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Investigation of Benzimidazole Derivates as Corrosion Inhibitor by DFT

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Abstract. Benzimidazole derivates are investigated the activity of corrosion inhibitor molecules.In quantum chemical calculation, different parameters such as E_{HOMO}, E_{LUMO}, ΔE (HOMO-LUMO energy gap), electronegativity, chemical hardness, global softness, nucleophilicity are calculated by Gaussian 09 software. Studied molecules were performed using the Hartree-Fock (HF) and Becke, 3-parameter, Lee-Yang-Parr (B3LYP) method with sdd, cep-4g, 3-21G, 6-31G, 6-31++G, lanl2dz basis set in gas and aqueous phase. We can see the corrosion inhibitor ranking as: 4NPBI > 4APBI > 2NPBI > 2APBI > 4BPBI > 4MPBI > 4CPBI > PBI in B3lyp method with sdd and lanl2dz.

***Keywords*:** Benzimidazole, DFT, corrosion, activity.

DFT ile benzimidazol türevlerinin korozyon inhibitörü olarak incelenmesi

Özet. Benzimidazol türevleri, korozyon önleyici moleküllerin aktivitesini araştırıldı. Kuantum kimyasal hesaplamasında, E_{HOMO}, E_{LUMO}, ΔE (HOMO-LUMO enerji aralığı), elektronegatiflik, kimyasal sertlik, global yumuşaklık, nükleofilik gibi farklı parametreler gaussian 09 yazılımı ile hesaplandı. Çalışılan moleküller, Hartree-Fock (HF) ve Becke, 3-parametre Lee-Yang-Parr (B3LYP) yöntemi kullanılarak sdd, cep-4g, 3-21G, 6-31G, 6-31 ++ G, lanl2dz temel sette gaz ve sulu fazda hesaplamaları yapıldı. Korozyon inhibitörü sıralamasını aşağıdaki gibi görebiliriz: 4NPBI> 4APBI> 2NPBI> 2APBI> 4BPBI> 4MPBI> 4CPBI> PBI, b3lyp metodunda lanl2dz ve sdd settinde.

***Anahtar Kelimeler*:** Benzimidazol, DFT, korozyon, aktivite.

1. INTRODUCTION

Metal corrosion is a very important problem in various industrial processes which is widely used water, alcohol and acid. The acid solutions used cause too much corrosion in the metal that is an iron, copper, aluminum. Corrosion inhibitors that are containing nitrogen, oxygen, Sulphur and aromatic ring, are used to prevent corrosion caused by acid solutions.

As it is well known that experimental studies have been used to understand the corrosion inhibition mechanism of molecules and to explain corrosion inhibition efficiencies. Quantum chemical calculations provide preliminary information on the activities of molecules. In quantum chemical calculations, parameters related to the activity of molecules are calculated using density functional theory (DFT) that are calculated HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), electrophilicity, electronegativity, chemical potential, chemical hardness and nucleophilicity.

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In this study, we can be seen that activity of studied molecules whose names are 2-(4-nitrophenyl) benzimidazole (4NPBI), 2-(4-aminophenyl) benzimidazole (4APBI), 2-(2-nitrophenyl) benzimidazole (2NPBI), 2-(2-aminophenyl) benzimidazole (2APBI), 2-phenyl benzimidazole (PBI), 2-(4-chlorophenyl) benzimidazole (4CPBI), 2-(4-metilphenyl) benzimidazole (4MPBI), 2-(4-bromophenyl) benzimidazole (4BPBI) in Figure 1 [1].

2. COMPUTATIONAL DETAILS

DFT calculation is the most popular method for the activity of molecules.In this study, we prepared the input files of the molecules studied by gaussian view 5.08 programs [2]. Calculations of studied molecules were performed with Gaussian IA32W-G09RevA.02 and Gaussian AS64L-G09RevD.01 programs [3-4]. Studied molecules were performed using the Hartree-Fock (HF)[5] and Becke, 3-parameter, Lee-Yang-Parr (B3LYP) [6-8] method with sdd, cep-4g, 3-21G, 6-31G, 6-31++G, lanl2dz basis set in gas and an aqueous phase. HOMO and LUMO are given information about activity of molecules.Chemical reactivity parameter of molecules isgiven to found a good corrosion inhibitor such as E_{HOMO}, E_{LUMO}, ΔE (HOMO-LUMO energy gap), electronegativity (χ), chemical potential (μ), chemical hardness (η), electrophilicity (ω), nucleophilicity (ε), global softness (σ) and proton affinity (PA) [9-18].

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

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

Ionization energy (I) and electron affinity (A) [19] of studied molecules are calculated with HOMO and LUMO energy that are interested Electronegativity, global softness and chemical hardness obtaining the following equations.

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

$$\eta = \frac{I - A}{2} \tag{4}$$

As it is well known that global softness is defined as the inverse of the chemical hardness [20].

$$\sigma = 1/\eta \tag{5}$$

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

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

The global electrophilicity index (ω) that is investigated by Parr et al., is the inverse of nucleophilicity and are given inequality (8). Electrophilicity and nucleophilicity are used for the prediction organic and inorganic reaction mechanisms. Nucleophilicity (ε) is defined as the inverse of the electrophilicity in equations (9).

$$\omega = \mu^2/2\eta = \chi^2/2\eta \tag{8}$$

$$\varepsilon = 1/\omega \tag{9}$$

3. RESULTS AND DISCUSSION

The corrosion inhibitor reactivity of benzimidazole derivatives is studied by quantum chemical calculation. The chemical reactivity of studied molecules that is obtained by the Gaussian software program, it is shown that a good inhibitor against different metal atoms. The studied of molecules are obtained the results are given in below.

The studied molecules are investigated quantum chemical parameter such as E_{HOMO}, E_{LUMO}, ΔE (HOMO-LUMO energy gap), electronegativity, chemical potential, chemical hardness, electrophilicity, nucleophilicity, global softness and proton affinity. These parameters are very important parameters which are compared the reactivity of studied molecules.

As it is well known that the properties of chemical reactivity of studied molecules were compared by molecular orbitals of an inhibitor molecule that have got two molecular orbitalswhose the name is

Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO).

The energy level of HOMO has defined the electron donating ability of studied molecules. The molecule has got the high values of energy of HOMO that is showingthe tendency to donate electrons of the molecule to appropriate that the acceptor molecules have low energy and empty molecular orbital [9-18]. From the light of the result given in the information, the energy level of LUMO of molecules is indicated electron accepting abilities of studied molecules. When the energy value of LUMO of inhibitor molecule is lower, this molecule has more electron accepting ability in lower energy of molecular orbitals. The calculated of HOMO and LUMO energy value is given in Table 1, 2, 3 and 4.

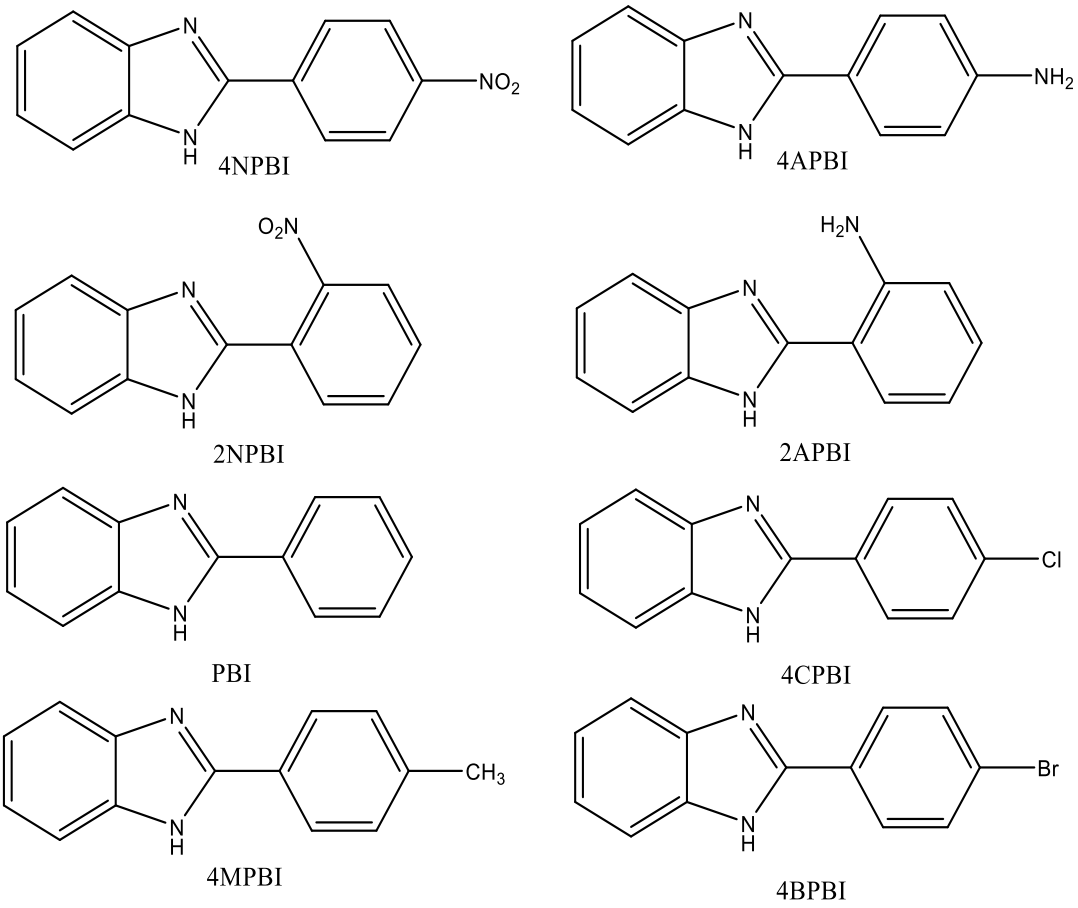

Figure 1. The structure and schematic representation of molecules of benzimidazole derivatives

In figure 2, structure of HOMO, LUMO and ESP studied molecules are given about some information of this molecule. In figure of HOMO of molecule, we look where highest occupied molecular orbital is. In this picture, HOMO orbitals appear to cover the entire molecule. In figure of LUMO of molecule, we look where lowest unoccupied molecular orbital is. In this picture, LUMO orbitals appear to cover the entire molecule. Last picture is ESP that is Molecular electrostatic potential (ESP) figure that given information about distribution of electrons in molecular. In this picture, the different value of the electrostatic potential represented by different colors [14]. This potential increases in the order red > orange > yellow > green > blue. The highest potential is on oxygen atoms.

The energy gap value (ΔE) in chemical reactivity of inhibitor molecule is a very important parameter in corrosion. As it is well known that inhibitor molecule has a small energy gap value, this molecule is a good corrosion inhibitor. Since the energy gap value of inhibitor molecule is indicated

that the binding ability of inhibitor molecules on metal surfaces [21]. On the basis of the calculated the energy gap value given in Table 1, 2, 3 and 4, the corrosion inhibition activity of benzimidazole derivatives molecules can be written as:4NPBI > 4APBI > 2NPBI > 2APBI > 4BPBI > 4MPBI > 4CPBI > PBI in B3lyp method with sdd and lanl2dz.

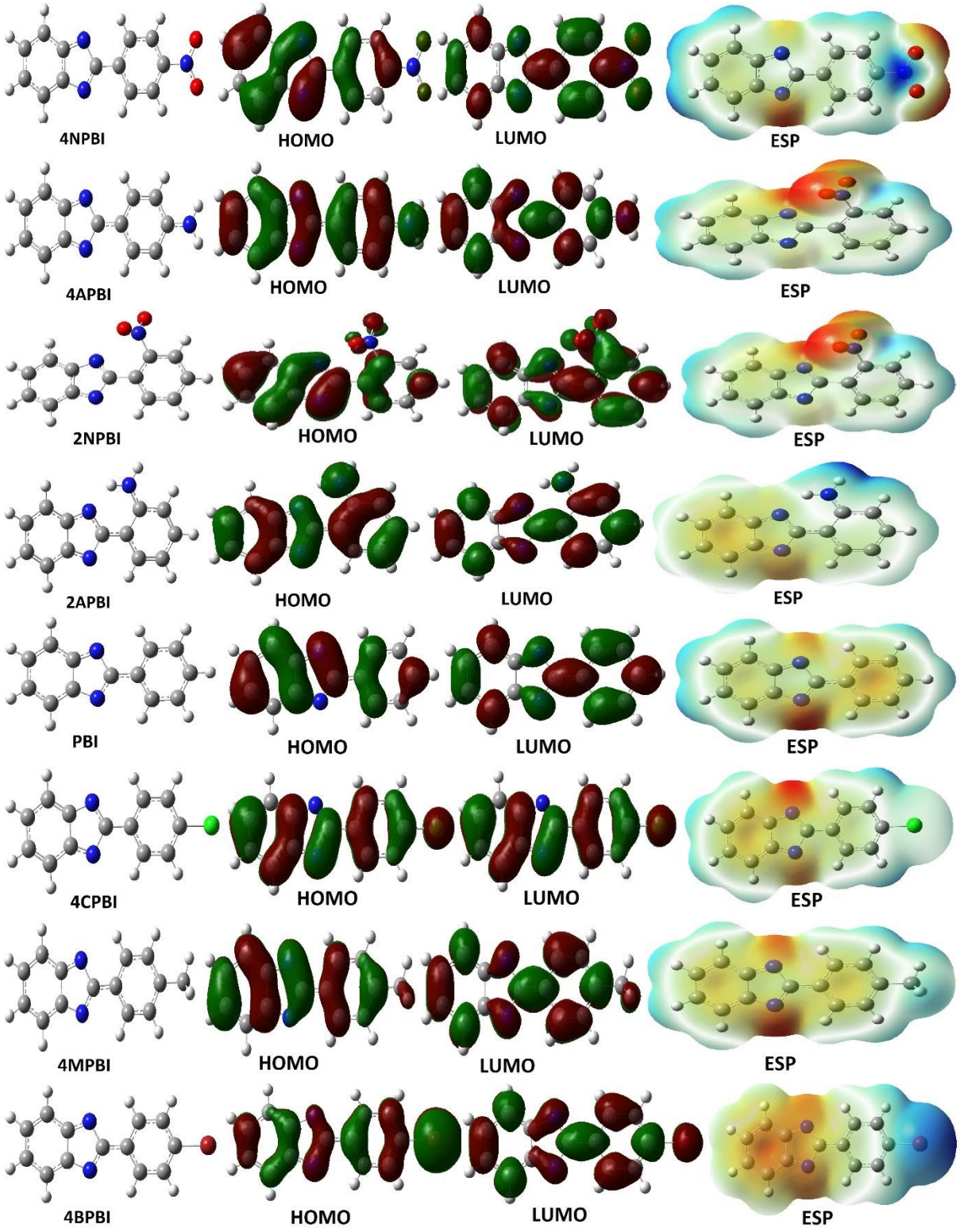

Figure 2. Structures of HOMO, LUMO and ESPs of benzimidazole derivatives

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

	E_{HOMO}	E_{LUMO}	I	A	ΔE	η	σ	χ	Pİ	ω	ε	dipol	Energy
B3LYP/SDD													
4NPBI	-6,903	-3,324	6,903	3,324	3,579	1,790	0,559	5,113	-5,113	7,305	0,137	8,811	-22163,416
4APBI	-5,376	-1,259	5,376	1,259	4,117	2,059	0,486	3,317	-3,317	2,673	0,374	5,861	-18105,389
2NPBI	-6,701	-2,566	6,701	2,566	4,136	2,068	0,484	4,633	-4,633	5,191	0,193	4,634	-22162,904
2APBI	-5,618	-1,471	5,618	1,471	4,147	2,073	0,482	3,544	-3,544	3,030	0,330	2,949	-18105,611
PBI	-6,193	-1,703	6,193	1,703	4,490	2,245	0,445	3,948	-3,948	3,471	0,288	0,998	-16599,339
4CPBI	-6,345	-1,920	6,345	1,920	4,425	2,213	0,452	4,132	-4,132	3,858	0,259	3,522	-29105,350
4MPBI	-6,009	-1,597	6,009	1,597	4,413	2,206	0,453	3,803	-3,803	3,277	0,305	0,391	-17668,447
4BPBI	-6,337	-1,939	6,337	1,939	4,398	2,199	0,455	4,138	-4,138	3,893	0,257	3,421	-16947,196
B3LYP/Cep-4g													
4NPBI	-8,192	-4,904	8,192	4,904	3,288	1,644	0,608	6,548	-6,548	13,041	0,077	8,251	-3762,591
4APBI	-6,682	-3,025	6,682	3,025	3,657	1,829	0,547	4,853	-4,853	6,440	0,155	3,823	-2932,975
2NPBI	-8,018	-4,466	8,018	4,466	3,552	1,776	0,563	6,242	-6,242	10,968	0,091	4,138	-3762,160
2APBI	-6,936	-3,193	6,936	3,193	3,743	1,872	0,534	5,065	-5,065	6,852	0,146	2,577	-2933,299
PBI	-7,652	-3,443	7,652	3,443	4,209	2,105	0,475	5,547	-5,547	7,310	0,137	1,906	-2649,286
4CPBI	-7,793	-3,739	7,793	3,739	4,054	2,027	0,493	5,766	-5,766	8,201	0,122	4,731	-3038,153
4MPBI	-7,498	-3,327	7,498	3,327	4,171	2,085	0,480	5,413	-5,413	7,024	0,142	0,913	-2833,735
4BPBI	-7,507	-3,506	7,507	3,506	4,001	2,000	0,500	5,507	-5,507	7,579	0,132	2,813	-2997,697
B3LYP/3-21g													
4NPBI	-6,653	-2,814	6,653	2,814	3,839	1,920	0,521	4,733	-4,733	5,836	0,171	7,293	-22043,816
4APBI	-5,108	-0,876	5,108	0,876	4,231	2,116	0,473	2,992	-2,992	2,116	0,473	6,020	-18008,316
2NPBI	-6,514	-2,448	6,514	2,448	4,067	2,033	0,492	4,481	-4,481	4,938	0,203	4,463	-22043,329
2APBI	-5,362	-1,146	5,362	1,146	4,216	2,108	0,474	3,254	-3,254	2,511	0,398	3,212	-18008,695
PBI	-6,055	-1,394	6,055	1,394	4,660	2,330	0,429	3,724	-3,724	2,977	0,336	1,122	-16510,517
4CPBI	-6,256	-1,660	6,256	1,660	4,595	2,298	0,435	3,958	-3,958	3,409	0,293	3,943	-28957,276
4MPBI	-5,886	-1,311	5,886	1,311	4,575	2,288	0,437	3,598	-3,598	2,830	0,353	0,200	-17573,972
4BPBI	-6,092	-1,568	6,092	1,568	4,524	2,262	0,442	3,830	-3,830	3,242	0,308	2,607	-86205,409
B3LYP/6-31g													
4NPBI	-6,699	-3,019	6,699	3,019	3,681	1,840	0,543	4,859	-4,859	6,414	0,156	8,360	-22160,493
4APBI	-5,171	-0,971	5,171	0,971	4,200	2,100	0,476	3,071	-3,071	2,246	0,445	5,850	-18103,585
2NPBI	-6,499	-2,190	6,499	2,190	4,309	2,154	0,464	4,345	-4,345	4,381	0,228	4,369	-22159,960
2APBI	-5,420	-1,196	5,420	1,196	4,224	2,112	0,474	3,308	-3,308	2,591	0,386	2,862	-18103,805
PBI	-6,008	-1,428	6,008	1,428	4,580	2,290	0,437	3,718	-3,718	3,018	0,331	0,968	-16597,877
4CPBI	-6,200	-1,682	6,200	1,682	4,519	2,259	0,443	3,941	-3,941	3,437	0,291	3,765	-29103,991
4MPBI	-5,838	-1,343	5,838	1,343	4,495	2,247	0,445	3,590	-3,590	2,868	0,349	0,307	-17666,882
4BPBI	-6,124	-1,644	6,124	1,644	4,479	2,240	0,446	3,884	-3,884	3,368	0,297	3,096	-86558,506
B3LYP/6-31++g													
4NPBI	-6,977	-3,443	6,977	3,443	3,534	1,767	0,566	5,210	-5,210	7,679	0,130	8,847	-22161,453
4APBI	-5,483	-1,352	5,483	1,352	4,130	2,065	0,484	3,417	-3,417	2,827	0,354	5,786	-18104,341
2NPBI	-6,769	-2,745	6,769	2,745	4,025	2,012	0,497	4,757	-4,757	5,623	0,178	4,581	-22160,962
2APBI	-5,716	-1,536	5,716	1,536	4,180	2,090	0,478	3,626	-3,626	3,145	0,318	2,846	-18104,506
PBI	-6,277	-1,757	6,277	1,757	4,520	2,260	0,442	4,017	-4,017	3,571	0,280	0,942	-16598,523
4CPBI	-6,440	-1,981	6,440	1,981	4,460	2,230	0,448	4,211	-4,211	3,975	0,252	3,607	-29104,649
4MPBI	-6,095	-1,664	6,095	1,664	4,431	2,216	0,451	3,879	-3,879	3,396	0,294	0,456	-17667,551
4BPBI	-6,385	-1,962	6,385	1,962	4,423	2,212	0,452	4,174	-4,174	3,939	0,254	3,097	-86559,996
B3LYP/Lanl2dz													
4NPBI	-6,908	-3,330	6,908	3,330	3,578	1,789	0,559	5,119	-5,119	7,323	0,137	8,827	-22163,371
4APBI	-5,379	-1,261	5,379	1,261	4,117	2,059	0,486	3,320	-3,320	2,677	0,374	5,862	-18105,360
2NPBI	-6,706	-2,574	6,706	2,574	4,131	2,066	0,484	4,640	-4,640	5,212	0,192	4,640	-22162,858
2APBI	-5,620	-1,473	5,620	1,473	4,147	2,074	0,482	3,547	-3,547	3,033	0,330	2,955	-18105,584
PBI	-6,196	-1,705	6,196	1,705	4,491	2,246	0,445	3,950	-3,950	3,475	0,288	1,003	-16599,313
4CPBI	-6,362	-1,931	6,362	1,931	4,430	2,215	0,451	4,147	-4,147	3,881	0,258	3,656	-16989,793
4MPBI	-6,013	-1,598	6,013	1,598	4,414	2,207	0,453	3,806	-3,806	3,281	0,305	0,387	-17668,421
4BPBI	-6,311	-1,920	6,311	1,920	4,391	2,195	0,455	4,116	-4,116	3,858	0,259	3,211	-16941,355

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

	E_{HOMO}	E_{LUMO}	I	A	ΔE	η	σ	χ	Pİ	ω	ε	dipol	Energy
B3LYP/SDD													
4NPBI	-6,795	-3,598	6,795	3,598	3,197	1,599	0,626	5,196	-5,196	8,446	0,118	11,794	-22163,836
4APBI	-5,643	-1,564	5,643	1,564	4,079	2,040	0,490	3,604	-3,604	3,184	0,314	11,666	-18105,943
2NPBI	-6,733	-3,252	6,733	3,252	3,481	1,740	0,575	4,992	-4,992	7,161	0,140	5,936	-22163,388
2APBI	-5,853	-1,665	5,853	1,665	4,188	2,094	0,478	3,759	-3,759	3,375	0,296	6,213	-18105,980
PBI	-6,402	-1,910	6,402	1,910	4,492	2,246	0,445	4,156	-4,156	3,845	0,260	1,504	-16599,635
4CPBI	-6,467	-2,028	6,467	2,028	4,439	2,220	0,451	4,248	-4,248	4,065	0,246	4,841	-29105,633
4MPBI	-6,235	-1,846	6,235	1,846	4,390	2,195	0,456	4,041	-4,041	3,719	0,269	0,928	-17668,758
4BPBI	-6,457	-2,046	6,457	2,046	4,411	2,205	0,453	4,252	-4,252	4,098	0,244	4,653	-16947,477
B3LYP/Cep-4g													
4NPBI	-8,178	-5,203	8,178	5,203	2,976	1,488	0,672	6,690	-6,690	15,043	0,066	10,258	-3763,007
4APBI	-7,004	-3,391	7,004	3,391	3,613	1,807	0,554	5,197	-5,197	7,476	0,134	7,187	-2933,601
2NPBI	-8,168	-5,044	8,168	5,044	3,124	1,562	0,640	6,606	-6,606	13,968	0,072	5,275	-3762,659
2APBI	-7,426	-3,335	7,426	3,335	4,091	2,045	0,489	5,381	-5,381	7,077	0,141	6,980	-2934,065
PBI	-7,914	-3,733	7,914	3,733	4,182	2,091	0,478	5,824	-5,824	8,111	0,123	2,767	-2649,691
4CPBI	-7,968	-3,940	7,968	3,940	4,027	2,014	0,497	5,954	-5,954	8,802	0,114	6,076	-3038,525
4MPBI	-7,811	-3,658	7,811	3,658	4,153	2,077	0,482	5,735	-5,735	7,918	0,126	1,585	-2834,169
4BPBI	-7,701	-3,739	7,701	3,739	3,962	1,981	0,505	5,720	-5,720	8,259	0,121	3,496	-2998,069
B3LYP/3-21g													
4NPBI	-6,621	-3,036	6,621	3,036	3,585	1,793	0,558	4,829	-4,829	6,503	0,154	9,425	-22044,112
4APBI	-5,384	-1,216	5,384	1,216	4,168	2,084	0,480	3,300	-3,300	2,612	0,383	11,861	-18008,855
2NPBI	-6,593	-2,818	6,593	2,818	3,775	1,887	0,530	4,706	-4,706	5,866	0,170	5,702	-22043,682
2APBI	-5,620	-1,355	5,620	1,355	4,265	2,133	0,469	3,487	-3,487	2,851	0,351	6,313	-18009,045
PBI	-6,281	-1,619	6,281	1,619	4,662	2,331	0,429	3,950	-3,950	3,346	0,299	1,734	-16510,766
4CPBI	-6,391	-1,785	6,391	1,785	4,606	2,303	0,434	4,088	-4,088	3,628	0,276	5,402	-28957,519
4MPBI	-6,133	-1,565	6,133	1,565	4,567	2,284	0,438	3,849	-3,849	3,244	0,308	0,297	-17574,226
4BPBI	-6,261	-1,731	6,261	1,731	4,530	2,265	0,442	3,996	-3,996	3,526	0,284	3,579	-86205,643
B3LYP/6-31g													
4NPBI	-6,601	-3,273	6,601	3,273	3,328	1,664	0,601	4,937	-4,937	7,324	0,137	11,136	-22160,860
4APBI	-5,421	-1,262	5,421	1,262	4,158	2,079	0,481	3,341	-3,341	2,685	0,372	11,164	-18104,077
2NPBI	-6,534	-2,835	6,534	2,835	3,699	1,849	0,541	4,684	-4,684	5,932	0,169	5,584	-22160,389
2APBI	-5,639	-1,381	5,639	1,381	4,258	2,129	0,470	3,510	-3,510	2,893	0,346	5,802	-18104,128
PBI	-6,202	-1,622	6,202	1,622	4,581	2,290	0,437	3,912	-3,912	3,341	0,299	1,437	-16598,127
4CPBI	-6,305	-1,773	6,305	1,773	4,532	2,266	0,441	4,039	-4,039	3,600	0,278	5,210	-29104,238
4MPBI	-6,046	-1,571	6,046	1,571	4,475	2,237	0,447	3,809	-3,809	3,242	0,308	0,679	-17667,162
4BPBI	-6,246	-1,755	6,246	1,755	4,491	2,246	0,445	4,000	-4,000	3,563	0,281	4,269	-86558,747
B3LYP/6-31++g													
4NPBI	-6,842	-3,731	6,842	3,731	3,111	1,556	0,643	5,286	-5,286	8,982	0,111	12,184	-22161,881
4APBI	-5,706	-1,608	5,706	1,608	4,098	2,049	0,488	3,657	-3,657	3,263	0,306	11,631	-18104,879
2NPBI	-6,834	-3,491	6,834	3,491	3,343	1,671	0,598	5,162	-5,162	7,972	0,125	6,520	-22161,520
2APBI	-5,908	-1,691	5,908	1,691	4,217	2,109	0,474	3,799	-3,799	3,423	0,292	6,113	-18104,858
PBI	-6,446	-1,927	6,446	1,927	4,519	2,259	0,443	4,186	-4,186	3,878	0,258	1,385	-16598,804
4CPBI	-6,522	-2,049	6,522	2,049	4,473	2,236	0,447	4,286	-4,286	4,106	0,244	5,005	-29104,924
4MPBI	-6,278	-1,877	6,278	1,877	4,401	2,200	0,454	4,078	-4,078	3,778	0,265	1,185	-17667,850
4BPBI	-6,477	-2,044	6,477	2,044	4,433	2,217	0,451	4,260	-4,260	4,094	0,244	4,225	-86560,265
B3LYP/Lanl2dz													
4NPBI	-6,801	-3,606	6,801	3,606	3,195	1,598	0,626	5,203	-5,203	8,473	0,118	11,813	-22163,791
4APBI	-5,648	-1,568	5,648	1,568	4,080	2,040	0,490	3,608	-3,608	3,191	0,313	11,672	-18105,916
2NPBI	-6,738	-3,263	6,738	3,263	3,475	1,738	0,575	5,000	-5,000	7,194	0,139	5,944	-22163,343
2APBI	-5,858	-1,668	5,858	1,668	4,189	2,095	0,477	3,763	-3,763	3,380	0,296	6,222	-18105,954
PBI	-6,408	-1,913	6,408	1,913	4,495	2,247	0,445	4,161	-4,161	3,851	0,260	1,520	-16599,610
4CPBI	-6,482	-2,037	6,482	2,037	4,444	2,222	0,450	4,259	-4,259	4,082	0,245	5,016	-16990,077
4MPBI	-6,240	-1,849	6,240	1,849	4,391	2,195	0,455	4,045	-4,045	3,726	0,268	0,921	-17668,733
4BPBI	-6,442	-2,039	6,442	2,039	4,403	2,202	0,454	4,241	-4,241	4,084	0,245	4,386	-16941,636

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

	E_{HOMO}	E_{LUMO}	I	A	ΔE	η	σ	χ	Pİ	ω	ε	dipol	Energy
HF/SDD													
4NPBI	-9,731	1,063	9,731	-1,063	10,793	5,397	0,185	4,334	-4,334	1,740	0,575	8,069	-22027,634
4APBI	-7,518	2,499	7,518	-2,499	10,017	5,009	0,200	2,509	-2,509	0,629	1,591	1,251	-17988,851
2NPBI	-9,606	0,988	9,606	-0,988	10,593	5,297	0,189	4,309	-4,309	1,753	0,570	5,060	-22026,633
2APBI	-7,286	2,280	7,286	-2,280	9,566	4,783	0,209	2,503	-2,503	0,655	1,527	5,928	-17987,967
PBI	-8,307	2,265	8,307	-2,265	10,572	5,286	0,189	3,021	-3,021	0,863	1,158	1,206	-16492,155
4CPBI	-9,140	0,209	9,140	-0,209	9,349	4,675	0,214	4,466	-4,466	2,133	0,469	4,423	-28979,512
4MPBI	-8,148	2,403	8,148	-2,403	10,552	5,276	0,190	2,872	-2,872	0,782	1,279	0,584	-17553,403
4BPBI	-9,059	2,072	9,059	-2,072	11,131	5,565	0,180	3,494	-3,494	1,097	0,912	4,188	-16834,371
HF/Cep-4g													
4NPBI	-11,048	-0,994	11,048	0,994	10,054	5,027	0,199	6,021	-6,021	3,606	0,277	7,817	-3662,891
4APBI	-8,991	1,491	8,991	-1,491	10,481	5,241	0,191	3,750	-3,750	1,342	0,745	0,917	-2849,671
2NPBI	-11,022	0,115	11,022	-0,115	11,136	5,568	0,180	5,453	-5,453	2,670	0,374	4,664	-3662,380
2APBI	-8,604	1,346	8,604	-1,346	9,951	4,975	0,201	3,629	-3,629	1,323	0,756	2,482	-2849,719
PBI	-10,075	1,128	10,075	-1,128	11,203	5,601	0,179	4,473	-4,473	1,786	0,560	1,478	-2573,138
4CPBI	-10,547	0,580	10,547	-0,580	11,127	5,564	0,180	4,984	-4,984	2,232	0,448	4,665	-2955,887
4MPBI	-9,973	1,282	9,973	-1,282	11,256	5,628	0,178	4,345	-4,345	1,678	0,596	0,721	-2751,804
4BPBI	-10,274	2,506	10,274	-2,506	12,780	6,390	0,156	3,884	-3,884	1,180	0,847	3,356	-2916,891
HF/3-21g													
4NPBI	-9,509	1,425	9,509	-1,425	10,934	5,467	0,183	4,042	-4,042	1,494	0,669	7,167	-21909,792
4APBI	-7,264	2,858	7,264	-2,858	10,122	5,061	0,198	2,203	-2,203	0,479	2,086	0,472	-17893,170
2NPBI	-9,416	1,386	9,416	-1,386	10,802	5,401	0,185	4,015	-4,015	1,492	0,670	4,741	-21908,839
2APBI	-7,310	2,611	7,310	-2,611	9,921	4,960	0,202	2,349	-2,349	0,556	1,798	1,916	-17893,832
PBI	-8,354	2,571	8,354	-2,571	10,925	5,462	0,183	2,892	-2,892	0,765	1,307	1,096	-16404,596
4CPBI	-8,659	2,177	8,659	-2,177	10,836	5,418	0,185	3,241	-3,241	0,969	1,032	4,153	-28832,859
4MPBI	-8,181	2,665	8,181	-2,665	10,845	5,423	0,184	2,758	-2,758	0,701	1,426	0,553	-17460,279
4BPBI	-8,490	2,259	8,490	-2,259	10,749	5,375	0,186	3,115	-3,115	0,903	1,108	3,201	-86052,485
HF/6-31g													
4NPBI	-9,507	1,349	9,507	-1,349	10,856	5,428	0,184	4,079	-4,079	1,533	0,652	7,884	-22024,747
4APBI	-7,504	3,068	7,504	-3,068	10,572	5,286	0,189	2,218	-2,218	0,465	2,150	1,393	-17987,154
2NPBI	-8,786	1,942	8,786	-1,942	10,727	5,364	0,186	3,422	-3,422	1,092	0,916	4,966	-22023,629
2APBI	-7,769	2,864	7,769	-2,864	10,633	5,316	0,188	2,453	-2,453	0,566	1,768	1,602	-17987,206
PBI	-8,150	2,601	8,150	-2,601	10,751	5,375	0,186	2,775	-2,775	0,716	1,396	1,157	-16490,647
4CPBI	-8,422	2,264	8,422	-2,264	10,686	5,343	0,187	3,079	-3,079	0,887	1,127	4,171	-28977,756
4MPBI	-7,993	2,697	7,993	-2,697	10,690	5,345	0,187	2,648	-2,648	0,656	1,524	0,608	-17551,797
4BPBI	-8,350	2,280	8,350	-2,280	10,630	5,315	0,188	3,035	-3,035	0,867	1,154	3,734	-86402,492
HF/6-31++g													
4NPBI	-9,086	0,216	9,086	-0,216	9,302	4,651	0,215	4,435	-4,435	2,114	0,473	8,026	-22024,899
4APBI	-7,524	1,058	7,524	-1,058	8,582	4,291	0,233	3,233	-3,233	1,218	0,821	0,384	-17988,099
2NPBI	-9,541	0,832	9,541	-0,832	10,373	5,186	0,193	4,355	-4,355	1,828	0,547	5,083	-22024,461
2APBI	-7,948	1,053	7,948	-1,053	9,001	4,501	0,222	3,447	-3,447	1,320	0,757	1,618	-17987,709
PBI	-8,323	1,056	8,323	-1,056	9,379	4,689	0,213	3,633	-3,633	1,408	0,710	1,159	-16491,100
4CPBI	-8,557	0,974	8,557	-0,974	9,531	4,766	0,210	3,792	-3,792	1,508	0,663	4,066	-28978,198
4MPBI	-8,155	1,084	8,155	-1,084	9,239	4,619	0,216	3,535	-3,535	1,353	0,739	0,536	-17552,232
4BPBI	-8,506	0,982	8,506	-0,982	9,489	4,744	0,211	3,762	-3,762	1,492	0,670	3,766	-86403,766
HF/Lanl2dz													
4NPBI	-9,686	0,357	9,686	-0,357	10,044	5,022	0,199	4,664	-4,664	2,166	0,462	8,602	-22027,001
4APBI	-7,512	2,501	7,512	-2,501	10,013	5,006	0,200	2,506	-2,506	0,627	1,595	1,248	-17988,792
2NPBI	-9,598	0,989	9,598	-0,989	10,587	5,293	0,189	4,305	-4,305	1,750	0,571	5,061	-22026,572
2APBI	-7,922	2,486	7,922	-2,486	10,407	5,204	0,192	2,718	-2,718	0,710	1,409	1,681	-17988,964
PBI	-8,306	2,262	8,306	-2,262	10,568	5,284	0,189	3,022	-3,022	0,864	1,157	1,210	-16492,099
4CPBI	-9,153	2,081	9,153	-2,081	11,233	5,617	0,178	3,536	-3,536	1,113	0,898	4,567	-16877,010
4MPBI	-8,143	2,404	8,143	-2,404	10,546	5,273	0,190	2,869	-2,869	0,781	1,281	0,587	-17553,340
4BPBI	-9,042	2,096	9,042	-2,096	11,138	5,569	0,180	3,473	-3,473	1,083	0,924	4,187	-16828,705

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

	E_{HOMO}	E_{LUMO}	I	A	ΔE	η	σ	χ	Pİ	ω	ε	dipol	Energy
HF/SDD													
4NPBI	-9,572	0,857	9,572	-0,857	10,428	5,214	0,192	4,358	-4,358	1,821	0,549	9,390	-22028,075
4APBI	-8,474	2,114	8,474	-2,114	10,587	5,294	0,189	3,180	-3,180	0,955	1,047	2,646	-17989,032
2NPBI	-9,607	0,626	9,607	-0,626	10,233	5,116	0,195	4,490	-4,490	1,970	0,508	6,386	-22027,146
2APBI	-8,186	2,262	8,186	-2,262	10,447	5,224	0,191	2,962	-2,962	0,840	1,191	2,161	-17989,338
PBI	-8,525	2,050	8,525	-2,050	10,576	5,288	0,189	3,237	-3,237	0,991	1,009	1,492	-16492,429
4CPBI	-8,633	1,922	8,633	-1,922	10,555	5,277	0,189	3,355	-3,355	1,067	0,937	4,965	-28979,199
4MPBI	-8,392	2,167	8,392	-2,167	10,559	5,279	0,189	3,112	-3,112	0,917	1,090	0,749	-17553,678
4BPBI	-8,596	1,864	8,596	-1,864	10,460	5,230	0,191	3,366	-3,366	1,083	0,923	4,650	-16834,047
HF/Cep-4g													
4NPBI	-11,038	-1,211	11,038	1,211	9,827	4,913	0,204	6,125	-6,125	3,817	0,262	8,804	-3663,269
4APBI	-8,517	1,842	8,517	-1,842	10,359	5,179	0,193	3,337	-3,337	1,075	0,930	19,751	-2847,722
2NPBI	-11,159	-0,967	11,159	0,967	10,192	5,096	0,196	6,063	-6,063	3,607	0,277	5,968	-3662,986
2APBI	-9,023	0,973	9,023	-0,973	9,996	4,998	0,200	4,025	-4,025	1,621	0,617	2,910	-2850,076
PBI	-10,381	0,826	10,381	-0,826	11,207	5,604	0,178	4,777	-4,777	2,036	0,491	1,638	-2573,449
4CPBI	-10,770	0,403	10,770	-0,403	11,173	5,587	0,179	5,184	-5,184	2,405	0,416	5,309	-2956,186
4MPBI	-10,326	0,937	10,326	-0,937	11,262	5,631	0,178	4,695	-4,695	1,957	0,511	0,767	-2752,114
4BPBI	-10,176	0,713	10,176	-0,713	10,888	5,444	0,184	4,732	-4,732	2,056	0,486	3,325	-2915,754
HF/3-21g													
4NPBI	-9,143	0,508	9,143	-0,508	9,651	4,826	0,207	4,318	-4,318	1,931	0,518	8,571	-21909,680
4APBI	-7,485	2,568	7,485	-2,568	10,053	5,027	0,199	2,458	-2,458	0,601	1,663	1,165	-17894,129
2NPBI	-9,442	1,506	9,442	-1,506	10,948	5,474	0,183	3,968	-3,968	1,438	0,695	5,566	-21909,660
2APBI	-8,609	3,072	8,609	-3,072	11,681	5,841	0,171	2,769	-2,769	0,656	1,524	3,304	-17893,970
PBI	-8,607	2,313	8,607	-2,313	10,920	5,460	0,183	3,147	-3,147	0,907	1,102	1,341	-16404,854
4CPBI	-8,796	2,030	8,796	-2,030	10,826	5,413	0,185	3,383	-3,383	1,057	0,946	5,007	-28833,117
4MPBI	-9,120	3,045	9,120	-3,045	12,165	6,082	0,164	3,037	-3,037	0,758	1,319	1,831	-17460,878
4BPBI	-8,664	2,083	8,664	-2,083	10,747	5,373	0,186	3,291	-3,291	1,008	0,992	3,817	-86052,729
HF/6-31g													
4NPBI	-8,831	0,336	8,831	-0,336	9,167	4,584	0,218	4,247	-4,247	1,968	0,508	9,396	-22024,616
4APBI	-7,350	2,192	7,350	-2,192	9,541	4,771	0,210	2,579	-2,579	0,697	1,435	13,029	-17986,720
2NPBI	-8,817	1,732	8,817	-1,732	10,549	5,274	0,190	3,542	-3,542	1,189	0,841	6,228	-22024,133
2APBI	-8,042	2,633	8,042	-2,633	10,675	5,337	0,187	2,704	-2,704	0,685	1,460	2,063	-17987,498
PBI	-8,373	2,377	8,373	-2,377	10,750	5,375	0,186	2,998	-2,998	0,836	1,196	1,445	-16490,898
4CPBI	-8,522	2,162	8,522	-2,162	10,684	5,342	0,187	3,180	-3,180	0,947	1,056	5,078	-28978,014
4MPBI	-8,241	2,455	8,241	-2,455	10,696	5,348	0,187	2,893	-2,893	0,782	1,278	0,783	-17552,044
4BPBI	-8,469	2,164	8,469	-2,164	10,633	5,316	0,188	3,152	-3,152	0,935	1,070	4,524	-86402,741
HF/6-31++g													
4NPBI	-8,942	-0,031	8,942	0,031	8,911	4,456	0,224	4,486	-4,486	2,259	0,443	9,556	-22025,334
4APBI	-7,956	1,127	7,956	-1,127	9,083	4,541	0,220	3,414	-3,414	1,283	0,779	1,791	-17988,068
2NPBI	-8,769	1,250	8,769	-1,250	10,018	5,009	0,200	3,760	-3,760	1,411	0,709	0,050	-5258,296
2APBI	-8,199	1,136	8,199	-1,136	9,335	4,667	0,214	3,532	-3,532	1,336	0,748	2,086	-17988,013
PBI	-8,522	1,118	8,522	-1,118	9,640	4,820	0,207	3,702	-3,702	1,422	0,703	1,465	-16491,364
4CPBI	-8,639	1,136	8,639	-1,136	9,775	4,888	0,205	3,751	-3,751	1,440	0,695	4,977	-28978,465
4MPBI	-8,384	1,137	8,384	-1,137	9,521	4,760	0,210	3,623	-3,623	1,379	0,725	0,731	-17552,497
4BPBI	-6,477	-2,044	6,477	2,044	4,433	2,217	0,451	4,260	-4,260	4,094	0,244	4,225	-86560,265
HF/Lanl2dz													
4NPBI	-9,464	0,170	9,464	-0,170	9,633	4,817	0,208	4,647	-4,647	2,242	0,446	10,080	-22027,451
4APBI	-7,719	2,243	7,719	-2,243	9,962	4,981	0,201	2,738	-2,738	0,753	1,329	0,565	-17989,775
2NPBI	-9,598	0,627	9,598	-0,627	10,225	5,112	0,196	4,486	-4,486	1,968	0,508	6,389	-22027,085
2APBI	-7,820	1,992	7,820	-1,992	9,812	4,906	0,204	2,914	-2,914	0,865	1,156	5,161	-17988,423
PBI	-8,518	2,053	8,518	-2,053	10,571	5,285	0,189	3,232	-3,232	0,988	1,012	1,495	-16492,373
4CPBI	-8,636	1,915	8,636	-1,915	10,551	5,276	0,190	3,360	-3,360	1,070	0,934	5,144	-16876,701
4MPBI	-8,384	2,170	8,384	-2,170	10,554	5,277	0,190	3,107	-3,107	0,915	1,093	0,752	-17553,614
4BPBI	-8,585	1,891	8,585	-1,891	10,475	5,238	0,191	3,347	-3,347	1,069	0,935	4,679	-16828,383

Chemical hardness [20,22-24] is the resistance to electron cloud polarization or deformation of chemical species.Chemical hardness is a very important parameter that is investigating a reactivity of molecules in both experimental and theoretical chemistry.Global softness, ΔE, and chemical hardness are related to each other.In the light of information of Koopman's theory [23], both chemical hardness value and global softness value are taken place HOMO and LUMO energy value. If the hard molecules have high HOMO-LUMO energy gap, this molecule is not a good corrosion inhibitor. This molecule can't very easy give electron of HOMO to metal. From the light of

the result given in table 1, 2, 3, and 4, we can see the corrosion inhibitor ranking of chemical hardness value as: 4NPBI > 4APBI > 2NPBI > 2APBI > 4BPBI > 4MPBI > 4CPBI > PBI in B3lyp method with sdd and lanl2dz.

The electronegativity value of molecules is a parameter that helps to compare the reactivity of molecules. Value of this parameter is given to predict the electron transfer between the metal and inhibitor. The molecule that has high electronegativity value, this molecule is hardly given the valances electron. Because these electrons are attracted more than other molecules by the nucleus. According to Sanderson's electronegativity equalization [24-25], we are work out the value of electrons transferred from corrosion inhibitor molecule by the following equation:

$$\Delta N_{max} = \frac{\chi_M - \chi_{inh}}{2(\eta_M + \eta_{inh})} \quad (10)$$

where χ_M and χ_{inh} are electronegativity of metal and inhibitor molecule, respectively. η_M and η_{inh} are chemical hardness of inhibitor molecule and metal, respectively.

In all parameter, we can write that 4NPBI is the best corrosion inhibitor more than another molecule. The activities of these molecules may be calculated using different programs [26-27].Moreover, a similar ranking was given in the experimental study managed by Dutta and his co-worker [1].

4. CONCLUSION

Benzimidazole derivatives were performed at Hartree-Fock and b3lyp with different basis set to investigate the corrosion inhibition activity.The result of quantum chemical parameters was shown that the corrosion inhibition efficiency ranking of these molecules can be givenas: 4NPBI > 4APBI > 2NPBI > 2APBI > 4BPBI > 4MPBI > 4CPBI > PBI in B3lyp method with sdd and lanl2dz.From the light of the result given in table 1, 2, 3, and 4, these molecules are very important towards rational design new benzimidazole derivate as corrosion inhibitor.

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