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Comparative Study of Halogen Substituted Isocyanatophosphine as an Adsorptive Inhibitor on Al (110) Crystal Surface, using Density Functional Theory.

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A B S T R A C T

To shield aluminium metals from the corrosion, a theoretical investigation on the ability to resist corrosion was carried out using the local density function Becke, 3-parameter, Lee-Yang-Parr (B3LYP) under limited spin polarization DNP+ basis in aqueous solution. The aim of the research was to obtain a stable geometry of the halogen substituted Isocyanatophosphine molecule, the local reactivity, and the global reactivity of the molecules as simulated on Al (110) surface. Some of the reactivities include the $(\omega +)$ electron accepting power which is in the order of 0.614<1.404<1.739<3.165 eV with DIP having highest accepting power and $(\omega$ -) electron donating power from 4.579< 6.015< 6.445< 7.891 eV and DFP having the highest accepting power. The energy gap (ΔEg) was in the order of 4.243<5.142<5.993<7.361eV; hence, DIP with 4.243eV is less stable and capable of been more reactive compare to DBP, DCP, and DFP. Fraction of electron transfer (ΔN) and Back-donation energy were in good agreement with each other in the order of 0.222<0.200<0.206<0.257% having DBP as the highest efficient molecule for the inhibition. The mode of interaction between the molecules and the surface of Al (110) was therefore established to be physisorption. The Binding energy of the molecules ranges between 15.708-22.298 kJmol⁻¹. The Fukui function findings suggest the heteroatoms in a molecule nitrogen, oxygen, and halogen atoms been the focal point for the selectivity of electron donation and acceptance between the metal and the molecules. The molecules are tetragonal planar on the surface of the aluminium crystals.





1. INTRODUCTION

Corrosion inhibitors are chemicals that efficiently slow the rate of corrosion of metals and alloys when used in relatively low concentrations, particularly in cooling systems, storage vessels and boilers, oil and gas pipelines, as well as in construction [1-2]. Corrosion itself is an ugly phenomenon that causes threat in the field of science and engineering [3]. Corrosion is known as a gradual destruction of materials with the help of some conditions, such as temperature, pressure, high concentration of corrosive acids, etc. [4-5]. These involve oxidation of metals there by destroying the useful properties of materials and structures like appearance, strain and stress and most importantly reduced the weight of such metal among others [6].

Corrosion transforms the metal back into it stable state, ore $[\underline{7}]$.

Therefore, it became crucial to keep track of how metals interact with their surroundings because corrosion results from the deterioration or destruction of metallic materials when they come into contact with their surroundings, which causes the collapse of crucial structures such as bridges and the perforation of storage tanks [8-9]. Building collapse has grown prevalent around the world, and many attributed the ugly phenomenon

inhibitors of corrosion of metallic surfaces (such as aluminium, iron, etc.), despite their high effectiveness. Although organic corrosion inhibitors are biodegradable and ecologically beneficial, they have further the ability to prevent corrosion. Organic corrosion inhibitors can be adsorbed on the metal surface and shield the surface from acidic solutions because they include electron donor atoms including phosphorous, sulphur, oxygen, and nitrogen [29]. To check if other atoms like Halogen group could have the same effect, this present research aims to determine the effect and nature of interaction between the aluminium surface and halogenated derivatives of isocyanatophosphine, as indicate in Fig. 1 using theoretical investigation of the inhibiting aluminium metal using computational method. This is hoping to be achieving with the aid of local reactivity, global reactivity, binding, and adsorption energy, derived from simulations of the molecule on the stated aluminium surface. The study is limited to the adsorptive impact of the halogen substituted isocyanatophosphine on the Al (11 0) crystal surface using computational quantum analysis and molecular simulation method. For the best of our knowledge, this compounds halogen substituted Isocyanatophosphine has not been used as a corrosion inhibitor on the aluminium surface in the literature.



Fig1. The structure of the halogen substituted Isocyanatophosphine

2. EXPERIMENTAL

2.1. Computational Method

2.1.1. Sketching and Geometric Optimization of the molecules

ChemDraw Ultra 7.0.3 CambridgeSoft was used to create sketches of the investigated compounds. Each molecular structure needs to be optimized once it has been constructed to bring it to a stable configuration. The atoms' coordinates are changed iteratively during this process to bring the structure's energy to a stationary point or where the forces acting on the atoms are zero. During the energy reduction, a relative minimum on the energy hyper surface was sought after. It is anticipated that the geometry corresponding to this structure will closely resemble the system's real physical structure when it is in equilibrium [8]. The molecules' torsional and conformational energies were reduced using the algorithms in Materials Studio DMoL3. From ChemDraw, the chemicals were imported into Materials Studio. The following parameters were used to do the optimization: limited spin polarization DNP+ basis for DFT-D. B3LYP was chosen as the local density functional in the water solvent [10-12].

2.1.2. Quantum Chemical Parameters Calculations

Calculations involving quantum chemistry were performed using density functional theory impacted in algorithms in Materials Studio DMoL3 Modules. Dmol3 is software that computes the electronic characteristics of molecule clusters, surfaces, and crystalline solid materials from the first principle using the density functional theory (DFT) and a numerical radial function basis set [13].

The double numeric with polarization (DNP) basis set and the functional methods B3LYP from the name Becke, 3-parameter, and Lee-Yang-Parr (B3LYP) for the correlation component were used to do the density functional theory (DFT) computations because it is the best set available in Dmol3. The calculations of the global reactivity indicators were obtained from the number of quantum-reactivity-descriptors (QRDs) and the local reactivity was evaluated from Fukui Functions. Some of QRDs are directly extracted from the output files such as the energy of the lowest unoccupied molecular orbital (ELUMO), energy of the highest occupied molecular orbital (E_{HOMO}), while other parameters were derived using appropriate mathematical equations and dependent parameters [13-14].

According to Koopman's theory, the energy of the border molecular orbital, the energy of the highest

occupied molecular orbital (EHOMO), and the energy of the lowest unoccupied molecular orbital (ELUMO) are connected in equation (2) and (3), respectively [<u>12</u>-<u>17</u>].

The value of global hardness (η), according to Pearson, is roughly described as given in Equation (3). The global softness (σ) of the system, as shown in Equation (4), is the opposite of the global hardness.

$$\eta = \frac{IE - EA}{2} \tag{3}$$

$$\sigma = \frac{1}{\eta} \tag{4}$$

The energy gap of the molecules is calculated using Equation (5). The energy gap is a parameter that determines in the how easy a molecule moves between the two surfaces capable of adsorption on the surface.

$$\Delta Eg = ELUMO - EHOMO \tag{5}$$

The fraction of electrons transferred (ΔN), of the inhibitor and Al-surface was calculated using Equation (6). The half electron transfer (ΔN), of the molecule is a parameter that demonstrates if the inhibition of molecule is strictly by transfer of electrons between the surface and the molecule within the threshold value of 3.6, or not.

$$\Delta N = \frac{\chi Fe - \chi Inh.}{2(\eta Fe + \eta Inh)}$$
(6)

According to the simple charge transfer model for donation and back donation of charges, when a molecule receives a certain amount of charge, ΔN^+ , then: $\Delta E^+ = \mu^+ \Delta N^+ + \frac{1}{2} \prod (\Delta N^+)^2$ and when a molecule back-donates a certain amount of charge, ΔN^- , then: $\Delta E^- = \mu^- \Delta N^- + \frac{1}{2} \prod (\Delta N^-)^2$. Assuming the amount of charge back-donation is equal to the amount of charge received, the total energy change will approximately be the sum of the contributions [15-18].

$$\Delta E_{t} = \Delta E^{+} + \Delta E^{-}$$

$$= (\mu^{+} - \mu^{-}) \Delta N^{+} \frac{1}{2} \eta (\Delta N^{+})^{2} + \frac{1}{2} \eta (\Delta N^{-})^{2}$$

$$= (\mu^{+} - \mu^{-}) \Delta N^{+} + \eta (\Delta N^{+})^{2}$$
(7)

However, the most favourable condition corresponds to the case when the total energy change (ΔE back-donation) becomes minimum with respect to ΔN^+ , which implies $\Delta N^+ = -(\mu^+ + \mu^-)/2 \eta$.

$$\Delta E_{bd} = (\mu^{+} - \mu^{-})^{2}/4 \eta = \frac{-\eta}{4}$$
(8)

The electron donating (ω^{-}) and electron accepting (ω^{+}) powers of the molecules has been defined, as shown in the Equations (9) and (10) [<u>19-20</u>].

$$\omega \approx \frac{(3I+A)^2}{16(I-A)} \tag{9}$$

$$\omega^{+} \approx \frac{(l+3A)^2}{16(l-A)} \tag{10}$$

$$\chi$$
 = Absolute electronegativity (eV) $\chi = \frac{l+A}{2}$ (11)

$$\Delta E back donation = \frac{1}{8} (E_{HOMO} - E_{LUMO})$$
(12)

The second order Fukui function (f^2) the dual descriptor $\Delta f(k)$, was used in describing the donating and acceptability of the molecule and the metal which has theoretical

3. RESULTS AND DISCUSSION

3.1. Quantum chemical parameters

The relationship between quantum chemical properties and corrosion inhibition is often based on the Lewis theory of acids-bases and Pearson's hard and soft acids and bases [10]. Chemical potential (μ) and softness (S) are also two features to characterize any chemical system [2]. The calculations of the global reactivity indicators of the inhibitors such as the localization of frontier molecular orbitals, *E* _{HOMO}, *E*_{LUMO}, energy gap (Δ Eg), absolute electronegativity (χ), hardness (η), dipole moment (μ), electrophilicity index (ω), softness (S), fraction of electrons transferred (Δ N), and back donation energy (Δ E _{b-d}) were used

to explicate the electron transfer mechanism between the inhibitor molecules and the steel surface in <u>Table 2 [5]</u>.

3.2. Fukui Functions

In this work, a local reactivity function called the Fukui function was utilized to evaluate the reactivity of various atomic positions inside a molecule. The molecules contained several halogen atoms (F, Cl, Br, and I). The condensed Fukui function and the local reactivity indices were thought to be a useful descriptor of the molecular elements since the halogen moieties include substituted hetero-atoms. The attack type (radical, electrophilic, or any mix of the three) is described by the Fukui indices. The most reactive sites within an inhibitor molecule are those with the biggest values for Pk+(M) and Pk-(M) because they have the largest reaction. The atoms having the greatest Fukui functions for both nucleophilic and electrophilic assaults are shown by the values of the atoms in bold as presented in <u>Table 1</u>a [15]. The results of the condensed dual descriptor computation utilizing f2 (M) Mulliken atomic charges are presented in <u>Table 1</u>b. The nucleophilic and electrophilic Parr functions, respectively, are represented by the Mulliken atomic spin densities Pk+(M) and Pk-(M) [7-9].

The results of the local reactivity descriptor in Table 1 indicated that the molecule will donate electrons to the empty p-orbital of the metal surface at same rate as received. Atom per molecule rate for electrophilic was equivalent with that of nucleophilic rate [1-3]. The highest Fukui value of the attack in the respective molecules is in the order of DFP>DCP>DBP>DIP, on P(1) for DFP, Cl(5) for DCP, Br(5) for DBP, and I (6) for DIP making the atoms having high probability of donating electrons compare to other atoms in the molecules [8]. The second Fukui function, demonstrated that a molecule has an equal potential for transfer of electrons to the metal surface. In <u>Table 1b</u>, f^2 (M) is equal with the same positive values as it is with the negative values. The sole exception to this rule is DIP, where the outcome should be a molecule that donates more electrons than it takes them off the surface [12].

Atom DFP	P_k^+ (M)	$P_k^-(\mathbf{M})$	Atom DBP	P_k^+ (M)	$P_k^-(\mathbf{M})$	Atom DCP	P_k^+ (M)	$P_k^-(\mathbf{M})$	Atom DIP	P_k^+ (M)	$P_k^-(\mathbf{M})$
P (1)	0.44	0.38	P (1)	0.186	0.23	P (1)	0.286	0.213	P (1)	0.148	0.115
N (2)	0.067	0.056	N (2)	0.021	-0.001	N (2)	-0.002	0.049	N (2)	0.021	-0.002
C (3)	0.139	0.189	C (3)	0.081	0.08	C (3)	0.139	0.07	C (3)	0.072	0.127
0 (4)	0.213	0.141	0 (4)	0.112	0.125	0 (4)	0.128	0.13	0 (4)	0.104	0.089
F (5)	0.058	0.117	Br (5)	0.312	0.238	Cl (5)	0.26	0.255	I (5)	0.328	0.314
F (6)	0.083	0.117	Br (6)	0.288	0.327	Cl (6)	0.188	0.284	I (6)	0.328	0.357

Table 1a. The Fukui function of the molecules in Milliken values

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f²(M)	f²(M)	f²(M)	f²(M)		
0.06	-0.044	0.073	0.033		
0.011	0.022	-0.051	0.023		
-0.05	0.001	0.069	-0.055		
0.072	-0.013	-0.002	0.015		
-0.059	0.074	0.005	0.014		
-0.034	-0.039	-0.096	-0.029		

Table1b. The second Fukui function of the molecules

3.2. Frontier orbital energies

Global reactivities which describe the potential behaviour of molecules on the metal surface were calculated and evaluated. The global reactivity includes: electronegativity (χ), global hardness (η), electron donating power(ω ⁻), electron accepting power (ω ⁺) global softness (σ), global hardness (η), and fraction of electron transfer (Δ N). These global reactivities describe the reactivity of a molecule in terms of the initial electron distribution in the molecule [13]. A molecule's capacity to take electrons from the porbital of the Al (110) metal surface is indicated by its ELUMO Eigen value.

The ability of the inhibitor to donate electrons to the unoccupied orbital p of the aluminium employed in this investigation would increase with a larger value of EHOMO. Similarly, the ELUMO value indicates a molecule's capacity to take electrons; the lower the value, the more likely it is that an inhibitor molecule will accept electrons from the p-orbital [11]. When compared to the other molecules of halogenated isocyanatophosphine, the molecule DFT has a higher possibility of taking an electron from the vacant orbital of aluminium because the order of the E LUMO value in the molecules under study is DFP>DIP>DBP>DCP. The superior DIP tendency to give off electrons than other molecules like DBP, DCP, and DFP is shown by the larger EHOMO (-6.840eV) value. As a result, the adsorption

phenomena for DIP will be identified, increasing inhibitory efficiency [2, 7]. Global chemical descriptors that gauge molecule stability was assessed, such as global softness (σ) and global hardness (ŋ). The energy gap (ΔEg) between E_{LUMO} and E_{LUMO} suggests a significant level of stability and reactivity. The molecule with the lowest Energy gap is refers as having the highest reactivity with instability while and the highest energy gap is related with high stability which result to low reactivity of the molecule. The DIP appears to be more reactive than the remaining halogenated isocyanatophosphine, according to the Δ Eg values, as indicated in Table 2. These concluded that the lower value of DIP (4.243 eV) is more able to interact with the Al surface than DCP, DBP, and DFP [11].

The value of electron transfer (Δ N) was determined to further analyse the adsorptive behaviour of the compounds on Al (110) surface. The molecule with the highest value of the fraction of electron transfer is suggested to have a greater efficiency of the inhibition on the metal surface. Ayuba *et al.* and *Nyijime et al.* in their various research concluded that the higher the values of electron transfer of the molecule demonstrate how the molecule inhibition on the surface depends on the transferred electrons, but not the molecular weight of the molecule and the effectiveness of the inhibition is directly related to the molecules' capacity to donate electrons [23, <u>26-27</u>]. The maximum proportion of electron transfer between the molecule and the surface of metal is predicted to occur in the molecule DBP, as listed in Table 2. The values obtained are significantly lower than the threshold value of 3.6% of the electron transfer (ΔN).

The interaction between the inhibitor molecule and the metal surface can be further demonstrated via the back donation ΔE_{b-d} energy. The process of back donation is improved if the global hardness is positive and the energy of back donation ($\Delta Eb-d$) value is negative. All backdonation values of the molecules were positive, according to Nyijime *et al.*, the transfer of charge from the inhibitor molecules to the metal surface occurs when the inhibitor molecules connect with the surface [12,26]. The ω - electron donating power and ω + electron accepting power of the molecules were calculated. It follows that a larger (ω +) electron accepting power value corresponds to a better capability of accepting charge, whereas a smaller value of (ω -) electron donating power value of a system makes it a better electron donor.

Properties	DFP	DCP	DBP	DIP
EHOMO (eV)	-7.646	-7.395	-6.847	-6.840
ELUMO (eV)	-0.285	-1.402	-1.705	-2.604
ΔE (eV)	7.361	5.993	5.142	4.243
(I) (eV)	7.646	7.395	6.847	6.847
(A) eV	0.285	1.402	1.705	2.604
(η)	3.681	2.997	2.571	2.122
(σ)	0.272	0.334	0.389	0.471
(x)	3.966	4.399	4.276	4.726
(ΔN)	0.222	0.200	0.257	0.206
(ω-)	4.579	6.445	6.015	7.891
(ω+)	0.614	1.404	1.739	3.165
ΔE _{b-d}	-0.920	-0.749	-0.643	-0.531

3.3. Molecular Geometry

<u>Table 3</u>(a, b, c, and d) presents the values of the bond length before and after simulation. The geometry showed that the single bonds were longer than the double bonds between the atoms of the molecules [12]. In DFP, the P1-N2 bond was the longest, followed by those between halogen atoms and P1. The simulation led to changes in the bond lengths of all the molecules [13]. This proved

that every molecule actively participated in the inhibition of the metal surface. The results of the examination into the bond angle before and after simulation of molecules were not completely planar; the values varied from 0 to 178, which is less than 180, and showed that the molecules would not have a flat orientation on the aluminium and iron surfaces to optimize surface adsorption [23-25].

Bond length	Before	Al Simulated (nm)	
DFP	Optimized (nm)		
P1-F6	1.540	1.538	
P1-F5	1.540	1.542	
P1-N2	1.650	1.653	
N2-C3	1.198	1.198	
C3-04	1.160	1.160	
Bond Angle	Before	Al Simulated (^o)	
DFP	Optimized (°)		
F6-P1-F5	109.558	109.021	
F6-P1-N2	109.578	110.138	
F5-P1-N2	109.520	109.362	
P1-N2-C3	179.737	179.938	
N2-C3-O4	173.320	173.354	

Table3b. The bond length of the DCP atoms in the molecule before and after simulation

Bond length	Before	Al Simulated(nm)
DCP	Optimized (nm)	
P1-Cl6	2 044	2 043
P1-Cl5	2.043	2.045
P1-N2	1.650	1.651
N2-C3	1.198	1.198
C3-04	1.159	1.159
Bond Angle	Before	Al Simulated(^e)
DCP	Optimized(^o)	
Cl6-P1-Cl5	109.545	110.604
Cl6-P1-N2	109.636	110.338
Cl-P1-N2	109.406	109.667
P1-N2-C3	179.714	179.451
N2-C3-04	173.487	172.821

Table3c. The bond length of the DBP atoms in the molecule before and after simulation

Bond length DBP	Before Optimized (nm)	Al Simulated (nm)
P1-Br6	2.176	2.173
P1-Br5	2.176	2.176
P1-N2	1.637	1.638
N2-C3	1.195	1.195
C3-04	1.159	1.158

Bond Angle DBP	Before Optimized (º)	Al Simulated (º)
Br6-P1-Br5	109.482	109.464
Br6-P1-N2	107.819	108.995
Br5-P1-N2	107.762	107.374
P1-N2-C3	179.986	179.856
N2-C3-O4	173.027	172.287

Table3d. The bond length of the DBP atoms in the molecule before and after simulation

Bond length	Before	Al Simulated (nm)
DIP	Optimized (nm)	
P1-I6	2.307	2.301
P1-I5	2.307	2.304
P1-N2	1.639	1.640
N2-C3	1.193	1.195
C3-04	1.158	1.158
Bond Angle	Before	Al Simulated(^o)
DIP	Ontimized(^o)	
	openinzed()	
I6-P1-I5	109.499	108.136
I6-P1-N2	107.960	108.643
I5-P1-N2	107.999	107.009
P1-N2-C3	179.953	179.488
N2-C3-O4	173.274	173.051

3.4. Frontier molecular orbitals

In Fig. 2 (a-d), the molecules under investigation's optimize structure, total electron density, HOMO orbitals, and LUMO orbitals. It was feasible that the

complete molecule boosts the corrosion inhibition on metal surfaces during the inhibition process based on the overall electron density of the molecules



Fig2a. The optimized structure, electron density, and HOMO and LUMO orbitals of the molecules DFP



Fig2b. The optimized structure, electron density, and HOMO and LUMO orbitals of the molecules DCP



Fig2c. The optimized structure, electron density, and HOMO and LUMO orbitals of the molecules DBP



Fig2d. The optimized structure, electron density, and HOMO and LUMO orbitals of the molecules DIP

3.5. Dynamic Simulation of Molecules

Understanding how molecules interact with metal surfaces to minimize the severity of corrosion when exposed to hazardous conditions is provided by the halogenated isocyanatophosphine derivatives modelled on the surfaces of Al (110) [24]. The highly populated surface of the aluminium Al (110) crystal was chosen in order to provide an accurate result because of their excellent atomic coverage and density on the surface [17, 20]. Following modelling of the molecules on the metal's surface,

demonstrates Figure. 3 the halogenated isocyanatophosphine structures on the Al surface. The characteristics of the predicted molecular dynamics were used to describe the potential for the inhibition of molecules on the surface of the simulated metal. The determined characteristics were total energy (kinetic and potential), surface energy, molecule energy, adsorption energy, and binding energy [20-21]. Table 4 indicates the statistical information for binding adsorption energy, system total potential and kinetic energy, and molecule and surface energy.

Properties	DFP	DCP	DBP	DIP
Total Kinetic Energy	4.623±1.7	3.578±2.1	5.323±0.0	3.551±2.4
Total potential energy	-31.5330±0.7	-36.908±0.0	-62.055±0.0	-46.231±0.0
Energy of the molecule	-12.488±0.0	-21.198±14.9	-39.757±0.0	-43.151±0.0
Energy of the surface	0.000±0.0	0.000±0.0	0.000±0.0	0.000±0.0
Adsorption Energy	-19.045±0.0	-15.708±14.9	-22.298±0.0	-20.079±0.2
Binding Energy	19.045±0.0	15.708±14.9	22.298±0.0	20.079±0.2

3.6. Mechanism of inhibition

The study of the molecules on Al (110) surfaces revealed that the molecules are spontaneous on the metal surface due to the negative adsorption energy obtained during simulation [10, 21]. A physical adsorption process is suggested by the simulation's binding and adsorption energies on the surface of metal. Hence, the values were both greater than -100 kcal/mol for adsorption energy and less than binding energy. This was demonstrated by Afandiyeva *et al.*, and Ayuba and Umar as a result of such lower binding energy the molecules interaction suggested mild inhibition and physical adsorption on the aluminium surface.



DCP side View

DCP Front view



DIP side view



DIP front View





Fig3. The molecule on the surface of Al (110) crystal side and top view

Conclusion

The interactions between a metal and the inhibitors cause changes in the inhibitors characteristics as studied by some parameters. Therefore, corrosion inhibitor halogen derivative of isocyanatophosphine could be used to protect the metallic surface from corrosion. A corrosion inhibitor was investigated using Density Function Theorey (DFT). The analysis revealed that:

(1) The low ELUMO combined with the high EHOMO reveals that the halogen derivative of isocyanatophosphine molecules was reactive by serving as a donor, hence confirming the predicted inhibition. The electronegativity atoms have a significant effect on the corrosion inhibition efficiency of Halogen derivative of isocyanatophosphine molecules, and the atom with a negative charge depicts the potential of a HOMO centre.

(2) Halogen derivative of isocyanatophosphine molecules show high significant corrosion protection properties and are thought to be highly effective

(3) By donating and receiving electrons, the heteroatoms in the inhibitor molecules boost the capacity to adsorb on the aluminium surface. The inhibitor is efficient due to oxygen and nitrogen atoms in the inhibitor molecules and that the inhibitor molecules bonded coordinative with the

p-orbital of aluminium atoms on the halogen atoms.

(4) That the binding energy of the simulation depicts low energy values suggesting a mild inhibition with the surface which also suggests physical adsorption because of the low value of binding and absorption energy.

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