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Research Article

THEORETICAL STUDY USING DFT CALCULATIONS ON INHIBITORY ACTION OF SOME PYRAZOLE DERIVATIVES ON STEEL

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ABSTRACT

The inhibition activity of two pyrazole derivatives, namely 1-{[benzyl-(2-cyano-ethyl)amino]methyl}-5-methyl-1H-pyrazole-3-carboxylic acid methyl ester (P1) and 1-{[benzyl-(2-cyano-ethyl)amino] methyl}-5-methyl-1H-pyrazole-3-carboxylic acid ethyl ester (P2) has been performed using density functional theory (DFT) at the B3LYP/6-31G(d,P) basis set level in order to elucidate the different inhibition efficiencies and reactive sites of these compounds as corrosion inhibitors. The calculated structural parameters correlated to the inhibition efficiency are the frontier molecular orbital energies E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), energy gap (ΔE), dipole moment (μ), hardness (η), softness (S), the absolute electronegativity (χ), the electrophilicity index (ω) and the fractions of electrons transferred (ΔN) from pyrazole molecules to iron . The local reactivity has been analyzed through the condensed Fukui function and condensed softness indices using population analysis. The calculated % IE was found to be in agreement with experimental corrosion inhibition efficiencies.

Keywords: Corrosion inhibition, Pyrazole , reactivity, DFT, Fukui function, softness indices.

1. INTRODUCTION

Corrosion of steel is an inevitable process during cleaning, pickling, scaling and etching in acidic medium. The study of corrosion processes and their inhibition by organic compounds is a very active field of research [1]. Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media [2]. It has been commonly recognized that organic inhibitor usually promotes formation of a chelate on the metal surface, which includes the transfer of electrons from the organic compounds to metal, forming coordinate covalent bond during such chemical adsorption process [3]. Most of the organic inhibitors containing nitrogen, oxygen, sulfur atoms, and multiple bonds in their molecules facilitate adsorption on the metal surface [4, 5]. Researchers conclude that the adsorption on the metal surface depends mainly on the physicochemical properties of the inhibitor, such as the functional group, molecular electronic structure, electron density at the donor atom, π orbital character and the molecular size [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 geometry of an inhibitor also has an important influence in determining its adsorbability at the metal-solution interface. Molecules that are planar have a greater tendency to adsorb at the metal surface than molecule that has less planar geometry [8]. Quantum chemical calculations have been widely used to study reactive mechanism and also an effective tool in the analysis and elucidation of many experimental observations. They have been proved to be a very powerful tool for studying corrosion inhibition mechanism [9, 10].

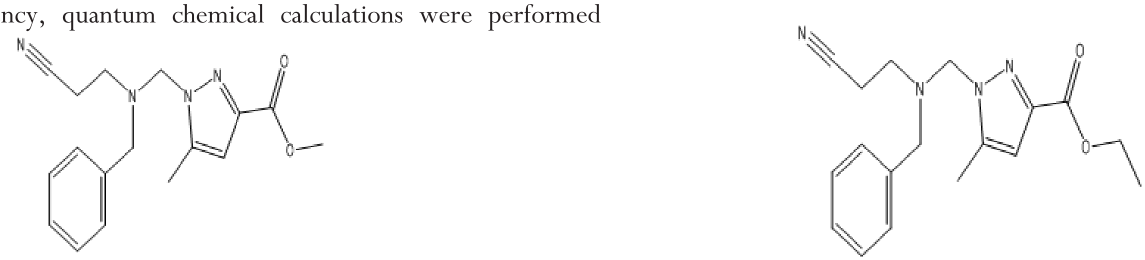
Pyrazole derivatives have attracted considerable attention in the recent years for their diverse biological [11] and also for their anticancer activities [12]. In literature, a few reports have been presented on the use of pyrazole and some of its derivatives as corrosion inhibitors in different media [13, 14]. Although experimental work of L. Herrag *et al.* [15] provide valuable information on the corrosion inhibition efficiency of 1-{[benzyl-(2-cyano-ethyl)amino]methyl}-5-methyl-1H-pyrazole-3-carboxylic acid methyl ester (P1) and 1-{[benzyl-(2-cyano-ethyl)amino]methyl}-5-methyl-1H-pyrazole-3-carboxylic acid ethyl ester (P2), a deep understanding of the inhibition property remain unclear. The objective of the present paper is to extend the study of L. Herrag *et al.* [15] by analyzing the inhibition efficiency of P1and P2 on theoretical chemical parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital

(E_{LUMO}), the energy gap (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η), softness (S), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and back donation(ΔE). 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 using DFT calculations

2. MATERIAL AND METHODS

2.1 Quantum Chemical Calculation

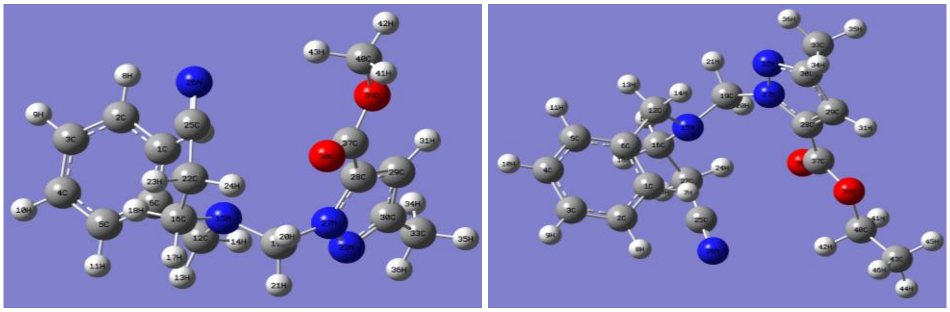
In order to explore the theoretical-experimental consistency, quantum chemical calculations were performed using Gaussian-03 software package [16]. Complete geometrical optimizations of the investigated molecules are performed using density functional theory(DFT) with the Becke's three parameter exchange functional along with the Lee– Yang–Parr nonlocal correlation functional (B3LYP) [17,18] at 6-31G(d,p) basis set level. These calculations have been widely used to study reaction mechanisms [19]. They have also been proved to be a very powerful tool for studying inhibition of the corrosion of metals [20, 21). 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 [22]. The chemical and optimized structures of the compounds studied are given in fig 1. and fig. 2.



1-{[benzyl-(2-cyano-ethyl)amino]methyl}-5-methyl-1H-pyrazole-3-carboxylic acid methyl ester (P1)

1-{[benzyl-(2-cyano-ethyl)amino]methyl}-5-methyl-1H-pyrazole-3-carboxylic acid ethyl ester (P2)

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



P1 P2

Fig. 2: Optimized structure of P1 and P2 calculated with the B3LYP/6-31G (d,p)

2.2. Global and local reactivity descriptors

Density functional theory (DFT) [23] has been found to be successful in providing theoretical insights into the chemical reactivity and selectivity, in terms of popular qualitative chemical concepts like electronegativity (χ), hardness (η), softness(S), electrophilicity index (ω) and local reactivity descriptors 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 [24], 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.

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)} = -\chi \qquad (1)$$

Where μ is the 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 as $v(r)$ property which measures both the stability and reactivity of the molecule [25].

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

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

According to, the Koopmans' theorem [26] for closed-shell molecules, ionization potential (*I)* and electron affinity *(A)* can be expressed as follows in terms of E_{HOMO}, E_{LUMO} the highest occupied molecular orbital energy, and the lowest unoccupied molecular orbital energy, respectively:

$$I = -E_{HOMO} \qquad (3)$$

$$A = -E_{LUMO} \qquad (4)$$

When the values of I and A are known, one can determine through the following expressions [27] the values of the absolute electronegativity χ, the absolute hardness η and the softness S (the inverse of the hardness):

$$\chi = \frac{I+A}{2} \qquad (5)$$

$$\eta = \frac{I-A}{2} \qquad (6)$$

The global softness(S) is the inverse of the global hardness [28]

$$S = \frac{1}{\eta} \qquad (7)$$

For a reaction of two systems with different electronegativities the electronic flow will occur from the molecule with the lower electronegativity (the organic inhibitor) towards that of higher value (metallic surface), until the chemical potentials are equal [29]. Therefore the fraction of electrons transferred (ΔN) from the inhibitor molecule to the metallic atom was calculated according to Pearson electronegativity scale [30]

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{\left[2(\eta_{Fe}+\eta_{inh}\right]} \qquad (8)$$

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 [31] and $\eta_{Fe} = 0$ by assuming that for a metallic bulk I = A [32] because they are softer than the neutral metallic atoms. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance [23]. The local selectivity of a corrosion inhibitor is best analyzed by means of condensed Fukui function.

The electrophilicity is a descriptor of reactivity that allows a quantitative classification of the global electrophilic nature of a molecule within a relative scale. Parr *et al* [33] have proposed electrophilicity index as a measure of energy lowering due to maximal electron flow between donor and acceptor. They defined electrophilicity index(ω) as follows.

$$\omega = \frac{\mu^2}{2\eta} \qquad (9)$$

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.

2.3. Local molecular reactivity

The Fukui function provides an avenue for analyzing the local selectivity of a corrosion inhibitor [34]. Their values are used to identify which atoms in the inhibitors are more prone to undergo an electrophilic or a nucleophilic attack. 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 [35].

$$f_k^{+} = q_{N+1} - q_N \qquad (10)$$

$$f_k^{-} = q_N - q_{N-1} \qquad (11)$$

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 $s(r)$ [36]

$$s(r) = \left(\frac{\partial\rho(r)}{\partial N}\right)_{v(r)} \left(\frac{\partial N}{\partial\mu}\right)_{v(r)} = f(r)S \qquad (12)$$

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.

According to the simple charge transfer model for donation and back-donation of charges proposed recently by Gomez *et al.*, [37] an electronic back-donation process might be occurring governing the interaction between the inhibitor molecule and the metal surface. The concept establishes that if both processes occur, namely charge transfer to the molecule and back-donation from the molecule, the energy change is directly related to the hardness of the molecule, as indicated in the following expression.

$$\Delta E_{\text{Back-donation}} = -\frac{\eta}{4}$$

The $\Delta E_{Back\text{-}donation}$ implies that when $\eta > 0$ and $\Delta E_{Back\text{-}donation} < 0$ the charge transfer to a molecule, followed by a back-donation from the molecule, is energetically favored. In this context, hence, it is possible to compare the stabilization among inhibiting molecules, since there will be an interaction with the same metal, then, it is expected that it will decrease as the hardness increases.

3. RESULTS AND DISCUSSION

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 [38]. Table 1 represents the quantum chemical parameters for the inhibitors P1and P2. The energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency towards the donation of electron by a molecule. 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 P1 and P2 is represented in fig. 3.

Table 1: Quantum chemical parameters for P1and P2 calculated using B3LYP/6-31G(d,p).

Parameters	P1	P2
E_{HOMO}(eV)	-6.246	-6.227
E_{LUMO} (eV)	-1.128	-1.121
Energy gap(ΔE) (eV)	5.118	5.106
Dipole moment (Debye)	2.0019	1.8430

The energy of the HOMO (EHOMO) provides information about the electron donating ability of the molecule. The molecule with the highest EHOMO value often has the highest tendency to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy [39]. 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} -6.227 (eV) of P2 indicates the better inhibition efficiency than the other inhibitor P1.

The energy gap between the HOMO and the LUMO (ΔE) provides information about the overall reactivity of a molecule. As ΔE decreases, the reactivity of the molecule increases leading to increase in the inhibition efficiency of the molecule [40]. Low values of the ($\Delta E = E_{LUMO} - E_{HOMO}$) gap will render good inhibition efficiencies since the energy to remove an electron from the last occupied orbital will be minimized [41]. 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 [42]. In our study, the trend for the (ΔE) values follows the order P2<P1, which suggests that inhibitor P2 has the highest reactivity in comparison to the other compound P1 and would therefore likely interact strongly with the metal surface.

The dipole moment (μ in Debye) is another important electronic parameter which provides the information on the polarity and the reactivity indicator of the molecule. Literature survey reveals that several irregularities appeared in case of correlation of dipole moment with inhibitor efficiency [43]. In general, there is no significant relationship between the dipole moment values and inhibition efficiencies [44]. It is shown from the calculations that there was no obvious correlation between the values of the dipole moment with the trend of inhibition efficiency obtained experimentally.

Table 2 summarized the important global chemical parameters. 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 [45]. The low ionization energy 6.227 (eV) of P2 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[46]. In our present study P2 with low hardness value 2.553 (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 [47]. 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 [48]. P2 with the softness value of 0.392 has the highest inhibition efficiency.

Table 2: Quantum chemical parameters for P1 and P2 calculated using B3LYP/6-31G(d,p).

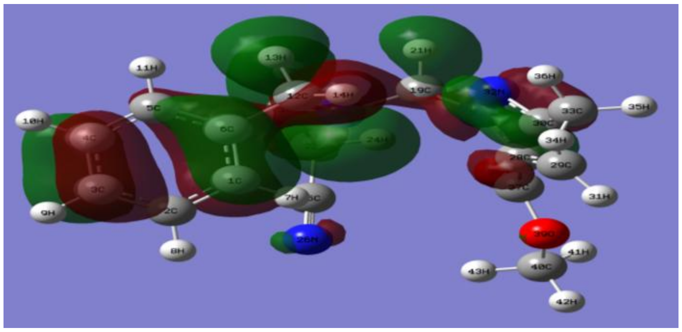
Parameters	P1	P2
IE(eV)	6.246	6.227
EA(eV)	1.128	1.121
η (eV)	2.559	2.553
S	0.391	0.392
χ (eV)	3.687	3.674
ω	2.656	2.644
μ	-3.687	-3.674

Table 2 shows the order of electronegativity as P1> P2. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order P2> P1. According to Sanderson's electronegativity equalization principle [49], P1 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.

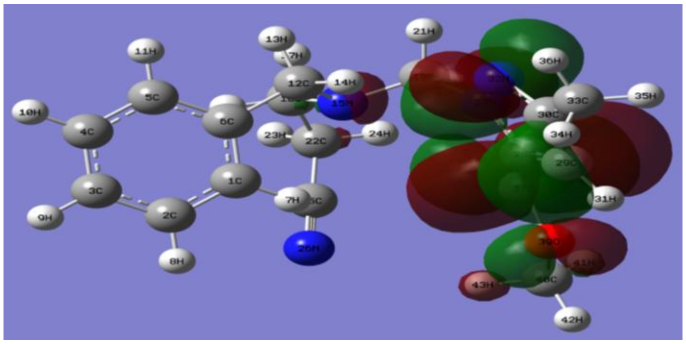
The number of electrons transferred (Δ*N*) and *back-donation (ΔE)* was also calculated and tabulated in Table 3. Values of Δ*N* show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study [50]. If Δ*N* < 3.6, the inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface and it increases in the following order: P1 < P2. 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 (P2), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (P1).

Table 3: The number of electron transferred (ΔN) and $\Delta E_{\text{back donation}}$ (eV) calculated for inhibitor P1 and P2.

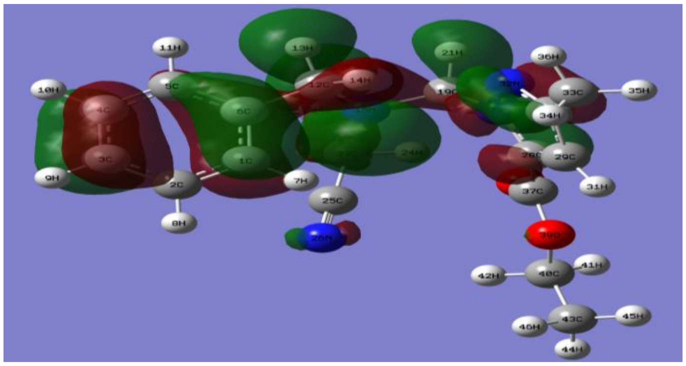
Parameters	P1	P2
Transferred electrons fraction (ΔN)	0.64732	0.65139
ΔE back-donation / (eV)	-0.63975	-0.63825



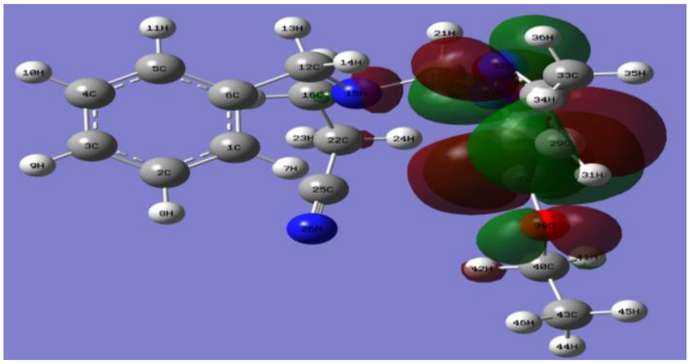
HOMO of P1



LUMO of P1



HOMO of P2



LUMO of P2

Fig. 3: Frontier molecular orbital diagrams of P1 and P2 by B3LYP/6-31G (d,p)

There is a general consensus by several authors that the more negatively charged a heteroatom, is the more it can be adsorbed on the metal surface through the donor-acceptor type reaction [51]. 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 [37].

Local Selectivity

The condensed Fukui functions and condensed local softness indices allow us to distinguish each part of the molecule on the basis of its distinct chemical behavior due to the different substituent functional groups. It is known that the Fukui indices were widely used as descriptors of site selectivity for the soft–soft reactions [52]. Parr and Yang proposed that larger value of Fukui function indicate more reactivity [53]. Hence greater the value of condensed Fukui function, the more reactive is the particular atomic centre in the molecule. 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. The calculated Fukui functions for the inhibitor P1 and P2 are presented in Tables 4 and 5.

In our study, the preferred site for nucleophilic attack in both the compound P1 and P2 is at C37 atoms. These results agree well with the analysis of the LUMO densities which also predicted these sites as the most electron deficient center. The electrophilic attack would preferably occur at N15 atoms in both the inhibitor P1 and P2. These results agree well with the analysis of the HOMO densities which also predicted these sites as the most electron rich centers. The results also show that back donation might take place on the N atom in both P1 and P2 structures.

Table 4. Fukui and local softness indices for nucleophilic and electrophilic attacks on P1 atoms calculated Mulliken atomic charges ; maxima in bold

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	-0.00586	-0.01453	-0.00229	-0.00568
2 C	-0.00132	0.00981	-0.00052	0.00384
3 C	0.00446	0.02181	0.00175	0.00853
4 C	0.00227	0.00975	0.00089	0.00381
5 C	0.00156	0.04858	0.00061	0.01899
6 C	-0.00653	0.00179	-0.00255	0.00070
7 H	-0.01899	0.03136	-0.00743	0.01226
8 H	0.01388	0.04177	0.00542	0.01633
9 H	0.02728	0.05558	0.01066	0.02173
10 H	0.02793	0.05865	0.01091	0.02293
11 H	0.01870	0.04078	0.00731	0.01594
12 C	-0.01395	-0.05862	-0.00545	-0.02292
13 H	0.03545	0.08526	0.01386	0.03334
14 H	-0.0113	0.04390	-0.00441	0.01716
15 N	-0.01030	**0.13649**	-0.00403	**0.05337**
16 C	-0.01068	-0.02515	-0.00417	-0.00983
17 H	0.02703	0.09987	0.01057	0.03905
18 H	0.03403	0.03494	0.01330	0.01366
19 C	0.00465	-0.02572	0.00181	-0.01005
20 H	0.01025	0.05535	0.00401	0.02164
21 H	0.05165	0.07574	0.02019	0.02962
22 C	0.00467	-0.01852	0.00183	-0.00724
23 H	0.03982	0.05159	0.01556	0.02017
24 H	-0.04258	0.02486	-0.01665	0.00972
25 C	0.03733	-0.03546	0.01459	-0.01387
26 N	0.01051	0.06522	0.00411	0.02550
27 N	0.0287	-0.00794	0.01120	-0.00311
28 C	0.02431	-0.01077	0.00950	-0.00421
29 C	0.04575	0.01687	0.01788	0.00659
30 C	-0.00612	0.02089	-0.00239	0.00817
31 H	0.06943	0.04205	0.02714	0.01644
32 N	0.08840	-0.01419	0.03456	-0.00555
33 C	-0.00823	-0.00203	-0.00322	-0.00079
34 H	0.03867	0.02444	0.01512	0.00955
35 H	0.03532	0.03444	0.01381	0.01347
36 H	0.03444	0.01341	0.01346	0.00524
37 C	**0.12703**	0.01438	**0.04967**	0.00562
38 O	0.12436	0.00011	0.04862	0.00004
39 O	0.05369	0.01167	0.02099	0.00456
40 C	-0.06196	-0.00338	-0.02423	-0.00132
41 H	0.04198	0.02338	0.01642	0.00914
42 H	0.06109	0.03345	0.02388	0.01308
43 H	0.07315	-0.01193	0.02860	-0.00466

Table 5. Fukui and local softness indices for nucleophilic and electrophilic attacks in P2 atoms calculated from Mulliken atomic charges ; maxima in bold.

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	-0.00481	-0.01416	-0.00188	-0.00555
2 C	-0.001	0.00966	-0.00039	0.00378
3 C	0.00452	0.02153	0.00177	0.00844
4 C	0.00214	0.00933	0.00085	0.00366
5 C	0.00138	0.04735	0.00054	0.01856
6 C	-0.00511	-0.00018	-0.00200	-0.00007
7 H	-0.01915	0.03193	-0.00750	0.01252
8 H	0.01332	0.04144	0.00522	0.01625
9 H	0.02684	0.05516	0.01052	0.02162
10 H	0.02750	0.05827	0.01078	0.02284
11 H	0.01819	0.04055	0.00713	0.01589
12 C	-0.01521	-0.05675	-0.00596	-0.02225
13 H	0.03541	0.08494	0.01388	0.03329
14 H	-0.01161	0.04453	-0.00455	0.01746
15 N	-0.00983	**0.13648**	-0.00385	**0.05350**
16 C	-0.01073	-0.02426	-0.00421	-0.00951
17 H	0.02684	0.09972	0.01052	0.03909
18 H	0.03324	0.03553	0.01303	0.01393
19 C	0.00461	-0.02563	0.00181	-0.01004
20 H	0.01005	0.05605	0.00394	0.02197
21 H	0.05122	0.07540	0.02007	0.02956
22 C	0.00525	-0.02015	0.00206	-0.00790
23 H	0.03892	0.05157	0.01525	0.02022
24 H	-0.04155	0.02519	-0.01628	0.00987
25 C	0.03681	-0.03595	0.01443	-0.01409
26 N	0.01049	0.06524	0.00411	0.02558
27 N	0.02853	-0.00780	0.01118	-0.00306
28 C	0.02615	-0.00956	0.01025	-0.00375
29 C	0.04443	0.01565	0.01742	0.00613
30 C	-0.00574	0.02183	-0.00225	0.00856
31 H	0.06821	0.04141	0.02674	0.01623
32 N	0.08670	-0.01505	0.03399	-0.00590
33 C	-0.00752	-0.00198	-0.00295	-0.00077
34 H	0.03748	0.02459	0.01469	0.00964
35 H	0.03511	0.03382	0.01376	0.01326
36 H	0.03385	0.01318	0.01327	0.00517
37 C	**0.1258**	0.01375	**0.04931**	0.00539
38 O	0.12150	-0.00144	0.04763	-0.00056
39 O	0.05471	0.01265	0.02144	0.00496
40 C	-0.06864	-0.00848	-0.02691	-0.00332
41 H	0.03698	0.02158	0.01449	0.00846
42 H	0.07307	-0.01296	0.02864	-0.00508
43 C	-0.01060	-0.0043	-0.00416	-0.00169
44 H	0.04439	0.02393	0.01740	0.00938
45 H	0.02075	0.02012	0.00814	0.00789
46 H	0.02702	0.00621	0.01059	0.00243

4. CONCLUSION

Quantum chemical calculations, using the Density Functional Theory method, have been performed on two pyrazole derivatives, namely 1-{[benzyl-(2-cyano-ethyl)amino]methyl}-5-methyl-1H-pyrazole-3-carboxylic acid methyl ester (P1) and 1-{[benzyl-(2-cyano-ethyl)amino]methyl}-5-methyl-1H-pyrazole-3-carboxylic acid ethyl ester (P2) to investigate their geometric and electronic properties in an attempt to elucidate the reactivity and selectivity centres of the compounds. The inhibition efficiency of P1 and P2 increases with the increase in E_{HOMO}, and decreases in energy gap (ΔE). P2 has the highest inhibition efficiency because it had the highest HOMO energy and ΔN values and it was most capable of offering electrons. 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 P2 >P1. The inhibitor P1 and P2 differs from each other only by the attachment of $-CH_2$ in ester functional group of P2. So most of the quantum chemical parameters of P1 and P2 shows very close values. Fukui function shows the nucleophilic and electrophilic attacking sites of the inhibitor P1 and P2**.**

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