Geometry optimization, FTIR, molecular electrostatic surface potential and fukui function of 3-hydroxy-4-methoxybenzaldehyde: A DFT study

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Abstract

The theoretical analyses of 3-hydroxy-4-methoxybenzaldehyde have been carried out using the density functional theory (DFT) based on B3LYP level at 6-311G(d, p) by Gaussian program. The molecular geometry shows good agreement with the experimental and theoretical bond lengths and bond angles. The atomic charges and vibrational wavenumbers of FTIR for 3-hydroxy-4-methoxybenzaldehyde were also calculated using the same basic set. The reactivity of a molecule was analysed using ionization potential (I), electron affinity (A), electronegativity (χ) chemical potential hardness (μ), global hardness (η), global softness (δ) and electrophilicity index (ω). The molecular electrostatic surface potential (MESP) and local reactivity descriptors (fukui functions) have undergone the same level of theoretical study for the title compound.

Keywords: Density Functional Theory, FTIR, Molecular Electrostatic Surface Potential and Fukui Function.

1. Introduction

The development of the functional organic materials is rapidly growing in the area of science to enhance the technological devices [1]. Single crystals of aromatic aldehyde shows excellent physicochemical and optical characteristics.. The grown 3-hydroxy-4-methoxy benzaldehyde, is an isomer of vanillin also known as isovanillin, its functional groups include aldehyde, hydroxyl and ether [2,3]. In the structure of the isovanillin the aldehyde and the methoxy groups are almost non-planar in nature. The theoretical calculations using density functional theory(DFT) methods with B3LYP combined with standard 6-311G(d,p) basic set have been performed to search for investigating the chemical reactivity and structural properties of 3-hydroxy-4-methoxy benzaldehyde molecule. In the present study, the optimization of the molecular structure was calculated using B3LYP exchange correlation functional. The vibrational spectral studies have been analysed on the basis of calculated potential energy distribution (PED) [4]. The intramolecular interactions of a molecule are determined by the Molecular electrostatic Surface Potential (MESP). The electrophilic and nucleophilic properties of a compound are revealed by a Fukui function.

2. Computational Techniques

The quantum chemical calculation was performed by the DFT method with the Becke's three parameter hybrid functional (B3) for the exchange part and the Lee-Yang-Parr (LYP) [5] correlation function with a 6–311G(d,p) basis set using the Gaussian 09 W program [6]. Using B3LYP 6-311G(d,p) level of theory, the optimal shape and vibrational wavenumbers of FTIR are calculated in the gas phase. Using Gaussian software, the global reactivity descriptors of the growing crystal are computed. Using the theoretical tool UCA-FUKUI, the condensed Fukui function and related local and global parameters are calculated to understand the chemical reactivity [7].

3. Result and Discussion

3.1 Molecular geometry

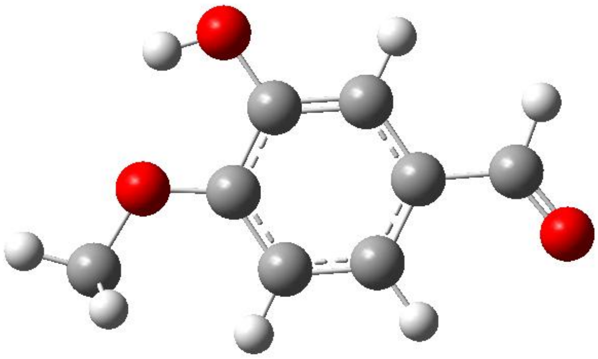

Fig. 1 Optimized structure using B3LYP/6-311G(d,p) of 3-hydroxy-4-methoxybenzaldehyde

The optimized structural parameters like bond lengths, bond angles, and torsional angles of 3-hydroxy-4-methoxybenzaldehyde were calculated by using the DFT method with B3LYP/6-311G(d,p) level of theory. The optimized structure of the compound was shown in Fig. 1 and the theoretical data's along with the experimental values are listed in Table 1. The bond length C_{12}-H_{13} in the phenyl ring is increased when compared to other C-H bonds due to the influence of steric effect. The bond angle C_6-C_7-C_9 is also decreases due to the presence of steric effect and the attachment of methoxy group. The dihedral angle H_2-C_4-O_5-C_6 shows the compound is in non-planar nature.

Table 1

Optimized geometry of 3-hydroxy-4-methoxybenzaldehyde at B3LYP/6-311G(d,p) level

Parameters	Experimental values (Å)	Calculated Values (Å)
C_{12}-H_{13}	0.93	1.084
C_6-C_7-C_9	120.4(13)	119.6
H_2-C_4-O_5-C_6	59.8	61.1

3.2 Natural Charge Analysis

Natural charge analysis has been calculated by using B3LYP/6-311G(d,p) level of theory. The calculated natural atomic charges are shown in Fig.2. The largest negative charge occurs at O_{15} atom and the highest positive charge occurs at H_{16} atom, which is due to the possibility of intramolecular O_{15}-H_{16}...O_5 hydrogen bonding. Among the benzene ring, the carbon atoms of C_6 and C_{14} shows positive charge and all other carbon atoms show negative charge. The other two atoms such as O_5 and O_{19} have a negative charge of -0.55 and -0.53e.

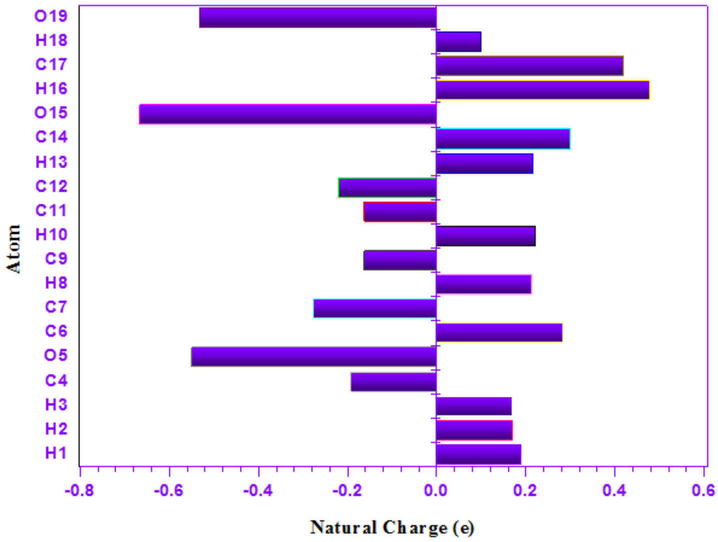

Fig. 2 Natural charge plot of 3-hydroxy-4-methoxybenzaldehyde

3.3 FTIR analysis

The absorption spectral bands recorded in FTIR was shown in Fig. 3, having different functional groups present in a material can be identified using vibrational spectroscopy. The OH stretching vibration is expected in the region between 3500-3300 cm^{-1} [8] which is observed in FTIR at 3578cm^{-1}. This change occurs due to intramolecular O-H...O hydrogen bonding. The C-H stretching vibrations normally lie between 3100 and 3000 cm^{-1}[9]. The peak observed in FTIR at 3040cm^{-1}. The aldehyde group of H-C=O stretching vibration is expected in the range of 2830–2695 cm-1. In the present study it is observed at 2763 cm^{-1}. The carbonyl C=O stretching vibration in aldehyde is expected in the region of 1740–1720 cm^{-1}. In 3-hydroxy-4-methoxybenzaldehyde C=O stretching vibration occurs at 1740 cm^{-1}.

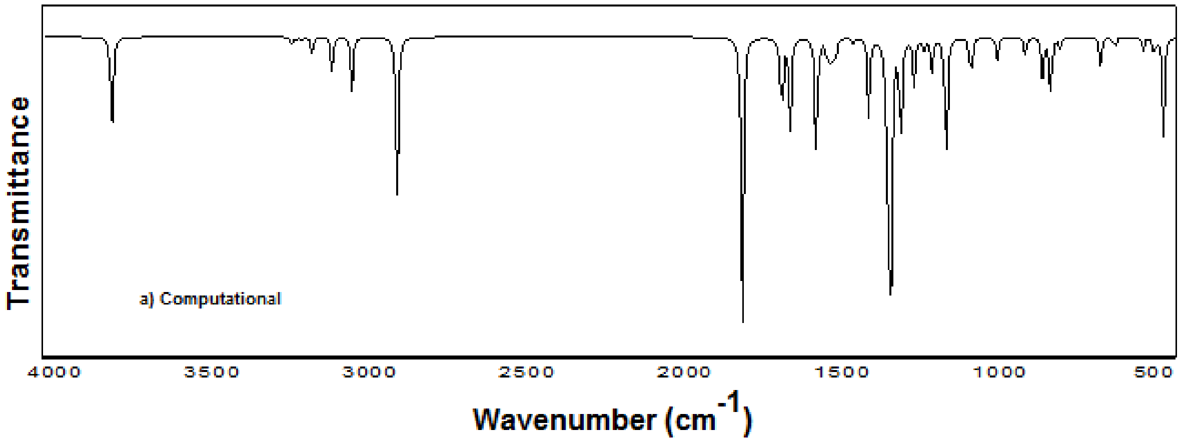

Fig. 3 FTIR Spectrum of 3-hydroxy-4-methoxybenzaldehyde

3.4 Global reactivity descriptors

From the geometrical parameters the molecular orbitals such as highest occupied molecular orbital energy (E_{HOMO}) and the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (E_{HOMO}-E_{LUMO}), ionization potential (I), electron affinity (A), electronegativity (χ) chemical potential hardness (μ), global hardness (η), global softness (δ) and electrophilicity index (ω) were calculated to analyse the reactivity of a molecule. According to the Koopman's theorem [10] the ionization potential (I) and electron affinity (A) values can be interacted with Frontier orbitals using the relation,

$$I = -(E_{HOMO}) \; and \; A = -(E_{LUMO})$$

and the other descriptors are also calculated using the following relations.

$$\chi = \frac{I + A}{2}$$

$$\mu = -\chi = -\frac{I + A}{2}$$

$$\eta = \frac{I - A}{2}$$

$$S = \frac{1}{2\eta}$$

$$\omega = \frac{\mu^2}{2\eta}$$

In 3-hydroxy-4-methoxybenzaldehyde crystal, the global hardness (η) is decreases and the global softness (S) is increases in gaseous phase due to the charge transfer in intramolecular aspects. The calculated values are shown in Table 2.

Table 2
Global reactivity descriptors of 3-hydroxy-4-methoxybenzaldehyde

Global reactivity descriptors	Values (eV)
Ionization Potential (I)	6.299
Electron Affinity (A)	1.834
Chemical Potential (μ)	-4.067
Electronegativity (χ)	7.216
Chemical Hardness (η)	2.232
Chemical Softness (S)	0.447
Electrophilicity Index (ω)	3.704

3.5 Molecular Electrostatic Surface Potential (MESP) Analysis

Molecular electrostatic surface potential (MESP), determines the interaction energy between charge distribution of molecules and a unit positive charge [11]. The explicit data on the chemical reactivity and a biological activity of the grown crystal are mainly applicable for electrophilic and nucleophilic reactions besides hydrogen bonding interactions. The MEP was studied and established within the range of -9.285e^{-2} to 9.285e^{-2} from the optimized molecular structure using B3LYP/6-311G(d,p) level of method. The graphical representation of MEP is shown in Fig.4. In 3-hydroxy-4-methoxybenzaldehyde, it is obvious that the red colour (negative charge) enclose the C=O group. The blue colour (positive charge) is over methoxy group, O-H group, H_{18} and benzene ring hydrogen atoms. The delocalization of electron covers O_{15} and O_{19} due to the presence of intramolecular O_{15}-H_{16}...O_5 hydrogen bonding.

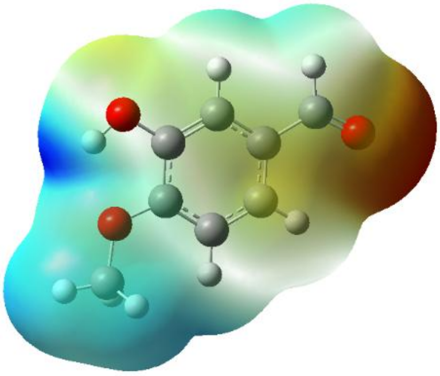

Fig. 4 Graphical representation of MESP

3.6 Fukui Functions

The Fukui function is used to study the reactivity indicators. These reactivity descriptors used to identify the reactive sites in electrophilic or nucleophilic reactions within a molecule. Due to the change of density function of a molecule the electrons (N) changes consequently, under the limitation of constant external potential. Perhaps it is to characterize the condensed or atomic fukui functions behind kth atoms[12].

$$f_k^{\,-} = q_j\,(\mathrm{N}) - q_j\,(\mathrm{N}-1)$$

$$f_k^{\,+} = q_j\,(\mathrm{N}+1) - q_j\,(\mathrm{N})$$

$$f_k^{\,0} = \frac{1}{2}[q_j\,(\mathrm{N}+1) - q_j\,(\mathrm{N}-1)]$$

In these equations, q is the atomic charge at $a^2 + b^2 = c^2$ the site of anion (N+1), cation (N-1), neutral (N) chemical categories [13]. A dual descriptor Δf(r), interprets the difference between electrophilic and nucleophilic Fukui function and is given by the equation,

$$\Delta \mathrm{f}(\mathrm{r}) = [f^{+}(\mathrm{r}) - f^{-}(\mathrm{r})]$$

When Δf(r)>0, then the position specifies an electrophilic attack, however when Δf(r)<0, its position specifies an nucleophilic attack. The order of the electrophilic position at Δf(r)>0 for the 3-hydroxy-4-methoxybenzaldehyde is 5O>4C>15O>11C>14C>9C>2H>3H>10H>13H>16H>1H>8H, while the nucleophilic position Δf(r) <0 is 17C>19O>12C>6C>18H>7C are ordered in descending order. The Fukui functions of (f_k^{+}), (f_k^{-}) and Δf(r) is shown in Table 3.

Table 3
Fukui Analysis of 3-hydroxy-4-methoxybenzaldehyde

Atoms	Anion q_{N-1}	Cation q_{N+1}	Neutral N	f_k^-	f_k^+	f_k^0	Δf(r)
1H	0.167	0.226	0.194	0.026	0.031	0.029	0.004
2H	0.157	0.204	0.175	0.017	0.028	0.023	0.010
3H	0.157	0.204	0.175	0.017	0.028	0.023	0.010
4C	0.194	-0.221	-0.202	-0.396	-0.018	-0.207	0.378
5O	0.594	-0.459	-0.563	-1.157	0.103	-0.526	1.260
6C	0.153	0.378	0.286	0.133	0.091	0.112	-0.041
7C	-0.282	-0.270	-0.272	0.010	0.002	0.006	-0.008
8H	0.181	0.251	0.214	0.032	0.037	0.034	0.004
9C	-0.261	-0.033	-0.157	0.104	0.123	0.113	0.019
10H	0.204	0.258	0.227	0.023	0.031	0.027	0.008
11C	-0.200	-0.064	-0.175	0.025	0.110	0.067	0.085
12C	-0.262	-0.192	-0.204	0.057	0.012	0.035	-0.044
13H	0.189	0.258	0.219	0.030	0.038	0.034	0.007
14C	0.253	0.384	0.278	0.024	0.106	0.065	0.081
15O	-0.705	-0.532	-0.668	0.036	0.135	0.086	0.099
16H	0.470	0.505	0.486	0.015	0.020	0.017	0.009
17C	0.228	0.397	0.420	0.192	-0.023	0.084	-0.215
18H	0.049	0.138	0.102	0.053	0.035	0.044	-0.017
19O	-0.714	-0.434	-0.538	0.176	0.104	0.140	-0.071

Conclusion

The compound 3-hydroxy-4-methoxybenzaldehyde was identified and analyzed at the DFT level. The geometrical parameters of 3-hydroxy-4-methoxybenzaldehyde were found to be in good agreement with the experimental results. The observed and simulated infrared wave numbers of the compound was analyzed by using vibrational analysis. MESP map confirms the intramolecular interactions which justifies the presence of hydrogen bonding. The Fukui function which helps to identify the region of the molecule exposed to electrophilic and nucleophilic attack.

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