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Theoretical and experimental prediction of corrosion inhibition efficiency of isatin and its derivatives by DFT calculations and weight loss method – A comparative study

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Abstract: The corrosion inhibition performance of isatin and its N1/C5 substituted derivatives were analyzed by DFT calculation (B3LYP, 6311g, dp) in gas phase and solvation method with the help of Gaussian 09W and Gaussian 16. The calculated quantum chemical parameters such as E_{LUMO}, E_{HOMO}, Ionization potential (I), Electron affinity (A), Electronegativity (χ), band gap energy (ΔE), Softness (σ), Hardness (η), Electrophilicity (ω) proved that isatin and its derivatives have the tendency to donate the electrons to the surface of metal ion on adsorption. The number of electron transfer (ΔN) from isatin and its derivatives to iron metal was calculated theoretically and said to possess the order IX>III>VII>IV>II>V>I>VIII>VI. The experimental studies reveal that the same order of inhibition as like theoretical studies. Mulliken's charge distribution analysis of the same compounds indicates the high negative magnitude on N1 atom. The negative magnitude of N1 atom was altered by substitution in N1 and C-5 position of isatin which was identified theoretically. Fukui local parameters were also calculated and used in the prediction of the compounds local selectivity.

Keywords: adsorption; HOMO; LUMO; Fukui local selectivity; Mulliken's charge distribution.

INTRODUCTION

Density functional theory (DFT) is an important tool in modern quantum chemistry in analyzing the electronic parameters of the compounds. It is also

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having versatile applications like drug design, solar cells, water splitting, materials discovery and design, corrosion inhibition, etc., with reduced computational cost.[1-6] Amongst corrosion inhibition behavior, prediction of metal surface interaction with inhibitor molecules is one of the crucial field of research over two decades.[7-9] Corrosion means destruction of metals, plastics, concrete and wood by various environmental substances surrounding it.[7-10] There are various metals used in the industry for storage of acids, bases and petrochemical products, wine, etc., Among them iron is the most used metal in various industries.[7-9]Added to that, acids have been utilized for pickling, descaling, acid cleaning, acidifying of oil wells and etc., This may also attack the surface of the metal resulting in the formation of metal oxide layers on the surface of the iron by dissolution of the metal.[7,8,11-15] For this, various types of inhibitors like organic/green/bio inhibitors have been reported in the last two decades.[16-19] Among these three inhibitors, organic inhibitors are suitable in preventing the corrosion of mild steel due to the known structure of the inhibitor. This helps to analyze the surface adsorption mechanism exactly. The above points make organic inhibitor better than bio/green inhibitor. In green inhibitors various chemical compounds are present and in addition prediction of mechanism and preserving of bio inhibitor is too difficult in varying temperature, pH and acidity.

Isatin is an organic compound and its derivatives were reported and well documented as non-toxic corrosion inhibitor for iron in various acid solution in the last decade.[20-30] The available report of isatin as inhibitor determined by weight loss method is supported by electrochemical studies.[30] There is a lack of availability of computational data in the prediction of the mechanism of the surface adsorption of the metal by inhibition. Recent days, exact evaluation of nucleophilicity/electrophilicity by electron donor/acceptor has been documented with a help of fukui indices.[31-36] This is an important parameter, to analyze the part of the compound attached for interaction with the surface of metal. In previous reports of isatin derivatives as corrosion inhibitor, fukui indices calculation are lacking[20-30] because the maximum reports were concentrated only on the Schiff bases of the isatin with free N-H groups. This free N-H is useful in formation of azanion in acidic solution which might be useful for surface interaction on the metal.[20-22,25-27,30] In this work the main focus is on comparison of isatin and its derivatives with electron donating/withdrawing moiety in the nitrogen N1- and C5-carbon to predict the better acceptor and donor parts of the derivatives by computational methods.

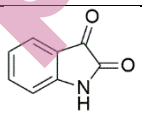
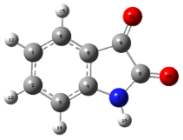
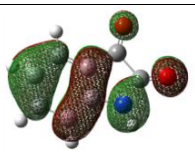
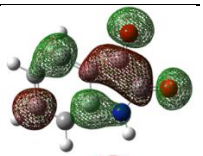
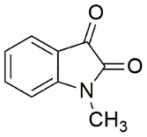
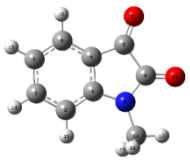
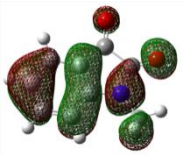
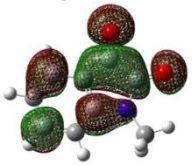
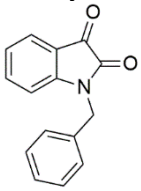
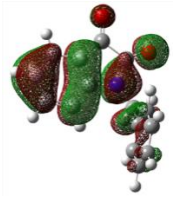
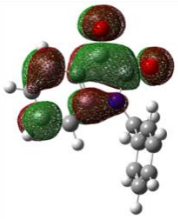
EXPERIMENTAL

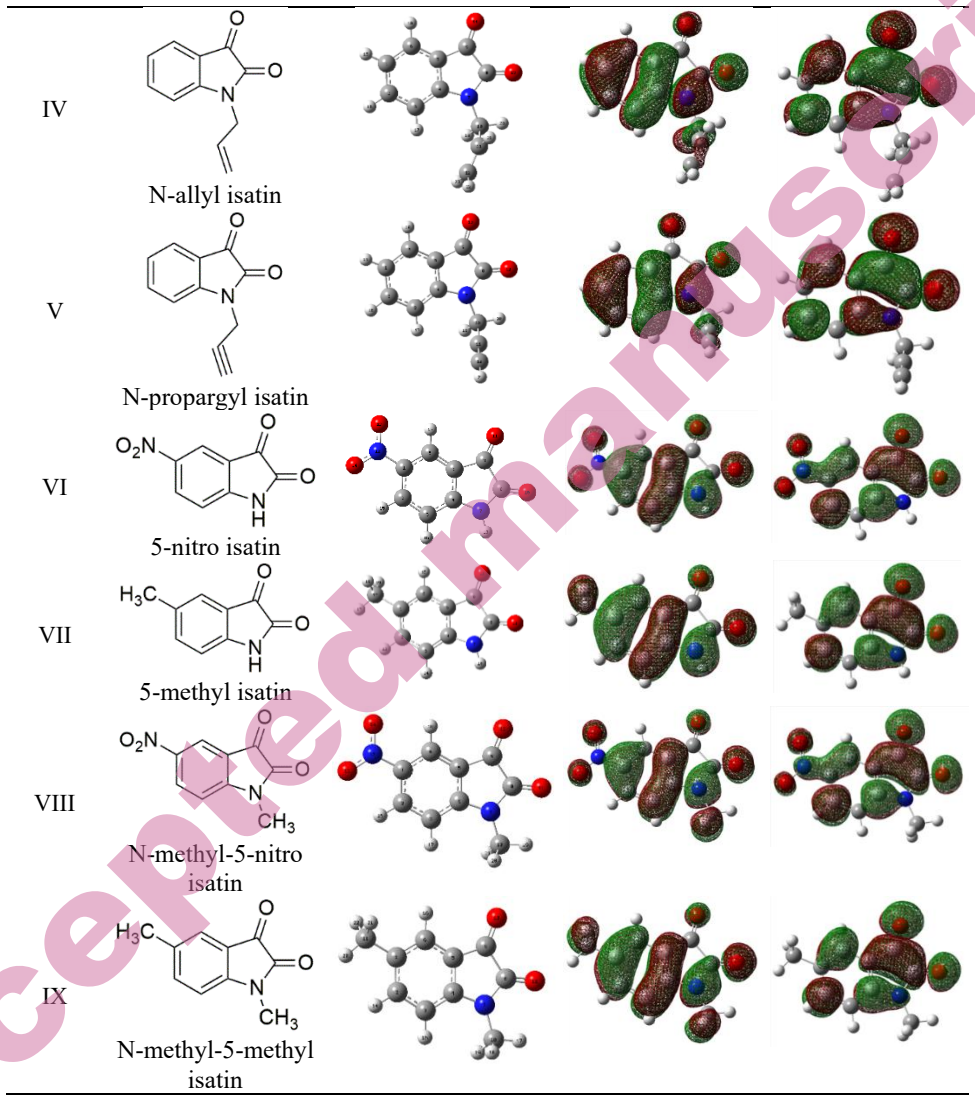
DFT calculations

Isatin and its derivatives as the chosen inhibitors are subjected to DFT calculations and all the calculations were performed by Gaussian 09W and Gaussian 16 with B3LYP and 6311G basic set for optimization.[37,38] All optimized geometries were confirmed as true minima by

vibrational frequency analysis using the same basic set. The calculation of energy was done with B3LYP and 6-311G basic set. Grimme's D3(BJ) provides a gas-phase London dispersion correction to total energies and geometries were analysed using PBE0-GD3BJ/6-31G (d,p). Solvent polarization was modeled separately using the IEFPCM-water implicit solvent model using B3LYP and 6-311G (d,p). The non-covalent interactions in the gas phase of the proposed inhibitor were calculated by using with Grimme's D3 method and the results were provided in the supporting information (Table s9). Corrosion on the metal surface mainly occurred in the presence of aqueous region, for this cause the energy analysis were performed using IEFPCM-water implicit solvent model for the proposed inhibitors and the results were provided in the supporting information (Table s10). The calculation parameters of compounds were provided in table s1. The comparison of the calculations with and without dispersion correction reveals the change in the bandgap energies. The DFT calculation with dispersion correction exhibits higher local parameters such as ionization potential (I), Electron affinity (A), electronegativity (χ), band gap energy (ΔE), softness (σ), hardness (η), electrophilicity (ω) than the calculation without dispersion correction. This is because of presence of non-covalent interactions like Vander walls force of attraction and London forces between the molecules. There is energy differences occurred in the DFT calculations with or without dispersion correction but the orders of local parameters is not changed. The comparison of the local parameters between the gas phase DFT studies and IEFPCM-water studies have very slight changes due to the protonation effects of the inhibitors. The obtained result from the energy calculation (gas phase DFT) has been utilized to predict the fukui global parameters and local parameters of the compound by using UCA FUKUI software.[38] The name of the compound, optimized structure, HOMO, LUMO diagrams have been given in Table I. The numbering of the atoms has been assigned by DFT in the compounds in Table I.

Table I. Compound number, name, structure, optimized structure, HOMO and LUMO structure of the compound.

Comp. No	Name and structure	Optimized structure	HOMO	LUMO
I	 Isatin			
II	 N-methyl isatin			
III	 N-benzyl isatin			



By having E_{HOMO} and E_{LUMO} energy values from DFT calculation following quantum chemical parameters such as ionization potential (I), Electron affinity (A), electronegativity (χ), band gap energy (ΔE), softness (σ), hardness (η), electrophilicity (ω) were calculated.[21,38]

Ionization potential (I.E) is related with highest occupied molecular orbital E_{HOMO} and the expression as follows.

$$I = -E_{HOMO} \quad (1)$$

Electron affinity (A) is related to the least unoccupied molecular orbital (E_{LUMO}) the expression is

$$A = -E_{LUMO} \quad (2)$$

The energy gap (ΔE) of isatin and its derivatives is energy difference between highest occupied molecular orbital E_{HOMO} and least unoccupied molecular orbital E_{LUMO}. The energy gap is calculated by the following equation

$$\Delta E = E_{HOMO} - E_{LUMO} \quad (3)$$

$$\Delta E = I - A \quad (4)$$

The hardness (η) of the compound is defined as the second derivative of electronic energy (E) with respect to number of electrons (N) at constant external potential. This originates from the Lewis theory and theory of hard and soft acid and base. The expression for hardness is follows

$$\eta = \frac{1}{2}(I - A) \quad (5)$$

$$\eta = \frac{1}{2}(E_{HOMO} - E_{LUMO}) \quad (6)$$

Softness (σ) is reciprocal of hardness and expressed as

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

Electronegativity is the descriptor of the direction of flow of electrons between metal and an inhibitor and it is related to I and A (E_{HOMO} and E_{LUMO})

$$\chi = \frac{1}{2}(I + A) \quad (8)$$

$$\chi = -\frac{1}{2}(E_{HOMO} - E_{LUMO}) \quad (9)$$

Nucleophilicity (ω) is the reciprocal of electrophilicity and expressed as

$$\omega = \frac{\mu^2}{2\eta} \quad (10)$$

The number of electrons transferred (ΔN) were calculated by the following expression using electrophilicity and hardness of Fe from the previous reported literature

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} - \eta_{inh})} \quad (11)$$

Weight loss method

Mass loss method was conducted at different temperatures in the range 308–333 K for 2 h in 1 M HCl. The specimens were immersed in 100 ml of the respective inhibitor and the test solution in a thermostatic bath. The specimens were weighed before and after immersion. The difference in weight was taken as the weight loss of mild steel. From the weight loss (ΔW), corrosion rate (ʎ) and the percentage of inhibition efficiency (IE %) were calculated using the following equation:

$$\lambda\ (mpy) = 534\ \mathrm{X}\frac{\Delta W}{DAT} \quad (12)$$

$$IE\ \% = \frac{W_0 - W_1}{W_0}\ \mathrm{X}\ 100 \quad (13)$$

Here ΔW = (W_b–Wa), where Wb and Wa are the specimen weights before and after immersion in the tested solution, W_0 and W_1 are the weight loss of mild steel in the absence and presence of inhibitor respectively, D is the density of the iron (g/cm3), A is the area of the specimen in $inch^2$ and T is the period of immersion in hours.

RESULTS AND DISCUSSION

From the literature reports, there seems to be a relationship between corrosion inhibition property and the electronic property of the compound.[39] The quantum chemical parameters like ionization potential (I), Electron affinity (A), electronegativity (χ), band gap energy (ΔE), softness (σ), hardness (η), electrophilicity (ω) is used to predict the electronic property and how it is working on the adsorption process.[39,40] The adsorption of the organic species on the surface of the metal has been deduced by the above-mentioned parameters which is calculated by using highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) calculated by DFT studies. The calculated values for various isatin derivatives is showed in Table II In general, the interaction between the metal and the inhibitor takes place due to the transfer of electron from the inhibitor HOMO to metal d-orbital or the electron transfer from metal d-orbital to LUMO of the inhibitor. From this statement, the inhibitor molecule has highest HOMO value, it has tendency to donate electron to the metal orbital. In the same way, the inhibitor also has lowest LUMO value, it has to tendency to accept the d-orbital electron of the metal. The both HOMO and LUMO were localized throughout the whole molecule in the isatin and its derivaties (compound I - IX) which is witnessed in the table 1. Compare the HOMO and LUMO of isatin (compound I) with N-substituted isatin (Compound II-V), there is change in N-1 atom in compound II-V from highest occupied to lowest unoccupied due to the substitution of electron donating and electron withdrawing group on the N-1 atom which altered the energies of the excited states. In addition the substitution in N-1 position of isatin (compound II to V) alters the C5 carbon from highest occupied to lowest unoccupied which also witnessed in the HOMO and LUMO images in the table I. On the other hand, the substitution on C5 position of isatin with electron donating $-CH_3$ (compound VII) and electron withdrawing $-NO_2$ (compound VI) did not alter the HOMO and LUMO present in the N1 position of the isatin moiety. Which resulted that the alteration of HOMO and LUMO by the substitution in N1 and C5 resulted the active donating and accepting of electron towards the metal. In this case, both HOMO and LUMO values of the 5-nitro isatin and 1-methyl-5-nitro isatin is comparatively higher than the other derivatives such as isatin, N1-substituted and C5-substituted isatin. This confirms that the electron donating/withdrawing group (nitro/methyl) substitution polarizes the isatin molecule by electron rich position and electron deficient position on it. This might be useful as of to act as good inhibitor for corrosion.

The energy gap (ΔE) is an important parameter of the molecule in analyzing the reactivity of the inhibitor towards the metal.[38-40] Moreover, band gap energy decreases and the reactivity of the molecule increases towards the adsorption of metal surface which leads to the increasing inhibition efficiency of the molecule with the change in redox property of the ligand. The results exhibited band gap

energy adjustment of isatin by substituting electron withdrawing/donating group on its C-5, N-1 position in it. The bandgap energy of isatin was decreased on introducing electron donating groups like methyl, benzyl, propargyl and allyl. The band gap energy of isatin (ΔE = 3.7793 eV) was reduced by introducing a methyl group in its N-1 position (ΔE = 3.7258 eV) and C-5 position (ΔE = 3.6188 eV) alone. The bandgap energy is reduced further to 3.4942 eV by substituting both N-1 and C-5 position of isatin simultaneously. This indicates the methyl substituted isatin possessing highest activity towards adsorption by donating electrons to the metal surface. On the other hand, the bandgap energy of isatin increased while introducing electron withdrawing group (NO_2) in C-5 position of isatin. From all the isatin derivatives 5-nitro isatin possess the highest bandgap energy (ΔE = 3.8798 eV) which is also reduced by substituting methyl group in N-1 position of isatin (ΔE = 3.6939 eV). This indicates that the nitro substituted isatin has higher activity towards adsorption by accepting electrons from the metal. All the nine derivatives have the bandgap energy in the same range. Among them methyl substituted and nitro substituted were highly warranted for electron accepting and donating to metals respectively in order to prevent corrosion. In addition, the HOMO and LUMO of all the compounds localized over the benzene ring helps in attachment to metal atom by inhibitors π-electron which doesn't alter the skeleton of the inhibitors while adsorbing on the metal. This exhibits the good redox property of the inhibitors by sharing its π-electron with metal.

Table II. Calculated global parameters by HOMO and LUMO energies

Comp. No	ΔE (eV)	I (eV)	A (eV)	χ (eV)	η (eV)	σ (eV)	ΔN (eV)	ω (eV)	ε (eV)
I	3.7793	6.9271	3.1478	5.0324	1.8846	0.5306	0.5219	6.7189	0.1488
II	3.7258	6.7438	3.0180	4.8809	1.8629	0.5367	0.5687	6.3941	**0.1563**
III	3.6131	6.6812	3.0680	4.8746	1.8065	0.5535	0.5882	6.5766	**0.1520**
IV	3.6259	6.7054	3.0795	4.8924	1.8129	0.5515	0.5812	6.6014	**0.1514**
V	3.6749	6.8172	3.1423	4.9798	1.8374	0.5442	0.5497	6.7481	0.1481
VI	3.8798	**7.7435**	**3.8637**	**5.8036**	1.9399	0.5154	0.3083	**8.6814**	0.1151
VII	3.6188	6.6888	3.0699	4.8794	1.8094	0.5526	0.5859	6.5790	**0.1519**
VIII	3.6939	**7.4850**	**3.7886**	**5.6368**	1.8481	0.5410	0.3687	**8.6252**	0.1159
IX	**3.4942**	6.4959	3.0016	4.7487	**1.7471**	**0.5723**	**0.6442**	6.4538	**0.1549**

Ionization potential (I) and electron affinity (A) is the measuring tool for the electron donating and accepting nature of the ligand respectively. The case study of ionization potential and electron affinity resulted that the 5-methyl substituted isatin has the highest tendency to accept/donate electrons from/to the metal orbitals than other reported isatin derivatives. This caused the strongest interaction between the metal and molecule. This doesn't mean only 5-nitro substituted isatin is the only compound with corrosion inhibition efficiency than other reported isatin

derivatives. All the reported isatin derivatives have the corrosion inhibition efficiency but 5-methyl substituted isatin has higher efficiency than other derivatives which was accounted by ionization potential and electron affinity, especially electron donating group substituted isatin derivative has the higher tendency to adsorb on the surface of the metal by donating/accepting electrons from the ligand. The parameters ionization potential, electron affinity resulted that the electron donating/accepting nature of the isatin derivatives are in the order VI>VIII>I>V>II>IV>VII>III>IX.

Electronegativity (χ) is the descriptor for the flow of electron in direction between ligand and metal which is giving the E_{HOMO} and E_{LUMO} values. isatin (I) has electronegativity of 5.0324 eV, it was increased to 5.8036 eV by introducing electron withdrawing nitro group (VI). The electronegativity is reduced by adding electron donating methyl group to compound VI and the value is found to be 5.6368 eV. Other compounds having the degeneracy values around 4.6 - 4.9 eV. According to Sanderson's electronegativity equivalization principle, high electronegativity quickly reaches to equalization. It results in low reactivity and low inhibition. From this statement N-methyl -5-methyl isatin (IX) may have highest inhibition efficiency than other compounds by having lowest electronegativity (χ).

The measurement of stability and reactivity of the molecule is the important properties for analyzing the polarization of electron clouds of the atoms. Hardness (η) and softness (σ) of isatin derivatives which were calculated by DFT calculation is related to their molecular reactivity and stability. Generally hard molecule has lowest tendency to polarize the electron cloud of atoms or ions or molecules which has highest band gap energy and hardness value. In addition, soft molecule has highest tendency to polarize or deformation of electron clouds of atoms or ions or electrons which has lowest band gap energy and hardness value. From this statement N-methyl-5-methyl isatin softness (IX) possess lower hardness value and lowest bandgap energy then other isatin derivatives which has been reported in this work. Softness is the inversive relationship with the hardness which is also resulted the same.

The electrophilicity (ω) and nucleophilicity (ε) index is another parameter to predict whether the molecule is electrophile or nucleophile and it reflects the stabilization energy of a system by receiving or donating electron from environment. Electrophilicity and nucleophilicity both have inversion relation with each other. Electron donating substituted isatin derivatives are acting as nucleophiles but electron accepting substituted isatin derivatives act as electrophiles. The highest electrophilicity (ω) and lowest nucleophilicity value of compound VI and VIII represents its electron accepting nature of a compound from metal surface. Moreover, high nucleophilicity (ε) and low electrophilicity compounds II, III, IV, VII, IX have tendency to donate electrons to metals surface.

All the compound has tendency to donate/accept electron from/to metal surface due to the polarization of a compound. In addition, DFT calculations were performed in gas phase, it may be protonated in various solution phase which is altered the nucleophilic/electrophilic approaches of a compound. From this study, substituted isatin derivatives have high tendency to donate or accept electrons from metal surface than isatin.

The number of electrons transferred (ΔN) were also calculated for iron metal and it is tabulated in Table II. The values of ΔN shows that the inhibition efficiency resulted all the compounds having tendency to donate electrons to metal surface by having the value of $\Delta N < 3.6$, This resulted that the inhibition efficiency of the compounds has order of IX>III>VII>IV>II>V>I>VIII>VI.

The solvation (IEFPCM-Water) effect in water of the proposed inhibitors also remains and follows same order of the local parameters as like exhibited in gas phase DFT studies (table s10). The difference in energy gap (ΔE) in this study is due to protonation effects of the inhibitors. The comparison of compound I (isatin) with its derivatives (compound II-IX), compound II (N-methyl isatin) exhibits the higher difference in the energy gap (ΔE) is about 0.1388 eV which is higher than 0.0679 eV of compound I. This reveals that electron donating $–CH_3$ substituted on nitrogen atom in isatin increases the availability of the lone pair on the nitrogen. The other compounds III to IX does not exhibit characteristic changes in the energy gap (ΔE) of the studies.

Charge distribution on the atoms of a molecule is theoretically identified by mulliken charge distribution. From this study, all the above discussed isatin and its derivatives have the tendency to donate electrons to the empty metal orbitals by having the negative magnitude on the heteroatoms present in the isatin derivatives as shown in Fig. 1. Especially negative magnitude of N-1 nitrogen is highly altered by the substituents in both N-1 and C-5 position, to be precise substituents in C-5 position highly increased the negative magnitude of N-1 nitrogen in isatin from -0.488 to -0.824 whether the substituent is EWG or EDG. It is also altered the negative magnitude of oxygen present in the neighboring and adjacent carbon slightly. This suggest that, negative charge nitrogen and oxygen present in the isatin derivatives were the most predictive adsorption sites.

Fukui functions are the best tool to identify the local selectivity of molecules active binding site by analyzing whether it undergoes electrophilic or nucleophilic substitution. For this cause, aforementioned molecules were analyzed for Fukui indices to predict the local selectivity of the molecule. The global parameters of examined isatin and its derivatives has been given in Table III. From the table, the global parameters possess the high electron density, high softness and low hardness to compound VI and VIII than other derivatives. This confirms compound VI and VIII has highest electron donating property to metal d orbitals than other isatin derivatives due to the high electron density, high softness and low

hardness which allows the molecule to polarize the electron cloud in high order. Fukui indices for isatin and its derivatives have been analyzed and the data were tabulated and given in the supporting information. From the above results compound VI and VIII has the higher tendency to make the coordination with metal surfaces than other compounds. Hence, Fukui indices for compounds VI and VIII are shown in Table IV and V (Fukui indices of other compounds is given in supporting information Table s2 to s8). In addition fukui indices are commonly negative values but in our case there is a non negative atomic fukui indices were obtained due to the large number of electron involvement (ΔN~1). [40]

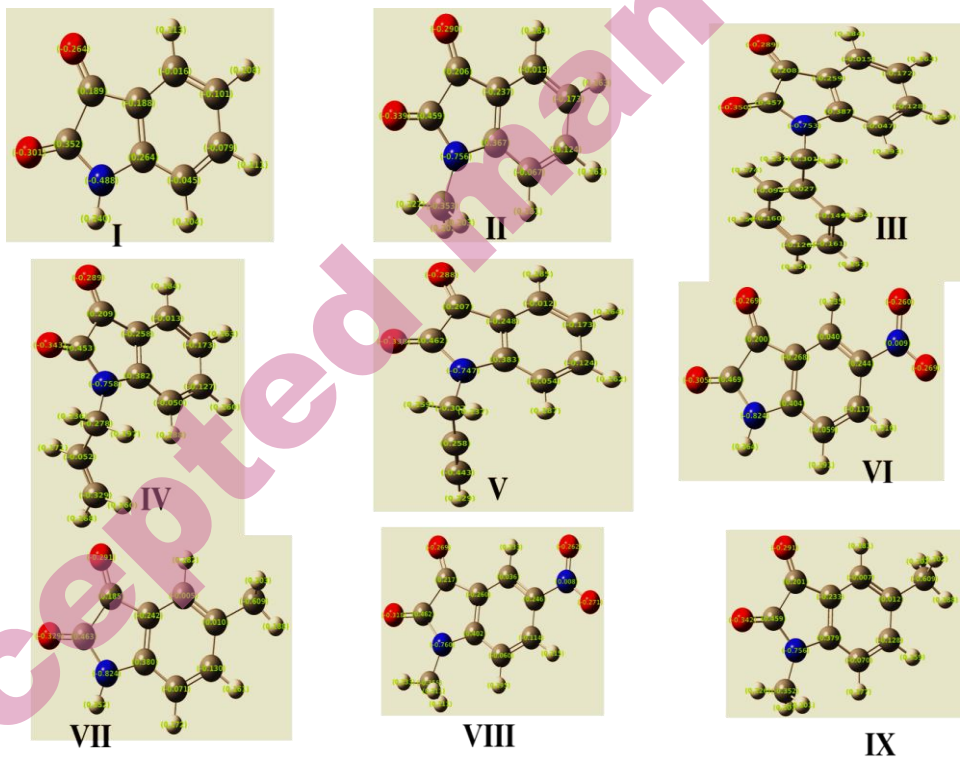


Fig. 1. Mulliken charge population analysis of isatin derivatives.

To identify the interaction between iron and inhibitors (compound I - IX) with different concentration (0,10,15,20 ppm) and different temperature (308,313,323 k) were analyzed in 1M HCl by weight loss method and the results were shown in figure s1. From these figures, the optimum concentration of the inhibitors for 1M HCl is15 ppm and the inhibition efficiency increases with increasing temperature. The thermodynamic parameters such as the apparent activation energy Ea, the enthalpy of activation ΔH* and the entropy of activation ΔS* for corrosion of mild

steel in 1 M HCl solutions in the absence and presence of compounds I to IX at 308–323 K were calculated by Arrhenius and transition plots which were shown in figure s2 and s3 respectively and calculated values were displayed in table s11.[8] The positive ΔH values and negative ΔS values indicates that dissolution of steel process is endothermic and decreasing the disordering of the film formation on the mild steel in 1M HCl by compound I to IX. The θ values of different concentrations of inhibitor were tested by fitting to various isotherms including Langmuir, Freundlich and Temkin isotherm. The obtained results were fitted to all the three adsorption isotherms and shown in figure s4, s5 and s6 respectively.[8] Adsorption parameters k_{ads} and free energy (ΔG) were calculated using Langmuir, Freundlich and Temkin isotherm and shown in table s12, s13 and s14 respectively. From the calculated free energy (ΔG) values from Langmuir, Freundlich, and Temkin isotherms were around -10 KJ mol^{-1} which is consistent with electrostatic interaction between charged molecules and a charged metal. This indicates the adsorption between the metal and all nine isatin and its detivative is physisorption. The presence of electrostatic interaction between the isatin and its derivatives with mild steel in 1M HCl is supported by the adsorption studies as prescribed in the computational studies.

Table III. Global Parameters calculated by Fukui function

Comp. No	Electronic potential (eV)	Hardness (eV)	Softness (eV)	Electrophilicity (eV)
I	3.7878	7.0613	104.8615	1.0158
II	3.7279	7.0613	104.8642	0.9836
III	3.6218	6.7865	109.1255	0.9665
IV	3.7578	7.0695	104.7227	0.9983
V	3.8531	7.0967	104.3227	1.0451
VI	**6.2150**	**3.4503**	**214.6347**	**5.5959**
VII	3.7143	7.0504	105.0193	0.9789
VIII	**6.1524**	**3.4531**	**214.3816**	**5.4801**
IX	3.6572	7.0477	105.0602	0.9491

Table IV. Fukui local parameters of compound VI (5-nitro isatin).

N	Z	f-	f+	f0	Dual-desc.	Hardness(au)	W-(eV)	W+(eV)
1	C	0.0009	0.0338	0.0173	0.0329	-0.0053	0.0049	**0.1892**
2	C	0.0042	0.0052	0.0047	0.001	0.0004	0.0234	0.0292
3	C	0.0042	0.0037	0.004	-0.0005	0.0006	0.0235	0.021
4	C	0.0044	0.0022	0.0033	-0.0023	0.0009	0.0248	0.012
5	C	0.0248	0.0013	0.0131	-0.0235	0.007	**0.139**	0.0072
6	C	0.0024	0.0019	0.0022	-0.0005	0.0004	0.0134	0.0108
7	N	0.0572	0.0022	0.0297	-0.0549	0.0163	**0.3199**	0.0126
8	C	0.0612	0.0002	0.0307	-0.0611	0.0178	**0.3427**	0.0009
9	C	**0.1234**	0	0.0617	**-0.1234**	0.036	**0.6907**	0.0002
10	O	**0.7117**	0.0005	**0.3561**	**-0.7111**	**0.2075**	**3.9824**	0.003
11	O	0.0015	0.0001	0.0008	-0.0014	0.0004	0.0083	0.0006
12	N	0.0002	**0.4553**	**0.2277**	**0.4551**	-0.0751	0.0009	**2.5479**
13	O	0	**0.2611**	**0.1305**	**0.261**	-0.0431	0.0002	**1.4608**
14	O	0.0001	**0.2324**	**0.1162**	**0.2323**	-0.0383	0.0003	**1.3005**
15	H	0	0	0	0	0	0.0002	0
16	H	0.0005	0	0.0002	-0.0005	0.0001	0.0027	0
17	H	0.0001	0	0	-0.0001	0	0.0004	0
18	H	0.0033	0	0.0016	-0.0033	0.001	0.0184	0

Table V. Fukui local parameters of compound VIII (1-methyl-5-nitro isatin).

N	Z	f-	f+	f0	Dual-desc.	Hardness(au)	W-(eV)	W+(eV)
1	C	0.0005	0.0346	0.0176	0.0341	-0.0055	0.0029	**0.1896**
2	C	0.0028	0.0054	0.0041	0.0026	-0.0001	0.0153	0.0296
3	C	0.0026	0.004	0.0033	0.0015	0.0001	0.014	0.022
4	C	0.0028	0.002	0.0024	-0.0008	0.0005	0.0154	0.0111
5	C	0.0233	0.0014	0.0124	-0.0219	0.0065	**0.1278**	0.0076
6	C	0.0017	0.0018	0.0018	0.0001	0.0002	0.0096	0.0101
7	N	0.0577	0.0024	0.0301	-0.0553	0.0163	**0.3161**	0.0133
8	C	0.0523	0.0002	0.0263	-0.0521	0.0151	**0.2866**	0.0012
9	C	**0.1025**	0	0.0512	-0.1024	0.0297	**0.5616**	0.0002
10	O	0.0064	0	0.0032	-0.0064	0.0019	0.0351	0
11	O	**0.7401**	0.0007	**0.3704**	**-0.7395**	**0.2142**	**4.0565**	0.0036
12	O	0.0013	0.0001	0.0007	-0.0012	0.0003	0.0069	0.0006
13	N	0.0001	**0.4551**	**0.2276**	**0.455**	-0.074	0.0006	**2.4944**
14	O	0	**0.2603**	**0.1302**	0.2603	-0.0423	0.0001	**1.4266**
15	O	0	**0.2316**	**0.1158**	0.2315	-0.0377	0.0002	**1.2691**
16	H	0.0001	0	0	-0.0001	0	0.0003	0
17	H	0.0002	0	0.0001	-0.0002	0.0001	0.0013	0
18	H	0.0001	0	0	-0.0001	0	0.0003	0
19	H	0.0054	0	0.0027	-0.0054	0.0016	0.0298	0
20	H	0	0.0002	0.0001	0.0002	0	0.0001	0.001
21	H	0	0.0002	0.0001	0.0002	0	0.0001	0.001

CONCLUSION

The band gap energy of isatin and its derivatives were successfully identified in both gas phase and solvation effects by DFT optimization. By having DFT calculations, the quantum chemical parameters such as ionization potential (I), Electron affinity (A), electronegativity (χ), band gap energy (ΔE), softness (σ), hardness (η), electrophilicity (ω) were calculated using HOMO and LUMO values. Comparison of adsorption behavior of isatin and its derivatives were analysed theoretically by quantum chemical parameters. The quantum chemical parameters possess all the studied derivatives has the tendency to donate the electron to the metal surface on adsorption. In addition, number of electron transfer from isatin and its derivatives to iron metal were calculated theoretically and possess the order IX>III>VII>IV>II>V>I>VIII>VI. In both gas phase and solvent phase, same trend exist in all the inhibitors. The protonation of compound I (isatin) and compound II (N-methyl isatin) were identified by the energy gap (ΔE) difference in gas phase and solvation models. Mulliken charge analysis confirms the donation of ligands from the heteroatoms present in isatin and its derivative to the metal ions. From the Fukui indices calculation for isatin and its derivatives, it shows that all the compounds have local selectivity for donating or accepting electrons towards the metal surface by the presence of hetero atoms. Among the derivatives, compound VI and VIII have high tendency to donate or accept electrons towards the metals. The adsorption studies supports the presence of electrostatic interaction between the Fe and compounds I-IX means the transfer of electrons from/to the metal surfaces.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/13336, or from the corresponding author on request.

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ИЗВОД

ТЕОРИЈСКА И ЕКСПЕРИМЕНТАЛНА ПРЕДВИЂАЊА ЕФИКАСНОСТИ ИНХИБИЦИЈЕ КОРОЗИЈЕ ИЗАТИНА И ЊЕГОВИХ ДЕРИВАТА ПРИМЕНОМ DFT ПРОРАЧУНА И МЕТОДЕ ГУБИТКА МАСЕ – УПОРЕДНА СТУДИЈА

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Перформансе инхибиције корозије изатина и његових деривата супституисаних на N1/C5 позицији анализиране су применом DFT прорачуна (B3LYP, 6311g, dp) у гасној фази, као у солватавионом методом помоћу Gaussian 09W и Gaussian 16 програмских пакета. Израчунати квантно-хемијски параметри, као што су E_{LUMO}, E_{HOMO}, јонизациони потенцијал (I), афинитет према електрону (A), електронегативност (χ), енергетски јаз (ΔE), мекоћа (σ), тврдоћа (η) и електрофилност (ω), показали су да изатин и његови деривати имају тенденцију да доniрају електроне ка површини металног јона током адсорпције. Теоријски је израчунат број пренетих електрона (ΔN) са изатина и његових деривата на гвожђе, при чему је утврђен редослед IX>III>VII>IV>II>V>I>VIII>VI. Експериментални резултати потврдили су исти редослед инхибиције као и теоријски. Анализа расподеле Миликенових наелектрисања за ова једињења указала је на високу негативну вредност на N1 атому. Негативна вредност на N1 атому се мења супституцијом на N1 и C-5 позицији изатина, што је теоријски потврђено. Локални Фукуи параметри такође су израчунати и коришћени за предвиђање локалне селективности ових једињења.

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