Molecular structure and electronic characteristics study of imidazole and dioxol derivatives as corrosion inhibitors. A quantum methodology investigation.

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ABSTRACT

The quantum chemical calculations were performed for four organic molecules differ in the number and type of hetero atoms namely1,2-di(1H-benzo[d]imidazol-2-yl)ethane(DBIE)**;** 1,2-di(benzo[d][1,3]dithiol-2-yl)ethane(DBTE)**;**1,2-di(benzo[d][1,3]dioxol-2-yl)ethane(DBOE)**;**and(*E*)-N'-(benzo[d][1,3]dioxol-2-ylmethyl)-*N*-(benzo[d][1,3]dithiol-2-yl) formimidamide (BDBF). Their efficiency as inhibitors for iron corrosion were evaluated in two phases, the first is a studying of molecular structure effect and its physic-chemical properties which included the molar refractivity, lipophilicity coefficient(log$P$),molecular electrostatic potential(MEP), molecular volume, molecule surface area and molecular polarizability(pol). Either second phase comprised studying electronic characteristics of molecules such as energy of the highest occupied molecular orbital E_{HOMO}, the energy of the lowest unoccupied molecular orbital E_{LUMO}, $\Delta E_{Back-donation}$, dipole moment (μ), ΔE_{gap}, global softness (σ), global hardness(η), number of transferred electrons(ΔN), global electrophilicity(ω), chemical potential (ρ),electronegativity (*x*), ionization potential(E), electron affinity(A), the energy each of electronic, hydration, total, solvation, potential, kinetic, binding and adsorption energy. The local reactive was studied through Fukui functions where appropriate sites for electrophilic and nucleophilic attacks have been identify and are necessary for adsorption processes on iron surface. Electronic characteristics of the molecules depends orbital analysis of HOMO and LUMO. Where it was noted there is satisfactory agreement on that these characteristics clearly affect on inhibition process. Finally, it was noted that molecules efficiency increases as the following: DBOE<DBIE<BDBF< DBTE .

Keywords: Quantum methodology, Corrosion inhibitors, Molecular structure, Molecular orbital's, Electronic characteristics, Physic-chemical properties**.**

1. Introduction

The corrosion is a degradation phenomenon of a metallic materials properties thus it is an inevitable part, meanwhile is considered a basic process plays an important role in safety and economics due to industrial use especially in the chemical, petrochemical industries and oil production fields, therefore we need to studies about corrosion and find ways to control it and its prevent[1-3]. There are common examples of corrosion in our daily life and they are found in various forms, such as the corroded tools, reddish-orange spots in car bodies, leaking hot-water tanks etc., therefore the corrosion researches are considered very important, and the focus must be on them[4,5]. Theoretical chemistry include different types of studies such as quantum chemical study where used to illustrate the mechanism of corrosion inhibition, due to the pivotal roles which its play as acceptable theoretical tool in elucidating the electronic structure and reactivity of compound[6,7]. Recently, the density functional theory (DFT) was used as a very useful technique for many uses such as analyze the characteristics of inhibitor and its structure, interpret the experimental results, electrons distribution, interpret of adsorption processes, and studying of metals surface inhibition mechanism using organic molecules[7-9]. In the last decade the methods of quantum chemistry confirmed on they already valuable at discovery the molecular structure the appropriate for inhibiting processes, therefore become quantum calculations from common cases in explanation of corrosion. Quantum chemistry could help on the understanding and identify of appropriate sites for interaction between the inhibitor and the metal surface[10,11]. On the other hand the quantum chemistry can provide us the information about the configuration of lowest adsorption energy onto a metal surface, which cannot be evaluated experimentally[12]. There are general consensus by several researchers on that molecules which work as inhibitors should contain electrons pair in hetero atoms (such as oxygen, nitrogen and sulfur), or contain polar functional groups (e.g. -OH,-CO_2H, -NH_2, -NO_2 etc.), or possess plentiful of π electrons, therefore these compounds provide large protection for metals via adsorbing on metallic surface which depends mainly on the physical and chemical properties of inhibitor hence they are excellent for corrosion inhibition[10,13-15]. At generally, the inhibition efficiency of compounds increases as the following: O < N < S < P[16]. In addition to, that ability of compounds to interact are closely linked with their molecular orbitals, including highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and other characteristics such as hardness, softness, electronic energy, solvation energy, potential energy and number of transferred electrons [17,18]. Recently, some compounds which contain of a phenyl rings and hetero atomic aromatic system with presence of imine (azomethine)(-HC=N-) were used as a good inhibitors of corrosion[19]. Our aim in this research has been devoted

to study the appropriate molecules characteristics for inhibiting with attempt to correlate and understanding the molecular structure effect and its physical, chemical and electronic characteristics on the inhibition of iron corrosion, which facilitates the process of selecting the compounds which will be prepared in future for control on corrosion.

2. Quantum chemical calculations

All calculations were performed on the Pentium(R)4/IPM-PC-CPU 3.00GHz, 2.00GB. Bond lengths, total energy and various electronic properties of molecules such as dipole moments, energy of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}) have been calculated by Gaussian09 software program using B3LYP /6-31G(d) within DFT method. Also, some physic-chemical properties of the studied molecules such as log$P$, MASS, polarizability, refractivity, molecular volume, molecules surface area (Grid) have been calculated by hyperchem program version7.5,semi-empirical method, PM3 model. Hydration energy, adsorption energy, solvation energy, total kinetic energy, total potential energy and electronic energy were calculated using PC Gamess (Firefly) and using 6-31G(d) basis set and PBE method [20,21].

3.   Results and discussion

3.1. Structure effect

3.1.1. Molecular structure effect

The effect of molecular structure on the chemical reactivity is an important and intense subject in different of the chemistry disciplines especially at inhibition processes. In order the effect study of molecular structure on inhibition efficiency and finding the relation between them, the charge density, molecular size, determination of favorite sites for adsorption and mode of its interaction with metal surface have been study, furthermore there are many of the physic-chemical properties for molecules should be also studied[22-24]. The studied molecules have the same number of carbon and hydrogen atoms and they are 14 hydrogen atom and 16 carbon atom but they differ in the number of nitrogen, sulfur and oxygen atoms, as well as they are differ in π bonds and molecular weights as shown in Table1and Fig.1. The reason in these molecules study are for contain them electron pairs in hetero atoms (oxygen, nitrogen and sulfur) and π electrons, therefore these molecules provides large protection for metals by adsorbing. With respect to molecules efficiency of DBIE, DBTE, DBOE and BDBF it was noted that the inhibition efficiency of DBTE molecule higher than DBIE, DBOE and BDBF because the sulfur atoms possess a high nucleophilic characteristics hence their ability will be stronger in interact and adsorption on iron surface through forming coordinate covalent bonds between electrons pairs of sulfur atoms and the unsaturated

orbital of iron (3*d* orbit). This mean that sulfur atoms ability at donate electrons to unoccupied orbit is a greater than oxygen and nitrogen atoms on donate the electrons for same orbit, meanwhile there is another center for absorption of molecule is a π electrons of planar benzene ring. In the same vein, the BDBF molecule has inhibition efficiency higher than DBIE and DBOE, due to its possess a lot of active centers which included π electrons of benzene rings, azomethine group (-HC=N-) and electron pair for each atom of nitrogen, oxygen and sulfur, whereby this molecule be able to form several of coordinate covalent bonds with 3*d*-orbit, as well as forming a protective film on surface, therefore adsorption increase causes increase of inhibition efficiency, and this is called a synergistic inhibition. Either reason the decreased of inhibition efficiency of DBIE molecule as compared with DBTE and BDBF may be due to weak ability to interact with iron surface because the π electrons of hetero-cyclic rings are a weak and not stable. Finally, it was noted that the efficiency of DBOE molecule less than efficiency all molecules because the ability of oxygen atoms on donate at electrons to *3d* orbit of iron are a less than ability the atoms of sulfur and nitrogen, or perhaps due to its possess non-planer structure as shown in Fig.1 which diminishes the molecule adsorption area on iron surface. In conclusion proved that each of π electrons of hetero-cyclic ring, aromatic rings, azomethine group and type of hetero atoms have a direct and different effect on inhibition efficiency, and the molecules which posses these specifications considered a good inhibitors. It was observed that efficiency of studied molecules increases as the following: DBOE < DBIE < BDBF < DBTE, in another words O < N < (O, N and S tandem) < S and which corresponds with several studies [14-16].

DBTE

DBTE

BDBF

BDBF

DBIE

DBIE
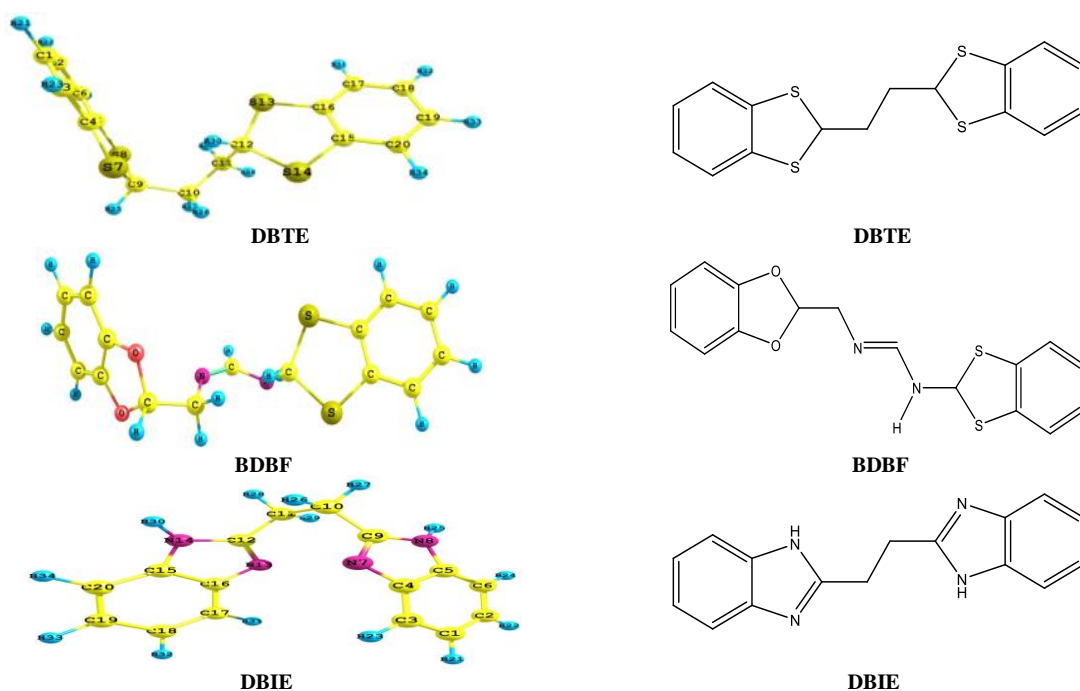
DBOE
Geometry-optimized structures

DBOE
Schematic structures

Figure (1): Elucidates the optimized and schematic structure of studied molecules.

Table (1): The IUPAC name, molecular formula and molecular weight of studied molecules.

Molecules	Abbreviations	IUPAC Names	Molecular formula	Molecular weights g/mol
1	DBTE	1,2-di(benzo[*d*][1,3]dithiol-2-yl)ethane.	$C_{16}H_{14}S_4$	334.53
2	BDBF	(*E*)-*N'*-(benzo[*d*][1,3]dioxol-2-ylmethyl)-*N*-(benzo[*d*][1,3]dithiol-2-yl) formimidamide.	$C_{16}H_{14}N_2S_2O_2$	330.42
3	DBIE	1,2-di(1*H*-benzo[*d*]imidazol-2-yl)ethane.	$C_{16}H_{14}N_4$	262.31
4	DBOE	1,2-di(benzo[*d*][1,3]dioxol-2-yl)ethane.	$C_{16}H_{14}O_4$	270.28

3.1.2 Physic-chemical properties effect

Physic-chemical properties are important for elucidates the molecules efficiency as a corrosion inhibitors, where it was calculated each of lipophilicity coefficient (log*P*), molecular volume, molecule surface area, molecular polarizability (pol) and molar refractivity, also the electrostatic potential has been elucidated. The results were shown that surface area of studied molecules is a large as shown in Table 2, and it was observed that efficiency increases with increasing surface area of molecule, this attributed to the expansion in coverage for largest possible area on the iron surface exposed for the corrosion[23,25,26]. Hence it was noted that the DBTE molecule has largest area 522.57 Å^2 which explains that highest inhibition efficiency was to this molecule. Lipophilicity coefficient is a characterizes the hydrophobicity and hydrophilicity of the molecule, the high of log*P* value mean that molecule is a more hydrophobic and the relation is inverse between log*P* and water solubility. According to the basics and principles of corrosion science that hydrophobic molecule tend to form a protective oxide layer or hydroxide layer on the iron surface which reduces the corrosion process significantly. Through the results obtained it was noted that highest value of log*P* is a 0.84 for the DBTE molecule, therefore this molecule are likely to form a protective layer over the iron surface for its protect, and already this molecule was given the highest inhibition efficiency[23]. Similarly, another molecules efficiency increases with increasing log*P* values, but this is not compatible with results of E.E. Ebenso *at el* [26, 27]. Besides, the polarizability is a factor plays important role in the corrosion inhibition, where that high values of the polarizability facilitate of adsorption process of inhibitors onto metal surface, and increase its value mean that molecules will leave of corrosive medium and adsorb on iron surface to form a protect film from oxide or iron

hydroxide. In our present study it was noted that efficiency increases with increasing the polarizability, which explains formation of the protective film on the iron surface for its protect from corrosion. As for the molecular volume, that small size of molecules leads to low surface coverage consequently give low inhibition efficiency, in this study it was noted that molecules size of DBIE and DBOE are smaller than molecules size of BDBF and DBTE, hence the efficiency of BDBF and DBTE are higher than DBIE and DBOE. In another words, the efficiency increases with increased each of molecular volume and molar refractivity as the following: DBOE < DBIE < BDBF < DBTE and all results are shown in Table 2 [23,26,28].

Table (2): Important physic-chemical properties of studied molecules

Abbreviations	Lipophilicity coefficient	Molar refractivity	Molecular volume $Å^3$	Molecular polarizability $Å^3$	Molecules surface area $Å^2$
DBTE	0.84	106.4	974.29	37.89	522.57
BDBF	0.11	99.64	908.81	35.45	511.56
DBIE	-1.46	87.91	803.49	30.46	498.00
DBOE	-1.53	80.71	682.45	28.43	486.12

3.1.3 Molecular electrostatic potential effect (MEP)

The molecular electrostatic potential is a very useful for revealed the locations of electrons density which located on specific atoms. Therefore, its importance can be insert in explain the electrostatic potential the positive, negative and neutral of molecule atoms, as well as it elucidates the molecular size and the shape. The maximum negative region is a preferred site for electrophilic attack while the maximum positive region is a preferred site for nucleophilic attack. The electrostatic potential effects are explains role of molecular structure in the inhibition efficiency so the molecules get closer to the iron surface through the maximum positive and negative regions which improves the physical adsorption process on the surface[6,29]. Through the electrostatic potential surfaces (EPS) of molecules shown in Fig. 2, it was observed that negative potential of DBIE molecule on nitrogen atoms while the negative potential of BDBF molecule on sulfur atoms. Either DBOE molecule that its negative potential has been observed on electronegative oxygen atoms and finally the negative potential of DBTE molecule on sulfur atom. It is apparent that regions which have the maximum negative potential and which it was noted over those atoms considered preferred centers for electrophilic attack (major centers for supplying electronic)due to their possess more negative charges, thus the certainly to be play major role in adsorption processes then inhibition. On the another hand, those atoms will be under the effect of dipole-dipole interactions between inhibitor molecule and iron surface, this likely to develops and activates the inhibition efficiency [6]. Meanwhile these atoms will be provide the electrons to form more coordinate bonds with iron atoms, indicating that adsorption will be occurs over multiple sites in

each molecule and not on a single site which increases the stability of adsorption then enhance of inhibition efficiency. The molecule containing more positive and negative regions is a better in the inhibition process, and this it was observed in the DBTE molecule where already possess a highest efficiency as compared to the other molecules due to provide more centers of physical adsorption on the iron surface. On the other hand, the sites which have maximum positive potential are present on the hydrogen and carbon atoms instead of the heterogeneous atoms and are preferred sites for nucleophilic attack. The different gradient of electrostatic potential (positive, negative and neutral) on the molecule surface is represent by different colors as shown in Fig. 2 where the potential increases in the system map according to order: red < orange < yellow < light blue < blue < dark blue. The colors code in electrostatic maps is a within the range -5.399e-2 a.u. (dark red) to +5.399e-2 a.u. (dark blue), where the blue color shows the strongest attract region (region poor in electrons), either red color on the contrary will be shows the strongest repulsion (region rich in electrons), in this distribution the positive regions for molecules are an directly related with protect of iron surface through forming the protected positive sites as a result of anodic reactive [6].
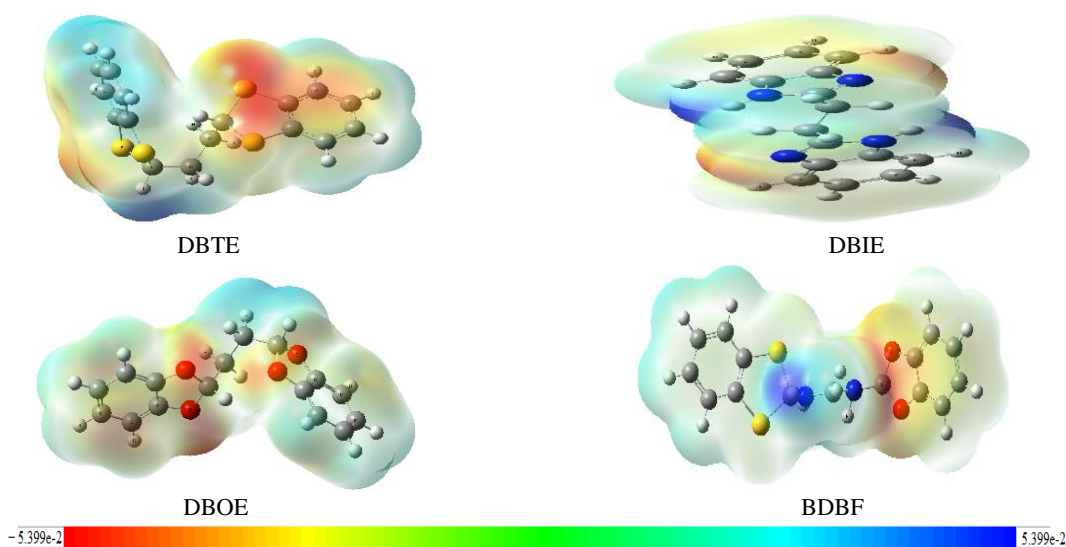

Figure2:Electrostatic potential surfaces (EPS) of the molecules with isopotential value ±5.399e-2 a.u. (Electrostatic maps)

3.2 Electronic characteristics
3.2.1 Molecular orbital energies

Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) are important quantum electronic characteristics and correlated to one another, thus we need to their interpretation to estimate effectiveness of molecules as an inhibitors for corrosion. It well known that the high value of the E_{HOMO} indicate that the molecule has strong tendency to donate in electrons to appropriate acceptor molecule with low energy, while the low value of the

E_{LUMO} is likely refer to ability on accepting electrons to form stable bonds, consequently the inhibition efficiency will be sensitive to   the changes in the HOMO and LUMO energies [23,30].

In this study, the results of DBIE and BDBF molecules revealed that whenever nitrogen atoms number increased, the energy levels dropped slightly from-5.509 to-5.802eV for the HOMO, and from -0.611 to -0.653eV for the LUMO. While, through comparison between DBTE molecule and BDBF molecule it was observed that whenever sulfur atoms number increased, the energy levels each of the HOMO and LUMO boosted slightly (-5.509 to -5.234eV), (-0.611 to -0.603eV) respectively. Meanwhile, the comparison between molecules of DBOE and BDBF revealed that whenever oxygen atoms number increased, the HOMO energy level is a dropped slightly from -5.509 to -6.324eV, while the LUMO energy boosted slightly from -0.611 to -0.333eV as shown in Table 3. Also, the energies of molecular orbital revealed that BDBF molecule possess values of low energies each of HOMO and LUMO due to existence several hetero atoms as shown in Fig.1. Through looking to the electronic configuration of iron atom[Ar]^{18} $4s^2$ $3d^6$ it was noted that $3d$ orbit is a not fully filled in electrons while the $4s$ orbit is a fully filled ($4s$ is a occupied and $3d$ is a unoccupied), therefore the $3d$ orbit can be accept the electrons from the hetero atoms in the molecules using HOMO energy to relate the inhibitor molecule with iron surface where the adsorption occurs through formation a coordinate covalent bond, hence the iron surface behaves as a electrophilie center while the hetero atoms in molecule behaves as nucleophilie centers and occurs of the inhibition [13]. Also, the inhibitor molecule can accepts the electrons rather than donate them, in another meaning that inhibitor molecule can accepts the electrons from anti-bonding orbit ($4s$ orbit of iron) using the LUMO energy of molecule to form back donating bond. However, the interaction between $3d$-orbit and HOMO energy stronger than interaction between $4s$-orbit and LUMO energy [23,31,32]. Furthermore, perhaps the adsorption occurs due to the interaction between the π-orbital of inhibitor and d-orbit of the iron atoms, which evokes a greater number of the inhibitor molecules for adsorption onto the surface and this leads to form a protective layer to protect the iron surface[5]. It is apparent that increase the HOMO values causes increase the inhibition efficiency, where it was noted that DBTE molecule posses highest HOMO value, meanwhile give highest inhibition efficiency, vice versa for DBOE molecule as shown in Table 3. Higher the value for HOMO represents higher ability on donate in electrons for iron to form a coordinate covalent bond, either smaller the value for LUMO represents higher ability on accept electrons from iron to form back donation bond, hence consists the donation and back-donation together, which increases the adsorption process to give the highest possible efficiency.

The electronic distribution density of HOMO and LUMO illustrated in Fig.3, where that density of HOMO for DBIE molecule was distributed over most the molecule almost. The density of molecules DBTE and BDBF were distributed on two of sulfur atoms and some π bonds of aromatic ring. As for the DBOE molecule was distributed on two of oxygen atoms and some π bonds of aromatic ring, all these location   indicate they centers for active sites (Nucleophilic centers) which donates in electrons to the vacant *d*-orbit of iron to interacts with surface where the inhibition occurs. Either electronic distribution density of LUMO are an acts as electrophile and the centers shown in Fig. 3 are those that accepts electrons from the occupied 4*s*-orbit of iron.

Moreover, it was observed that all values of hydration energies are negative, thus explains that dissolution of molecules in water are an exothermic interactions, also it was observed that inhibition efficiency increases with increase of the hydration energy. The negativity increase in molecules hydration energy is due to the hydrogen bonding which form between the atoms of nitrogen, sulfur, oxygen and water molecules[22]. Whenever negativity increase of hydration energy whenever was energy needed to break the hydrogen bond highest. The efficiency of molecules follows the order DBTE > BDBF > DBIE > DBOE with decrease of hydration energy values - 4.54 > - 6.18 > -7.97 > - 8.08 kcal/ mol. Total energy of the molecule (DBOE, DBIE, BDBF and DBTE) is consist of potential and kinetic energy, it was observed that inhibition efficiency decreases with increase each of total energy, electronic energy and solvation energy(SE) as shown in Table 3 [23,31].

Table (3): Quantum chemical energies of the molecules.

| Molecules	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔEgap (eV)	Electronic energy(eV)	Total energy (eV)	Potential energy	Kinetic energy	Hydration energy(kcal/mol)	Solvation energy (kJ/mol)
DBTE	-5.234	-0.603	4.631	-2484.025	-2210.897	-4410.623	2199.726	-4.54	33.19
BDBF	-5.509	-0.611	4.898	-1948.608	-1674.314	-3336.343	1662.029	-6.18	65.01
DBIE	-5.802	-0.653	5.149	-1116.506	-837.190	-1666.505	829.315	-7.97	112.98
DBOE	-6.324	-0.333	5.991	-1097.936	-818.908	-1529.702	710.794	-8.08	164.11

DBIE

DBIE

DBTE

DBTE
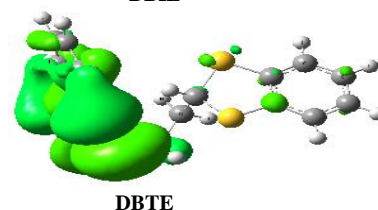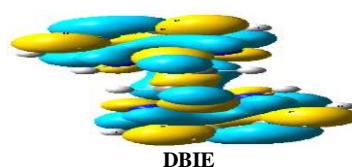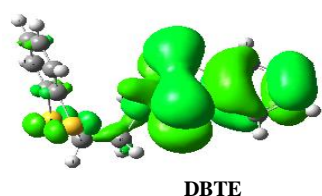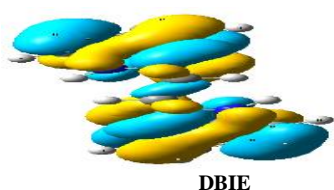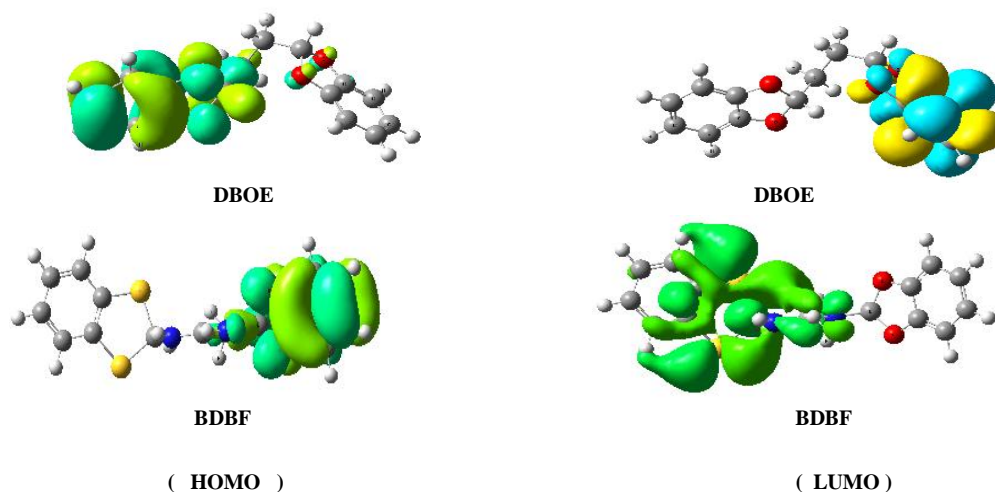
Figure (3): Molecular frontier orbital of the molecules density distribution

3.2.2 Energy gap

Energy gap(ΔE_{gap})is a very important characteristic as a function for molecule reactivity as inhibitor through the adsorption on the metallic surface, also it a measure to the hardness and softness of the molecule. Hard molecules are an characterized by large values of ΔE_{gap}, vice versa where the soft molecules are characterized by small values, therefore the hard molecules are less reactive from the soft molecules because of the large gap between the last occupied orbital and the first virtual orbit, or may due to that soft molecules are an more polarized. The low value of the energy gap renders a good inhibition efficiency because the energy needed to remove electron from the last occupied orbit will be low, the $\Delta E_{gap}$was calculated using Equation 1 [23,33,34].

$$\Delta E_{gap} = E_{LUMO} - E_{HOMO} \qquad (1)$$

The results of the molecules revealed that whenever increased the nitrogen atoms number, the energy gap boosted slightly from 4.898to5.149eV, similarly whenever increased the oxygen atoms number, the energy gap boosted slightly from 4.898 to 5.991eV. While, whenever increased the sulfur atoms number, the energy gap is a dropped slightly from 4.898 to 4.631eV as shown in Table 3. Therefore we can conclude that relation between the inhibition efficiency and energy gap are an inversely. The ΔE_{gap} values for molecules of DBTE, BDBF, DBIE and DBOE are an 4.631, 4.898, 5.149 and 5.991 eV respectively, these results are indicated in Table 3. Results shown that DBTE molecule has the lowest energy gap consequently this molecule acts as soft molecule, where a better performance as a corrosion inhibitor has been given as compared with the other molecules [5,29]. Order of inhibition efficiency of the molecules are as the following order DBTE > BDBF >DBIE > DBOE. On the other hand, the energy gap between HOMO and LUMO are use in intramolecular charge transfer because it a measure of electron conductivity. Fig. 4 shows the

relation between the molecular frontier orbitals of studied molecules and energy gap, where that DBTE molecule possess lower energy gap which facilitate its adsorption on the iron surface[29].
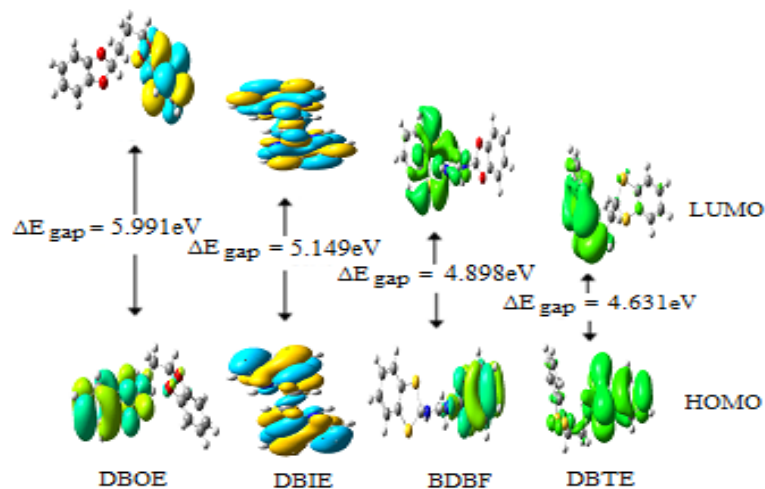
Figure(4): Correlation diagram between molecular orbitals of the molecules and their energies gap.

3.2.3 Dipole moment

The dipole moment (μ) is important electronic index and provides several information e.g the prediction at occurred of the inhibition processes, also, it is the measure of polarity each of inhibitor and covalent bond. Finally is describes the electronic distribution in molecule [23,32,35].The molecule which has a high dipole moment tend to form force of Vander Waals from type dipole-dipole interactions with the metal surface, this leads to strong adsorption on the surface then gives high inhibition efficiency [8,36,37]. The increase of dipole moment lead to increase volume of inhibitor molecule and this increases the adsorption area between the inhibitor and metal surface, hence ability increases on corrosion inhibition[8]. In this study, the dipole moment values of molecules DBIE, DBTE, DBOE and BDBF are 2.602 Debye (8.677×10^{-30}Cm), 3.123Debye (10.41×10^{-30}Cm), 2.022Debye(6.74×10^{-30}Cm) and 2.997Debye (9.994×10^{-30}Cm) respectively and they higher than dipole moment value of H_2O ($\mu = 6.26 \times 10^{-30}$ Cm). This confirms on increase of inhibitor molecules volume thereby increase molecules adsorption on iron surface via quasi-substitution process between the inhibitor molecules in the aqueous solution [Inhibitor in solution] and water molecules on iron surface [H_2O (ads)] as shown in Equation 2[8,32,38,39]. In addition to, these high values are an suggest they are polar compounds and can be easily donates in electrons to form dπ-pπ bonding [25], also, likely to refer that dipole–dipole interactions between molecules and surface of iron will be strong where gives high inhibition efficiency [39].

$$\text{Inhibitor}_{(sol.)} + x\text{H}_2\text{O}_{(ads.)} \longrightarrow \text{Inhibitor}_{(ads.)} + x\text{H}_2\text{O}_{(sol.)} \qquad \textbf{(2)}$$

The inhibition efficiency of molecules increases with increase of dipole moment [11,40], in another study on the contrary where that inhibition efficiency decrease with increase of dipole moment

[41,42]. To illustrate this difference and contradiction, the Obi-Egbedi *et al* were suggested not there are clear relation between dipole moment and inhibition efficiency[43]. According to results shown in Table 4, it was noted that molecules efficiency DBTE, BDBF, DBOE and DBIE have been increased with increase of dipole moment as follows: DBTE> BDBF >DBIE >DBOE[11,40] due to accumulation of inhibitor molecules on the iron surface [41,42,44], where that DBTE possess highest value 3.123(Debye) and gave the best inhibition efficiency as compared with another molecules pointing out that DBTE molecule more reactive [8,11,40].

3.2.4 Number of transferred electrons

Often the number of transferred electrons(ΔN) indicates to ability of inhibitor molecule to donate electrons, where whenever higher the value of ΔN whenever the ability of molecule a good on donate electrons to receptive species characterized by scarcities of electrons. In corrosion inhibitors field, the high values of ΔN are mean there are high tendency to interact with the metal surface through adsorption processes, indicating increase the inhibition efficiency[45]. According to the Lukovits's *et al* and Al-Sabagh *et al*, if the value of transferred electrons < 3.6 can be assume that inhibition efficiency increases with increase the ability of electronic donation from the inhibitor molecule to the orbit of metal surface atoms[23,45]. According to the Pearson theory the ΔN has been calculated through Equation 3[34,46], and according to the Sastri and Perumareddi, the initial molecule-metal interaction energy ($\Delta\psi$) was calculated using Equation4[47].

$$\Delta N = \frac{\chi Fe - \chi inh}{[2(\eta Fe + \eta inh)]} \qquad (3)$$

$$\Delta\psi = \frac{(\chi Fe - \chi inh)^2}{4(\eta Fe + \eta inh)} \qquad (4)$$

Where χFe and χinh are absolute electro negativity of iron and inhibitor molecule respectively, as for the ηFe and ηinh are absolute hardness of iron and inhibitor molecule respectively. The theoretical values of χFe and ηFe are 7.0eV/mol and 0eV/mol respectively. The electronegativity(χ) and global hardness(η) of the inhibitors have been calculated according to Pearson using the following relations[46,48].

$$\chi = \frac{E+A}{2} = \frac{-E_{HOMO} + (-E_{LUMO})}{2} = -\frac{(E_{HOMO} + E_{LUMO})}{2} \qquad (5)$$

$$\eta = \frac{E-A}{2} = \frac{-E_{HOMO} - (-E_{LUMO})}{2} = \frac{E_{LUMO} - E_{HOMO}}{2} = \frac{\Delta E_{gap}}{2} \qquad (6)$$

Where **E** is ionization potential and **A** is electron affinity of inhibitors and have been calculated through the Equations7 and 8 [48,49].

$$E = -E_{HOMO} \qquad (7)$$

$$A = -E_{LUMO} \qquad (8)$$

The ionization potential (E) directly related with the energy of highest occupied molecular orbital, while the electron affinity (A) is a directly related with the energy of lowest unoccupied molecular orbital, in another words, the ionization potential is a negative value of HOMO, and the electron affinity is a negative value of LUMO according to Equations 7 and 8.The ionization potential is a unique index, used to describe the chemical reactivity of atoms and molecules, also plays important role in the interpretation of inhibition and adsorption of the inhibitors on metal surface. The high value of ionization potential indicates the more stable molecules with inertness in chemical reactivity while its low value mean that molecules are more effective and gives high inhibition efficiency[34,50]. The ionization potential values of molecules DBIE, DBTE, DBOE and BDBF are 5.802, 5.234, 6.324 and 5.509eV respectively as shown in Table 4. It was noted the value of DBOE is a highest (stable and inert molecule) therefore gives low inhibition efficiency. The ΔN values of the molecules DBIE, DBTE, DBOE and BDBF are 0.7326, 0.8813, 0.6128 and 0.8044 respectively(Table4). ΔN is a represents the number ratio of transferred electrons from adsorbed molecules to iron surface. From our results (Table4)show that all ΔN values are an less than 3.6 and this mean that inhibition efficiency increases with increasing ability of the electronic donation, hence the DBTE molecule possess highest value of ΔN (0.8813) where give highest inhibition efficiency(89.92%), pointing out that DBTE molecule possess the higher ability to the electron donation as compared with the molecules of DBIE, DBOE and BDBF[23,45]. Furthermore, the positive values which were got from the present study mean that these molecules in addition to their ability on donate electrons, they are possess the ability to accept electrons from the occupied 4*s*-orbit of iron to form back-donation bond [51].

Table (4): The energetic electronic indices for molecules and their inhibition efficiency

Molecules	Transferred electrons	Electronegativity (eV/mol)	Ionization potential (eV)	Electron affinity(eV)	Dipole moment (Debye)	Metal interaction energy (Δψ)	Inhibition efficiency(%)
DBTE	0.8813	2.9185	5.234	0.603	3.123	1.798	89.92
BDBF	0.8044	3.060	5.509	0.611	2.997	1.584	86.93
DBIE	0.7326	3.2275	5.802	0.653	2.602	1.381	84.33
DBOE	0.6128	3.3285	6.324	0.333	2.022	1.125	83.05

3.2.5 Global softness and Global hardness

First of all, the softness(σ) and hardness (η) of molecule considered from important characteristics which provides information about behavior of molecules reactivity and their stability. Depending on the principle of the hard–soft acid base, the hard molecule is a associated with low of basicity and this confirms on low of ability on donation electronically, while the soft molecule is a directly related with high of basicity this asserting it possess a high ability on donation

electronically. The softness and hardness of molecules are an correlated with one another to give idea that inhibition efficiency increases with increasing of softness but decrease with increasing of hardness[8,52,53], also, the high value of the hardness is a indication on the stability of molecule with low of reactivity[22]. The soft molecule has a small energy gap while the hard molecule has a large energy gap, from this can be infer that soft molecules are an more reactive from the hard molecules as earlier reported [54,55]. Briefly, the low of η and high of σ implies that molecule is a more reactive, more polarized and gives high inhibition efficiency[56]. The hardness(η) was calculated through the Equation 6, while the global softness(σ) is inverse of global hardness therefore was calculated as shown in Equation 9 [48,56,57].

$$\sigma = \frac{1}{\eta} = -\frac{2}{E_{HOMO} - E_{LUMO}} \qquad (9)$$

In our present study, the DBTE molecule has highest value of softness 0.4318eV and lowest value of hardness 2.3155eV/mol as compared with the molecules of DBIE, DBOE and BDBF, which a possess the   values 0.3884, 0.3338, 0.4083eV for the softness, and values 2.5745, 2.9955, 2.449eV/mol for the hardness respectively as shown in Table 5. Indicating that best inhibitor is a DBTE molecule, and this likely to pointing that larger number of electrons have been transferred for contribute in the adsorption process on the iron surface. Similarly, the inhibition efficiency according to hardness will be as the following order DBTE>BDBF>DBIE>DBOE and this agree with calculated inhibition efficiency as shown in Table 4 [52,53,56].

On the another hand, there are status interesting is a relation between global hardness and ΔE $_{Back-donation}$ where that hardness is related with ΔE $_{Back-donation}$ through Equation 10 [58,59]. If the value of global hardness (η) > 0 and value of ΔE $_{Back-donation}$< 0, this mean that charge transfer to the molecule followed the back-donation from the molecule.

$$\Delta E_{Back-donation} = \frac{-\eta}{4} \qquad (10)$$

Meanwhile our results were identical with previously mentioned, if observed that values of η greater than zero and are 2.5745, 2.3155, 2.9955 and 2.449, while the values of ΔE $_{Back-donation}$ less than zero and are -0.6436,-0.5788, -0.7488 and -0.6122 for molecules DBIE, DBTE, DBOE and BDBF respectively, this explains that these molecules have ability and possibility on configure donor-acceptor interactions with iron surface and this confirm that molecules posses a good inhibition efficiency [34,58,59]. The values each of ΔE $_{Back-donation}$ and hardness have been listed in Table 5.

3.2.6 Global electrophilicity index

Global electrophilicity index(ω) represents measure factor for energy stabilization through the system acquisition to additional number of gained electrons from corrosion environment, whenever high the value of ω whenever increased the ability of molecule on accept electrons. In another

words, the electrophilicity index consider as a measure of electrophilic power and its low value means that molecule is a more reactive (nucleophile), while the molecule behavior will be electrophile rather than nucleophile when be its high value[7,34,60]. In order to provide a standard case for chemical reactivity and selectivity a new form of philicity has been recently introduced. The local philicity index is a illustrates in Equation 11, either the atomic site k in the molecule is a explained in Equation 12 [60].

$$\omega^{\alpha}(r) = \omega f^{\alpha}(r) \qquad\qquad (11)$$

$$\omega_{k^{\alpha}} = \omega f^{\alpha} k \qquad\qquad (12)$$

Where α is either (+) or (-) or (0) and refer to nucleophilic, electrophilic and radical attacks respectively. The electrophilic or nucleophilic ability is a distributed over all atomic sites in a molecule, hence the atomic site which has largest value of ω_k^+ will be the most favorable site for nucleophilic attack, and the largest value of ω_k^- will be for the electrophilic attack, either largest value of ω_k^o will be for radical attack[60]. Global electrophilicity has been calculated using the Equation 13, where χ is a electronegativity and $\boldsymbol{\eta}$ is a global hardness[61].

$$\omega = \frac{\chi^2}{2\eta} \qquad\qquad (13)$$

In another studies, the electrophilicity index has been calculated depending on chemical potential$\rho$and global hardness η as shown in Equation14[62] or through depend on chemical potential and global softnessσ as shown in Equation 15[22].

$$\omega = \frac{\rho^2}{2\eta} \qquad\qquad (14)$$

$$\omega = \frac{\sigma\rho^2}{2} \qquad\qquad (15)$$

Where the chemical potential $\boldsymbol{\rho}$ represent the first derivative of energy and was calculated through Equation 16, where that v_r is the external potential of system[7,63,64]. On the same token, the equations from 13 to 16 have been listed in one Equation as shown in 17.

$$\rho = (\partial E/\partial N_{electrons})_{v_r} = -\chi = \frac{E_{HOMO}+E_{LUMO}}{2} \qquad\qquad (16)$$

$$\omega = \frac{\chi^2}{2\eta} = \frac{\rho^2}{2\eta} = \frac{\sigma\rho^2}{2} = \frac{[(E_{HOMO}+E_{LUMO})/2]^2}{2\eta} = \frac{\sigma[(E_{HOMO}+E_{LUMO})/2]^2}{2} \qquad (17)$$

In present study, the $\boldsymbol{\omega}$ values of DBIE, DBTE, DBOE and BDBF molecules are 2.023, 1.8392, 1.8492 and 1.9117 respectively. It is clear that electrophilicity value for DBIE molecule is a highest and this infers that this molecule has higher ability on accept electrons from $4s^2$ orbit of iron as compared with another molecules and this mean that behavior of DBIE molecule is a strong electrophile. While the DBTE molecule behavior is a strong nucleophile due to its posses of least value(1.8392)[7,34,60], this fact can be noted through maps forms of electrostatic potential shown in

Fig. 2 the mentioned earlier. Hence the order of the electrophilicity for molecules will be as follows DBIE >BDBF > DBOE > DBTE, vice versa for nucleophilicity, all results are shown in Table 5.

Table5: Important electronic parameters of the molecules.

Parameters	Molecules			
	DBTE	BDBF	DBIE	DBOE
Global softness(eV)	0.4318	0.4083	0.3884	0.3338
Global hardness(eV/mol)	2.3155	2.449	2.5745	2.9955
Global electrophilicity(eV)	1.8392	1.9117	2.0230	1.8492
Chemical potential (eV/mol)	-2.9185	-3.060	-3.2275	-3.3285
Adsorption energy (kcal/mol)	-0.042	-0.031	-0.029	-0.013
Binding energy (kcal/mol)	0.042	0.031	0.029	0.013
$\Delta E_{\text{Back-donation}}$ (eV)	-0.5788	-0.6122	-0.6436	-0.7488

3.2.7 Fukui functions and chemical reactivity.

The local reactivity of molecules is a analyzed according to principle of Fukui functions, on the other hand the Fukui functions $f_{(k)}$ directly correlated with local softness indices $\sigma_{(k)}$ as shown in relation 18, where allows for distinguish each part of molecule on basis its chemical behaviour[65,66]. Mulliken population analysis widely used to calculation the charge distribution over whole molecular structure, hence determines the adsorption centers of inhibitors on metal surface and explains how the metal interacts with inhibitor molecule[67]. There is general agree by several researchers that hetero atoms most negative are faster and more effective to adsorption on metal surface through donor-acceptor interactions [68]. Parr and Yang suggested that largest value of Fukui function indicate to greater reactivity(more effective)[69] similarly Li and Evans suggested that favorite reactive site is which possess high value of Fukui indices[70]. Briefly, Fukui indices use for predicting favorite sites for nucleophilic, electrophilic and radical attacks depending on direction of electron transfer as shown in Equations 19, 20 and 21[70-73].

$$\sigma_{(k)} = \left(\frac{\partial \rho_{(r)}}{\partial N}\right) v_{(r)} \left(\frac{\partial N}{\partial \mu}\right) v_{(r)} = f_{(k)}\sigma \qquad (18)$$

$$f_k^+ = q_k(N+1) - q_k(N) \qquad \text{For nucleophilic attack} \qquad (19)$$

$$f_k^- = q_k(N) - q_k(N-1) \qquad \text{Forelectrophilic attack} \qquad (20)$$

$$f_k^o = [q_k(N+1) - q_k(N-1)]/2 \qquad \text{For radical attack} \qquad (21)$$

Where q(N), q(N+1) and q(N-1) are electronic population of the atom *k* in neutral, anionic and cationic systems respectively. As for another indices which can used for predicting in active sites of the inhibitor are an local softnessσ^+andσ^- for atom, which can considered as a product for Fukui

function and global softness as shown in Equations 22 and 23[26,58,74]. The high values of the σ^+ indicate to high electrophilicity, and the high values of the σ^- indicate to high nucleophilicity. At generally the information obtained from local softness are an similar to information obtained from Fukui function, in addition to, that local softness gives the information about the total molecule softness[26,74].

$$\sigma^+ = (f^+)\sigma \qquad\qquad \text{For nucleophilic attack} \qquad\qquad (22)$$

$$\sigma^- = (f^-)\sigma \qquad\qquad \text{For electrophilic attack} \qquad\qquad (23)$$

Regarding to Fukui functions for this study, the nucleophilic and electrophilic centers for each molecule have been determination and these centers are an suitable for adsorption on iron surface. The most reactive sites for the nucleophilic attack f_k^+ in the molecules of DBIE, DBTE, DBOE and BDBF are an atoms of H_{21}, H_{27}, H_{21} and H_{24} respectively which have a electrophilic characteristics and involved in chemical reactivity to provide appropriate conditions for adsorption mechanism on the metal surface, where found that highest values to these atoms are an 0.558922, 0.359739, 0.443496 and 0.342852 respectively. Either more reactive sites for the electrophilic attack f_k^- in the molecules of DBIE, DBTE, DBOE and BDBF are on the atoms of N_7, C_9, O_{14} and S_{18}, where found that highest values to these atoms are an 0.602128, 0.438765, 0.553436 and 0.399143 respectively and all results are shown in Tables 6-9. In another words, the highest values obtained for sites f_k^+ and f_k^- represent most probable centers for nucleophilic and electrophilic attacks respectively, which considerers as an adsorption centers in molecules and the necessary for occurrence of inhibition. Furthermore, the active sites for nucleophilic and electrophilic attacks in the molecules can be determined by similarly method to Fukui functions but depending on local softness indices σ_k^- and σ_k^+. Where the highest values of σ_k^- for molecules of DBIE, DBTE, DBOE and BDBF are on atoms of N_7**,** C_9**,** O_{14} and S_{18} respectively, indicating to these atoms are an favorite sites for electrophilic attack, while the atoms of H_{21}, H_{27}, H_{21} and H_{24} are most reactive sites for nucleophilic attack. According to Mulliken distribution that nucleophilic centers are in red color, and electrophilic centers are in green color as shown in Fig.5. Besides, there are another active centers have possibility to the reaction with iron surface and they are represented in the atoms which have a largest value on the radical sites f_K° as listed in Tables 6-9. All these results confirms ability of molecules on donation and back-donation between them and iron surface to gives high inhibition efficiency.
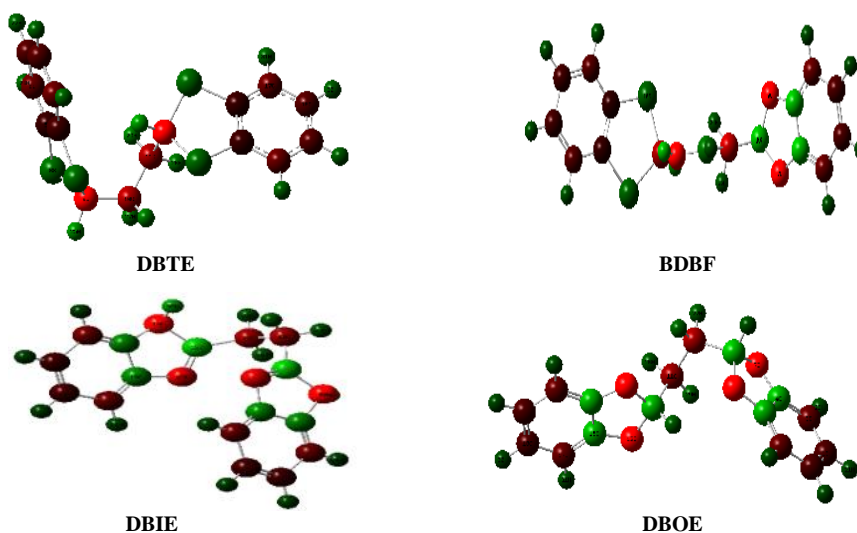
DBTE

BDBF

DBIE

DBOE

Figure (5): Mulliken distribution on atoms of the molecules.

Table 6: Fukui and softness indices for nucleophilic, electrophilic and radical attacks in the **DBIE** molecule calculated from Mulliken charges (maximum value in bold).

No.	Atomic	f_k^+	f_k^-	f_k°	σ_k^+	σ_k^-	σ_k^o
1	C	-0.144176	0.116517	-0.145341	-0.264176	0.100517	0.124259
2	C	-0.138614	0.192611	-0.238767	-0.148614	0.143611	0.187676
3	C	-0.226743	0.136748	-0.198647	-0.116709	0.131448	-0.145476
4	C	0.302438	-0.202222	0.298745	0.201436	-0.201352	0.289765
5	C	0.287509	0.217501	0.165473	0.232209	0.127241	0.176209
6	C	-0.233541	0.133041	0.163547	-0.211141	0.293042	-0.176541
7	**N**	-0.502128	**0.602128**	0.125398	-0.215128	**0.522128**	0.136128
8	N	-0.358768	0.458768	0.634252	-0.256768	0.318768	0.428657
9	C	0.138133	-0.236233	0.291875	0.247813	-0.186233	-0.187565
10	C	-0.343796	0.243719	-0.218004	-0.139796	0.193710	-0.123765
11	C	-0.343796	0.223711	-0.037336	-0.129796	0.143705	-0.214357
12	C	0.238133	-0.118331	0.182203	0.222133	-0.218541	0.133453
13	N	-0.502128	0.342128	-0.193830	-0.382128	0.212108	-0.323232
14	N	-0.658768	0.231761	-0.354262	-0.267768	0.471235	-0.243588
15	C	0.287509	0.197529	0.278929	0.324509	0.137520	0.320098
16	C	0.302438	-0.102435	0.109283	0.278643	-0.112437	0.018643
17	C	-0.226743	0.216203	-0.211194	-0.134743	0.140215	0.032452
18	C	-0.144176	0.244226	-0.136363	-0.192176	0.219226	0.192131
19	C	-0.138614	0.298114	-0.227789	-0.172614	0.212114	0.123242
20	C	-0.233541	0.183354	-0.537333	-0.198501	0.122359	-0.023242
21	**H**	**0.558922**	0.119422	0.153768	**0.459422**	0.217425	0.121109

22	H	0.133347	-0.313341	-0.129876	0.191047	-0.213391	-0.122090
23	H	0.147846	-0.227846	-0.298570	0.122146	-0.177844	-0.154367
24	H	0.127857	-0.182785	0.165757	0.217844	-0.192225	-0.212111
25	H	0.229340	-0.221941	-0.329340	0.237340	-0.191931	0.232423
26	H	0.179026	-0.129014	0.122334	0.213026	-0.126714	0.163534
27	H	0.168851	-0.128811	0.233646	0.128051	-0.125611	0.187654
28	H	0.168851	-0.238711	0.198096	0.155851	-0.212311	0.109756
29	H	0.179026	-0.121926	0.103425	0.200026	-0.186526	0.123121
30	H	0.329340	-0.229190	0.300343	0.110340	-0.167190	0.198076
31	H	0.147846	-0.127867	0.145464	0.224846	-0.119867	0.113209
32	H	0.133422	-0.213409	0.190987	0.103427	-0.216709	0.102341
33	H	0.133347	-0.113397	0.213190	0.221342	-0.214397	0.143557
34	H	0.127857	-0.167821	0.123232	0.136657	-0.119811	0.109121

Table 7: Fukui and softness indices for nucleophilic, electrophilic and radical attacks in the **DBTE** molecule calculated from Mulliken charges (maximum value in bold)

No.	Atomic	f_k^+	f_k^-	f_k°	σ_k^+	σ_k^-	σ_k^o
1	C	-0.125599	0.165499	-0.144176	-0.134019	0.123499	0.147846
2	C	-0.125137	0.119837	-0.138614	-0.111132	0.123837	0.133422
3	C	-0.155543	0.191243	-0.226743	-0.112341	0.119843	0.133347
4	C	-0.084858	0.022258	0.302438	-0.184001	0.176458	0.127857
5	C	-0.082992	-0.123092	0.217501	-0.023492	-0.254092	-0.128811
6	C	-0.157145	-0.121645	0.133041	-0.111242	-0.112945	-0.238711
7	S	0.157861	-0.278061	0.602128	0.112766	-0.270911	-0.121926
8	S	0.166944	-0.145674	0.558768	0.119344	-0.228174	-0.214490
9	**C**	-0.428698	**0.438765**	-0.236233	-0.419498	**0.391765**	-0.212108
10	C	-0.282875	0.223405	0.243719	-0.212573	0.182405	0.471235
11	C	-0.254342	0.221347	0.223711	-0.219344	0.179342	0.137520
12	C	-0.452571	0.351271	0.222133	-0.439466	0.157271	0.123242
13	S	-0.165394	0.413899	0.182128	-0.163244	0.312994	-0.023242
14	S	0.154647	0.191240	-0.267768	0.142336	0.136747	-0.121109
15	C	-0.084485	-0.123405	0.324509	-0.011185	-0.100105	-0.122090
16	C	-0.081047	-0.032147	0.278643	-0.023447	0.072247	0.598710
18	C	-0.127017	0.141954	0.113209	-0.100125	0.101983	0.121254
19	C	-0.127447	-0.121147	0.102341	-0.119411	-0.124567	0.112322
20	C	-0.158696	-0.158876	0.143557	-0.152343	-0.112376	0.111760
21	H	0.136461	-0.133245	0.109121	0.191769	-0.190145	0.112217
22	H	0.236041	-0.187652	0.208413	0.128142	-0.134652	0.119822
23	H	0.245926	-0.154320	0.171321	0.119822	-0.119932	0.111071

24	H	0.245070	-0.102130	0.159739	0.111071	-0.156730	0.212912
25	H	0.208413	0.265313	0.124329	0.212912	-0.212313	0.124329
26	H	0.171321	0.132451	0.101932	0.124329	0.100251	-0.122980
27	**H**	**0.359739**	-0.143231	-0.151942	**0.501932**	-0.123232	-0.123435
28	H	0.165548	0.198768	0.126542	0.151942	0.194233	-0.735356
29	H	0.189349	-0.034289	-0.267768	0.126542	-0.123204	-0.122271
30	H	0.240636	0.265432	0.324509	0.272631	0.223432	-0.174343
31	H	0.141362	-0.198762	0.278643	0.133531	-0.132962	-0.554322
32	H	0.131265	-0.432905	-0.134743	0.111819	-0.122905	0.312345
33	H	0.131144	-0.143214	-0.127447	0.121634	-0.122290	-0.532288
34	H	0.140859	0.112989	-0.158696	0.117251	0.256785	0.125347

Table 8: Fukui and softness indices for nucleophilic, electrophilic and radical attacks in the **DBOE** molecule calculated from Mulliken charges (maximum value in bold)

No.	Atomic	f_k^+	f_k^-	f_k°	σ_k^+	σ_k^-	σ_k^o
1	C	-0.138890	0.123410	-0.419498	-0.122990	0.102390	-0.164545
2	C	-0.140487	0.367887	-0.212573	-0.112347	0.122187	-0.134353
3	C	-0.225983	0.212383	-0.219344	-0.298653	0.209384	-0.223185
4	C	0.258710	0.323410	-0.439466	0.328210	0.334567	0.109874
5	C	0.251871	-0.398771	-0.112376	0.351231	-0.234561	0.398760
6	C	-0.225154	0.276554	-0.190145	-0.128154	0.164754	-0.109867
7	O	-0.532592	0.131982	-0.134652	-0.554322	0.238373	-0.512324
8	C	0.213576	0.118076	-0.023447	0.312345	0.135353	0.126583
9	O	-0.537980	0.331230	-0.100125	-0.532288	0.393434	-0.182636
10	C	-0.316424	0.313440	-0.143231	-0.322764	0.122609	-0.109877
11	C	-0.294498	0.138678	0.198768	-0.233658	0.123398	-0.154768
12	C	0.283327	0.351677	-0.034289	0.221397	0.187987	-0.210987
13	O	-0.534765	0.323458	0.163244	-0.345665	0.222096	0.123455
14	**O**	-0.528767	**0.553436**	0.142336	-0.587657	**0.463536**	0.099222
15	C	0.354832	0.352151	-0.011185	0.354302	0.234432	0.187664
16	C	0.353920	-0.363530	0.168851	0.353280	-0.328820	0.312324
18	C	-0.141678	0.195857	0.179026	-0.112398	0.064548	-0.109890
19	C	-0.142382	0.146353	0.329340	-0.158672	0.074882	-0.151213
20	C	-0.233965	0.132325	-0.122905	-0.265675	0.043465	-0.015675
21	**H**	**0.443496**	-0.424296	-0.122290	**0.487656**	-0.143436	-0.181324
22	H	0.143999	-0.043213	0.102390	0.143549	-0.143536	0.113242
23	H	0.150810	-0.003410	0.122187	0.143560	-0.101130	0.091761

| No	Atomic					
24	H	0.154435	-0.100335	0.283327	0.154356	-0.129876	0.120982
25	H	0.162460	-0.042390	-0.534765	0.198765	-0.122980	-0.113242
26	H	0.180245	-0.054645	-0.528767	0.154120	-0.123435	0.111109
27	H	0.165116	-0.132316	-0.217820	0.198406	-0.535356	0.193122
28	H	0.168641	-0.086641	-0.234500	0.154121	-0.122271	0.132425
29	H	0.174075	-0.143434	-0.129366	0.165385	-0.174343	0.132655
30	H	0.203196	-0.282720	0.160305	0.222316	-0.118976	0.265780
31	H	0.145371	-0.003731	-0.309426	0.176543	-0.118371	-0.143535
32	H	0.137306	-0.054646	0.198745	0.121876	-0.166301	0.143537
33	H	0.136839	-0.118279	0.190763	0.187649	-0.132433	-0.125464
34	H	0.143032	-0.053433	0.104374	0.193442	-0.143857	-0.190989

Table 9: Fukui and softness indices for nucleophilic, electrophilic and radical attacks in the **BDBF** molecule calculated from Mulliken charges. (maximum value in bold)

No	Atomic	f_k^+	f_k^-	f_k°	σ_k^+	σ_k^-	σ_k^o
1	C	0.137992	-0.121392	-0.118371	0.278635	-0.176592	-0.513203
2	C	0.142936	-0.112836	-0.166301	0.187356	-0.187866	-0.121226
3	C	0.236220	-0.217820	-0.132433	0.233918	-0.299800	-0.165481
4	C	0.315780	-0.234500	-0.143857	0.165920	-0.120500	0.143123
5	C	0.241110	-0.312340	-0.181324	0.248801	-0.032340	-0.169124
6	C	0.209898	-0.124430	0.113242	0.242328	-0.187530	-0.330136
7	O	0.252258	-0.287979	-0.091761	0.398758	-0.297979	-0.129422
8	C	0.261104	0.300123	0.137306	0.220204	0.302933	-0.191047
9	O	0.310003	-0.298710	-0.136839	0.333203	-0.112010	0.120146
10	C	-0.126626	0.121254	0.143032	-0.121232	-0.187654	-0.211844
11	C	-0.133948	0.112322	0.102341	-0.134248	0.198282	0.230340
12	C	-0.137485	0.111760	-0.143557	-0.123871	0.198760	-0.213026
13	C	-0.139153	0.112217	0.109121	-0.198125	0.198717	-0.382128
14	C	-0.130038	0.112745	0.208413	-0.132286	0.198745	-0.267768
15	C	-0.129366	0.143563	0.598710	-0.126539	0.190763	0.324509
16	S	0.160305	0.269734	0.127794	0.154287	0.304374	0.278643
17	C	-0.309426	0.335436	-0.112432	-0.352432	0.287636	0.187656
18	**S**	0.193543	**0.399143**	0.111980	0.132278	**0.322343**	0.143549
19	C	-0.191793	0.009793	0.112317	-0.123375	0.019873	-0.143260
20	N	-0.342528	0.287988	0.276554	-0.354272	0.223438	0.161005
21	C	0.155765	0.121298	0.531982	0.188254	0.198428	-0.309426
22	N	-0.538742	0.354987	0.118076	-0.511954	0.287397	-0.193543

23	H	0.328166	0.322287	0.531230	0.234363	0.120032	-0.191193
24	**H**	**0.342852**	-0.142852	0.313440	**0.423332**	-0.100232	0.118774
25	H	0.137380	0.064530	0.138678	0.128766	0.039870	0.221765
26	H	0.146627	-0.035400	-0.121232	0.017777	-0.022340	-0.254405
27	H	0.149571	-0.053591	-0.134248	0.034363	-0.023131	-0.165752
28	H	0.238991	-0.114641	-0.123871	0.122209	-0.119871	0.154371
29	H	0.159052	-0.122908	-0.186233	0.125465	-0.121001	0.111124
30	H	0.144096	-0.100236	-0.193710	0.165431	-0.186206	0.114530
31	H	0.148330	-0.104530	0.143705	0.113242	-0.187650	-0.164550
32	H	0.159450	-0.167350	0.019093	0.192325	-0.121343	0.211450
33	H	0.223270	-0.228750	-0.323238	0.298716	-0.209110	-0.130243
34	H	0.169534	0.163243	0.192328	0.123354	0.109323	-0.198704
35	H	0.177977	0.132324	0.412097	0.132498	0.109898	0.154647
36	H	0.275507	0.109287	0.098236	0.112983	0.100764	0.017567

3.2.8 Strength of nucleophilic center

One of agreed constants that electrons be more related whenever bond length increased [75] accordingly the bonds length were calculated to determine strength of nucleophilic centers in molecules. The results indicate to that bonds length for (C_4–N_7–C_9); (S_7–C_9–S_8); (C_{12}–O_{14}–C_{16}) and (C_{11}–S_{18}–C_{17}) in nucleophilic centers of the molecules DBIE, DBTE, DBOE and BDBF are (1.414, 1.342); (1.854, 1.853); (1.445, 1.373); and (1.777, 1.851) Å respectively. It was noted that bonds length for S_7–C_9 and S_8–C_9 in nucleophilic center for DBTE molecule are longest as compared with the nucleophilic centers of the another molecules, hence the electrons to those bonds are more related and considered strongest nucleophile. While the bonds length in the nucleophilic center for DBIE molecule are shortest and considered weakest nucleophile. These results agree with results of global electrophilicity index, they also confirms that efficiency of DBTE molecule is higher than molecules efficiency DBIE, DBOE and BDBF due to strength of nucleophilic center the necessary to adsorption on surface of iron. Besides, the bonds length showed that molecules structure have asymmetrical lengths except DBIE molecule as shown in Fig 6, hence we can conclude that efficiency of symmetrical and asymmetrical structures are a good for reducing corrosion.
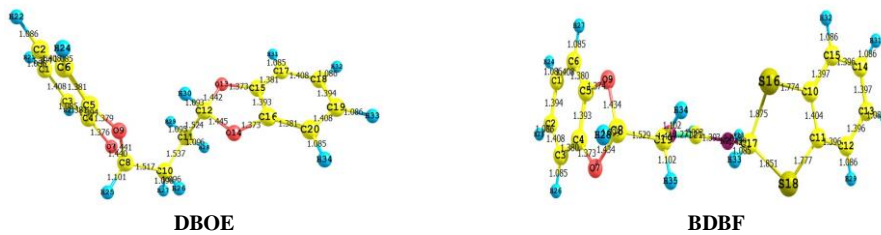

DBIE   DBTE
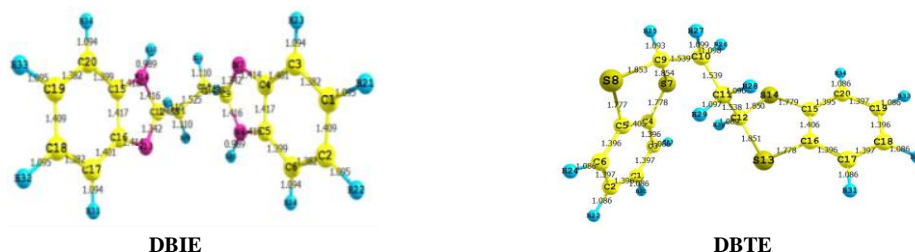
DBOE   **BDBF**
Figure (6): Symmetrical and asymmetrical bonds lengths of the molecules (in Å).

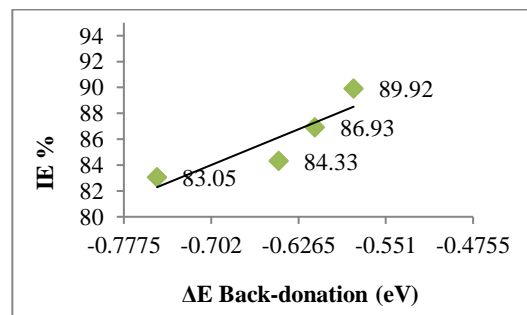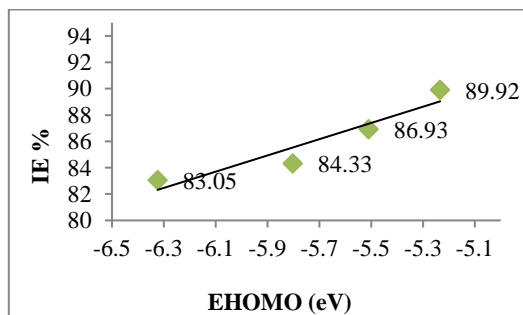## 3.2.9 Relation between molecules characteristics and their inhibition efficiency.

The physic-chemical properties and electronic characteristics which affect on inhibition efficiency have been explained as mentioned earlier. Where it was observed that these characteristics plays an important role at interpretation of molecules efficiency but not there are simple and direct relation between the characteristics and corrosion inhibition efficiency. So, the molecules efficiency differs because of different influences for chemical parameters, therefore the difficulty obtain on direct relation confirm the nature of complex interactions for inhibition processes. However, it possible calculate the theoretical inhibition efficiency based on Equation 24 [7,23,24,26].

$$\text{IE}_{\text{Theor}} = 123.418 - 9.334 \times \mu - 0.131 \times (\text{SE}) \tag{24}$$

The results shown that inhibition efficiency has been increased with increasing E_{HOMO} values due to increase the activation energy of interaction [23]. Also the results revealed that efficiency affected by several factors and this agree with E.E. Ebenso *et al* as describe in Equation 25 [26], therefore it can be conclude that relation between each of lipophilicity coefficient ($\log P$), polarizability (pol), dipole moment (μ), $\Delta E_{\text{Back-donation}}$ and number of transferred electrons(ΔN) directly proportional with inhibition efficiency as shown in Fig.7, but the total energy, global hardness, solvation energy and E_{gap} inversely proportional with the efficiency as shown in Fig.8. All these characteristics confirms that inhibition efficiency of molecules increases as the following order DBOE<DBIE<BDBF< DBTE

$$\text{eff} = \frac{\left(1.0127 \times E_{\text{HOMO}} + E_{\text{LUMO}} + 0.99 \times E_{\text{gab}} + \mu + \text{Log}P + \text{Pol} + 69.12\right) \times C_i}{\left[1 + \left(1.0127 \times E_{\text{HOMO}} + E_{\text{LUMO}} + 0.99 \times E_{\text{gab}} + \mu + \text{Log}P + \text{Pol} + 69.12\right)\right] \times C_i} \times 100 \tag{25}$$
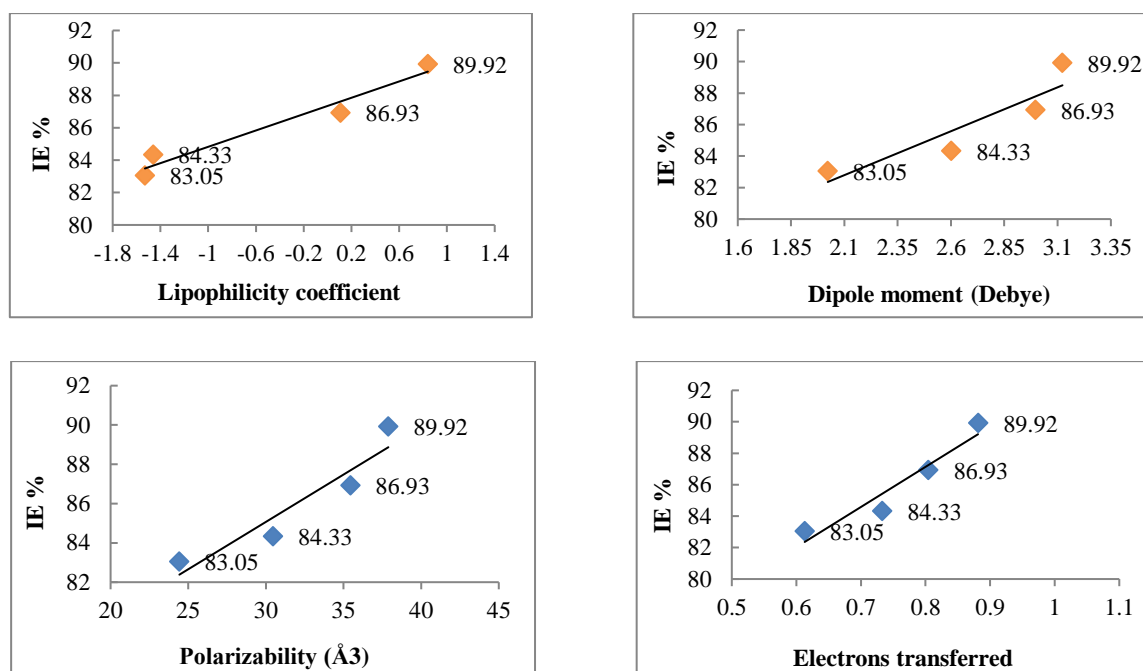
Figure (7): Demonstrates the directly proportional between theoretical inhibition efficiency of molecules and some important characteristics.
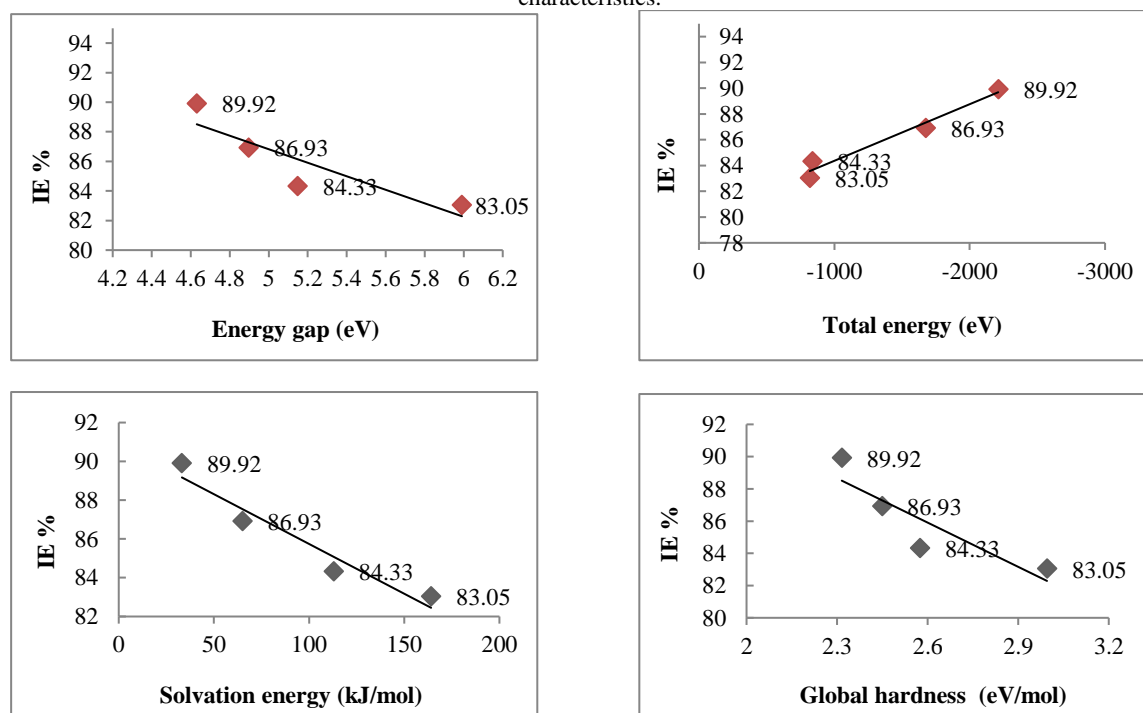

Figure (8): Demonstrates the inverse relation between theoretical inhibition efficiency of molecules and some important characteristics.

3.2.10 Adsorption and binding energies

Adsorption behavior of inhibitory molecules on metal surface is an important to understand of inhibition mechanism. Accordingly, the quantitative appraisal of the interaction between each molecule and iron surface has been studied where the molecules efficiency were evaluate through calculate of the

adsorption energyE_{ads} and binding energyE_{bin} depending on that binding energy of inhibitor with iron surface   is a negative value to the adsorption energy according to Equation 26 [19,53,76,77].

$$E_{binding} = - \ E_{adsorption} \qquad\qquad (26)$$

 Table 5 showed that all adsorption energies are negativity and they are - 0.042, -0.031,- 0.029 and -0.013 kcal.mol^{-1} for molecules of DBTE, BDBF, DBIE and DBOE respectively. Where the negative values indicate that adsorption processes of inhibitory molecules on iron surface are fast, strong, stable and spontaneous while the positive values indicate that a repulsive interaction. The calculated values revealed that binding energies decreased in the order DBTE > BDBF > DBIE > DBOE hence the DBTE molecule has highest binding energy during the whole simulation process, which indicates that this molecule strongly adsorb on iron surface and has best performance at inhibition. Also, the positive values of binding energies means the chemical adsorption occurrence, which affirms on the electrons acceptance from iron atoms then back donation to iron atoms at same site [19,76-79].

4. CONCLUSIONS

    In conclusion, the studied molecules are characterized at a good inhibition efficiency, and that all electronic characteristics and physic-chemical properties are affect on inhibition efficiency, where efficiency increases as the   following: DBOE< DBIE <BDBF<DBTE. The compounds containing sulfur atoms have inhibition efficiency higher than compounds containing atoms each of nitrogen, sulfur and oxygen together (tandem) and these have efficiency higher than compounds containing nitrogen atoms, finally the compounds containing oxygen atoms possess the least inhibition efficiency. The inhibition efficiency of compounds increases whenever increased the HOMO energy, polarizability, molar refractivity, dipole moment, molecular volume, molecule surface area, lipophilicity coefficient, hydration energy, transferred electrons, $\Delta E_{Back-donation}$ and global softness, but decreases with increase each of total energy, solvation energy, energy gap and global hardness. Also, it can be concluded that each of molecular weight, global electrophilicity and LUMO energy do not have a regular effect on inhibition efficiency of compounds. The molecules containing hetero atoms can use as inhibitors for make iron resistant to corrosion, and molecule which contains sulfur atoms consider strongest nucleophile as compared with another molecules. Fukui functions revealed that preferred sites for nucleophilic attack are an hydrogen atoms, and in same vein the preferred sites for electrophilic attack are an mainly on the hetero atoms. The studied heterocyclic molecules are possessed negative adsorption energies and this mean that molecules adsorb on iron surface strongly through physical and chemical adsorption meanwhile.

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دراسة التركيب الجزيئي والخصائص الالكترونية لمشتقات الايميدازول و الدايوكسول كمثبطات للتآكل (دراسة منهجية الكم)

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مديرية تربية البصرة ، البصرة ، العراق[1]

مركز ابحاث البوليمر ، جامعة البصرة ، العراق [2]

الخلاصة

في هذا البحث أجريت الحسابات الكيميائية الكمية لأربعة جزيئات عضوية جديدة تختلف في عدد ونوع الذرات غير المتجانسة لغرض دراسة خصائصها الالكترونية والفيزيائية والكيميائية لمعرفة وتقييم كفاءتها كمثبطات لتآكل الحديد حيث تم تقييم كفاءة هذه المركبات على مرحلتين، الأولى تضمنت دراسة تأثير التركيب الجزيئي وخصائصه الفيزيائية والكيميائية على عملية التثبيط أما الثانية فتتضمن دراسة الخصائص الالكترونية للجزيئات. أيضا تم دراسة التفاعل المحلي الموقعي من خلال وظائف فوكوي حيث تم تحديد المواقع المناسبة للهجوم النيوكلوفيلي والالكتروفيلي الضرورية لعمليات الامتزاز على سطح الحديد. ولوحظ من خلال هذه الدراسة إن طبيعة التركيب الجزيئي وخصائصه لها تأثير واضح وبشكل مباشر على كفاءة الجزيء كمثبط لتآكل الحديد.

الكلمات المفتاحية:- منهجية الكم , مثبطات التآكل , الاوربيتال الجزيئي , التركيب الجزيئي, الخصائص الالكترونية , الخصائص الفيزيائية والكيميائية