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Theoretical Analysis of 1,4-Dioxane by Hartree-Fock and Density Functional Theory

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Abstract

1,4 dioxane is a very important organic solvent in both laboratory and industry at large due to its dissolving effect it has on many organic solvents. It also serves as a stabilizer in chlorinated solvents especially when organic synthesis is taking place. In this work, the dioxane compound is thoroughly analyze using computational calculations. The properties determined are spectroscopic properties which include nuclear magnetic resonance, ultraviolet spectroscopy and infrared spectroscopy. The energy between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is also analyzed.

Keywords: 1,4-Dioxane, Ultraviolet, NMR, Spectroscopy, Hartree-Fock, DFT

1. Introduction

Due to its unique property of being miscible and water and other organic solvents, 1,4-dioxane is a very imortant organic solvent in both laboratory and has many industrial applications[1-7]. One of its main property is dissolving many organic compounds [8-16]. It serves as a stabilizer in chlorinated solvents of organic synthesis and can be use as a replacement of glacial acetic acid [17-25]. It can be use as driver of Schenk equilibrium due to its reaction with Grignard reagent to precipitate the magnesium dihalide and its excellent chelating diether ligand [26-32].

This paper focuses on the analysis of the dioxane and improving its effectiveness through theoretical calculations of spectroscopic properties of the compound. The work concentrate on theoretical calculations of spectroscopic properties such as bandgap and electronic structure through structural optimization.

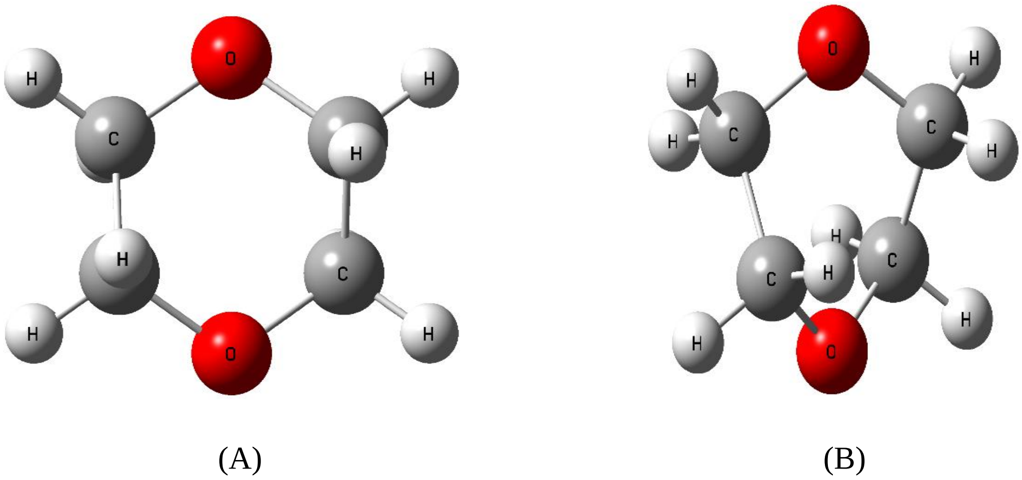
The ground state energy and geometry optimization is achieved by using trial and error between two method (Density functional theory and Hatree-Fock) and eight basis set. The molecular orientations were investigated using potential energy maps. To have an advance understanding of electrical and spectrocopic properties, UV-Visible, NMR, and FT-IR spectra were computed.

2. Methods

The density functional theory (DFT) was implemented in this work using Gaussian 09 software package. The molecular optimization of 1,4 dioxane is achieved using B3LYP functional together with the 6-311G basis in the DFT method [10-12]. The method has been used by many researchers to explain the geometries and bandgap energies of the complex covalent molecular systems [13-14]. Different basis set in both HF and DFT were exploited using trial and error to achieve the smallest energy possible (ground-state energy) for the rest of our calculation. It was found that the energy value for the 6-311G basis set is in agreement many research papers, which is the main incentive for the continuation for the rest of quantum mechanical calculations in this research. The ultraviolet spectroscopy (UV-VIS) was computed using the optimized structure. The Fourier transform infrared calculation was used to done using the optimized structure to achieve the minimum potential energy surface and at the end of calculations FT-IR results have been multiplied by a factor of 0.2. The optimized structure was also computed to calculate theoretical nuclear magnetic resonance (NMR) to determine the chemical shift when the doping took place. The three-dimensional plotting of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) was carried out using the same functional and basis set. The bandgap energy is also achieved from the 3-D plot of the HOMO and LUMO. The theoretical calculations in this work are carried out by Gaussian software package. The density of state (DOS) calculations has been achieved using the below equation

$$DOS(E) = \sum g(E - \varepsilon i) \tag{1}$$

here g is a function dependent on energy E and I, respectively. I is the energy levels of the calculated system which is a function of electronic orbitals.



(A) (B)

Figure 1. The geometry optimized structure of (A) 1,4-dioxane (B) side-view of dioxane

3 Result

In this paper, two methods (Hartree-Fock HF and density functional theory DFT) were tested with eight different basis set for the comprising of lowest ground-state energy and a suitable basis set for the remaining analysis. The analysis in this work includes the analysis of 1,2 dioxane through spectroscopic analysis such as ultraviolet (UV), Fourier transform spectroscopy (FT-IR), and nuclear magnetic resonance (NMR). Table 1 gives the values of the comparison between the methods. The calculation in this research were conducted using Gaussian 09 software program.

3.1 The molecular orbital

The titled compound 1,4-dioxane having twenty-five (25) molecular orbitals which can be used to analysed the bandgap and other important properties. The investigation of molecular orbital is very important because it explains the electrons distribution in the 1,4-dioxane molecule [37-40]. The orbitals in the molecule that are already occupied by the electrons are twenty-five (25). It can be seen from figure 3 that the highest occupied molecular orbitals (HOMO) resided on the portion of the ring while at the same time the lowest unoccupied molecular orbital (LUMO) totally resides and localised on the ring part. The energy difference between the HOMO and LUMO can be describe as the bandgap energy. To form a correlation between the chemical reaction and biochemical systems, the bandgap energy is used as a pointer. The bandgap energy of the titled molecule in this work is found to be 1.14 eV.

Table 1. The comparison of optimization of the basis set between Hartree-Fock and DFT

Basis Set	Hatree-Fock (eV)	DFT(eV)
STO-3G	0.42	1.37
3-21G	5.15	5.02
6-31G	5.15	5.05
6-31G*	5.16	5.05
6-311G	5.58	1.14
LanL2DZ	5.81	4.79
LanL2MB	0.315	1.37
SDD	5.815	4.76

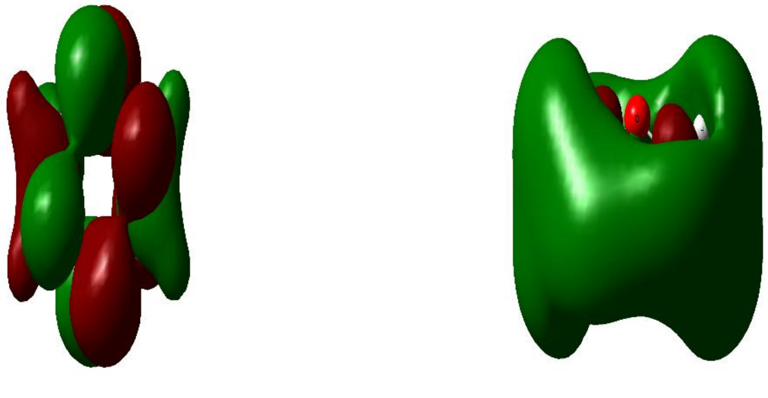

(A) (B)

Figure 2. The simulated (A) HOMO and (B) LUMO of 1,4-dioxane

3.2 Infrared spectroscopy (FT-IR)

This section of the research focuses on the vibrational frequencies in the 1,4-dioxane when analysed theoretically. The frequency calculations were done using Gaussian 09 with DFT method and 6-311G/B3LYP basis set. Later the Origin is used to plot IR after the IR was plot in Gaussian. In figure 5, the dioxane ring present can be investigated through C-C, C=C, C=O and C-H bond. In literature, the normal carbon hydrogen (C-H) stretching vibrations of dioxane occur at about 3000 cm^{-1} and moderate bands (multiplicity) can be present when compared to normal C-H stitching vibrations [16-18]. In these investigations, the modes of vibrational associated with C-H bond of dioxane is present at about 3900-3024 cm^{-1}. This indicates the accuracy of the selected basis set due to its agreement with the literature. The stretching vibrations of aliphatic C-H is about 3200 cm^{-1}. The C-O bond stretching occurs at around 790-810 cm^{-1}.

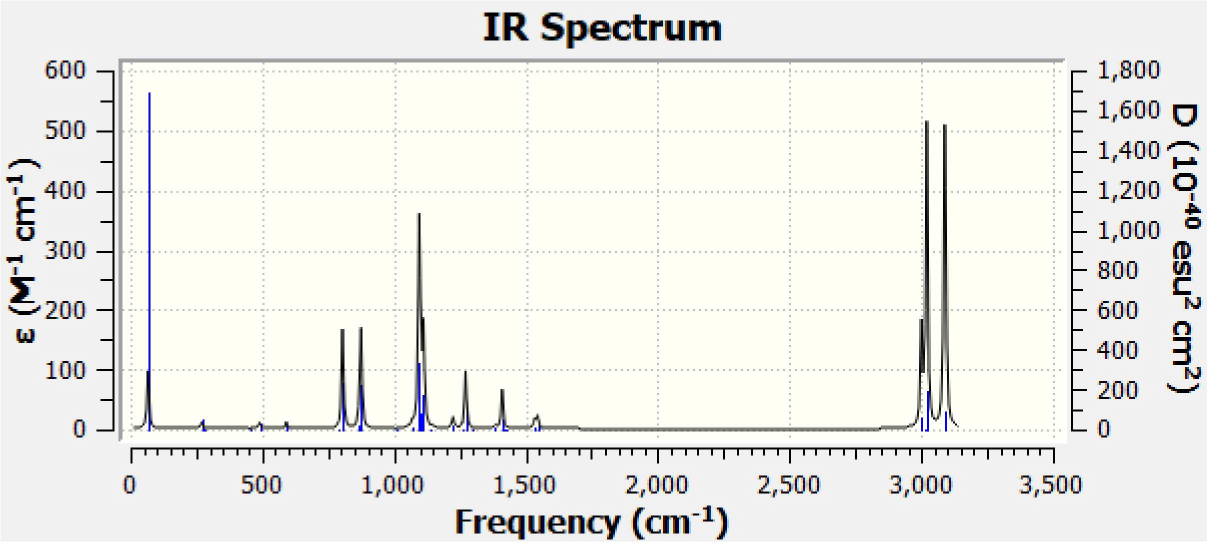


Figure 3. The simulated infrared spectra of 1,4-dioxane

3.3. Ultraviolet spectroscopy (UV)

Ultraviolet spectroscopy (UV-VIS) is another tool use in spectroscopy for the structure determination of complex molecules because it can measure the absorption. In this work, the UV-vis is implemented to measure the wavelength and the intensity of dioxane molecule. Table 2 shows a comprehensive data analysis of both the wavelength and intensity of the titled molecule. The titled molecule has a first absorption at around 155 nm. There is a second band at around 175 cm which may come from the higher excited states of the system (electrons migrating to other states of higher energy). Figure shows a clear a Picture of the two peaks that occur as a result of the first and second absorption.

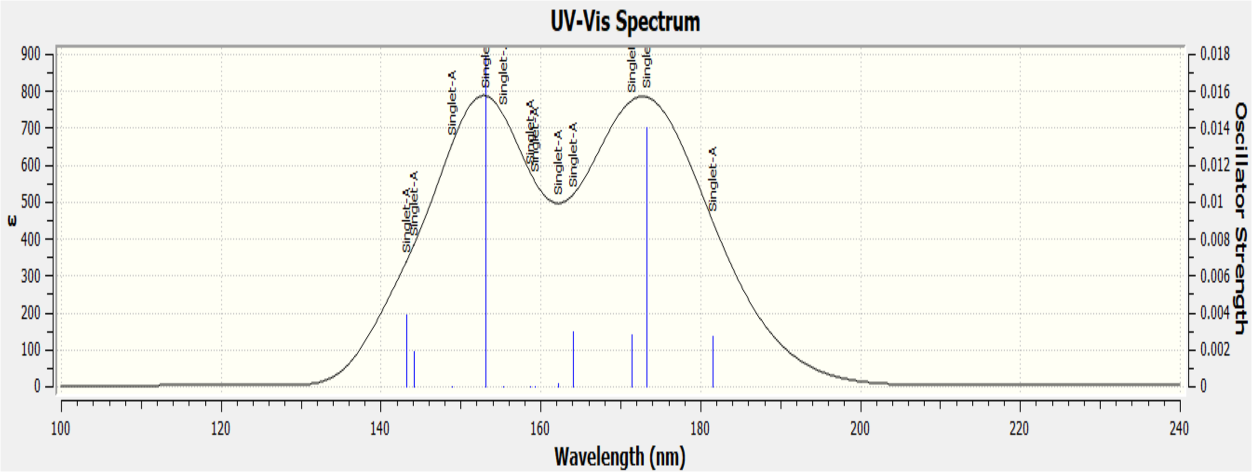


Figure 4. The simulated UV-visible absorbtion spectra of 1,4-dioxane

3.4. C-NMR

One of the methods for the determination of the structure of a chemical compound in the chemistry is nuclear magnetic resonance. The method is very efficient in showing the absorption peak, chemical environment and the shielding effect of a particular molecule. In this research the method was implemented to determine the proton and carbon absorption. The figures above show the absorption carbon and proton as well. There are four carbon atoms in the molecule and they all have absorption at the same chemical environment due to the fact that the titled molecule is symmetric molecule. All the four showed peak at around 121 ppm. The absorption is not the same with the proton. The four of the eight protons have peak around 28.6 ppm while the remaining four protons has absorption around 29.2 ppm.

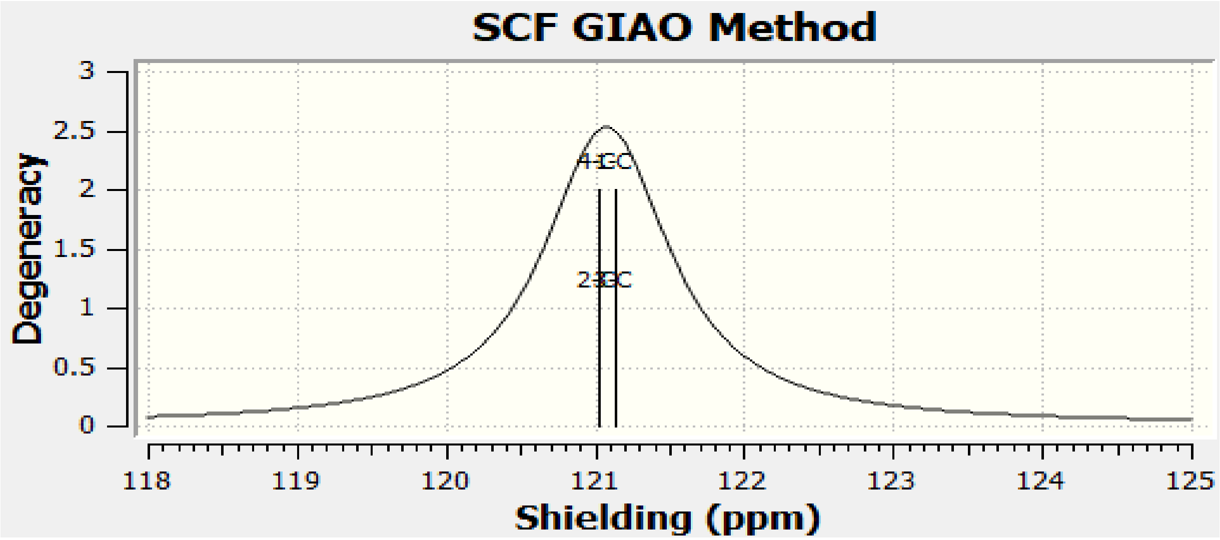


Figure 5. The simulated ^{13}C-NMR of dioxane

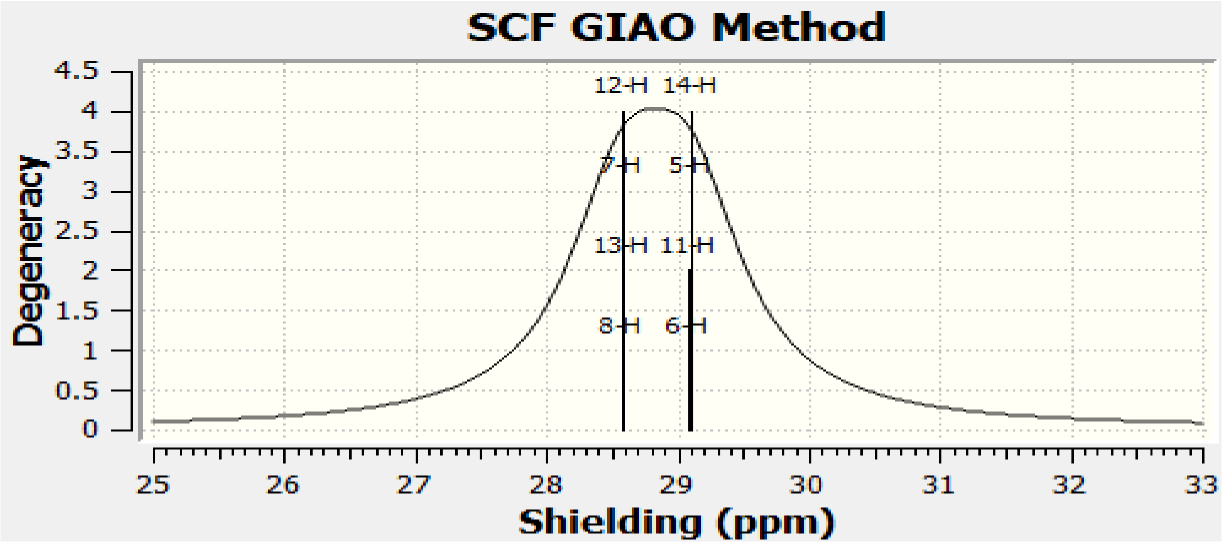


Figure 6. The simulated ^{1}H-NMR of dioxane

5. Conclusion

This work is directly focus on the analysis of dioxane due to its importance. The compound was designed and optimized by a strong computation method. The spectroscopic properties of the titled compound are then calculated. The properties calculated are bandgap energy, infrared spectroscopy, ultraviolet and nuclear magnetic resonance. The energy between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is also analysed. Both the two NMR (^{13}C-NMR and ^{1}H-NMR) that has been calculated gives result that are close to the literature which indicates the accuracy of the theoretical method and basis set use in the computation.

Contributions

All the authors have contributed equally.

Conflict of Interest Statement

Authors declare that they have no known conflict of interest.

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