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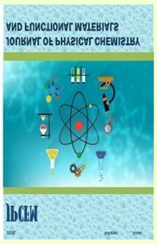

Investigation of Spectroscopic and Electronic Properties of 5-Bromo-1,2,3-Trimethoxybenzene Molecule

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ABSTRACT

In this thesis, the optimization of 5-Bromo-1,2,3-Trımethoxybenzene molecule was done by using the DFT method. After optimization, with the same basis set we have calculated Nuclear Magnetic Resonances (NMR) Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of the molecules that considered in this thesis. The 5-Bromo-1, 2, 3-Trımethoxybenzene compound which is considered here in this thesis was studied at B3LYP/6-311G (d) level. Fourier Transform Infrared (FTIR) calculations also have been done and our results were compared with the available data in literature.

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1. Introduction

This C9H11BrO3 molecular is not found in nature and is produced only experimentally. To a solution of 4 (1.91 g, 11.3 mmol) in dry CH2Cl2 (46 ml), triphenylphosphine (5.95 g, 22.6 mmol) was added at room temperature. After being stirred for 10 min, carbon tetrabromide (7.52 g, 22.6 mmol) was added at 2788C, and was stirred at 2508C for 80 min. The reaction mixture was treated with hexane – EtOAc mixture (20 ml) and passed through flash short column chromatog- raphy (EtOAc 300 ml). Concentration and flash column chromatography (hexane:EtOAc ¼ 20:1) gave product 5 (2.57 g, 11.1 mmol, 98%): white powder; C9H11BrO3, mp 73–758C; IR (KBr): nmax 3060, 3003, 2936, 2837, 1721, 1595, 1477, 1331, 1167, 1069, 941, 853, 822, 697, 646, 608, 526, 475 cm21; 1H NMR (300 MHz, CDCl3) d 6.54 (2H, d, J ¼ 2.4 Hz, Ar), 6.40 –6.39 (1H, t, J ¼ 2.4 Hz, Ar), 4.42 (2H, s, CH2Br), 3.80 (6H, s, OMe); 13C NMR (75 MHz, CDCl3) d 161.1, 139.9, 107.1, 100.8, 55.5, 33.8; EI-MS m/z 230 $[M]^+$ [1].

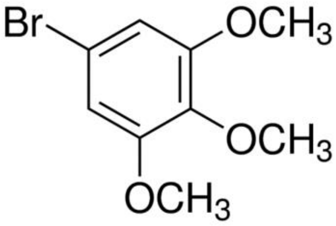

Figure 1. Molecular structure of 5-Bromo-1,2,3-Trimethoxybenzene compounds [2].

2. Calculation Method

The geometrical, spectroscopic and electronic properties of $C_9H_{11}BrO_3$ molecular have been investigated DFT at the B3LYP level. The B3LYP/6-311G(d) level has

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been in the calculations. The calculations have been performed using the GAUSSIAN09 program.

3. Results and Discussion

3.1. Optimized structure

Optimized structure of investigated compound was obtained to using at B3LYP/6-311G(d) level. The resulting optimized structures are given in Figure 2.

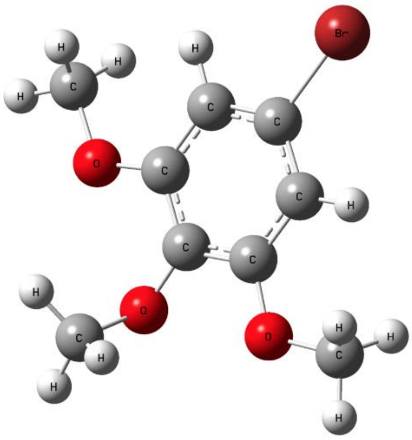

Figure 2. Optimized structure.

3.2. Frontier molecular orbitals

Since the majority of the energy gain in a reaction between two molecules is a result of the HOMO of a molecule that reacts with the LUMO of a second molecule, this interaction is called the Frontier Molecular Orbital (FMO) interaction. Therefore, a reaction is preferred when HOMO (nucleophile) is high in energy and LUMO (electrophile) is low energy. he HOMO and LUMO energies of the compounds studied in our study were given in Figure 3 and 4 to determine the active regions of molecules in electron exchange.

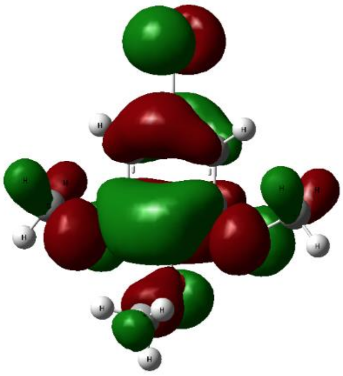

Figure 3. Frontier molecular orbitals of HOMO

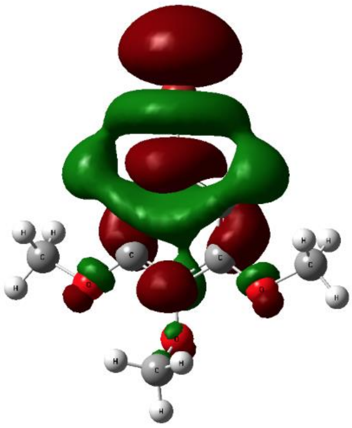

Figure 4. Frontier molecular orbitals of LUMO

4. Conclusion

In order to study the molecule, firstly the optimized geometry of the molecule was obtained. For the optimization, Hartree-Fock and Density function theory (DFT) were taken and tests were made for each method by considering the base sets in all possible cases. The results obtained from these tests are given in Table 4.1. Gaussian 09W program was used in all calculations. As a result of all optimization calculations, the energy gap of the studied molecule was calculated for each base and method. These calculated energy values are given in Table 1. The reason why different basis sets were used is that each basis sets involves different functionalities and characteristics. Table 1 shows the energy band gaps for the two methods of different basis sets. The geometry system of diphenhydramine at the B3LYP (DFT), 6-311G basis set has been chosen [3]. Also, the originlab program was performed for drawing the IR as in figure 8.

Table 1. The energy bandgap for different basis sets for both HF and DFT methods.

	E_G	
B. SETS	HF	DFT
STO-3G	13.40742eV	5.97485 eV
3-21G	12.29746eV	5.79960 eV
6-31G	12.18562eV	5.76042 eV
6-31G^{+}	12.18562eV	5.76042 eV
6-311G	11.99949eV	5.60314 eV
LANL2DZ	11.95868eV	5.64423 eV
LANL2MB	13.36742eV	4.93591 eV
SDD	11.30533eV	5.50354 eV

The energy gap available in the literature is 0.1223 eV for the 5-Bromo-1,2,3-trimethoxybenzene molecule. When looking at Table 1, the method and base set closest to this value 6-311G / DFT value was obtained.

4.1. C-C /C=C vibrations:

As shown in Figure 5, the molecule has five different chemical carbon atoms. As seen from the C-NMR spectrum, the C13 and C11 atoms have the highest chemical shift value. The C5 and C2 carbons also gave the highest chemical shift value in the electronegativity.

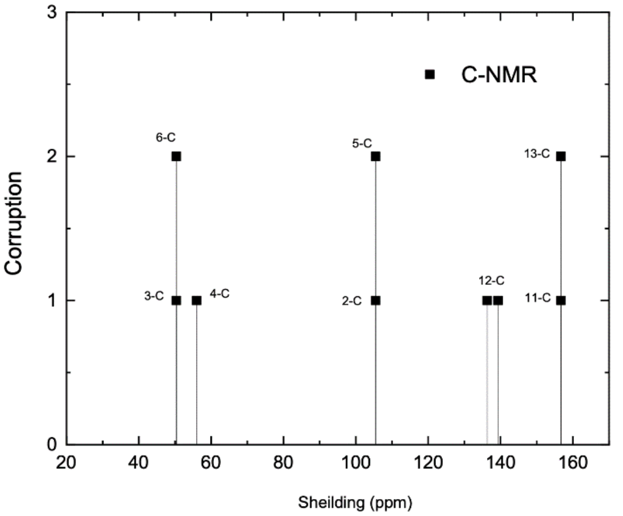

Figure 5. NMR spectrum for the C atom of the molecule

4.2. H-H vibrations

As shown in Figure 6, the molecule has three different chemical hydrogen atoms. As seen from the H-NMR spectrum, the atoms H24 and H23 have the highest chemical shift value. The H22 and H15 carbons also gave the highest chemical shift value with the highest electronegativity.

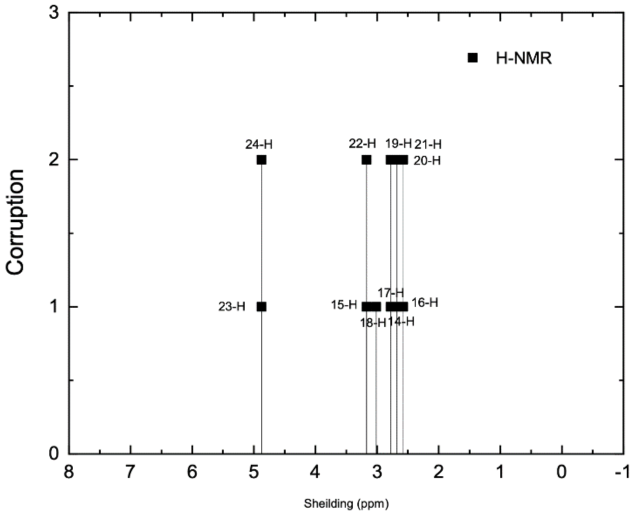

Figure 6. NMR spectrum for the H atom of the molecule

4.3. O-O vibrations

As seen in Figure 7, the molecule has two different chemical oxygen atoms. As can be seen from the O-NMR spectrum, the O10 and O8 atoms have the highest chemical shift value. O9 carbon also gave the highest chemical shift value of electronegativity.

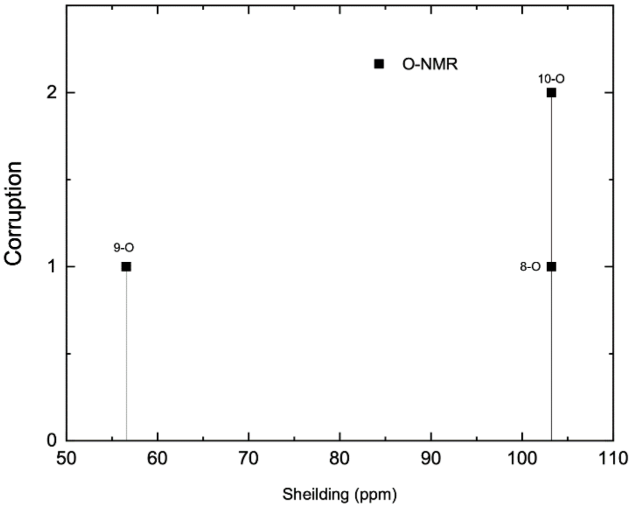

Figure 7. NMR spectrum for the O atom of the molecule

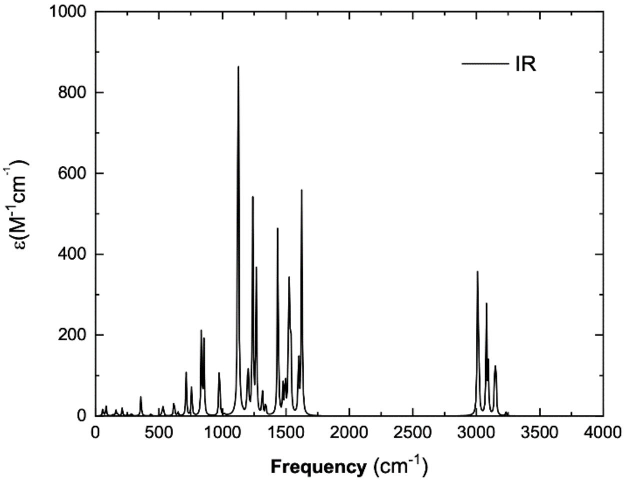

Figure 8. IR spectrum of the molecule

4.4. NMR analysis

In Figure 8, all vibration frequencies are positive when the molecule is in the basic state. In computational chemistry, the vibrational frequencies of molecules are calculated assuming that the vibrations are harmonic. Therefore, only the fundamental vibrational frequencies are obtained. By this factor, harmonic frequencies are multiplied and anharmonic frequencies are obtained. Each peak in Figure 8 corresponds to the vibration frequency between atoms in the molecule. The highest peak is that the molecules in the whole system vibrate in the direction of bond lengths and the peaks of 3000 cm^{-1} correspond to the C-H stretching mode. The magnitude of a peak intensity is directly proportional to the magnitude of the vibration mode of the molecule.

The ^{13}C NMR chemical shifts used to identify chemical compounds [4,5]. GIAO (Gauge Including Atomic Orbital) is the faster procedure to calculation upon the basis set used. A GIAO method was preferable for many aspects state of the subject [6]. Consequently, these are theoretically expected results of the molecule. In this work, all basis sets with both HF and DTF methods investigated to calculation bandgap energy for 5-Bromo-1,2,3-Trimethoxybenzene molecule. Proposed the better basis set is 6-311G according to the literature previous. The IR shows the vibration for all atoms that is good agreement with the kinds of literature. NMR has determined the identity of the molecular structure. The peaks of atoms in NMR were the relation with the types of references which was used on it. Molecular orbital energy diagrams (MOED), contour diagrams of leading orbitals [highest filled molecular orbital (HOMO) and lowest empty molecular orbitals (LUMO)], maps of molecular electrostatic potential (MEP), and electronic charges of atoms indicate electronic structures of molecules. Since most biological events occur in the water phase, it may be necessary to calculate the electronic structures in the water phase. Polarizable continuity model (PCM) is a widely used method for modeling solvent effects in computational chemistry. In this method, in order to facilitate the calculations, instead of considering each solvent molecule as a separate molecule, a continuous polarity is considered. There are two types of PCM methods. These are dielectric PCM (DPCM) and conductor like PCM (CPCM). In this study, aqueous phase calculations were performed by using CPCM method.

Acknowledgments

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Reference

[1] Tanakaa, A. Araia, Y. Kimb, Su-Nam. Hamb, J. Usukia, T. Synthesis and biological evaluation of bilobol and adipostatin A. Journal of Asian Natural Products Research. Vol. 13, No. 4, April 2011, 290–296.

[2]https://www.sigmaaldrich.com/catalog/product/aldrich/634530?lang=en&region=TR

[3] Smith DW, Peterson MR, DeBerard SC (August 1999). "Local anesthesia. Topical application, local infiltration, and field block". Postgraduate Medicine. 106 (2): 57–60, 64–6. doi:10.3810/pgm.1999.08.650. PMID 10456039.

[4] American Academy of Hospice and Palliative Medicine, "Five Things Physicians and Patients Should Question", Choosing Wisely: an initiative of the ABIM Foundation, American Academy of Hospice and Palliative Medicine, archived from the original on 1 September 2013, retrieved 1 August 2013, which cites.

[5] Subramanian, N., N. Sundaraganesan, and J. Jayabharathi, Molecular structure, spectroscopic (FT-IR, FT-Raman, NMR, UV) studies and first-order molecular hyperpolarizabilities of 1, 2-bis (3-methoxy-4-hydroxybenzylidene) hydrazine by density functional method. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2010. 76(2): p. 259-269.

[6] Smith TJ, Ritter JK, Poklis JL, Fletcher D, Coyne PJ, Dodson P, Parker G (May 2012). "ABH gel is not absorbed from the skin of normal volunteers". Journal of Pain and Symptom Management. 43 (5): 961–6. doi:10.1016/j.jpainsymman.2011.05.017. PMID 22560361.