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Adsorption and Quantum Chemical studies on the Inhibition potentials of some Formazan Derivatives

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ABSTRACT

Density functional theory (DFT) at the B3LYP/6-31G(d,p) basis set level was performed on two Formazan 2-(phenyl(2-phenylhydrazinyl) methylene) hydrazinecarboxamide (FB) and 2-((4-(dimethylamino)phenyl)(2-phenylhydrazinyl)methylene)hydrazinecarboxamide (FD) and the inhibitive effect of these formazans against the corrosion of mild steel in acidic medium is elucidated. The calculated quantum chemical parameters correlated to the inhibition efficiency are E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), the energy gap(ΔE), hardness(η), Softness(S), dipole moment(μ), electron affinity(EA), ionization potential(IE), the absolute electronegativity(χ) and the fraction of electron transferred (ΔN). The order of inhibition efficiency of the formazan derivatives was found to be in agreement with experimental corrosion inhibition efficiencies. The local reactivity has been analyzed through the condensed Fukui function and local softness indices using mulliken population analysis.

Keywords: Corrosion inhibition, Formazan, Density functional theory(DFT), Fukui function, softness indices.

INTRODUCTION

The protection of metal surfaces against corrosion is an important industrial and scientific topic. Many chemical phenomena cannot be explained by classical physics and need quantum mechanics for the complete analysis. In that case quantum chemical studies are used to analyze the inhibition efficiency of certain compounds on corrosion. A number of heterocyclic compounds containing nitrogen, oxygen and sulphur either in the aromatic or long chain carbon system have been reported to be effective inhibitors [1,2]. The planarity and the lone electron pairs in the hetero atoms are important features that determine the adsorption of molecules on the metallic surface[3].The inhibition efficiency has been closely related to the inhibitor adsorption

abilities and the molecular properties for different kinds of organic compounds[4-9]. The power of the inhibition depends on the molecular structure of the inhibitor. Organic compounds, which can donate electrons to unoccupied d orbital of metal surface to form coordinate covalent bonds and can also accept free electrons from the metal surface by using their anti bonding orbital to form feedback bonds, constitute excellent corrosion inhibitors.

Quantum chemical calculations have been proved to be a very powerful tool for studying corrosion inhibition mechanism [10-14]. Density functional theory (DFT)[15,16] has provided a very useful framework for developing new criteria for rationalizing, predicting, and eventually understanding many aspects of chemical processes[17-21]. A variety of chemical concepts which are now widely used as descriptors of chemical reactivity, e.g., electronegativity [18] hardness or softness quantities etc., appear naturally within DFT[16]. The Fukui function[20] representing the relative local softness of the electron gas, measures the local electron density/population displacements corresponding to the inflow of a single electron.

The reactive ability of the inhibitor is closely linked to their frontier molecular orbital (MO), including highest occupied molecular orbital, HOMO, and lowest unoccupied molecular orbital, LUMO, and the other parameters such as hardness and softness. Quantum chemical studies have been successfully performed to link the corrosion inhibition efficiency with molecular orbital (MO) energy levels for some kinds of organic compounds [22,23].

Claudia Nadejde et al. have studied the spectral investigation of Triphenylformazan derivatives in ultraviolet light[24]. A series of new substituted formazan derivatives has been synthesized from corresponding aryl diazonium chloride and Schiff base in pyridine and were identified by spectral studies and screened for their antimicrobial activities by Marjadi et al.[25].

The Formazan derivatives investigated in the present work are:

(2-(phenyl(2-phenylhydrazinyl)methylene)hydrazinecarboxamide (FB)

2-((4-(dimethylamino)phenyl)(2-phenylhydrazinyl)methylene)hydrazinecarboxamide (FD)

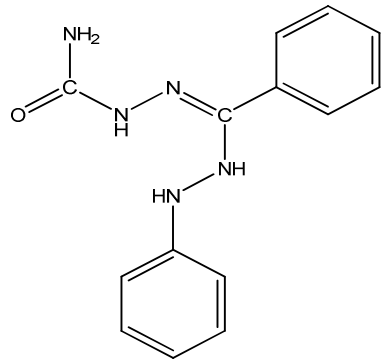
The inhibition efficiency of the formazan derivatives investigated in this work has been studied experimentally using weight loss method, potentiodynamic polarization and electrochemical impedance spectroscopic techniques. Results obtained showed that FB<FD [26].The objective of this work is therefore, to present a theoretical study of the electronic and structural parameters of formazan derivatives and the effect of these parameters on their inhibition efficiency of corrosion of mild steel using the quantum chemically calculated parameters. Molecular orbital calculations are performed looking for good theoretical parameters to characterize the inhibition property of inhibitors, which will be helpful to gain insight into the mechanism of corrosion inhibition. Also from the calculations we will try to explain which adsorption site is favoured to bind to the metal surface. Computational calculations were obtained by means of B3LYP/6-31G(d,p) method. Parameters like E_{HOMO}, E_{LUMO}, energy gap(ΔE), dipolemoment(μ), global hardness(η), softness(S), the fraction of electron transfered (ΔN) and total energy change (ΔE) were calculated. The local reactivity has been analyzed by means of the Fukui indices, since they

indicate the reactive regions, in the form of the nucleophilic and electrophilic behaviour of each atom in the molecule.

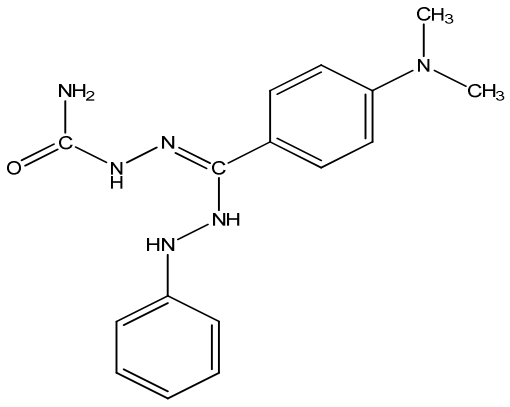
MATERIALS AND METHODS

Computational Details

All the quantum chemical calculations were performed with complete geometry optimizations using Gaussian-03 software package [27]. Geometry optimization were carried out by B3LYP functional at the 6-31G(d,p) basis set and at the density functional theory (DFT) level. BLYP functional is obtained by adding gradient corrections to the LDA method—specifically the exchange correction of Becke [28] and the correlation function of Lee *et al.* [29]. Recently, Density functional theory (DFT) has been used to analyze the characteristics of the inhibitor/ surface mechanism and to describe the structural nature of the inhibitor in the corrosion process [30,31].

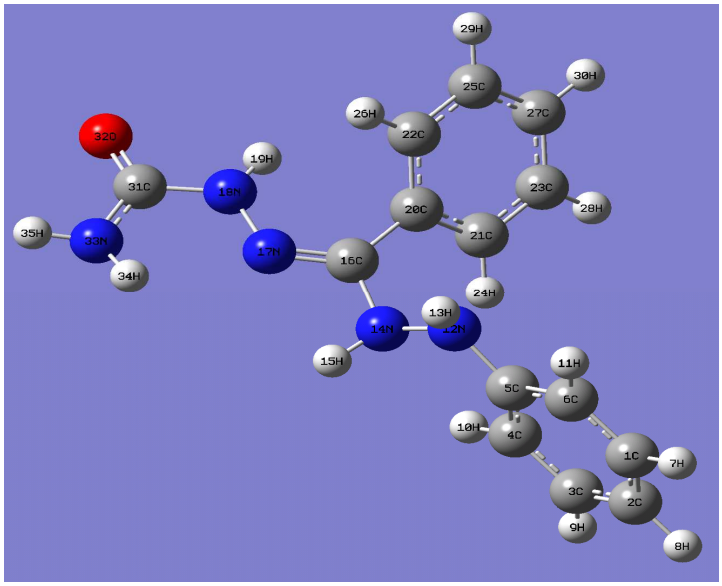


(2-(phenyl(2-phenylhydrazinyl) methylene)hydrazinecarboxamide (FB)

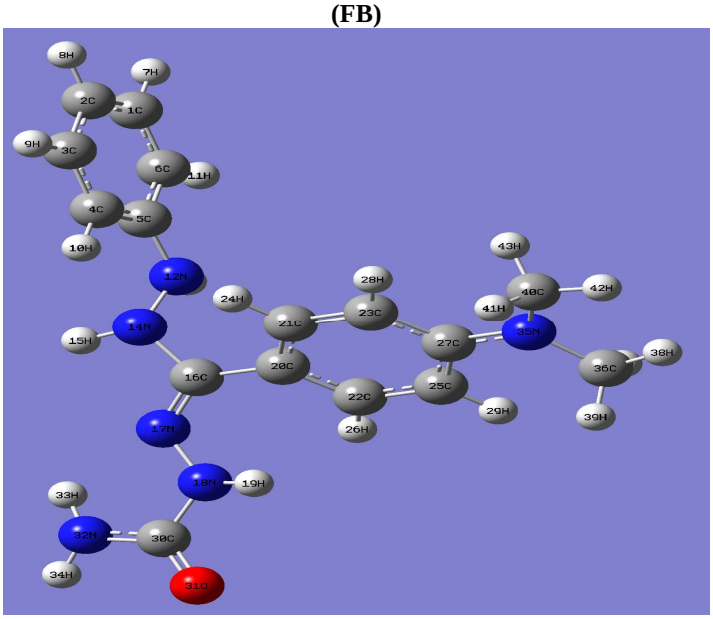


2-((4-(dimethylamino)phenyl)(2-phenylhydrazinyl)methylene)hydrazinecarboxamide (FD)

Figure 1. Names, molecular structure and the abbreviation of the inhibitors investigated



(FB)



(FD)

Figure 2. Optimized structure of FB and FD calculated with the B3LYP/6-31G(d,p)

Density functional theory (DFT) [16] has been quite successful in providing theoretical basis for popular qualitative chemical concepts like electronegativity (χ), hardness (η), softness(S) and local ones such as Fukui function(F(r) and local softness(s(r). For an N-electron system with total energy E, these reactivity indices are defined as the following first-order derivative [32].

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)}$$

Hardness (η) has been defined within the DFT as the second derivative of the E with respect to N as $v(r)$ property which measures both the stability and reactivity of the molecule [33].

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)}$$

where $v(r)$ and μ are, respectively, the external and electronic chemical potentials.

According to Koopman's theorem [34] the ionization potential (IE) and electron affinity (EA) of the inhibitors are calculated using the following equations and hence χ and η are calculated.

$$IE = -E_{HOMO}$$

$$EA = -L_{LUMO}$$

The higher HOMO energy corresponds to the more reactive molecule in the reactions with electrophiles, while lower LUMO energy is essential for molecular reactions with nucleophiles[35].

$$\chi = \frac{IE + EA}{2}$$

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

The global softness(S) is the inverse of the global hardness [33]

$$S = \frac{1}{\eta}$$

When two systems, Fe and inhibitor, are brought together, electrons will flow from lower χ(inhibitor) to higher χ(Fe), until the chemical potentials become equal. The number of transfered electrons (ΔN) was also calculated [36] by using the equation below.

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{\left[2(\eta_{Fe} + \eta_{inh}\right]}$$

Where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule respectively η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of χ_{Fe}=7.0 eV and η_{Fe} = 0 for the computation of number of transferred electrons[36]. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance [37]. The local selectivity of a corrosion inhibitor is best analyzed by means of condensed Fukui function.

The change in electron density is the nucleophilic (f^+) and electrophilic (f^-) Fukui functions, which can be calculated using the finite difference approximation as follows [38**].**

$f_k^+ = q_{N+1} - q_N$ (for nucleophilic attack)

$f_k^- = q_N - q_{N-1}$ (for electrophilic attack)

where q_N, q_{N+1} and q_{N-1} are the electronic population of the atom k in neutral, anionic and cationic systems.

Condensed softness indices allowing the comparison of reactivity between similar atoms of different molecules can be calculated easily starting from the relation between the Fukui function $f(r)$ and the local softness $s(r)$ [39]

$$s(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} = f(r)S$$

RESULTS AND DISCUSSION

According to Wang *et al.* [39], the frontier orbital (highest occupied molecular orbital-HOMO and lowest unoccupied molecular orbital-LUMO) of a chemical species play major role in defining its reactivity. As E_{HOMO} is often associated with the electron donating ability of a molecule, high value of E_{HOMO} are likely to indicate the tendency of the molecule to donate electrons to appropriate acceptor molecules with lower energy MO. Increasing values of E_{HOMO} facilitate adsorption and therefore enhance the inhibition efficiency, by influencing the transport process through the adsorbed layer. E_{LUMO} indicates the ability of the molecule to accept electrons. The binding ability of the inhibitor to the metal surface increases with increasing of the HOMO and decreasing of the LUMO energy values. Frontier molecular orbital diagrams of FB and FD is represented in figure 3.

Table 1. Quantum chemical parameters for FB and FD calculated using B3LYP/6-31G(d,p).

Parameters	FB	FD
E_{HOMO}(eV)	-5.55602	-5.13479
E_{LUMO} (eV)	-1.10152	-0.68845
Energy gap(ΔE) (eV)	4.45451	4.44634
Dipole moment (Debye)	3.9276	4.7028

According to the frontier molecular orbital theory(FMO) of chemical reactivity, transition of electron is due to interaction between highest occupied molecular orbital(HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting species. The higher values of E_{HOMO} indicate the greater its ability of offering electrons to unoccupied d-orbital of the metal, and higher the corrosion inhibition efficiency through better adsorption. The inhibitor does not only donate electron to the unoccupied d orbital of the metal ion but can also accept electron from the d-orbital of the metal leading to the formation of a feed back bond. The highest value of E_{HOMO} -5.13479 eV indicates the better inhibition efficiency of FD.

ΔE (*energy gap* $\Delta E = E_{LUMO} - E_{HOMO}$) is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on the metallic surface. As ΔE decreases the reactivity of the molecule increases leading to increase in the %IE of the molecule. Lower values of the energy difference will render good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low [40]. Reportedly, excellent corrosion inhibitors are usually organic compounds which not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal [11]. A molecule with a low energy gap is more polarizable and is generally associated with the high chemical activity and low kinetic stability and is termed soft molecule[41]. The results as indicated in table 1 shows that inhibitor FD has the lowest energy gap, this means that the molecule could have better performance as corrosion inhibitor.

The dipole moment (μ in Debye) is another important electronic parameter that results from non uniform distribution of charges on the various atoms in the molecule. The high value of dipole moment probably increases the adsorption between chemical compound and metal surface [42]. The energy of the deformability increases with the increase in μ , making the molecule easier to adsorb at the Fe surface. The volume of the inhibitor molecules also increases with the increase of μ. This increases the contact area between the molecule and surface of iron and increasing the corrosion inhibition ability of inhibitors. In our study the value 4.7028(eV) of FD enumerates its better inhibition efficiency.

Ionization energy is a fundamental descriptor of the chemical reactivity of atoms and molecules. High ionization energy indicates high stability and chemical inertness and small ionization energy indicates high reactivity of the atoms and molecules[43]. The high ionization energy 5.55602 (eV) of FB indicates the low inhibition efficiency.

Absolute hardness and softness are important properties to measure the molecular stability and reactivity. It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap[44]. In our present study FD with low hardness value 2.22317(eV) compared with FB have a low energy gap. Normally, the inhibitor with the least value of global hardness(hence the highest value of global softness) is expected to have the highest inhibition efficiency [45].

For the simplest transfer of electron, adsorption could occur at the part of the molecule where softness(S), which is a local property, has a highest value[46]. FD with the softness value of 0.449808 correlates the above statement.

The table 2 shows the order of electronegativity as FD<FB. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order FD>FB. According to Sanderson's electronegativity equalization principle [47], FB with a high electronegativity and low difference of electronegativity quickly reaches equalization and hence low reactivity is expected which in turn indicates low inhibition efficiency.

The values of ΔN presented in the table 2 represents the number of electronic charges that will be exchanged between the surface and the adsorbed species. The greater value of 0.919493 for FD indicates the maximum transfer of electron and hence greater inhibition efficiency.

Table 2. Quantum chemical parameters for FB and FD calculated using B3LYP/6-31G(d,p).

Parameters	FB	FD
E_N (au)	-891.494426	-1025.470690
E_{N-1}(au)	-891.256647	-1025.224731
E_{N+1}(au)	-891.495437	-1025.461112
IE(eV)	5.55602	5.13479
EA(eV)	1.10152	0.68845
η (eV)	2.22725	2.223171
S (eV)	0.448984	0.449808
χ (eV)	3.32877	2.91162
ΔN	0.824162	0.919493

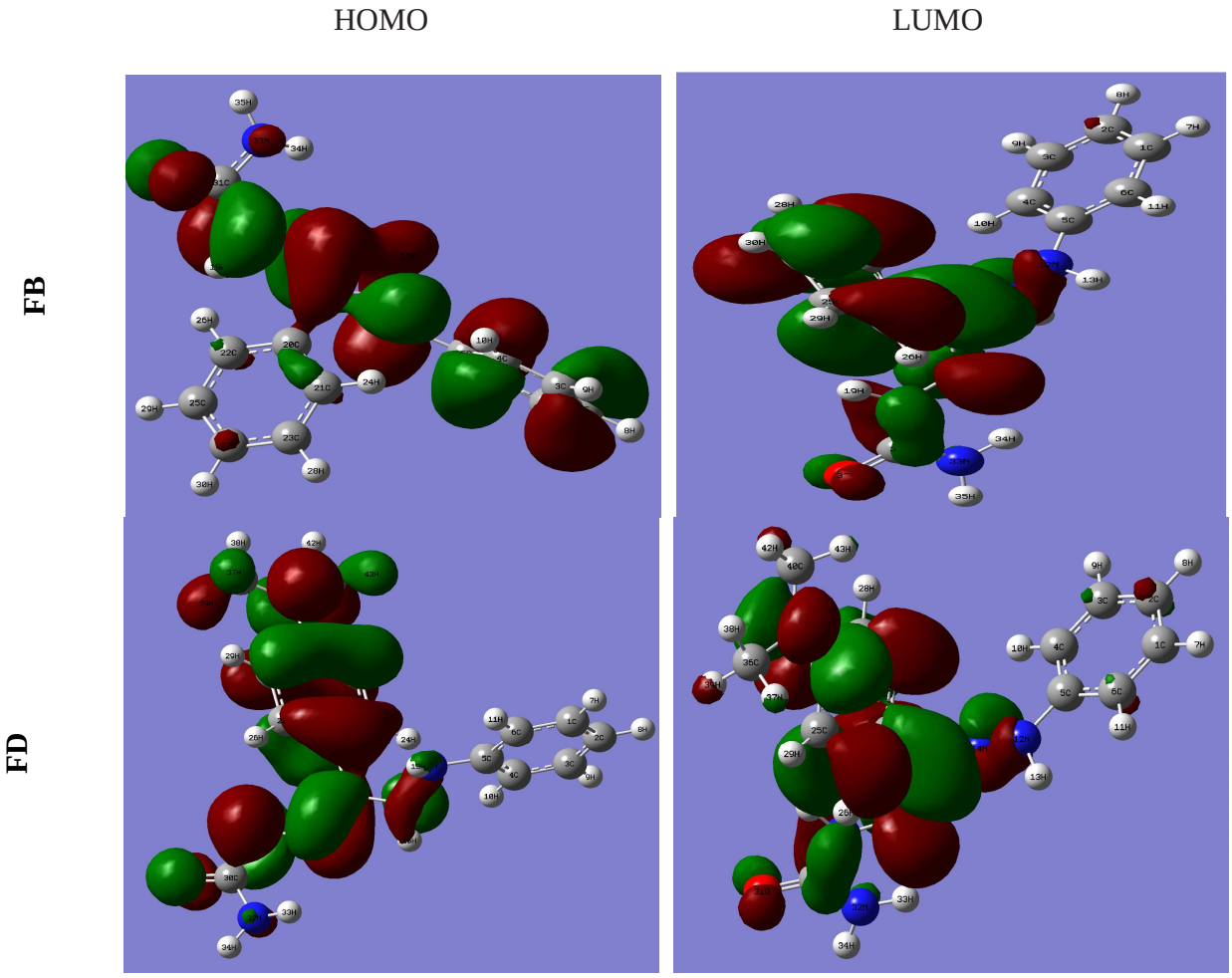


Figure 3. Frontier molecular orbital diagrams of FB and FD by B3LYP/6-31G(d,p)

Table 3. Fukui and local softness indices for nucleophilic and electrophilic attacks on FB atoms calculated from mulliken charges

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	0.00125	0.00411	0.004167	0.013671
2 C	0.01383	0.02203	0.046033	0.073339
3 C	-0.00038	0.00862	-0.001278	0.028694
4 C	0.00097	-0.00428	0.003242	-0.014234
5 C	-0.03466	0.01772	-0.115375	0.059002
6 C	-0.00162	0.02101	-0.005399	0.069924
7 H	0.03596	0.04849	0.119722	0.161435
8 H	0.04011	0.05229	0.133513	0.174078
9 H	0.03364	0.04649	0.111999	0.154777
10 H	0.00534	0.01534	0.017782	0.051046
11 H	0.02205	0.04218	0.073396	0.140417
12 N	0.02647	0.04913	0.088109	0.163549
13 H	0.02044	0.05283	0.068046	0.175865
14 N	0.00794	0.09562	0.026420	0.318283
15 H	0.01831	0.05869	0.060959	0.195365
16 C	**0.18363**	0.02323	**0.611258**	0.077344
17 N	0.01194	**0.13366**	0.039735	**0.444916**
18 N	-0.02568	0.05612	-0.085479	0.186817
19 H	0.02273	0.02618	0.075662	0.087157
20 C	0.01535	-0.13951	0.051103	-0.464407
21 C	0.06118	-0.01754	0.203654	-0.0584
22 C	0.10102	-0.04115	0.336285	-0.136986
23 C	-0.00123	0.01328	-0.004104	0.044199
24 H	0.03471	0.02349	0.115538	0.078219
25 C	-0.00533	0.01664	-0.017729	0.055377
26 H	0.02223	0.04409	0.074011	0.146772
27 C	0.05435	0.00673	0.180908	0.022412
28 H	0.06240	0.04203	0.207715	0.139891
29 H	0.06289	0.04556	0.209333	0.151655
30 H	0.07441	0.04643	0.247710	0.154548
31 C	0.01047	0.07059	0.034838	0.234971
32 O	0.06331	0.05829	0.210744	0.194037
33 N	0.01395	-0.00269	0.046446	-0.008944
34 H	0.01083	0.02386	0.036067	0.079424
35 H	0.03717	0.04042	0.123727	0.134542

Table 4. Fukui and local softness indices for nucleophilic and electrophilic attacks in FD atoms calculated from mulliken charges

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	0.002133	0.00305	0.006210	0.008880
2 C	0.012599	0.0103	0.036683	0.029989
3 C	-0.001466	0.00574	-0.004268	0.016712
4 C	0.007017	0.002747	0.020430	0.007998
5 C	-0.009138	-0.033289	-0.026606	-0.096925
6 C	0.000226	0.001267	0.000658	0.003689
7 H	0.03072	0.033208	0.089444	0.096689
8 H	0.034246	0.034647	0.099711	0.100878
9 H	0.027581	0.025405	0.080305	0.073969
10 H	-0.000103	-0.025909	-0.000299	-0.075437
11 H	0.015689	0.024838	0.045680	0.072318
12 N	-0.007197	0.014135	-0.020954	0.041155
13 H	0.012066	0.034985	0.035131	0.101863
14 N	0.010181	0.009773	0.029643	0.028455
15 H	0.025032	0.038675	0.072883	0.112606
16 C	0.140796	0.058231	0.409944	0.169546
17 N	0.104075	0.046825	0.303026	0.136336
18 N	-0.028897	0.072894	-0.084137	0.212239
19 H	0.015535	0.064099	0.045232	0.186631
20 C	-0.033704	0.020008	-0.098133	0.058255
21 C	0.04251	0.025402	0.123772	0.073961
22 C	0.047375	0.041463	0.137938	0.120724
23 C	-0.033182	0.006529	-0.096613	0.019010
24 H	0.030862	0.028025	0.089858	0.081598
25 C	-0.017700	0.013094	-0.051535	0.038124
26 H	0.036800	0.018612	0.107147	0.054191
27 C	**0.150490**	0.019046	**0.438169**	0.055454
28 H	0.049892	0.038014	0.145266	0.110682
29 H	0.048299	0.038626	0.140628	0.112464
30 C	0.052513	-0.011088	0.152897	-0.032284
31 O	0.04769	**0.095099**	0.138855	**0.276892**
32 N	0.001512	0.022457	0.004402	0.065386
33 H	0.015636	0.017905	0.045526	0.052132
34 H	0.035422	0.042663	0.103135	0.124218
35 N	-0.035297	0.016515	-0.102771	0.048085
36 C	-0.027288	-0.023728	-0.079452	-0.069087
37 H	0.057459	0.029536	0.167298	0.085997
38 H	0.03847	0.035046	0.112010	0.102040
39 H	0.015137	0.033282	0.044073	0.096904
40 C	-0.027816	-0.022844	-0.080989	-0.066513
41 H	0.013231	0.032391	0.038523	0.094310
42 H	0.040819	0.035517	0.118849	0.103412
43 H	0.059774	0.026812	0.174039	0.078066

The maxima of the nucleophilic Fukui function f^+indicate the preferred site for adsorption of nucleophilic agents[48]. On the other hand f^-corresponds to reactivity with respect to electrophilic attack. Table 3and 4 represents the Fukui and local softness indices of FB and FD . In FB the preferred sites for attack by nucleophilic agent is near C16 atom. This is due to the π electron density is slightly shifted towards N17 and at the approach of a reagent the electromeric shift results in complete transfer of this π electron pair to N. This leads to the electrophilic attack at N17. The powerfully activating dialkyl amino group makes C27 to be the site for the nucleophilic attack and O31 to be the site for electrophilic attack in FD.

CONCLUSION

The following conclusions can be drawn from this study:

1. The inhibition efficiency of formazan derivatives obtained Quantum chemically increase with the increased in E_{HOMO}, and with decreased in E_{LUMO} and energy gap (ΔE). FD has the highest inhibition efficiency because it had the highest HOMO energy and ΔN values and it was most capable of offering electrons.
2. The parameters like hardness(η), Softness(S), dipole moment(μ), electron affinity(EA) ionization potential(IE), electronegativity(χ) and the fraction of electron transferred (ΔN) confirms the inhibition efficiency in the order of FD>FB.
3.Fukui function shows the nucleophilic and electrophilic attacking sites in the formazan derivatives.

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