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Design of Nano-Inhibitor of Dichlorobenzene and It's Adduct and Study of Its Structural and Electronic Properties: DFT Calculations

Abstract- *Corrosion in oil pipelines is one of the biggest problems in the oil sector companies because of the high cost resulted from repairing the corroded parts, or replace it with another non-corroded ones, so, in this research, we study the design of nano-inhibitor and study of its structural and electronic properties of dichlorobenzene molecule ($C_6H_4Cl_2$) and the effect of adding groups of Hydroxy on those properties, density functional theory (DFT) at B3LYP level with (6-31G) basis sets. The study included four new molecules, which are including monohydroxy dichlorobenzene molecule, dihydroxy dichlorobenzene, trihydroxy dichlorobenzene, and tetrhydroxy dichlorobenzene. The structural and electronic calculations have been done by using Gaussian 09 program and Gaussian View in DFT calculations. The geometry optimization using both methods for dichlorobenzene (nano-inhibitor) and group's Hydroxy molecules has been found in good agreement with experimental data. While the electronic properties included calculate total energy, ionization potential, electron affinity, chemical potential, electronegativity, electrochemical hardness and electronic softness for molecules under study. These results show that the energy gap reduced with the increase of the number of groups; also, the electron affinity and electronegativity for dichlorobenzene molecule Ben-Cl-2OH are the lowest, while the chemical potential be the highest for the same inhibitor. Nano-inhibitor result reduces corrosion of internal surfaces of tubes that used for transporting oil and gas to the importance of these molecules in terms of their high ability for interaction. Those dichlorobenzene can restrain corrosion from claiming steel toward framing an inactive layer for this molecule on the metal's surface.*

Keywords- *Inhibitor, Dichlorobenzene, Structural and Electronic Properties, DFT.*

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1. Introduction

A corrosion inhibitor is a synthetic compound that, the point when included to a fluid, abatements the corrosion rate of a material, commonly a metal or a compound [1]. The viability of a corrosion inhibitor relies on liquid composition, amount from claiming water, Also stream administration. An normal component for hindering erosion includes creation of a coating, regularly a passivation layer, which keeps entry of the destructive substance of the metal [1,2].

Benzene is a natural synthetic compound with those molecular recipes (C_6H_6). It is sometimes abbreviated Ph–H. Benzene is a colorless and highly flammable liquid with a sweet smell. Because it is a known carcinogen, its use as an additive in gasoline is now limited, but it is an important industrial solvent and precursor in the production of drugs, plastics, synthetic rubber, and dyes [3].

Kekule first recognized the tetravalency of carbon in 1858, and numerous attempts to formulating the structure of the benzene molecule have since been made. The comparatively large carbon content of aromatic compounds made the structure difficult to formulate, and early attempts produced unacceptable linear structures, such compounds would be expected to readily undergo addition reactions across the unsaturated bonds, whereas benzene shows little tendency to undergo this type of reactions [3,4]. In 1865, Kekule produced the first reasonably acceptable cyclic structure for benzene: of the gasses.

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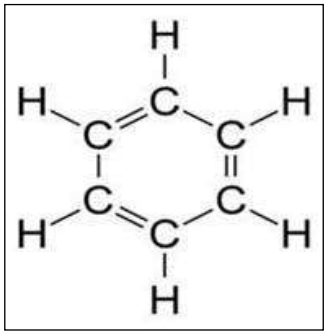

Figure 1: Benzene Structure (C_6H_6) [3]

Dichlorobenzene may be a natural compound with those recipes C6H4Cl2. It is those minimum regular of the three isomers of dichlorobenzene, it is a boring fluid that is insoluble on water. It is handled Similarly as An minor result of the chlorination from claiming benzene, However could Additionally make ready in An guided way Toward those Sandmeyer response for 3-chloroaniline. It also arises starting with the isomerization of the other dichlorobenzenes toward high engineering [5,6]. It is the properties of a molecule of Dichlorobenzene (molar mass(MS) 147.00 g·mol−1, density (D) 1.25 g/cm^3, melting point(MP) 53.5 °C, solubility in water (SIW) 10.5 mg/100 mL (20 °C) [5,7,8].

2. Theoretical Methods

Figure 2 explain to the molecules under study are intended at Gauss View 5.0.8 [9]. All the computational investigations were executed using the DFT methods execute in the Gaussian 09 suite of programs [10].

The sub-atomic properties of the exacerbates bring been registered by DFT utilizing the standard 6-31G basis set. In the DFT calculations the Lee, Yang Also parr relationship functional (correlation) [11] is utilized together for Becke's three parameters return utilitarian B3LYP [12].

The hybrid functional need indicated with a chance to be exceptionally great to count those electronic properties for example, such as ionization potentials, electronic states and energy gaps [13-16].

The DFT partitions the electronic energy as $E=E_T + E_V + E_J + E_{XC}$, where E_T, E_V, and E_J are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms respectively [17].

In this investigation, the more relevant electronic potential (IP), electron affinities (EA), chemical potential (μ) it is the negative of electro negativity (χ), hardness (η) and softness (S) were calculated. The HOMO and LUMO vitality was also utilized to valuation the IP and EA in the scope of Koopmans' hypothesis [18,19]:

$$IP = -\varepsilon_{HOMO} \quad \text{and} \quad EA = \varepsilon_{LUMO} \tag{1}$$

Limited divergence estimation to chemical potential gives,

$$\mu \approx \frac{1}{2}(E_{HOMO} + E_{LUMO}) \approx -\frac{1}{2}(IP + EA) \tag{2}$$

The theoretical definition about chemical hardness has been provided by the DFT as the second subordinate from claiming electronic vitality for admiration to those numbers from claiming electrons N, for a constant external potential v(r) [19.20]:

$$\eta = \frac{1}{2}\left[\frac{\partial^2 E}{\partial N^2}\right]_{V(\vec{r})} = \frac{1}{2}\left[\frac{\partial \mu}{\partial N}\right]_{V(\vec{r})}$$
$$\eta = \frac{(IP - EA)}{2} \tag{3}$$

The softness is given as [19]:

$$S = \frac{1}{2\eta} = \left(\frac{\partial^2 N}{\partial E^2}\right)_{V(\vec{r})} = \left(\frac{\partial N}{\partial \mu}\right)_{V(\vec{r})} \tag{4}$$

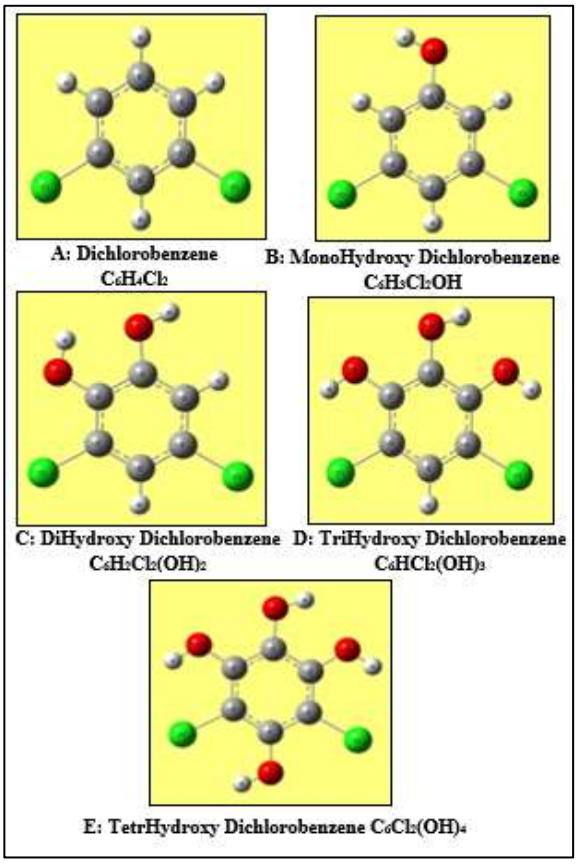

Figure 2: (A-B-C-D-E) Structures of nano-inhibitor of dichlorobenzene and it's adduct discussed in this work

3. Results and Discussion

Figure 2 represents the relaxation structure of

Nano-inhibitor design at Gauss View 5.0.8. and relax by employing the B3LYP/DFT at Gaussian 09 program. Table 1 shows the result of the relaxation of the nano-inhibitor included the optimized coordinates for atoms in nano-inhibitor, and the standard orientations (optimized coordinates) in Angstroms for all atoms in the studied structures. It may be clear starting with Table 1 that those geometrical parameters calculations clinched alongside display study would for a great concurred upon for test information. [21].

Figure 3 shows the decreasing of the total energy of nano-inhibitor with the increasing the number of groups hydroxy molecules, this result is a reflection of the binding energy of each structure and indicates to that these structures have good relaxation. This leads to be certain that the effect of adding hydroxy molecules nano-inhibitor (Dichlorobenzene) on the total energy of the molecule is effective.

The results showed that the forbidden energy gap Eg of all structures are large, and therefore the studied nano-inhibitors have low conductivity and big forbidden energy gap. In other words, the values of the forbidden energy gap of the studied structures are of the order ($C_6H_4Cl_2$> $C_6H_3Cl_2OH$ > $C_6H_2Cl_2(OH)_2$ > $C_6HCl_2(OH)_3$ >$C_6Cl_2(OH)_4$, as seen in Figure 4.

The molecular orbitals (E_{HOMO} and E_{LUMO}) values for nano-inhibitor of Dichlorobenzene and its additions are calculated according to the LCAO – MO theory. Figure 3 shows the shapes of HOMO (higher occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), these shapes illustrate the contributions for each atom in construction HOMO and LUMO. Note from Figure 5 symmetrical distribution of shipments and this shows that the nano-inhibitor (dichlorobenzene) ability restrain corrosion from claiming steel Toward shaping an inactive layer for this molecule on the metal's surface [5,21].

The down results are correspond to the IP and EA of the structures, where the IP is decrease and EA is increase with the increasing the number of groups hydroxy molecules. Note that the inhibitor (DiHydroxy Dichlorobenzene) have EA less valuable, this shows the increasing possibility of formation inert layer on the inner surface of the pipe to increase corrosion protection, as we see in Figures 6 and 7. That means the doped Dichlorobenzene has low ability to donating or accepting an electron to become cation or anion [6,21].

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Table 1: Optimized coordinates (Å) for nano-inhibitor of dichlorobenzene and it's adduct discussed in this work

Tag	Symbol	X	Y	Z	Tag	Symbol	X	Y	Z
A : Dichlorobenzene $C_6H_4Cl_2$					MonoHydroxy Dichlorobenzene $C_6H_3Cl_2OH$				
1	C	-0.0000110	2.0996850	-0.0000030	1	C	1.2152500	1.0632370	-0.0000820
2	C	1.2174670	1.4082320	0.0000220	2	C	1.1937190	-0.3249750	0.0000790
3	C	1.1914580	0.0150700	0.0000140	3	C	0.0102440	-1.0667240	0.0000280
4	C	0.0000040	-0.7092060	0.0000190	4	C	-1.1814610	-0.3468660	-0.0001050
5	C	-1.1914470	0.0150520	0.0000010	5	C	-1.2236570	1.0452900	0.0000730
6	C	-1.2174680	1.4082250	-0.0000160	6	C	-0.0093700	1.7445540	0.0000390
7	H	-0.0000010	3.1842940	-0.0000260	7	H	2.1393120	1.6239520	-0.0003360
8	H	2.1611150	1.9386970	0.0000180	8	H	0.0195350	-2.1471230	0.0000580
9	H	0.0000180	-1.7905370	0.0000310	9	H	-2.1741940	-1.5659280	0.0001990
10	H	-2.1611340	1.9386580	-0.0000160	10	Cl	-2.7572830	-1.2639620	-0.0000150
11	Cl	-2.7677340	-0.9027480	-0.0000020	11	Cl	2.7781780	1.2243420	0.0000090
12	Cl	2.7677330	-0.9027490	-0.0000110	12	O	0.0572250	3.1284140	-0.0000230
DiHydroxy Dichlorobenzene $C_6H_2Cl_2(OH)_2$					13	H	-0.8262170	3.5439890	0.0001650
1	C	1.1850460	1.2080830	-0.0000230	TriHydroxy Dichlorobenzene $C_6HCl_2(OH)_3$				
2	C	1.4891760	-0.1546510	-0.0000220	1	C	-1.2196340	0.7867050	-0.0000310
3	C	0.5030710	-1.1348460	-0.0000200	2	C	-1.2051030	-0.6143480	-0.0000340
4	C	-0.8341480	-0.7286190	-0.0000240	3	C	-0.0289910	-1.3586540	-0.0000750
5	C	-1.1868590	0.6187220	-0.0000390	4	C	1.1757200	-0.6636710	-0.0000630
6	C	-0.1564810	1.5776000	-0.0000280	5	C	1.2091920	0.7293890	-0.0000100
7	H	1.9739400	1.9510320	-0.0000690	6	C	0.0122310	1.4580640	-0.0000120
8	H	0.7552680	-2.1859990	0.0000270	7	H	-0.0523650	-2.4392110	-0.0000860
9	Cl	-2.1384480	-1.9798330	0.0000760	8	Cl	2.7632090	-1.5657090	0.0000430
10	Cl	3.2415070	-0.6587870	-0.0000060	9	Cl	-2.8127100	-1.4831100	0.0000010
11	O	-2.5044630	1.0105110	-0.0002480	10	O	2.3576610	1.5069130	-0.0000600
12	O	-0.6224870	2.8930670	0.0001020	11	O	0.0349150	2.8334520	-0.0000470
13	H	0.0917910	3.5553990	0.0004700	12	O	-2.3600690	1.5522140	0.0001060
14	H	-2.5562230	1.9897300	0.0004910	13	H	3.1716260	0.9665110	0.0005190
TetrHydroxy Dichlorobenzene $C_6Cl_2(OH)_4$					14	H	0.9651050	3.1441030	0.0000300
1	C	-1.1844890	1.0328280	-0.0000530	15	H	-3.1633950	0.9929900	0.0001580
2	C	-1.2071090	-0.3682250	-0.0000440					
3	C	-0.0460050	-1.1495710	-0.0000480					
4	C	1.1787560	-0.4787410	-0.0000580					
5	C	1.2300840	0.9142510	-0.0000040					
6	C	0.0575420	1.6784990	0.0000140					
7	Cl	2.7331510	-1.4102390	0.0000180					
8	Cl	-2.8298340	-1.2159140	0.0000150					
9	O	2.4009960	1.6548530	0.0000100					
10	O	0.1130780	3.0572400	-0.0000500					
11	O	-2.3106560	1.8202810	0.0000120					
12	O	-0.0409700	-2.5262090	0.0000080					
13	H	3.1966450	1.0869360	0.0001850					
14	H	1.0510090	3.3421240	0.0002210					
15	H	-3.1282070	1.2834630	0.0003710					
16	H	-0.9481180	-2.8914740	-0.0000110					

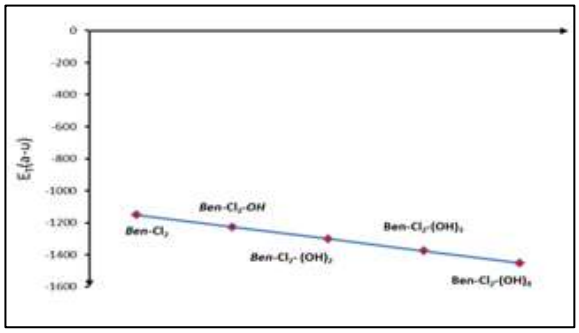

Figure 3: The total energy in a.u of the nano-inhibitor of dichlorobenzene and it's adduct

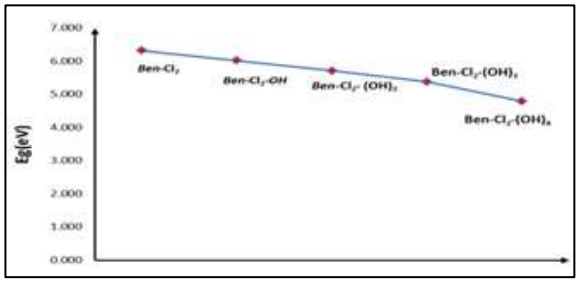

Figure 4: The forbidden energy gap in eV of the nano-inhibitor of dichlorobenzene and it's adduct

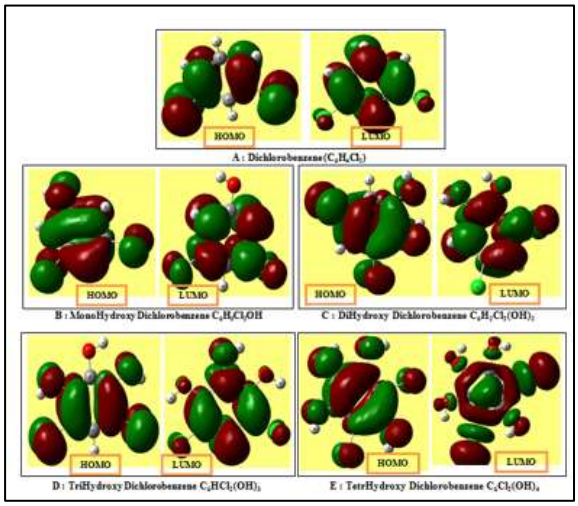

Figure 5: The shapes of HOMO and LUMO for studied structures

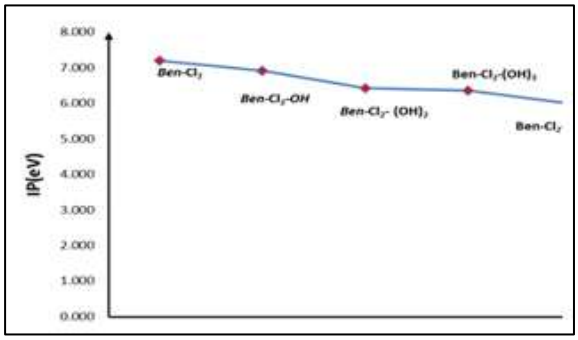

Figure 6: The ionization potential in eV of the nano-inhibitor of dichlorobenzene and it's adduct

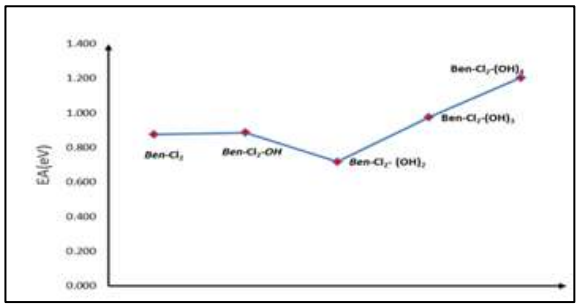

Figure 7: The electron affinity in eV of the nano-inhibitor of dichlorobenzene and it's adduct

The results in Figure 8 showed that the chemical potential μ values are increased with the increasing the number of O and H atoms. In general, the values of μ of the $C_6H_2Cl_2(OH)_2$ is large, that means the electrons in these structures have a large escaping tendency, and this indicates to the decline in the values of HOMO and LUMO energies [7.22].

Figures 9 and 10 showed that the nano-inhibitor of dichlorobenzene and it's adduct have low electrochemical hardness η and high electronic softness S. These results correspond to the result of energy gap that the structures have, and indicate to the high activity of the inhibitors in reaction with the surrounding species [21-23].

Figure 11 shows the electronegativity values in eV of inhibitors. It is clear that from the below figure, $C_6H_2Cl_2(OH)_2$ inhibitor has less electronegativity, the reason is because it has a higher chemical potential. This is very important to protect from corrosion in oil pipelines [21].

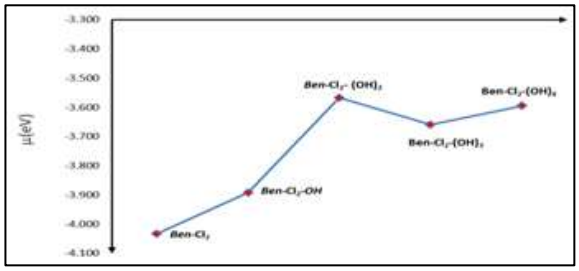

Figure 8: The chemical potential in eV of the nano-inhibitor of dichlorobenzene and it's adduct

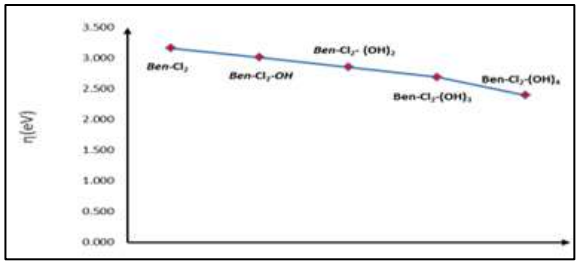

Figure 9: The electrochemical hardness in eV of the nano-inhibitor of dichlorobenzene and it's adduct

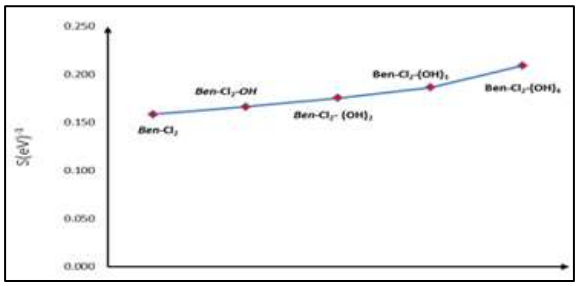

Figure 10: The electronic softness in(eV)-1 of the nano-inhibitor of dichlorobenzene and it's adduct

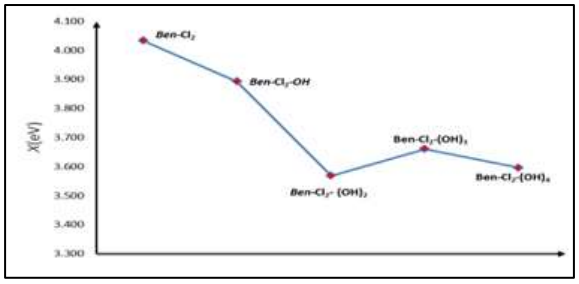

Figure 11: The electronegativity in eV of the nano-inhibitor of dichlorobenzene and it's adduct

4. Conclusion

Nano-inhibitor was design at Gauss View 5.0.8. and relax by employing the B3LYP/DFT at Gaussian 09 program. From the results, one can conclude: The relax structure under study has geometrical parameters lie in the same range of the aromatic rings, which means the method we used in the relaxation is a suitable for these kinds of structures. The E_T of the Dichlorobenzene is decrease with increasing the number of groups (OH). The inhibitors under study have differnt values of IE, EA, η , S and X, with adding groups hydroxy. These results are correspond to the high resultant energy band gap. Note through the results of the energies of calculating HOMO and LUMO, this assists to form an inert layer to protect from corrosion found in oil pipelines.

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