Structural and solvent dependence of the electronic properties and corrosion inhibitive potentials of 1,3,4-thiadiazole and its substituted derivatives- a theoretical investigation.

ABSTRACT

The frontier molecular orbitals (FMOs) are very important for describing chemical reactivity and understanding the static molecular reactivity. The HOMO and LUMO energies of 1,3,4-thiadiazole and its substituted derivatives were calculated using the hybrid B3LYP method with a large polar 6-31G* basis set in vacuum, acetone, ethanol and tetrahydrofuran (THF). It was revealed that substitution at position -2 with -NO_2, -CH_3, -NH_2, -CN and -CH=C(CN)COOH results in enhanced reactivities due to reduction of the energy band gap, E_g. It also altered some important molecular properties like η, S, ΔN, μ, α and β. Substituted -NO_2, -CN and -CH=C(CN)COOH may possess better inhibitive potentials and better reactivities than other derivatives on the basis of studied parameters. It was observed that solvent media affect molecular properties.

Keywords: 1,3,4-thiadiazole, substituent effects, solvent effects, structural properties, electronic properties, global reactivity descriptors

1. Introduction

To understand chemical phenomena and reactions, it is important to study the conformation a particular molecule prefers [1,2]. The conformation of molecules is therefore, important. Changes in structure of molecules are expected when substituents are inserted or when solvents are added; and they lead to variations in the physical and electronic properties like the energy band gap, E_g, electron affinity and intra-molecular charge transfer, brought about by either a new environment (substituent) or (solvent). It has been observed that the dipole moments (μ), polarizabilities (α) and hyperpolarizabilities (β) increase with an increase in the dielectric constants, ε, of solvents [2,3]. The frontier energies could be stabilized (reduced) by solvents, especially polar solvents [4].

Heterocycles like 1,3,4-thiadiazole and their different derivatives have been studied for various applications in biological [5,6], chemical [3,7], optical [8-10] and pharmaceutical fields [11,12]. Thiadiazole is a five-membered heterocycle containing two nitrogen atoms and a sulphur atom, it has different isomers including 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole and 1,3,4-thiadiazole. However, 1,3,4-thiadiazole isomer has been investigated more than other isomers. The inductive effect of the sulphur atom makes it a weak base, it is also electron deficient due to the electron-withdrawing nature of the atoms and therefore inert to electrophiles but can undergo nucleophilic reactions readily. 1,3,4-thiadiazole and its derivatives could be studied for various applications, computational studies can help in predicting probable applications for example as corrosion inhibitor (owing to the presence of some heteroatoms like sulphur, oxygen, nitrogen and phosphorus) [13] and compare them with that of the substituted analogues. This is because O, N, S and P are active centers for adsorption process on metal surface. Studies have shown that organic inhibitors usually displace water molecules from the surface of the metal, forming a protective barrier [14]. The strength of the chemisorption bond depends upon the electron density on the donor group and also the α values of the group, this is because chemisorption involves the formation of a chelate on the metal surface and it is usually achieved by the transfer of electrons from the organic compounds to metals- a coordinate covalent bond [24]. When an H atom attached to the C in the ring is replaced by a substituent group (–NH_2, –NO_2, – CHO, or – COOH) it improves inhibition, owing to the addition of more heteroatoms with nonbonded electrons [15]. This facilitates electron transfer from the inhibitor to the metal surface. Structural and electronic properties are affected by molecular size, substituent groups [16] and this can in turn affect the global reactivity descriptors which are important parameters to investigate when studying materials for their corrosion inhibitive potentials [17,18].

Recently, a lot of experimental and theoretical studies have been done on the structural and electronic properties of organic materials for certain applications like nonlinear optical (NLO) applications [19,20], corrosion inhibitive applications [21-23] and so on. If the properties of a simple aromatic system are well investigated, there will be a better understanding of its structure-property relationship, which in turn provides a guideline for the design of novel NLO material or an inhibitor, an important responsibility of material scientists. Quantum chemical calculations have proven to be successful in studying molecular, electronic properties and the global reactivity descriptors like the chemical hardness, η, chemical softness, S, global electrophilicity index of molecules with several researches based on the use of density functional theory (DFT) approach [24-28,41]. As such, quantum chemical studies were employed to investigate the effect of substituents and solvents on the structural, optical, electronic properties of 1,3,4-thiadiazole and some its substituted derivatives. This work therefore draws motivation from the fact that few reports about the structural and solvent dependence on ground state electronic properties of 1,3,4-thiadiazole and its derivatives exist. 1,3,4-thiadiazole (A), 2-cyano-1,3,4-thiadiazole (B), 2-methyl-1,3,4-thiadiazole (C), 2-nitro-1,3,4-thiadiazole (D), 2-amino-1,3,4-thiadiazole (E), 1,3,4-thiadiazole-2-cyanoacrylic acid (F) and the dimeric form of 1,3,4-thiadiazole (G) were considered. The substituents vary in size and donor capacity so it is expected that the molecular and electronic properties will vary, it is also expected that there might also be variations in their properties in different solvent media. Ab-initio Becke's three hybrid parameter DFT-Hatree Fock (20% of Hartree Fock approximation) and Lee-Yang-Parr correlation functional (B3LYP) procedures with high polar 6-31G* basis set. The B3LYP/6-31G* has proven to be an efficient method of describing the ground state electronic properties of organic molecules as it corroborates experimental findings [22,24-26]. Improving on the molecular properties by insertion of substituents increase molecular size and improves electronic properties in that the molecule because the substituted molecules have more space to form instantaneous dipoles, this improves the dipole moments and polarizabilities of such molecules. This work therefore, presents a theoretical study on the molecular and electronic properties like the frontier orbital energies (energies of the highest occupied molecular orbital, E_{HOMO} and the lowest unoccupied molecular orbital, E_{LUMO}), energy band gaps, E_g values (E_{LUMO} – E_{HOMO}), the global reactivity descriptors which are responsible for inhibition efficiency like the chemical hardness, η, softness, S, electronegativity, χ.

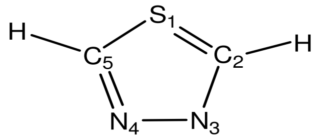

Fig. 1.1: Structural representation of 1,3,4-thiadiazole.

2. Computational details

Quantum mechanical investigations were carried out on 1,3,4-thiadiazole and its substituted analogues with Spartan 14 software package [29] on intel®Core (TM) i5-3317U CPU @1.70GHz 1.70Hz computer with the *ab* initio restricted pure and hybrid Density Functional Theory (DFT) and the time dependent Density Functional Theory (TDDFT) [30,31], B3LYP exchange-correlation method with 6-31G* basis set, all implemented on Spartan 14 software package. The DFT calculations were carried out in vacuum and in different solvent media like acetone (ε= 20.7), ethanol (ε= 24.55) and Tetrahydrofuran, THF (ε= 7.58). Structural optimization was done without any constraints. The experimental data for 2-amino-1,3,4-thiadiazole were used as a reference and investigated to ascertain if any/all theoretical methods employed correlated well with experimental observations. Such method(s) were employed in understanding structure-property relationships of other molecules. The global reactivity descriptors were all obtained from the E_{HOMO}, E_{LUMO} and E_g values. E_g is given by eq. 1.1:

$$E_g = E_{LUMO} - E_{HOMO} ....1.1$$

Hardness is given by half of the energy band gap:

$$\eta = \frac{Eg}{2} \ldots\ldots\ldots 1.2$$

The softness of a molecule is just the inverse of its chemical hardness:

$$S = \frac{1}{\eta} ....1.3$$

According to Koopman's theorem [33], the ionization potential, I = $-E_{HOMO}$ while the electron affinity, A = $-E_{LUMO,}$ so that E_g in eq. 1.1 becomes I – A.

The electronegativity is given by [34]:

$$\chi = \frac{(I + A)}{2} ....1.4$$

η, S and χ are the global properties of the molecules.

The metal, say iron and inhibitor are brought in contact in order for the inhibitor to form a chelate on the metal surface. There is a flow of electrons from the lower χ (inhibitor) to a higher χ (Fe). The fraction of electron transferred, ΔN, therefore, is always used to measure the inhibition efficiency. ΔN is given by [32]:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} ....1.5$$

Where χ_{Fe} and χ_{inh} are the electronegativities of bulk Fe and inhibitor respectively, η_{Fe} and η_{inh} are the chemical hardness of bulk Fe and inhibitor respectively. The theoretical value of χ_{Fe} is given as 7 eV [32], while η_{Fe} is zero (brought about by the assumption that E_{HOMO} and E_{LUMO} are the same for metallic bulk).

In order to extend this work beyond the structural and inhibitive potentials of the systems under investigation, molecular parameters like the polarizabilities and hyperpolarizabilities were calculated. This was done in a bid to explain the trend of the substituted molecules follow from 1,3,4-thiadiazole to know if they have better nonlinear optical responses.

The polarizability of a molecule is related to its dipole moment by:

$$\mu = \alpha\varepsilon \quad \text{..............1.6}$$

where α is the polarizability, μ is the dipole moment and ε is the electric field strength. μ and α usually increase with a decrease in E_g values [16,24,35]. The dipole moment is necessary in order to understand the intermolecular interactions and is found to increase with a decrease in the E_g values of molecular systems [16,35].

The molecular first hyperpolarizability (β) is a third-rank tensor that is described by a 3 x 3 x 3 matrix from a reduced 27 components of the 3D matrix which becomes 10 components owing to Kleimann symmetry [36] and is given by:

$$\beta_{eff} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} \quad \text{...........1.7}$$

The second order susceptibility of a nonlinear opical (NLO) material, χ^2 strongly depends on β_{eff} value. β_{eff} value increases with reduced E_g values and increased α values [37].

3. Results and discussion

The geometry of 1,3,4-thiadiazole is defined using the structure in Fig 1.1. In this structure, different substituent groups are put in place of H (i.e. 2- position). The optimized geometry is shown in fig.1.2.

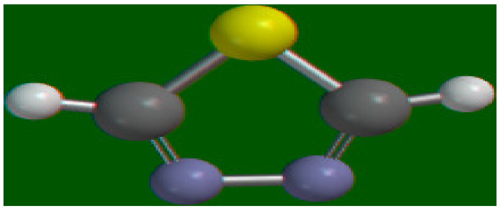

Fig. 1.2: Optimized structure of 1,3,4-thiadiazole

The E_g values in vacuum, acetone, ethanol and THF are presented in table 1. It is observed that E_g values are more stabilized as different substituent groups replace the hydrogen atom at position 2. 1,3,4-thiadiazole has E_g value of 6.22 eV, 2-methyl-1,3,4-thiadiazole has almost the same value of 6.21 eV while 2-amino-1,3,4-thiadiazole has a lower value of 5.86 eV, with the other derivatives reducing E_g values significantly with 2-cyano-1,3,4-thiadiazole, dimer, 2-nitro-1,3,4-thiadiazole and 1,3,4-thiadiazole-2-acrylic acid of 5.50, 4.89, 4.83 and 4.43 eV respectively in vacuum, indicating that there is transfer of electrons from the donor to the acceptor groups. Similar trend was observed in the solvent media with the values decreasing generally, and further reducing with substituents and with a decrease in the dielectric constant of the solvents. This improves the reactivity and electronic properties of the molecules. The molecules are arranged in decreasing order of E_g values as R = H > $-CH_3$ > $-NH_2$ > -CN > dimer > $-NO_2$ > -CH=C(CN)COOH, this may be attributed to the molecular sizes of the molecules. The chemical hardness is expected to follow the same trend as it is derived directly from E_g, eq. 1.2 while the softness follows a reverse trend as it is the inverse of η, eq. 1.3. -CH=C(CN)COOH and $-NO_2$ are the with the least E_g values, softest, largest of the molecules and are therefore possess the highest charge transfer character and are more reactive than other analogues and are expected to form instantaneous dipoles more readily than others. The $-CH_3$ group did not reduce E_g values significantly, this is owing to the fact that it is a weaker electron donor than $–NH_2$, while others are deactivating groups, with cyano, nitro and cyano acrylic acid groups differ in size and withdrawing ability. All the substituted derivatives have lower E_g values than the unsubstituted 1,3,4-thiadiazole. The electronegativities of $–CH_3$ and $-NH_2$ are lower than that of unsubstituted 1,3,4-thiadiazole, they are higher in other substituted derivatives, this may be due to the electron donating abilities of $–CH_3$ and $-NH_2$ and electron withdrawing abilities of others. These values reduced in solvents and with reduced dielectric constants. The values of ΔN describes the donating ability of a material and it is reported that this value increase with increased inhibition [38]. However, this study shows that there is no correlation between ΔN and inhibition efficiency, an observation also made by Kara and co-workers [24].

The values of the dipole moments as seen on table 2 shows that unsubstituted 1,3,4-thiadiazole has a value of 3.08 D in vacuum while $–CH_3$ derivative increased the value a bit to 3.10 D and $–NH_2$ to 3.56 D, this may be because only a slight decrease in the E_g was observed for $–CH_3$ unlike $–NH_2$. Other substituted derivatives increased μ values significantly. All values increased with the addition of solvent; also with an increase in dielectric constant. Although there are some inconsistences on the use of μ as a predictor for the direction of a corrosion inhibition reaction, it could be argues that molecules with high μ values are more reactive and soft; they can easily give up electrons that will bind to metal surfaces. The polarizabilities of the molecules increase with an increase in molecular size but there is no much difference in their values in different solvents. On the overall, the $–CH=(CN)COOH$ is the most reactive of the molecules and probably with the best optical response , followed by $–NO_2$, dimer, -CN, $-NH_2$ and $–CH_3$ considering their optical/energy band gaps, size, polararizabilities and dipole moments. Their electro-optical responses however, will be confirmed by the values of molecular first hyperpolarizbilities and UV absorptions.

β values increased but not too significantly for $–CH_3$ unlike other substituted derivatives with -CH=CNCOOH and dimer having the highest values of 1.21×10^{-30} esu and 0.57×10^{-30} esu respectively. All units were all in Debye $Å^2$, and converted to esu units (1 Debye $Å^2 = 1 \times 10^{-30}$ esu) [40]. β values also increased in solvent media and also with an increase with dielectric constants of the solvents. Only -CH=CNCOOH can be considered a potential candidate for NLO applications because it is the only molecule having better β value than urea (0.65×10^{-30} esu) [9].

The UV absorption was carried out using the TD-DFT. All substituted derivatives bathochromically shifted the absorption wavelength, with $–NH_2$ comparing well with experimental result available [39]. -CH=CNCOOH and dimer increasing the λ_{max} the most from 186 nm to 259 nm and 262 nm respectively. The λ_{max} tends to increase with decrease E_g and it also decreased in the solvents used.

Table 1: The electronic properties of 1,3,4-thiadiazole and substituted analogues with B3LYP/6-31G* in vacuum, acetone (ε = 20.7), Ethanol (ε = 24.55) and THF (ε = 7.58)

Molecules	E_{LUMO}(eV)	E_{HOMO}(eV)	E_g(eV)	η(eV)	$S(eV^{-1})$	χ(eV)	ΔN
			VACUUM				
R = H	-1.27	-7.49	6.22	3.11	0.32	4.38	0.42
2-NO$_2$	-3.42	-8.25	4.83	2.42	0.41	5.84	0.24
2-CH$_3$	-1.07	-7.28	6.21	3.11	0.32	4.18	0.45
2-NH$_2$	-0.63	-6.49	5.86	2.93	0.34	3.56	0.59
2-CN	-2.67	-8.17	5.50	2.75	0.36	5.42	0.29
2-CH=C(CN)COOH	-3.07	-7.50	4.43	2.23	0.45	5.29	0.38
Dimer	-2.54	-7.43	4.89	2.45	0.41	4.99	0.41
			ACETONE				
R = H	-1.17	-7.40	6.23	3.12	0.32	4.29	0.43
2-NO$_2$	-3.43	-7.91	4.48	2.24	0.45	5.67	0.29
2-CH$_3$	-1.09	-7.30	6.21	3.11	0.32	4.19	0.45
2-NH$_2$	-0.57	-6.09	5.52	2.76	0.36	3.33	0.66
2-CN	-2.56	-8.04	5.48	2.74	0.36	5.30	0.31
2-CH=C(CN)COOH	-2.88	-7.27	4.39	2.19	0.46	5.08	0.44
Dimer	-2.57	-7.27	4.70	2.35	0.43	4.92	0.44
			ETHANOL				
R = H	-1.19	-7.48	6.29	3.15	0.32	4.34	0.42
2-NO$_2$	-3.51	-8.08	4.55	2.28	0.44	5.79	0.27
2-CH$_3$	-1.12	-7.40	6.28	3.19	0.31	4.26	0.43
2-NH$_2$	-0.64	-6.23	5.59	2.80	0.36	3.44	0.64
2-CN	-2.53	-8.09	5.56	2.78	0.36	5.31	0.30
2-CH=C(CN)COOH	-2.89	-7.34	4.45	2.23	0.45	5.12	0.42
Dimer	-2.57	-7.38	4.81	2.41	0.41	4.98	0.42
			THF				
R = H	-1.18	-7.36	6.18	3.09	0.32	4.27	0.44
2-NO$_2$	-3.42	-7.78	4.36	2.18	0.46	5.60	0.32
2-CH$_3$	-1.08	-7.18	6.10	3.05	0.33	4.13	0.47
2-NH$_2$	-0.56	-5.89	5.33	2.67	0.37	3.23	0.71
2-CN	-2.57	-7.93	5.36	2.68	0.37	5.25	0.33
2-CH=C(CN)COOH	-2.90	-7.11	4.21	2.11	0.47	5.01	0.47

Dimer	-2.56	-7.16	4.60	2.30	0.43	4.86	0.47

Table 2: The dipole moments, polarizabilities, λ_{max} and molecular first hyperpolarizabilities of 1,3,4-thiadiazole and substituted analogues with B3LYP/6-31G* in vacuum, acetone ($\varepsilon = 20.7$), Ethanol ($\varepsilon = 24.55$) and THF ($\varepsilon = 7.58$)

Molecules	**μ (D)**	**α (Cm^{2}V^{-1})**	**λ_{max}(nm)**	**β(x10^{-30} esu)**
		VACUUM		
R = H	3.08	45.83	185.51	0.14
2-NO_2	4.45	47.92	242.91	0.22
2-CH_3	3.10	46.33	193.36	0.14
2-NH_2	3.56	46.96	241.35 (241)	0.27
2-CN	4.53	47.60	222.98	0.50
2-CH=CNCOOH	5.50	52.74	259.82	1.21
Dimer	5.68	50.83	262.41	0.57
		ACETONE		
R = H	3.91	45.77	182.96	0.18
2-NO_2	5.7	47.95	241.55	0.29
2-CH_3	4.03	47.27	191.52	0.19
2-NH_2	4.95	46.80	225.60	0.37
2-CN	6.02	47.59	221.99	0.66
2-CH=CNCOOH	7.57	52.72	256.76	1.58
Dimer	7.34	50.82	260.06	0.72
		ETHANOL		
R = H	3.99	45.77	182.88	0.18
2-NO_2	5.89	47.96	244.94	0.32
2-CH_3	4.08	47.27	191.33	0.19
2-NH_2	4.9	46.79	224.62	0.36
2-CN	6.04	47.59	221.94	0.65
2-CH=CNCOOH	7.95	52.72	257.62	1.63
Dimer	7.48	50.82	259.93	0.73
		THF		
R = H	3.81	45.78	183.22	0.17
2-NO_2	5.53	47.95	240.13	0.29
2-CH_3	3.92	47.28	191.72	0.19
2-NH_2	4.78	46.79	225.20	0.36
2-CN	5.83	47.59	221.94	0.64
2-CH=CNCOOH	7.22	52.72	256.40	1.52
Dimer	7.12	50.82	260.27	0.69

Experimental result in bracket [39].

4. Conclusion

The FMOs are very important for describing chemical reactivity and understanding the static molecular reactivity. The HOMO and LUMO energies of 1,3,4-thiadiazole and its substituted derivatives were calculated using the hybrid B3LYP method with a large polar 6-31G* basis set in vacuum, acetone, ethanol and tetrahydrofuran (THF). It was revealed that substitution at position -2 with -NO_2, -CH_3, -NH_2, -CN and -CH=C(CN)COOH results in enhanced reactivities due to reduction of the energy band gap, E_g. It also altered some important molecular properties like η, S, ΔN, μ, α and β. Substituted -NO_2, -CN and -CH=C(CN)COOH may possess better inhibitive potentials and better reactivities than other derivatives on the basis of studied parameters. It was observed that solvent media affect molecular properties.

References

1. Islam MM, Bhiuyan MDH, Bredow T, Try AC. Theoretical investigation on the non-linear optical properties of substituted anilines and N,N-dimethylanilines. Comput. Theor. Chem. 2011; 165-170.

2. Kosar B, Albayrak C, Ersanli CC, Odabasoglu M, Buyukgungor O. Molecular structure, spectroscopic investigations, second-order nonlinear optical properties and intra-molecular proton transfer of (E)-5-(diethylamino)-2-[(4-propylphenylimino) methyl]phenol: a combined experimental and theoretical study. Spectrochim Acta Part A. 2012; 1-9.

3. Praveen PL, Ojha DP. Substituents and solvent effects on UV-visible absorption spectra of liquid crystalline di-substituted bi-phenylcyclohexane derivatives - a computational approach, Crys. Res. Technol. 47: 2012; 91-100.

4. Anbarasan, PM, Kumar PS, Geetha M, Rovindan R, Manimegalia S, Velmurugan K. Geometries, electronic structures and electronic absorption spectra of silicon dichloride substituted phthalocyanine for dye sensitised solar cells. *Rec. Res. Sci. Tech.* 2010; 8-16

5. Abhishek Kumar Jain, Simant Sharma, Ankur Vaidya, Veerasamy Ravichandran, Ram Kishore Agrawal. 1,3,4-Thiadiazole and its derivatives: A Review on Recent Progress in Biological Activities. *Chem. Biol. Drug. Des.* 2013; 557-576

6. Matysiak J, Malinski Z. 2-(2,4-dihydroxyphenyl)-1,3,4thiadiazole analogues: antifungal activity *In Vitro* against *Candida species.* Russ. J. Bioorg. Chem. 2007; 594-601.

7. Nabati M. 1,3,4-thiadiazole rings as π-spacers in triphenylamine based dyes: A density functional theory study of reactivity, UV/Visible spectra, structural and optical properties. Iranian Journal of Organic Chemistry. 2015; 1669-1678.

8. Alyar H, Kantarci Z, Bahat M, Kasap F. Investigation of torsional barriers and nonlinear optical (NLO) properties of phenyltriazines. *Journal of Molecular Structure.* 2006; 834-836: 516-520.

9. Quifang X, Zhou J, Hu J, Peng D, Liu Y, Liao Y, Zhu C, Zhong C. Synthesis and Photovoltaic properties of branched chain polymeric metal complexes containing Phenothiazine and Thiophene derivatives for dye-sensitized solar cells. J. Chem. Sci. 2015; 127(3): 395-403.

10. Lipinski J, Bartkowiak W. Conformation and solvent dependence of the first and second molecular hyperpolarizabilities of charge-transfer chromophores. Quantum-chemical calculations. Chemical Physics. 1999; 245: 263-276.

11. Kumar D, Kumar NM, Chang K, Shan K. Synthesis and anticancer activity of 5-(3-indolyl)-1,3,4-thiadiazoles. Eur. J. Med. Chem. 2010; 45: 4664-4668.

12. Chou J, Lai S, Pan S, Jow G, Chern J, Guh J. Investigation of anticancer mechanism of thiadiazole-based compound in human non-small cell lung cancer A549 cells. Biochem. Pharma-col. 2003; 66: 115-124.

13. Amitha RBE, Basu BBJ. Green Inhibitors for Corossion Protection of Metals and Alloys: An Overview. International Journal of Corossion. 2012; 1

14. Obot. IB, Obi-Egbedi NO, Umoren SA. Antifungal drugs as corrosion inhibitors for aluminium in 0.1 M HCl. Corossion Science. 2009; 1868-1875.

15. Evans UR. The Corrosion and Oxidation of Metals, Hodder Arnold. 1976.

16. Adejoro IA, Oyeneyin OE, Ogunyemi BT. Computational Investigation on substituent and Solvent Effects on the Electronic, Geometric and Spectroscopic Properties of Azobenzene and Some Substituted Derivatives. International Journal of Computational and Theoretical Chemistry. 2015; 3 (6): 50-57.

17. Obot IB, Obi-Egbedi NO. HSAB descriptors of thiadiazole derivatives calculated by DFT: possible relationship as mild steel corrosion inhibitors. Der. Pharma Chemica. 2009; 1(1): 106-123.

18. Arukalam IO, Madufor IC, Ogbobe O, Oguzie E. Experimental and Theoretical Studies of Hydroxyethyl Cellulose Inhibitor for Acid Corrosion Inhibition of Mild Steel and Aluminium. The Open Corrosion Journal. 2014; 6: 1-10.

19. Marder SR, Gorman CB, Cheng LT, Teimann BG. Optimizing the optical nonlinearities of organic molecules: Asymmetric cyanines and highly polarized polyenes. SPIE. 1993; 1775: 19-31.

20. Hui-Yin W, Ajay C, Shyi-Long L. Theoretical Studies on Nonlinear Optical Properties of Formaldehyde Oligomers by *Ab Initio* and Density Functional Theory Methods. Wiley Periodicals, Inc. J. Comput. Chem. 2005; 26: 1543–1564.

21. Naimen PM, Trokourey A, Sissouma D. Copper Corrosion Inhibition in 1M HNO_3 by 2-Thiobenzylbenzimidazole: Adsorption and Chemical Modeling of the Inhibition Efficiency. International Journal of Research in Chemistry and Environment. 2012; 4: 204-214.

22. Obot IB, Umoren SA, Obi-Egbedi NO. Corrosion inhibition and adsorption behaviour for aluminum by extract of *Aningeria robusta* in HCl solution:

Synergistic effect of Iodide ions. J. Mater. Envirin. Sci.,2011; 2(1): 60-71.

23. Fekry AM, Ameer MA. Corrosion Inhibition of mild steel in acidic media using newly synthesized heterocyclic organic molecules. International Journal of Hydrogen Energy. 2010; 35: 7641.

24. Kara YS, Sagdinc SG, Esme A. Theoretical study on the relationship between the molecular structure and corrosion inhibition efficiency of long alkyl side chain acetamide and isoxazolidine derivatives. Protection of metals and Physical Chemistry of Surfaces. 2012; 48(6): 710-721.

25. Rajendran M, Keerthika K, Kowsalya M, Devapiriam D. Theoretical studies on corrosion inhibition efficiency of pyridine carbonyl derivatives using DFT method. Der Pharma Chemica. 2016; 8(3):71-79.

26. Lashkari M, Arshadi MR. DFT studies of pyridine corrosion inhibitors in electrical double layer: solvent, substrate and electric effects. Chemical Physics. 2004; 131-137.

27. Camacho-Mendoza RL, Gutiérrez-Moreno E, Guzmán-Percástegui E, Aquino-Torres E, Cruz-Borbolla J, Rodríguez-Ávila JA, Alvarado-Rodríguez JG, Olvera-Neria O, Thangarasu P, Medina-Franco JL. DFT and Electrochemical Studies: Structure–Efficiency Relationship on Corrosion Inhibition. J. Chem. Inf. Model. 2015; DOI: 10.1021/acs.jcim.5b00385.

28. Udhayakala P. Density functional theory calculations on corrosion inhibitory action of five azlactones on mild steel. Journal of Chemical and Pharmaceutical Research. 2014; 6(7): 117-127.

29. Shao Y, Molnar LF, Jung Y, Kussmann J, Ochsenfeld C, Brown ST, Gilbert ATB, Slipchenko LV, Levchenko SV, O'Neill DP, DiStasio Jr, RA, Lochan RC, Wang T, Beran GJO, Besley NA, Herbert J. M, Lin CY, Van Voorhis T, Chien SH, Sodt A, Steele RP, Rassolov VA, Maslen PE, Korambath PP, Adamson RD, Austin B, Baker J, Byrd EFC, Dachsel H, Doerksen RJ, Dreuw A, Dunietz BD, Dutoi AD, Furlani TR, Gwaltney SR, Heyden A, Hirata S, Hsu CP, Kedziora G, Khalliulin RZ, Klunzinger P, Lee AM, Lee MS, Liang WZ, Lotan I, Nair N, Peters B, Proynov EI, Pieniazek PA, Rhee YM, Ritchie J, Rosta E, Sherrill CD, Simmonett AC, Subotnik JE, Woodcock III HL, Zhang W, Bell AT, Chakraborty AK, Chipman DM, Keil FJ, Warshel A, Hehre WJ, Schaefer HF, Kong J, Krylov AI, Gill PMW, Head-Gordon M, Deepmer BJ, Driessen AJ, Hehre TS, Johnson JA, Pietro WJ, Yu J. SPARTAN '14, build 1.01. Wavefunction Inc. Irvine CA. 2014.

30. Hohenberg P, Kohn W. Inhomogeneous electron gas. Phys. Rev., 1964; 136 (B): 864–871.

31. Kohn W, Sham L J Phys. Rev., 1965; 140 (A): 1133.

32. Pearson RG. Absolute electronegativity and hardness: application to inorganic chemistry Inorganic Chemistry. 1988; 27:734.

33. Koopman T. On the assignment of wave functions and eigenvalues to the individual electrons of an atom. Physica. 1934; 104-113.

34. Wang H, Wang X, Wang L, Wang A, Liu J. DFT study of new bipyrazole derivatives and their potential activity as corrosion inhibitors. J. Mol. Model. 2007; 13: 147.

35. Targema M, Obi-Egbedi NO, Adeoye MD. Molecular structure and solvent effects on the dipole moments and polarizabilities of some aniline derivatives. Computational and Theoretical Chemistry. 2013; 1012: 47-53.

36. Kleinman DA. Nonlinear dielectric polarization in optical media. Physical Review. 1962; 2: 1977-1979.

37. Adhikari S, Kar T. Experimental and theoretical studies on physicochemical properties of ^{L}-leucine nitrate- a probable nonlinear optical material. Journal of Crystal Growth. 2012; 356: 4-9.

38. Lukovits I, Kalman E, Zucchi F. Corrosion Inhibitors—Correlation between Electronic Structure and Efficiency. Corrosion. 2001; 3-8.

39. Bio-Rad Laboratories, Inc. 2017.

40. Sanusi K, Khene S, Nkoyong T. Enhanced optical limiting performance in pthalocyanine-quantum dot nanocomposites by free-carrier absorption mechanism. Optical materials. 2014; 572-582.

41. Bourass M, Touimi Benjelloun A, Benzakour M, Mcharfi M, Hamidi M, Bouzzine SM, Serein-Spirau F, Jarrosson T, Lère-Porte JP, Sotiropoulos JM, Bouachrine M. Theoretical Studies by Using the DFT and TD-DFT of the effect of the bridge formed of thienopyrazine in solar cells. J. Mater. Environ. Sci. 2015; 6 (6): 1542-1553.