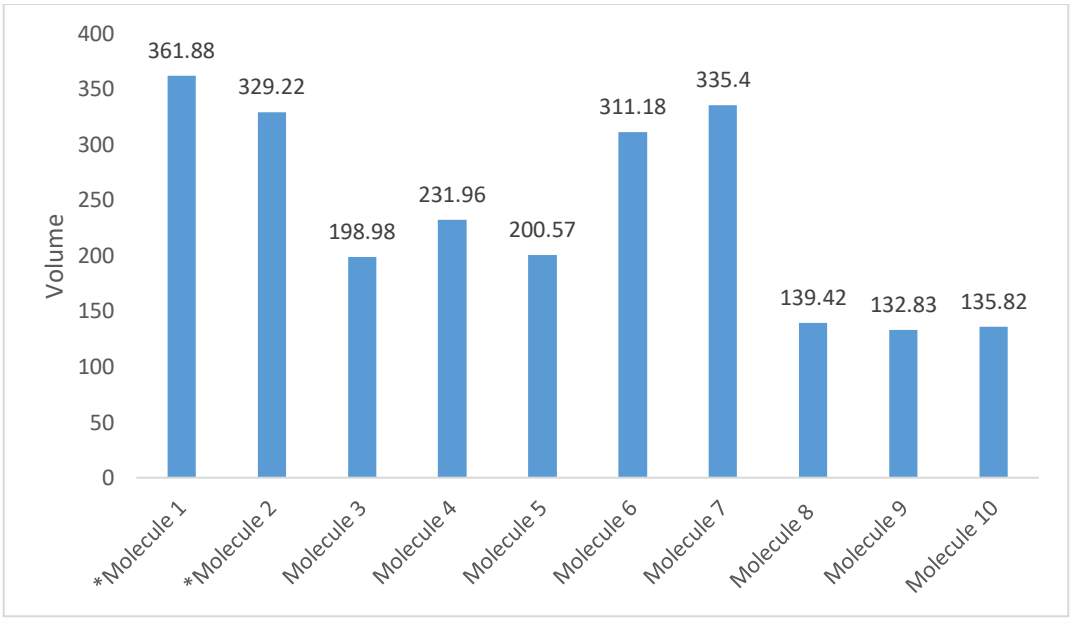

Fig 10: Volume vs Molecule

Names of molecules 1-10

a) Molecule 1: 6-styryl-5H-benzo[α]phenoxazin-5-one
b) Molecule 2: 6-phenyl-5H-benzo[α]phenoxazin-5-one
c) Molecule 3: Alloxazine (Ali et al, 2003)
d) Molecule 4: 1,2-diaminoanthraquinone (Tang et al, 2005)
e) Molecule 5: Xanthione (Cruz et al, 2005)
f) Molecule 6: 2-(6-methyl pyridine-2-yl)oxazdo[5,4-f][1,10]phenanthroline (Popova et al, 2004)
g) Molecule 7: 4-methoxy-2-(3H-phenanthro[9-10-d]-imidazol-2-yl)phenol (Ita et al, 2007)
h) Molecule 8: Triethylamine (Cardoso et al, 2007)
i) Molecule 9: Indole (Popova et al, 2007)
j) Molecule 10: 2-oxyindole (Wang et al, 2004)

After comparing the quantum chemical parameters of the ten molecules listed in table 1, it can be said that the benzo-phenoxazinone derivatives (Molecule 1 and Molecule 2) generally possess greater efficiency as

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corrosion inhibitors compared to the other known organic corrosion inhibitors listed (Molecules 3-10). This is done by evaluating the values of the different quantum chemical parameters to know which value will possess a greater inhibiting efficiency compared to the values obtained by the benzo-phenoxazinone derivatives. This is explained in detail below:

The E_{HOMO} is often associated with the electron donating ability of a molecule (Khaled, 2009). Therefore, increasing values of E_{HOMO} indicates a higher tendency for donation of electrons to the appropriate acceptor molecule with low energy and empty molecular orbital. Thus, increasing values of the adsorption of the inhibitor. Hence the higher the value of E_{HOMO}, the greater the inhibition potential of the molecule.

The E_{LUMO} indicates the ability of the molecule to accept electrons. Hence, to serve as an effective corrosion inhibitor, the lower the value of the $E_{LUMO,}$ the greater the inhibition potential of the molecule.

The separation energy which indicates reactivity is the difference between the HOMO and the LUMO (**E_L-E_H)**. The energy gap also relates how soft or hard a molecule is. A larger energy gap indicates low reactivity to chemical specie, thus a soft molecule is more reactive than a hard molecule (Khaled, 2009). In summary, the binding ability of the inhibitor to the metal surface increases with increasing energy of HOMO, decreasing energy of LUMO and low separating energy values.

Dipole moment (μ) is another useful quantum index for the prediction of the direction of a corrosion inhibition process. It is a measure of the polarity in a bond and is related to the distribution of electrons in a molecule. Although literature is inconsistent on the use of dipole moment as a predictor for the direction of a corrosion inhibition reaction, it is generally agreed that the adsorption of polar compounds possessing higher dipole moments on the metal surface should lead to better inhibition efficiency.

Polarizability is the ratio of induced dipole moment to the intensity of the electric field. The induced dipole moment is proportional to polarizability. Hence, the greater its value, the better the inhibition potential of that molecule (Wang et al, 2003).

The values of log P (substituent constant) were also found to have a good relationship with the corrosion inhibition efficiencies of the studied inhibitors. Substituent constants are empirical quantities which account for the variation of the structure and do not depend on the parent structure but vary with the substituent. Hence, increasing the value of log P increases the inhibition efficiencies of organic inhibitors (Gece, 2011).

Molecular volume and weight are quantum parameters that determine molecular size and effective surface coverage. These invariably determine how effective a molecule can be adsorbed on and cover a metal surface, thereby isolating it from the corroding environment. As the value of these parameters increase, so also the likely corrosion inhibition potentials of the molecules increase.

Also, when comparing the corrosion inhibition efficiency of the two benzo-phenoxazinone derivatives based on these calculated quantum chemical parameters, it is observed that molecule 1 generally has greater corrosion inhibition efficiency than molecule 2. This is due to the presence of the conjugated double bond in molecule 1 which makes more electrons available to be donated to the metal and thus promotes better the inhibition of corrosion.

CONCLUSION AND RECOMMENDATIONS

Conclusion

Quantum chemical calculations using AM1 semi-empirical method were performed to find the relation between the molecular structure of the inhibitor and the inhibition efficiency. It also compared the inhibition efficiency of benzo-phenoxazinone derivatives with other known organic inhibitor compounds.

The calculated quantum chemical indices confirm that the benzo-phenoxazinone derivatives are potentially effective corrosion inhibitors. The calculated quantum chemical indices also confirm that the benzo-

phenoxazinone derivatives actually possess inhibiting properties which are generally more efficient than those of the other known organic inhibitors used in oil and gas systems.

Recommendations

1. The inhibitory potentials of the benzo-phenoxazinone derivatives should be further investigated using Density Functional Theory (DFT).
2. The adsorption of the molecules on the surface of metal iron should be studied.
3. Experimental methods should be employed to further investigate the inhibition potentials of benzo-phenoxazinone derivatives.
4. Detailed study of the molecular structure of the organo-iron complexes responsible for the inhibition should be undertaken.

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