



Theoretical assessment of Inhibitive behaviour of some Benzohydrazide Derivatives on Mild Steel

P.Udhayakala^{a*}, T.V. Rajendiran^b, S. Gunasekaran^c

^a Department of Chemistry, Dr.MGR Educational and Research Institute, Chennai -600095, India

^b Department of Chemistry, Pachaiyappa's College, Chennai - 600 030, India

^c Department of Physics, Spectrophysics Research Laboratory, Pachaiyappa's College, Chennai- 600 030, India

*Corresponding author: udhayakala_kumar@yahoo.in

ABSTRACT

In the present work, a theoretical study of two benzohydrazide derivatives N'-benzylidene benzohydrazide(BBH) and N'-(3-phenylallylidene) benzohydrazide(PABH), 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 quantum chemical properties/descriptors most relevant to their potential action as corrosion inhibitors have been calculated. They include 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 fraction of electrons transferred (ΔN) and the electrophilicity index (ω). The local reactivity has been analyzed through the condensed Fukui function and condensed softness indices in order to compare the possible sites for nucleophilic and electrophilic attacks. The theoretical results were found to be consistent with the experimental data reported.

Keywords: Benzohydrazide, reactivity, DFT, Fukui function, softness indices.

1. INTRODUCTION

Corrosion of mild steel is an inevitable process that produces a deterioration of materials and their properties resulting in massive economic losses that has attracted many investigation and researches [1, 2]. One of the most common, effective and economic method to protect metals against corrosion is use of organic compounds, as corrosion inhibitors. A number of heterocyclic compounds containing N, O, and S either in the aromatic or long chain carbon system have been reported as effective inhibitors of metal corrosion [3, 4]. Most efficient inhibitors are organic compounds containing electronegative functional groups and π -electrons in triple or conjugated double bonds. 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 [5, 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, 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 [10].

Recently the effectiveness of an inhibitor molecule has been related to its spatial as well as electronic structure [11, 12]. Quantum chemical calculations have been widely used to study reaction mechanism. They have been proved to be a powerful tool for studying corrosion inhibition mechanism [13-15]. Density functional theory (DFT) [16, 17] has provided a very useful framework for developing new criteria for rationalizing, predicting, and eventually understanding many aspects of chemical processes [18-20]. A variety of chemical concepts which are now widely used as descriptors of chemical reactivity, e.g., electronegativity [19] hardness or softness quantities etc., appear naturally within DFT [16]. 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 [21, 22]. Arjunan et al. have studied the systematic vibrational spectroscopic assignment and analysis of benzohydrazide [23]. An experimental and theoretical study on the acetylation reaction of benzohydrazide derivatives towards *p*-nitrophenyl acetate was investigated by Paola R. Campodonico et al. [24]. Quantum chemical study of the efficiency of some *o*-, *m*-, and *p*-substituted benzohydrazides were studied by El Sayed H. El Ashry et al. [25].

The benzohydrazide derivatives investigated in the present work are:

N'-benzylidene benzohydrazide (BBH)

N'-(3-phenylallylidene) benzohydrazide (PABH)

The objective of this paper is to extend the study of P.Mohan et al. [26] to investigate the dependence of inhibition efficiency of BBH and PABH 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.

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 [27]. 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 non local correlation functional (B3LYP) [28,29]. The calculations were based on 6-31G (d,p) basis set. This method has been widely implemented to study the relationship between corrosion inhibition efficiency of the molecules and their electronic properties [30]. Recently, Density functional theory (DFT) has been used to analyze the characteristics of the inhibitor mechanism and to describe the structural nature of the inhibitor in the corrosion process [31]. The chemical and optimized structures of the compounds studied are given in Fig 1. and Fig 2.

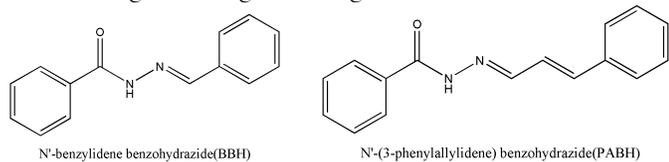


Fig. 1. Names, molecular structure and the abbreviation of the inhibitors investigated

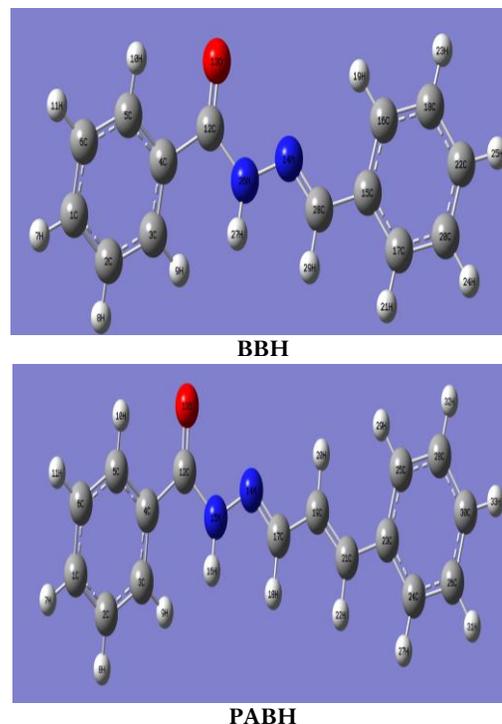


Fig. 2: Optimized structure of BBH and PABH calculated with the B3LYP/6-31G (d,p)

2.2. Global and local reactivity descriptors

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), 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 [32], 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 .

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

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 [33].

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

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

According to, the Koopman's theorem [34] 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:

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

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

When the values of I and A are known, one can determine through the following expressions [35] the values of the absolute electronegativity χ , the absolute hardness η and the softness S (the inverse of the hardness):

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

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

The global softness (S) is the inverse of the global hardness [36]

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

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 [37]. Therefore the fraction of electrons transferred (ΔN) from the inhibitor molecule to the metallic atom was calculated according to Pearson electronegativity scale [38].

$$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})} \quad (8)$$

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 $\chi_{\text{Fe}} = 7.0$ eV [39] and $\eta_{\text{Fe}} = 0$ by assuming that for a metallic bulk $I = A$ [40] 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 [41]. 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 electrophile nature of a molecule within a relative scale. Parr *et al* [42] 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.

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

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

Fukui functions are the relevant reactivity indicators in the electron-transfer controlled reactions such as corrosion inhibition process [42]. 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 [43].

$$f^+(r) = \rho_{N+1}(r) - \rho_N(r) \text{ (for nucleophilic attack)} \quad (10)$$

$$f^-(r) = \rho_N(r) - \rho_{N-1}(r) \text{ (for electrophilic attack)} \quad (11)$$

Where, ρ_{N+1} , ρ_N and ρ_{N-1} are the electronic densities of anionic, neutral and cationic species respectively.

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 $s(r)$ [44].

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

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.*, [45] 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 proportional to the hardness of the molecule, as indicated in the following expression.

$$\Delta E_{\text{Back-donation}} = -\frac{\eta}{4} \quad (13)$$

The $\Delta E_{\text{Back-donation}}$ implies that when $\eta > 0$ and $\Delta E_{\text{Back-donation}} < 0$ 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 [46]. 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 BBH and PABH are represented in fig. 3.

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

Parameters	BBH	PABH
E_{HOMO} (eV)	-5.98119	-5.66391
E_{LUMO} (eV)	-1.53993	-1.80715
Energy gap(ΔE)	4.44126	3.85676
Dipole moment (Debye)	4.3719	4.6456

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 [47]. 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} -5.66391 (eV) of PABH indicates the better inhibition efficiency than the other compound.

The energy of the lowest unoccupied molecular orbital, E_{LUMO} , indicates the ability of the molecule to accept electrons [36]. So, lower the value of E_{LUMO} , more probable the molecule to accept electrons. In our study the PABH having low value of E_{LUMO} could have better performance as corrosion inhibitor.

The energy gap, ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) 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 [48]. Hard molecules have high HOMO-LUMO gap [49] and thus soft bases inhibitors are the most effective for metals [50]. 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 [15]. 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 PABH 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 [51]. 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 4.6456 (Debye) of PABH 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 [52]. The low ionization energy 5.66391 (eV) of PABH 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 PABH with low hardness value 1.92838(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 [54]. 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 [55]. PABH with the softness value of 0.51857 has the highest inhibition efficiency.

The table 2 shows the order of electronegativity as $\text{BBH} > \text{PABH}$. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order $\text{PABH} > \text{BBH}$. According to Sanderson's electronegativity equalization principle [56], BBH 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.

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

Parameters	BBH	PABH
I(eV)	5.98119	5.66391
A(eV)	1.53993	1.80715
η (eV)	2.22063	1.92838
S (eV)	0.45032	0.51857
χ (eV)	3.76056	3.73553
ω	3.184189	3.61811
μ	-3.76056	-3.73553

The number of electrons transferred (ΔN) and *back-donation* (ΔE) was also calculated and tabulated in Table 3. Values of ΔN show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study [57]. If $\Delta N < 3.6$, 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: BBH < PABH. The results indicate that ΔN values correlates strongly with experimental inhibition efficiencies. Thus, the highest fraction of electrons transferred is associated with the best inhibitor (PABH), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (BBH).

Table 3. The number of electron transferred (ΔN) and ΔE back donation (eV) calculated for inhibitor BBH and PABH.

Parameters	BBH	PABH
Transferred electrons fraction (ΔN)	0.729397	0.84643
ΔE back-donation / (eV)	-0.55516	-0.48210

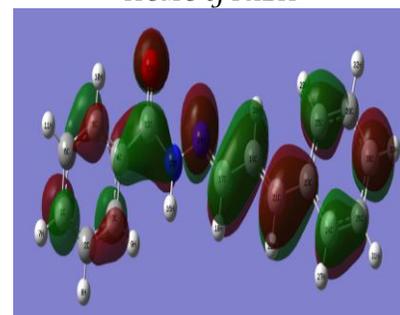
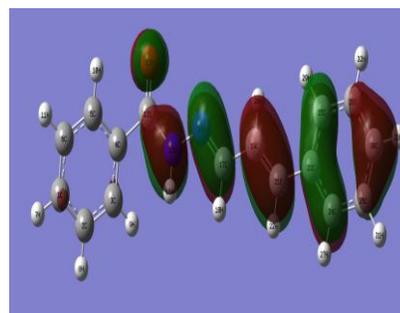
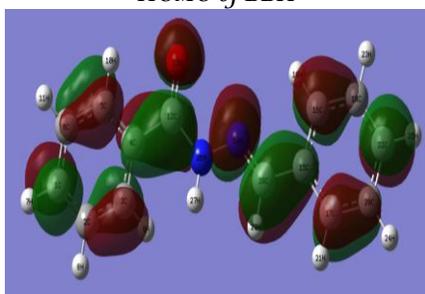
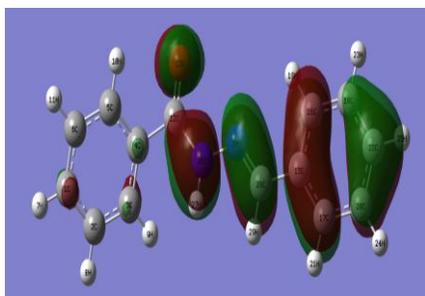


Fig. 3: Frontier molecular orbital diagrams of BBH and PABH by B3LYP/6-31G (d,p)

Table 4. Fukui and local softness indices for nucleophilic and electrophilic attacks on BBH atoms calculated from electron densities.

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	-0.240357	0.092708	-0.108237	0.041748
2 C	-0.046054	0.086501	-0.020739	0.038953
3 C	-0.207955	0.131371	-0.093646	0.059158
4 C	-0.009009	-0.018585	-0.004056	-0.008369
5 C	-0.179868	0.090904	-0.080998	0.040935
6 C	-0.050173	0.094728	-0.022593	0.042657
7 H	0.102180	-0.094245	0.046013	-0.042440
8 H	0.091019	-0.092293	0.040987	-0.041561
9 H	0.090152	-0.086102	0.040597	-0.038773
10 H	0.125365	-0.120922	0.056454	-0.054454
11 H	0.094898	-0.096242	0.042734	-0.043340
12 C	0.456771	-0.606247	0.205693	-0.273005
13 O	-0.616222	0.534748	-0.277497	0.240807
14 N	-0.364738	0.364212	-0.164248	0.164011
15 C	0.079197	-0.011357	0.035663	-0.005114
16 C	-0.213024	0.232966	-0.095928	0.104909
17 C	-0.205098	0.225534	-0.092359	0.101562
18 C	-0.035826	0.013121	-0.016133	0.005908
19 H	0.130380	-0.130635	0.058712	-0.058828
20 C	-0.049439	0.040030	-0.022263	0.018026
21 H	0.084448	-0.085029	0.038028	-0.038290
22 C	-0.241337	0.326692	-0.108678	0.147115
23 H	0.091053	-0.090639	0.041002	-0.040817
24 H	0.087271	-0.087252	0.039299	-0.039291
25 H	0.097320	-0.099263	0.043825	-0.044700
26 N	-0.350342	0.713615	-0.157766	0.321355
27 H	0.251486	-0.263877	0.113249	-0.118829
28 C	-0.045602	0.005618	-0.020535	0.002529
29 H	0.073510	-0.070055	0.033098	-0.031547

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 [58]. 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 [45]. Parr and Yang proposed that larger value of Fukui function indicate more reactivity [20]. 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.

Table 5. Fukui and local softness indices for nucleophilic and electrophilic attacks in PABH atoms calculated from electron densities.

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	-0.16334	0.085278	-0.084703	0.044223
2 C	-0.066638	0.088397	-0.034556	0.045840
3 C	-0.16925	0.128452	-0.087767	0.066611
4 C	0.018992	-0.026192	0.009848	-0.013582
5 C	-0.14436	0.092519	-0.074860	0.047977
6 C	-0.066337	0.092806	-0.034400	0.048126
7 H	0.09786	-0.093709	0.050747	-0.048595
8 H	0.091417	-0.092109	0.047406	-0.047765
9 H	0.087814	-0.085757	0.045537	-0.044471
10 H	0.123471	-0.120933	0.064028	-0.062712
11 H	0.095154	-0.09601	0.049344	-0.049788
12 C	0.494258	-0.597266	0.256307	-0.309724
13 O	-0.572959	0.529522	-0.297119	0.274594
14 N	-0.412623	0.388582	-0.213973	0.201507
15 N	-0.363199	0.640681	-0.188344	0.332238
16 H	0.251479	-0.260828	0.130409	-0.135258
17 C	0.058894	-0.109082	0.030540	-0.056567
18 H	0.069508	-0.066622	0.036044	-0.034548
19 C	-0.142067	0.188697	-0.073671	0.097852
20 H	0.113276	-0.114147	0.058741	-0.059193
21 C	-0.325036	0.304322	-0.168553	0.157812
22 H	0.089171	-0.08639	0.046241	-0.044799
23 C	0.141641	-0.118018	0.073450	-0.061201
24 C	-0.22193	0.236662	-0.115086	0.122725
25 C	-0.232379	0.222948	-0.120504	0.115614
26 C	-0.037907	0.026978	-0.019657	0.013990
27 H	0.087499	-0.087631	0.045374	-0.045443
28 C	-0.029159	0.027041	-0.015120	0.014022
29 H	0.096221	-0.095326	0.049897	-0.049433
30 C	-0.243279	0.270681	-0.126157	0.140367
31 H	0.087293	-0.087085	0.045267	-0.045160
32 H	0.089162	-0.089356	0.046236	-0.046337
33 H	0.097353	-0.097106	0.050484	-0.050356

According to fukui indices, C12 is the most reactive site for nucleophilic attack in both the compounds BBH and PABH. In case of HOMO of BBH the dense electron cloud around N26

indicates the electrophilic attack. The same is around N15 in PABH as confirmed by the Fukui function f_k^- too.

4. CONCLUSION

Through DFT quantum chemical calculations, a correlation between parameters related to the electronic structures of benzohydrazide derivatives N'-benzylidene benzohydrazide (BBH) and N'-(3-phenylallylidene) benzohydrazide (PABH) and their inhibition efficiencies have been established. The inhibition efficiency increase with the increase in E_{HOMO} , and decrease in E_{LUMO} and energy gap (ΔE). PABH 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(A) ionization potential(I), electronegativity(χ) and the fraction of electron transferred (ΔN) confirms the inhibition efficiency in the order of PABH > BBH. Fukui function shows the nucleophilic and electrophilic attacking sites in the PABH and BBH.

5. REFERENCES

- Eddy NO, Ebenso EE. *Pigment and Resin Tech*, 2010; **39(2)**:77-83.
- Arab ST, Turkustani AMAl. *Portugaliae Electrochimica Acta*, 2006; **24**:53-69.
- Popova A, Christov M, Rachieva S, Sokolova E. *Corros. Sci*, 2004; **46**:1333-1350.
- Fouda AS and Elithy AS, *Corros Sci*, 2009; **51(4)**:868-875.
- Obot IB, Obi-Egbedi NO. *Surface Review and Letters*, 2008; **15(6)**: 903-910.
- Ju H, Kai ZP, Li Y. *Corros Sci*, 2008; **50**:865.
- Abd El-Rehim SS, Ibrahim MAM, Khaled FFJ. *Appl Electrochem*, 1999; **29**:593-599.
- Ebenso EE. *Bull Electrochem*, 2003; **19**:209-216.
- Granese SL. *Corros Sci*, 1988; **44**: 322-327.
- Udhayakala P, Rajendiran TV, Gunasekaran S, *J Comput Methods Mol Des*, 2012; **2(1)**:1-15.
- Stoyanova AE, Peyerimhoff SD, *Electro Chim Acta*, 2002; **47**: 1365-1371.
- Valdez LMR, Villafane AM, Maitnik DG. *J Mol Struct (THEOCHEM)*, 2005; **716**:61-65.
- Vosta J, Eliasek J. *Corros Sci*, 1971; **11**:223-229.
- Bentiss F, Lebrini M, Lagrenee M. *Corros Sci*, 2005; **47**:2915-2931.
- Choa P, Liang Q, Li Y. *Appl Surf Sci*, 2005; **252**:1596-1601.
- Hohenberg P, Kohn W. *Phys Rev*, 1964; **136**:B864-B871.
- Parr RG and Yang W, *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
- Cohen MH, *In Topics in Current Chemistry*; R.F.Nalewajski, Ed.; Springer-Verlag: Heidelberg, Germany, 1996; **183**:143.
- Sanderson RT. *J Am Chem Soc*, 1952; **74**:272-274.
- Parr RG, Yang W. *J Am Chem Soc*, 1984; **106**: 4049-4050.
- Fang J, Li J. *J Mol Struct (THEOCHEM)*, 2002; **593**:179-186.

22. Arslan T, Kandemirli F, Ebenso EE, Love I, Alemu H. *Corros Sci.*, 2009; **51**:35-47.
23. Arjunan V, Rani T, Mythili CV, Mohan S. *Spectrochim Acta Part A*, 2011; **79(3)**:486-496.
24. Paola R. Campodonico, Margarita E. Aliaga, Jose G. Santos, Enrique A. Castro, Renato Contreras. *Chem Phys Letters*, 2010; **488(1-3)**:86-89.
25. El Sayed H. El Ashry, Ahmed El Nemr, Samy A. Essawy and Safaa Ragab, *ARKIVOC*, 2006; **(XI)**:205-220.
26. Mohan P, Usha R, Paruthimal Kalaigan G, Muralidharan VS, *Journal of Chemistry*, 2012; 7.
27. Frisch MJ, Trucks GW, Schlegel HB et al. Gaussian 03, Gaussian, Inc.: Pittsburgh PA, 2003.
28. Becke AD. *J Chem Phys*, 1993; **98**:1372-1377.
29. Lee C, Yang W, Parr RG, *Phys. Rev.*, 1988; **B 37**:785-789.
30. Young D C 2001 *A practical guide for applying techniques to realworld problems in computational chemistry* (New York: JohnWiley & Sons Inc.) p. 630.
31. Lashkari M, Arshadi MR, *Chem. Phys.*, 2004; **299**:131-137.
32. Parr RG, Donnelly RA, Levy M, Palke WE. *J Chem Phys*, 1978; **68**:3801-3807.
33. Parr RG, Pearson RG. *J Am Chem Soc*, 1983; **105**:7512-7516.
34. Koopmans T. *Physica*, 1933; **1**:104-113.
35. Pearson RG. *JAmChemSoc*, 1963; **85(22)**:3533-3539.
36. Lesar A, Milosev I. *Chem Phys Lett*, 2009; **483(4-6)**:198-203.
37. Martinez S. *Mater Chem Phys*, 2002; **77**:97-102.
38. Pearson RG. *Inorg Chem*, 1988; **27**:734-740.
39. Sastri VS, Perumareddi JR. *Corros Sci*, 1997; **53**:617-622.
40. Dewar MJS, Thiel W. *J Am Che Soc*, 1977; **99**:4899-4907.
41. Chermette H. *J Comput Chem*, 1999; **20**:129-154.
42. Parr RG, Szentpaly L, Liu S. *J Am Chem Soc*, 1999; **121**:1922-1924.
43. Quijano MA, Pardav MP, Cuan A, Romo MR, Silva GN, Bustamante RA et al. *Int J Electrochem Sci*, 2011; **6**:3729-3742.
44. Wang H, Wang X, Wang H, Wang L, Liu A. *J Mol Model*, 2007; **13**:147-153.
45. Gomez B, Likhanova NV, Dominguez-Aguilar MA, Martinez-Palou R, Vela A Gasquez J. *J Phy Chem B*, 2006; **110**:8928-8934.
46. Musa AY, Kadhum AH, Mohamad AB, Rohoma AB Mesmari H. *J Mol Struct*, 2010; **969**:233-237.
47. Gece G Bilgic S. *Corros.Sci*, 2009; **51**:1876-1878.
48. Obot IB, Obi-Egbedi NO, Umoren SA. *Int J Electro Chem. Sci*, 2009; **4**:863-877.
49. Awad MK, Mustafa MS Abo Elnga MM. *J Mol Struct*, 2010; **959(1-3)**:66-74.
50. Li X, Deng S, Fu H, Li T. *Electrochim Acta*, 2009; **54**:4089-4098.
51. Quraishi MA, Sardar R. *J Appl Electrochem*, 2003; **33(12)**:1163-1168.
52. Sip K Rajak, Nazmul Islam, Dulal C Ghosh. *J Quantum information Science*, 2011; **1**:87-95.
53. Obi-Egbedi NO, Obot IB, El-Khaiary MI, Umoren SA Ebenso EE, *Int J Electro Chem Sci*, 2011; **6**:5649-5675.
54. Ebenso EE, Isabirye DA, Eddy NO. *Int J Mol Sci*, 2010; **11**:2473-2498.
55. Hasanov R, Sadikglu M, Bilgic S. *Appl Surf Sci*, 2007; **253**:3913-3921.
56. Geerlings P De Proft F. *Int J Mol Sci*, 2002; **3**:276-309.
57. Lukovits I, Kalman E, Zucchi F. *Corrosion*, 2001; **57**:3-8.
58. Breket G, Hur E, Ogretir C. *J Mol Struct (THEOCHEM)*, 2002; **578**:79-88.