HSAB descriptors of thiadiazole derivatives calculated by DFT: possible relationship as mild steel corrosion inhibitors

I. B. Obot[a]*, N.O. Obi-Egbedi[b]

[a]*Department of Chemistry, Faculty of Science, University of Uyo, Uyo, Nigeria.*

[b]*Department of Chemistry, University of Ibadan, Ibadan, Nigeria.*

Abstract

The inhibitive effect of some substituted thiadiazoles, 2-amino-1,3,4-thiadiazoles (AT), 2-amino-5-methyl-1,3,4-thiadiazoles (AMT), 2-amino-5-ethyl-1,3,4-thiadiazoles (AET) and 2-amino-5-propyl-1,3,4-thiadiazoles (APT) against the corrosion of mild steel in formic and acetic acid is studied theoretically using DFT at the B3LYP/6-31G(d) level in order to elucidate the different inhibition efficiencies and reactive sites of these compounds as corrosion inhibitors. The calculated quantum chemical parameters correlated to the inhibition efficiency are, $E_{HOMO,}$ $E_{LUMO,}$ energy of the gap (ΔE) and other parameters, including electronegativity (χ), global hardness (η), global softness (S) and the fraction of electrons transferred from the inhibitor molecule to the metallic atom (ΔN). The calculated results are in agreement with the experimental data. In addition, the local reactivity has been analyzed through the Fukui function and condensed softness indices as well as Mulliken population analysis.

Keywords: Thiadiazole, corrosion inhibitors, density functional theory (DFT), Fukui function, softness indices.

Introduction

The use of inhibitors is one of the most practical methods to protect metals against corrosion, especially in acidic media [1]. Most efficient inhibitors are organic compounds containing electronegative functional groups and π-electrons in triple or conjugated double bonds. The remarkable inhibitory effect is reinforced by the presence of heteroatoms such as sulphur, nitrogen and oxygen in the ring which facilitates its adsorption on the metal surface following the sequence O < N < S [2]. Researchers conclude that the adsorption on the metal surface depends mainly on the physicochemical properties of the inhibitor group, such as the functional group, molecular electronic structure, electronic density at the donor atom, π orbital character and the molecular size [3-5].

Quantum chemical calculations have been widely used to study reaction mechanisms. They have also proved to be a very powerful tool for studying corrosion inhibition mechanisms [6]. Recently, theoretical prediction of the efficiency of corrosion inhibitors has become very popular in parallel with the progress in computational hardware and the development of efficient algorithms which assisted the routine development of molecular quantum mechanical calculations [7].

Several reports have appeared in literature using DFT as a theoretical tool in correlating inhibition efficiency and electronic properties/molecular structures of azoles and their derivatives used as corrosion inhibitors. The electronic and molecular structures of 1,3,4-thiadiazole and its derivatives have been calculated by Rodriguez-Valdez et al. [8] by means of B3LYP/STO-3G* method. Such parameters as the total energy, ΔE, the HOMO and LUMO energies, dipole moment, and global hardness (η) were calculated for each one of the derivatives of 1,3,4-thiadiazole, both in the gas and liquid phases. No significant differences were found for the structures of these compounds in gaseous and liquid phases.

Feng et al. [9] performed calculations of a self-assembled monolayer of 2-mercaptobenzothiazole (MBT) in order to investigate the adsorbate-surface interactions by the B3LYP/6-31+G*. They calculated such parameters as the atomic charges for two tautomeric forms of the MBT molecule (i.e. thiol and thione), the HOMO and LUMO energies and the interaction energy between MBT and iron. They chose benzothiazole to compare the results obtained by MBT. The HOMO energies of the two forms of MBT (-624.1kJ/mol for thiol form and -583.5kJ/mol for thione form) were larger than that of benzothiazole (-647.9kJ/mol). These results showed the importance of the exocyclic sulphur atom in forming the self-assembled monolayers on iron. The interaction energy calculations also predicated that MBT chemically adsorbed on the iron surface most probably via the exocyclic sulphur atom.

Some new 2,5-disubstituted 1,3,4-thiadiazole as corrosion inhibitors of mild steel in 1 M HCl was investigated using the B3LYP/6-31G (d,p) (2d,2p) method by Bentiss et al. [10]. In order to find a correlation between experimentally determined corrosion inhibition data and a number of quantum molecular properties, inhibition performance of six thiadiazole compounds (2,5-bis(phenyl)-1,3,4-thiadiazole (DPTH), 2,5-bis(4-methoxyphenyl)-1,3,4-thiadiazole (4-MTH), 2,5-bis(4-dimethylaminophenyl)- 1,3,4-thiadiazole (4-DATH), 2,5-bis(4-methylphenyl)- 1,3,4-thiadiazole (4-MPTH), 2,5-bis(4-nitrophenyl)- 1,3,4-thiadiazole (4-NPTH) and 2,5-bis(4-chloroxyphenyl)- 1,3,4-thiadiazole (4-CPTH) was subjected to correlation analysis with the calculated quantum chemical parameters (E_{HOMO}, E_{LUMO}, ΔE and dipole moment using linear and non-linear models to establish direct links between them. The linear model was not found to be satisfactory. A good correlation ($R = 0.98$) was found when non-linear model was used.

Ma et al. [11] studied the inhibition efficiency of self-assembled films of 1-methyl-5-mercapto-1,2,3,4-tetrazole (MMT) for iron using the B3LYP/LANL2DZ method. In order to investigate the adsorption between MMT and iron, they calculated the enthalpies, entropies and free energy changes of the MMT/iron system. They concluded from the results obtained from the calculations that MMT molecule is bound to the iron surface by sharing electrons between the nitrogen and iron atoms.

The inhibitive action of some thiadiazole derivatives, namely 2,5-bis(2-thienyl)-1,3,4-thiadiazole (2-TTH), and 2,5-bis(3-thienyl)-1,3,4-thiadiazole (3-TTH) against the corrosion of mild steel in 0.5 M H_2SO_4 was investigated by Lebrini et al. [12] using the B3LYP/6-31+G(d,p) (2d,2p) method. The calculated the HOMO and LUMO energies, energy gap and the dipole moment of the molecules. Small energy difference was found between E_{HOMO} and E_{LUMO} and no direct correlation could be seen between the dipole moment, energy gap and inhibition efficiency. Thus they used a linear resistance model (LR) to correlate the corrosion inhibition properties with the calculated quantum chemical parameters. A good correlation (R = 0.91) was found between the coefficient of $E_{HOMO,}$ E_{LUMO} and inhibition efficiency.

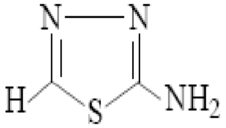
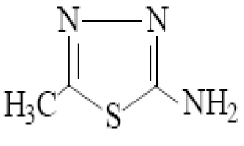
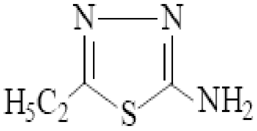
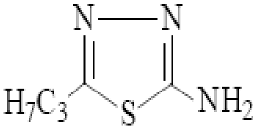
Zhang et al. [13] studied the inhibition efficiencies of imidazole, benzimidazole and their derivatives using the B3LYP/6-31G* method. They calculated a number of quantum chemical parameters such as $E_{HOMO,}$ E_{LUMO}, energy gap, charge distribution, dipole moment, and molecular connectivity index (MCI) which reveals the steric hindrance effect of the molecule. According to their results, the E_{HOMO} was the most statistically significant term influencing the corrosion inhibition efficiencies. Thus the greater the $E_{HOMO,}$ the greater is the inhibition efficiency.

The thiadiazole derivatives investigated in this work has been studied experimentally as corrosion inhibitors for mild steel and their inhibition efficiency measured using weight loss method, potentiodynamic polarization and electrochemical impedance techniques. Results obtained showed that 2-amino-5-propyl-1,3,4-thiadiazoles (APT) has the highest inhibition efficiency while 2-amino-1,3,4-thiadiazoles (AT) has the least inhibition efficiency [14].

The objective of this work therefore, is to present a theoretical study of the electronic and structural parameters of thiadiazole derivatives and the effect of these parameters on their inhibition efficiency of corrosion of mild steel from the data presented by Rafiquee and co-workers [14]. Molecular orbital calculations are performed looking for good theoretical parameters to characterize the inhibition property of inhibitors, which will be helpful to gain insight into the mechanism of corrosion inhibition. Also from the calculations we will try to explain which adsorption site is favoured to bind to the metal surface, the sulphur atom or the nitrogen atom.

The investigated thiadiazole derivatives are: 2-amino-1,3,4-thiadiazoles (AT), 2-amino-5-methyl-1,3,4-thiadiazoles (AMT), 2-amino-5-ethyl-1,3,4-thiadiazoles (AET) and 2-amino-5-propyl-1,3,4-thiadiazoles (APT), Table 1.

Table 1. Name and abbreviations of the compound used.

S.No	Structure	Designation and abbreviation
1		2-amino-1, 3, 4- thiadiazole, AT
2		5-methyl-2- amino-1, 3, 4- thiadiazole, AMT
3		5-ethyl-2-amino-1, 3, 4- thiadiazole, AET
4		5-propyl-2-amino-1, 3, 4- thiadiazole, APT

Results and discussion

The chemical structures of the compounds under investigation are presented in Table 1. The optimized molecular structures of the studied molecules using hybrid DFT functional (B3LYP/6-31G (d) are shown in Fig.1(a-d)

According to Wang et al. [15], the frontier orbitals (highest occupied molecular orbital-HOMO) and (lowest unoccupied molecular orbital-LUMO) of a chemical species are very important in defining its reactivity. Fukui [16] first recognized the importance of frontier orbitals as principal factors governing the ease of chemical reactions and the stereoselective path. Parr and Yang [34] demonstrated that most frontier theory can be rationalized from DFT. A good correlation has been found between the corrosion inhibition efficiency and E_{HOMO} that is often associated with the electron-donating ability of the molecule. It is well known that the adsorption of an inhibitor on the metal surface can occur on the basis of donor-acceptor interactions between the π-electrons of the heterocyclic compound and the vacant d-orbitals of the metal surface atoms [17].

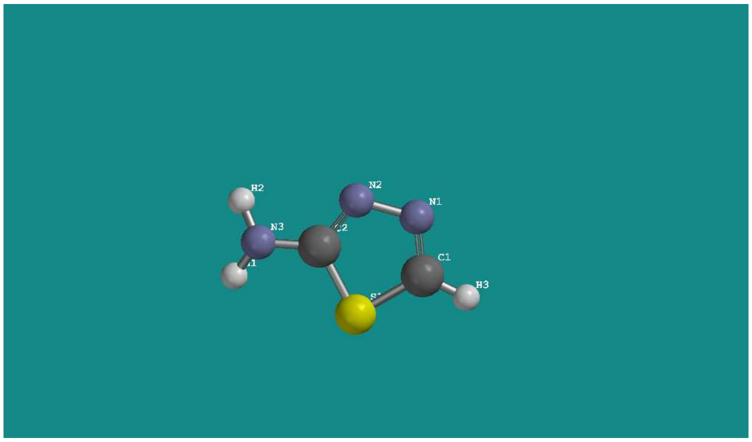


Fig. 1(a): Optimized structure of AT calculated with the B3LYP/6-31G(d) model chemistry

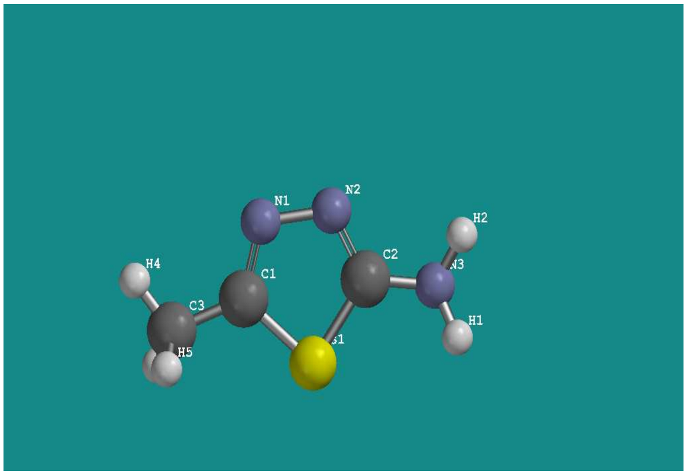


Fig. 1(b): Optimized structure of AMT calculated with the B3LYP/6-31G(d) model chemistry

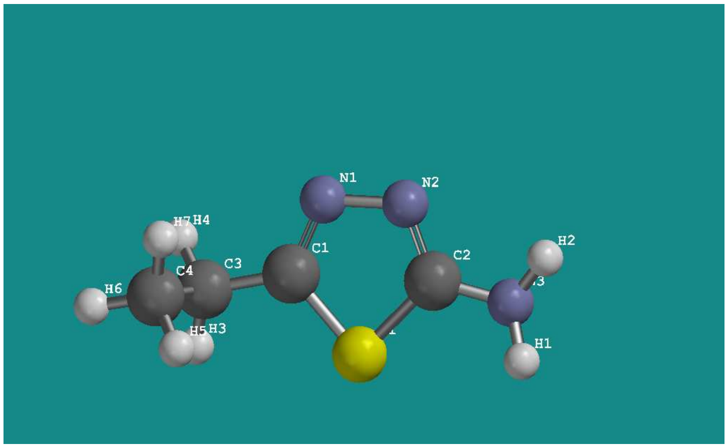


Fig. 1(c): Optimized structure of AET calculated with the B3LYP/6-31G(d) model chemistry

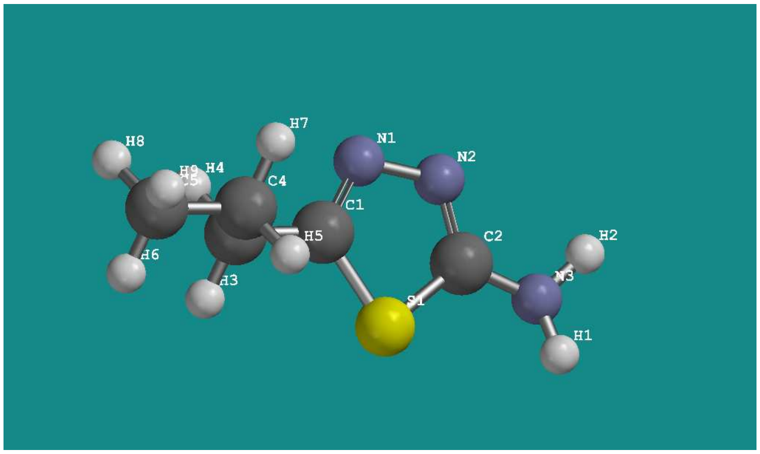


Fig. 1(d): Optimized structure of APT calculated with the B3LYP/6-31G(d) model chemistry

A Higher 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. Increasing values of E_{HOMO} facilitate adsorption and therefore enhance the inhibition efficiency, by influencing the transport process through the adsorbed layer. On the other hand, the energy of the lowest unoccupied molecular orbital indicates the ability of the molecule to accept electrons. The lower the value of E_{LUMO}, the more probable it is that the molecule would accept electrons. Concerning the value of the energy of the gap $\Delta E = E_{LUMO} - E_{HOMO}$, larger values of the energy difference will provide low reactivity to a chemical species. Lower values of the energy difference will render good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low [18].

Table 2 shows the calculated quantum-chemical parameters which are related to the molecular electronic structure of the molecules under consideration such as: E_{HOMO}, E_{LUMO} and $\Delta E = E_{LUMO} - E_{HOMO}$. The values of E_{HOMO} show the relation APT > AET > AMT > AT for this property. The calculations show that APT has the highest HOMO level at -6.0031 eV. This is in a good agreement with the experimental observations suggesting that the APT has the highest inhibition efficiency among the investigated inhibitors. According to the experimental results obtained from the work of Rafiquee and co-workers [14], when H atom from AT was substituted by a propyl group (C_3H_7-) (i.e. transforming AT to APT), the corrosion inhibition efficiency increased significantly. Quantum chemical calculation reveals that the substitution of H by C_3H_7- results in a great increase of HOMO energy level (and a decrease of energy of the gap $E_{LUMO} - E_{HOMO}$) obviously. The increase of inhibition efficiency due to H/C_3H_7 substitution should arise from the increase of HOMO level, implying the ability of APT to offer free electrons to the metal surface. The result is not surprising as C_3H_7 which is an alkyl group is an electron donor. AT has the lowest E_{HOMO} value, also the lowest inhibition efficiency. Thus, the order of inhibition efficiency APT > AET > AMT > AT is due the nature of the alkyl group attached to the 2-amino-1, 3, 4-thiadizole ring.

Table 2. HOMO and LUMO energies, HOMO-LUMO gap and for the studied compounds obtained with the DFT at the B3LYP/6-31G(d) level

Molecules	**E_{HOMO}(eV)**	**E_{LUMO}(eV)**	**ΔE (eV)**	**% IE[a]**
AT	-6..331	-0.510	5.820	79.12
AMT	-6.069	-0.338	5.731	82.62
AET	-6.030	-0.338	5.692	86.96
APT	-6.003	-0.309	5.693	90.06

[a] Values of inhibition efficiency in 20% acetic acid at 100 ppm from Ref. [14]

In addition, the values of the energy of the gap ($E_{LUMO} - E_{HOMO}$), show the relation AT > AMT > AET ≈ APT for this property. Value of ΔE for AET and APT are lower and close as compared to AT which has the highest energy gap value (Table 2). Although molecular structures are quite different (i.e. substitution of C_2H_5 with C_3H_7), experimental results show that AET and APT have somehow close values of inhibition efficiency. Thus, AET and APT provide an excellent evidence to confirm the relationship between macroscopic properties and their microscopic structures.

In order to calculate the fraction of electrons transferred, a theoretical value for the electronegativity of bulk iron was used χ_{Fe} =7eV [29], and a global hardness of η_{Fe} = 0, by assuming that for a metallic bulk $I = A$ [15] because they are softer than the neutral metallic atoms. From Table 3, it is possible to observe that the values of global hardness for APT and AET are almost similar and lower than AMT and AT. However, the fraction of electrons transferred is the largest for APT and, in turn, is AET, AMT and AT. According to Lukovits [19], if $\Delta N < 3.6$, the inhibition efficiency increased with increasing electron donating ability at the metal surface. In this study, APT was the highest donor of electrons, and the mild steel surface was the acceptor. This result supports the assertion that the adsorption of inhibitor on the metal surface can occur on the bases of donor- acceptor interactions between the π electrons of the heterocyclic compound and the vacant d- orbitals of the metal surface [17]. According to Issa et al. [28], adsorption of inhibitor onto a metallic surface occurs at the part of the molecule which has the highest softness. The calculations show that APT has the highest softness similar to the value obtained for AET whereas AMT and AT have lower values. This result agrees well with the experimental results obtained.

Table 3. Quantum-chemical descriptors for the studied compounds obtained with the DFT at the B3LYP/6-31G (d) level

Molecules	I	A	χ	η	ΔN	S
AT	6.331	0.510	3.420	2.910	0.614	0.343
AMT	6.069	0.338	3.204	2.865	0.662	0.348
AET	6.030	0.338	3.184	2.846	0.670	0.351
APT	6.003	0.309	3.156	2.844	0.675	0.352

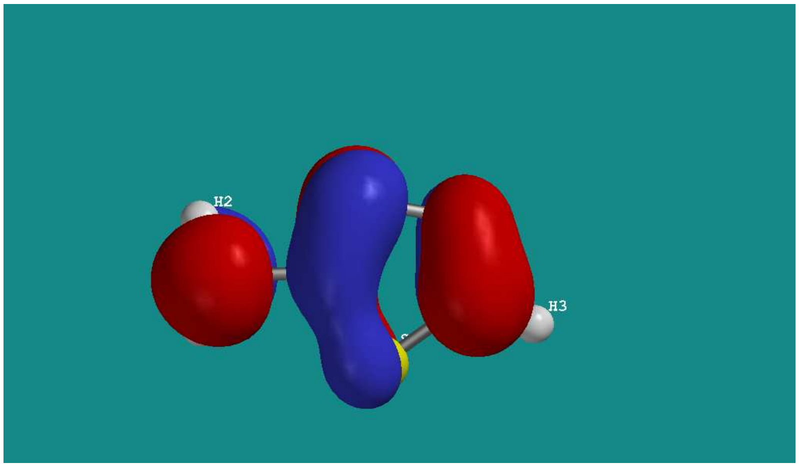
The local reactivity is analyzed by means of the condensed Fukui function and condensed local softness. These indices allow us to distinguish each part of the molecule on the basis of its distinct chemical behaviour due to the different substituent functional groups. Thus, the site for nucleophilic attack will be the place where the value of f_k^+ is a maximum. In turn, the site for electrophilic attack is controlled by the value of f_k^- . The condensed local softness indices S_k^+ and S_k^- are related to the condensed Fukui functions through Eq.12. In Table 4, in order to obtain an overall conception with regard to the values of the Fukui functions and local softness for each thiadizole ring (the 2 Nitrogen atoms and 1 Sulphur atom including the Nitrogen of the NH_2 attached to the ring), their average values are adopted for comparison. It can be observed that the order of the average values of Fukui functions f_k^+ for the 2 Nitrogen atoms and 1 Sulphur atom of the thiadiazole ring including the Nitrogen of the NH_2 attached to the ring for the investigated compounds is APT > AET > AMT > AT. In the same way, the order of the averaged local softness indices S_k^+ values is APT > AET > AMT > AT. Thus, the thiadiazole ring of APT will be more reactive than the thiadiazole ring of the other molecules in a nucleophilic reaction. These results are not surprising. This is because of the presence of propyl group (C_3H_7-) attached to thiadiazole ring of APT which has the ability to donate more electrons to the ring when compared to ethyl group (C_2H_5-), methyl group (CH_3-) and H attached to the thiadiazole rings of AET, AMT and AT respectively.

Table 4. Fukui function and local softness average values for 4 atoms (2 nitrogen and 1 sulphur atom including the nitrogen of the NH_2 attached to the ring) of the thiadiazole and its derivatives obtained with the DFT at the B3LYP/6-31G (d) level

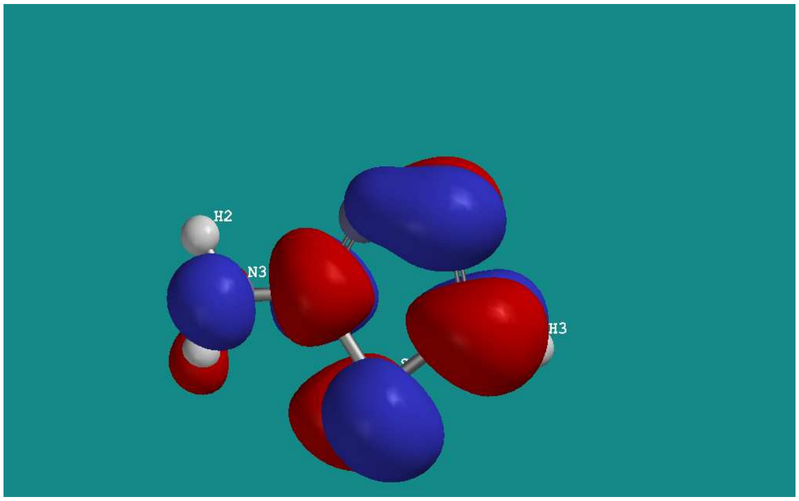
Average	*AT*	*AMT*	AET	APT
f_k^+	-0.1276	-0.1203	-0.1195	-0.1193
f_k^-	-0.1555	-0.1453	-0.1419	-0.1389
S_k^+	-0.0438	-0.0420	-0.0419	-0.0417
S_k^-	-0.0533	-0.0506	-0.0492	-0.0488

Fig. 2 shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the compounds under investigations. From these figures it can be concluded that the compounds adsorbed on the mild steel surface by using the thiadiazole moiety which contains the heteoatoms Nitrogen and Sulphur

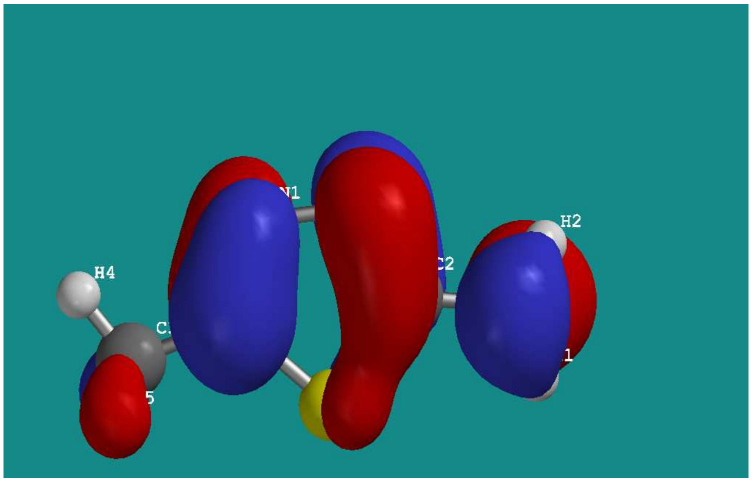
HOMO of AT



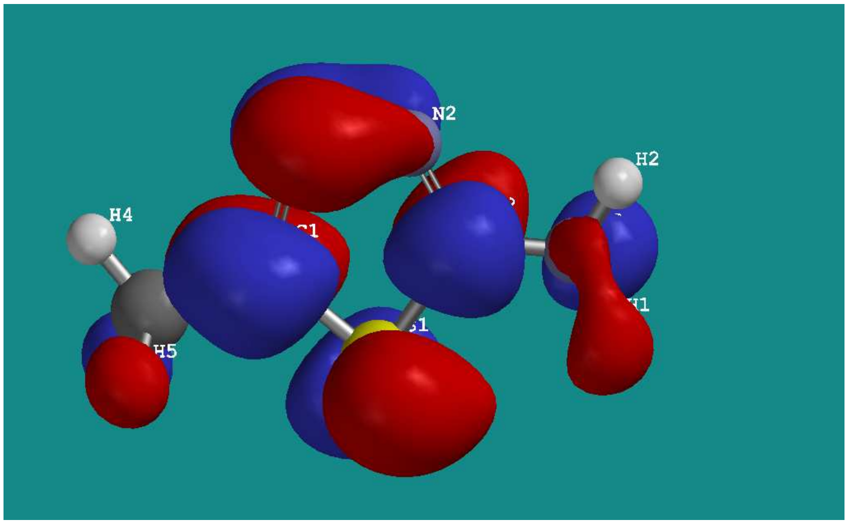
LUMO of AT



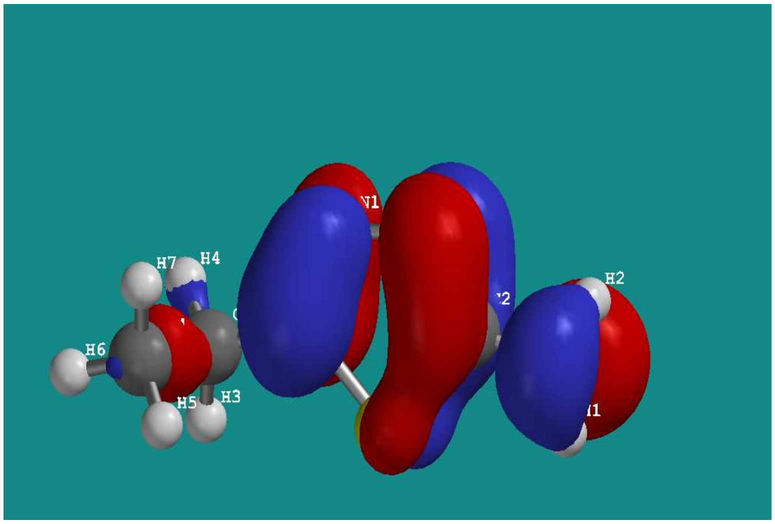
HOMO of AMT



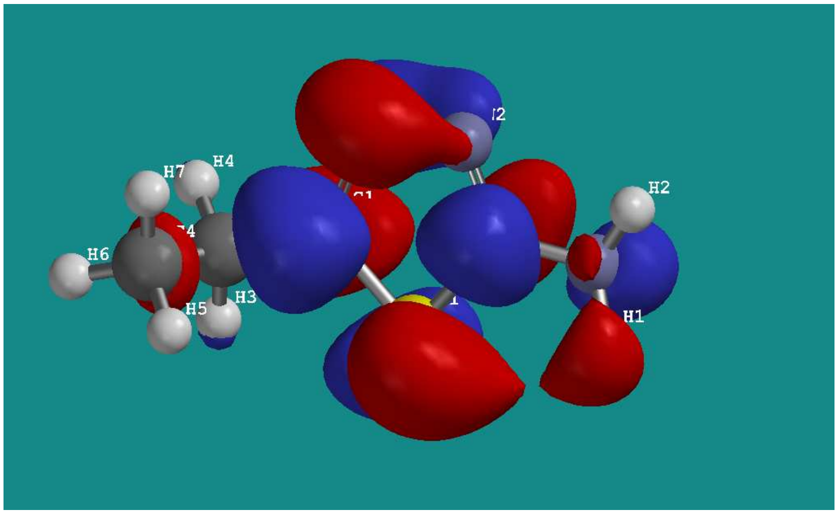
LUMO of AMT



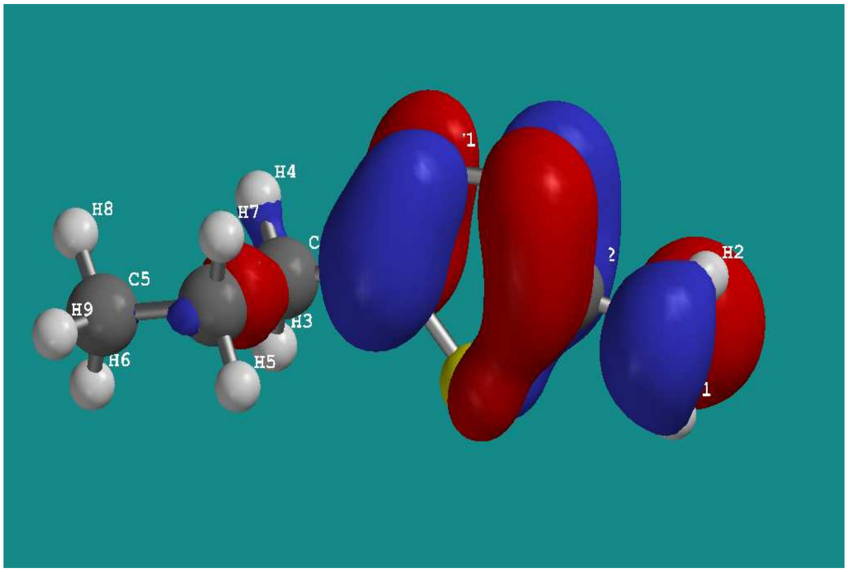
HOMO of AET



LUMO of AET



HOMO of APT



LUMO of APT

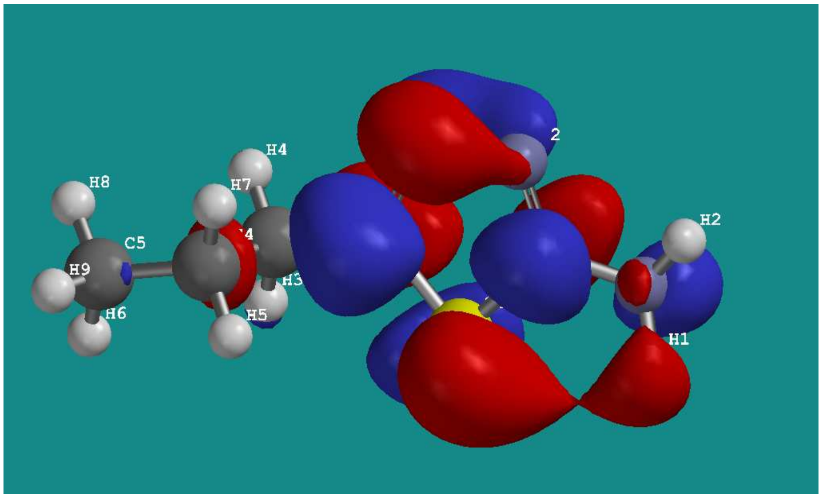


Fig. 2. Frontier molecular orbital diagrams of AT, AMT, AET and APT by the B3LYP/6-31G(d) model chemistry

In Table 5, the results derived from the application of Mulliken population analysis are reported. The objective of this is to obtain a wider knowledge of the reactive site responsible for the adsorption and to show whether the atom responsible for the adsorption is nitrogen or sulphur of the thiadiazole ring. For all the studied compounds, it is possible to observe that all the nitrogen atoms of the thiadiazole ring present and the nitrogen atom of the NH_2 group attached to the ring have considerable excess of negative charge (Table 5). In all the molecules studied, the sulphur atoms present positive charges, being the greatest value of 0.207 for the sulphur atom of AT, thus probably experiencing the greater repulsive effect towards metallic atom when the molecule acts as a nucleophile and the least value of the positive charge being 0.185 for the sulphur atom of APT. This makes the APT to probably experience the greatest attractive effect towards metallic atoms when the molecule acts as a nucleophile thus making it to probably exhibit the highest inhibitive effect. Thus the likely reactive centres of adsorption of the thiadiazole and its derivatives are the nitrogen atoms. Similar observation has been reported by Rodriguez-Valdez et al [8] on their study of computational simulation of the molecular structure and properties and properties of heterocyclic organic compounds (1,3,4-thiadiazole and its derivatives) with possible corrosion inhibition properties.

Table 5. Mulliken population analysis obtained for the heteroatoms with the DFT at the B3LYP/6-31G (d) level.

Molecules	***1N***	***2N***	**3N**	**1S**
AT	-0.207	-0.316	-0.746	0.207
AMT	-0.265	-0.318	-0.756	0.186
AET	-0.273	-0.317	-0.757	0.186
APT	-0.274	-0.318	-0.758	0.185

Materials and methods

The use of density functional theory (DFT) for the evaluation of corrosion inhibitors has been shown to have some merits over other quantum chemical methods [20]. B3LYP, a version of the DFT method that uses Becke'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) [21], has been recognized especially for systems containing transition metal atoms [22]. It has much less convergence problems than those commonly found for pure DFT methods. Thus, B3LYP was used in this work to carry out quantum calculations. Then, full geometry optimizations of all inhibitors were carried out at the B3LYP/6-31G(d) level using the Spartan'06 V112 program package. Many quantum chemical parameters that indicate structural characteristics of these organic inhibitors such as $E_{HOMO,}$ E_{LUMO}, energy gap, charge distribution and so on, were obtained.

The recent impact of density functional theory (DFT) in the development of quantum chemistry is considerable, and can be linked to achievement of so-called "chemical accuracy" at the end of the 1980s when gradient-corrected and hybrid functional methods were introduced [23]. Based on the well-known Hohenberg-Kohn theorems [24], DFT focuses on the electron density, $\rho(r)$, itself as the carrier of all information in the molecular (or atomic) ground state.

DFT also provides a convenient theoretical framework and has extra-ordinary potential for calculating global and local indices that describe the inherent reactivity of chemical species quantitatively. The electronegativity χ has been identified as the negative of the chemical potential μ, which is the Lagrange multiplier in the differential equation in DFT [25]:

$$\chi = \left(\frac{\partial E}{\partial N}\right)_{v(r)} = -\mu \qquad (1)$$

Where E is the total electronic energy, N is the number of electrons, and v(r) is the external electrostatic potential that the electrons feel due to the nuclei.

The global hardness is defined as [26]:

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} = \left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \qquad (2)$$

While the global softness is the inverse of the hardness [27]:

$$S = \frac{1}{\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} \qquad (3)$$

For χ and η, their operational and approximate definations are [28]:

$$\chi = \frac{I + A}{2} \qquad (4)$$

$$\eta = \frac{I - A}{2} \qquad (5)$$

χ, η and S are global properties characterizing the molecules as a whole.

When two systems, Fe and inhibitor, are brought together, electrons will flow from lower χ (inhibitor) to higher χ (Fe), until the chemical potentials become equal. As a first approximation, the fractions of electrons transferred [29], ΔN, will be given by:

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

where Fe is the Lewis acid according to HSAB theory [30]. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance [30, 31].

According to Koopman's theorem [32], the energies of the HOMO and the LUMO orbitals of the inhibitor molecule are related to the ionization potential, I, and the electron affinity, A, respectively, by the following relation [33]:

$$I = -E_{HOMO} \qquad (7)$$

$$A = -E_{LUMO} \qquad (8)$$

The Fukui function $f(r)$, as proposed by Parr and Yang [34], is defined as the partial derivative of the electron density $\rho(r)$ with respect to the total number of electrons N of the system at the constant external potential $v(r)$:

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} = \left(\frac{\partial \mu}{\partial v(r)}\right)_{N} \tag{9}$$

The condensed Fukui function calculations are based on the finite difference approximation and partitioning of the electron density $\rho(r)$ between atoms in a molecular system. Yang and Mortier [35] proposed f_k calculations from atomic charges using the following equations:

For reaction with the electrophiles:

$$f_k^- = q_N - q_{N-1} \tag{10}$$

For reaction with the nucleophiles:

$$f_k^+ = q_{N+1} - q_N \tag{11}$$

where q_N, q_{N+1} and q_{N-1} are the atomic charges of the systems with N, $N+1$ and $N-1$ electrons, respectively. The condensed Fukui function is local reactivity descriptor and can be used only for comparing reactive atomic centers within the same molecule.

Condensed softness indices allowing the comparison of reactivity between similar atoms of different molecules can be calculated easily starting from the relation between the Fukui function $f(r)$ and the local softness $S(r)$ [28]:

$$S(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} = f(r)S \tag{12}$$

From this relation, one can infer that local softness and Fukui function are closely related, and they should play an important role in the field of chemical reactivity. Indeed, local softness combines the site reactivity index, $f(r)$, with the global softness measure, S. It can be considered as a distribution of global softness weighted by the Fukui function over the molecule, so that it may be considered as a softness density.

All calculations including geometry optimization for all structures were performed with B3LYP exchange-correlation corrected functional [21, 36] with the 6-31G (d) basis set using the spartan’06 V116 package [37]. As shown by De Proft et al. [38], the B3LYP function appears to be reliable for calculation $f(r)$ and f_k indices.

Conclusion

The following conclusions can be drawn from this study:

1. The inhibition efficiency of thiadiazole and its derivatives obtained experimentally increase with the increased in E_{HOMO}, and with decreased in E_{LUMO} and energy of the gap (ΔE). APT has the highest inhibition efficiency because it had the highest HOMO energy and ΔN values, and it was most capable of offering electrons.

2. The order of the average values of Fukui functions f_k^+ for the 2 nitrogen atoms and 1 sulphur atom of the thiadiazole ring including the nitrogen of the NH_2 attached to the ring for the investigated compounds is APT > AET > AMT > AT. In the same way, the order of the averaged local softness indices S_k^+ values is APT > AET > AMT > AT. Thus, the thiadiazole ring of APT is more reactive than the thiadiazole ring of the other molecules in a nucleophilic reaction confirming its highest inhibiting capacity when adsorbed on the mild steel surface.

3. Mulliken population analysis shows that the mechanism of adsorption between the thiadiazole and its derivatives and the mild steel surface occurs mainly through the nitrogen atoms and not the sulphur atom.

References

[1] S.A. Umoren, I.B.Obot, N.O. Obi-Egbedi, *Mater. Sci*,. **2009**, 44(1) 274.
[2] I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, *Corros. Sci.* **2009** ,51 276.
[3] I.B. Obot, N.O. Obi-Egbedi, *Surface Review and Letters*., **2008**, 15(6) 903.
[4] I.B. Obot, N.O. Obi-Egbedi, *Colloids and surfaces A: Physicochem.Eng. Aspects*, **2008**, 330, 207.
[5] H. Ju, Z.P. Kai, Y. Li, *Corros. Sci*., **2008**, 50, 865.
[6] F.B. Growcock, *Corrosion*, **1989**, 45, 1003.
[7] A. Domenicano, I. Hargittai, Accurate Molecular Structures, Their Determination and Importance, Oxford University Press, New York, **1992**.
[8] L.M. Rodriguez-Valdez, A. Martinez-Villafane, D. Glossman-Mitnik, *J. Mol. Struct.* **2005**, 713, 65.
[9] Y. Feng, S. Chen, H. Zhang, P. Li, L. Wu, W. Guo, *Appl. Surf. Sci.* **2006**, 253, 2812.
[10] F. Bentiss, M. Lebrini, M. Lagrenee, M. Traisnel, A. Elfarouk, H. Vezin, *Electrochim Acta*, **2007**,52, 6865.
[11] H. Ma, T. Song, H. Sun, X. Li, *Thin Solid Films*, **2008**, 516, 1020.
[12] M. Lebrini, M. Lagrenee, M. Traisnel, I. Gengembre, H. Vezin, F. Bentiss, *Appl. Surf. Sci.*, **2007**, 253, 9267.
[13] S.G. Zhang, W. Lei, M.Z. Xia, F.Y. Wang, *J. Mol. Struct. (THEOCHEM),* **2005**, 732, 173.
[14] M.Z.A. Rafiquee, S. Khan, N. Saxena, M.A. Quraishi, *Port. Electrochimica Acta,* **2007**, 25, 419.
[15] H. Wang, X. Wang, H. Wang, L. Wang, A Liu, *J. Mol. Model*, **2007**, 13, 147.
[16] K. Fukui, T. Yonezawa, H. Shingu, *J. Chem. Phys*., **1952**, 20, 722.

[17] I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, *Int. J. Electrochem. Sci*.,**2009,** 4, 863.
[18] I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, Corros. Sci., **2009,** doi:10.1016/j.corsci.2009.05.017.
[19] I. Lukovits, E. Lalman, F. Zucchi, *Corrosion*, **2001**, 57, 3.
[20] N. Lopez, F. Illas, *J. Phys, Chem.,***1998**, *B*102, 1430.
[21] C. Lee, W. Yang, R.G. Parr, *Phys. Rev.*, **1988**, *B*37, 785.
[22] M. Lashkari, M.R. Arshadi, *Chem. Phys*., **2004**, 299, 131.
[23] T. Ziegler, *Chem. Rev*., **1991**, 91, 651.
[24] P. Hohenberg, W. Kohn, *Phys. Rev*., **1964**, A136, 864.
[25] R.G. Parr, R.A. Donnelly, M. Levy, W.E. Palke, *J. Chem. Phys*.,**1978**, 68, 3801.
[26] R.G. Parr, R.G. Pearson, *J. Am. Chem. Soc.*,**1983**, 105, 7512.
[27] W. Yang, R.G. Parr, *Proc. Natl. Acad. Sci*.,**1985**, 82, 6723.
[28] H. Wang, X. Wang, H. Wang, L. Wang, A. Liu, *J. Mol. Model*, **2007**, 13, 147.
[29] R.G. Pearson, *Inorg. Chem*., **1988**, 27, 734.
[30] R.G. Pearson, *J. Am. Chem. Soc.*,**1963**, 85, 3533.
[31] H. Chermette, *J. Computational Chem*., **1999**, 20, 129.
[32] V.S. Sastri, J.R. Perumareddi, *Corrosion*,**1996**, 53, 671.
[33] R. M. Issa, M. K. Awad, F.M. Atlam, *Appl. Surf. Sci.*, **2008**, 255, 2433.
[34] R.G. Parr, W. Yang, *J. Am. Chem. Soc.*,**1984**, 106, 4049.
[35] W. Yang, W.J. Mortier, *J. Am. Chem. Soc.*,**1986**, 108, 5708.
[36] A.D. Becke, *J. Chem. Phys*., **1993**, 98, 5648.
[37] Spartan,06 Wavefunction, Inc. Irvine, CA: Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipehenko, S.V. Levehenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T.Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C.P. Hsu, G. Kedziora, R.Z. Khalliulin, P.Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I.Lotan, N. Nair, B.Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W.Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A. Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. krylov, P.M.W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 8 (**2006**) 3172.
[38] F. de Proft, J.M.L. Martin, P. Geerlings, *Chem. Phys. Lett*., **1996**, 256, 400.