Structural and electronic properties of 3,4-DimethoxyBenzaldehyde – Quantum Chemical Approach

***S.J. Jenepha Mary, D. Ashni Renisha and G. Jaya Gayathri**

Department of Physics, Holy Cross College (Autonomous), Nagercoil – 4
Affiliated to Manonmaniam Sundaranar University, Tirunelveli - 627012
*Corresponding Author - E-mail: jenephaashok@gmail.com

ABSTRACT

A novel type of benzaldehyde derivative known as 3,4-Dimethoxy Benzaldehyde has been studied using density functional theory (DFT) model, performed by GAUSSIAN 09 packages, based on the Becke, 3-parameter, Lee–Yang–Parr (B3LYP) exchange correlation functions augmented with 6–311++(d,p) basis set. The geometric equilibrium, charge transfer interactions and the stereo-electronic interactions, leading to the stability, bioactivity, has been confirmed using natural bond orbital analysis.

Keywords: *Density functional theory (DFT), Natural bond orbital, HOMO-LUMO, Hirshfeld surface*

Introduction

3,4- DimethoxyBenzaldehyde is an organic compound that is widely used as an flavorant and odorant. The compound is structurally related to benzaldehyde. The molecule consists of two methoxy group and acarbonyl groups on benzene. Benzaldehyde (C6H5CHO) an extremely straight forward agent of fragrant aldehydes, happens normally as glycoside amygdalin. Benzaldehyde is a colorless liquid with the scent of almond oil It has a liquefying point of -26°c(-14.8°F) 179°c(354.2°F). It is slightly soluble in water and completely soluble in ethanol and diethyl ether. Benzaldehyde goes through concurrent oxidation and decreases with alcoholic potassium hydroxide (Cannizzaro response) [1], giving potassium benzoate and benzyl liquor; with alcoholic potassium cyanide. Veratraldehyde can be used as an intermediate in the synthesis of some pharmaceutical drugs including amiquinsin [2], hoquizil, piquizil, toborinone, verazide and vetrabutine [3]. The prime focus of the present study is on the investigation of the structure of 3,4-DimethoxyBenzaldehyde to elucidate the electronic properties.

Computational details

Quantum chemical calculations was done with the Gaussian ’09 program package, using density functional theory (DFT) with B3LYP function and 6-31G+(d,p) basis set. Natural bond analysis has been carried out using NBO 3.1 version [4,5,].

Results discussion

Optimized geometry

The optimized structure of the isolated 3,4-dimethoxy benzaldehyde molecules

calculated using DFT theory at the B3LYP functional together with the 6-311G (d,p) basis set is shown in Figure 1. The calculated parameters were compared with the experimental parameters [6]

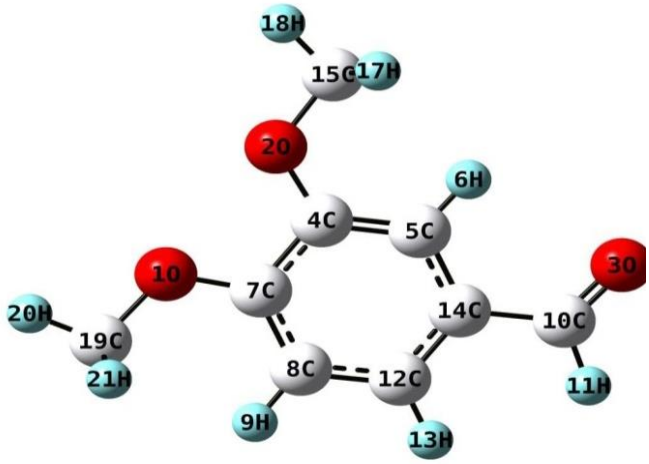

Figure 1. Optimized molecular structure of 3,4-dimethoxy benzaldehyde

The molecular structure of 3,4-dimethoxy benzaldehyde consists of a benzene ring with two methoxy group at 3,4 position and a alcohol group in the 1-position. Calculated geometrical parameters agree well with the experimental values except some exceptions. The planarity of the benzene ring is distorted owing to the heavy substituted methoxy group at the 3,4 position as revealed by an increase in the O2 — C4 — C7 —O1torsional angle by 1.28°. In the phenyl ring the bond angle C4— C5—C14 has been increased by 1° and the bond angle C5— C4—C7 has been decreased by 1° from the experimental value due to the presence of the adjacent methoxy group. A significant decrease in bond lengths of O1—C7,O1—C14, O2—C15 and O2—C15 is noticed. The occurrence of this effect is due to the redistribution of partial charges on O2 as the lone pair electron is delocalized and thereby reveals the effects of resonance in this part of the molecule [7,8]. Calculated geometrical parameters are given in the supplementary table Table S1, S2 and S3

Natural bond orbital study

In order to probe the second order perturbation energy of the hyperconjugative interactions between the donor and acceptor atoms natural bond orbital analysis was carried out[9]. The most prominent interactions resulting from the second order perturbation energy E(2) of the Fock matrix have been tabulated (Table 1). The second-order perturbation theory analysis of Fock matrix in 3,4- Dimethoxybenzaldehyde shows the presence of intramolecular hyperconjugative interactions [9]. The quantum of charges transferred from lone pairs of n(O1), n(O2) of the methyl group and n(O3) into the σ antibond orbitals of the phenyl ring

leads to the stabilization energy of 5–8 kcal mol−1 except for the second lone pairs n2(O1), n2(O2) involved in the π bond interactions show stabilization energies of 33.56 kcal mol−1 and 31.68 kcal mol−1 Also, The quantum of charges transferred from lone pairs of n(O3) of the keto group into the σ antibond orbitals of the phenyl ring leads to the stabilization energy of 22.45 kcal mol−1 and 18.93 kcal mol−1 because of the energy differences between orbitals. Considerable changes are noticed in para substituted keto group than the ortho and meta substituted methyl group.

Table 1. Second Order Perturbation Theory Analysis of Fock Matrix of 3,4-Dimethoxybenzaldehyde

Donor (i)	Acceptor (j)	E(2)kcal/mol	E(j)− E(i) a.u.	F(i,j) a.u
n1(O 1)	σ*(C7 - C8)	7.45	1.11	0.081
n2(O 1)	π*(C7 - C8)	33.56	0.34	0.1
n2(O 1)	σ*(C 19 - H 21)	5.25	0.74	0.058
n2(O 1)	σ*(C 19 - H 22)	5.25	0.74	0.058
n1(O2)	σ*(C4 - C5)	7.44	1.13	0.082
n2(O2)	π*(C4 - C5)	31.68	0.34	0.097
n2(O2)	σ*(C 15 - H 16)	5.3	0.74	0.058
n2(O2)	σ*(C 15 - H 17)	5.3	0.74	0.058
n2(O3)	σ*(C 10 - H 11)	22.45	0.67	0.111
n2(O3)	σ*(C 10 - C14)	18.93	0.72	0.106

Mullikan population analysis

Atomic charge distribution based on Mullikan Charge analysis has been represented in Table2. From the table it has been observed that, in 3,4- Dimethoxybenzaldehyde the carbon atom attached to the oxygen atom are more positively charged when compared to the carbon atoms attached to the hydrogen atom.

Table 2. Mullikan charge of 3,4- Dimethoxybenzaldehyde

SI NO	Atom Number	Charge (e)
1	O1	-0.50063
2	O2	-0.513224
3	O4	-0.428977
4	C4	0.329946
5	C5	-0.161024

6	H6	0.115357
7	C7	0.336616
8	C8	-0.140584
9	H9	0.091427
10	C10	0.252797
11	H11	0.053215
12	C12	-0.136921
13	H13	0.089851
14	C14	0.047146
15	C15	-0.082298
16	H16	0.118509
17	H17	0.118499
18	H18	0.126987
19	C19	-0.083463
20	H20	0.132267
21	H21	0.117256
22	H22	0.117248

It has been observed that C7 has the most positive charge (0.336616) followed by C4 (0.329946). The distribution of charge over C7 and C4 is due to the charge transfer interactions take place between n1(O 1) → σ*(C7 - C8), n2(O 1) → π*(C7 - C8), n1(O2) → σ*(C4 - C5) and n2(O2) → π*(C4 - C5) with the stabilization energy of 7.45 kcal/mol, 33.56 kcal/mol, 7.44 kcal/mol, 31.68 kcal/mol respectively. Fig. 2 illustrates the plot of atomic charges to the atom number.

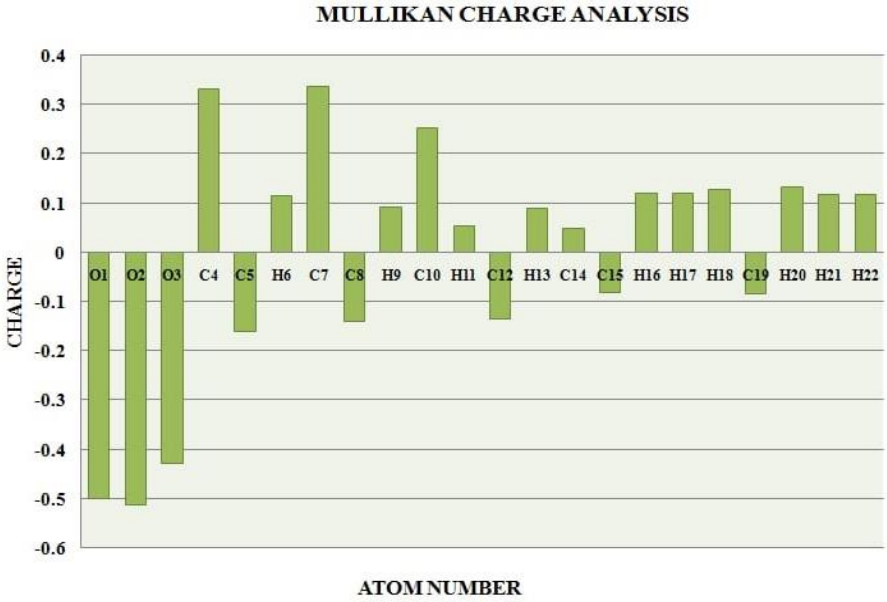

Figure 2. Mullikan charge of 3,4- Dimethoxybenzaldehyde

HOMO - LUMO

The frontier molecular orbitals, HOMO and LUMO plays an important role in the electric and optical properties, as well as in chemical reactions. The frontier molecular orbital gives a clear description about the reactivity of the molecule and the active sites of the molecule. The calculated energy for HOMO and LUMO s been shown in Table 3.

Table 3. Global reactivity descriptors of 3,4-Dimethoxybenzaldehyde

Parameters	Value
EHOMO	- 5.2193
ELUMO	- 2.1307
Electron affinity (A)	2.1307
Ionization potential (I)	5.2193
Electronegetivity	3.656
Chemical potential (μ)	-4.776
Chemical Hardness (η)	1. 8443
Chemical Softness(S)	0.27110

In HOMO, the charges are concentrated on the phenyl moiety whereas in LUMO, the charge distribution is over the entire molecule except the methyl group. The calculated low energy gap (ΔE=3.089 ev) reflects that the molecule is highly active. From the HOMO-LUMO energies, the global reactivity descriptors such as ionization potential I=-EHOMO, electron affinity A= -ELUMO, chemical hardness η= (I-A)/2; chemical potential μ = -(I+A) / 2 and electrophilicity index ω = μ 2 /2η were calculated.

Conclusion

The Spectrocopic study of molecule 3,4 dimethoxybenzaldehyde has been investigated. The influence of CH3, C-H, C-C and C=O on the vibrational frequencies of the molecule 3,4 dimethoxy benzaldehyde were also discussed. The optimized structure of isolated 3,4 dimethoxy benzaldehyde molecules calculated using DFT theory at B3LYP functional together with the 611G (dp) basic set. The optimized bond length, bond angle, and dihydral angle of the molecule has been estimated with the experiment value. NBO reveals the transferred of charges from lone pair to antibond and π bond. Muliken charge analysis reveal the atomic charge distribution, from this 3,4 dimethoxybenzaldehyde the carbon atom attached to oxygen atom are more positively charged when compared to carbon atom attached to hydrogen atom. From HOMO - LUMO, energies of global reactivity descriptors such as ionization potential, electron affinity, chemical hardness, chemical potential and electrophilicity index were calculated.

References

1. Hester R.E., Girling R.B. Ftir studies of bacteriorhodopsin structural and functional aspects. Spectroscopy of Biological Molecules. 1991; 5: 1 - 6.
2. Sun Y., Chen J., Chen X., Huang L., Li X. Inhibition of cholinesterase and monoamine oxidase-B activity by Tacrine-Homoisoflavonoid hybrids. Bioorg Med Chem. 2013; 21(23): 7406 - 17.
3. Li X., Liu L., Schlegel HB. On the physical origin of blue-shifted hydrogen bonds. J Am Chem Soc. 2002; 124 (32): 9639 - 47.
4. Glendening E. D., Reed A. E., Carpenter J. E., Weinhold F. A. NBO, Version 3.1; 1995.
5. Erik de Ronde., Sander J.T. Brugman., Niels Koning., Paul Tinnemans., Elias Vlieg. 3,4-Dimethoxybenzaldehyde, data reports. Acta Cryst E. 2017; 467 - 471.
6. Bernstein Davis R.E., Shimoni L., Chang N. Patterns in hydrogen bonding: functionality and graph set analysis in crystals. Angewandte Chemie International Edition in English. 1995; 34 (15): 1555 - 1573.
7. Jeffrey A.G., Salinger W. Hydrogen Bonding in Biological Structures. Computational chemistry. 1991; 4(12): 2345 - 2350.
8. Jeffrey A.G., Salinger W. Hydrogen Bonding in Biological Structures. Computational chemistry 1995; 12(22): 1845 - 1856.
9. Davies DR. The structure and function of the aspartic proteinases. Annual review of biophysics and biophysical chemistry. 1990; 19(1): 189 - 215.