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# Exploring the Geometric Configuration of N-(4-Bromobenzylidene)-2,3-dihydrobenzo[b][1,4]dioxin-6-amine by Density Functional Theory

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**Abstract:**

The accurate determination of molecular geometry is paramount in understanding the structure, reactivity, and properties of compounds in chemical research. This study focuses on N-(4-Bromobenzylidene)-2,3-dihydrobenzo[b][1,4]dioxin-6-amine (BBDDA), a compound of significant interest in medicinal chemistry and materials science due to its diverse pharmacological activities. Employing density functional theory (DFT), we optimized the geometry of BBDDA, revealing its three-dimensional arrangement of atoms and providing insights into its structural stability, electronic properties, and potential reactivity. The results showcased that BBDDA exhibits a promising range for light absorption and emission, suggesting applications in photonics and optoelectronic devices. Its narrow energy gap indicates stability and potential for catalytic reactions, while its capacity to both donate and accept electrons makes it suitable for redox processes. Moreover, non-covalent interaction analysis illustrated various intramolecular hydrogen bonds and intermolecular interactions, enhancing our understanding of BBDDA's behaviour. This research contributes to the growing body of knowledge in molecular structure analysis, with implications for diverse scientific and practical applications.

## 1. Introduction

The optimization of molecular geometry plays a fundamental role in the characterization and understanding of molecular structures, reactivity, and properties in the realm of chemical research [1-5]. Accurate determination of the three-dimensional arrangement of atoms within a molecule is pivotal for predicting its behavior and interactions in various chemical and biological contexts [6-10]. One class of compounds that has attracted significant interest due to its diverse pharmacological activities and potential applications in medicinal chemistry is N-(4-Bromobenzylidene)-2,3-dihydrobenzo[b][1,4]dioxin-6-amine [11].

This compound belongs to the family of dihydrobenzo[b][1,4]dioxin derivatives and features a substituted benzylidene moiety. The presence of a bromine atom and the unique structural scaffold confer distinct properties to this molecule, making it a subject of considerable research. Understanding the precise geometric arrangement

of atoms within N-(4-Bromobenzylidene)-2,3-dihydrobenzo[b][1,4]dioxin-6-amine is essential for elucidating its chemical reactivity, intermolecular interactions, and potential biological activities.

Density functional theory (DFT) is a widely used computational approach for geometry optimization, offering a reliable and efficient method for calculating the electronic structure and energetics of molecules [12-21]. In this context, the current study aims to employ DFT methods to optimize the geometry of N-(4-Bromobenzylidene)-2,3-dihydrobenzo[b][1,4]dioxin-6-amine. By doing so, we seek to unravel the precise spatial arrangement of its constituent atoms, gaining insights into its structural stability, electronic properties, and potential reactivity. Furthermore, the results of this research may shed light on the compound's potential applications in drug design, materials science, or other chemical disciplines.

This article outlines the computational methodologies, provides detailed results, and discusses the implications of the geometry optimization of N-(4-Bromobenzylidene)-2,3-dihydrobenzo[b][1,4]dioxin-6-amine, contributing to the growing body of knowledge in the field of molecular structure analysis and its broader scientific and practical implications.

## 2. Experimental section

We performed structural geometry optimization and subsequent energy calculations for N-(4-Bromobenzylidene)-2,3-dihydrobenzo[b][1,4]dioxin-6-amine (BBDDA) utilizing the density functional theory (DFT) with the 6-311++G(d,p) basis set within the Gaussian 09 software program [22]. In these DFT calculations, we employed a three-parameter hybrid function for the exchange component, complemented by the Lee-Yang-Parr (LYP) correlation function [23]. Subsequent to the geometry optimization, we conducted a comprehensive analysis of various molecular properties and characteristics. This analysis encompassed the determination of Kohn-Sham frontier molecular orbitals (FMOs), the computation of the molecular electrostatic potential (MEP), and an evaluation of the reduced density gradient (RDG), all of which were based on the optimized geometry. To gain insights into the electronic structure and reactivity of BBDDA, we estimated frontier molecular orbitals, their associated energy gap, and pertinent global reactive parameters using Koopman's approximation [24].

We also generated visual representations of the frontier molecular orbitals using GaussView 6.0 software [25]. In summation, our comprehensive approach, which melds theory with visualization tools, allows for a profound exploration of the electronic properties, reactivity, and structural aspects of BBDDA, shedding light on its potential applications and contributions to the field of chemistry.

We conducted Reduced Density Gradient (RDG) and Non-Covalent Interaction (NCI) analyses using the powerful computational tool Multiwfn 3.8 [35]. These analyses are essential for understanding the nature of non-covalent interactions in molecular systems. RDG analysis, in particular, provides insights into the distribution of electron density in the molecular system, offering valuable information about weak interactions, such as hydrogen bonds, van der Waals forces, and other non-covalent interactions. By analyzing the RDG, we can pinpoint regions of electron density concentration that are indicative of these interactions.

To further enhance our understanding of the results obtained from Multiwfn, we employed Visual Molecular Dynamics (VMD) software [36]. VMD is a versatile visualization tool, often used in molecular dynamics

simulations and structural biology. In our case, we utilized VMD to create visually intuitive representations of the non-covalent interactions revealed by the RDG analysis. This visualization allows us to directly observe and comprehend the spatial distribution of electron density associated with various non-covalent interactions within the molecular system.

## 3. Results and discussion

### *Geometry optimization and Frontier molecular orbitals*

Figure 1 and 2 vividly presents the ground state optimized geometry and the frontier molecular orbitals of the of the BBDDA. Figure 2 display the three-dimensional plots showcasing the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). These orbitals are marked by orange and green regions denoting positive and negative lobes, respectively. The color-coded segments effectively convey information about the electron-donating and electron-accepting traits of these orbitals. Analyzing the computed energies of the HOMO and LUMO provides insights into charge transfer within the molecule, aiding the assessment of its redox potential. Higher HOMO value and a lower LUMO value indicates its propensity to transfer its least tightly bound electron to suitable acceptor orbital of the molecule. HOMO of the BBDDA is localized predominantly over the entire molecule. whereas LUMO is distributed over the molecule except dioxin ring.

**Table 1:** Global chemical reactivity descriptors of BBDDA molecule.

| **Parameters** | **value** |
|---|---|
| EHOMO(eV) | -5.8627 |
| ELUMO(eV) | -0.1944 |
| Energy gap (ΔE) (eV) | 3.9144 |
| Ionisation potential (IP) (eV) | 5.8627 |
| Electrin affinity (EA) (eV) | 1.9445 |
| Electronegativity (χ) (eV) | 3.9036 |
| Chemical potential(μ) (eV) | -3.9036 |
| Global Hardness (η) (eV) | 1.9591 |
| Softness(σ) (eV-1) | 0.5104 |
| Electrophilicity index (ω) (eV) | 3.8891 |

Crucial global reactivity parameters, as outlined in table 1, encompass significant insights into the complex's reactivity. These parameters include the global electrophilicity index (ω), global hardness (η), chemical potential (ν), and global softness (s). Notably, the energy levels of EHOMO and ELUMO (-5.8627 eV and -0.1944 eV, respectively) suggest an optimal range for light absorption and emission, hinting at potential applications in photonics and optoelectronic devices. The relatively narrow energy gap (ΔE) of 3.9144 eV signifies the molecule's stability, which holds promise for catalytic reactions. The values of ionization potential (IP) and electron affinity (EA) indicate the molecule's capacity to both donate and accept electrons, a trait crucial for redox processes in catalysis. The global electrophilicity index (ω = 3.8891 eV) reflects the molecule's inclination to donate electrons, underlining its potential for active participation in chemical reactions, particularly pertinent in biological applications.

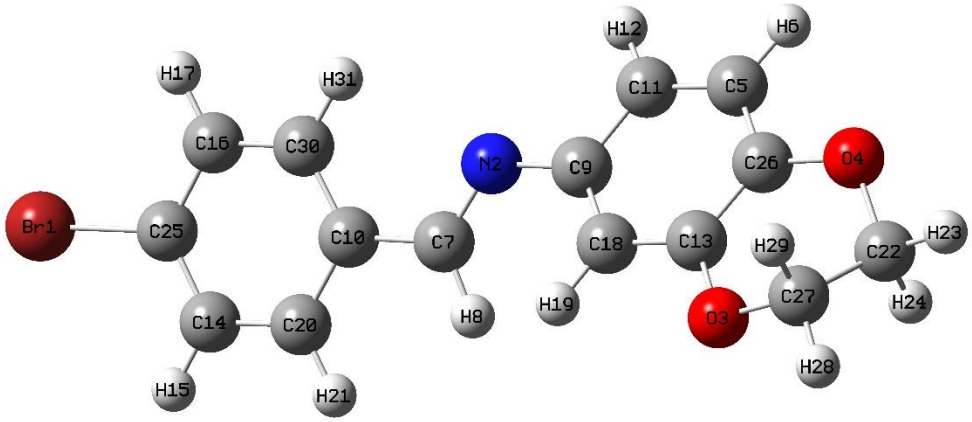


**Figure 1:** Ground state optimized three-dimensional geometrical structure of N-(4-Bromobenzylidene)-2,3-dihydrobenzo[b][1,4]dioxin-6-amine.

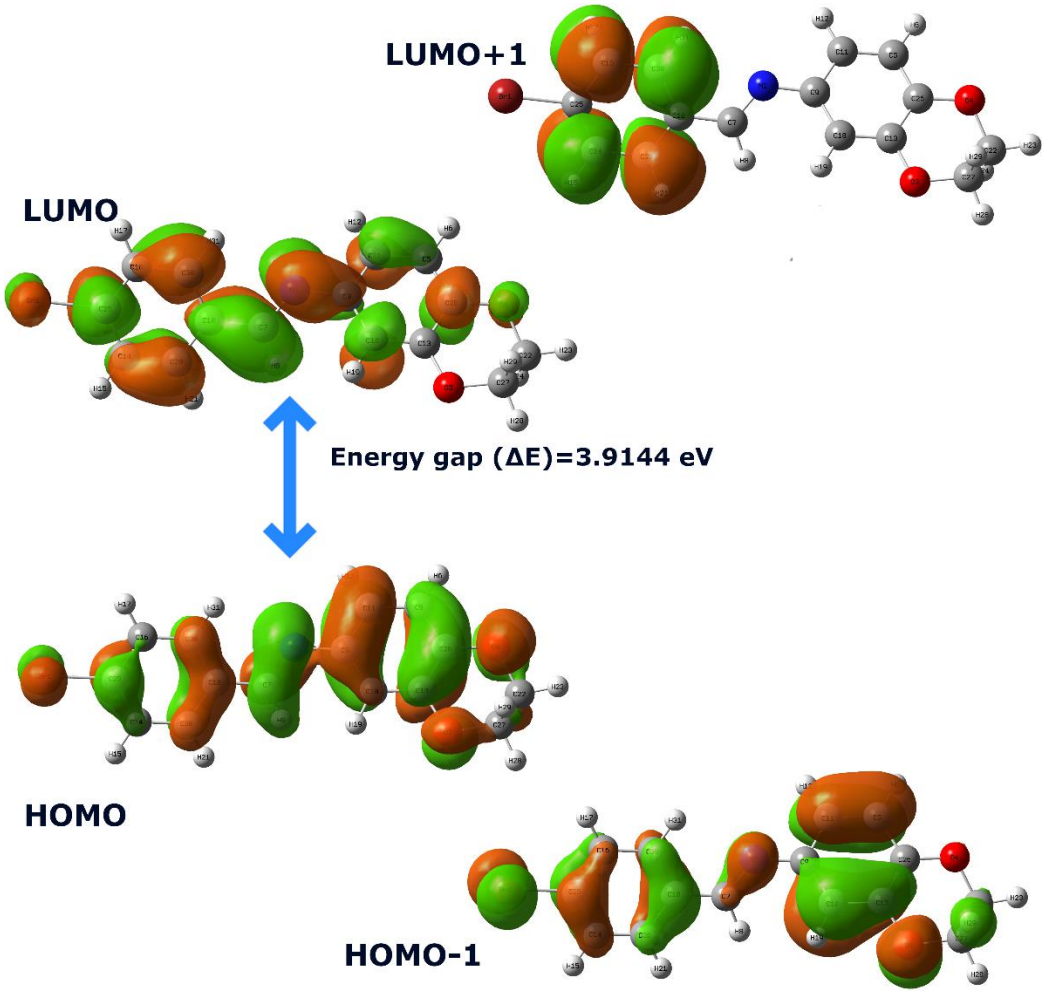


**Figure 2:** Three-dimensional plots of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) with their energy gap (a) and mMolecular electrostatic potential (b) of BBDDA molecule.

### *Molecular electrostatic potential*

In Figure 3, we are presented with a molecular electrostatic potential (MEP) plot showcasing the DDMP molecule. This plot is a valuable tool for comprehending electron density localization and interaction characteristics among molecules through a visual spectrum of colors. Consequently, the MEP map serves as a predictive tool for identifying reactive sites and potential hydrogen bonding within a molecular system, thereby enhancing our understanding of molecular interactions and reactivity. In this representation, red signifies regions of negative electrostatic potential, blue indicates areas of the most positive electrostatic potential, and green marks zones of neutral potential. Notably, the negative potential is notably concentrated

over specific sites such as the nitrogen (N2), the dioxin oxygen atoms (O3 and O4) and bromine atom. This concentration highlights these points as potential centers for electrophilic attacks. On the contrary, the blue shading over the dioxin hydrogen atoms designates them as centres for nucleophilic attack.

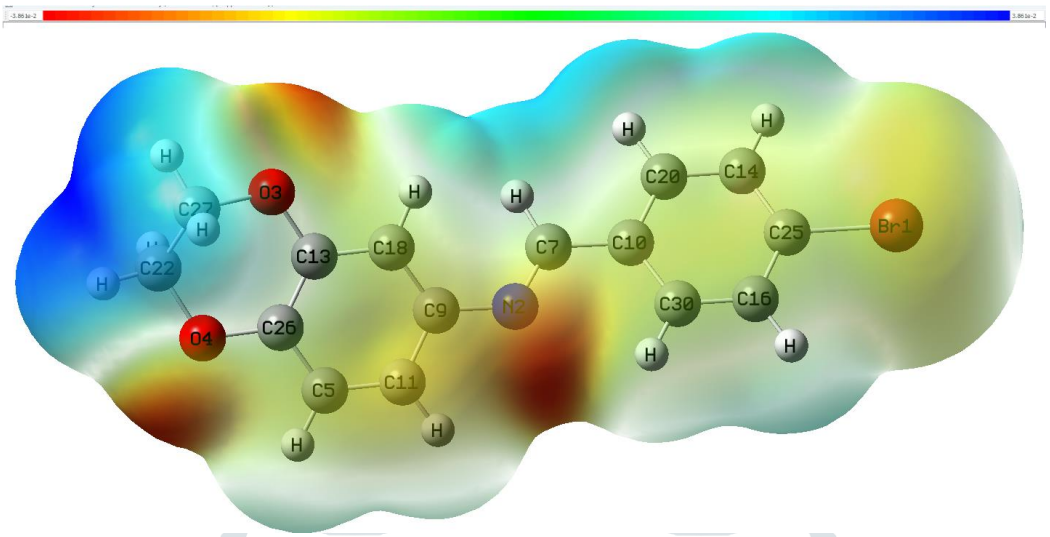


**Figure 3:** Molecular electrostatic potential plot of N-(4-Bromobenzylidene)-2,3-dihydrobenzo[b][1,4]dioxin-6-amine.

***Non-covalent interaction analysis***

NCI analysis was carried out to understand the nature of the intra and intermolecular interactions in which it predicts weak interactions in real space based on electron density. The NCI analysis consists of 3D isosurfaces and 2D reduced density gradient (RDG) graphs. The 2D-RDG graph and 3D isosurfaces of the NCI analysis for the BBDDA molecule are presented in figure 4.

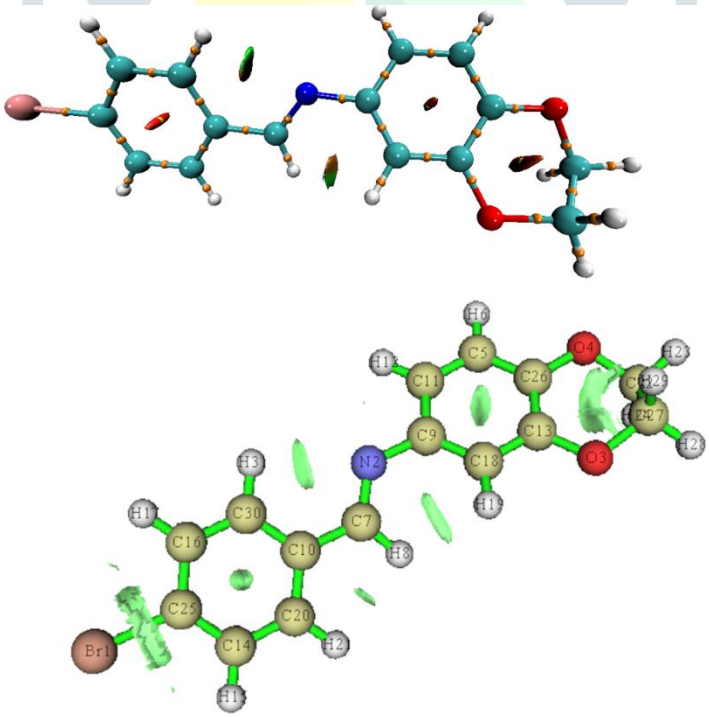


**Figure 4:** Intra molecular non-covalent interactions of BBDDA molecule obtained by NCI electron densities.

In Figure 4, the 3D isosurfaces effectively reveal intramolecular interactions by displaying distinctive green and red patches or discs. Notably, a green isosurface discs between N2 and H30 indicates the C30-H30…N2

intramolecular hydrogen bond interaction. The occurance of short interaction between H18 and H7, within the molecule, is vividly shown with red and green discs. Additionally, the presence of red cylindrical discs at the centers of the rings in indicates intermolecular C-H…π and π...π interactions.

## 4. Conclusion

In this study, we conducted a comprehensive investigation of N-(4-Bromobenzylidene)-2,3-dihydrobenzo[b][1,4]dioxin-6-amine (BBDDA), a compound with significant relevance in medicinal chemistry and materials science. Through density functional theory (DFT) calculations, we optimized the geometry of BBDDA, revealing its structural stability and electronic properties. The presence of a narrow energy gap suggests potential applications in light absorption and emission, as well as catalytic reactions. The molecule's capacity to donate and accept electrons, as indicated by its ionization potential and electron affinity, makes it suitable for redox processes.

Moreover, our non-covalent interaction analysis unveiled various intramolecular hydrogen bonds and intermolecular interactions, providing a deeper understanding of BBDDA's behavior. The visual representation of electron density localization, as well as predictive molecular electrostatic potential (MEP) maps, highlighted potential sites for electrophilic and nucleophilic attacks. This research contributes to the body of knowledge in molecular structure analysis and opens doors for potential applications in diverse fields, including drug design, materials science, and catalysis. The combination of DFT and non-covalent interaction analysis has enriched our understanding of BBDDA, shedding light on its potential in various chemical disciplines.

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