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Density Functional Theory Investigation of Electronic Structure of Benzimidazole Derivatives Using B3LYP and PBEPBE Functionals

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Abstract: *A systematic density functional theory (DFT) investigation was conducted on two pharmacologically significant benzimidazole derivatives: 2-(1H-benzo[d]imidazol-2-yl)-4-bromophenol (Compound 1) and 2-(1H- benzo[d]imidazol-2-yl)phenol (Compound 2). Quantum chemical calculations were performed employing the B3LYP and PBEPBE exchange-correlation functionals with the 6-311G basis set using Gaussian software. The energy gap (ΔE), frontier molecular orbital energies (HOMO and LUMO), chemical potential (μ), electronegativity (χ), electrophilicity index (ω), ionization potential (IP), chemical hardness (η), chemical softness (S), and energy gap were all systematically derived and compared. Results indicate that Compound 1 (the bromo-substituted derivative) exhibits a narrower HOMO–LUMO gap at the B3LYP/6-311G level (4.31 eV) compared to Compound 2 (4.82 eV), suggesting enhanced reactivity and polarizability conferred by the electron-withdrawing bromo substituent. PBEPBE/6-311G calculations yielded reduced gap values of 1.36 eV and 1.27 eV, respectively, consistent with the tendency of GGA functionals to underestimate energy gaps. These findings provide molecular-level insight into the electronic properties, charge transfer capability, and potential biological activity of these benzimidazole scaffolds.*

Keywords: Benzimidazole; DFT; B3LYP; PBEPBE; HOMO–LUMO; Reactivity Descriptors; Chemical Hardness

I. INTRODUCTION

Benzimidazole and its derivatives constitute one of the most pharmacologically versatile classes of heterocyclic compounds in medicinal chemistry. [1], [2]The bicyclic aromatic framework, comprising a fused benzene and imidazole ring, imparts a unique combination of electron-rich and electron-deficient sites, making benzimidazoles highly amenable to interactions with diverse biological macromolecules.[3], [4] Over the past few decades, benzimidazole scaffolds have been identified as key structural motifs in a broad spectrum of clinically approved drugs, including antiulcer agents (omeprazole, lansoprazole), antifungals, antiparasitics, antihypertensives, and anticancer compounds.[5], [6]. The introduction of substituents onto the benzimidazole core, such as phenolic hydroxyl groups and halogen atoms, significantly modulates the electronic distribution, frontier orbital energetics, and consequently the biological potency of these molecules.[1], [7] In particular, the phenol-benzimidazole hybrid — 2-(1H-benzo[d]imidazol-2-yl)phenol — has attracted considerable attention owing to its capacity for intramolecular proton transfer, photophysical properties, and biological activity [8]. The introduction of a bromine substituent at the para-position of the phenol ring introduces a strong electron-withdrawing inductive effect and considerable steric influence, further perturbing the molecular electronic landscape.[9], [10].

The quantum mechanical framework that provides the best combination of computing efficiency and predictive accuracy for studying molecular electrical structure computationally is density functional theory (DFT)[11]. For precise

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representation of ground-state geometries and frontier orbital features of organic molecules, the gold standard among density-functional theory (DFT) functionals is Becke's three-parameter hybrid functional paired with Lee-Yang-Parr correlation (B3LYP)[12], [13]. The pure generalized gradient approximation functional PBEPBE (Perdew-Burke-Ernzerhof) provides an important methodological benchmark, particularly relevant for systems requiring accurate electron density distributions.[14], [15] In his initial postulate, Fukui laid out the frontier molecular orbital (FMO) theory, which states that the HOMO and LUMO are the primary determinants of molecular reactivity[16]. Measurements of molecule kinetic stability, optical polarizability, and charge transfer capabilities are provided by the HOMO-LUMO energy gap (ΔE)[17]. The conceptual density-functional theory (DFT) framework also allows for the exact calculation of global reactivity descriptors, which together describe a molecule's tendency to donate or accept electron density, including chemical hardness (η), chemical softness (S), chemical potential (μ), electronegativity (χ), and electrophilicity index (ω)[18], [19].

The present study undertakes a comparative DFT analysis of two benzimidazole derivatives at the B3LYP/6-311G and PBEPBE/6-311G levels of theory[20]. The objectives are: (i) to compute and compare HOMO–LUMO energies and energy gaps; (ii) to derive global chemical reactivity descriptors; and (iii) to rationalize the influence of bromine substitution on electronic structure and reactivity.[21], [22]

II. COMPUTATIONAL METHODOLOGY

Using the Gaussian 09W software suite, all quantum chemical calculations were carried out. Using the hybrid B3LYP functional and the GGA-based PBEPBE functional in conjunction with the triple-zeta split-valence 6-311G basis set, full geometry optimization was carried out using ethanol as the solvent for both Compound 1 and Compound 2. The absence of imaginary vibrational frequencies upon frequency analysis revealed that the initial molecular geometries, which were built using standard bond parameters, were optimized to a minimum on the potential energy surface.

Upon geometry convergence, single-point energy calculations yielded the frontier molecular orbital energies. To get the HOMO and LUMO energies in electron-volts (eV), the Hartree atomic unit conversion factor was used, which is 1 Hartree = 27.2114 eV. The use of the Koopmans' theorem yielded global chemical reactivity descriptors.

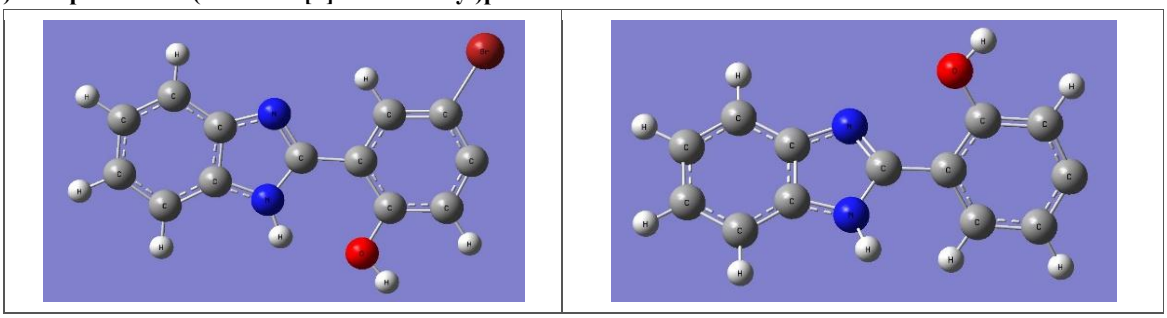
Using GaussView 6, plots of frontier orbital isosurfaces and molecular visualizations were created. All our calculations were carried out at 1 atm pressure and room temperature (298.15 K) using ethanol as the solvent.

III. RESULTS AND DISCUSSION

3.1 Molecular Structures and Optimized Geometries

The optimized molecular structures of the two benzimidazole derivatives are presented below. Compound 1, 2-(1H-benzo[d]imidazol-2-yl)-4-bromophenol, incorporates a bromine atom at the para-position of the phenol substituent. Compound 2, 2-(1H-benzo[d]imidazol-2-yl)phenol, retains only the phenolic hydroxyl group without halogenation. Both compounds share the core benzimidazolyl-phenol connectivity, enabling a controlled comparison of the halogen substitution effect.

Figure 1. Optimized molecular structures of (a) Compound 1: 2-(1H-benzo[d]imidazol-2-yl)-4-bromophenol and (b) Compound 2: 2-(1H-benzo[d]imidazol-2-yl)phenol at the B3LYP/6-311G level.



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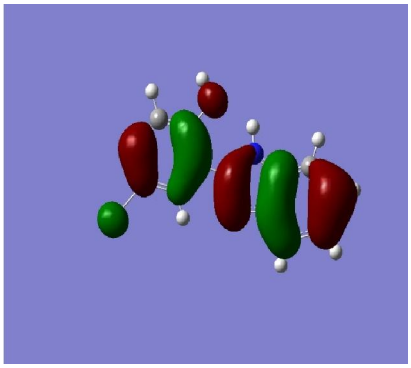
(a) Compound 1 2-(1H-benzo[d]imidazol-2-yl)-4-bromophenol	(b) Compound 2 2-(1H-benzo[d]imidazol-2-yl)phenol

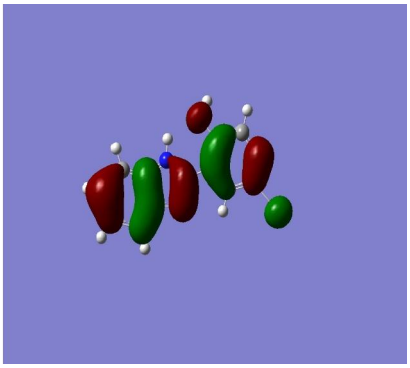
3.2 HOMO–LUMO Orbital Visualizations

The frontier molecular orbital isosurface plots computed at the B3LYP/6-311G and PBEPBE/6-311G levels are depicted in Figures 2 and 3, respectively. The spatial distribution of the HOMO and LUMO provides qualitative insight into the sites of electron donation and acceptance within each molecule.

Figure 2. HOMO–LUMO orbital isosurfaces of Compound 1 (2-(1H-benzo[d]imidazol-2-yl)-4-bromophenol). Left: B3LYP/6-311G. Right: PBEPBE/6-311G.

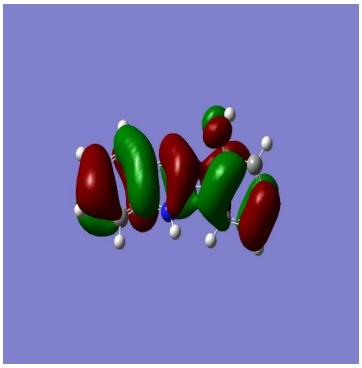


B3LYP/6-311G

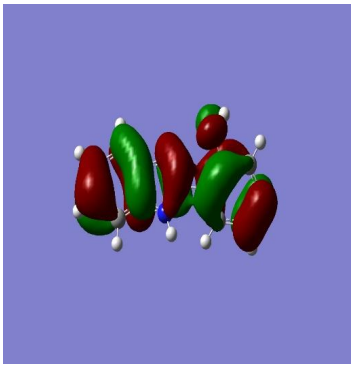


PBEPBE/6-311G

Figure 3. HOMO–LUMO orbital isosurfaces of Compound 2 (2-(1H-benzo[d]imidazol-2-yl)phenol). Left: B3LYP/6-311G. Right: PBEPBE/6-311G.



B3LYP/6-311G



PBEPBE/6-311G

In both compounds, the HOMO electron density is predominantly delocalized across the entire π-conjugated system, encompassing both the benzimidazole and the phenol rings, with notable electron density on the nitrogen atoms of the imidazole moiety. In Compound 1, the presence of the bromo substituent introduces a slight asymmetry in the HOMO distribution, reflecting the partial withdrawal of electron density from the ring system. The LUMO, in contrast, exhibits a more pronounced contribution from the electron-deficient benzimidazole ring and the carbonyl-adjacent region, consistent with the electrophilic character of this portion of the molecule. The PBEPBE orbital plots display qualitatively similar distributions but with subtly different contour shapes, reflecting the different electron density description inherent to GGA vs. hybrid functionals.

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3.3 HOMO–LUMO Energies and Energy Gap

In Table 1 we can see the frontier molecular orbital energies calculated for both compounds at the B3LYP/6-311G and PBEPBE/6-311G levels. Compound 1 has an energy gap of 4.3108 eV at the B3LYP/6-311G level, with a HOMO energy of -6.1286 eV and a LUMO value of -1.8177 eV. The second compound, which does not have the bromine substituent, has an energy gap of 4.8227 eV because its HOMO is slightly lower (-6.3092 eV) and its LUMO is greater (-1.4866 eV). Based on bromine's well-known electron-withdrawing properties, which stabilize the LUMO by reducing electron density through inductive effects, Compound 1's narrower gap allows for easier charge transfer and less kinetic stability compared to the unsubstituted analogue.

At the PBEPBE/6-311G level, both compounds exhibit markedly reduced energy gaps of 1.3551 eV and 1.2670 eV for Compounds 1 and 2, respectively. This systematic underestimation of the energy gap by GGA functionals relative to hybrid functionals is a well-documented characteristic arising from the self-interaction error and the absence of exact exchange in the functional. The PBEPBE gaps should thus be interpreted in a relative rather than absolute sense, confirming the same trend of Compound 1 possessing a narrower gap.

Table 1. HOMO and LUMO Energies (eV) and Energy Gap (ΔE, eV) of Benzimidazole Derivatives

Compound	HOMO (eV) B3LYP	LUMO (eV) B3LYP	ΔE (eV) B3LYP	ΔE (eV) PBEPBE
2-(1H-benzo[d]imidazol-2-yl)-4-bromophenol	–6.1286	–1.8177	4.3108	1.3551
2-(1H-benzo[d]imidazol-2-yl)phenol	–6.3092	–1.4866	4.8227	1.2670

Note: B3LYP values from B3LYP/6-311G; PBEPBE values from PBEPBE/6-311G calculations.

3.4 Global Chemical Reactivity Descriptors

Table 2 displays the worldwide chemical reactivity descriptors estimated using the B3LYP/6-311G program. Ionization potential (IP) is a measure of the energy needed to remove an electron from the hole-opening multiplication state (HOMO). Compound 2 displays a marginally higher IP (6.3092 eV) relative to Compound 1 (6.1286 eV), implying that the bromo-substituted compound donates electrons somewhat more readily. Conversely, the electron affinity (EA) of Compound 1 (1.8177 eV) is substantially greater than that of Compound 2 (1.4866 eV), confirming the enhanced electron-accepting ability conferred by the electronegative bromine substituent.

Chemical hardness (η) quantifies resistance to electron cloud deformation. Compound 2 is the harder species (η = 2.4113 eV) compared to Compound 1 (η = 2.1554 eV), consistent with its wider energy gap and greater thermodynamic stability. Chemical softness (S = 1/2η) follows the inverse trend: Compound 1 is the softer molecule (S = 0.2320 eV^{-1}), indicating greater polarizability and a tendency to engage in covalent interactions with soft biological targets. The electrophilicity index (ω) of Compound 1 (3.6619 eV) exceeds that of Compound 2 (3.1505 eV), indicating a greater propensity to accept electron density from nucleophilic biological partners.

Table 2. Global Chemical Reactivity Descriptors at B3LYP/6-311G Level (eV)

Descriptor	IP	EA	η	S	μ	χ	ω
2-(1H-benzo[d]imidazol-2-yl)-4-bromophenol	6.1286	1.8177	2.1554	0.2320	–3.9731	3.9731	3.6619
2-(1H-benzo[d]imidazol-2-yl)phenol	6.3092	1.4866	2.4113	0.2074	–3.8979	3.8979	3.1505

IP: ionization potential; EA: electron affinity; η: chemical hardness; S: chemical softness; μ: chemical potential; χ: electronegativity; ω: electrophilicity index.

Table 3. Global Chemical Reactivity Descriptors at PBEPBE/6-311G Level (eV)

Descriptor	IP	EA	η	S	μ	χ	ω
2-(1H-benzo[d]imidazol-2-	5.4923	4.1372	0.6776	0.7379	–4.8148	4.8148	17.107

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yl)-4-bromophenol							
2-(1H-benzo[d]imidazol-2-yl)phenol	5.4012	4.1342	0.6335	0.7893	–4.7677	4.7677	17.941

Note: Elevated ω values reflect the characteristic GGA underestimation of chemical hardness.

3.5 Influence of Bromine Substitution and Functional Comparison

The comparative analysis unambiguously reveals that bromine substitution at the para-position of the phenol ring exerts a multifaceted influence. The bromine atom, being a σ-withdrawing but π-donating substituent, engages in complex interaction with the aromatic system. The net effect manifests as: (i) a destabilization of the HOMO (–6.1286 vs. –6.3092 eV); (ii) a stabilization of the LUMO (–1.8177 vs. –1.4866 eV); and (iii) a reduced HOMO–LUMO gap (4.31 vs. 4.82 eV), collectively rendering Compound 1 a more reactive, more polarizable, and stronger electrophile. B3LYP/6-311G consistently predicts larger and more reliable energy gaps than PBEPBE/6-311G due to its partial Hartree-Fock exchange content, while both functionals confirm identical qualitative trends in reactivity.

IV. CONCLUSIONS

In this density-functional theory (DFT) investigation, two benzimidazole derivatives are thoroughly characterized quantum chemically utilizing the B3LYP and PBEPBE functionals on the 6-311G basis set. 2-(1H-benzo[d]imidazol-2-yl)-4-bromophenol possesses a narrower HOMO–LUMO energy gap (B3LYP: 4.31 eV; PBEPBE: 1.36 eV) compared to 2-(1H-benzo[d]imidazol-2-yl)phenol (B3LYP: 4.82 eV; PBEPBE: 1.27 eV), indicating higher chemical reactivity and polarizability of the bromo-substituted derivative. Bromine substitution elevates the HOMO energy, lowers the LUMO energy, reduces chemical hardness, and increases the electrophilicity index — effects attributable to the inductive electron-withdrawing character of the halogen substituent. Frontier molecular orbital visualizations confirm predominant HOMO delocalization across the π-system, with bromine-induced asymmetry in 2-(1H-benzo[d]imidazol-2-yl)-4-bromophenol, while LUMO density concentrates on the electron-deficient benzimidazole ring. The derived global reactivity descriptors provide a coherent, physically interpretable picture of differential reactivity, with implications for rational development of halogenated benzimidazole scaffolds as bioactive agents. These results lay a quantitative foundation for the further computational screening and rational molecular design of halogenated benzimidazole derivatives as candidates in drug discovery programmes.

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