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Research Article

Quantum Chemical Studies on The Efficiencies of Vinyl Imidazole Derivatives as Corrosion Inhibitors For Mild Steel

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ABSTRACT

The corrosion inhibition characteristics of two vinyl imidazole derivatives, ie., 2,4,5-triphenyl-1-vinyl-1*H*-imidazole (C1) and 2-(4-methoxyphenyl)-4,5-diphenyl-1-vinyl-1*H*-imidazole(C2), on mild steel has been studied using Density functional theory (DFT).Quantum chemical parameters such as 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) , electrophilicity index(ω) and the fraction of electron transferred (ΔN) have been calculated using B3LYP/6-31G(d,p) basis set. The local reactivity has been studied through the Fukui and condensed softness indices in order to predict both the reactive centres and to know the possible sites of nucleophilic and electrophilic attacks. The obtained correlations and theoretical conclusions agree well with the experimental data.

Keywords: Vinyl imidazole, corrosion inhibitors, DFT, Fukui function, softness indices, electrophilicity index

1. INTRODUCTION

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. The study of corrosion of mild steel and iron is a matter of tremendous theoretical and practical concern and as such has received a considerable amount of interest. Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media [1–3].

Among efficient corrosion inhibitors used to prevent the deterioration of mild steel are heterocyclic organic compounds consisting of a π-system and / or O, N, or S hetero atoms [4-6]. The planarity and the lone electron pairs in the hetero atoms are important features that determine the adsorption of molecules on the metallic surface [7]. The inhibition efficiency has been closely related to the inhibitor adsorption abilities and the molecular properties for different kinds of organic compounds [8-10]. 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. Free electron pairs on heteroatoms or π electrons are readily available for sharing to form a bond and act as nucleophile centres of inhibitor molecules and greatly facilitate the adsorption process over the metal surface, whose atoms act as electrophiles[11]. Recently the effectiveness of an inhibitor molecule has been related to its spatial as well as electronic structure [12,13]. Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity [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. The Fukui function [20] represents 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 (FMO), 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].

Theoretical investigation of corrosion inhibition effect of imidazole and its derivatives on mild steel using cluster model has been investigated by Mehdi Mousavi *et al*.[24] K. F. Khaled *et al*.[25] have investigated the electrochemical and molecular dynamics simulation studies on the corrosion inhibition of aluminum in molar hydrochloric acid using some imidazole derivatives. Quantum mechanical calculations on some 4-methyl-5-substituted imidazole derivatives as acidic corrosion inhibitor for zinc was calculated by G. Bereket *et al*. [26].Y.C.He *et al* [27] have investigated the corrosion and scaling inhibition by imidazoline derivatives. Zhang *et al.* [28] studied the inhibition efficiencies of imidazole, benzimidazole and their derivatives using B3LYP/6-31G (d,p) method.

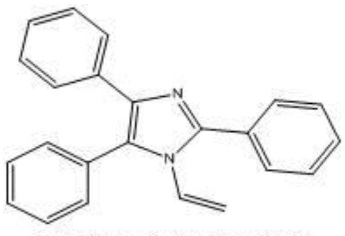
The Vinyl imidazole derivatives investigated in the present work are:
2,4,5-triphenyl-1-vinyl-1*H*-imidazole (C1)
2-(4-methoxyphenyl)-4,5-diphenyl-1-vinyl-1*H*-imidazole(C2)

The objective of the present paper is to extend the study of Deana Wahyuningrum *et al.* [29] by analyzing the inhibitive properties of C1 and C2 using DFT calculations. Molecular orbital calculations are performed looking for good theoretical parameters to characterize the inhibition property of inhibitor, which will be helpful to gain insight into the mechanism of the corrosion inhibition. Results obtained showed that the inhibition efficiency of C2>C1. It is well correlated with the experimental results. From the calculations we have explained which adsorption site is favoured to bind to the metal surface.

2. MATERIAL AND METHODS

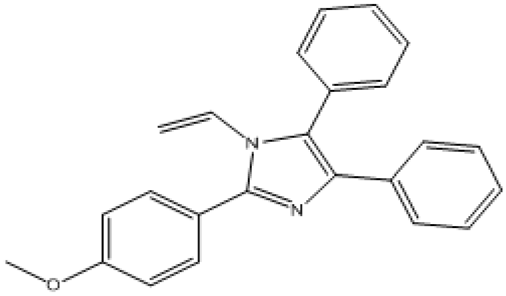
2.1. Computational Details

In computational chemistry tools, the DFT offers the fundamentals for interpreting multiple chemical concept used in different branches of Chemistry. In order to explore the theoretical-experimental consistency, quantum chemical calculations were performed with complete geometry optimizations using standard Gaussian-03 software package[30]. Geometry optimization were carried out by B3LYP functional at the 6-31G (d,p) basis set and at the density functional theory (DFT) level. 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 [31,32]. Furthermore, DFT is considered a very useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data.



2,4,5-triphenyl-1-vinyl-1H-imidazole

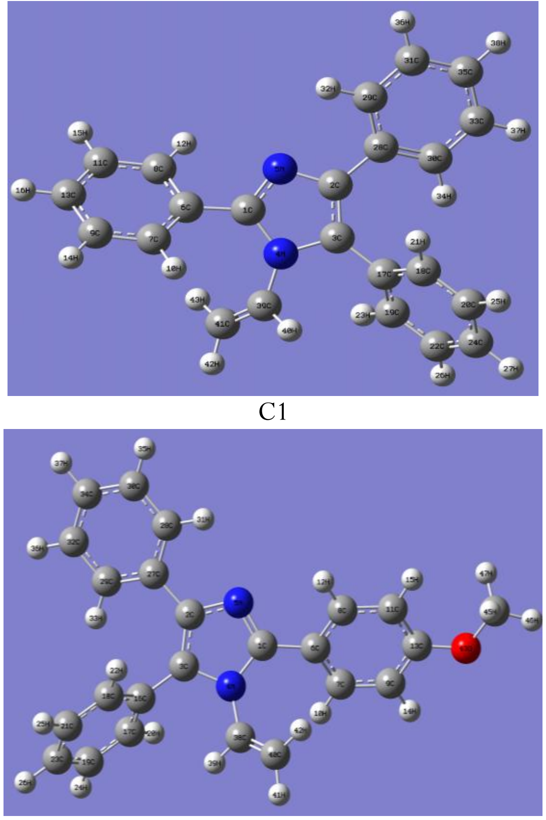
(C1)



2-(4-methoxyphenyl)-4,5-diphenyl
-1-vinyl-1H-imidazole

(C2)

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



C1

C2

Figure 2. Optimized structure of C1 and C2 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). The basic relationship of the density functional theory of chemical reactivity is precisely, the one established by Parr, Donnelly, Levy and Palke [33], that links the chemical potential of DFT with the first derivative of the energy with respect to the number of electrons, and therefore with the negative of the electronegativity χ.

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

Where μ is the electronic chemical potential, E is the total energy, N is the number of electrons, and $v(r)$ is the external potential of the system.

Hardness (η) has been defined within the DFT as the second derivative of the E with respect to N at $v(r)$ property which measures both the stability and reactivity of the molecule [34].

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

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

According to Koopman's theorem [35] the ionization potential (IE) and electron affinity (EA) of the inhibitors are calculated using the following equations and hence χ and η are calculated.

$$IE = -E_{HOMO}$$
$$EA = -E_{LUMO}$$

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 [36].

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

The global softness(S) is the inverse of the global hardness [37].

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

Electronegativity, hardness and softness have proved to be very useful quantities in the chemical reactivity theory. 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 fraction of transferred electrons (ΔN) from the inhibitor molecule to the metallic atom was calculated according to Pearson [38]. For a reaction of two systems with different electronegativities (as a metallic surface and an inhibitor molecule) the following mechanism will take place: the electronic flow will occur from the molecule with the lower electronegativity toward that of higher value, until the chemical potentials are the same. For the calculation the following formula was used [39].

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

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 ηFe = 0 for the computation of number of transferred electrons [37]. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance [40]. The local selectivity of a corrosion inhibitor is best analyzed by means of condensed Fukui function.

The global electrophilicity index was introduced by Parr [41] and is given by $\omega = \mu^2/2\eta$. According to the definition, this index measures the propensity of chemical species to accept electrons. A good, more reactive, nucleophile is characterized by lower value of μ, ω; and conversely a good electrophile is characterized by a high value of μ, ω. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment.

The change in electron density is the nucleophilic f^+(r) and electrophilic f^- (r) Fukui functions, which can be calculated using the finite difference approximation as follows [42].

$$f_k^+ = q_{N+1} - q_N$$

$$f_k^- = q_N - q_{N-1}$$

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 $s(r)$ [43].

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

From this relation, one can infer that local softness and Fukui function are closely related, and they should play an important role in the field of chemical reactivity.

3. RESULTS AND DISCUSSION

The inhibition effect of inhibitor compound is usually ascribed to adsorption of the molecule on metal surface. There can be physical adsorption (physisorption) and chemical adsorption (chemisorption) depending on the adsorption strength. When chemisorption takes place, one of the reacting species acts as an electron pair donor and the other one acts as an electron pair acceptor. The energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency towards the donation of electron by a molecule [44]. High values of E_{HOMO} have a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy, empty molecular orbital. Increasing values of E_{HOMO} facilitate adsorption and therefore enhance the inhibition efficiency, by influencing the transport process through the adsorbed layer. Therefore, higher values of E_{HOMO} indicate better tendency towards the donation of electron, enhancing the adsorption of the inhibitor on mild steel and therefore better inhibition efficiency. 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 C1 and C2 is represented in figure 3.

Table 1. Quantum chemical parameters for C1 and C2 calculated using B3LYP/6-31G (d,p).

Parameters	C1	C2
E_{HOMO}(eV)	-5.28811	-5.13409
E_{LUMO} (eV)	-1.00276	-0.87459
Energy gap(ΔE)(eV)	4.28535	4.2595
Dipole moment (Debye)	3.3922	2.6832

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 [45]. E_{HOMO} is a quantum chemical parameter which is often associated with the electron donating ability of the molecule. High value of E_{HOMO} is likely to a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy [46]. 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 feedback bond. The highest value of E_{HOMO} -5.13409 (eV) of C2 indicates the better inhibition efficiency.

The 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 [47]. 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 [48]. 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 [49]. The results as indicated in table 1 shows that inhibitor C2 has the lowest energy gap, this means that the molecule could have better performance as corrosion inhibitor.

It is shown from the calculation that there was no obvious correlation between the values of dipole moment with the trend of inhibition efficiency obtained experimentally. In the literature there is a lack of agreement on the correlation between the dipole moment and inhibition efficiency [50, 51]. 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 [52]. The low ionization energy 5.13409 (eV) of C2 indicates the high 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 [53]. In our present study C2 with low hardness value 2.12975 (eV) compared with other compound 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 [38]. 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 [54]. C2 with the softness value of 0.46954 has the highest inhibition efficiency.

According to Sanderson's electronegativity equalization principle [55], C1 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 table 2 shows the order of electronegativity as C1>C2. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order C2>C1.

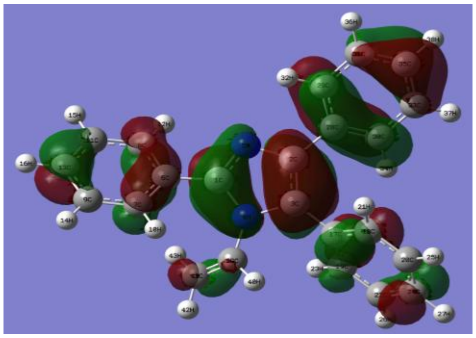
The number of electrons transferred (Δ*N*) was also calculated and tabulated in Table 2. Values of Δ*N* show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study [38]. If Δ*N* < 3.6, the inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface and it increases in the following order: C2>C1. The results indicate that Δ*N* values correlates strongly with experimental inhibition efficiencies. Thus, the highest fraction of electrons transferred is associated with the best inhibitor (C2), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (C1).

Table 2. Quantum chemical parameters for molecule C1 and C2 calculated using B3LYP/6-31G (d,p)

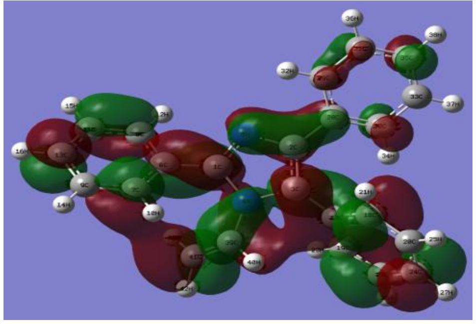
Parameters	**C1**	**C2**
E_N (au)	-569.60802	-530.29463
E_{N-1}(au)	-569.31709	-529.99744
E_{N+1}(au)	-569.61160	-530.29883
IE(eV)	5.28811	5.13409
EA(eV)	1.00276	0.87459
η (eV)	2.14267	2.12975
S	0.46671	0.46954
χ (eV)	3.14544	3.00434
ω	2.30874	2.11904
ΔN	0.89948	0.93806

The use of Mulliken population analysis to estimate the adsorption centres of inhibitors has been widely reported and it is mostly used for the calculation of the charge distribution over the whole skeleton of the molecule [56]. There is a general consensus by several authors that the more negatively charged an heteroatom, is the more it can be adsorbed on the metal surface through the donor-acceptor type reaction [48]. It is important to consider the situation corresponding to a molecule that is going to receive a certain amount of charge at some centre and is going to back donate a certain amount of charge through the same centre or another one [57]. Parr and Yang proposed that larger value of Fukui function indicate more reactivity [26]. Hence greater the value of condensed Fukui function, the more reactive is the particular atomic centre in the molecule.

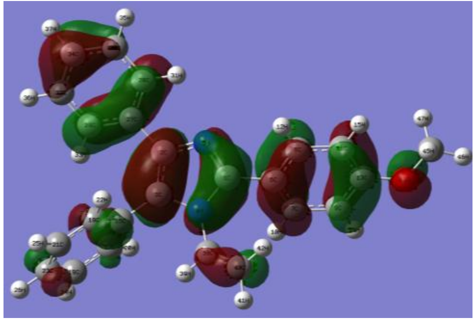
The local reactivity of molecule C1 and C2 is analyzed by means of the condensed Fukui function. The condensed Fukui function and local softness indices allow one distinguish each part of the molecule on the basis of its distinct chemical behaviour [58] due to the different substituted functional group. The f_k^+ measures the changes of density when the molecules gains electrons and it corresponds to reactivity with respect to nucleophilic attack. On the other hand, f_k^- corresponds to reactivity with respect to electrophilic attack or when the molecule loss electrons. For nucleophilic attack the most reactive site of molecule C1 and C2 is on the C41 and C40. It is clear that C41 and C40 of molecule C1 and C2 has more nucleophilic character and is involved in the chemical reactivity of the molecules with metal surface which exhibit the adsorption mechanism. The Fukui function f_k^- is confirmed by the electrophilic attack at the site C3 in both the compounds.



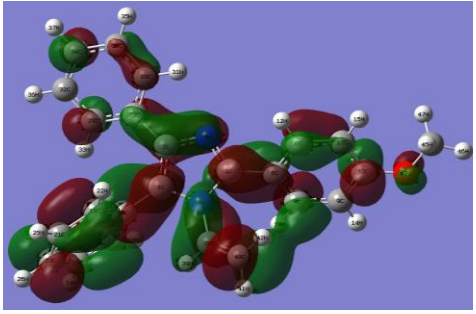
HOMO of C1



LUMO of C1



HOMO of C2



LUMO of C2

Figure 3. Frontier molecular orbital diagrams of C1 and C2 by B3LYP/6-31G (d,p)

Table 3. Fukui and local softness indices for nucleophilic and electrophilic attacks in C1 atoms calculated from Mulliken atomic charge

Atom No	f_k^{+}	f_k^{-}	s_k^{+}	s_k^{-}
1 C	0.020833	0.077189	0.004861	0.018012
2 C	0.007388	0.060242	0.001723	0.014057
3 C	0.013654	**0.081489**	0.003186	**0.019015**
4 N	0.036989	-0.020867	0.008631	-0.004869
5 N	0.037075	0.000343	0.008651	0.000080
6 C	-0.008514	0.002736	-0.001986	0.000638
7 C	0.047875	-0.008675	0.011172	-0.002024
8 C	0.019681	0.013549	0.004592	0.003161
9 C	0.004275	0.003238	0.000997	0.000755
10 H	0.016714	0.029264	0.003900	0.006828
11 C	0.002029	0.006557	0.000473	0.001530
12 H	0.023718	0.033793	0.005534	0.007885
13 C	0.030076	0.021683	0.007018	0.005059
14 H	0.045204	0.041129	0.010548	0.009597
15 H	0.047003	0.041482	0.010968	0.009679
16 H	0.053148	0.047555	0.012402	0.011097
17 C	-0.021931	0.002183	-0.005117	0.000509
18 C	0.020249	0.011147	0.004725	0.002601
19 C	0.022087	0.005357	0.005154	0.001250
20 C	0.002911	0.001085	0.000679	0.000253
21 H	0.036926	0.011314	0.008616	0.002640
22 C	0.003487	0.00581	0.000814	0.001356
23 H	0.025187	0.026558	0.005877	0.006197
24 C	0.030326	0.014464	0.007076	0.003375
25 H	0.051183	0.03737	0.011943	0.008720
26 H	0.047289	0.039695	0.011034	0.009263
27 H	0.056059	0.043477	0.013081	0.010145
28 C	0.008313	-0.013015	0.001939	-0.003040
29 C	-0.000393	0.027018	-9.170650	0.006305
30 C	0.00659	0.021509	0.001537	0.005019
31 C	0.005768	0.00639	0.001345	0.001491
32 H	0.018244	0.030881	0.004257	0.007206
33 C	0.002371	0.004418	0.000553	0.001031
34 H	-0.001717	0.030414	-0.000400	0.007097
35 C	0.014337	0.02374	0.003345	0.005539
36 H	0.035548	0.047889	0.008295	0.011175
37 H	0.030697	0.045564	0.007163	0.010632
38 H	0.039293	0.053806	0.009169	0.012555
39 C	-0.002361	-0.046334	-0.000550	-0.010812
40 H	0.038819	0.034779	0.009058	0.008115
41 C	**0.056866**	0.039995	**0.013269**	0.009333
42 H	0.053838	0.043323	0.012563	0.010109
43 H	0.022868	0.020459	0.005336	0.004774

Table 4. Fukui and local softness indices for nucleophilic and electrophilic attacks in C2 atoms calculated from Mulliken atomic charges

Atom No	f_k^{+}	f_k^{-}	s_k^{+}	s_k^{-}
1 C	0.050964	0.074968	0.011965	0.017600
2 C	0.013448	0.051556	0.003157	0.012104
3 C	0.016722	**0.083559**	0.003926	**0.019617**
4 N	0.016925	-0.024573	0.003973	-0.005769
5 N	0.026917	-0.004483	0.006319	-0.001052
6 C	-0.060048	0.004579	-0.014097	0.001075
7 C	0.117062	-0.004926	0.027482	-0.001156
8 C	0.077782	0.016112	0.018260	0.003783
9 C	0.047748	0.007704	0.011209	0.001808
10H	-0.030027	0.028622	-0.007049	0.006719
11 C	0.027312	0.013859	0.006412	0.003254
12 H	-0.024521	0.044505	-0.005757	0.010448
13 C	0.046155	0.029802	0.010835	0.006996
14 H	-0.002089	0.042901	-0.000490	0.010072
15 H	-0.00882	0.03965	-0.002070	0.009308
16 C	-0.048108	0.003637	-0.011294	0.000854
17 C	0.070676	0.023476	0.016592	0.005512
18 C	0.106793	-0.009496	0.025071	-0.002229
19 C	0.043907	0.000015	0.010308	0.000035
20 H	-0.019595	0.015038	-0.004600	0.003530
21 C	0.048808	0.001942	0.011458	0.000456
22 H	-0.016349	0.019676	-0.003838	0.004619
23 C	0.076687	0.012155	0.018004	0.002854
24 H	0.004872	0.033986	0.001144	0.007979
25 H	0.005564	0.033528	0.001306	0.007871
26 H	0.012026	0.038295	0.002823	0.008990
27 C	-0.018539	-0.016868	-0.004352	-0.00396
28 C	0.057605	0.022226	0.013524	0.005218
29 C	0.069329	0.019066	0.016276	0.004476
30 C	0.048278	0.004567	0.011334	0.001072
31 H	-0.028481	0.023466	-0.006686	0.005509
32 C	0.046069	0.003885	0.010816	0.000912
33 H	-0.054372	0.02577	-0.012765	0.0061
34 C	0.056636	0.018997	0.013296	0.004459
35 H	-0.011	0.041188	-0.002582	0.009669
36 H	-0.015295	0.03984	-0.003590	0.009353
37 H	-0.007522	0.046687	-0.001766	0.010961
38 C	0.042222	-0.063438	0.009912	-0.014893
39 H	-0.016755	0.042091	-0.003933	0.009882
40 C	**0.158741**	0.047588	**0.037267**	0.011172
41 H	0.01504	0.042929	0.003531	0.010078
42 H	-0.031752	0.022033	-0.007454	0.005173
43 O	0.016696	0.037496	0.003919	0.008803
44 C	0.103872	-0.026617	0.024386	-0.006249
45 H	-0.016115	0.029271	-0.003783	0.006872
46 H	-0.003358	0.03743	-0.000788	0.008787
47 H	-0.012106	0.026312	-0.002842	0.006177

4. CONCLUSION

The following conclusions can be deduced from the present study:

1. Through DFT calculations a correlation between parameters related to the electronic and molecular structures of Vinyl imidazole derivatives (C1 and C2) and their ability to inhibit the corrosion process could be established.

2. The inhibition efficiency of the molecules C1 andC2 obtained Quantum chemically increase with the increase in E_{HOMO}, and decrease in energy gap (ΔE). C2 has the highest inhibition efficiency because it had the highest HOMO energy and ΔN values and lowest energy gap it was most capable of offering electrons and it could have a better performance as corrosion inhibitor.

3. 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 C2>C1.

4. Fukui function shows the nucleophilic and electrophilic attacking sites in the molecule C1 and C2.

5. Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the method employed here.

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