Traveling the Regular Shape of N-(4-Bromobenzylidene)-2,3-dihydrobenzo[b][1,4]dioxin6-amine by Compactness Handy Model

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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.

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.

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.

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].

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.

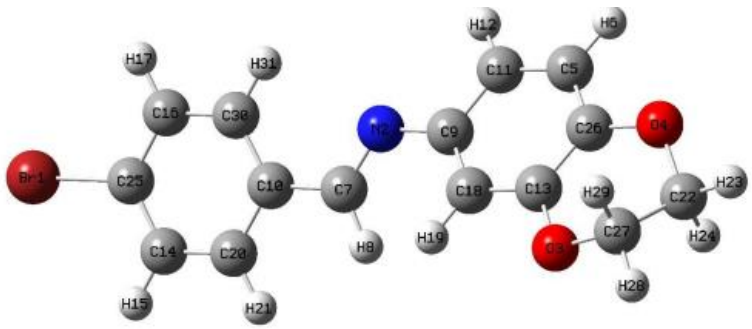
Results and discussion

Geometry optimization and Frontier molecular orbitals

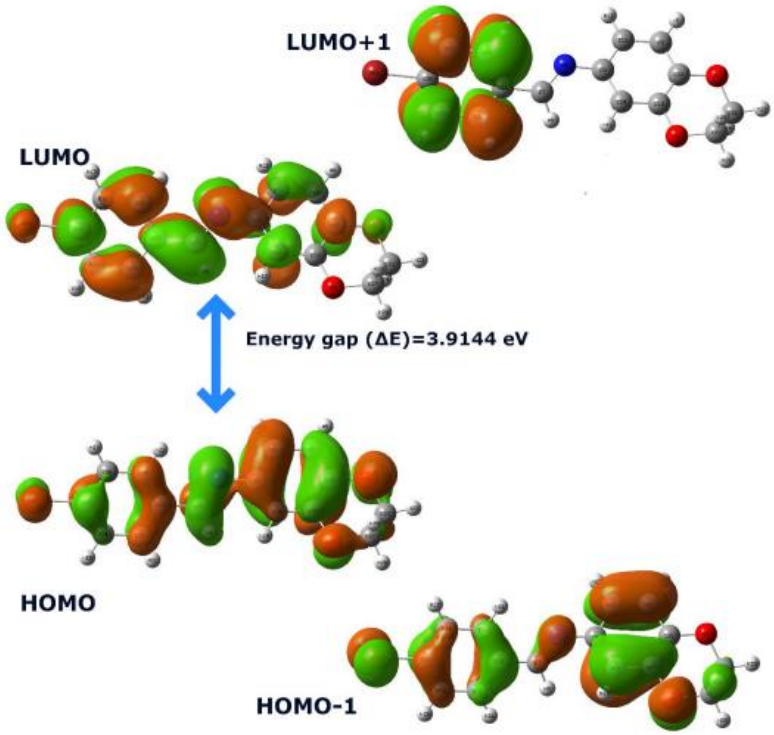
Figure vividly presents the ground state optimized geometry and the frontier molecular orbitals of the of the BBDDA. Figure display the three-dimensional plots showcasing the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). These orbitals are marked by orange 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.

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

Crucial global reactivity parameters, as outlined in table, 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 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.



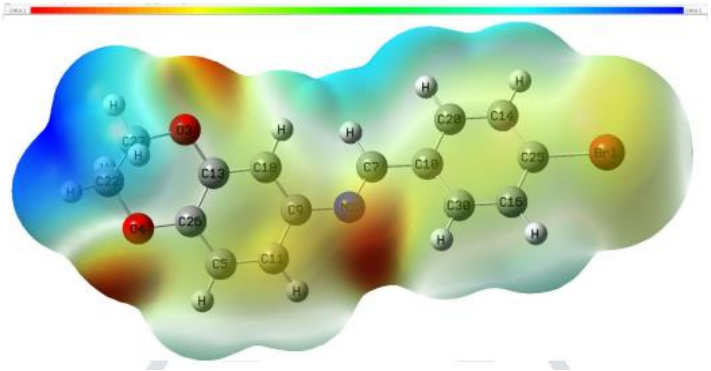
Ground state optimized three-dimensional geometrical structure of N-(4-Bromobenzylidene)-2,3-dihydrobenzo[b][1,4]dioxin-6-amine.



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.

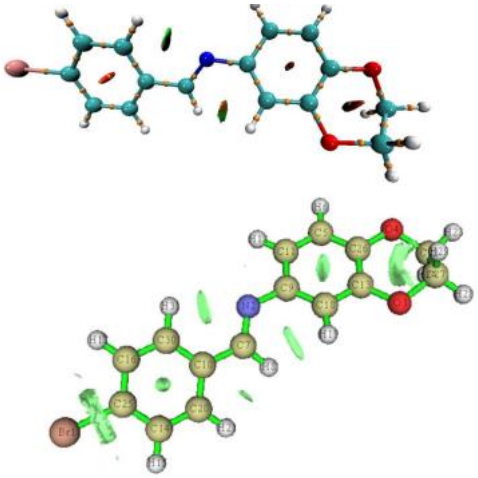
Molecular electrostatic potential

In Figure, 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. 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.



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 2D-RDG graph and 3D isosurfaces of the NCI analysis for the BBDDA molecule are presented in figure.



Intra molecular non-covalent interactions of BBDDA molecule obtained by NCI electron densities.

Conclusion

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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