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Theoretical Evaluation of Six Indazole Derivatives as Corrosion Inhibitors Based on DFT

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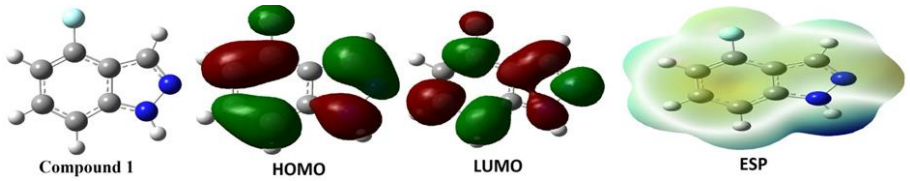
Abstract: This article deals with the calculation of the quantum chemical parameters of 1-substituted βCCM (methyl 9H-pyrido[3,4-b]indole-3-carboxylate) compounds that can be used as effective drugs in the treatment of many diseases. All DFT (density functional) geometry optimizations and frequency calculations have been performed to explain both the solvent and basis set effects on chemical reactivity behavior using 10 different solvent environments (by using the PCM, Polarized Continuum Model) except for the gas phase and with 3 different basis sets which are 6-31G(d,p), 6-31+G(d,p) and 6-311++G(d,p). The study revealed that the anthracen-9-yl substituted structure is the most reactive structure because its energy gap is the lowest one among the other structures, also in according with calculated global hardness values of the each di-substituted structure it is the soft structure which means it can easier interact with any receptor site than the other di-substituted structures while the structure 6-methoxynaphthalene-2-yl substituted compound has the highest energy gap which seems it is the less reactive structures in according with these results. Quantitative chemical identifiers were used to determine which molecules were more active or less active but also mapped electric potential (MEP) diagrams were drawn to illustrate the reactive sites of the molecules which were easier interact with an external molecule group in electrophilic/ nucleophilic reactions and, to show whether they possess electrophilic or nucleophilic properties. We expect that the findings of this study obtained from extensive and time-consuming calculations and analyzes will be an important source of information in the synthesis of less side effect ligands or compounds that can treat many diseases in the future.

Keywords: *Quantum chemical descriptors, Solvent effect, Substituent effect, Chemical reactivity*

Graphical Abstract



- Investigations of corrosion inhibition are performed by using HF, B3LYP methods.
- B3LYP/6-31g is found as the best calculation level and it is taken into consideration in other calculations,
- E_{HOMO}, E_{LUMO}, HOMO–LUMO energy gap (ΔE) have been calculated and discussed.

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1. Introduction

Corrosion is a very important problem in many chemical industries. Many methods are used in the industry to prevent corrosion. The most commonly used method to prevent corrosion on metal surfaces is provided by corrosion inhibitors which are adsorbed on metal surfaces. The most effective corrosion inhibitors adsorbed on metal surfaces are p-conjugated systems and heterocyclic organic compounds [1-2]. In many studies, many of the organic inhibitors containing nitrogen, oxygen, sulfur and an aromatic ring are highly effective against corrosion.

Experimental studies for corrosion inhibition are both time consuming and very expensive. The work of corrosion inhibitors has been very useful in the theoretical applications in recent years [3]. Quantum chemical parameters which are based on the Density Functional Theory such as HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), chemical hardness, electronegativity, chemical potential, nucleophilicity, electrophilicity have been the guide for investigating the agreement with experimental data of the results of computational chemistry works [4]. In this study, we have studied in detail the inhibition performance of six indazole compounds, 4-fluoro-1H-indazole (compound 1), 4-chloro-1H-indazole (compound 2), 4-bromo-1H-indazole (compound 3), 4-methyl-1H-indazole (compound 4), 4-amino-1H-indazole (compound 5), 4-hydroxy-1H-indazole (compound 6) in Fig 1.

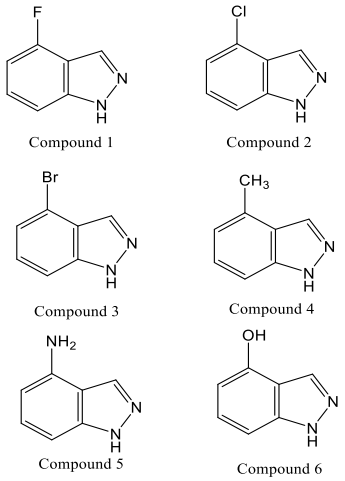

Fig. 1. The structure and schematic representation of indazole derivatives.

Koopmans theorem is the most commonly used method for describing calculations in computational chemistry [5]. Koopmans' theorem states that in closed-shell Hartree–Fock theory (HF), the first ionization energy of a molecular system is equal to the negative of the orbital energy of the highest occupied molecular orbital (HOMO). With the help of this theory, the Hard and Soft Acid-Base (HSAB) method needs to be discussed in detail [6,7]. According to HSAB theory, Lewis acid and bases classified by Pearson as hard and soft. Hard Lewis acids are described by high positive charge, empty orbital in high energy LUMOs. Soft Lewis acids are described by low positive charge, completely filled atomic orbitals in low energy LUMOs [4]. As can be understood from this definition, hard acids prefer to interact with hard bases and soft acids prefer to interact with soft bases. Because, the hard-hard interaction is basically an electrostatic interaction and soft-soft interaction is basically a covalent interaction. Since corrosion inhibitors are Lewis bases, HSAB theory should be considered in corrosion studies.

In the conceptual Density Functional Theory (DFT), quantum chemical parameters such as chemical hardness (η), softness (σ) [8], electronegativity (χ) [9], proton attraction [10], electrophilicity [11], chemical potential (μ) and nucleophilicity (ε) are considered in predicting the chemical reactivities of the compounds studied. The mathematical formulas for these concepts are as follows [12-21].

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

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(r)} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right) \tag{2}$$

As it is well-known ionization energy is the negative of the highest occupied molecular orbital energy and electron affinity is the negative of the lowest unoccupied molecular orbital energy.

$$\chi = -\mu = \left(\frac{I + A}{2}\right) \tag{3}$$

$$\eta = \frac{I - A}{2} \quad (4)$$

The global electrophilicity index (ω) reported by Parr et al. is the inverse of nucleophilicity and this equation is shown below.

$$\sigma = 1/\eta \quad (5)$$

$$\chi = -\mu = \left(\frac{-E_{HOMO} - E_{LUMO}}{2} \right) \quad (6)$$

$$\eta = \left(\frac{E_{LUMO} - E_{HOMO}}{2} \right) \quad (7)$$

$$\omega = \mu^2 / 2\eta = \chi^2 / 2\eta \quad (8)$$

$$\varepsilon = 1/\omega \quad (9)$$

Electrophilicity is the measure of electron withdrawal from a nucleophile of chemical species. Pearson and Parr were presented operational and approximate definitions using the finite differences method depending on electron affinity (A) and ionization energy (I) of any chemical species (atom, ion or molecule) for chemical hardness, softness (σ) electronegativity and chemical potential [22-24].

2. Method

The Density Function Theory is a common method used to predict the chemical reactivity of molecules. Computational chemistry studies have been widely used in recent years. In this study, the input files of studied molecules were prepared with Gauss View 5.0.8 [25]. DFT calculations were carried out using Gaussian 9.0 Program [26]. The molecules studied have been studied both in the gas phase and in the aqueous phase. All molecular structures were optimized on the B3LYP / 6-31++g basis set. all molecular structures were studied in sdd, Cep-4g, 3-21g, 6-31g, 6-31++g basis sets in HF and DFT / B3 LYP methods. Structures of HOMO, LUMO and ESPs of indazole derivatives were indicated in Fig. 2.

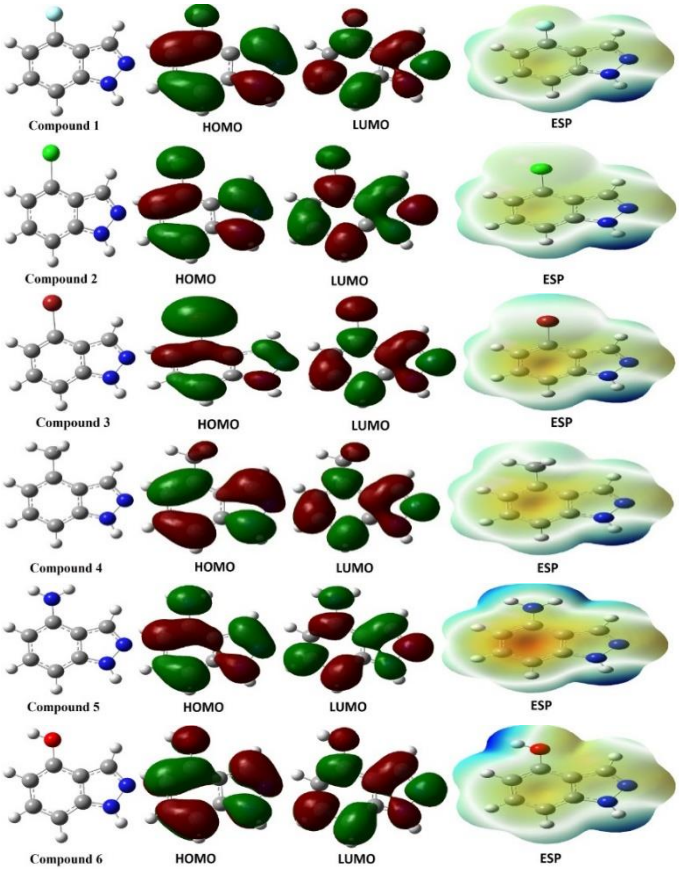

Fig. 2. Structures of HOMO, LUMO and ESPs of indazole derivatives.

3. Results and discussion

Quantum chemical parameter such HOMO, LUMO, and energy gap Quantum chemistry parameters are needed to compare as corrosion inhibitors the derivatives of indazole molecules. In Table 1 and 2, the derivatives of indazole molecules are demonstrated calculation results in B3LYP method in gas and aqueous phase. In Table 3 and 4, the derivatives of indazole molecules are demonstrated calculation results in HF method in gas and aqueous phase.

When it is desired to compare the reactivities of the working molecules, an analysis of the boundary molecule orbitals should be made. The numerical value of the HOMO energy of the molecules studied shows the ability of electron donation. The high value of HOMO energy of molecules is able to give electrons easier to molecules with low energy and empty molecular orbitals. On the other hand, the numerical value of the LUMO energy shows the ability of electron accepting. It should be remembered that the molecule studied will accept more electrons if it has a lower LUMO energy value. When we look at tables 1, 2, 3 and 4, in many basis sets we can write the corrosion inhibition efficiency order as: compound 5 < compound 6 < compound 4 < compound 1 < compound 3 < compound 2 (in LUMO energy value) in B3lyp/6-31g level. in experimental complex corrosion systems, the quantum chemical parameter values obtained by the theoretical studies may not be compatible with all the basic sets.

Chemical hardness is the resistance to electron cloud polarization or deformation of chemical species. In the light of this information, the chemical hardness of the molecules studied is inversely proportional to the inhibition yield. As molecular hardness increases, electron donation becomes more difficult. Chemical hardness, ΔE values, and softness are concepts related to each other. As it is well known that both chemical hardness and softness are based on HOMO and LUMO energy value as a result of HSAB's theorem. Hard molecules with high HOMO-LUMO energy gap are not a good corrosion inhibitor. Soft molecules with low HOMO-LUMO energy gap can be used as a good corrosion inhibitor because they easier give electrons. It is obvious that the same corrosion inhibition ranking in consideration of these three quantum chemical parameters.

The electrophilicity index (ω) is an important parameter that indicates the tendency of the inhibitor molecule to accept the electrons. This quantity is frequently used in the analysis of chemical reactivity of molecules. Nucleophilicity (ε) is physically the inverse of electrophilicity (1/ω). For this reason, it should be stated that a molecule that has large electrophilicity value is ineffective against corrosion while a molecule that has large nucleophilicity value is a good corrosion inhibitor.

Electronegativity is an important parameter for predicting the electron transition between the metal and the corrosion inhibitor. It is seen that as electronegativity of corrosion inhibitor molecules increases, the transfer of electrons from metallic to metallic surfaces decreases from the equation given below. On the basis of Sanderson's electronegativity equalization principle, the electron transfer between the metal and the inhibitor continues until the electronegativity values are equal to each other [27-28]. The fraction of electrons transferred from corrosion inhibitor to metal (DN) can be calculated by Pearson via following equation (11) [29]. The data obtained with this equation are in agreement with the experimental results. In recent studies, the use of Mulliken population analysis has become widespread in finding the adsorption center of inhibitors.

Table 1. The calculated quantum chemical parameters with B3LYP method in gas phase (eV)

	E_{HOMO}	E_{LUMO}	I	A	ΔE	η	σ	χ	PA	ω	ε	dipole	Energy
B3LYP/SDD LEVEL													
Compound 1	-6.511	-1.339	6.511	1.339	5.172	2.586	0.387	3.925	-3.925	2.979	0.336	3.626	-13032.833
Compound 2	-6.490	-1.428	6.490	1.428	5.062	2.531	0.395	3.959	-3.959	3.096	0.323	3.560	-22837.984
Compound 3	-6.475	-1.465	6.475	1.465	5.010	2.505	0.399	3.970	-3.970	3.146	0.318	3.466	-10679.834
Compound 4	-6.086	-0.992	6.086	0.992	5.094	2.547	0.393	3.539	-3.539	2.458	0.407	1.882	-11401.061
Compound 5	-5.281	-0.597	5.281	0.597	4.684	2.342	0.427	2.939	-2.939	1.844	0.542	2.180	-11837.836
Compound 6	-5.962	-0.924	5.962	0.924	5.038	2.519	0.397	3.443	-3.443	2.352	0.425	3.511	-12378.590
B3LYP/Cep-4g LEVEL													
Compound 1	-7.737	-3.317	7.737	3.317	4.419	2.210	0.453	5.527	-5.527	6.912	0.145	3.755	-2332.478
Compound 2	-7.698	-3.323	7.698	3.323	4.375	2.188	0.457	5.511	-5.511	6.941	0.144	3.641	-2081.299
Compound 3	-7.325	-2.959	7.325	2.959	4.365	2.183	0.458	5.142	-5.142	6.057	0.165	2.435	-2040.902
Compound 4	-7.261	-2.695	7.261	2.695	4.566	2.283	0.438	4.978	-4.978	5.428	0.184	1.686	-1876.918
Compound 5	-6.431	-2.339	6.431	2.339	4.092	2.046	0.489	4.385	-4.385	4.699	0.213	2.236	-1976.157
Compound 6	-7.096	-2.771	7.096	2.771	4.325	2.162	0.462	4.934	-4.934	5.628	0.178	3.387	-2124.771
B3LYP/3-21g LEVEL													
Compound 1	-6.150	-0.823	6.150	0.823	5.327	2.663	0.375	3.487	-3.487	2.282	0.438	2.735	-12962.585
Compound 2	-6.380	-1.133	6.380	1.133	5.247	2.623	0.381	3.757	-3.757	2.690	0.372	3.552	-22723.306
Compound 3	-6.163	-1.003	6.163	1.003	5.160	2.580	0.388	3.583	-3.583	2.488	0.402	2.757	-79971.472
Compound 4	-5.924	-0.665	5.924	0.665	5.259	2.629	0.380	3.295	-3.295	2.064	0.484	1.514	-11339.967
Compound 5	-4.961	-0.118	4.961	0.118	4.843	2.421	0.413	2.540	-2.540	1.332	0.751	1.994	-11774.167
Compound 6	-5.638	-0.447	5.638	0.447	5.191	2.595	0.385	3.043	-3.043	1.783	0.561	2.878	-12311.925
B3LYP/6-31g LEVEL													
Compound 1	-6.284	-1.013	6.284	1.013	5.271	2.636	0.379	3.648	-3.648	2.525	0.396	3.269	-13030.835
Compound 2	-6.376	-1.200	6.376	1.200	5.176	2.588	0.386	3.788	-3.788	2.772	0.361	3.610	-22836.939
Compound 3	-6.277	-1.152	6.277	1.152	5.124	2.562	0.390	3.715	-3.715	2.693	0.371	3.238	-80291.476
Compound 4	-5.938	-0.749	5.938	0.749	5.189	2.595	0.385	3.343	-3.343	2.154	0.464	1.797	-11399.814
Compound 5	-5.083	-0.294	5.083	0.294	4.789	2.395	0.418	2.688	-2.688	1.509	0.663	2.100	-11836.334
Compound 6	-5.762	-0.621	5.762	0.621	5.141	2.570	0.389	3.191	-3.191	1.981	0.505	3.314	-12376.828
B3LYP/6-31++g LEVEL													
Compound 1	-6.635	-1.436	6.635	1.436	5.199	2.599	0.385	4.035	-4.035	3.133	0.319	3.661	-13031.476
Compound 2	-6.628	-1.536	6.628	1.536	5.092	2.546	0.393	4.082	-4.082	3.272	0.306	3.634	-22837.384
Compound 3	-6.551	-1.513	6.551	1.513	5.038	2.519	0.397	4.032	-4.032	3.226	0.310	3.351	-80292.762
Compound 4	-6.215	-1.122	6.215	1.122	5.093	2.547	0.393	3.669	-3.669	2.643	0.378	1.942	-11400.267
Compound 5	-5.436	-0.759	5.436	0.759	4.677	2.338	0.428	3.097	-3.097	2.051	0.487	2.197	-11836.890
Compound 6	-6.099	-1.040	6.099	1.040	5.058	2.529	0.395	3.569	-3.569	2.519	0.397	3.550	-12377.416
B3LYP/Lanl2dz LEVEL													
Compound 1	-6.515	-1.343	6.515	1.343	5.172	2.586	0.387	3.929	-3.929	2.985	0.335	3.632	-13032.810
Compound 2	-6.510	-1.443	6.510	1.443	5.067	2.534	0.395	3.976	-3.976	3.120	0.320	3.631	-10722.435
Compound 3	-6.440	-1.433	6.440	1.433	5.006	2.503	0.399	3.936	-3.936	3.095	0.323	3.370	-10674.005
Compound 4	-6.088	-0.993	6.088	0.993	5.095	2.548	0.393	3.541	-3.541	2.460	0.406	1.885	-11401.045
Compound 5	-5.283	-0.599	5.283	0.599	4.684	2.342	0.427	2.941	-2.941	1.847	0.541	2.183	-11837.817
Compound 6	-5.966	-0.927	5.966	0.927	5.039	2.520	0.397	3.446	-3.446	2.357	0.424	3.517	-12378.568

Table 2. The calculated quantum chemical parameters with B3LYP method in aqueous phase (eV)

	E_{HOMO}	E_{LUMO}	I	A	ΔE	η	σ	χ	PA	ω	ε	dipole	Energy
B3LYP/SDD LEVEL													
Compound 1	-6.525	-1.381	6.525	1.381	5.144	2.572	0.389	3.953	-3.953	3.037	0.329	4.753	-13033.120
Compound 2	-6.520	-1.472	6.520	1.472	5.048	2.524	0.396	3.996	-3.996	3.163	0.316	4.755	-22838.254
Compound 3	-6.505	-1.506	6.505	1.506	4.999	2.500	0.400	4.005	-4.005	3.209	0.312	4.628	-10680.103
Compound 4	-6.194	-1.147	6.194	1.147	5.048	2.524	0.396	3.671	-3.671	2.669	0.375	2.434	-11401.330
Compound 5	-5.385	-0.828	5.385	0.828	4.557	2.279	0.439	3.106	-3.106	2.117	0.472	2.832	-11838.228
Compound 6	-6.061	-1.098	6.061	1.098	4.963	2.481	0.403	3.579	-3.579	2.581	0.387	4.631	-12378.988
B3LYP/Cep-4g LEVEL													
Compound 1	-7.874	-3.456	7.874	3.456	4.418	2.209	0.453	5.665	-5.665	7.263	0.138	4.769	-2332.849
Compound 2	-7.840	-3.455	7.840	3.455	4.385	2.193	0.456	5.648	-5.648	7.273	0.137	4.651	-2081.660
Compound 3	-7.453	-3.108	7.453	3.108	4.345	2.173	0.460	5.281	-5.281	6.417	0.156	2.968	-2041.242
Compound 4	-7.503	-2.947	7.503	2.947	4.556	2.278	0.439	5.225	-5.225	5.993	0.167	2.036	-1877.318
Compound 5	-6.635	-2.630	6.635	2.630	4.004	2.002	0.499	4.633	-4.633	5.359	0.187	2.781	-1976.700
Compound 6	-7.291	-3.015	7.291	3.015	4.276	2.138	0.468	5.153	-5.153	6.210	0.161	4.201	-2125.280
B3LYP/3-21g LEVEL													
Compound 1	-6.219	-0.920	6.219	0.920	5.299	2.649	0.377	3.569	-3.569	2.404	0.416	3.502	-12962.822
Compound 2	-6.445	-1.207	6.445	1.207	5.238	2.619	0.382	3.826	-3.826	2.795	0.358	4.692	-22723.566
Compound 3	-6.257	-1.109	6.257	1.109	5.148	2.574	0.389	3.683	-3.683	2.635	0.380	3.621	-79971.717
Compound 4	-6.068	-0.840	6.068	0.840	5.228	2.614	0.383	3.454	-3.454	2.282	0.438	1.909	-11340.220
Compound 5	-5.099	-0.364	5.099	0.364	4.735	2.368	0.422	2.731	-2.731	1.575	0.635	2.570	-11774.548
Compound 6	-5.762	-0.646	5.762	0.646	5.116	2.558	0.391	3.204	-3.204	2.007	0.498	3.678	-12312.285
B3LYP/6-31g LEVEL													
Compound 1	-6.297	-1.056	6.297	1.056	5.241	2.621	0.382	3.677	-3.677	2.579	0.388	4.259	-13031.084
Compound 2	-6.393	-1.229	6.393	1.229	5.164	2.582	0.387	3.811	-3.811	2.813	0.355	4.822	-22837.191
Compound 3	-6.311	-1.196	6.311	1.196	5.115	2.557	0.391	3.754	-3.754	2.755	0.363	4.327	-80291.719
Compound 4	-6.028	-0.880	6.028	0.880	5.148	2.574	0.388	3.454	-3.454	2.317	0.432	2.338	-11400.051
Compound 5	-5.172	-0.503	5.172	0.503	4.669	2.334	0.428	2.837	-2.837	1.724	0.580	2.741	-11836.691
Compound 6	-5.847	-0.783	5.847	0.783	5.064	2.532	0.395	3.315	-3.315	2.170	0.461	4.362	-12377.187
B3LYP/6-31++g LEVEL													
Compound 1	-6.613	-1.447	6.613	1.447	5.166	2.583	0.387	4.030	-4.030	3.144	0.318	4.904	-13031.768
Compound 2	-6.613	-1.540	6.613	1.540	5.073	2.537	0.394	4.076	-4.076	3.275	0.305	4.938	-22837.654
Compound 3	-6.546	-1.524	6.546	1.524	5.022	2.511	0.398	4.035	-4.035	3.241	0.309	4.551	-80293.026
Compound 4	-6.276	-1.231	6.276	1.231	5.045	2.522	0.396	3.753	-3.753	2.793	0.358	2.629	-11400.531
Compound 5	-5.488	-0.940	5.488	0.940	4.548	2.274	0.440	3.214	-3.214	2.271	0.440	2.975	-11837.272
Compound 6	-6.156	-1.180	6.156	1.180	4.975	2.488	0.402	3.668	-3.668	2.704	0.370	4.843	-12377.806
B3LYP/Lanl2dz LEVEL													
Compound 1	-6.530	-1.385	6.530	1.385	5.145	2.572	0.389	3.958	-3.958	3.045	0.328	4.760	-13033.098
Compound 2	-6.536	-1.483	6.536	1.483	5.053	2.526	0.396	4.009	-4.009	3.181	0.314	4.841	-10722.708
Compound 3	-6.480	-1.484	6.480	1.484	4.997	2.498	0.400	3.982	-3.982	3.173	0.315	4.506	-10674.273
Compound 4	-6.198	-1.149	6.198	1.149	5.049	2.524	0.396	3.674	-3.674	2.673	0.374	2.437	-11401.316
Compound 5	-5.388	-0.831	5.388	0.831	4.557	2.279	0.439	3.109	-3.109	2.122	0.471	2.836	-11838.211
Compound 6	-6.065	-1.102	6.065	1.102	4.963	2.482	0.403	3.584	-3.584	2.588	0.386	4.638	-12378.967

Table 3. The calculated quantum chemical parameters with HF method in gas phase (eV)

	E_{HOMO}	E_{LUMO}	I	A	ΔE	η	σ	χ	PA	ω	ε	dipole	Energy
B3LYP/SDD LEVEL													
Compound 1	-8.944	2.356	8.944	-2.356	11.300	5.650	0.177	3.294	-3.294	0.960	1.041	3.765	-12955.328
Compound 2	-8.905	2.193	8.905	-2.193	11.097	5.549	0.180	3.356	-3.356	1.015	0.985	3.757	-22751.932
Compound 3	-8.829	2.105	8.829	-2.105	10.933	5.467	0.183	3.362	-3.362	1.034	0.967	3.552	-10606.790
Compound 4	-8.375	2.678	8.375	-2.678	11.053	5.526	0.181	2.849	-2.849	0.734	1.362	1.969	-11326.422
Compound 5	-7.631	3.086	7.631	-3.086	10.716	5.358	0.187	2.272	-2.272	0.482	2.075	2.154	-11761.990
Compound 6	-8.372	2.788	8.372	-2.788	11.160	5.580	0.179	2.792	-2.792	0.699	1.431	3.721	-12301.711
B3LYP/Cep-4g LEVEL													
Compound 1	-9.941	1.024	9.941	-1.024	10.964	5.482	0.182	4.458	-4.458	1.813	0.552	3.965	-2274.814
Compound 2	-9.908	0.957	9.908	-0.957	10.865	5.432	0.184	4.476	-4.476	1.844	0.542	4.048	-2026.119
Compound 3	-9.488	1.336	9.488	-1.336	10.823	5.412	0.185	4.076	-4.076	1.535	0.651	2.860	-1985.774
Compound 4	-9.327	1.716	9.327	-1.716	11.043	5.522	0.181	3.806	-3.806	1.312	0.762	1.778	-1822.065
Compound 5	-8.653	1.954	8.653	-1.954	10.607	5.303	0.189	3.350	-3.350	1.058	0.945	2.019	-1919.967
Compound 6	-9.328	1.576	9.328	-1.576	10.903	5.452	0.183	3.876	-3.876	1.378	0.726	3.592	-2067.627
B3LYP/3-21g LEVEL													
Compound 1	-8.721	2.925	8.721	-2.925	11.646	5.823	0.172	2.898	-2.898	0.721	1.387	3.120	-12886.454
Compound 2	-8.873	2.587	8.873	-2.587	11.460	5.730	0.175	3.143	-3.143	0.862	1.160	3.691	-22638.871
Compound 3	-8.646	2.694	8.646	-2.694	11.341	5.670	0.176	2.976	-2.976	0.781	1.281	2.985	-79858.533
Compound 4	-8.309	3.106	8.309	-3.106	11.414	5.707	0.175	2.601	-2.601	0.593	1.687	1.737	-11266.290
Compound 5	-7.446	3.655	7.446	-3.655	11.102	5.551	0.180	1.895	-1.895	0.324	3.090	2.037	-11699.402
Compound 6	-8.198	3.337	8.198	-3.337	11.535	5.767	0.173	2.431	-2.431	0.512	1.952	3.302	-12236.272
B3LYP/6-31g LEVEL													
Compound 1	-8.763	2.742	8.763	-2.742	11.505	5.753	0.174	3.011	-3.011	0.788	1.269	3.586	-12953.453
Compound 2	-8.793	2.514	8.793	-2.514	11.307	5.653	0.177	3.140	-3.140	0.872	1.147	3.773	-22751.131
Compound 3	-8.684	2.542	8.684	-2.542	11.226	5.613	0.178	3.071	-3.071	0.840	1.190	3.444	-80175.891
Compound 4	-8.239	3.013	8.239	-3.013	11.253	5.626	0.178	2.613	-2.613	0.607	1.648	1.997	-11325.166
Compound 5	-7.468	3.482	7.468	-3.482	10.950	5.475	0.183	1.993	-1.993	0.363	2.758	2.171	-11760.533
Compound 6	-8.213	3.170	8.213	-3.170	11.383	5.692	0.176	2.521	-2.521	0.558	1.791	3.673	-12300.039
B3LYP/6-31++g LEVEL													
Compound 1	-8.935	0.915	8.935	-0.915	9.849	4.925	0.203	4.010	-4.010	1.633	0.612	3.740	-12953.845
Compound 2	-8.913	0.907	8.913	-0.907	9.820	4.910	0.204	4.003	-4.003	1.632	0.613	3.757	-22751.419
Compound 3	-8.828	0.918	8.828	-0.918	9.746	4.873	0.205	3.955	-3.955	1.605	0.623	3.522	-80177.024
Compound 4	-8.379	1.053	8.379	-1.053	9.432	4.716	0.212	3.663	-3.663	1.423	0.703	2.018	-11325.469
Compound 5	-7.649	0.999	7.649	-0.999	8.648	4.324	0.231	3.325	-3.325	1.278	0.782	2.179	-11760.900
Compound 6	-8.378	0.935	8.378	-0.935	9.313	4.657	0.215	3.721	-3.721	1.487	0.673	3.721	-12300.420
B3LYP/Lanl2dz LEVEL													
Compound 1	-8.938	2.358	8.938	-2.358	11.296	5.648	0.177	3.290	-3.290	0.958	1.044	3.765	-12955.298
Compound 2	-8.922	2.174	8.922	-2.174	11.096	5.548	0.180	3.374	-3.374	1.026	0.975	3.873	-10649.453
Compound 3	-8.812	2.168	8.812	-2.168	10.980	5.490	0.182	3.322	-3.322	1.005	0.995	3.560	-10601.156
Compound 4	-8.369	2.679	8.369	-2.679	11.048	5.524	0.181	2.845	-2.845	0.733	1.365	1.969	-11326.383
Compound 5	-7.625	3.088	7.625	-3.088	10.712	5.356	0.187	2.268	-2.268	0.480	2.082	2.153	-11761.955
Compound 6	-8.366	2.789	8.366	-2.789	11.156	5.578	0.179	2.789	-2.789	0.697	1.435	3.720	-12301.678

Table 4. The calculated quantum chemical parameters with HF method in aqueous phase (eV)

	E_{HOMO}	E_{LUMO}	I	A	ΔE	η	σ	χ	PA	ω	ε	dipole	Energy
B3LYP/SDD LEVEL													
Compound 1	-8.921	2.338	8.921	-2.338	11.259	5.629	0.178	3.291	-3.291	0.962	1.039	4.817	-12955.647
Compound 2	-8.897	2.176	8.897	-2.176	11.072	5.536	0.181	3.361	-3.361	1.020	0.980	4.913	-22752.227
Compound 3	-8.829	2.066	8.829	-2.066	10.895	5.447	0.184	3.381	-3.381	1.049	0.953	4.651	-10607.079
Compound 4	-8.461	2.521	8.461	-2.521	10.981	5.491	0.182	2.970	-2.970	0.803	1.245	2.502	-11326.714
Compound 5	-7.722	2.849	7.722	-2.849	10.571	5.285	0.189	2.437	-2.437	0.562	1.780	2.751	-11762.403
Compound 6	-8.444	2.618	8.444	-2.618	11.062	5.531	0.181	2.913	-2.913	0.767	1.304	4.803	-12302.141
B3LYP/Cep-4g LEVEL													
Compound 1	-10.014	0.940	10.014	-0.940	10.954	5.477	0.183	4.537	-4.537	1.879	0.532	4.922	-2275.150
Compound 2	-9.978	0.889	9.978	-0.889	10.867	5.434	0.184	4.544	-4.544	1.900	0.526	5.074	-2026.443
Compound 3	-9.563	1.248	9.563	-1.248	10.811	5.405	0.185	4.158	-4.158	1.599	0.625	3.471	-1986.068
Compound 4	-9.514	1.504	9.514	-1.504	11.018	5.509	0.182	4.005	-4.005	1.456	0.687	2.103	-1822.407
Compound 5	-8.868	1.684	8.868	-1.684	10.552	5.276	0.190	3.592	-3.592	1.223	0.818	2.400	-1920.406
Compound 6	-9.475	1.380	9.475	-1.380	10.856	5.428	0.184	4.048	-4.048	1.509	0.663	4.381	-2068.076
B3LYP/3-21g LEVEL													
Compound 1	-8.763	2.842	8.763	-2.842	11.604	5.802	0.172	2.960	-2.960	0.755	1.324	3.907	-12886.729
Compound 2	-8.920	2.518	8.920	-2.518	11.437	5.719	0.175	3.201	-3.201	0.896	1.116	4.779	-22639.158
Compound 3	-8.719	2.595	8.719	-2.595	11.314	5.657	0.177	3.062	-3.062	0.829	1.207	3.837	-79858.805
Compound 4	-8.449	2.917	8.449	-2.917	11.366	5.683	0.176	2.766	-2.766	0.673	1.485	2.147	-11266.576
Compound 5	-7.581	3.393	7.581	-3.393	10.974	5.487	0.182	2.094	-2.094	0.400	2.502	2.561	-11699.807
Compound 6	-8.311	3.130	8.311	-3.130	11.441	5.720	0.175	2.590	-2.590	0.587	1.705	4.142	-12236.673
B3LYP/6-31g LEVEL													
Compound 1	-8.758	2.701	8.758	-2.701	11.459	5.729	0.175	3.028	-3.028	0.800	1.250	4.560	-12953.748
Compound 2	-8.798	2.481	8.798	-2.481	11.279	5.640	0.177	3.158	-3.158	0.884	1.131	4.922	-22751.416
Compound 3	-8.704	2.497	8.704	-2.497	11.200	5.600	0.179	3.103	-3.103	0.860	1.163	4.493	-80176.167
Compound 4	-8.331	2.859	8.331	-2.859	11.190	5.595	0.179	2.736	-2.736	0.669	1.495	2.545	-11325.442
Compound 5	-7.567	3.244	7.567	-3.244	10.811	5.406	0.185	2.161	-2.161	0.432	2.315	2.780	-11760.927
Compound 6	-8.293	2.990	8.293	-2.990	11.283	5.642	0.177	2.651	-2.651	0.623	1.605	4.724	-12300.448
B3LYP/6-31++g LEVEL													
Compound 1	-8.909	1.200	8.909	-1.200	10.109	5.055	0.198	3.854	-3.854	1.470	0.680	4.852	-12954.166
Compound 2	-8.897	1.211	8.897	-1.211	10.107	5.054	0.198	3.843	-3.843	1.461	0.684	4.966	-22751.716
Compound 3	-8.818	1.213	8.818	-1.213	10.030	5.015	0.199	3.802	-3.802	1.441	0.694	4.649	-80177.313
Compound 4	-8.452	1.180	8.452	-1.180	9.632	4.816	0.208	3.636	-3.636	1.373	0.728	2.651	-11325.762
Compound 5	-7.726	1.182	7.726	-1.182	8.908	4.454	0.225	3.272	-3.272	1.202	0.832	2.873	-11761.312
Compound 6	-8.440	1.171	8.440	-1.171	9.611	4.805	0.208	3.635	-3.635	1.375	0.727	4.914	-12300.847
B3LYP/Lanl2dz LEVEL													
Compound 1	-8.914	2.341	8.914	-2.341	11.255	5.627	0.178	3.286	-3.286	0.960	1.042	4.817	-12955.617
Compound 2	-8.907	2.165	8.907	-2.165	11.073	5.536	0.181	3.371	-3.371	1.026	0.974	5.057	-10649.751
Compound 3	-8.814	2.146	8.814	-2.146	10.960	5.480	0.182	3.334	-3.334	1.014	0.986	4.667	-10601.444
Compound 4	-8.453	2.524	8.453	-2.524	10.977	5.488	0.182	2.965	-2.965	0.801	1.249	2.502	-11326.674
Compound 5	-7.715	2.852	7.715	-2.852	10.567	5.283	0.189	2.432	-2.432	0.560	1.787	2.750	-11762.367
Compound 6	-8.437	2.621	8.437	-2.621	11.058	5.529	0.181	2.908	-2.908	0.765	1.308	4.804	-12302.108

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

where ΔN is electron transfer between metal and inhibitor. χ_M and χ_{inh} are electronegativity of metal and electronegativity of inhibitor, respectively. η_M and η_{inh} represent chemical hardness value of metal and chemical hardness value of inhibitor, respectively. The partial atomic charges in the inhibitor molecule help to find the reactive center in the inhibitor molecule. The highest negatively charged atoms are the atom that interacts most with the metal surface. The inhibitors can easily interact with the metal surface through such atoms.

It is clearly known that the figure of molecular electrostatic potential (ESP) of six molecules givens an indication of the total charge distribution (electron + nuclei) of the molecule and correlates with dipole moments, electronegativity, partial charges and chemical reactivity of six molecules in Figure 2. It provides that a visual method to understand the relative polarity of the molecules. An electron density isosurface of six molecules mapped with the electrostatic potential surface the size, shape, charge density and site of chemical reactivity of molecules [15].

The different value of the electrostatic potential represented by different colors: red represents the region of the most negative electrostatic potential, blue represents the regions of the most positive electrostatic potential and green represents the region of zero potential. The potential increases in the order red < orange < yellow < green < blue. From the light of the result given in the mapped have been plotted for title molecules in 6-311++G** basis set using the computer software gauss view.

Experimental studies for compounds 1, 2 and 3 are available by Qiang et al [30]. This experiment has a similar order for the three molecules studied in the study, but only for compounds 1, 2 and 3. Theoretical calculations do not always fit experimentally for all basis sets. The best fit was achieved in the b3lyp / 6-31g basis set.

4. Conclusion

Hartree Fock (HF), density functional theory at B3LYP with different basis sets was employed to evaluate the corrosion inhibition efficiencies of some indazole derivatives at the molecular level. The following conclusions could be drawn from this study:

1. Remarkable correlations have been obtained between theoretical results and experimental inhibition efficiencies of indazole derivatives investigated.
2. The results of both DFT approach showed that the corrosion inhibition efficiency ranking of studied compounds can be given as in B3lyp/6-31++g: compound 5 < compound 6 < compound 4 < compound 1 < compound 3 < compound 2
3. The theoretical results obtained in this study are important towards rational design new indazole derivatives as a corrosion inhibitor.

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