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Chemistry

Highlights

- Effect of DFT Exchange
- Passivation Enhancing Potentials
- Determination of Lead Levels
- Introduction of the Informatics Potential

Discovering Thoughts, Inventing Future

VOLUME 19 ISSUE 2 VERSION 1.0

Global Journal of Science Frontier Research: B
Chemistry

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Effect of DFT Exchange Correlation Functionals and Basis Set Quality on the Calculations of the Magnetic Coupling Parameter J.

By Mohamed A. Makhyoun, Nicholas Lees-Gayed & Raghdaa A. Massoud
Alexandria University

Abstract- The J magnetic coupling parameters were calculated theoretically by the aid of ORCA software. Seven exchange-correlation functionals combined with seven different basis set including low quality and high quality types. The calculations were done for two different geometries of the same dimer anion Cu_2Cl_6. The first geometry is a square planar, the second is distorted tetrahedral. The differences is due to the accompanied cation. For testing the approach the calculations have extended to the other dimers using only two combinations of the above that seems to give good results. The values of the computed J for all cases were compared to experiments.

It termed out that some of the combinations functionals/basis set gave satisfactory results for both anion.

A regression analysis were done to correlate the coupling constant with certain theoretical parameters chosen carefully for the above combinations. Because the electronic transitions are sensitive to small geometry variations of the same anion , we have used different approaches to calculate the first two transitions (mainly d-d).

Keywords: *magnetic coupling parameter, DFT calculations, copper dimers.*

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Keywords: magnetic coupling parameter; DFT calculations; copper dimers.

I. Introduction

The study of the anion Cu_2Cl_6 is a subject of interest. Many compounds of the formula $([\text{cation}]^+ [CuCl_3])_2$ were synthesized and X-ray or/and magnetic data were determined [1-6]. Although we deal with the same anion, different properties are exhibited when we alter the associate cation. Here we have studied six dimmers these are (where the geometry around each copper is given):

1. $(\text{Dibenzotetrathiafulvalenium})_2^{++}$ Cu2Cl6^{--} square planar [1]
2. $(Ph4P)_2^{++}$ Cu2Cl6^{--} distorted tetrahedreal [2]
3. melaminiumH2 $^{++}$ Cu2Cl6^{--} square planar [3]
4. $(Ph4As)_2^{++}$ Cu2Cl6^{--} distorted tetrahedral [4]
5. $(Ph4Sb)_2^{++}$ Cu2Cl6^{--} distorted tetrahedral [5]
6. (propyl-triphenyl $P)_2^{++}$ Cu2Cl6— square planar [6]

Calculations of the J parameter of some of these compounds were previously done using one combination B3LYP/pVDZ, using G94 software. The authors claimed to get good correlation.[7]

For calculating J theoretically The total energy of the wave function of spin (3,1), a triplet wave function was calculated. Second the total energy of wave function with (3,0) with broken symmetry was also calculated. According to the work of Bencini and Gatteschi[8], a combination of the two energies in one equation led to:

$$[E_{\text{high spin}} - E_{\text{broken symmetry}}]/(S_{max}(S_{max}+1)) = -J \qquad (1)$$

This means that if J is negative the system is anti-ferromagnetic, while positive value implies ferromagnetic interaction.

All our calculations are provided by the ORCA program [9-11].

The angle X(bridging)-Cu-Y (terminal) sometimes is correlated with J.[7]

Instead a relation connecting calculated J with five parameters chosen carefully by us resulting in good correlations.

II. Method of Calculations

We utilize seven functionals in our calculations these are: the hybrid types B3LYP, O3LYP, PW6B95, TPSS0, and the range-separated types cam-B3LYP, LC-BLYP and wB97X-D3. These are combined with seven basis set which are : def2-SVP, 6-311+G*, TZVPP, def2-TZVPP, ma-def2-QZVPP, def2-QZVPP and aug-PC-2 resulting in a total of 49 computations for each of the two anions dimers **1**,**2**. These computations were aimed to calculate J parameters according to equation (1).

The geometries determined by X-ray were used in the calculations without further optimization. The calculations involved only the anion Cu2Cl6^{2-}, because this part is expected to contribute exclusively to the magnetic properties.

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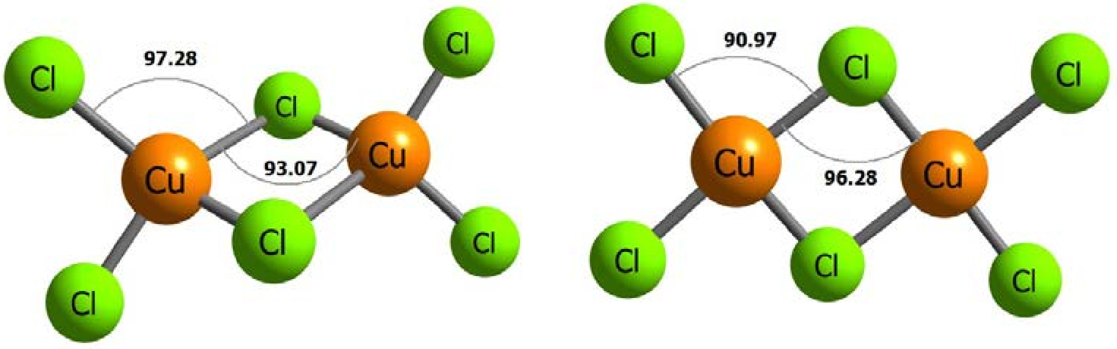
Figure 1 Shows the two possible geometries of Cu2Cl6^{2-}



Anion (**2**) distorted tetrahedral. Anion (**1**) square planar

Fig. 1: The anion geometrical structures after X-ray determination[1, 2]

III. Discussion

a) Calculation of magnetic coupling parameter (J)

We notice from experimental finding that the square planar configuration is mostly anti-ferromagnetic, while the tetrahedral one is mostly ferromagnetic. In our opinion this is dependent on the Cu-Cu distance. It is shorter in the square planar types which felicitate the interaction of the electrons.

Tables 1. and 2. display the calculated J parameters after equation (1) for the 49 combinations of dimers **1** and **2.**

Table 1: Magnetic coupling parameter of compound **1**

	Def2-SVP	6-311+G*	TZVPP	Def2-TZVPP	ma-def2-QZVPP	Def2-QZVPP	Aug-PC-2
B3LYP	-38.6	-25.3	-30.8	-27.7	-23.7	-22.9	-22.6
O3LYP	-46.4	-29.0	-38.0	-34.7	-28.1	-28.6	-29.5
PW6B95	-24.9	-25.6	-16.3	-13.7	-9.7	-10.0	-10.7
TPSS0	-20.5	-21.0	-12.5	-9.6	-6.1	-6.3	-7.3
cam-B3LYP	-20.8	-20.6	-13.6	-11.0	-7.0	-7.3	-8.0
LC-BLYP	-27.9	-34.2	-21.9	-19.3	-14.5	-14.9	-15.6
wB97X- D3	-18.4	-6.4	-9.2	-6.9	-9.7	-3.7	-4.0

Experimental = -41.8 cm-1.[13]

Table 2: Magnetic coupling parameter for compound **2**

	Def2-SVP	6-311+G*	TZVPP	Def2-TZVPP	Ma-def2-QZVPP	Def2-QZVPP	Aug-PC-2
B3LYP	33.3	34.5	31.8	31.5	31.1	31.0	31.6
O3LYP	44.2	48.0	44.2	44.1	44.1	43.9	44.6
PW6B95	30.9	31.2	29.0	28.5	28.0	27.9	28.4
TPSS0	27.5	27.3	25.3	24.8	24.1	24.0	24.5
Cam-B3LYP	28.7	29.0	26.8	26.3	25.9	25.8	26.2
LC-BLYP	30.2	32.5	30.0	19.7	29.5	29.4	29.8
wB97X-D3	26.5	27.9	26.1	25.6	25.1	25.1	25.1

Experimental =+26.5 cm-1.[13]

The values shaded by yellow color in tables 1 & 2 are those near the expermimental finding. If you examine the two tables you can find that (a) both calculations predict the right sign of J. (b) The most correlated combinations of J values for dimer **1** is not necessary those for dimer **2.** According to the two tables the combinations: O3LYP/def2-TZVPP and TPSS0/def2-TZVPP seems reasonable to be used in calculations of the rest of the dimers (table 3). (c) Small differences in the structure (e.g. compounds **2,4,5**) resulting in remarkable differences in J. Which means that J is sensitive to small variations in the geometery.

It is worth to mention here that some of the dimers may be weakly interacting with other dimers in the lattice forming some kind of a linear polymer with weak Second coupling (J')[6].

We have tried to connect the calculated J constants over the different combinations with some chosen DFT output variables. We found that calculated J values are dependent (with good statistical correlations) on the HOMO energy, LUMO energy, natural copper charge (CM), natural chlorine charge (CL) (the one at the bridging position), natural spin population on copper center (M*), natural spin population on bridging chlorine (L*) and finally on the exchange correlation energy dependent on the type of functional used (E(XC). Charges and spin population have been calculated using GENBO5 software [12]

We have found that there is poor correlation between calculated J values and the above parameters if we use all the 49 combinations mentioned above together, instead we found that if we take each seven combinations belonging to the same basis set at a time, as shown in table 3, the correlation is very good.

The J values were found to be strongly dependent on only five parameters.

Each basis set has it own five parameters.

Table 3: Indicates which five parameters that give best correlation for dimer **1**

HOMO LUMO C_M C_L M* L* E(XC)

6-311+G* 3+4+5+6+7
R=0.99986 S= 0.69

TZVPP 2+3+4+6+7
R=0.99999 S= 0.25

Def2-TZVPP 1+2+3+4+6
R=0.99999 S=0.22

Def2-QZVPP 1+2+3+4+7
R=0.999999 S=0.034

ma-def2-QZVPP 2+3+4+5+7
R=0.999999 S= 0.036

Aug-P-C2 2+3+5+6+7
R=0.9998 S=0.93

Def2-SVP 2+4+5+6+7
R=0.99995 S=0.49

R=correlation coefficient, S=standard error.

Another dependence was visualized by drawing a contour diagrams of dimers **1** & **2**, of calculated J over the different combinations reflected in the basis set dimension (Number of contracted functions) against exchange-correlation energy of the DFT functional. (Figures 2&3).

Table 4: J values for compounds 1-6 using only two combinations

Dimer	O3LYP/ def2-TZVPP	TPSS0/ def2-TZVPP	Experimental[13]
1	-34.7	-9.6	-41.8
2	+44.1	+24.8	+26.5 cm^{-1}
3	-7.0	-7.0	- 19.0 [3]
4	+47.9	+28.7	+19.5[14]
5	+46.9	+29.1	+43.9
6	+6.4	+19.2	+46.5

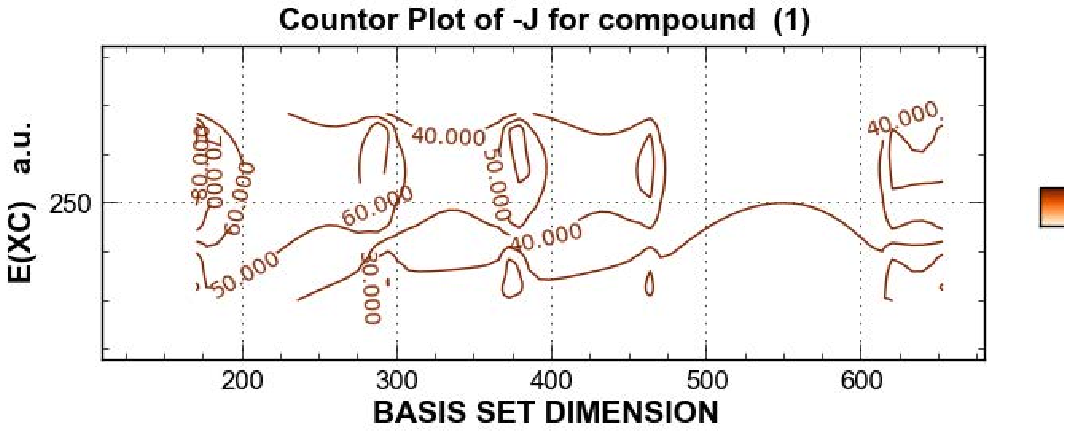


Fig. 2

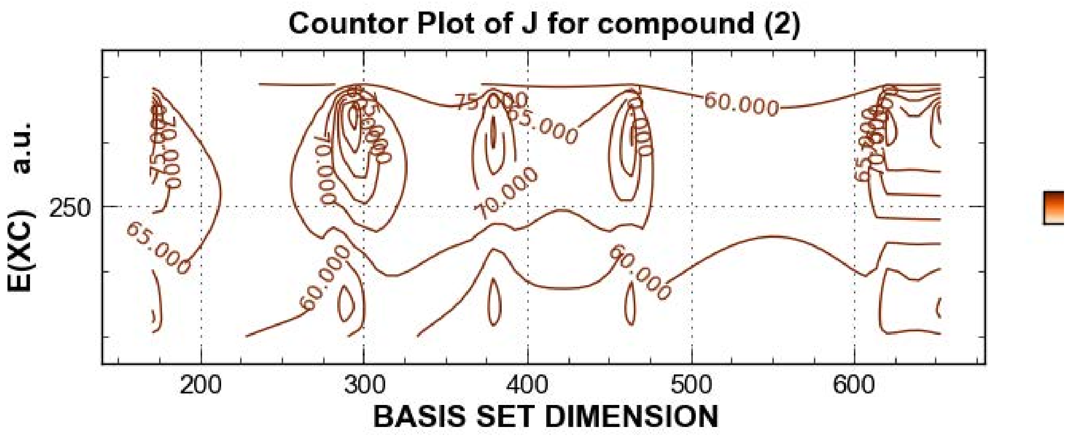


Fig. 3

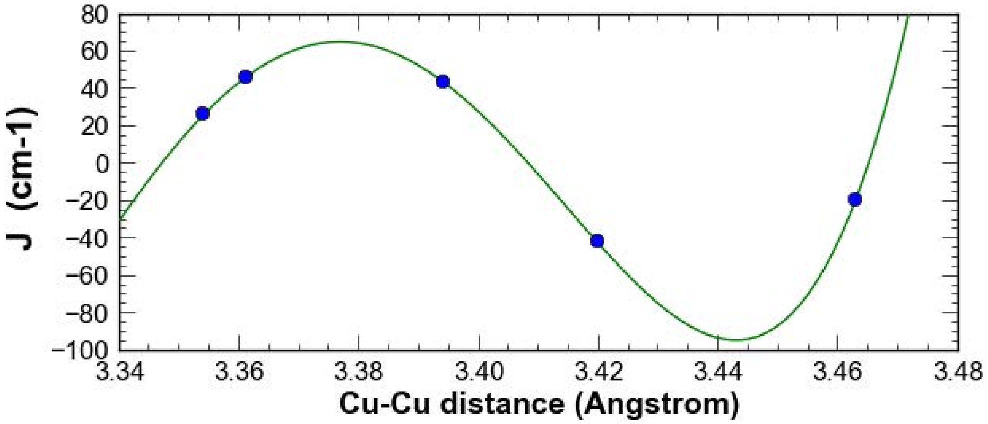


Fig. 4: Dependence of J on the Cu-Cu distance through a cubic equation

It is well establish the relation of J with the the Cl-Cu-Cl in Cu2Cl6 anion[7].
In this work a relation between J and Cu-Cu distance is also proposed (see figure 4).

One can notice that the larger distances belong to anti-ferromagnetic Systems ,while smaller distances are for ferromagnetic systems.

b) Calculations of the first electronic transition energy

Table 5: Transition energy is given in cm^{-1}

	TDDFT/ Cam-B3LYP/ def2-TZVPP	CI(D)/ def2-TZVPP	CASSCF(10,12)/ def2-TZVPP	EE-EOM-CCSD/ TZVP	Experimental Reference 15,16
1	14962	11760	7796	12640	9900
2	9352	7748	6655	5750	8000
3	14138	10639	9140	11844	11760
4	9925	8224	7008	8507	8700
5	10456	8585	7294	8915	9524
6	14271	10733	7020	11804	10000

The first electronic transition of our dimers has been calculated theoretically by four different methods, together with their corresponding experimental values.

The one which approximate closely the experiments is the CI(D) approach, next to it the CASSCF(10,12) method.

IV. CONCLUSION

The use of 49 combinations (compounds **1&2**) of calculation variables (Exchange-correlation functionals/basis set) widen the scope for the search of good correlated set with respect to the magnetic coupling parameters. Many combinations satisfy close resemble with experiment. At least good prediction of ferro/antiferro coupling properties was achieved very well in our six dimers.

We succeeded to get equations relating the J constants with five theoretical parameters extracted mainly form ORCA program output. Although the correlation between J and the five parameters is very good, unfortunately they are basis set dependent. The J constant was known to be related to the angle employing the bridging atoms in the polymer. We found that it is also related to the Cu-Cu distance in our systems.

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Supplementary Material

Table S1: Calculated HOMO, LUMO, M*, L* for compound **1**

	Def2-SVP	6-311+G*	TZVPP	Def2-TZVPP	ma-def2-QZVPP	Def2-QZVPP	aug-PC-2
B3LYP	.994	1.076	1.065	1.068	1.106	1.068	1.106
	-.601	-.612	-.614	-.611	-.629	-.611	-.629
	.450	.478	.492	.485	.483	.485	.483
	.186	.2118	.204	.210	.211	.210	.211
O3LYP	.955	1.026	1.016	1.012	1.016	1.013	1.052
	-.587	-.593	-.596	-.594	-.590	-.5894	-.608
	.454	.427	.437	.437	.4282	.429	.427
	.202	.232	.224	.225	.233	.2325	.233
PW6B95	1.033	1.116	1.109	1.109	1.114	1.113	1.150
	-.618	-.631	-.635	-.634	-.631	-.631	-.649
	.534	.520	.531	.535	.530	.530	.529
	.171	.1936	.186	.186	.191	.191	.191
TPSS0	1.077	1.139	1.138	1.138	1.140	1.140	1.175
	-.632	-.638	-.644	-.643	-.640	-.640	-.657
	.566	.546	.558	.562	.558	.558	.556
	.162	.1848	.177	.177	.181	.182	.182
Cam-B3LYP	1.041	1.123	1.118	1.116	1.121	1.121	1.156
	-.621	-.633	-.638	-.636	-.633	-.633	-.651
	.537	.520	.532	.536	.530	.531	.529
	.169	.193	.182	.185	.191	.191	.191
LC-BLYP	.987	1.065	1.057	1.054	1.059	1.057	1.094
	-.603	-.612	-.616	-.613	-.610	-.610	-.628
	.496	.468	.480	.481	.473	.473	.472
	.181	.212	.202	.205	.212	.212	.211

wB97X-D3	1.061 -.630 .545 .166	1.133 -.638 .529 .190	1.128 -.643 .539 .182	1.127 -.641 .543 .182	1.130 -.637 .537 .188	1.130 -.638 .538 .188	1.166 -.655 .537 .188

Table S2: Calculated HOMO, LUMO, M*,L * for compound **2**

	Def2-SVP	6-311+G*	TZVPP	Def2-TZVPP	ma-def2 QZVPP	Def2-QZVPP	aug-PC-2
B3LYP	1.033 -.639 .546 .148	1.115 -.654 .526 .172	1.112 -.659 .540 .162	1.109 -.657 .542 .146	1.115 -.654 .539 .168	1.115 -.654 .539 .167	1.149 -.670 .537 .168
O3LYP	.988 -.623 .493 .166	1.0583 -.633 .4658 .194	1.0527 -.637 .479 .184	1.0485. -.636 .479 .185	1.0538 -.632 .473 .191	1.0529 -.632 .474 .191	1.0889 -.648 .472 .192
PW6B95	1.0709 -.654 .582 .135	1.155 -.671 .570 .155	1.153 -.676 .584 .146	1.153 -.676 .588 .145	1.159 -.672 .586 .149	1.1600 -.673 .586 .149	1.194 -.689 .584 .150
TPSS0	1.081 -.659 .589 .130	1.180 -.678 .600 .145	1.182 -.684 .615 .137	1.1823 -.684 .618 .136	1.1868 -.681 .617 .139	1.188 -.681 .617 .139	1.221 -.697 .615 .140
Cam-B3LYP	1.0804 -.659 .589 .130	1.165 -.676 .574 .151	1.164 -.681 .589 .142	1.1630 -.679 .592 .142	1.170 -.677 .591 .146	1.1701 -.677 .591 .146	1.203 -.693 .589 .147
LC-BLYP	1.0200 -.641 .541 .141	1.102 -.656 .514 .169	1.0969 -.661 .529 .158	1.0936 -.659 .529 .160	1.101 -.656 .524 .165	1.1008 -.656 .525 .165	1.135 -.672 .523 .166
wB97X-D3	1.0989 -.667 .595 .128	1.174 -.680 .582 .148	1.172 -.685 .594 .140	1.170 -.684 .597 .140	1.1760 -.680 .596 .144	1.177 -.681 .596 .144	1.211 -.697 .595 .144

Table S3

	B3LYP	O3LYP	PW6B95	TPSS0	Cam-B3LYP	LC-BLYP	wB97X-D3
E(XC)*	-245.3	-268.9	-225.3	-230.4	-235.3	-273.9	-228.8

**Exchange-correlation energy a.u.*

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Metal Catalyzed Synthesis and Antimicrobial Studies of Some New Amido Derivatives of Non-Linear Polycyclic Diazapheno-thiazinone

By Evelyn Uloma Godwin-Nwakwasi, Uchechukwu Chris. Okoro, Mercy Amarachukwu Ezeokonkwo, Ifeoma Chinyere Ugwu & Fidelia Ngozi Ibeanu
Gregory University Uturu

Abstract- The synthesis of novel non-linear polycyclic diazaphenothiazine and its amido derivatives via Buchwald – Hartwig reaction protocol is reported. By reacting 2-amino-5-bromopyrazine-3[4*H*]-thione and 2, 3-dichloro-1, 4-naphthoquinone in the presence of anhydrous sodium carbonate, 9-bromo-6-chloro-8, 11-daiza-5*H*-benzo[a] phenothiazin-5-one was obtained. The arylation of 9-bromo-6-chloro-8, 11-daiza-5*H*-benzo[a]pheno-thiazin-5-one with some amides under palladium catalysis gave the amido derivatives in good yield. The stability of these cyclic quinoneimine systems, which has been attributed to ionic resonance effect, is noted. Structural assignments were based on UV, IR and NMR spectra as well as elemental analysis. These compounds showed significant antimicrobial activity against *E. coli*, *Staphylococcus spp*, *Bacillus spp*. and *Pseudomonas aeruginosa* at varying concentrations.

Keywords: synthesis, arylation, amido derivatives and palladium catalysis.

GJSFR-B Classification: *FOR Code: 030399p*

Strictly as per the compliance and regulations of:

Metal Catalyzed Synthesis and Antimicrobial Studies of Some New Amido Derivatives of Non-Linear Polycyclic Diazaphenothiazinone

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Abstract- The synthesis of novel non-linear polycyclic diazaphenothiazine and its amido derivatives via Buchwald – Hartwig reaction protocol is reported. By reacting 2-amino-5-bromopyrazine-3[4*H*]-thione and 2, 3-dichloro-1, 4-naphthoquinone in the presence of anhydrous sodium carbonate, 9-bromo-6-chloro-8, 11-daiza-5*H*-benzo[a] phenothiazin-5-one was obtained. The arylation of 9-bromo-6-chloro-8, 11-daiza-5*H*-benzo[a]pheno-thiazin-5-one with some amides under palladium catalysis gave the amido derivatives in good yield. The stability of these cyclic quinoneimine systems, which has been attributed to ionic resonance effect, is noted. Structural assignments were based on UV, IR and NMR spectra as well as elemental analysis. These compounds showed significant antimicrobial activity against *E. coli*, *Staphylococcus spp*, *Bacillus spp*. and *Pseudomonas aeruginosa* at varying concentrations.

Keywords: synthesis, arylation, amido derivatives and palladium catalysis.

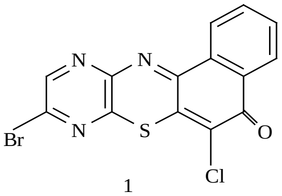
I. Background

It is a well-known fact [1] that transition metal-catalyzed reactions represent an elegant approach to complex molecular scaffolds. The use of reactions catalyzed by transition-metal complexes especially palladium has changed the face of modern organic synthesis and led to the development of radically new methods of building carbon-carbon and carbon-heteroatom bonds [2 – 5]. Besides their esthetics and increase in structural complexity, they have also become tools for combating the challenges posed by the difficulties in constructing C-C, C-N and C-O bonds. Palladium catalyzed substitution reactions forming carbon-carbon and carbon-heteroatom coupling reactions as well as nickel-catalyzed reactions [6-9] across multiple bonds are extensively used in the synthesis of complex organic moieties.

There exist two different aspects in the application of transition metal-catalyzed reactions to the chemistry of heterocyclic compounds. The first involves the building of the heterocyclic backbone and the second, using the heterocyclic fragment as one of the reactions components. Both groups of reactions are equally important though the second one usually has no individual features of its own, replicating the regularities observed in the chemistry of aromatic compounds.

Some of the transition-metal cross-coupling reactions that have revolutionized synthetic strategies include the (i) Buchwald-Hartwig coupling reactions (ii) Heck – Mizoroki Cross-coupling reactions (iii) Suzuki – Miyaura (SM) coupling reactions (iv) Sonogashira reaction of aryl halides using acetylene (alkylnylation), (v) Stille reaction of aryl halides using stannanes, (vi) Migita-Kosugi-Stille Cross-coupling reactions involving organotin compounds, (vii) Negishi pd-catalyzed allyl-alkenyl coupling reactions among others. The influence of metal catalyzed cross-coupling reactions was recognized with Richard Heck, Akira Suzuki and Ei-ichi Negishi being declared the 2010 Chemistry Nobel Laureates for their development of these reactions [10,11].

Although significant advances have occurred in the metal-catalyzed amination and amidation of aryl halides during the last decade, application of this coupling to various heterocyclic structures such as angular azaphenothiazines is still grossly understudied [6,12]. Palladium-catalyzed C-N bond forming reactions between 9-bromo-6-chloro-8, 11-diaza-5*H*-benzo[a]phenothiazin-5-one, 1 and nucleophiles such as amides and amines are still unknown despite continued interest in the chemistry of phenothiazines [13-16] with annular nitrogen atoms. More so, the diverse biological activities of these new compounds spurred our interest the more; hence, we report our studies on these useful reactions.



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II. METHODS

a) *General Information*

Most of the chemicals were purchased from Sigma-Aldrich and were used as purchased because they were of analytical grade. Melting points of the novel compounds were determined using Fisher-Johns melting point apparatus and were uncorrected. ^{1}HNMR, ^{13}CNMR, IR, UV/Visible spectroscopic methods and elemental analysis were employed in their structural characterization. Nuclear Magnetic Resonance (^{1}HNMR and ^{13}CNMR) spectra were done using Varian NMR Mercury-200BB in Central Science Lab. Obafemi Awolowo University Ife. Chemical shifts are reported on the δ-scale (neat). Infrared spectra were recorded using SHIMADZU FTIR-8400S Fourier Transform Infrared Spectrophotometer (KBr discs), at NARICT, Zaria. UV-Visible spectra were done on a JENWAY 6405 UV/VIS Spectrophotometer using matched 1cm quartz cells at the Department of Pure and Industrial Chemistry, University of Nigeria Nsukka. The elemental analyses were carried out at the Central Science laboratory, University of Cairo, Egypt on a CE440 Elemental Analyzer.

b) *Synthesis of 2-Amino-3,5-dibromopyrazine, 3*

Preparation of compound **3** was achieved using literature procedure [13a,17,18]. 9.5 g, (100 mmol) 2-Aminopyrazine was placed in a three-necked flask into which glacial acetic acid (70 ml) has been added. The mixture was warmed on a steam bath until it dissolved. Sodium acetate trihydrate (33 g, 243 mmol) was then added with constant swirling. The reaction mixture was placed in an ice-salt bath and stirred, maintaining the temperature at -5°C while bromine (16 ml) was added drop wise over a 4 h period.

Stirring continued in the ice bath after the addition of bromine for 2 h and then at room temperature for 24 h. The entire crude was poured into ice (50 g) and neutralized with concentrated ammonia (pH 8). 2-amino-3,5-dibromopyrazine (16.8 g, 66%), m.p 113-114°C (Lit.[13a17, 18] 114-115°C) was recrystallized from methanol (Norit) as colourless needles

c) *Synthesis of 2-Amino-5-bromopyrazine-3[4H]–thione, 4*

This intermediate was prepared according to literature[13a, 18]. 2-amino-3,5-dibromopyrazine (7.69 g, 30 mmol) and sodium hydrosulphide (13.33 g, 238 mmol) were added to methanol (60 ml) in a 250 ml three-necked flask equipped with a reflux condenser and a magnetic stirring bar and the mixture was refluxed for 4.5 h.

The solvent (methanol) was then removed by distillation and the residual mixture worked up. Recrystallization using DMF (Norit) furnished pure 2-amino-5-bromopyrazine-3[4*H*]-thione (3.75g, 61%) as a yellow solid, m.p 209-211°C (dec); (lit.[18]208-210°C).

UV-Vis (MeOH): λ_{max} 222 (2.46), 249 (4.16), 340 (3.89), 425 (1.61) nm.

Ir (KBr): ʋmax 3446, 3173, 1563, 1524, 1318, 674cm^{-1}

d) *Synthesis of 9-Bromo-6-chloro-8,11-diaza-5H-benzo[a]phenothiazin-5-one (also known as 9-bromo-6-chloro-8,11,12 triazabenzo[a]anthracen-5-one[18]), 1*

Compound 4 (1.03 g, 5 mmol), anhydrous sodium carbonate (1.06 g, 10 mmol) and benzene (40ml) mixed with dimethylformamide (5 ml) were charged into 100 ml three-necked round-bottom flask fitted with a short magnetic stirring bar and a reflux condenser. The mixture was refluxed for 45 min on a water-bath at 70-75°c while stirring. 2,3-Dichloro-1,4-naphthoquinone (1.14 g, 5 mmol) was added and the mixture refluxed for 7h. At the end of the 7h., the solvent was removed by vacuum distillation. Crushed ice was added and filtration was carried out. The residue was recrystallized from DMF-acetone-water mixture (1:2:2) after treatment with activated charcoal to yield a purplish red crystalline solid which weighed 0.98 g (52%); melted at 238-240°c (lit.[18]>200°c) and identified as 9-bromo-6-chloro-8,11-diaza-5*H*-benzo[a]phenothiazin-5-one, 1.

UV-Vis (MeOH): λ_{max}245 (3.82), 285 (3.76), 335 (3.92) nm.

Ir (KBr): ʋmax 3172, 1674, 1562, 1220, 1121, 820, 702cm^{-1}

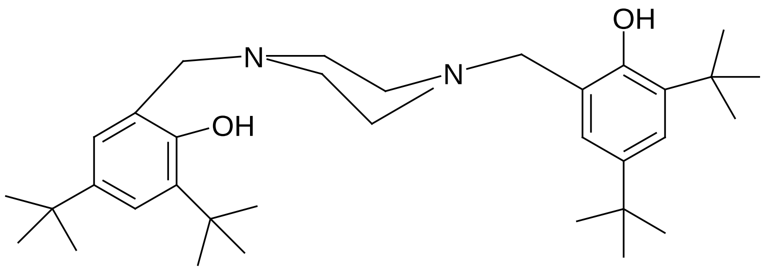
^{1}HNMR (DMSO): δ7.8 - 8.4 (4H, m), 7.2(1H, s),

^{13}CNMR (DMSO): δ160 (C=O), 143 (C-10), 134 (C-10), 127 (C-6), 76 -77(DMSO)

Anal. Calcld for $C_{14}H_5N_3BrSOCl$: C, 44.39; H, 1.32; N, 11.10; Br, 21.14; S, 8.45; Cl, 9.40

Found: $C_{14}H_5N_3BrSOCl$: C, 44.40; H, 1.29; N, 11.20, Br, 21.28; S, 8.50; Cl, 9.49

Preparation of 1,4-bis(2-hydroxy-3,5-di-tert-butylbenzyl)piperazine, $C_{34}H_{54}N_2O_2$,10.



10

The preparation of the ligand, 10 was achieved following Balakrishna *et al* method [22]. Piperazine (2.2 g, 25.54 mmol) was mixed with 40% aqueous formaldehyde solution (5.30 ml, 75.36 mmol) and dissolved in methanol (40 ml). The reaction mixture was refluxed until a clear solution was obtained. After cooling, 2,4-di-*tert*-butylphenol (10.3 g, 50.41 mmol) in methanol (60 ml) was added. The resulting solution was further refluxed for 12 h at 60°C. The mixture was allowed to cool to room temperature and colourless crystals of compound **10** were obtained. Yield: 64% (8.35 g, 15.98 mmol); m.p >250°C (dec) (lit[22]>250°C (dec).

e) *General Procedure for the Palladium-Catalyzed C-N Cross-Coupling Reactions [20]*

An oven-dried 50 ml three-necked flask equipped with a magnetic stir bar and a reflux condenser was charged with $Pd(OAc)_2$(1mol %) and ligand (3mol %). The reaction vessel was flashed with nitrogen and the solvent (2 ml) and degassed water (4mol %) were added via syringe. After the addition of the water, the solution was heated to 110°C for 1.5 min.

Another 50 ml three-necked flask equipped with a magnetic stir bar was charged with base (1.4 mmol), the phenothiazine (1.0 mmol) and amide/amine (1.4mmol) and flashed with nitrogen. The activated catalyst solution was transferred from the first reaction vessel into the second. The entire reaction mixture was heated to 110°C for 3h. At the end of the reflux period, the reaction mixture was cooled to room temperature. After removal of the solvent in vacuo, the compound of interest was recrystallized from ethyl acetate-water mixture.

f) *6-Chloro-9-ethanamido-8,11-diaza-5H-benzo[a]-phenothiazin-5-one, 9a.*

A mixture of 9-bromo-6-chloro-8,11-diaza-5*H*-benzo[a]phenothiazin-5-one (0.378 g, 1.0mmol), acetamide (0.083 g, 1.4 mmol), K_3PO_4 (0.297 g, 1.4 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), 1,4-bis(2-hydroxy-3,5-di-*tert*-butyl-benzyl)piperazine (0.016 g, 0.03 mmol), H_2O (1μl, 0.04 mmol) and t-BuOH (2 ml) was heated to 110°C for 3h. After removal of the solvent in vacuo, the compound of interest was recrystallized from ethyl acetate-water mixture as a dark brown solid (0.403 g, 80.4%), m.p 106-108°C.

UV-Vis (MeOH): λ_{max}221.8 (4.40), 251.2 (4.32), 345.6 (3.92), 514.4 (3.06) nm.

Ir (KBr): υmax 3300, 3158, 2861,1672, 1553, 705 cm^{-1}

^{1}HNMR (DMSO): δ8.5 (1H, s, N-H), 8.1 (4H, m), 7.0 (1H, s), 1.8 (3H, s, CH_3).

^{13}CNMR (DMSO): δ166 (C=O), 153 (C-9), 143 (C α to C-6), 135 (C-10), 127 (C-1 & C-4), 123 (C-6), 38.7 – 41.2 (DMSO).

*Anal.*Calcld for $C_{16}H_9N_4SO_2Cl$: C, 53.86; H, 2.52; N, 15.71; S, 8.97; Cl, 9.96

Found: $C_{16}H_9N_4SO_2Cl$: C, 53.80; H, 2.45; N, 15.60; S, 9.06; Cl, 10.09

g) *9-Benzamido-6-chloro-8,11-diaza-5H-benzo[a]phenothiazin-5-one, 9b*

9-bromo-6-chloro-8,11-diaza-5*H*-benzo[a]phenothiazin-5-one (0.378 g, 1.0mmol), benzamide (0.169 g, 1.4 mmol), K_3PO_4 (0.297 g, 1.4 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), ligand (0.016 g, 0.03 mmol), H_2O (1μl, 0.04 mmol) and t-BuOH (2 ml) as a mixture was heated to 110°C for 3h. After removal of the solvent in vacuo, the compound of interest was recrystallized from ethyl acetate-water mixture as a reddish-brown solid (0.421 g, 80%) m.p 115-117°C.

UV-Vis (MeOH): λ_{max}245.2 (4.38), 317 (4.13), 3661.6 (3.73), 502.4 (3.47) nm.

Ir (KBr): υmax 3300, 3173,1665, 1566, 1277, 697 cm^{-1}

^{1}HNMR (DMSO): δ8.3 (1H, s, N-H), 8.1(4H, m), 7.5 (4H, m), 6.9 (1H, s,).

^{13}CNMR (DMSO): δ168(C=O), 153.7 (C-9), 134 (C-2), 131(C-3), 129 (C-1, C-4 & C-10), 128(C at *m*-position in benzamido moiety), 115(C-6), 38.7 – 41.2 (DMSO).

*Anal.*Calcld for $C_{21}H_{11}N_4SO_2Cl$: C, 60.22; H, 2.63; N, 13.40; S, 7.65; Cl, 8.48

Found: $C_{21}H_{11}N_4SO_2Cl$: C, 60.35; H, 2.60; N, 13.42; S, 7.80; Cl, 8.36

h) *6-Chloro-9-(4-nitrobenzamido)-8,11-diaza-5H-benzo [a]phenothiazin-5-one, 9c.*

A mixture of 9-bromo-6-chloro-8,11-diaza-5*H*-benzo[a]phenothiazin-5-one (0.378 g, 1.0mmol), 4-

nitrobenzamide (0.232 g, 1.4 mmol), K_3PO_4 (0.297 g, 1.4 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), ligand (0.016 g, 0.03 mmol), H_2O (1 µl, 0.04 mmol) and t-BuOH (2 ml) was heated to 110°C for 3h. After removal of the solvent in vacuo, the compound of interest was recrystallized from ethyl acetate-water mixture as a reddish-brown solid (0.374 g, 57.7%), m.p 129-131°C.

UV-Vis (MeOH): λ_{max}222 (4.43), 249.8 (4.47), 338.6 (3.92), 494 (1.97) nm.

Ir (KBr): υmax 3452, 3167,1688, 1609, 1538, 1334, 711 cm^{-1}

^{1}HNMR (DMSO): δ8.5 (1H, s, N-H), 8.2 (4H, m), 7.8 (4H, m), 6.9 (1H, s).

^{13}CNMR (DMSO): δ166 (C=O), 153 (C-9), 150 (C-NO_2), 143.5 (C α to C-6), 136.9 (C α to C-4), 134 (C-2), 131 (C-3), 129 (C-1, C-4 & C-10),127.5 (C at *o*-position in the nitrobenzamido moiety), 124 (C-6 & C at *m*-position in the benzamido moiety), 38.7 – 41.2 (DMSO).

*Anal.*Calcld for $C_{21}H_{10}N_5SO_4Cl$: C, 54.37; H, 2.24; N, 15.10; S, 6.90; Cl, 7.66

Found: $C_{21}H_{10}N_5SO_4Cl$: C, 54.40; H, 2.19; N, 15.25; S, 6.80; Cl, 7.81

i) 6-Chloro-9-ureacyl-8,11-diaza-5H-benzo[a]phenolthiazin-5-one, 9d.

A mixture of 9-bromo-6-chloro-8,11-diaza-5*H*-benzo[a]phenothiazin-5-one (0.378 g, 1.0mmol), urea (0.084 g, 1.4 mmol), K_3PO_4 (0.297 g, 1.4 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), ligand (0.016 g, 0.03 mmol), H_2O (0.04 mmol) and t-BuOH (2 ml) was heated to 110°C for 3h. After removal of the solvent in vacuo, the title compound was recrystallized from ethyl acetate-water mixture as a brown solid (0.343 g, 47%), m.p 102-104°C (dec).

UV-Vis (MeOH): λ_{max}249.6 (4.50), 340.2 (4.08), 496.2 (3.16) nm.

Ir (KBr): υmax 3458, 3359, 3168, 1680, 1609, 1454, 1284, 712 cm^{-1}

^{1}HNMR (DMSO): δ8.5 (1H, s, N-H), 7.8 (4H, m), 6.9 (1H, s), 5.5 (2H, s, N-H).

^{13}CNMR (DMSO): δ180, 177 (C=O), 153 (C-9), 143 (C α to C-Cl), 135 (C-2), 133 (C-3), 127 (C-1, C-4 & C-10), 123 (C-6), 38.7 – 41.2 (DMSO).

*Anal.*Calcld for $C_{15}H_8N_5SO_2Cl$: C, 50.35; H, 2.24; N, 19.58; S, 8.98; Cl, 9.93

Found: $C_{15}H_8N_5SO_2Cl$: C, 50.50; H, 2.10; N, 19.60; S, 9.00; Cl, 9.95

j) 6-Chloro-9-(3-nitroanilino)-8,11-diaza-5H-benzo[a]-phenothiazin-5-one, 9e.

A mixture of 9-bromo-6-chloro-8,11-diaza-5*H*-benzo[a]phenothiazin-5-one (0.378 g, 1.0mmol), 3-nitroaniline (0.193 g, 1.4 mmol), K_3PO_4 (0.297 g, 1.4 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), ligand (0.016 g, 0.03 mmol), H_2O (1 µl, 0.04 mmol) and t-BuOH (2 ml) was heated to 110°C for 3h. After removal of the solvent in vacuo, the compound of interest was recrystallized from ethyl acetate-water mixture as a dark brown solid (0.518 g, 85%), m.p, 96-98°C.

UV-Vis (MeOH): λ_{max}241.2 (4.80), 341.8 (4.19), 497 (3.12) nm.

Ir (KBr): υmax 3302, 3087,1674, 1523, 1342, 725 cm^{-1}

^{1}HNMR (DMSO): δ8.4 (1H, s), 8.2 (4H, m), 7.5 (1H, s), 7.3 (3H, m), 7.0 (1H, s), 5.8 (1H, s.N-H)

^{13}CNMR (DMSO): δ161(C=O), 150.5 (C-9), 143 (C α to C-Cl), 130 [(C -3 & to C-9-(5)], 120 [(C-6 & C-9-(6)], 107 [(C-9-(2)], 38.7 – 41.2 (DMSO).

*Anal.*Calcld for $C_{20}H_{10}N_5SO_3Cl$: C, 55.11; H, 2.30; N, 16.07; S, 7.35; Cl, 8.15

Found: $C_{20}H_{10}N_5SO_3Cl$: C, 55.21; H, 2.36; N, 16.00; S, 7.45; Cl, 8.20

k) 6-Chloro-9-phthalimido-8,11-diaza-5H-benzo[a]-phenothiazin-5-one, 9f.

A mixture of 9-bromo-6-chloro-8,11-diaza-5*H*-benzo[a]phenothiazin-5-one (0.378 g, 1.0mmol), phthalimide (0.206 g, 1.4 mmol), K_3PO_4 (0.297 g, 1.4 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), 1,4-bis(2-hydroxy-3,5-di-*tert*-butyl-benzyl)piperazine (0.016 g, 0.03 mmol), H_2O (1µl, 0.04 mmol) and t-BuOH (2 ml) was heated to 110°C for 3h. After removal of the solvent in vacuo, the title compound was recrystallized from ethyl acetate-water mixture as a greyish-brown solid (0.420 g, 67.9%), m.p, 118-120°C.

UV-Vis (MeOH): λ_{max}222.2 (4.46), 245.8 (4.56), 273.8 (4.39), 338 (4.16), 360 (4.00), 498 (3.44) nm.

Ir (KBr): υmax 3156, 1674, 1674, 1494, 1367, 705 cm^{-1}

^{1}HNMR (DMSO): δ8.5 (1H, s), 8.1 (4H, m), 7.8 (4H, m), 6.9 (1H, s).

^{13}CNMR (DMSO): δ180, 176 (C=O), 153.7 (C-9), 143 (C α to C-6), 135 (C-2), 131(C-3), 127 (C at phthalimido moiety), 123 (C-6), 38.7 – 41.2 (DMSO).

*Anal.*Calcld for $C_{22}H_9N_4SO_3Cl$: C, 59.39; H, 2.02; N, 12.59; S, 7.20; Cl, 7.99

Found: $C_{22}H_9N_4SO_3Cl$: C, 59.25; H, 2.06; N, 12.58; S, 7.33; Cl, 8.00

l) Antibacterial Activity of the Synthesized Angular Diazaphenothiazinones

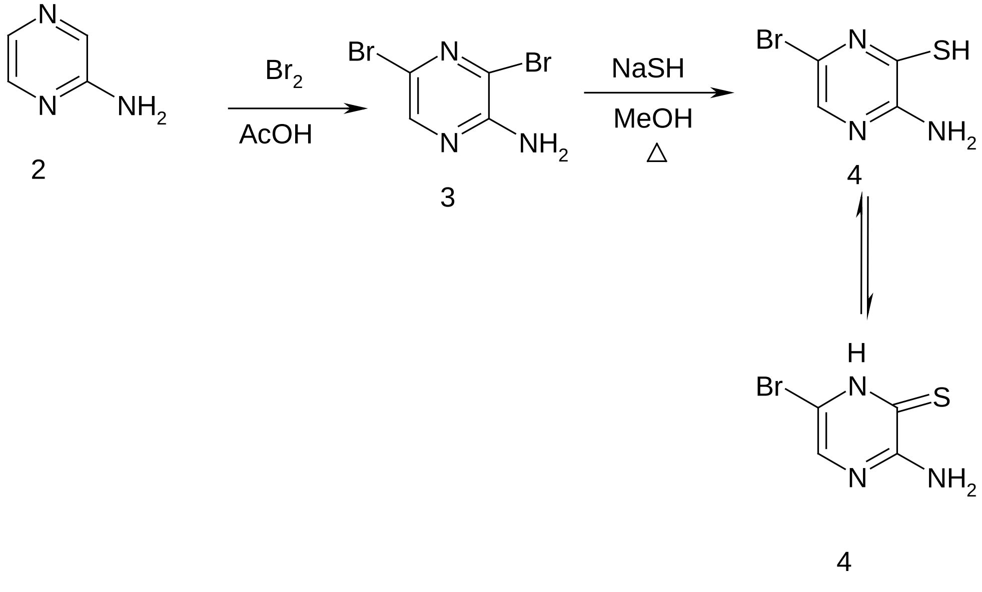
The antibacterial activity of the synthesized Angular Phenothiazinones was conducted using agar-well diffusion method [23]. Solution of each compound with a 20 mg/ml concentration was made by dissolving 0.04 g of each compound in 2 ml dimethyl sulfoxide (DMSO). A colony of each test bacteria isolate was picked and mixed with 2ml of sterile nutrient broth in a bijoux bottle. Each mixture of test bacteria isolate was standardized to correspond to 0.5 McFarland turbidity standards (approximately 10^8 cfu/ml). This suspension was used to inoculate onto the surface of iso-sensitest agar and the excess fluid drained into discard pot containing disinfectant. The inoculated agar was allowed to air dry and the petri dishes were appropriately labelled. A cork borer with a diameter of 6mm was used to bore wells onto the inoculated iso-sensitest agar. Then a micropipette was used to deliver 50µl of each test compound solution into each well. The petri dishes were left on the bench for 30 minutes so that the compound would diffuse into the solid agar. Thereafter, the petri dishes were put in the incubator at 37°C for 24h. After 24h incubation, the petri dishes were checked for zone of inhibition around the wells. The inhibition zone diameters were measured with metre rule and recorded to the nearest whole millimetre.

m) Minimum Inhibitory Concentration (MIC) of the Synthesized Angular Diazapheno-thiazinones.

The minimum inhibitory concentration of these non-linear diazaphenothiazines was done using agar dilution method as stated by Clinical Laboratory Standards Institute (CLSI) [24]. One millilitre of DMSO was put into sterile test tubes that were lined up on a test tube rack. Two-fold serial dilution of each compound suspension was done by transferring 1 ml of each compound solution (20mg/ml) into the first test tube and from the first to the second test tube and so on till the seventh one. The concentration of the solutions in each test tubes were as follows: 10, 5, 2.5, 1.25, 0.625, 0.3125, and 0.15625 (mg/ml)(i.e, graded concentrations of the compounds). After the dilutions, 1ml of each resultant solution was added into 19 ml each of sterilized molten agar, mixed very well and poured onto sterilized petri dishes. These petri dishes with compound amended agar were left to cool and gel on the bench. Then, a colony of each test bacteria isolate was picked and used to inoculate 2ml sterile nutrient broth making a suspension of each test bacterium. All the suspensions of the test bacteria were standardized. Ten microlitre of each bacterial suspension was spot-inoculated onto the surface of the agar using a micropipette. Agar without any of the test compound was also spot-inoculated as positive controls. The inoculated petri dishes were incubated at 37°C for 24 h. After incubation they were checked for any visible bacterial growth. MIC was recorded as the least concentration of the compounds that showed no visible bacteria growth on the agar surface.

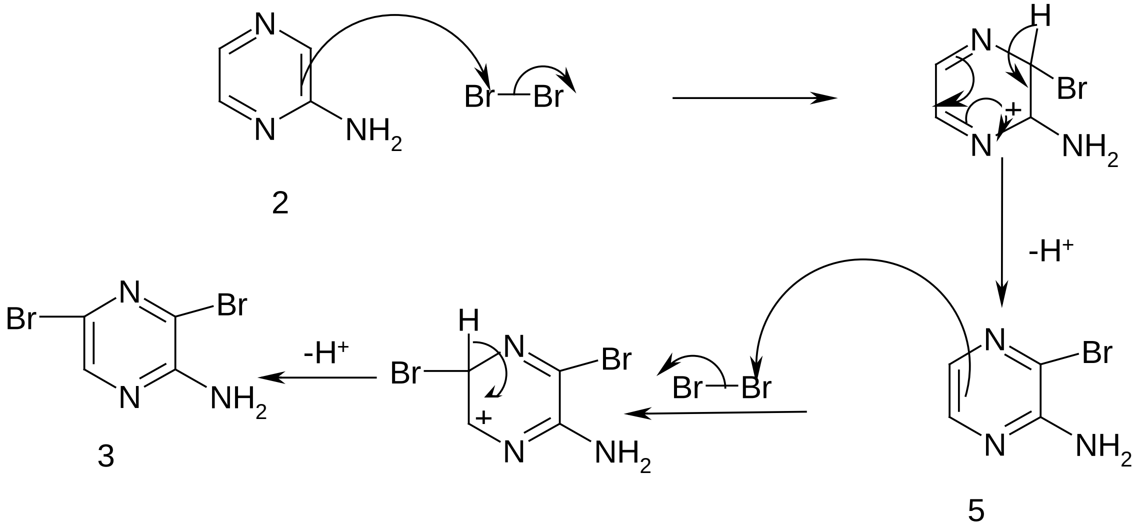
III. Results and Discussion

2-Aminopyrazine, 2, was converted to the 3,5-dibromo derivative, 3, by the action of bromine in glacial acetic acid as also reported by Okafor [17]. Thiation of product 3 using sodium hydrosulphide (NaSH) in methanol furnished 2-amino-5-bromopyrazine-3[4*H*]-thione, 4 (scheme 1).



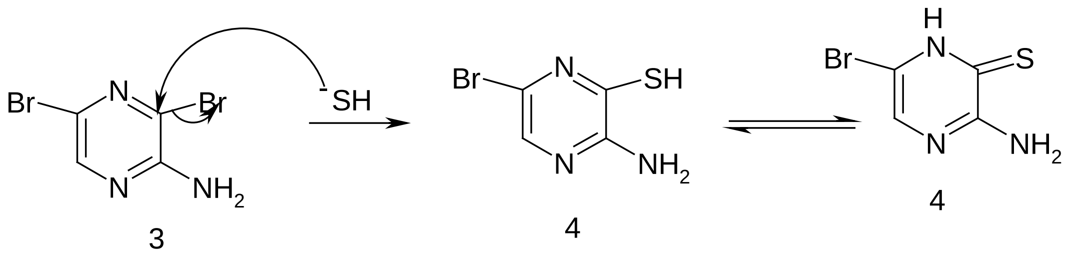
Scheme 1: Synthesis of compound **4**

The possible mechanisms of these reactions are shown in schemes 2 and 3. Under acidic condition, bromine mounts electrophilic attack on carbon in position 3 followed by proton elimination to give compound **5**. Another electrophilic attack is mounted on carbon in position 5 and with hydride elimination; compound 3 is produced as colourless needles on recrystallization from methanol (Norit). It melted at 113 – 115°C (Lit[17], 114 – 115°C).



Scheme 2: Possible mechanism of forming compound 3

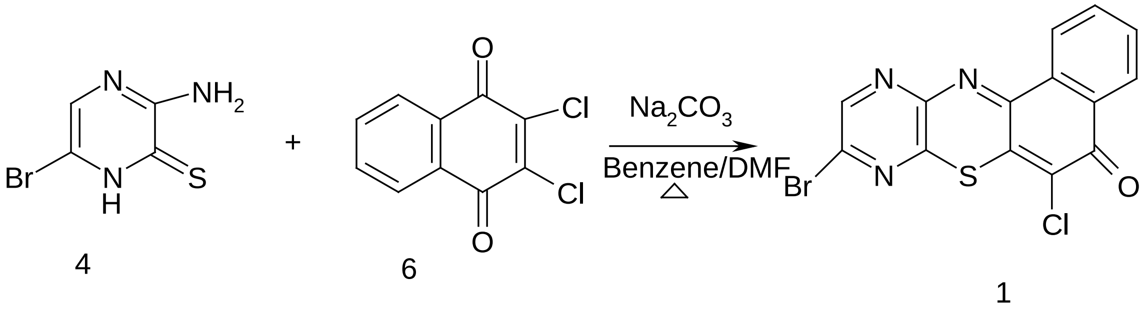
Because of the high reactivity of pyrazine derivatives with nucleophilic agents such as sodium hydrosulphide the displacement of bromine in bromopyrazines like compound 3 proceeds with relative ease. The mercapto group SH$^-$ attacks the carbon at the 3-position displacing the bromine atom giving compound 4 and there could also be hydride shift.



Scheme 3: Possible mechanism for forming compound 4

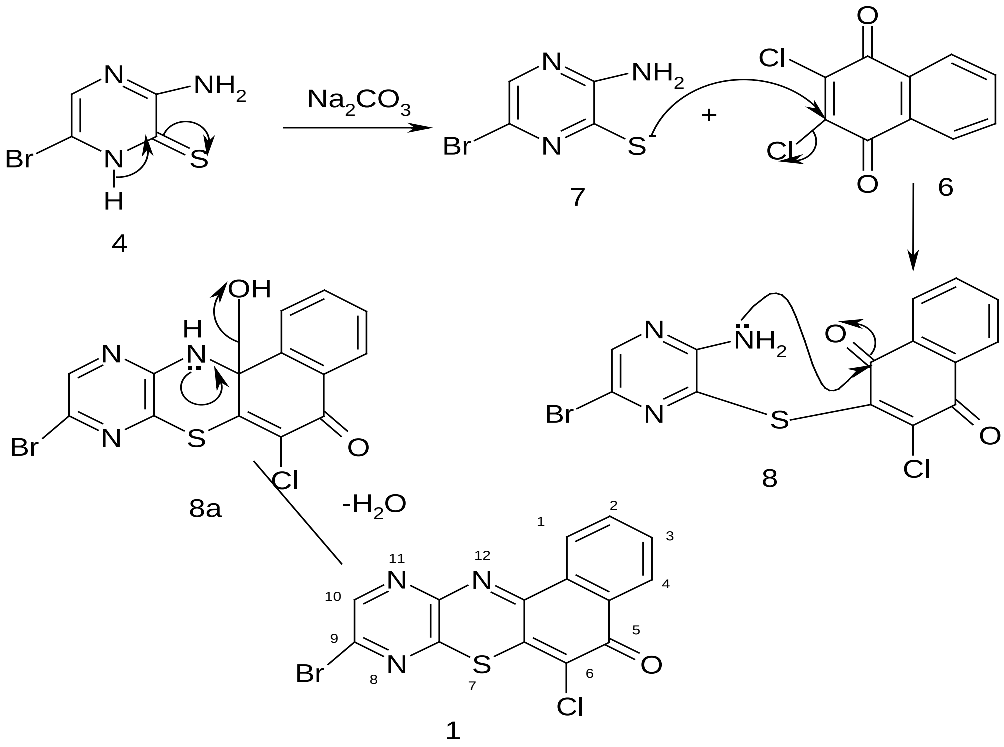
The UV-Vis spectrum gave absorptions at λmax 222 (ε=2.46), 249 (4.16), 340 (3.89) and 425 (1.61) nm. Infrared spectrum (cm^{-1}) showed absorption signals at 3446 (N-H stretch), 3173 (C-H aromatic rings), 1563, 1524 (C =C aromatic rings) and 674 (C – Br stretch). Other bands also agree with the assigned structure.

Condensation reaction (scheme 4) between 2-amino-5-bromopyrazin-3[4*H*]-thione, 4 and 2,3-dichloro-1, 4-naphthoquinone,6, in the presence of anhydrous sodium carbonate furnished compound 1 which was a purplish red crystalline solid melting at 238 – 240°C dec. (Lit[18], > 200°C dec.)



Scheme 4: Synthesis of compound **1**

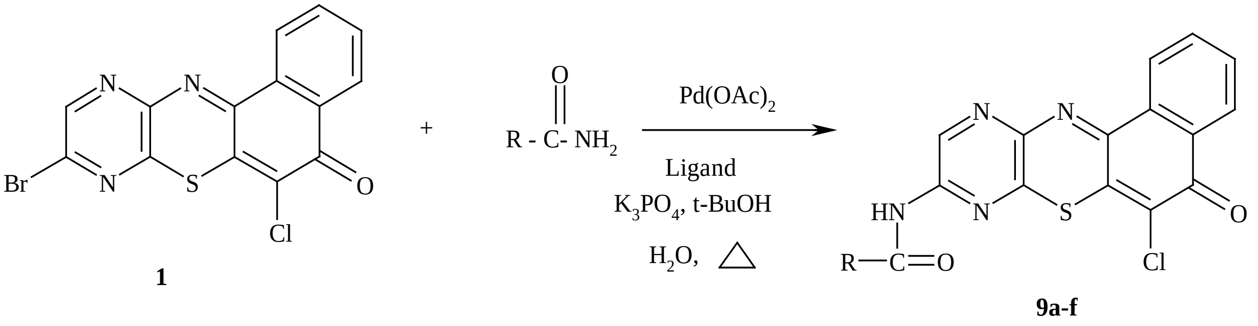
The proposed mechanism (scheme 5) for this reaction could be by an initial nucleophilic attack of the dichloronaphthoquinone, 6, by the mercaptide ion, 7, which results in the formation of the diaryl sulphide, 8. Cyclization takes place by the condensation of the amino group with the carbonyl group in the naphthoquinone moiety. Eliminationoccurs giving 9-bromo-6-chloro-8, 11-diaza-5*H*-benzo[a]phenothiazin-5-one, 1. Compound 1 is an intensely coloured solid due to its extended conjugated system and it is air stable.



Scheme 5

Microanalysis and spectroscopy agree with the assigned structure. The UV-Vis spectrum showed bands at λmax 245 (ε=3.82), 285 (3.76) and 335 (3.92) nm. The infrared spectrum gave signals (cm^{-1}) at 3172 (C-H aromatic rings), 1674 (C=O), 1562 (C=C aromatic rings), 1220, 1121 (C=-N stretch), 820 (C-Cl and 720 (C – Br). The ^{1}HNMR gave peaks at 8.4 (m, 4H) and 7.2 (s,1H). The absorption at δ2.3 is due to dimethyl sulfoxide (DMSO). The ^{13}CNMR showed signals at δ160 (C = O), 143 (C – 10), 134 (C – 2), 127 (C – 6). Peaks at δ76 - 77 were attributed to the solvent used (DMSO).

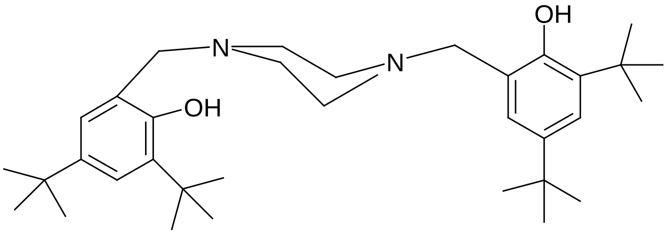
Using Pd(OAc)$_2$, 1,4-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)piperazine, t-BuOH, K$_3$PO$_4$, water and at 110°C, cross-coupling reactions were carried out between compound 1 and some amides/amines (Buchwald-Hartwig reaction) to furnish compounds 9a-f (scheme 6).



R = Me, Phenyl or substituted phenyl

Scheme 6: Synthesis of compounds 9a-f

The protocol utilized water and piperazine ligand, 10, to reduce Pd(OAc)$_2$ and generate the active LnPd(0) complex. The activation was monitored visually by colour change.



10

a) *1,4-bis(2-hydroxy-3,5-di-tert-butylbenzyl)piperazine,* $C_{34}H_{54}N_2O_2$, *10*

This type of activation was first published in 1992 by Ozawa and Hayashi [19] in which they were able to reduce $Pd(OAc)_2$ in the presence of 3 equivalents of BINAP. According to their report, in the absence of water, the reduction did not proceed; however by adding extra equivalents of water, the rate of activation could be accelerated. Similarly, Buchwald et al [20] successfully coupled even electron-deficient 4-nitroaniline and 2-nitroaniline with 4-n-butylchlorobenzene in excellent yield by performing a water-mediated catalyst pre-activation of $Pd(OAc)_2$. The reaction sequence of this type of activation can be deduced as follows:

$$2L + Pd(II)(OAc)_2 \rightleftharpoons L_2Pd(II)(OAc)_2$$

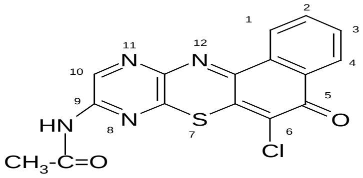
$$LPd(0) + L(oxide) \xleftarrow[-2HOAc]{H_2O} LPd(0)(OAc)^- + AcOL^+$$

This can be simplified as:

$$dX_2 + Ph_3P + H_2O \longrightarrow Pd(0) + Ph_3PO + 2HX$$

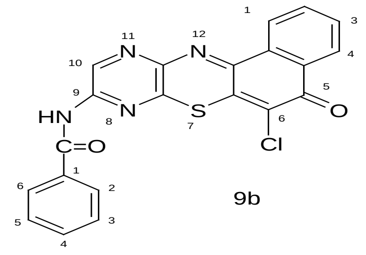
The achievement here is that we have been able to utilize piperazine compound (a bidentate ligand) instead of Ph_3P to achieve the purpose of reduction of Pd(II) to Pd(0). This is in agreement with an earlier report by Buchwald *et al*[20]who used XPhos as their ligand, although XPhos is a monodentate ligand.

Compounds 9a-f were identified based on their microanalysis and the spectroscopic data available as 6-chloro-9-ethanamido-8,11-diaza-5*H*benzo[a]phenothiazin-5-one, 9a; 9-benzamido-6-chloro-8, 11-diaza-5*H*-benzo{a}phenothiazin-5-one, 9b; 6-chloro-9- (4-nitrobenzamido)-8, 11-diaza-5*H*-benzo[a]phenothiazin-5-one, 9c; 6-chloro-9-ureacyl-8, 11-diaza-5*H*-benzo[a]phenothiazin-5-one, 9d; 6-chloro-9-(3-nitroanilino)-8, 11-diaza-5*H*-benzo[a]phenothiazin-5-one, 9e and 6-chloro-9-phthalimido-8, 11-diaza-5*H*-benzo[a]phenothiazin-5-one,9f.

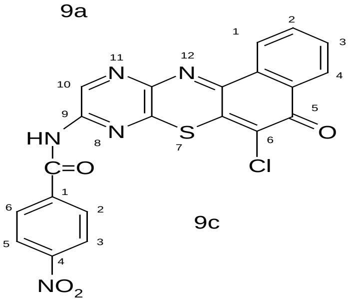


9a

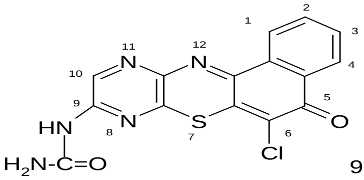
+ ;



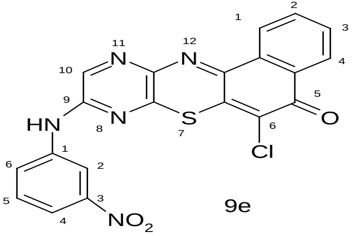
9b



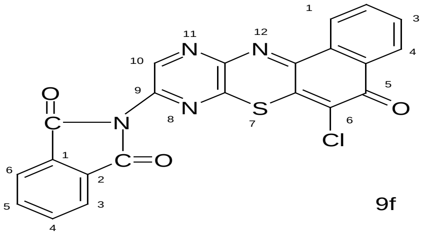
9c



9d



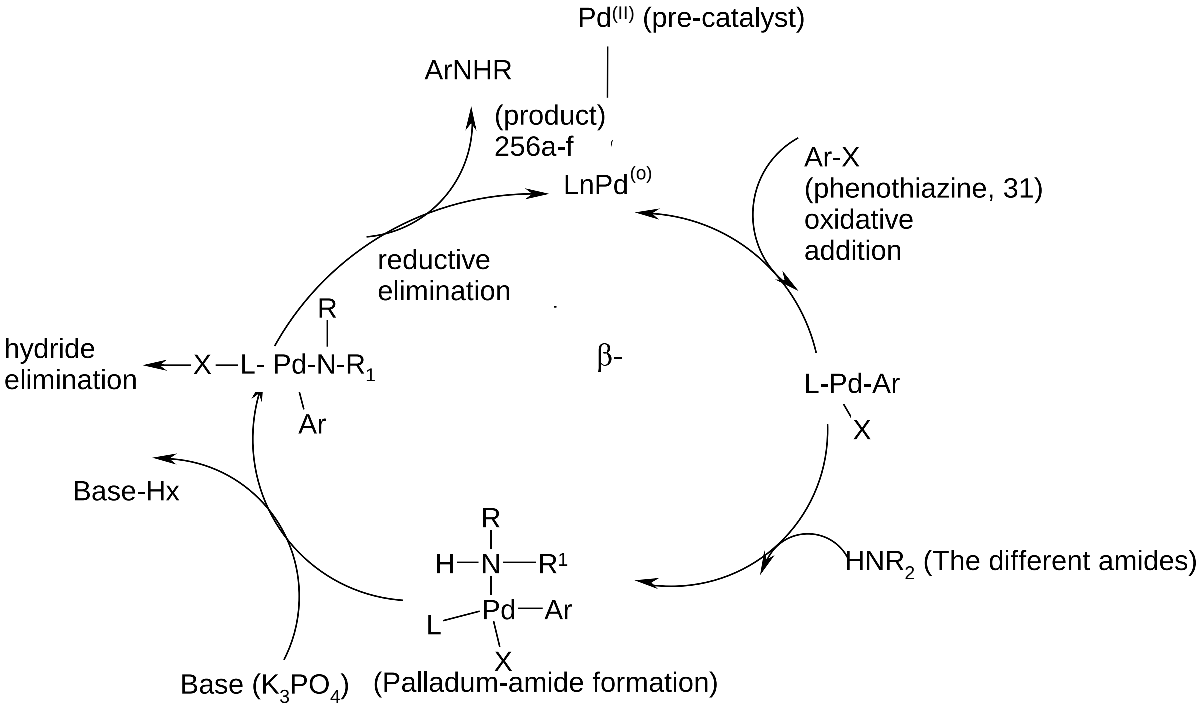
9e



9f

The physical, analytical and spectroscopic data for compounds 9a-f are summarized in the experimental section.

The mechanism of these reactions (scheme 7) follows the general mechanism[21] for Buchwald-Hartwig coupling reactions. The reaction mechanism has been demonstrated to proceed through steps similar to those known for palladium-catalyzed C-C coupling reactions. The steps involve oxidative addition; palladium-amide formation and finally reductive elimination.



Scheme 7: Possible mechanism for the synthesis of compounds 9a-f

The antimicrobial activity of these newly synthesized compounds was evaluated and the data obtained showed they had significant inhibitory effects. An effective approach of antimicrobial therapy of an infection is based on the isolation and identification of the infected organism and determining its sensitivity to antimicrobial drugs. The bacteria tested were three*E. coli* strains (Eco 3, Eco 4 and Eco 12), 2 *Staphylococcus species (Staphylococcus pseudointermedius* and *Staphylococcus scuiri)*, *Bacillus subtilis* and *Pseudomonas aeruginosa*. Table 1 below shows the result of the antibacterial susceptibility test. Seven compounds tested against seven bacteria isolates comprising of Gram Positive and Gram negative bacteria. The result of the preliminary screening of the seven compounds tested against the above mentioned Gram negative and Gram positive bacteria are shown in Table 1.

Table 1: Antibacterial Activity of Synthesized Angular Phenothiazinones showing Inhibition Zone Diameter (mm) produced by the Compounds tested (20mg/ml)

Cpd	*S. pseudointermedius*	*S. scuiri*	Eco 3	Eco 4	Eco 12	*Bacillus subtilis*	*Pseudomonas aeruginosa*
1	16	19	14	12	11	16	0
9a	17	16	12	12	15	18	0
9b	15	15	11	11	11	18	0
9c	17	17	17	18	16	17	0
9d	19	20	17	18	18	30	0
9e	15	16	11	12	12	16	0
9f	16	14	11	12	12	16	0

Cpd = compound

The figures in Table 1 show the inhibition zone diameter (IZD) produced by each compound against the test bacteria at 20 mg/ml concentration. It ranged between 11 and 30 mm in diametre; the higher the IZD, the higher the sensitivity. The test compounds produced good activity against all the test bacteria except *Pseudomonas aeruginosa*. This implies that the compounds that produced high IZD have high antibacterial activity against the test bacteria.

The results of the MIC of the test compounds ranged between 0.625 and 5mg/ml. Hence, Table 2 below shows the result of MIC of the test compounds, Ampicillin and Gentamicin against Eco 3, *S. scuiri* and *Bacillus subtilis*.

Table 2: Minimum Inhibitory Concentration (mg/ml) of the Synthesized Compounds, Ampicillin and Gentamicin against test Bacteria

Compound/Drug	Eco3 (mm)	*S. scuiri*(mm)	*Bacillus subtilis*(mm)
1	5	1.25	1.25
9a	5	1.25	1.25
9b	5	1.25	1.25
9c	2.5	1.25	1.25
9d	1.25	1.25	0.625
9e	5	1.25	1.25
9f	5	1.25	1.25
Ampicillin	100	2.5	1.25
Gentamicin	6.25	2.5	0.15625

The MIC against the test bacteria ranged from 0.625 mg/ml to 5 mg/ml. It became necessary to compare the MICs of the synthesized compounds with some antibiotics against the bacteria tested. Ampicillin and Gentamicin were used as positive control because they are among the drugs used in the treatment of infections caused by similar strains of bacteria while DMSO served as the negative control.

The MIC of the drugs used ranged between 0.15625 mg/ml and100 mg/ml. From Table 2, most of the synthesized phenothiazine derivatives were active against E. coli strain (Eco 3) at very low concentrations whereas Ampicillin has its MIC against Eco 3 as 100 mg/ml which shows that the E. coli strain is highly resistant to Ampicillin. The MIC of Gentamicin showed MIC of 6.25 mg/ml against Eco 3 which is still greater than that of the test compounds especially compounds **9c** and **9d**. This same explanation goes for G84. It was only in the case of *Bacillussubtilis* that the MIC values of novel compounds compared favourably with those of the standard drugs with Gentamicin having the lowest MIC value, 0.15625 mg/ml. All these show that the synthesized phenothiazine derivatives are highly biologically active; hence, they are of pharmaceutical interest.

IV. CONCLUSION

The syntheses of these biologically active novel angular diazaphenothiazinones have in no small measure extended the list of phenothiazine derivatives of medicinal importance. Again, the carbon-nitrogen coupling reaction catalyzed by transition metal (palladium $^{(0)}$) leading to the synthesis of these derivatives has opened a new route of synthesis.

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Authors' Contributions

EUGN and UCO designed the work, carried out the syntheses and characterization of all the compounds. ICU and EUGN did the antimicrobial screening. EUGN, UCO and ICU contributed in the manuscript write-up. MAE and FNI edited and scrutinized the article. All authors read and approved the submission of this manuscript.

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The Introduction of the Informatics Potential and the Kinetics of Informatics: The Spontaneous and Non-Spontaneous Enmorphy

By Dimitrios Samios

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Abstract- In this paper the Informatics Potential is introduced as a consequence of the four energetic potentials, namely, dH the enthalpy, dA the free energy of Helmholtz, dG the free energy of Gibbs and dE the internal energy, and the chemical potential $d\mu_i$. In the informatics, the matter is the Information and the Enmorphy, and for this reason, the Informatics Potential was introduced. Then, a general and unified kinetic theory of informatics was presented, similar to chemical kinetic theory. The main issue is the transformation of Information into Order. The order, in this case, means: structure, organization, form, aligning, composition, establishment, grouping, layout, pattern, scale, sequence, symmetry and uniformity and all other notions which can be understood as the order. The general kinetic theory of informatics can be applied to all areas of science, i.e, physics, chemistry, medicine, biology, geosciences, agronomy, architecture and civil engineering, social sciences, and several other disciplines aiming knowledge.

GJSFR-B Classification : FOR Code: 030703

The Introduction of the Informatics Potential and the Kinetics of Informatics: The Spontaneous and Non-Spontaneous Enmorphy

Dimitrios Samios

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I. INTRODUCTION

Edgar Morin (1) in his book *The seven knowledge necessary for the education of the future* working with the notion complexity cited Claude Bastien (2) who said that *cognitive evolution does not lead to the establishment of increasingly abstract knowledge, but, instead, to its contextualization.* The physicist Stephen Hawking (3) answer to question: *Some say that while the twentieth century was the century of physics, we are now entering the century of biology. What do you think of this?* The answer of Hawking: *I think the next [21st] century will be the century of complexity. We have already discovered the basic laws that govern matter and understand all the normal situations. We don't know how the laws fit together, and what happens under extreme conditions. But I expect we will find a complete unified theory sometime this century. There is no limit to the complexity that we can build using those basic laws*.

Based on this and having in mind the complexity and contextualization and the expression of Hawking which said, *we don't know how the laws fit together*, this contribution aims to aggregate and elucidate the questions: what is the Informatics Potential, and how the unified kinetic theory of informatics works?

In previous publications (4,5) the notion of enmorphy was introduced and defined as a function of the logarithmic expression of the disorder. Considering that the information corresponds to energy, and enmorphy corresponds to the entropy, thinking analogically, we introduced the temperature and the time as the variables of the integrating factor. Following the same logic, the information is directly related to order created through equation 1. In this equation, I is the information, c the proportionality factor, it achieves values between 0 and 1, and O is the order created.

$$I = c\,O \qquad [1]$$

Equation 2 was proposed verbally by Schrödinger (6) in his work *what is life*. In this equation, O is the order, and D is the disorder.

$$O.D = 1 \qquad [2]$$

Physical-chemistry, according to Blinder (7), considers that there are four energetic potentials, namely: dH the enthalpy, dA the Free energy of Helmholtz, dG the free energy of Gibbs and dE the internal energy. Chemistry, on the other hand, introduces the chemical potential, $d\mu i$, that depends on the chemical composition of the reaction and the state (pressure and temperature) of the matter before the start of the reaction. To perform a chemical reaction we need at least two components, excluding nuclear reactions. The materials of the reactions are transformed and take another form and the nature of the product very little resembles the nature of the components. The number of reactions known to man is very high. These transformations, according to the chemical potential, are always spontaneous, depending on the temperature and pressure conditions, and on the chemical equilibrium that establishes the relationship between the components and the reaction product. To accelerate or slow down the reaction rate, we need to increase or decrease the temperature or pressure.

We can even alter the chemical equilibrium, and for this, we need more knowledge about the reaction and the consequences of changing the pressure and temperature parameters. Knowledge equals to information. The reaction needs to be fed with additional information.

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In Physical-chemistry, the part that refers to physicist is the part of the observer who tries to explain, with experiments and theories, the phenomena of nature; the part that refers to chemist is that the researcher studying the reactions creates information to be able to do intelligent or non-intelligent actions, in other words, to manipulate the chemical equilibrium.

The human being, through observation, experiment and theory, managed to overcome superstition, overcome magic and create physics as the first of science. Along with this path, great thinkers had the capacity for abstraction and sharp intelligence to replace magic with physical science. This process forces the thinker to be abstract from beliefs up to that moment valid as true.

Shannon [8-11] carried out the publication of computer mathematics in 1941. Between Szilard (12) and Shannon and after them, there are many other thinkers who have made important contributions in computer science. The researcher felt the weight of information in any area. That is why today we cannot exclude computing from any interdisciplinary research. Nowadays we cannot imagine interdisciplinary without the participation in computer science.

The history of science teaches us that physicists of the Renaissance could observe and did not interfere with nature. Physicists discovered the secrets of nature without interfering with nature or were observers and experimenters. This direction changed radically from the moment of Le Chatelier's (13, 14) formulation. This principle defined the chemical equilibrium between the products of the reaction and the materials before it, and is one among other principles of chemistry which received much attention from 19th-century researchers. On the other hand, early 20th-century, physicists with atomic science began using nuclear energy for peaceful and bellicose purposes, and biologists in recent years started working with mutagenesis of plants and animals, therefore assume an interference with nature.

At this moment we do feel the need to introduce the "Informatics Potential" presented as dI. Following the analogical method, we treated the Informatics Potential similarly to the Chemical Potential dμi. Then the Informatics Kinetics is presented alike to the Chemical Kinetics. However, in the case of chemistry and engineering, very small efforts have been applied to control the entropy produced, and the entropy corresponds to the enmorphy.

Then, for the case of chemistry we can write the general expression:

$$d\mu/dt = k1\, \mu_1{}^{n}\, \mu_2{}^{m} + k2\mu_3{}^{l}\mu_4{}^{p}, \qquad [3]$$

μ is the concentration of component μ during the reaction. k1 and k2 are the Arrhenius constant. n, m, l, and p are the orders or degrees of the reaction. μ_1, μ_2 μ_3, and μ_4 are the respective concentration of the components. Starting with this simple equation, it was possible to describe more complex systems of the reaction and finally the lows of Chemical Kinetics.

The mathematical description of the transformation of Information into the order and the deterioration of the order itself

The chemists and engineers do not care about the entropy created in the process of transformation. Do not care because the entropy it is an abstract notion, and in the words of John von Naumman *nobody knows what exactly is* [11]. Unlike entropy, enmorphy is a specific expression related to the disorder caused by the transformation to be performed.

The information existing before the transformation into order can be divided into two cases: a) continue existing. This effect is observed in DNA, plants of constructions of buildings, bridges and maps and others as patents and publications. The information can be used again and again with the same or similar purpose. The duplication of DNA reproduces the information included in DNA (15-18). However, the duplication of DNA is subject of mutagenesis and cannot work forever. b) The information transformed into order can be lost because of different events and catastrophes that we live daily. To recuperate the information lost it is needed knowledge and to recuperate the order is needed energy that means costs. The human civilization is based on electricity. Every scientific instrument and generally instruments and electronic devices, from the water heater to very complex international networks, work with electricity. The information is transferred electrically. For this reason, if we want to preserve our civilization, we must consider other means than electricity. This means new computers that work totally with the principle of light.

II. SPONTANEOUS AND NON-SPONTANEOUS TRANSFORMATION

For an established order, every change of the order is followed by the change of enmorphy. As established order, we consider the order that can remain constant for a relatively long time. Enmorphy is related to the disorder. This way, the discussion is elevated from the abstract level of energy and entropy to the concrete level of information, order or disorder, in other words in the enmorphy as defined before.

The spontaneous change of enmorphy is the event, characterized by a total lack or incipient information. Considering the earth we present as examples: the catastrophes caused by tsunamis and earthquakes, the recently Marianas and Brumadinho (MG) dam rupture [19], the change of the height of the mountains, the creation of new island the by volcanic activity, the aging of the marvels of the Acropolis, the physical and chemical aging of the materials including the processes of fatigue, the aging of any living organism, and many other examples. The former order stopped, slow or fast, to exist and give way to disorder.

Probably the information is hiding behind the physical and chemical properties of the matter. Specifically the structure of the matter and structure means order.

The non-spontaneous change of enmorphy is forced by the living organisms, in the sense of increased or decreased disorder. According to Szilard L [12], *any action resulting in a decrease in entropy must be preceded by the acquisition of information*. We transform the expression of Szilard to this, *any intelligent or non-intelligent action of the inhabitants of the earth (maybe the universe) needs acquisition of information.* Living organisms are constructed with the matter. Every kind of life possesses an elementary intelligence [5]. This fact is explained by the DNA which includes, in this stage of the evolution of the different species, previously defined information. The experience factors we do not want to discuss in this publication. The evolution of living nature is responsible for this fact.

We have to spend special attention to the catastrophes and conflicts caused by humans. First and Second world wars, the atomic bomb in Hiroshima and Nagasaki, the continuing civil war of Syria and other countries and the in-numerous conflicts around the earth are some examples. Additionally, the revolutions can be observed from this angle, the angle of enmorphy. The revolutions that failed to introduce the new order can be explained by failure and lack of information, consequently wrong and inadequate planning. They usually guide to civil wars and, consequently, catastrophe.

The transformation of information into the order can be discussed under the angle of non-spontaneous enmorphy. Any achievement, for example, the construction of a building (or monument) on clean ground, begins with the justification, search of the financing and the design of the building. In this stage, all this is called planning of the enterprise, the logistic works with virtual information, information that the scientists and engineers brought with them. Depending on what was initially planned at the virtual level, a percentage of the information will be transformed in order. If, on the other hand, the land is not cleared, planning should include the destruction of the old building, removal, and disposal of the rubble generated. The destruction of the old building should include information about it, and the process is quick and the execution of this work at the lowest possible cost. The issue is not just a problem of physical-chemistry, but for the engineers and computer science. It is accepted that physics and chemistry describe with approximations the reality, informatics, on the other hand, can describe with approximations the reality and virtuality. In this case, destroying the old structure, the old order is equivalent to expending energy to acquire the necessary information, the entropy is increased and parallel to this, the enmorphy increased too. *To change the created order, we have to pass from the step of the disorder and then established the new order.* The difference between humans and the animals is that, every human achievement includes Justification, Financial support, Planning, and Execution, for the animals there are no justification or financial support, the information necessary for planning is already available in the DNA and the previous experience.

To transform information into order, the information must include a logical sequence. In the construction of a building, first comes to the foundation and support parts, second the walls are constructed, and after the demand necessary for the finishing, etc. According to this, the information can be divided in to: the basic step information which has to be included to relatively finish the construction, the parallel steps and the consecutive steps. The parallel steps are those that the workers can perform at the same time. The consecutive steps are the ones the workers can complete one by one.

Considering that the degree of the transformation of the information is zero, then the equation that describes this transformation is the following one.

$$-dI/dt = k_0 I^0 \qquad [4]$$

$-dI/dt$ is the velocity of the transformation of information with the time, k_0 the velocity constant, I^0 indicate the zero degree of the transformation,

The integration of this equation gives the following result.

$$I = I_0 - k_0 t \qquad [5]$$

I_0: is the initial value of the information.

Figure 1 demonstrates the evolution of the information with time for the zero degree transformation. As seen, it follows a linear decay.

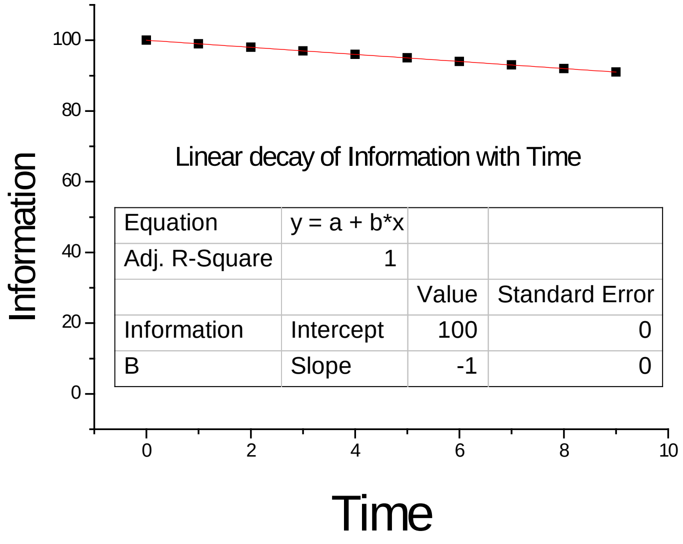

Figure 1: The zero degree transformation evolution of information with the time

In this paper, instead of *order of the transformation*, the expression *degree of the transformation* is used to avoid any misunderstanding with the word *order* indicating structure and the other synonyms giving in the abstract. The proportionality factor must be considered in all the operation, according to Eq. [2]. Additionally, arbitrarily it is used the number of information 100. In the cases of parallel and consecutive transformation the degree of transformation is equal to 1. All the following examples should accompany the same numbers.

According to equation [5], the construction of a building would initiate and be finished in determined time. However, the constant k_0 depends strongly on what is the material planned to be used in the construction. If parts are prefabricated, includes silt or/and reinforced concrete or/and wood, etc. The time to initiate, the work and the duration are predefined.

Assuming that the velocity of the transformation is described by the equation of the first degree.

$$-dI/dt = kI^1 \qquad [6]$$

I^1: indicate the first degree of transformation.

The integration of this equation gives the following result.

$$I = I_0 \exp(-kt) \qquad [7]$$

Figure 2 resumes the exponential decay for the first degree transformation with the time. The created order follows an exponential growth, considering the respective value of the proportionality factor.

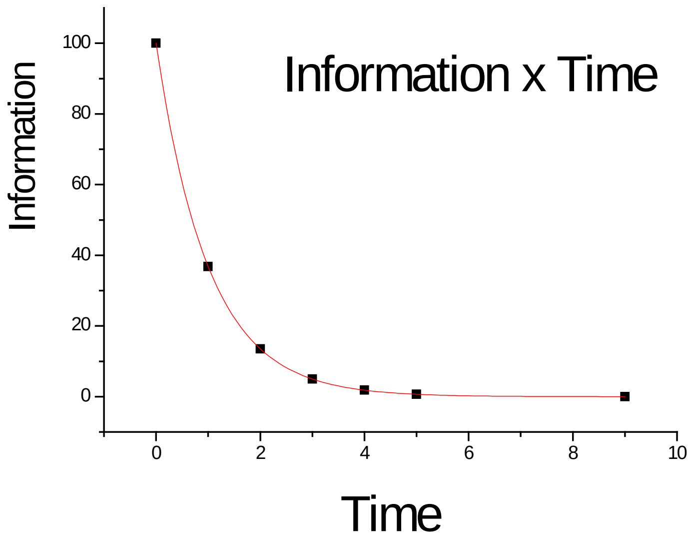

Figure 2: Exponential decay of information with the time

Assuming that the velocity of the transformation is described by the second degree equation.

$$-dI/dt = kI^2 \qquad [8]$$

I^2: indicate the second degree of transformation.

The integration of this equation gives the following result.

$$I = Io / (1+k\ Io\ t) \qquad [9]$$

Figure 3 describes the equation of second-degree kinetics for the transformation of the information to order, according to eq.(9).

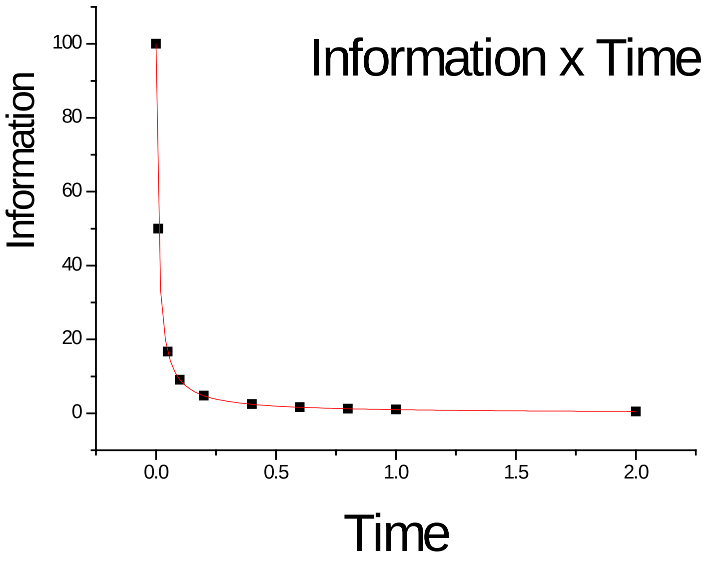

Figure 3: The evolution with the time of the information for a second-degree transformation

It is mentioned before, that there are three types of information to be transformed into the order: the basic, the parallel and the consecutive, however, the combinations of this can lead in a much more complex system.

Considering that planning includes parallel actions, then, we can describe the transformation of information into order according to the following scheme.

$$I \xrightarrow{k1} Or1 \qquad [10]$$

$$I \xrightarrow{k2} Or2 \qquad [11]$$

This scheme corresponds to tow parallel reaction of the first degree (order). For the corresponding velocities are valid following equations.

$$-dI/dt = k1I + k2I \qquad [12]$$

$$dOr1/dt = k1I \qquad [13]$$

$$dOr2/dt = k2I \qquad [14]$$

The integration of this scheme leads to following equation.

$$I = Io \exp [-(k1 + k2) t] \qquad [15]$$

$$Or1 = (k1\ Io / (k1 - k2)) [(1 - \exp(-(k1 + k2) t)] \qquad [16]$$

$$Or2 = (k2\ Io / (k1 + k2)) [(1 - \exp(-(k1 + k2) t)] \qquad [17]$$

The figures: 4, 5 and 6 describe the parallel scheme of the transformation of information to order. The exponential decay, according to Eq [15] and the products of order is presented according to Eq. [16] and [17].

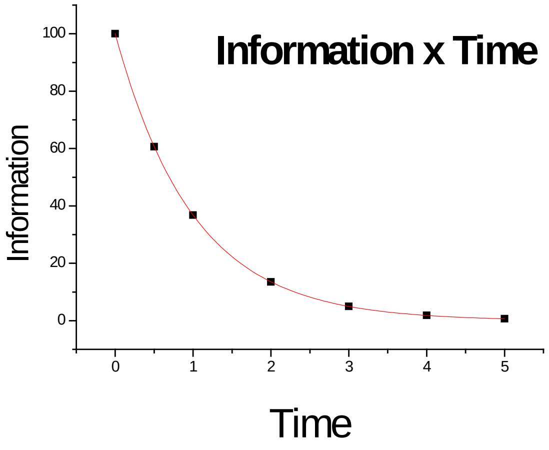

Figure 4: The exponential decay of information, according to Eq [15]

Figure 5: The first product according to the parallel scheme, Eq. [16]

Figure 6: The second product according to the parallel scheme, Eq. [17]

The other case to be discussed is the consecutive transformation of information to the order, represented by the scheme.

$$I \xrightarrow{k1} Or1 \xrightarrow{k2} Or2 \qquad [18]$$

This is represented by two sequential first order (order) processes.
For the velocities are valid following equations:

$$- dI/dt = k1\, I \qquad [19]$$

$$dOr1/dt = k1I - k2\, Or1 \qquad [20]$$

$$dOr2/dt = k2Or1 \qquad [21]$$

The integration of this scheme leads to following equation.

$$I = Io \exp [\,-k1\ t] \qquad [22]$$

$$Or \quad 1 = (k1/\ (k2 - k1))\ Io\ (\exp(-k1t) - \exp(-k2t)) \qquad [23]$$

$$Or \quad 2 = Io\ (1 + (k2/(k1-k2)) \exp(-k1t) + (k1/(k2-k1)) \exp(-k2t)) \qquad [24]$$

The case of consecutive transformation can be applied perfectly in the construction of a work, beginning with foundation, then follows the walls, the coating, the painting and other details to finish the work.

Figures 7, 8 and 9 show the result of the transformation of information into order in the case of consecutive transformation. The exponential decay of information, according to Eq. [22]. The products of order are described by eq. [23] and [24] respectively. The Eq. [23] presents a maximum, easily predicted. The Eq.[24] is a sigmoid curve.

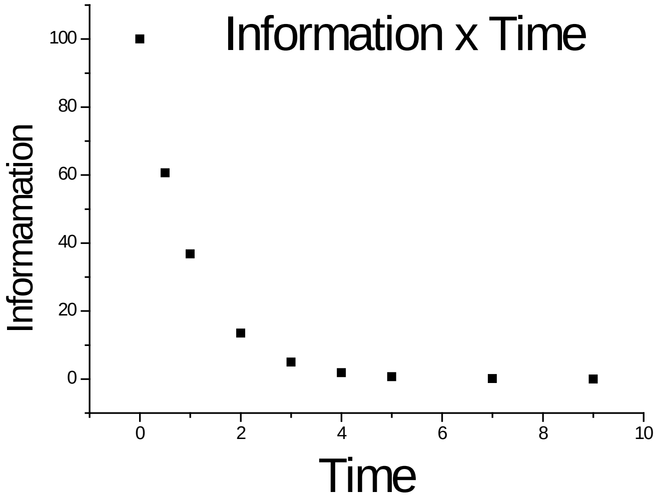

Figure 7: The evolution with time of the exponential decay of information, according to Eq. [22].

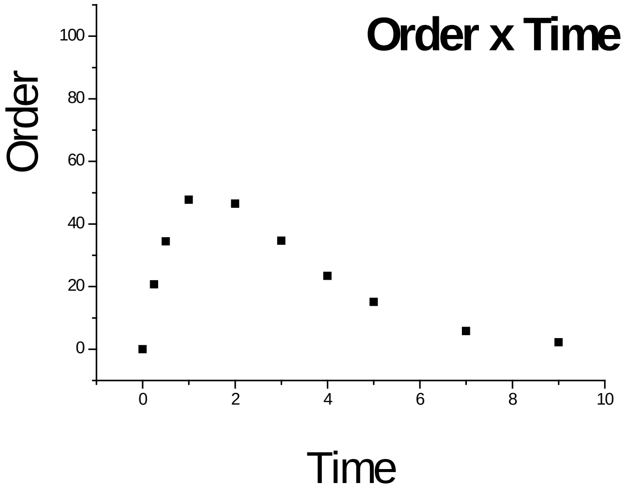

Figure 8: The evolution with the time of the first product (considered intermediate) according to Eq. [23]

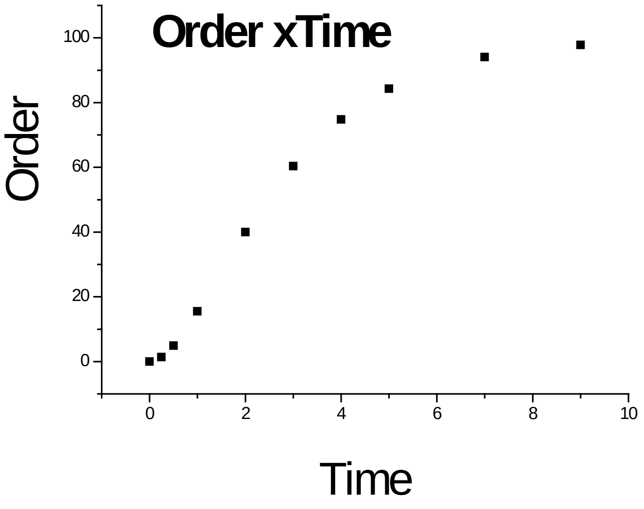

Figure 9: The evolution with the time of the second product (considered final product) according to Eq. [24]

The combination of the cases discussed above, specifically the two last, and the definition of the degree of transformation, would be an excellent instrument for the planning of any kind achievement.

III. THE DETERIORATION OF THE ORDER ITSELF

There is a natural phenomenon related to the deterioration of the order. This phenomenon obeys to the spontaneous and non-spontaneous processes discussed above. The deterioration of the order can be described by the same principles as the process of the transformation of the information into order, using the same formalism, that is zero or first or second or parallel and consecutive and more complex schemes. However, the product, in this case, is the disorder and disorder is related to the enmorphy, as previously defined (5).

A chemist would explain the deterioration of the order by the strength of the bonding of the molecules forming the materials used. Strength is related to vibration; consequently, according to Blinder (7), vibration is related to the temperature. All forms of deterioration of the order, namely: zero, first, second, parallel and consecutive and other more complex schemes, starts with decay: linear or exponential or even more complex forms. This is defined as the characteristic correlation time of the decay of the deterioration of the material. This way, it was justified the dependence of the integrating factor of the Enmorphy on the temperature and the time, as predicted in our earlier publication [5].

IV. SYNOPSIS

The Informatics Potential, dI was introduced as a consequence of the four energetic potentials, namely:

dH the enthalpy, dA the free energy of Helmholtz, dG the free energy of Gibbs and dE the internal energy, and the chemical potential $d\mu_i$. A general kinetic theory of informatics was presented, similar to chemical kinetic theory. The main issue is the transformation of Information into Order. In this case, order means: structure, organization, form, aligning, composition, establishment, grouping, layout, pattern, scale, sequence, symmetry and uniformity and all other notions which can be understood as the order. A discussion was presented of what is considered as spontaneous and non-spontaneous process in informatics. The aim to mathematically describe the transformation of Information into the order and the deterioration of the order itself was achieved. Some examples, considering different degrees of transformation, were demonstrated. The general kinetic theory of informatics can be applied to all areas of science, i.e: physics, chemistry, medicine, biology, geosciences, agronomy, architecture and civil engineering, social sciences, and other related areas. It is exactly the informatics that creates the link between the physical sciences and the human sciences. That is why today we cannot exclude computing from any interdisciplinary research. Nowadays we cannot imagine interdisciplinary without the participation of computer science.

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Determination of Lead Levels in Soil for Some Areas at East Gezira and Khartoum - Sudan, Africa

A Comparative Study between the Rural Areas and Urban Areas

By Mr. Abdirashid Adam Isak & Dr. Mohammed Mubarek Awad

Somali National University

Abstract- Lead is a chemical element with an atomic number 82 and symbol Pb and nowadays recognized as a heavy-metal poisonous, it affects every system of the body. Acute exposure to a high level of Lead can result in death or significant damage to the brain or other organs. The study aimed to determine the concentration of Lead in Soil of some areas in Khartoum and East of Gezira (Banat, Rufa'a, and Tambol) Specifically. Also, to make a comparison between the rural areas and the urban areas. Eighteen samples of soil havebeen collected from the bus stations, batteries repairing Market in Souk Sha'bi and specific distances away from them. Atomic Absorption Spectrometer method was used to do the analytical work. The concentration of Lead in samples of soil in this Investigation was ranged 0.78 ppm (Banat) – 10.58 ppm (Batteries Market Souk Sha'bi). We found a positive correlation between Urbanization and lead mean concentration of 1.22 ppm in Khartoum and 0.40 ppm in East of Gezira. A positive relationship was additionally found between the concentrations of lead as being closer to the Centre of each one of the transport station and Batteries repairing places and the Main road. So this study recommended that all Lead-related industries and markets should be far enough from human living to avoid environmental lead pollution.

Keywords: lead pollution, lead poisoning, pollution, environmental pollution, spectro- photometer, aas, and positive correlation.

GJSFR-B Classification: FOR Code: 030699p

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I. INTRODUCTION

Heavy metal is an Individual from a badly characterized subset of the chemical elements that show metallic properties. Many different descriptions of the term Heavy metal have been proposed, in light of either Density, Atomic number, Atomic weight, Chemical properties, or Toxicity (Cacar, 2003).The term heavy metal alludes to any metallic chemical element that has a comparatively high density and is poisonous at low concentrations (Cacar, 2003). Instances of Heavy Metals incorporate Mercury (Hg), Cadmium (Cd), Arsenic (As), Chromium (Cr), Thallium (Tl), and Lead (Pb) "Our focus element in this Examination"

Heavy metals are natural constituents of the Earth's crust. They are steady and can't be debased or devastated, and along these lines, they will result in general aggregate in soils and dregs. However, human activities have drastically altered the biochemical and geochemical cycles and balance of some heavy metals.

The vital man-made wellsprings of Heavy Metals are mechanical point sources, e.g., mines, foundries and smelters, and diffuse sources, such as ignition side-effects, traffic, and so on. Moderately unstable Heavy metals and those that become connected to air-borne particles (particulates) can be broadly scattered all through the climate, regularly being saved a great many miles from the site of introductory discharge. As a rule, the littler and lighter a molecule is, the more it will remain noticeable all around. In general bigger particles (greater than 10 micrometers (μm) in diameter) will settle to the ground by gravity in matter of hours whereas the littlest particles (under 1μm in diameter) can remain in the environment for a considerable length of time and are for the most part expelled by precipitation.

The main anthropogenic wellsprings of heavy metals are different industrial procedures, mining, foundries, and smelters, burning of non-renewable energy source and gasoline, and waste incinerators. The significant Heavy Metals of worry to EMEP are Hg, Cd, and Pb, since they are the most dangerous and have known actual impacts on, for example, human health. Environmental exposure to high concentrations of heavy metals has connected with, e.g., different diseases, cancers, and kidney harm. There are significantly more estimations information on Hg, Cd, and Pb in Europe than for other metals. (Ilyan et al. 2002)

Heavy metal contamination in wastewater and Soil are one of the issues confronting Individuals, Heavy Metal can be toxic or poisonous to life, as shown in [Table 1].

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Table 1: Classification of Elements According to Toxicity and Availability (Wood, 1974).

Non-critical Accessible	Toxic but rare	Very toxic
Al	Ba	Ag
Br	Cs	As
C	Ga	Au
Ca	Hf	Be
Cl	Ir	Bi
Li	La	Cd
Mg	Nb	Co
N	Re	Cu
Na	Rh	Hg
Rb	Ru	Ni
Sr	Ta	**Pb**
Si	Ti	Pd
F	Zr	Pt
Fe	W	Sb
Hg		Se
K		Ti
O		Te
P		Zn
S		

II. THE OBJECTIVE OF THE EXAMINATION

The propose of this Investigation was to determine and examine the level of lead in soil by using atomic absorption spectrometer Method and makes a comparison between the rural and the urban areas.

III. THE EXPERIMENT

a) Materials

Eighteen Samples of soil were collected from several random places from East of Gezira and Khartoum (Sudan), including three rural areas Rufa'a, Banat and Tambol (East of Gezira) and three urban areas Souk Arabi, Souk Sha'abi, and Mina Al-Barri (Khartoum) and preserved for a later laboratory test.

b) Chemical reagents

The grade of chemical reagents used in soil analysis for *Pb* element estimation was Analytical reagent (AR) with high purity (99.9%); which includes HCl and H_2SO_4.

c) Atomic Absorption Spectrometer

Atomic absorption Spectrometer (210/211 VGP Buck Scientific) double beam manufactured by The United States of America was used in a measuring the concentration of Pb in soil Samples (AAS, 1994). It's usually used for the determination of metal elements. This technique features high accuracy and precision of trace element determination on condition that analyze is adequately prepared.

IV. METHODS

a) Sample preparation

5.0 g of an air-dried ground and sieved sample was placed in an Erlenmeyer flask. 20 ml of extracting solution was added; (0.05N HCl + 0.025N H2SO4). Then Placed in a mechanical shaker for 15 minutes. After that filtrated through Whatman #42 filter paper into a 50-ml volumetric flask and diluted to 50 ml with extracting solution.

b) Analytical methods for Atomic Absorption

The analysis of soil samples for measuring Pb was done by Calibrated Atomic Absorption Spectrometer Instrument with known stock standard solutions prepared in ratio 1:3:6 mg/l to perform the linear curves within the linear ranges for the mentioned element, beside the reference sample materials (Certified Samples for the same elements) according to certain condition.

The techniques of instrument operation performed in steps, the desired lamp in the upper most position of the lamp turret was installed. This is an operating position to align the wavelength. {Library} key button was pressed to enter the library. {Sel} key button pressed until the lamp number (Top of the screen) matches the turret position. Either {Up/down} key arrow was pressed until the desired metal and method were shown in the library window.

c) Statistical Analysis

Data were analyzed as a completed randomized design. Analysis of variance (ANOVA) was performed According to the procedure described by Gomez (1984). Means were separated by using Duncan multiple ranges tests (DMRT). The results were used to compare between the two sample Areas.

d) *Sample Coding*

After taking the samples from their different areas what the researcher needed was making codes to deal with the different items and samples, the codes were assembled by taking the Urban Area as (A) and the rural area as (B). The below table gives more detail about the codes.

Table 2: Sample Codes and their Distribution

Urban Areas (Khartoum)		
Sample Code	mg/l	mg/kg
A1a	0.198	1.98
A1b	0.129	1.29
A1c	0.135	1.35
Mean of A1 area = 1.54		
A2a	0.192	1.92
A2b	0.157	1.57
A2c	0.277	2.77
Mean of A2 area = 2.09		
A3a	0.623	6.23
A3b	1.058	10.58
A3c	0.833	8.33
Mean of A3 area = 8.38		

V. RESULTS

The Experimental work was done in *Environmental and natural resource and desertification research Institute* (Khartoum – Sudan) under supervision of *Dr. Magdi Hashim Ahmed* (Central lab. Supervisor), and *Dr. Omer Mohamed Dafalla* (Chief of the chemical analysis Dep.) and this was the result.

Table 3: Lead Level in the Urban Areas

Urban Area (Khartoum)	Rural area (East of Gezira state)
A1a Bus Station (Mina al barri)	B1a Banat
A1b 50 meter away	B1b 50 meter away
A1c 100 meter away	B1c 100 meter away
A2a Bus station (Souk Arabi)	B2a Tambol – Veterinary medicine college
A2b Around the liberty bridge	B2b 50 meter away
A2c Sahafa shareg buses	B2c 100 meter away
A3a Souk sha'bi	B3a Rufa'a
A3b 50 meter away	B3b 50 meter away
A3c 100 meter away	B3c 100 meter away

Note: Uncontaminated soil contains lead concentrations less than 50 ppm, but soil lead levels in many urban areas exceed 200 ppm.

Calculation Formula:

[Mg/Kg = Reading (g/l) x Volume (ml) / Weight (g)]

Example: 0.198 x 50 / 5 = 1.98 mg/kg

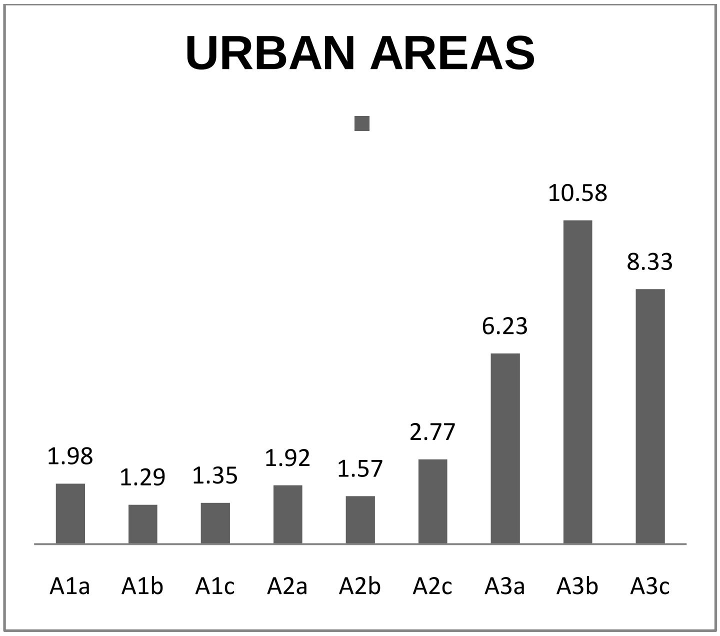

Figure 1: Level of Lead Concentration in Urban Areas

Note:

- Since the P value in the urban area is greater than 0.05, the null hypothesis is accepted which indicates that the lead level is higher in the urban area than the rural area.
- Values with different characters are significantly different using of DUNCANS Test (p<0.05).

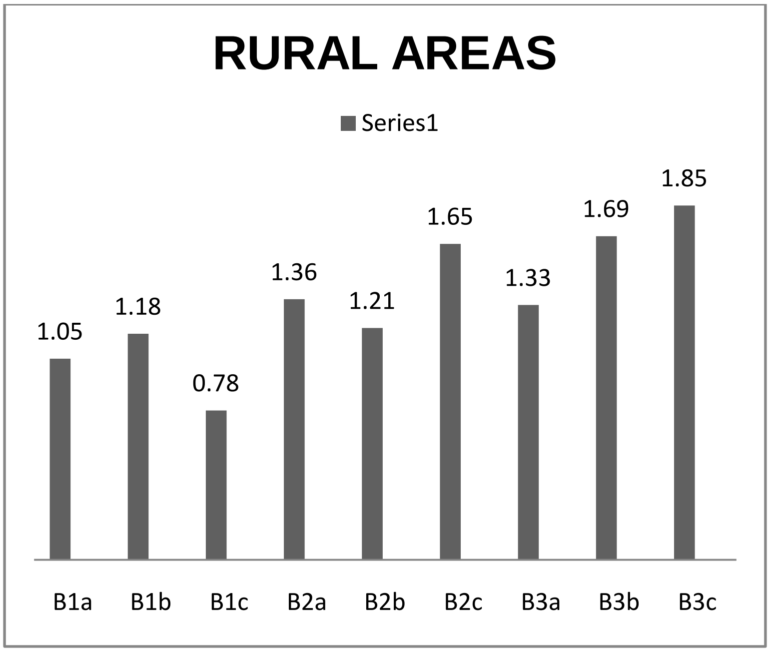

Figure 2: Level of Lead Concentration in Rural Areas

Table 2: Lead Level in the Rural Areas

Rural Areas		
Sample Code	mg/l	mg/kg
B1a	0.105	1.05
B1b	0.118	1.18
B1c	0.078	0.78
Mean of B1 area = 1.003		
B2a	0.136	1.36
B2b	0.121	1.21
B2c	0.165	1.65
Mean of B2 area = 1.41		
B3a	0.133	1.33
B3b	0.169	1.69
B3c	0.185	1.85
Mean of B3 area = 1.62		

VI. DISCUSSION

The highest point of Lead Pollution was found in souk sha'bi (A3b) which was 10.58mgkg^{-1} as expected because of the high level of lead pollution in this area, and the lowest point of Lead pollution was in the rural area as expected and was 0.78 mgkg^{-1} in Banat (B1c) area because of its flexible and rural maintained stability of purity (there is no source of pollution).

So we notice that there is a significant difference (sig. = 0.02) in the two sample areas because of their pollution's source. Among all the things, in general, the urban areas have highly a pollution source that doesn't exist in the rural area.

Mohamed Elmubarek, 2012 "Ph.D." *(Environmental Levels of Lead in Soil and Drinking water in some areas in Khartoum and Gezira State, University of Gezira*), did the same analysis on the soil in Khartoum area and get ranging about 11.24 ppm, by using the same method.

As well as Wafaa Sahib Abbood Alawsy College of Agriculture-University of Qadisia and Eman Abdul Mahdi Oleiwi College of Agriculture-University of Baghdad, 2014 "MSc" *(Study the Pollution of some Calcareous Soils with Cadmium and Lead and Its Relationship with the Accumulative Effect of Used Engines Oils on Mineralogical Soil Separates)* were done work on lead pollution in Soil of some areas in Iraq and their ranging was high between 12.8 – 13.6 ppm.

VII. CONCLUSION

7.1 A Soil with Contamination of *LeadPb* may expose a risk by direct ingestion, Smelling, take-up in vegetable ranches and Soil.

7.2 Uncontaminated soil contains lead fixations under 50 ppm; however, soil lead levels in numerous urban territories surpass 200 ppm.

7.3 The EPA's standard for lead in uncovered soil in play zones is 400 ppm by weight and 1200 ppm for non-play territories.

7.4 The results of this study were significant eligible by the meaning of this command.

VIII. RECOMMENDATION

This investigation suggests that:

8.1 All lead-related ventures and Batteries Market ought to be sufficiently far from human living to evade environmental lead contamination.

8.2 To accomplish more work on this contamination field (Heavy metal poisonous).

8.3 More research must be completed for another Heavy metal.

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Natural Products for Material Protection: Passivation Enhancing Potentials of *Spondias Mombin* as AISI 316L Corrosion Inhibitor in 3.5% NaCl Solution

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Abstract- The corrosion inhibition characteristics of *Spondias mombin* (SM) on stainless steel AISI 316L in 3.5% NaCl has been studied using gasometric, potentiodynamic polarization, surface and elemental analysis and computational techniques. Results showed that the inhibition occurs through adsorption of the inhibitor molecules on the metal surface. The effectiveness of protection became more pronounced with decreasing gas evolution as extract concentration increased. Electrochemical results revealed that the extracts' constituents adsorbed on the AISI 316L surface and enhanced the passivation mechanism which is in agreement with the reduced the anodic and cathodic current densities. Computational simulations were adopted to describe probable reactiveness of SM leaf extract constituents on Fe(110) slab.

Keywords: *corrosion inhibition, stainless steel, spondias mombin, elemental analysis, passivation enhancer, adsorption.*

GJSFR-B Classification: *FOR Code: 030599*

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Raphael S. Oguike [α] & Omolara Oni [σ]

Abstract- The corrosion inhibition characteristics of *Spondias mombin* (SM) on stainless steel AISI 316L in 3.5% NaCl has been studied using gasometric, potentiodynamic polarization, surface and elemental analysis and computational techniques. Results showed that the inhibition occurs through adsorption of the inhibitor molecules on the metal surface. The effectiveness of protection became more pronounced with decreasing gas evolution as extract concentration increased. Electrochemical results revealed that the extracts' constituents adsorbed on the AISI 316L surface and enhanced the passivation mechanism which is in agreement with the reduced the anodic and cathodic current densities. Computational simulations were adopted to describe probable reactiveness of SM leaf extract constituents on Fe(110) slab.

Keywords: corrosion inhibition, stainless steel, spondias mombin, elemental analysis, passivation enhancer, adsorption.

I. INTRODUCTION

Protection of stainless steel that finds service in several sectors of the economy has been of keen interest, especially the media which includes chloride ions [1]. AISI 316L type stainless steel are used in marine-relative environment and various engineering applications owing their excellent corrosion resistant properties, high ductility, aesthetic appearance and high work hardening rate [2-6]. However, when in contact with medium containing chloride ions, they are much susceptible to corrosion, leading to enormous economic losses and pose potential safety problems. These challenges are contained by the use of corrosion inhibitors to lengthen their in-service years. Most commercial corrosion inhibitors function as passivation enhancers via forming monoatomic or polyatomic oxide film on the metal surface which results in a reduction of corrosion reaction and metal surface protection. However, the main drawback is the toxicity, cost and carcinogenic nature of inhibitors involving chromates [7]. This has led to the investigation of alternative compounds that are environmentally acceptable and offer effective corrosion protection as well as enhance the metal's passivation potential.

Of the efficient methods to protect against corrosive attacks on AISI 316L deployed in service is the use of organic compounds which contain conjugated double bonds, triple bonds and electronegative species to form tight surface films [8–13].Numerous advancements have been made to address the growing need for proficient inhibition for stainless steel corrosion in a bid to find inhibitors of natural product origin [14]. Natural products of plant origin contain organic constituents with similar structures as the commercial inhibitors having aromatic rings, multiple bonds, electronegative functional groups as well as hetero-atoms like nitrogen, sulfur and oxygen in their molecular backbone. These species are beneficial to form complex chelating ligands with the metal surface against corrosive species, as they are regarded as major adsorption centers within the inhibitor molecule that form compact thin film on the metal.

The basis for corrosion control is a compromise between the benefits generated by the level of corrosion control versus the costs that would result if that level of control were not maintained Regrettably, several of these commercial inhibitors are expensive, toxic and hazardous to environment [15-16], hence the drive to develop eco-friendly corrosion inhibitors with adequate effectiveness and efficiency [17]. An attempt has been made in the present work to describe the inhibitory features and efficiency of *Spondias mombin* for corrosion of AISI 316L in 3.5% NaCl solutions.

II. EXPERIMENTAL

a) Material Preparation

The composition of AISI 316L which was obtained commercially from Advent research materials Ltd, England OX294JA has the following typical analysis (ppm) C < 300, Si <100, Ni < 1400, Mn < 200, Cr < 1800, Mo < 300, S < 300, P < 450 and Fe. The sheets were reduced to specimens mechanically and treated as described in our earlier work as well as inhibitor preparation [5].

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b) Gasometric Measurement

In the gasometric method, seventy milliliters of 2 M HCl solution without and with AM leaf extracts was introduced into the gasometric apparatus. AISI 316L specimen was introduced into the flask which was quickly corked. The initial volume of paraffin oil in the apparatus was recorded. The decrease in volume of the paraffin oil due to hydrogen gas evolution was taken after every five minutes. From the volume of hydrogen gas evolved, the corrosion rate was calculated using eqn (2) while the inhibition efficiency of the inhibitor was calculated using eqn (3) [5].

$$CR_{HE} = \frac{V_f - V_i}{t_f - t_i} \qquad (1)$$

$$IE_{HE}\% = 1 - \frac{CR_{HE\ (in\,hib)}}{CR_{HE\ (free)}} \qquad (2)$$

where CRHE is the corrosion rate, Vf and Vi is the final and initial volume of gas evolved, tf and ti the final and initial time in minutes and CRHE(inhib) and CRHE(free) are corrosion rates in the presence and absence of the inhibitor.

c) Electrochemical Measurement

A polarization cell with a three-electrode configuration was used for electrochemical measurements; steel specimens having a total exposed surface area of 1cm2 was used as working electrode, a graphite rod and a saturated calomel electrode (SCE) were used as counter and reference electrode respectively. The working electrode was used as obtained, however, were cleaned with distilled water, degreased with ethanol, and finally dried with acetone and warm air. Electrochemical experiments were conducted using a VERSASTAT 3 Complete DC Voltammeter and Corrosion System as described in [15]. The inhibition efficiency was calculated using eqn (4).

$$IE_{PS}\% = 1 - \frac{i_{corr}}{i_{corr}{}^{\circ}} x\,100 \qquad (3)$$

where icorr is the current density for the inhibited solution and $i_{corr}{}^{\circ}$ is the current density of the uninhibited solution.

d) Surface Examination

The morphologies of the corroded metal surfaces after 150 hours of immersion time were inspected by SEM on Vega Tescan scanning electron microscope, resolution 80 Angstroms, magnification range: 10 X – 180 000 X, SE detector, HV 20.0 kV.] while the energy dispersive X-ray emission spectroscopy (EDS) were recorded in a VG TC INCA PentaFET x3 spectrometer with Mg K_X-ray source (1486.7 eV photons energy) operated at 300 W (accelerating voltage 12.5 kV, emission current 24 mA). A detailed procedure for the surface examination is reported in [33]

III. RESULTS AND DISCUSSION

a) Gasometric technique

Fig. 1 shows the gas evolution-time curves for the corrosion of AISI 316L in 3.5% NaCl solution without and with different concentrations of SM leaf extracts. As observed from this figure, by increasing the concentration of SM, the volume of hydrogen gas evolved with time decreased. The stepwise progression of the plot indicates that AISI 316L surface experienced stages of passivation as the surface corrosion proceeds and the chloride ions usually situate at the bottommost areas of localized areas actually compromise the stability of the passive films formed on the steel surface [18]. However, with increasing SM leaf extracts concentration clearer and stable passivation periods were seen to be maintained suggesting that SM leaf extracts did enhance the compactness of the formed surface films which hindered the intrusion of further chloride ions thereby reducing corrosion rate. The cathodic reaction for hydrogen evolution of stainless steel corrosion in near neutral medium may require several steps involving either a chemical recombination mechanism and/or electrochemical recombination mechanism [19] where majority of pre-adsorbed atomic hydrogen will recombine to form molecular hydrogen which bubbles off of the surface. From the calculated corrosion rate 27.17, 45.65 and 72.83 % for 0.01, 0.1 and 1.0 g/L respectively, it is clear that the release of molecular hydrogen follows steel dissolution however, inhibition efficiency value for 1.0 g/L SM leaf extract indicates that its constituent molecules did obstruct the cathodic reaction via adsorption on the anodic substrate of AISI 316L. This reduced anodic dissolution and probably, the constituent molecules even got trapped within the metal/solution interface either by complex chelate formation and/or electron transfer [20].The %IE suggests that SM leaf extracts did obstruct the cathodic hydrogen reduction reaction via formation of surface films which indeed induced some modifications in the system double layer and diffusion boundary as a result of the adsorbed extracts' constituent at the metal/corrodent interface [21-24] and in turn enhanced the steel passivation properties.

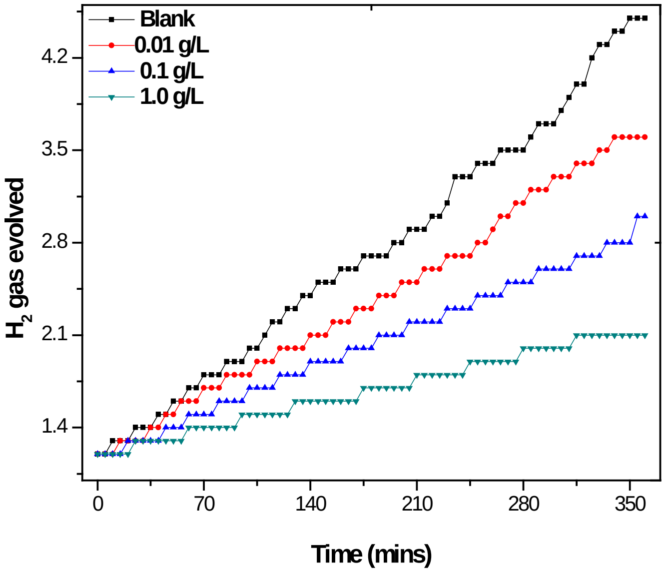


Fig. 1: Variation of H_2 gas evolved with time for AISI 316L in 3.5% NaCl solution without and with SM leaf extracts

b) Potentiodynamic polarization results

Table 1: Corrosion parameters for AISI 316 L in 3.5% NaCl solution in the absence and presence of SM leaf extracts

Solution	Parameters			
	i_{corr}	E_{corr}	θ	%IE
Blank	112.25	-110.02	--	--
0.1 g/L	16.32	109.32	0.8546	85.46
1.0 g/L	15.85	251.96	0.8588	85.88

Fig. 2 depicts the potentiodynamic polarization curves for AISI 316L in uninhibited and inhibited 3.5% NaCl solution while the polarization data obtained by extrapolating the Tafel segments of the anodic and cathodic curves are listed in Table 1.As clearly seen form the curves, the rest potential shifted toward the more positive potential with the inhibited solution which increased with inhibitor concentration indicating a preponderate anodic protection. This behaviour is characteristic of spontaneous blocking of chloride ions attack on the protective passive films associated with the steel hence reducing anodic dissolution of the steel. Spontaneous passivation was observed in the anodic branch of the polarization scan of AISI 316L in 3.5% NaCl solution in the presence of SM leaf extracts with a marginal increase in corrosion current density and decreased passive current density values. However, minimal anodic reaction occurred at higher corrosion potential as the concentration of SM leaf extracts increased recording a decrease in corrosion current density till about 0.98 mV. At this point, pitting action of the chloride ions initiate a breakdown of the passive film formed on AISI 316L surface aiding further dissolution of the metal [25-26].

According to Refaey *et al*[27], the passive layer formed on stainless steel in aqueous NaCl solutions consists of Fe_2O_3, Cr_2O_3 and FeCl while the corrosion resistant properties are determined by an inner Cr_2O_3 layer and outermost Fe_2O_3 layer that feature poor barrier. Examination of the potential-current plot reveals that the presence of chloride ions in the system is clearly seen to interferes with the steel surface property via introducing a discrete surface process due to local surface activation following passivity breakdown though in the presence of the inhibitor, the surface features were enhanced. The observed increase in current density above 0.98 mV could be explained on the grounds that the pre-adsorbed FeCl layer is oxidized to $FeCl^+$ whose action resulted in nucleation of pits on AISI 316L surface [24]. This made the current density to increase with increasing corrosion potentials in the positive direction before oxygen evolution [28] and sharplyrose at about 1.08 mV denoting breakdown of the passive layer and nucleation of pitting corrosion an indication of dissolution of the adsorbed inhibitor complex ligands and dissolution of the oxide films. Although a relatively good consensus prevails on the corrosion products that form on stainless steel surfaces under chloride ion bearing conditions and on the reaction processes particularly as it is known that the presence of chloride ions enables the formation of adsorbates and complexes [29-31]. SM leaf extracts were seen to reduce corrosion rate of AISI 316L compared to the uninhibited medium through formation of complex chelating ligands on the metal surface thereby played down on the formation of chloride ion adsorbate and complexes thereby enhancing the compactness of the surface film. This infers that the inhibitor did modify the charge transfer mechanisms at the electrolyte/metal interface and electric double layer region with an overall result of enhancing the metals' passivation potential as it gave an optimal protection efficiency of 85.9% at 1.0 g/L. However, considering the combined observations on the changes in Tafel slopes, current densities, and the direction of change in corrosion potentials, the inhibition process appeared to be mixed type in nature with pronounced anodic effects [24,32]. The significant anodic and cathodic branch shift of the potential-current plot to positive potential and decrease in current density with increase in inhibitor concentration suggests formation of a stronger film protective layer on AISI 316L surface.

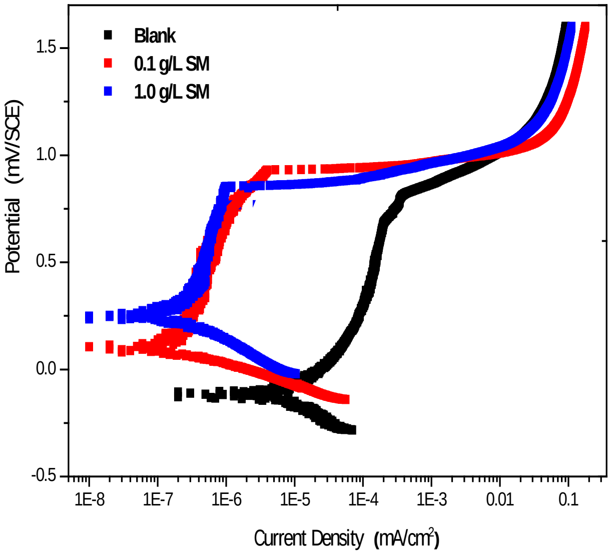


Fig. 2: Potentiodynamic polarization curves for AISI 316L in 3.5% NaCl solution in the absence and presence of SMleaf extracts

c) *SEM studies and elemental analysis*

Surface examination of the AISI 316L specimen exposed to a 3.5% NaCl solution in the uninhibited and inhibited solutions after 150 h was performed by SEM analysis as shown in the micrographs (Fig. 3). It is clearly shown in Fig. 3athat the action of chloride ion strongly damaged AISI 316L surface in the uninhibited solution due to the metal dissolution and pitting corrosion. The metal surface in uninhibited solution revealed depth of pits at various points and groove cracks along boundary grains. In contrast, the appearance of the steel surface is different in the inhibited solution with 1.0g/L SM leaf extracts after150 h immersion time. As observed from Fig. 3b, the steel surface improved greatly in the inhibited solution with reduced density cracks and no pits were seen in comparison with the surface of uninhibited solution. This observation could be interpreted as the inhibitor forming complex ligands with the metal surface via adsorption and prevented formation of chloride adsorbates and complexes such as FeCl formation and its oxidation. The observed damaged steel surface discloses that the formed chloride adsorbates on the surface further stationed as nucleation centers that further enhanced Fe ions migration from the surface into the bulk medium. SEM analysis further supports the fact that SM leaf extracts strengthened the compactness of the passive film formed thereby enhancing the passivation potentials of AISI 316L.

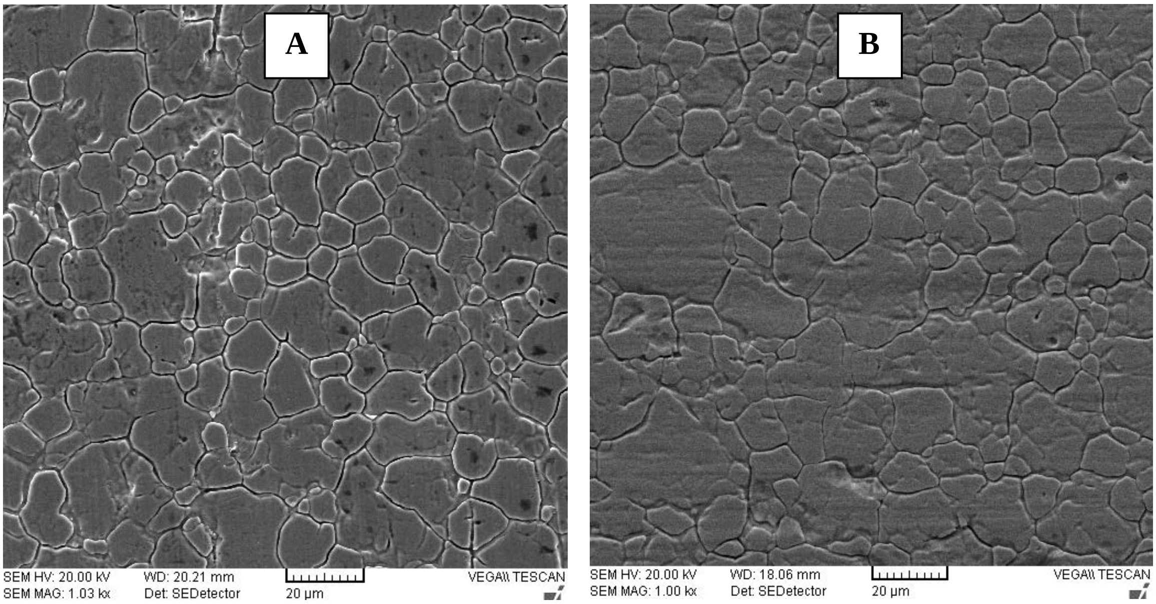


Fig. 3: SEM micrographs of AISI 316L surface after immersion for 150 h in 3.5% NaCl solution (a) uninhibited (b) inhibited

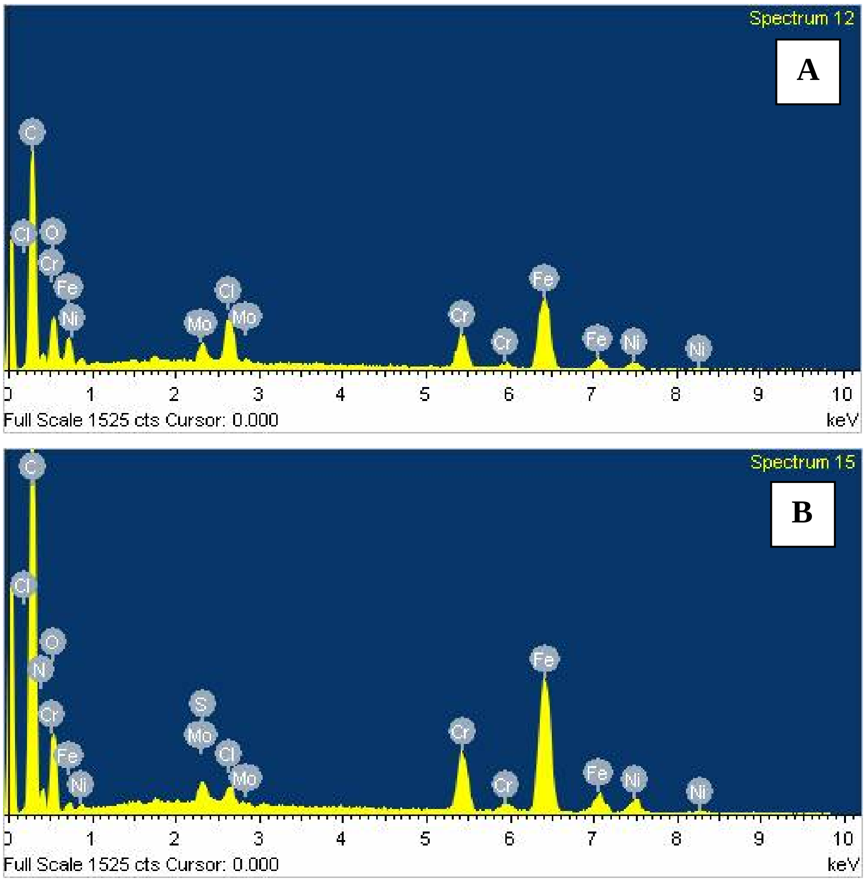


Fig. 4: EDS analysis of the corrosion product on AISI 316L surface in 3.5% NaCl solution (a) uninhibited (b) inhibited

Fig. 4 shows the spectra for AISI 316L in uninhibited and inhibited 3.5% NaCl solution while Table 2 reports the surface elemental composition and atomic% values. The elemental analysis for AISI 316L specimen in inhibited 3.5% NaCl solution discloses the presence of appreciable amount of oxygen and nitrogen atoms as well as traces of sulphur signifying that the leaf extract species did encounter bonding with the steel surface. The data revealed that the amount of Na and Cl atoms at the surface reduced in the presence of the inhibitor supporting the fact that the inhibitor reduced available active sites on the steel surface for corrosion.

Table 2 reports the atomic% values, weight% and application concentration for the uninhibited and inhibited solution. The atomic% values of oxygen in both media indicate that it played a major role at the surface film formation via Fe_2O_3 and Cr_2O_3 [27]. However, in the inhibited system, the reduced atomic representation of oxygen and better resulting surface suggests that there were complex chelating ligands on the surface that enhanced the compactness of the surface films such as (N-Fe-O)$_{ads}$, (N-Fe-S)ads and (Fe-Cl-TD)$_{ads}$[33]. This is supported with the energy dispersive spectrum in Fig. 4 showing peaks of the elements and elemental composition values in Table 2. The presence of Fe, Cr and O atoms in the analyzed corrosion products on the surface is consistent with the formation of a passivating layer of oxides although, hydroxides are not ruled out in serving passivation roles under various aqueous conditions [34] which of course, are enhanced by the inhibitor. Moreover, the low peaks along with reduced atomic representation for Fe, Cr, Na and chlorine atoms in the inhibited medium could only mean that the inhibitor molecules had a strong presence at the steel surface and replaced chloride ions on the surface thereby reduced the corrosive attacks on the steel surface. Hence, EDS analysis confirms that the protective film composed of strongly adhered inhibitor molecules on the metal surface via forming complex chelating ligands and inhibitor-chloride-complex deposits that mitigated the corrosion reaction which is consistent with results obtained from gasometric, electrochemical and SEM analysis.

Table 2: Elemental analysis value of AISI 316L surface corrosion products formed in 3.5% NaCl solution with and without SM leaf extracts

	Inhibited surface			Uninhibited surface		
Element	App Conc.	Weight%	Atomic%	App Conc.	Weight%	Atomic%
C K	114.07	52.80	69.68	7.00	16.10	29.86
N K	2.37	8.39	9.50	--	--	--
O K	17.07	13.10	12.98	33.03	36.57	50.90
Na K	1.06	0.55	0.38	0.42	0.95	0.92
Si K	0.77	0.34	0.19	--	--	--
S K	2.30	0.93	0.46	--	--	--
Cl K	0.91	0.43	0.19	0.51	0.80	0.50
Cr K	9.82	4.27	1.30	5.83	7.85	3.36
Fe K	34.07	16.24	4.61	20.61	30.81	12.29
Ni K	4.43	2.15	0.58	2.46	3.78	1.44
Mo L	1.61	0.79	0.13	1.86	3.13	0.73
Totals		100.00			100.00	

d) *Computational studies*

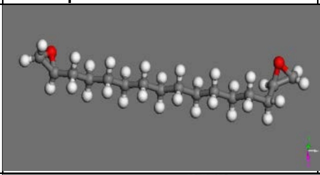
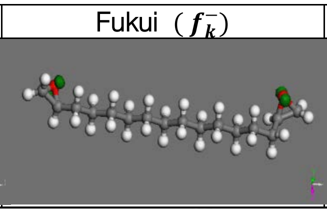
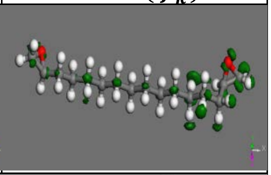
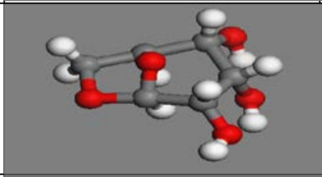
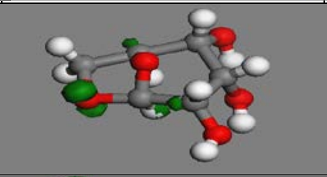
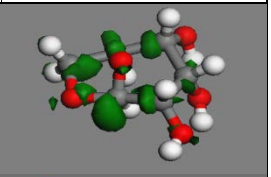
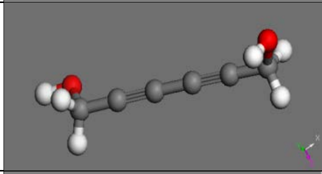
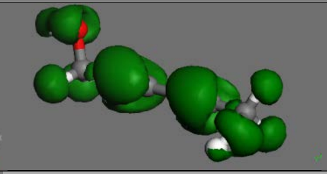
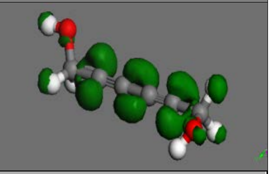
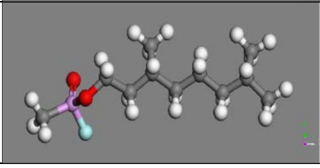
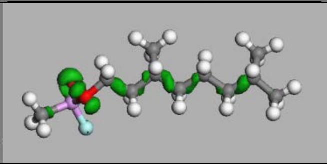
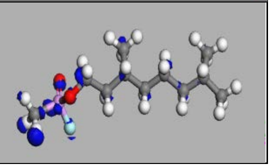
The electrochemical forces among molecular sites stabilize the orbitals in ways in which satisfy the linear combination of atomic orbitals merger [35]. Table 3 records computed quantum chemical analysis include the energy of highest occupied molecular orbital (EHOMO), energy of lowest unoccupied molecular orbital (ELUMO), EHOMO–ELUMO energy gap (ΔE) and binding energy obtained by means of molecular dynamics. The charge density plot of SM leaf extract constituents for EHOMO, ELUMO and total electron density are presented in Fig.5ashowing electron clouds at active sites within individual molecule for interaction with the metal surface. Interactions between frontier orbitals lead to the formation of a transition state with the HOMO as the outermost orbital having high energy which could act as electron donor while the LUMO is the innermost orbital which accepts electron through its vacant room [36]. This implies that low lying ELUMO induces an electrophile behaviour from the metal to the molecule whereas high EHOMO would preferably undergo electron transfer vacant d orbital of the metal surface resulting in a donor-acceptor bond hence, formation of chelating ligand bond via adsorption on the metal surface. The bond formed uses up available sites on the metal surface and reduce further intrusion of reactive species.

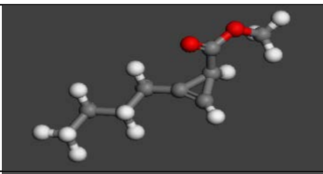
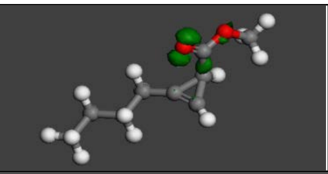
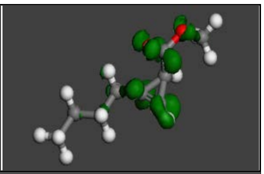
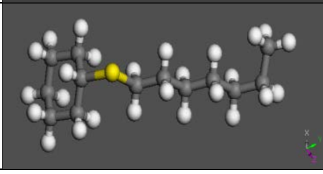
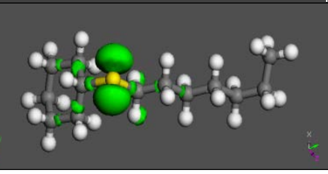
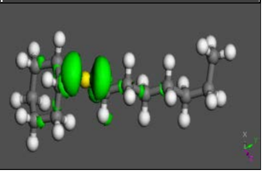
Herrag *et al* [37] reported that excellent corrosion inhibitors are usually molecules that not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal using their anti-bond orbital to form stable chelates. Accordingly Xia *et al* [38] stated that low lying LUMO induces a backdonation of charge from the metal to the molecule whereas high EHOMO facilitates adsorption by influencing the transport process through the adsorbed layer. This implies that SM leaf extract constituents do possess these qualities are good inhibitors as confirmed by the experimental results. It is well known fact that corrosion inhibitors which not only offer electrons to the unfilled d orbital but also have unoccupied orbitals with the tendency of accepting electrons from d-orbital of metal to form stable chelates are considered excellent inhibitors [39]. Examination of Fig. 5a reveal that the HOMO orbital of 1,2-15,16-diepoxyhexadecane molecule were found with high electric density at the oxy- O16 atom with modest electric density at oxy- O18 atom both with lone electron pairs available to donate to the d-orbital of the metal surface and hence provide adsorption centers with the metal surface while its

LUMO orbital were found at the same sites but spread from C8 to C13 atom indicating available sites through which the molecule could accept electrons from the metal resulting in a donor/acceptor bond. This reveals that the molecule has the propensity to adsorb on the metal via donation/backdonation coordinate bond forming ligands that protect the metal surface at the sites where they are attached. The very high value of ELUMO (Table 3) suggests that the molecule had weak electrostatic interaction with the metal via the carbon atoms. The HOMO orbital of 1,6-anhydro-beta-d-talopyranose had its electric density localized around O7, O10, O9 and O11 atoms indicating sites through which the molecule could adsorb and donate electrons to the metal surface while its LUMO orbital were located at same sites but also included the O1 however, the low value of ELUMO indicated that the molecule had affinity for electrons from the metal surface. The low value of EHOMO reveals low surface coverage as expected seeing that the molecule does not have planar geometry (Fig. 5a) hence, could not adsorb on a flat orientation. Examination of the HOMO and LUMO orbital, 2,4-hexadiyne-1,6-diol reveal that the electron rich triple bonds serves as sites for HOMO and LUMO electric density with modest electric density around hydroxyl O1, O8 atom for the formation of chelating ligands with the metal surface. However, considering the low ELUMO values in Table 3 with high EHOMO value suggest that the presence of highly electron releasing character of the triple bond and π-OH enhanced greater adsorption migration towards the metal surface. The orbital plot obtained for 3,7-dimethyl-1-octyl methylphosphonofluoridate showed that the HOMO is localized around the molecule exempting C1, and P2 atom with modest electric density at F13 while the LUMO is situated around C1 to C6 including the hydroxyl hydrogen suggesting the molecule to be of more electron acceptor. This indicates that 3,7-dimethyl-1-octyl methylphosphonofluoridate is preferably adsorbed on the metal surface by electron acceptance via backdonation, rather than by donation of π-electrons to the metal as confirmed by the values in Table 3[40]. Methyl 2-butyl-2-cyclopropene-1-carboxylate and cyclohexyl heptyl had the electric density for HOMO and LUMO located within the same region at the electron rich double bond and lone pair electrons available for donation. The unshared electron pair on the oxygen atoms are weakly basic and can be protonated in acidic or near neutral media, suggesting that the molecule will be attached at the cathodic site thereby forming adsorbed surface film due to electrostatic interaction at the metal/electrolyte interface which hinders cathodic reaction and reduce dissolution of the metal. This electrostatic interaction is suggested to be weak in nature considering the values of energy gap (ΔE) recorded in Table 3. Similarly, Fukui indices density plots reveals that the region of f_k^+ corresponds to the LUMO region of the same molecule whereas the f_k^- region assumes the regions where the HOMO charge densities are high [41].

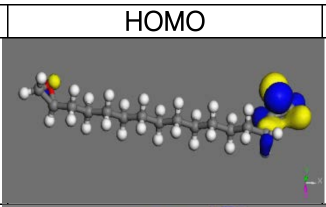
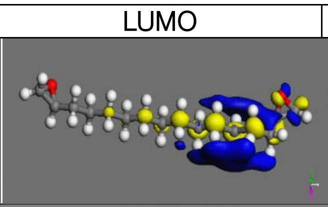
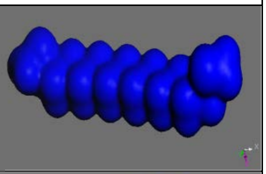
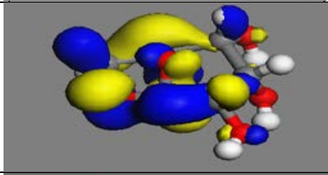
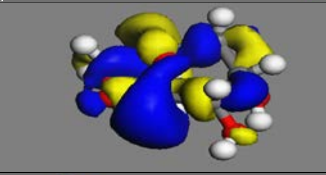
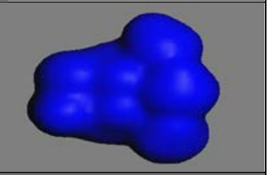
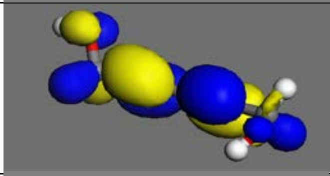
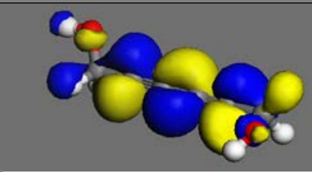
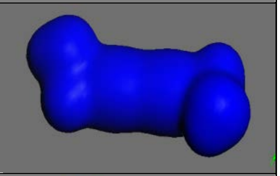
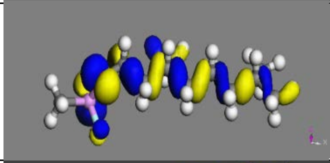
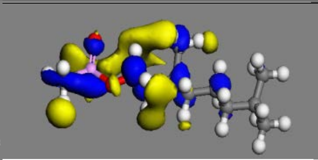
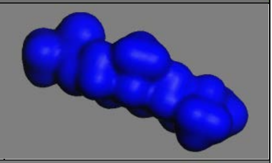
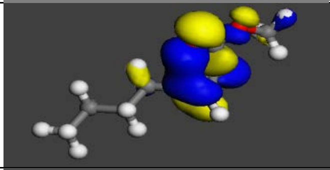
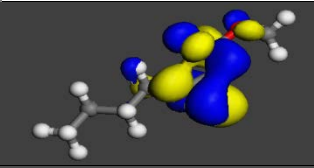
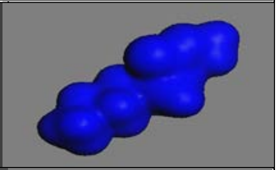
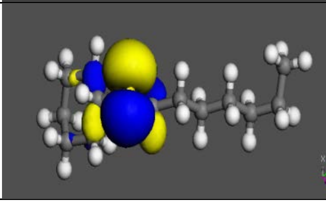
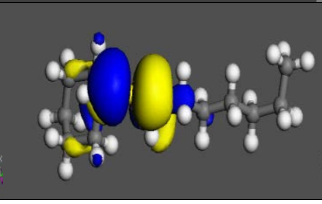
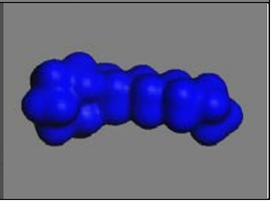
Fig. 5. A): Electronic structures and Fukui indices for SM leaf extract constituents. B). Electronic properties showing the highest occupied molecular orbitals (HOMO), highest unoccupied molecular orbital (LUMO) and total electron density (TED)

A

Molecule	Optimized structure	Fukui (f_k^-)	Fukui (f_k^+)
1,2-15,16-Diepoxyhexadecane			
1,6-Anhydro-beta-d-talopyranose			
2,4-hexadiyne-1,6-diol			
3,7-Dimethyl-1-octyl methyl-phosphonofluoridate			

Methyl 2-butyl-2-cyclopropene-1-carboxylate			
Cyclohexyl heptyl			

B

Molecule	HOMO	LUMO	TED
1,2-15,16-Diepoxyhexadecane			
1,6-Anhydro-beta-d-talopyranose			
2,4-hexadiyne-1,6-diol			
3,7-Dimethyl-1-octyl methyl phosphonofluoridate			
Methyl 2-butyl-2-cyclopropene-1-carboxylate			
Cyclohexyl heptyl			

The Mulliken population charges reference describes mainly the accumulation of potential energy among different species on which the lattice of electrostatic potential surfaces is ascribed [42] while the Fukui indices which describe reactive sites within a molecule as well as its tendency to accept/donate electrons [43] with the metal surface. Fig. 5b shows the Fukui density plots and molecule optimized structures. The reactive site with tendency to release electrons will be the place where the value of f_k^+ is a maximum, while reactive site for receiptibility of released electrons is controlled by the maximum value of f_k^-. The condensed Fukui functions distinguish each part of the molecule based on distinct chemical behavior of the different substituent functional groups [43]. Fig. 5b shows the Fukui density plots and the reactive sites of 1,2-15,16-diepoxyhexadecane were at O16, O18 and C13atom with Mulliken population charges to be -0.431, -0.428 and -0.204 respectively indicating species with the propensity to form coordinate bond with the metal surface. 1,6-anhydro-beta-d-talopyranose exhibited the ability to accept electrons at O7, O11, O1 atom from the metal surface Mulliken population charges to be -0.523, -0.445 and -0.417 while the possibility of donating electrons to the vacant sites on the metal via C6, C3 atom with Mulliken population charges +0.307 and +0.104 respectively. The population analysis data shows that O1, O7, O9, O10, O11 atom carries high negative charge indicating their participation in forming coordinate bonds with the metal surface. Analyzing the results obtained for 3,7-Dimethyl-1-octyl methylphosphonofluoridate revealed O12, O3, F13 atoms as sites where the molecule interact via accepting electrons with Mulliken population charges to be -0.573, -0.532, -0.373 respectively while possible electron donation was via through P2 atoms (+1.247) and probable chelating ligand formation as revealed by Mulliken charges. The affinity to donate/accept electrons for 2,4-hexadiyne-1,6-diol was chiefly at O1, O8 atom with Mulliken charges of -0.469 and -0.482 respectively. However, the population analysis had high charges for $f-$ values which suggests that it tends to adsorb on the metal surface via electrostatic electron transfer to form coordinate bonds on a flat orientation and reduce available active sites for corrosion. Methyl 2-butyl-2-cyclopropene-1-carboxylate used C1, C4 and C3 atom for interaction with the metal surface with Mulliken charges of -0.256, +0.470 and -0.156 respectively however, carbon atoms are known to form weak electrostatic bonds with the metal surface. The population charge analysis revealed O5 atom (-0.402) and O6 atom (-0.400) with high negative charges including it as potential zones through which the molecule adsorbed onto metal surface.

The efficiency of an organic compound as a successful inhibitor is mainly dependent on its ability to be adsorbed on the metal surface, which includes of the replacement of water molecule at a corroding interface [15]. To quantitatively evaluate the most suitable adsorption configuration of inhibitor molecule on optimized metal surface cleaved along (110) plane, the adsorption energy (E_{Bind}) was calculated and reported in Table 3. The obtained values show that 1,2-15,16-diepoxyhexadecane and 2,4-hexadiyne-1,6-diol exhibit the most favourable binding energy for SM leaf extract molecular composition during the simulation processes. The high values of binding energy for 1,2-15,16-diepoxyhexadecane and 2,4-hexadiyne-1,6-diol is attributed to existence of planar geometry and favourable electronic properties. Electron rich multiple bonds enhanced electrostatic interaction with the metal surface and the presence of p-π conjugation system at the O atoms resulted in a dissociative adsorption which is favourable to crack intramolecular bond of the adsorbate molecule [44]. Oxy- groups are generally known to hydrolyze in acidic/near neutral solutions which indicate that the molecule is suitable to displace water molecules at the metal surface. The high value of *E*Bind obtained for 2,4-hexadiyne-1,6-diol infers a probable chemisorption as expected which affirms the observed electron donation and backdonation at the same sites. The presence of lone pair electrons on O atoms provided electrons to the unfilled *3d* orbital of the metal surface thereby forming a protective layer via adsorption. Such protective film acts as steric barrier that hinders the reactiveness of corrosive species in the environment coming in contact with the metal surface hence, a mitigation of corrosion process. 1,6-Anhydro-beta-talopyranose exhibited low binding energy despite a number of O atoms present in the molecular structure which confirms that non planar molecular structure engenders low inhibition. Moreover, the energy gap was observed to be low suggesting that the presence of O atoms in the molecule with high population charges offer electrons to the metal surface to form coordinate bonds counteracted the non planar structure to exhibit inhibiting qualities against corrosion. The adsorption orientation of all inhibitor constituent molecules revealed that polarizable atoms in their molecular backbone aligned with vacant sites on the fcc lattice atop the metal surface and virtually avoided contact with the metal atoms along surface. This is expected considering that the electron deficient regions along Fe(110) surface are found within the vacant sites of the crystal plane. This supports the idea that constituent molecules of the present inhibitors did adsorb directly on the metal surface on the basis of donor–acceptor interactions between π-electrons, non-bonding lone pairs of S, O and F atoms and vacant d-orbitals of metal surface [45,46]. The S and N atoms probably formed ligands with the metal through lone pair electrons which acts as thin films that protect the steel surface along with the oxides of the metal.

Table 3: EHOMO, ELUMO, energy gap (Δ*E*), and Binding energy (*E*Bind) from the molecular dynamic simulations for SM leaf extracts molecular compositions

Property	EHOMO (Ha)	ELUMO (Ha)	*ΔE* (Ha)	*E*bind (Kcal/Mol)
1,6-Anhydro-beta-talopyranose	-0.1898	-0.0587	0.1311	-87.98
1,2-15,16-diepoxyhexadecane	-0.2263	0.0364	0.2627	-159
2,4-hexadiyne-1,6-diol	-0.2211	-0.0746	0.1465	-159
3,7-Dimethyl-1-octyl methylphosphonofluoridate	-0.2639	-0.0192	0.2447	-128
Methyl 2-butyl-2-cyclopropene-1-carboxylate	-0.2187	-0.0468	0.1719	-100.6
Cyclohexyl heptyl	-0.1807	0.0035	0.1842	-139.8

IV. CONCLUSION

The purpose of this study was to evaluate SM extracts for corrosion protection of AISI 316L in 3.5% NaCl solution and to attempt explanation of the mechanism of action. Obtained results in the study have shown that corrosion protection is attained because of the extracts' constituents being adsorbed on AISI 316L surface with pronounced effect on the passivation mechanism. This passivation enhancing effect was ascribed to the adsorbed organic matter which did modify the nature of electron transfer processes across the metal/solution interface. Quantum chemical simulations where used theoretically investigate the interaction of the extract constituents with the metal at the molecular level and data obtained revealed a strong and spontaneous adsorption of the constituents on Fe(110) slab, which should be responsible for the observed corrosion inhibiting efficacy of SM leaf extracts.

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Residual Silica in Raw Jute and Elimination Scope

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Abstract- Jute- the golden fibre of Bangladesh is used widely for various purposes. But it is reported that there is a draw back facing in the industrial machinery while processing the jute fibre for its product due to the presence of Residual Silica / Silicates. Under very warm condition the silicates may split into silica. Since silica and silicates are semi -metal, they exhibit conductive property in raw jute and also in jute products. An investigation was carried out in BJRI & PDB, Ghorasal Laboratory to find out the content of Residual silica /silicates by Spectrophotometric and Ashing methods in retted raw jute fiber of Faridpur zone for suggesting the remedial measure.

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RESIDUALSILICAINRAWJUTEANDELIMINATIONSCOPE

Residual Silica in Raw Jute and Elimination Scope

Mubarak Hossen α, Mohd. Sabder Ali Khan σ, Ayesha Khatton ρ & Mahmuda Begum ω

Abstract- Jute- the golden fibre of Bangladesh is used widely for various purposes. But it is reported that there is a draw back facing in the industrial machinery while processing the jute fibre for its product due to the presence of Residual Silica / Silicates. Under very warm condition the silicates may split into silica. Since silica and silicates are semi -metal, they exhibit conductive property in raw jute and also in jute products. An investigation was carried out in BJRI & PDB, Ghorasal Laboratory to find out the content of Residual silica /silicates by Spectrophotometric and Ashing methods in retted raw jute fiber of Faridpur zone for suggesting the remedial measure.

I. INTRODUCTION

Jute is an important raw material for producing paper and pulp, domestic purposes, body materials of vehicles, cloths, handicraft materials, gunny bag, etc. A long process is to follow to get the jute fibre in the hand of the user starting from its growth when there is every possibility to carry so many impurities among which Silica is one of them, and this Silica in jute creates a lot of problems (1,3). Some plants contain an appreciable amount of Silica in plant tissues. The green plant only from the soil usually absorbs most of the elements other than Carbon and Oxygen. Elements that enter into a plant from the soil might be presented to it in the form of its soluble component (2,5). During the last few decades, much diversity of opinions about the effect of silica on the plant growth has been expressed. It has been reported that the silicon is an element, which occurs in the plants universally and the amount of silica present in the plant varies greatly for different plants and again varies for different parts of the same plant (1,3,4,5). It has been reported that the silica content is commonly found more not only in leaves but also in the stem of the plant (5,6). A large amount of jute fibre is being used as raw material for paper and pulp. There is no doubt that if jute contains significant amounts of Silica in the process of pulping, it will be separated from the fibre and will appear in the black liquor (waste stem) in the form of Sodium Silicate and another complex Siliceous compound. Gradually the separated Silicate/ Siliceous compounds accumulating and causes hard Scaling in evaporator tubes and other associated parts of the recovery system, reducing their efficiency and ultimately increasing maintenance as well as production costs. Also, the other oxides/compounds along with Silica either will deposit or will cause corrosion in the machinery of the factory. The mineral matters associated with raw jute fibres are inorganic salts, oxides of metals, Silicates and Silica might be due to the contamination during retting, washing, drying, storing, marketing and, eventually transportation. On the other hand, water-soluble Silicates possess some polarity. In some specific warm condition, the silicates may split into Silica (4,6). Both Silica & Silicates may disburse the conductive property of raw jute. So, it is very important to have either Silica free or the least amount of silica content in the Jute fibre to avoid the above problems. Therefore, an investigation was conducted to find out the content of silica in the jute fibre for suggesting a remedial measure so that raw jute fibre could be used in producing good quality of its product and to maintain the machinery in good condition.

II. MATERIALS & METHODS

Retted Raw jute samples (conventional & control system) were collected from Faridpur zone. Green jute sample was taken from BJRI experimental field.

a) *Apparatus*

UV/VIS – Spectrophotometer, Glass wares, reagent grade chemicals, ashless filter paper etc. were used according to the need of experiment. Standard SiO_2 solution was stored in a clean dark plastic bottle.

b) *Reagents*

Ammonium hepta Molybdate (10% w/v), Oxalic Acid Solution (10% w/v), 1-Amino- 2- Naphthol - 4-Sulfonic Acid Solution (ANSA), 1:1 HCl acid, SiO_2 Standard Solution prepared by dissolving 0.4732 gm of $Na_2SiO_3.9H_2O$ ($SiO_2 = 100$ ppm), and Silica free water.

c) *Procedure*

To measure the content of silica- the Green Jute stick was washed and taken out the ribbon and cut into small pieces of about 2-3 cm long and was burnt in a platinum crucible and then a solution was prepared followed by fusion taking a certain quantity of ash for colorimetric (UV/VIS- spectrophotometric) analyses. Retted jute fibre was hydrolyzed using caustic & 0.1N HCl to extract both the soluble and insoluble Silica / Silicates. After hydrolysis, the jute fibre was taken out

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and rinsed several times. All the rinsing water collected together. The solution recovered by filtration was used for Colorimetric determination to measure the content of soluble silica and the residue left in the filter paper was used to find out the content of insoluble silica (7). The residue in the filter paper was treated by aqua regia to remove any heavy metal, which is not dissolved by HCl. Insoluble silica was determined by ashing method at 500°C ± 50°C using a Platinum crucible and Muffle furnace.

The amount of insoluble Silica was the difference between the weight of dried empty Crucible and the weight of crucible after making ash as stated above. The total silica was the sum of soluble Silica and insoluble Silica. The UV/ Vis - spectrophotometer was calibrated by using 0 ppm, 2 ppm, 4 ppm, 8 ppm, 12 ppm, 16 ppm, & 20 ppm of Standard SiO_2 solution according to ASTM D-859 procedure.

III. Results and Discussion

The results of Silica determined by Colorimetric and Ashing methods – presented below in tables 1,2 & 3.

Table 1: Determination of Silica / Silicates in different parts of Green Jute plant Collected from BJRI experimental field

Serial No.	Sample type	% of Silica content as SiO_2	Sample collected from
1	Top	0.0004	BJRI experimental field.
2	Middle	0.0003	
3	Bottom	0.00031	
4	Root	0.0013	

Table 2: Determination of Silica / Silicates in Jute collected from Faridpur zone retted under conventional system

Sl. No	Sample collected atea	Collection source	Retting water Condition & Jack material used.	Washing condi-tion	Drying Condition	% of total Silica Content as SiO_2.
01	Ragunan-dnpur	Produ-cer	Stagnant water under Grass& banana logs	Turbid water	Bamboo log	0.0129
02	Nakulhati	Whole-saler	Stagnant water under water hyacinth	Clean water	Bamboo log	0.0056
03	Talma	Produ-cer	Stagnant water under banana logs	Turbid water	Bamboo log	0.0142
04	Kaniepur	Whole-saler	Stagnant water under water hyacinth	Clean water	Bamboo log	0.0118

Table 3: Determination of Silica / Silicates in jute samples collected from Faridpur zone retted under control system

Sl. No.	Sample collected area	Collection source	Retting water Condition & Jack material used.	Washing condition	Drying Condition	% of total Silica Content as SiO_2.
01	Faridpur	BJRI	Stagnant water	Clean water	Bamboo log	0.0037
02	Faridpur	BJRI	Stagnant water	Clean water	Bamboo log	0.0028

The contaminants like silica in jute can cause a significant problem for machineries. Silica accumulates and hardens on machinery creating the need to frequently stop production and clean with chemicals. Frequent shutting down machinery in mill / industry decreases the chance of creating economically viable product. Again small mills will be more affected because chemical recovery does not make economical sense.

So, it is very important to reduce the amount of Silica content in Jute fibre. From the analyses results of green jute ribbon shown in Table 1, it seems that the silica in jute by nature is very negligible which in practical might not be any problem in industries. It is easily understood from the green jute analysis that the silica in it either could be the analysis error or a trace amount of soluble Silica exists naturally. It can be concluded from the analyses results shown in table 2 & 3 that the conventional retted & retted under control system respectively - the significant amount of Silica / Silicates in jute is nothing but a result of contamination causes at the time of retting, washing, drying, storing and transportation.

a) *Remedial measure*

Some investigations were done to reduce the content of Silica. From that experiment the following suggestions could be adopted for remedial measures.

(1) While retting the jute- use clean water, bamboo chunk beneath the jute for jag and use concrete block Bamboo/ Wooden log on the top of jag as

weight- should not use banana log, soil chunk, water hyacinth.

(2) Wash in clean water and dry on bamboo/ wooden log instead of using open filed and store on bamboo / wooden terrace- not on the floor.

(3) If the jute looks dirty due to water contamination- shock it with 4-5% detergent for one hour, then wash out the detergent and then finally wash with 4-5% HCl acid solution for 30-60 minutes.

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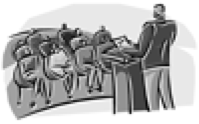

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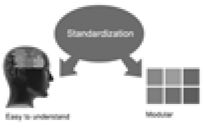

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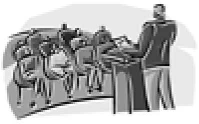

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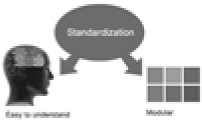

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- In addition to above, if one is single author, then entitled to 40% discount on publishing research paper and can get 10%discount if one is co-author or main author among group of authors.
- The Fellow can organize symposium/seminar/conference on behalf of Global Journals Incorporation (USA) and he/she can also attend the same organized by other institutes on behalf of Global Journals.
- The Fellow can become member of Editorial Board Member after completing 3yrs.
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- • This individual has learned the basic methods of applying those concepts and techniques to common challenging situations. This individual has further demonstrated an in–depth understanding of the application of suitable techniques to a particular area of research practice.

Note :

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- In future, if the board feels the necessity to change any board member, the same can be done with the consent of the chairperson along with anyone board member without our approval.
- In case, the chairperson needs to be replaced then consent of 2/3rd board members are required and they are also required to jointly pass the resolution copy of which should be sent to us. In such case, it will be compulsory to obtain our approval before replacement.
- In case of "Difference of Opinion [if any]" among the Board members, our decision will be final and binding to everyone.

"

PREFERRED AUTHOR GUIDELINES

We accept the manuscript submissions in any standard (generic) format.

We typeset manuscripts using advanced typesetting tools like Adobe In Design, CorelDraw, TeXnicCenter, and TeXStudio. We usually recommend authors submit their research using any standard format they are comfortable with, and let Global Journals do the rest.

Alternatively, you can download our basic template from https://globaljournals.org/Template.zip

Authors should submit their complete paper/article, including text illustrations, graphics, conclusions, artwork, and tables. Authors who are not able to submit manuscript using the form above can email the manuscript department at submit@globaljournals.org or get in touch with chiefeditor@globaljournals.org if they wish to send the abstract before submission.

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Authors must ensure the information provided during the submission of a paper is authentic. Please go through the following checklist before submitting:

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2. Authors must accept the privacy policy, terms, and conditions of Global Journals.
3. Ensure corresponding author's email address and postal address are accurate and reachable.
4. Manuscript to be submitted must include keywords, an abstract, a paper title, co-author(s') names and details (email address, name, phone number, and institution), figures and illustrations in vector format including appropriate captions, tables, including titles and footnotes, a conclusion, results, acknowledgments and references.
5. Authors should submit paper in a ZIP archive if any supplementary files are required along with the paper.
6. Proper permissions must be acquired for the use of any copyrighted material.
7. Manuscript submitted *must not have been submitted or published elsewhere* and all authors must be aware of the submission.

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- Findings
- Writings
- Diagrams
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- Illustrations
- Lectures

- Printed material
- Graphic representations
- Computer programs
- Electronic material
- Any other original work

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3. Final approval of the version of the paper to be published.

Changes in Authorship

The corresponding author should mention the name and complete details of all co-authors during submission and in manuscript. We support addition, rearrangement, manipulation, and deletions in authors list till the early view publication of the journal. We expect that corresponding author will notify all co-authors of submission. We follow COPE guidelines for changes in authorship.

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Unless specified in the notification, the Editorial Board's decision on publication of the paper is final and cannot be appealed before making the major change in the manuscript.

Acknowledgments

Contributors to the research other than authors credited should be mentioned in Acknowledgments. The source of funding for the research can be included. Suppliers of resources may be mentioned along with their addresses.

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PREPARING YOUR MANUSCRIPT

Authors can submit papers and articles in an acceptable file format: MS Word (doc, docx), LaTeX (.tex, .zip or .rar including all of your files), Adobe PDF (.pdf), rich text format (.rtf), simple text document (.txt), Open Document Text (.odt), and Apple Pages (.pages). Our professional layout editors will format the entire paper according to our official guidelines. This is one of the highlights of publishing with Global Journals—authors should not be concerned about the formatting of their paper. Global Journals accepts articles and manuscripts in every major language, be it Spanish, Chinese, Japanese, Portuguese, Russian, French, German, Dutch, Italian, Greek, or any other national language, but the title, subtitle, and abstract should be in English. This will facilitate indexing and the pre-peer review process.

The following is the official style and template developed for publication of a research paper. Authors are not required to follow this style during the submission of the paper. It is just for reference purposes.

Manuscript Style Instruction (Optional)

- Microsoft Word Document Setting Instructions.
- Font type of all text should be Swis721 Lt BT.
- Page size: 8.27" x 11'", left margin: 0.65, right margin: 0.65, bottom margin: 0.75.
- Paper title should be in one column of font size 24.
- Author name in font size of 11 in one column.
- Abstract: font size 9 with the word "Abstract" in bold italics.
- Main text: font size 10 with two justified columns.
- Two columns with equal column width of 3.38 and spacing of 0.2.
- First character must be three lines drop-capped.
- The paragraph before spacing of 1 pt and after of 0 pt.
- Line spacing of 1 pt.
- Large images must be in one column.
- The names of first main headings (Heading 1) must be in Roman font, capital letters, and font size of 10.
- The names of second main headings (Heading 2) must not include numbers and must be in italics with a font size of 10.

Structure and Format of Manuscript

The recommended size of an original research paper is under 15,000 words and review papers under 7,000 words. Research articles should be less than 10,000 words. Research papers are usually longer than review papers. Review papers are reports of significant research (typically less than 7,000 words, including tables, figures, and references)

A research paper must include:

a) A title which should be relevant to the theme of the paper.
b) A summary, known as an abstract (less than 150 words), containing the major results and conclusions.
c) Up to 10 keywords that precisely identify the paper's subject, purpose, and focus.
d) An introduction, giving fundamental background objectives.
e) Resources and techniques with sufficient complete experimental details (wherever possible by reference) to permit repetition, sources of information must be given, and numerical methods must be specified by reference.
f) Results which should be presented concisely by well-designed tables and figures.
g) Suitable statistical data should also be given.
h) All data must have been gathered with attention to numerical detail in the planning stage.

Design has been recognized to be essential to experiments for a considerable time, and the editor has decided that any paper that appears not to have adequate numerical treatments of the data will be returned unrefereed.

i) Discussion should cover implications and consequences and not just recapitulate the results; conclusions should also be summarized.
j) There should be brief acknowledgments.
k) There ought to be references in the conventional format. Global Journals recommends APA format.

Authors should carefully consider the preparation of papers to ensure that they communicate effectively. Papers are much more likely to be accepted if they are carefully designed and laid out, contain few or no errors, are summarizing, and follow instructions. They will also be published with much fewer delays than those that require much technical and editorial correction.

The Editorial Board reserves the right to make literary corrections and suggestions to improve brevity.

FORMAT STRUCTURE

It is necessary that authors take care in submitting a manuscript that is written in simple language and adheres to published guidelines.

All manuscripts submitted to Global Journals should include:

Title

The title page must carry an informative title that reflects the content, a running title (less than 45 characters together with spaces), names of the authors and co-authors, and the place(s) where the work was carried out.

Author details

The full postal address of any related author(s) must be specified.

Abstract

The abstract is the foundation of the research paper. It should be clear and concise and must contain the objective of the paper and inferences drawn. It is advised to not include big mathematical equations or complicated jargon.

Many researchers searching for information online will use search engines such as Google, Yahoo or others. By optimizing your paper for search engines, you will amplify the chance of someone finding it. In turn, this will make it more likely to be viewed and cited in further works. Global Journals has compiled these guidelines to facilitate you to maximize the web-friendliness of the most public part of your paper.

Keywords

A major lynchpin of research work for the writing of research papers is the keyword search, which one will employ to find both library and internet resources. Up to eleven keywords or very brief phrases have to be given to help data retrieval, mining, and indexing.

One must be persistent and creative in using keywords. An effective keyword search requires a strategy: planning of a list of possible keywords and phrases to try.

Choice of the main keywords is the first tool of writing a research paper. Research paper writing is an art. Keyword search should be as strategic as possible.

One should start brainstorming lists of potential keywords before even beginning searching. Think about the most important concepts related to research work. Ask, "What words would a source have to include to be truly valuable in a research paper?" Then consider synonyms for the important words.

It may take the discovery of only one important paper to steer in the right keyword direction because, in most databases, the keywords under which a research paper is abstracted are listed with the paper.

Numerical Methods

Numerical methods used should be transparent and, where appropriate, supported by references.

Abbreviations

Authors must list all the abbreviations used in the paper at the end of the paper or in a separate table before using them.

Formulas and equations

Authors are advised to submit any mathematical equation using either MathJax, KaTeX, or LaTeX, or in a very high-quality image.

Tables, Figures, and Figure Legends

Tables: Tables should be cautiously designed, uncrowned, and include only essential data. Each must have an Arabic number, e.g., Table 4, a self-explanatory caption, and be on a separate sheet. Authors must submit tables in an editable format and not as images. References to these tables (if any) must be mentioned accurately.

Figures

Figures are supposed to be submitted as separate files. Always include a citation in the text for each figure using Arabic numbers, e.g., Fig. 4. Artwork must be submitted online in vector electronic form or by emailing it.

PREPARATION OF ELETRONIC FIGURES FOR PUBLICATION

Although low-quality images are sufficient for review purposes, print publication requires high-quality images to prevent the final product being blurred or fuzzy. Submit (possibly by e-mail) EPS (line art) or TIFF (halftone/ photographs) files only. MS PowerPoint and Word Graphics are unsuitable for printed pictures. Avoid using pixel-oriented software. Scans (TIFF only) should have a resolution of at least 350 dpi (halftone) or 700 to 1100 dpi (line drawings). Please give the data for figures in black and white or submit a Color Work Agreement form. EPS files must be saved with fonts embedded (and with a TIFF preview, if possible).

For scanned images, the scanning resolution at final image size ought to be as follows to ensure good reproduction: line art: >650 dpi; halftones (including gel photographs): >350 dpi; figures containing both halftone and line images: >650 dpi.

Color charges: Authors are advised to pay the full cost for the reproduction of their color artwork. Hence, please note that if there is color artwork in your manuscript when it is accepted for publication, we would require you to complete and return a Color Work Agreement form before your paper can be published. Also, you can email your editor to remove the color fee after acceptance of the paper.

TIPS FOR WRITING A GOOD QUALITY SCIENCE FRONTIER RESEARCH PAPER

Techniques for writing a good quality Science Frontier Research paper:

1. Choosing the topic: In most cases, the topic is selected by the interests of the author, but it can also be suggested by the guides. You can have several topics, and then judge which you are most comfortable with. This may be done by asking several questions of yourself, like "Will I be able to carry out a search in this area? Will I find all necessary resources to accomplish the search? Will I be able to find all information in this field area?" If the answer to this type of question is "yes," then you ought to choose that topic. In most cases, you may have to conduct surveys and visit several places. Also, you might have to do a lot of work to find all the rises and falls of the various data on that subject. Sometimes, detailed information plays a vital role, instead of short information. Evaluators are human: The first thing to remember is that evaluators are also human beings. They are not only meant for rejecting a paper. They are here to evaluate your paper. So present your best aspect.

2. Think like evaluators: If you are in confusion or getting demotivated because your paper may not be accepted by the evaluators, then think, and try to evaluate your paper like an evaluator. Try to understand what an evaluator wants in your research paper, and you will automatically have your answer. Make blueprints of paper: The outline is the plan or framework that will help you to arrange your thoughts. It will make your paper logical. But remember that all points of your outline must be related to the topic you have chosen.

3. Ask your guides: If you are having any difficulty with your research, then do not hesitate to share your difficulty with your guide (if you have one). They will surely help you out and resolve your doubts. If you can't clarify what exactly you require for your work, then ask your supervisor to help you with an alternative. He or she might also provide you with a list of essential readings.

4. Use of computer is recommended: As you are doing research in the field of science frontier then this point is quite obvious. Use right software: Always use good quality software packages. If you are not capable of judging good software, then you can lose the quality of your paper unknowingly. There are various programs available to help you which you can get through the internet.

5. Use the internet for help: An excellent start for your paper is using Google. It is a wondrous search engine, where you can have your doubts resolved. You may also read some answers for the frequent question of how to write your research paper or find a model research paper. You can download books from the internet. If you have all the required books, place importance on reading, selecting, and analyzing the specified information. Then sketch out your research paper. Use big pictures: You may use encyclopedias like Wikipedia to get pictures with the best resolution. At Global Journals, you should strictly follow here.

6. Bookmarks are useful: When you read any book or magazine, you generally use bookmarks, right? It is a good habit which helps to not lose your continuity. You should always use bookmarks while searching on the internet also, which will make your search easier.

7. Revise what you wrote: When you write anything, always read it, summarize it, and then finalize it.

8. Make every effort: Make every effort to mention what you are going to write in your paper. That means always have a good start. Try to mention everything in the introduction—what is the need for a particular research paper. Polish your work with good writing skills and always give an evaluator what he wants. Make backups: When you are going to do any important thing like making a research paper, you should always have backup copies of it either on your computer or on paper. This protects you from losing any portion of your important data.

9. Produce good diagrams of your own: Always try to include good charts or diagrams in your paper to improve quality. Using several unnecessary diagrams will degrade the quality of your paper by creating a hodgepodge. So always try to include diagrams which were made by you to improve the readability of your paper. Use of direct quotes: When you do research relevant to literature, history, or current affairs, then use of quotes becomes essential, but if the study is relevant to science, use of quotes is not preferable.

10. Use proper verb tense: Use proper verb tenses in your paper. Use past tense to present those events that have happened. Use present tense to indicate events that are going on. Use future tense to indicate events that will happen in the future. Use of wrong tenses will confuse the evaluator. Avoid sentences that are incomplete.

11. Pick a good study spot: Always try to pick a spot for your research which is quiet. Not every spot is good for studying.

12. Know what you know: Always try to know what you know by making objectives, otherwise you will be confused and unable to achieve your target.

13. Use good grammar: Always use good grammar and words that will have a positive impact on the evaluator; use of good vocabulary does not mean using tough words which the evaluator has to find in a dictionary. Do not fragment sentences. Eliminate one-word sentences. Do not ever use a big word when a smaller one would suffice.

Verbs have to be in agreement with their subjects. In a research paper, do not start sentences with conjunctions or finish them with prepositions. When writing formally, it is advisable to never split an infinitive because someone will (wrongly) complain. Avoid clichés like a disease. Always shun irritating alliteration. Use language which is simple and straightforward. Put together a neat summary.

14. Arrangement of information: Each section of the main body should start with an opening sentence, and there should be a changeover at the end of the section. Give only valid and powerful arguments for your topic. You may also maintain your arguments with records.

15. Never start at the last minute: Always allow enough time for research work. Leaving everything to the last minute will degrade your paper and spoil your work.

16. Multitasking in research is not good: Doing several things at the same time is a bad habit in the case of research activity. Research is an area where everything has a particular time slot. Divide your research work into parts, and do a particular part in a particular time slot.

17. Never copy others' work: Never copy others' work and give it your name because if the evaluator has seen it anywhere, you will be in trouble. Take proper rest and food: No matter how many hours you spend on your research activity, if you are not taking care of your health, then all your efforts will have been in vain. For quality research, take proper rest and food.

18. Go to seminars: Attend seminars if the topic is relevant to your research area. Utilize all your resources.

19. Refresh your mind after intervals: Try to give your mind a rest by listening to soft music or sleeping in intervals. This will also improve your memory. Acquire colleagues: Always try to acquire colleagues. No matter how sharp you are, if you acquire colleagues, they can give you ideas which will be helpful to your research.

20. Think technically: Always think technically. If anything happens, search for its reasons, benefits, and demerits. Think and then print: When you go to print your paper, check that tables are not split, headings are not detached from their descriptions, and page sequence is maintained.

21. Adding unnecessary information: Do not add unnecessary information like "I have used MS Excel to draw graphs." Irrelevant and inappropriate material is superfluous. Foreign terminology and phrases are not apropos. One should never take a broad view. Analogy is like feathers on a snake. Use words properly, regardless of how others use them. Remove quotations. Puns are for kids, not grunt readers. Never oversimplify: When adding material to your research paper, never go for oversimplification; this will definitely irritate the evaluator. Be specific. Never use rhythmic redundancies. Contractions shouldn't be used in a research paper. Comparisons are as terrible as clichés. Give up ampersands, abbreviations, and so on. Remove commas that are not necessary. Parenthetical words should be between brackets or commas. Understatement is always the best way to put forward earth-shaking thoughts. Give a detailed literary review.

22. Report concluded results: Use concluded results. From raw data, filter the results, and then conclude your studies based on measurements and observations taken. An appropriate number of decimal places should be used. Parenthetical remarks are prohibited here. Proofread carefully at the final stage. At the end, give an outline to your arguments. Spot perspectives of further study of the subject. Justify your conclusion at the bottom sufficiently, which will probably include examples.

23. Upon conclusion: Once you have concluded your research, the next most important step is to present your findings. Presentation is extremely important as it is the definite medium though which your research is going to be in print for the rest of the crowd. Care should be taken to categorize your thoughts well and present them in a logical and neat manner. A good quality research paper format is essential because it serves to highlight your research paper and bring to light all necessary aspects of your research.

Informal Guidelines of Research Paper Writing

Key points to remember:

- Submit all work in its final form.
- Write your paper in the form which is presented in the guidelines using the template.
- Please note the criteria peer reviewers will use for grading the final paper.

Final points:

One purpose of organizing a research paper is to let people interpret your efforts selectively. The journal requires the following sections, submitted in the order listed, with each section starting on a new page:

The introduction: This will be compiled from reference matter and reflect the design processes or outline of basis that directed you to make a study. As you carry out the process of study, the method and process section will be constructed like that. The results segment will show related statistics in nearly sequential order and direct reviewers to similar intellectual paths throughout the data that you gathered to carry out your study.

The discussion section:

This will provide understanding of the data and projections as to the implications of the results. The use of good quality references throughout the paper will give the effort trustworthiness by representing an alertness to prior workings.

Writing a research paper is not an easy job, no matter how trouble-free the actual research or concept. Practice, excellent preparation, and controlled record-keeping are the only means to make straightforward progression.

General style:

Specific editorial column necessities for compliance of a manuscript will always take over from directions in these general guidelines.

To make a paper clear: Adhere to recommended page limits.

Mistakes to avoid:

- Insertion of a title at the foot of a page with subsequent text on the next page.
- Separating a table, chart, or figure—confine each to a single page.
- Submitting a manuscript with pages out of sequence.
- In every section of your document, use standard writing style, including articles ("a" and "the").
- Keep paying attention to the topic of the paper.
- Use paragraphs to split each significant point (excluding the abstract).
- Align the primary line of each section.
- Present your points in sound order.
- Use present tense to report well-accepted matters.
- Use past tense to describe specific results.
- Do not use familiar wording; don't address the reviewer directly. Don't use slang or superlatives.
- Avoid use of extra pictures—include only those figures essential to presenting results.

Title page:

Choose a revealing title. It should be short and include the name(s) and address(es) of all authors. It should not have acronyms or abbreviations or exceed two printed lines.

Abstract: This summary should be two hundred words or less. It should clearly and briefly explain the key findings reported in the manuscript and must have precise statistics. It should not have acronyms or abbreviations. It should be logical in itself. Do not cite references at this point.

An abstract is a brief, distinct paragraph summary of finished work or work in development. In a minute or less, a reviewer can be taught the foundation behind the study, common approaches to the problem, relevant results, and significant conclusions or new questions.

Write your summary when your paper is completed because how can you write the summary of anything which is not yet written? Wealth of terminology is very essential in abstract. Use comprehensive sentences, and do not sacrifice readability for brevity; you can maintain it succinctly by phrasing sentences so that they provide more than a lone rationale. The author can at this moment go straight to shortening the outcome. Sum up the study with the subsequent elements in any summary. Try to limit the initial two items to no more than one line each.

Reason for writing the article—theory, overall issue, purpose.

- Fundamental goal.
- To-the-point depiction of the research.
- Consequences, including definite statistics—if the consequences are quantitative in nature, account for this; results of any numerical analysis should be reported. Significant conclusions or questions that emerge from the research.

Approach:

  - Single section and succinct.
  - An outline of the job done is always written in past tense.
  - Concentrate on shortening results—limit background information to a verdict or two.
  - Exact spelling, clarity of sentences and phrases, and appropriate reporting of quantities (proper units, important statistics) are just as significant in an abstract as they are anywhere else.

Introduction:

The introduction should "introduce" the manuscript. The reviewer should be presented with sufficient background information to be capable of comprehending and calculating the purpose of your study without having to refer to other works. The basis for the study should be offered. Give the most important references, but avoid making a comprehensive appraisal of the topic. Describe the problem visibly. If the problem is not acknowledged in a logical, reasonable way, the reviewer will give no attention to your results. Speak in common terms about techniques used to explain the problem, if needed, but do not present any particulars about the protocols here.

The following approach can create a valuable beginning:

- Explain the value (significance) of the study.
- Defend the model—why did you employ this particular system or method? What is its compensation? Remark upon its appropriateness from an abstract point of view as well as pointing out sensible reasons for using it.
- Present a justification. State your particular theory(-ies) or aim(s), and describe the logic that led you to choose them.
- Briefly explain the study's tentative purpose and how it meets the declared objectives.

Approach:

Use past tense except for when referring to recognized facts. After all, the manuscript will be submitted after the entire job is done. Sort out your thoughts; manufacture one key point for every section. If you make the four points listed above, you will need at least four paragraphs. Present surrounding information only when it is necessary to support a situation. The reviewer does not desire to read everything you know about a topic. Shape the theory specifically—do not take a broad view.

As always, give awareness to spelling, simplicity, and correctness of sentences and phrases.

Procedures (methods and materials):

This part is supposed to be the easiest to carve if you have good skills. A soundly written procedures segment allows a capable scientist to replicate your results. Present precise information about your supplies. The suppliers and clarity of reagents can be helpful bits of information. Present methods in sequential order, but linked methodologies can be grouped as a segment. Be concise when relating the protocols. Attempt to give the least amount of information that would permit another capable scientist to replicate your outcome, but be cautious that vital information is integrated. The use of subheadings is suggested and ought to be synchronized with the results section.

When a technique is used that has been well-described in another section, mention the specific item describing the way, but draw the basic principle while stating the situation. The purpose is to show all particular resources and broad procedures so that another person may use some or all of the methods in one more study or referee the scientific value of your work. It is not to be a step-by-step report of the whole thing you did, nor is a methods section a set of orders.

Materials:

Materials may be reported in part of a section or else they may be recognized along with your measures.

Methods:

- Report the method and not the particulars of each process that engaged the same methodology.
- Describe the method entirely.
- To be succinct, present methods under headings dedicated to specific dealings or groups of measures.
- Simplify—detail how procedures were completed, not how they were performed on a particular day.
- If well-known procedures were used, account for the procedure by name, possibly with a reference, and that's all.

Approach:

It is embarrassing to use vigorous voice when documenting methods without using first person, which would focus the reviewer's interest on the researcher rather than the job. As a result, when writing up the methods, most authors use third person passive voice.

Use standard style in this and every other part of the paper—avoid familiar lists, and use full sentences.

What to keep away from:

- Resources and methods are not a set of information.
- Skip all descriptive information and surroundings—save it for the argument.
- Leave out information that is immaterial to a third party.

Results:

The principle of a results segment is to present and demonstrate your conclusion. Create this part as entirely objective details of the outcome, and save all understanding for the discussion.

The page length of this segment is set by the sum and types of data to be reported. Use statistics and tables, if suitable, to present consequences most efficiently.

You must clearly differentiate material which would usually be incorporated in a study editorial from any unprocessed data or additional appendix matter that would not be available. In fact, such matters should not be submitted at all except if requested by the instructor.

Content:

- Sum up your conclusions in text and demonstrate them, if suitable, with figures and tables.
- In the manuscript, explain each of your consequences, and point the reader to remarks that are most appropriate.
- Present a background, such as by describing the question that was addressed by creation of an exacting study.
- Explain results of control experiments and give remarks that are not accessible in a prescribed figure or table, if appropriate.
- Examine your data, then prepare the analyzed (transformed) data in the form of a figure (graph), table, or manuscript.

What to stay away from:

- Do not discuss or infer your outcome, report surrounding information, or try to explain anything.
- Do not include raw data or intermediate calculations in a research manuscript.
- Do not present similar data more than once.
- A manuscript should complement any figures or tables, not duplicate information.
- Never confuse figures with tables—there is a difference.

Approach:

As always, use past tense when you submit your results, and put the whole thing in a reasonable order.

Put figures and tables, appropriately numbered, in order at the end of the report.

If you desire, you may place your figures and tables properly within the text of your results section.

Figures and tables:

If you put figures and tables at the end of some details, make certain that they are visibly distinguished from any attached appendix materials, such as raw facts. Whatever the position, each table must be titled, numbered one after the other, and include a heading. All figures and tables must be divided from the text.

Discussion:

The discussion is expected to be the trickiest segment to write. A lot of papers submitted to the journal are discarded based on problems with the discussion. There is no rule for how long an argument should be.

Position your understanding of the outcome visibly to lead the reviewer through your conclusions, and then finish the paper with a summing up of the implications of the study. The purpose here is to offer an understanding of your results and support all of your conclusions, using facts from your research and generally accepted information, if suitable. The implication of results should be fully described.

Infer your data in the conversation in suitable depth. This means that when you clarify an observable fact, you must explain mechanisms that may account for the observation. If your results vary from your prospect, make clear why that may have happened. If your results agree, then explain the theory that the proof supported. It is never suitable to just state that the data approved the prospect, and let it drop at that. Make a decision as to whether each premise is supported or discarded or if you cannot make a conclusion with assurance. Do not just dismiss a study or part of a study as "uncertain."

Research papers are not acknowledged if the work is imperfect. Draw what conclusions you can based upon the results that you have, and take care of the study as a finished work.

- You may propose future guidelines, such as how an experiment might be personalized to accomplish a new idea.
- Give details of all of your remarks as much as possible, focusing on mechanisms.
- Make a decision as to whether the tentative design sufficiently addressed the theory and whether or not it was correctly restricted. Try to present substitute explanations if they are sensible alternatives.
- One piece of research will not counter an overall question, so maintain the large picture in mind. Where do you go next? The best studies unlock new avenues of study. What questions remain?
- Recommendations for detailed papers will offer supplementary suggestions.

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When you refer to information, differentiate data generated by your own studies from other available information. Present work done by specific persons (including you) in past tense.

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