

A Density Functional Theory Study of 4-OH Aldehydes [†]

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Abstract: According to certain theories, aldehydes play a significant role as precursor species in the creation of new atmospheric particles. In the current study, we first optimized the structure of the title compound by using the B3LYP 631-G (d, p) basic set. This compound's electrostatic potential, electrophilicity (ω), chemical potential (μ), chemical hardness (η), and maximum quantity of electronic charge transfer (Nmax) have all been carefully examined. The hyperconjugated electron interactions within the molecule that contribute to its stability were investigated using natural bond orbital analysis, in order to research the molecule's chemically active areas. Additionally, reactivity descriptors were determined. The moment of the electric dipole, initial static hyperpolarizability values, and polarizability have been studied for the title compound.

Keywords: 4-OH benzaldehyde; HOMO-LUMO; NLO; MESP

1. Introduction

The importance of benzaldehyde and its derivatives is highest in the food, cosmetics, chemical, and pharmaceutical sectors due to its many biological properties. Benzaldehyde and its derivatives are produced naturally, through a de novo process, from fruits and some fungi species [1]. The richest natural sources for the production of benzaldehyde and its derivatives are also peach leaf oil and cinnamon oil [2,3]. One of the benzaldehyde derivatives, which is mostly utilised as a flavouring ingredient in pharmaceuticals, foods, and drinks, is vanillin. Additionally, it contains psychotherapeutic qualities that were applied to the treatment of mental diseases [4]. Other aldehyde derivatives have been employed as tyrosinase inhibitors, antioxidants, and building blocks for the manufacture of coumarin and biocide polymers [5–8]. Bees sometimes escape from of honey supers using benzaldehydes [9]. Additionally, benzaldehyde derivatives have the ability to inhibit cytochrome P450 enzyme-dependent mono oxygenase and promote lipid peroxidation, both of which have anti-tumor effects [10].

One isomer of hydroxybenzaldehyde with the chemical formula C₇H₆O₂ is termed 4-formylphenol, also known as 4-hydroxybenzaldehyde. 4-hydroxybenzaldehyde is an aldehyde containing one hydroxyl group (-OH) in the para position of its structure. Several researchers have also looked into the structural and spectroscopic characteristics of various benzaldehyde derivatives [11–18]. However, no spectroscopic or structural studies of the 4-hydroxybenzaldehyde have been performed. Due to this, current research on the 4-hydroxybenzaldehyde has been focused on confirming its molecular structure through theoretical means.

2. Materials and Methods

Computational Details

All of the 4-hydroxybenzaldehyde quantum chemical calculations were carried out at the DFT/B3LYP level of theory [19–21] using the 6-31G(d,p) basis set and the Gaussian



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09W programme suite [22]. Gaussview 5.0 software [23] was used to determine optimized geometrical parameters, UV-spectra, and molecular electrostatic potential surfaces.

3. Results and Discussion

3.1. Optimized Structural Parameters

The optimized molecular geometry of 4-hydroxybenzaldehyde, including bond lengths and bond angles, was simulated at the DFT/B3LYP level of theory using the 6-31G(d,p) basis set. Figure 1 depicts the optimized molecular structure, while Table 1 lists the findings. The 4-OH benzaldehyde structure has C1 point group symmetry.

Table 1. Optimized table of 4-hydroxybenzaldehyde.

Bond Length (° Å)		Bond Angle (°)		Dihedral Angle (°)	
	B3LYP		B3LYP		B3LYP
C(1,2)	1.3843	A(2,1,6)	120.6882	D(6,1,2,3)	−0.0001
R(1,6)	1.4065	A(2,1,10)	121.0305	D(6,1,2,11)	−180.0001
R(1,10)	1.0853	A(6,1,10)	118.2813	D(10,1,2,3)	180.0
R(2,3)	1.405	A(1,2,3)	119.5664	D(10,1,2,11)	0.0
R(2,11)	1.0847	A(1,2,11)	121.745	D(2,1,6,5)	0.0001
R(3,4)	1.4015	A(3,2,11)	118.6886	D(2,1,6,7)	180.0001
R(3,8)	1.3593	A(2,3,4)	120.3802	D(10,1,6,5)	180.0
R(4,5)	1.3905	A(2,3,8)	117.0398	D(10,1,6,7)	0.0
R(4,12)	1.0877	A(4,3,8)	122.58	D(1,2,3,4)	0.0
R(5,6)	1.4006	A(3,4,5)	119.4648	D(1,2,3,8)	180.0
R(5,13)	1.0875	A(3,4,12)	119.98	D(11,2,3,4)	180.0001
R(6,7)	1.473	A(5,4,12)	120.5553	D(11,2,3,8)	0.0001
R(7,9)	1.218	A(4,5,6)	120.7194	D(2,3,4,5)	0.0
R(7,14)	1.1137	A(4,5,13)	119.7292	D(2,3,4,12)	180.0
R(8,15)	0.9667	A(6,5,13)	119.5514	D(8,3,4,5)	−180.0
		A(1,6,5)	119.181	D(8,3,4,12)	0.0
		A(1,6,7)	120.5982	D(2,3,8,15)	179.9998
		A(5,6,7)	120.2208	D(4,3,8,15)	−0.0002
		A(6,7,9)	124.8792	D(3,4,5,6)	0.0
		A(6,7,14)	114.4237	D(3,4,5,13)	−180.0
		A(9,7,14)	120.6971	D(12,4,5,6)	180.0
		A(3,8,15)	109.5344	D(12,4,5,13)	0.0
				D(4,5,6,1)	0.0
				D(4,5,6,7)	−180.0001
				D(13,5,6,1)	−180.0
				D(13,5,6,7)	0.0
				D(1,6,7,9)	−0.0006
				D(1,6,7,14)	180.001
				D(5,6,7,9)	−180.0006
				D(5,6,7,14)	0.001

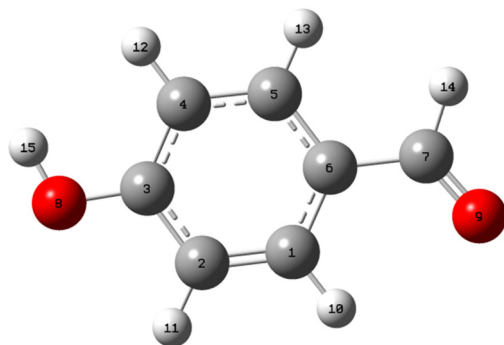


Figure 1. The optimized molecular structure of 4-hydroxybenzaldehyde.

3.2. Electronic Properties

For electronic spectrum studies in the UV-Vis range, 4-hydroxybenzaldehyde was dissolved in methanol. Theoretically, the TD-DFT approach with a B3LYP/6-31G(d,p) basis set was used for analysing the electronic spectrum. In Table 2, the major contributions of 4-hydroxybenzaldehyde are shown together with their wavelengths (λ), excitation energies (E), and oscillator strengths (f). Figure 2 depicts the predicted electronic spectra. Three bands were observed at 316.45 nm, 261.52 nm, and 256.48 nm in the theoretical electronic spectrum. Additionally, the HOMO and LUMO energy gaps were produced to assess the 4-hydroxybenzaldehyde chemical stability. In Figure 3, the HOMO and LUMO plots were displayed. According to Table 2, the HOMO-LUMO energy gap is predicted to be around 5.01 eV, and exhibits greater chemical stability. Positive phases are depicted in red in HOMO-LUMO plots, whereas negative phases are shown in green.

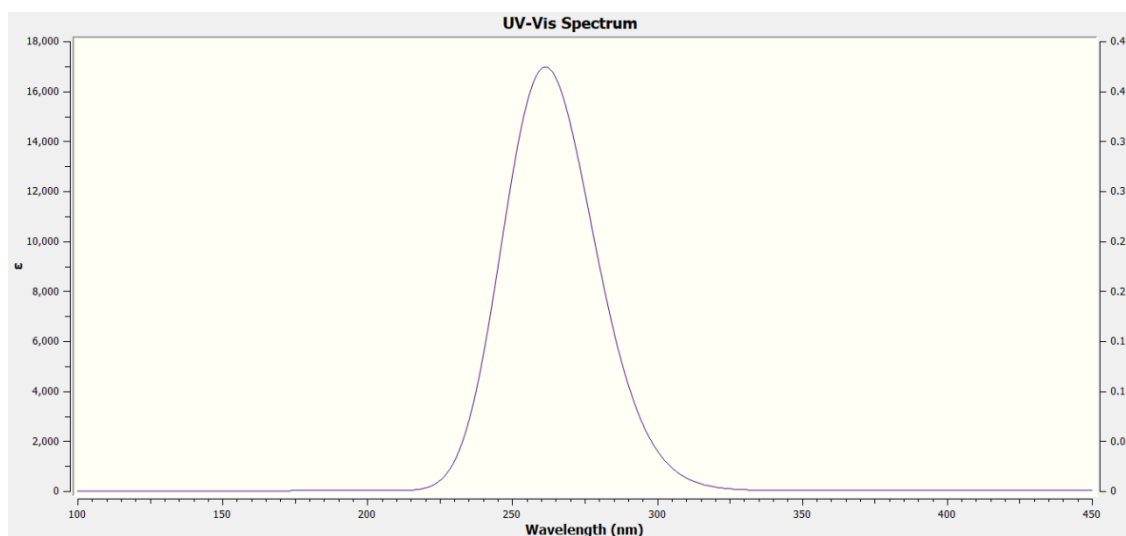


Figure 2. Theoretical electronic spectrum of 4-hydroxybenzaldehyde.

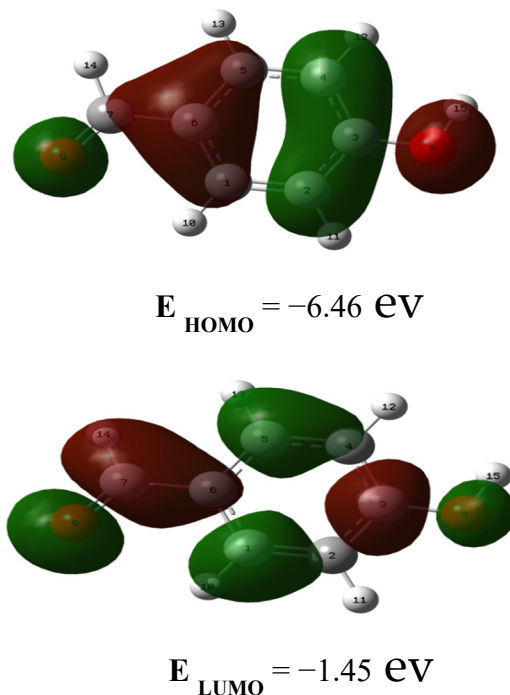


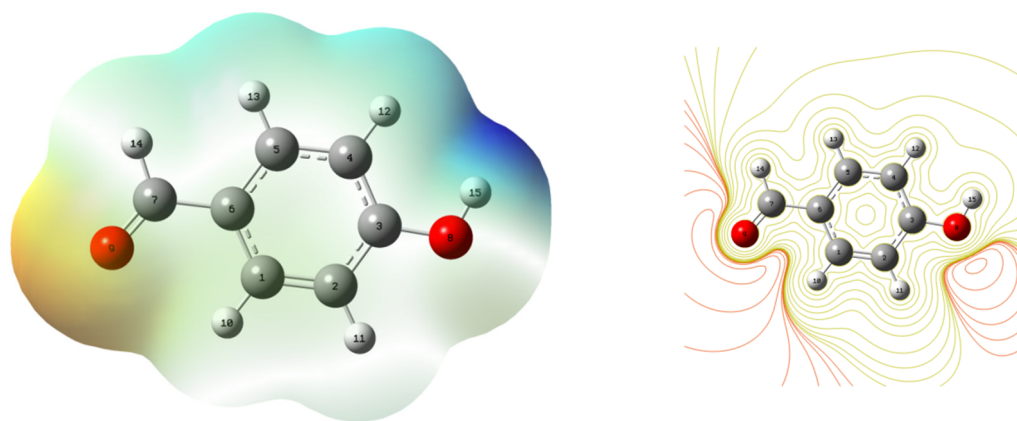
Figure 3. The HOMO-LUMO band gap plots of 4-hydroxybenzaldehyde.

Table 2. Calculated wavelengths (λ), excitation energies (E), and oscillator strengths (f) of 4-hydroxy benzaldehyde.

S. No.	Excitation	Energy (eV)	Wave Length (nm)	Oscillation Constant (f)
1.	HOMO-1-LUMO	3.9179 eV	316.45 nm	0.0001
2.	HOMO-LUMO	4.7408 eV	261.52 nm	0.4092
3.	HOMO-2 -> LUMO	4.8340 eV	256.48 nm	0.0061

3.3. Molecular Electrostatic Potential Surface

Nucleophilic and electrophilic areas have been identified using molecular electrostatic potential surfaces (MESP) [24]. In order to explain the changes in colour between the electron-rich and electron-poor regions, the molecular electrostatic potential surfaces (MESP) of 4-hydroxy benzaldehyde have been generated. The 4-hydroxybenzaldehyde has a colour code for MESP that maps between -7.673×10^{-2} and 7.673×10^{-2} a.u. Red denotes the highest electron repulsion, while blue denotes the strongest electron attraction in Figure 4. The resultant graphic shows that the hydrogen atoms, particularly the hydroxyl group hydrogens, are surrounded by electron-poor zones, which are denoted by blue colour mesh. Red colour mesh serves as an indicator that electron-rich areas are developing around the oxygen atoms of the carbonyl group.

**Figure 4.** Molecular electrostatic potential (MEP) surface analysis of 4-hydroxybenzaldehyde.

3.4. Global Reactivity Descriptors

The terms electronegativity (χ), global hardness (η), global softness (S), chemical potential (μ), and electrophilicity index (ω) are used to describe global reactivity. They are employed to calculate the chemical reactivity and site selectivity of the molecular systems, which were studied by DFT [25]. Accordingly, global reactivity descriptors are calculated based on Koopman's theorem [26] and supplied by the equations [27–29] presented below using the HOMO and LUMO energies [30].

$$IP = -\epsilon_{HOMO}, \quad (1)$$

$$EA = -\epsilon_{LUMO}, \quad (2)$$

$$\chi = -\frac{1}{2}(\epsilon_{LUMO} + \epsilon_{HOMO}), \quad (3)$$

$$\eta = \frac{1}{2}(\epsilon_{LUMO} - \epsilon_{HOMO}) \quad (4)$$

$$\mu = -\chi = \frac{1}{2}(\epsilon_{LUMO} + \epsilon_{HOMO}) \text{ and } \omega = \frac{\mu^2}{2\eta}. \quad (5)$$

$$(\Delta N_{\max}) = -\mu/\eta \quad (6)$$

According to Parr et al., the chemical potential and chemical hardness are comparable to the electrophilicity index [28]. The stability of the molecule is correlated with the hardness, which is represented by the difference between the HOMO and LUMO energies. Table 3 provides an overview of the theoretically determined HOMO, LUMO, energy gap, and global reactivity parameters of the selected molecule. Also measured was the electrophilicity index (ω), which measures the amount of energy reduction carried on by the maximal electron flow between acceptor and donor [31]. These variables are crucial in defining the system's stability and biological activity.

Table 3. Calculated chemical reactivity descriptors of 4-hydroxy benzaldehyde.

Compound Name	ϵ_H	ϵ_L	$\epsilon_L - \epsilon_H$	I	A	χ	η	μ	ω	δN_{\max}
4-OH benzaldehyde	−6.46	−1.45	5.01	6.46	1.45	3.955	2.505	−3.955	3.09	1.57

3.5. Nonlinear Optical Properties

Large first-order hyperpolarizabilities of molecules are a high potential component of non-linear optical (NLO) properties, which have a wide range of applications in engineering, physics, and chemistry. In the presence of an applied electric field, a molecule's hyperpolarizability, polarizability, and dipole moment are distinctive features [32–34].

The average linear polarizability (α_{tot}), the mean first-order hyperpolarizability (β_{tot}), and the total static dipole moment (μ_{tot}), using the x, y, and z components, are defined as follows:

$$\mu_{\text{tot}} = \left(\mu_x^2 + \mu_y^2 + \mu_z^2 \right)^{\frac{1}{2}} \quad (7)$$

$$\alpha_{\text{tot}} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (8)$$

$$\langle \beta \rangle = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyx} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzx} + \beta_{zxx} + \beta_{zyy})^2 \right]^{\frac{1}{2}} \quad (9)$$

Thus, in order to determine the NLO behaviour of the 4-OH benzaldehyde, the total molecule polarizability (α_{tot}), and its components, the total molecular dipole moment (μ_{tot}), and the first-order hyperpolarizability (β_{tot}) were computed. The results are shown in Table 4.

Table 4. Dipole moment (μ_{tot}), polarizability (α_{tot}), and hyperpolarizability (β_{tot}) of 4-hydroxybenzaldehyde.

Dipole Moment		Polarizability		Hyperpolarizability	
μ_x	3.7144	α_{xx}	121.266	β_{xxx}	702.65
μ_y	2.8260	α_{yy}	−1.689	β_{yyy}	108.85
μ_z	0.0721	α_{zz}	83.375	β_{zzz}	−50.65
μ	4.6678	α_{xy}	0.0024	β_{xyy}	45.83
		α_{xz}	−0.0010	β_{xxy}	−0.834
		α_{yz}	28.316	β_{xxz}	0.632
		α_0	67.65	β_{xzz}	−0.266
				β_{yzz}	−1.483
				β_{yyz}	0.965
				β_{xyz}	−0.0004
				β_0	757.35

It was found that the electronic dipole moment (μ_{tot}) value was 4.66 Debye. 4-hydroxybenzaldehyde's first hyperpolarizability value was determined to be 16.5181030 esu. The system's NLO feature is linked to intramolecular charge transfer, as indicated by the high value of hyper polarizability.

4. Conclusions

Spectroscopic methods have been used to explore the structural, and electronic features of 4-hydroxybenzaldehyde with the aid of quantum chemistry computer simulations. In order to analyse the chemical stability of 4-hydroxybenzaldehyde, HOMO-LUMO plots were used. MESP surfaces were used to identify the electron-poor and electron-rich locations. The computed small energy gap between HOMO and LUMO confirmed the charge transfer and showed that the compound has lower kinetic stability and is more chemically reactive, which makes it easier for the substance to be NLO active. The calculated first-order hyperpolarizability and dipole moment values further demonstrated the active NLO behaviour of the 4-OH benzaldehyde. From MEP analysis, the reactivity sites for electrophilic, nucleophilic, and radical attack have been identified.

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