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Theoretical Study of Some Cyclic Halogenated Compounds as Corrosion Inhibitors

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Abstract: *The molecular structure of Pyridine derivatives have been investigated by using abinitio Hartree Fock and density Functional Theory(DFT) using standard B3LYP functional and 6-311G(d)and6-311G(d,p) basis sets. Corrosion control can be achieved by many methods, being corrosion inhibitors one of the most effective alternatives for the protection of metallic surfaces against corrosion. A perusal of the literature on corrosion inhibitors reveals that most organic inhibitors employed as corrosion inhibitors contain nitrogen, oxygen, sulphur and/or aromatic ring in their molecular structure. The aim of this paper is to extend these investigations in order to discuss the relationship between quantum chemical calculations and experimental inhibition efficiencies of the inhibitors by determining the quantum chemical parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO} and dipole moment (μ). The chemical structures of the compounds studied are given in Figure. The optimized molecular structures of the studied molecules using hybrid DFT functional (B3LYP/6-31G*) and the calculated quantum chemical indices E_{HOMO}, E_{LUMO} ΔE and dipole moment (μ) are given in table 1, 2, 3. The atomic charge values were obtained by the Mulliken population analysis. Table 4 & 5 presents Mulliken charges of the selected atoms of the compounds studied.*

Keyword: *Pyridine derivatives, Quantum chemical parameters, Mullikan atomic charges.*

1. INTRODUCTION

Pyridine is a basic heterocyclic organic compound with the chemical formula C_5H_5N. It is structurally related to benzene, with one C-H group replaced by a nitrogen atom. The pyridine ring occurs in many important compounds, including azines and the vitamins niacin and pyridoxal. The structure of pyridine is shown in figure 1.

Pyridine was discovered in 1849 by the Scottish chemist Thomas Anderson as one of the constituents of bone oil. Two years later, Anderson isolated pure pyridine through fractional distillation of the oil. It is a colourless, highly flammable, weakly alkaline, water-soluble liquid with a distinctive, unpleasant fish-like odor. Pyridine is used as a precursor to agrochemicals and pharmaceuticals and is also an important solvent and reagent. Pyridine is added to ethanol to make it unsuitable for drinking. It is used in the synthesis of sulfapyridine (a drug against bacterial and viral infections), antihistaminic drugs tripelennamine and mepyramine, as well as water repellents, bactericides and herbicides. Some chemical compounds, although not synthesized from pyridine, contain its ring structure. They include B vitamins niacin and pyridoxal, an anti-tuberculosis drug isoniazed, nicotine and other nitrogen-containing plant products. Historically, pyridine was produced from coal tar and as a by-product of the coal gasification. However, increased demand for pyridine resulted in the development of more economical methods of synthesis from acetaldehyde and ammonia, and more than 20,000 tonnes per year are manufactured worldwide.

The bond angles and bond lengths in pyridine and the pyridinium ion are almost identical. This is because protonation of pyridine does

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not affect the aromatic π system. The structure of the pyridine molecule makes it polar. It is thus a polar but aprotic solvent. It is fully miscible with a broad of other solvents, including hexane and water.

2-chloropyridine is an organohalide with the formula C_5H_4ClN. It is primarily used to generate fungicides and insecticides in industry. It also to generate antihistamines and antiarrythymics for pharamaceutical purposes. It reacts with nucleophiles to generate pyridine derivatives substituted at the second and forth carbons on the heterocycle. Therefore, many reactions using 2-chloropyridine generate mixtures of products which require further workup isolate the desired isomer. The structure of 2-chloropyridine is shown in figure 1.

2-chloropyridine is primarily used to generate other pyridine derivatives. Some commercial products include pyrithione, pyripropoxyfen, chlorphenamine, and disopyramide. These reactions rely on chloride's nature as a good leaving group to facilitate the transfer of a substrate onto the pyridine ring. Pyrithione, the conjugate base of 2-mercaptopyridine-N-oxide, is a fungicide found in some shampoos. It is generated from 2-chloropyridine by reacting the N-oxide of 2-chloropyridine with Na_2S in a basic solution, before adding aqueous HCl. Used as an antihistamine, pheniramine may be generated via several different pathways. One synthesis is to hydroformylate functionalized olefins. This reaction proceeds by reacting phenylacetonitrile with 2-chloropyridine in the presence of a base. The resulting intermediate is then alkylated by 2-(dimethylamino) ethyl chloride and the cyano group removed.

2-Bromopyridine was prepared by beating 2-chloropyridine with HBr gas in the acetic acid. Thus 55g HBr gas were introduced into 30.8g 2-chloropyridine in 500mL acetic acid at 110-120°C for 10 hrs to give 81.4% 2-bromopyridine with purity of 98.6%. The effects of reaction temperature and time on the field of 2-bromopyridine were also investigated. Other names of 2-bromopyridine is α- Bromopyridine, O-Bromopyridine. The structure of 2-bromopyridine is shown in figure 1.

2. Method of Calculation

The compound under investigation is purchased from sigma-aldrich chemicals,U.S.A. which is of spectroscopic grade and hence used for recording the spectra as such without any further purification.The FTIR spectra of the compounds are recorded in the range of 4000-100cm^{-1},with scanning speed of 30cm^{-1}. The frequencies of all sharp bands are accurate to ± 1 cm^{-1}. Abinitio (HF/6-31G** basis set) calculations were done by the GAMESS program suite (2). Bulk solvent effects were estimated by single point calculations using the polarized continuum model (PCM) [1, 2].

3. Quantum Chemical Parameters

Quantum chemical methods and molecular modeling techniques enable the definition of a large number of molecular quantities characterizing the reactivity, shape, and binding properties of a complete molecule as well as of molecular fragments and substituents. The use of theoretical parameters presents two main advantages: firstly, the compounds and their various fragments and substituents can be directly characterized on the basis of their molecular structure only; and secondly, the proposed mechanism of action can be directly accounted for in terms of the chemical reactivity of the compounds under study [3].

3.1. Molecular Orbital Energies

Highest occupied molecular orbital energy (E_{HOMO}) and lowest unoccupied molecular orbital energy (E_{LUMO}) are very popular quantum chemical parameters. These orbitals, also called the frontier orbitals, overlap) method. INDO itself is an improvement over the CNDO (complete neglect of differential overlap) approximation. There are several such semiempirical LCAO MO methods, developed for specific purposes.

3.2. AM1 (Austin model 1)

AM1 is a semiempirical method based on the neglect of differential diatomic overlap integral approximation. Specifically, it is a generalization of the modified neglect of diatomic differential overlap approximation. AM1 was developed by Michael Dewar and coworkers reported in 1985 [4].

3.3. PM3 (Parameterized model number 3)

PM3 is another semiempirical method based on the neglect of differential diatomic overlap integral approximation. The PM3 method uses the same formalism and equations as the AM1 method.

4. Results and Discussion

Corrosion control can be achieved by many methods, being corrosion inhibitors one of the most effective alternatives for the protection of metallic surfaces against corrosion. A perusal of the literature on corrosion inhibitors reveals that most organic inhibitors

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employed as corrosion inhibitors contain nitrogen, oxygen, sulphur and/ or aromatic ring in their molecular structure [5-7]. In order to find optimized conformations of the compounds studied and to speed up the calculations, the molecular structures were optimized initially with PM3 semiemprical calculations. The convergence was to 0.001kcal/mol. The structures obtained from PM3 calculations were fully re-optimized by using DFT (density functional theory) methods to estimate the quantum chemical parameters. Calculations at the DFT level were performed using one basis sets, 6-31G(d). The chemical structures of the compounds studied are given Fig 1.the optimized molecular structures of the studied molecules using hybrid DFT functional (B3LYP/6-31G) and the calculated quantum chemical indices $E_{HOMO,}$ $E_{LUMO,}$ ΔE and dipole moment (μ) are given in table No;1,2,3. According to the frontier molecular orbital theory, the formation of a transition states is due to an interaction between frontier orbitals (HOMO and LUMO) of reacting species. Thus, the treatment of the general principles governing the nature of chemical reactions. HOMO is often associated with the electron donating ability of a molecule. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbital. Increasing values of the E_{HOMO} facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer. E_{LUMO} indicates the ability of the molecules to accept electrons. The lower values of E_{LUMO}, the more probable it is that the molecule would accept electrons. Low absolute values of the energy band gap (ΔE) gives good inhibition efficiencies, because the energy to remove an electron from the occupied orbital will be low. The results obtained by 6-311G(d,p)/B3LYP/6-11G(d,p) method (table 1) show that 2-Chloropyridine has the highest HOMO energy (E_{HOMO}) and the lowest LUMO energy (E_{LUMO}) among these organic heterocyclic compounds. Another point to be considered is the HOMO-LUMO gap (ΔE), that is the difference between the HOMO and LUMO energies for the compounds.

The binding capability of molecule with metal depends also on the electronic charge on the chelating atom. Thus the atomic charge values are obtained by Mulliken population analysis. Table 4 and 5 presents Mulliken charges of the selected atoms of the compounds studied. From the atomic charge value listed, 4N atoms of both compounds have excess electron density which increases the π-electron density in the aromatic ring. However 2C of the compounds would contribute less to the π-system. It is on the electronic charge on the chelating or active atoms that is more negative the charge, the stronger of the binding capability.

5. Conclusions

Through AM1, PM3 semiempirical and DFT quantum chemical calculations a correlation between parameters related to the electronic structure of halogenated compounds and their ability to inhibit the corrosion process could be established. The highest occupied molecular orbital energy levels and energy gap calculated by 6-311G(d,p) DFT study show reasonably good correlation as compared to other calculated data. Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the method employed here.

6. References

1. Miertus S, Scrocio E, Tomasi *J.Chem. Phys.*, (1981) 55, 117
2. Barone V.Cossi M,TomasiJ.J.comput.Chem.1998;19:404.
3. I.N. Levine, Quantum Chemistry, Prentice Hall, New Jersey, 1991. *J. Am. Chem. Soc.*, (1985) 107 3902–3909.
4. G. Bereket, E. Hür, C. Öğ˘retir, Quantum chemical studies on some imidazole derivatives as corrosion inhibitors for iron in acidic medium, *J. Mol. Struct. (THEOCHEM).*, (2002) 578 , 79–88.
5. E. Kraka, D. Cremer, Computer design of anticancer drugs, *J. Am. Chem. Soc.*, (2000) 122, 8245–8264.
6. A. Hinchliffe, Modelling Molecular Structures, John Wiley & Sons, (1994).
7. A. Hinchliffe, Chemical Modelling From Atoms to Liquids, John Wiley & Sons, (1999).

Calculated quantum chemical parameters of the studied compound

Table 1 AM1 (Austin model 1)

Molecule	E_{HOMO} Kcal/mol	E_{LUMO} Kcal/mol	ΔE Kcal/mol	ΔH Kcal/mol	μ debyes
2-Bromopyridine	-1.4802	- 0.0011	-46.12	37.53	2.88
2-Chloropyridine	-1.4804	-0.0006	-46.87	26.39	2.82

Table 2 PM3 (Parameterized model number 3)

Molecule	E_{HOMO} Kcal/mol	E_{LUMO} Kcal/mol	ΔE Kcal/mol	ΔH Kcal/mol	μ debyes
2-Bromopyridine	-1.44	-0.0093	-42.96	37.69	2.66
2-Chloropyridine	_	_	-41.62	23.36	2.44

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Table 3 DFT (density functional theory)

Molecule	E_{HOMO} Kcal/mol	E_{LUMO} Kcal/mol	ΔE Kcal/mol	ΔH Kcal/mol	μ debyes
2-Bromopyridine	-489.96	0.104	-2815.77	_	4.23
2-Chloropyridine	-104.82	0.102	-705.47	_	4.59

Table 4 & 5 Total Mulliken Population - 2-Bromopyridine & 2-Chloropyridine

2-Bromopyridine			2-Chloropyridine		
Atom	Mull.pop	Charge	Atom	Mull.pop	Charge
1C	6.153	- 0.153	1C	6.167	- 0.167
2C	6.112	- 0.112	2C	6.052	- 0.052
3C	6.154	- 0.154	3C	6.154	- 0.154
4N	7.484	- 0.480	4N	7.485	- 0.485
5C	6.236	- 0.236	5C	6.235	- 0.235
6C	5.945	0.055	6C	5.945	0.055
7BR	34.834	0.166	7CL	16.889	0.110
8H	0.759	0.241	8H	0.753	0.247
9H	0.772	0.227	9H	0.771	0.229
10H	0.776	0.224	10H	0.774	0.226
11H	0.775	0.225	11H	0.773	0.227

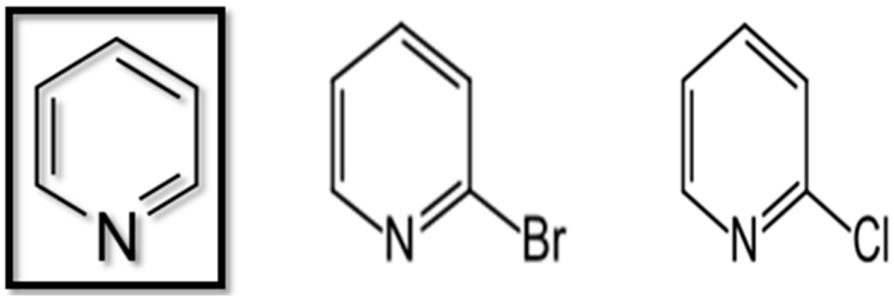

FIGURE 1: Molecular structure of Pyridine derivatives (Pyridine, 2-Bromopyridine, 2-Chloropyridine)

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