STRUCTURAL, SPECTROSCOPIC AND THEORETICAL STUDIES OF METHYL 5,6-DIMETHOXY-1H-INDOLE-2-CARBOXYLATE

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Abstract- The structural and spectroscopic characterization of Methyl 5,6-dimethoxy-1H-indole-2-carboxylate has been performed using DFT method. The vibrational frequencies and intensities of vibrational bands were evaluated using density functional theory (DFT) with standard B3LYP using 6-311G(D,P) basis set. Simulation of infrared spectra utilizing the result of these calculations led to excellent overall agreement with the observed spectral patterns. The complete assignments were performed on the basis of the potential energy distribution (PED) of the vibrational modes, calculated with scaled quantum mechanics (SQM) method. The stability of the molecule arising from hyperconjugative interactions and the charge delocalization has been analyzed using NBO analysis. The HOMO-LUMO energy gap also measured.
Keywords – PED, SQM, DFT, HOMO-LUMO, NBO

I. Introduction

Indole is a fused aromatic heterocyclic ring, consisting of a six-membered benzene ring fused to a five-membered nitrogen - containing pyrrole ring, Indole nucleus is present in compounds involved in research aimed at evaluating new products that possess interesting biological activities like antihypertensive, anti-viral, anti-inflammatory, anticancer, antidiabetic,etc.[1]. Spectral analysis have been carried out using computation and experimental methods. Intramolecular hydrogen bonding interaction have received much attention from both practical and theoretical values, as they can determine the structure and activities of biological molecules. Vibrational spectroscopic investigation with the help of quantum chemical computation have recently be used as an efficient tool in the structural analysis of cardiovascular compounds, DFT with the B3LYP method using Gaussian '09 program package is used for calculation. Hence, the present investigations aim to interpret the vibrational characteristics of Methyl 5,6-dimethoxy-1H-indole-2-carboxylate using FT-IR, HOMO-LUMO energies and NBO analysis.
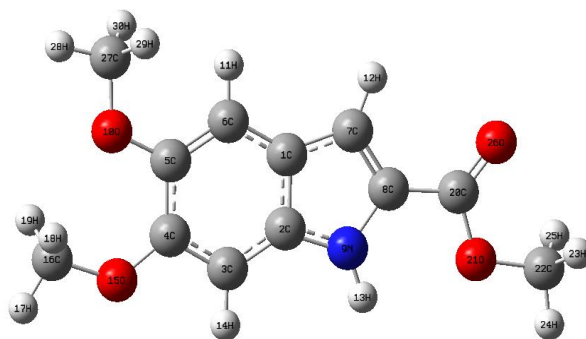

Fig 1. Structure of Methyl 5,6-dimethoxy-1H-indole-2-carboxylate.

II. Experimental details

Methyl 5,6-dimethoxy-1H-indole-2-carboxylate was purchased from Sigma–Aldrich (St. Louis, MO, USA) and used without further purification. The IR spectrum of each sample was recorded using a PerkinElmer Spectrum One FTIR spectrometer in the region 400–4000 cm^{-1}, using a KBr sample pellet. The resolution of the spectrum was 4 cm^{-1}.

III. Computation

The DFT computations for the Methyl 5,6-dimethoxy-1H-indole-2-carboxylate was carried out in the Gaussian 09 program package using "ultrafine" integration grids. The calculations were performed at the B3LYP level with the standard 6-311

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G(d,p) basis set in order to derive the optimized geometry, vibrational wavenumbers and natural bond orbital analysis of Methyl 5,6-dimethoxy-1H-indole-2-carboxylate.

IV. Result and Discussion
A. Optimized geometry
The calculated data of Methyl 5,6-dimethoxy-1H-indole-2-carboxylate are in close agreement with the experimental values [table1]. The longest bondlength C_1-C_2 is observed in the benzene ring at 1.404 Å and was calculated at 1.418 Å. This is due to the fusion of indole moiety at these carbons. Comparing the bond distances of the hetero ring, all varies significantly from each other due to the variation of electronegativities of the atoms [2]. The bondlengths C_4-O_{15} and C_5-O_{10} increases because of the presence of methoxy group. The bond length C_8-C_{20} is longer due to the electron withdrawing nature of carboxylic group. The angle C_3-C_4-C_5 and C_4-C_5-C_6 are similar to the typical hexagonal angle of 120º. This is because of the effect of O-CH_3 group attached to the C_4 and C_5 position of the benzene ring [3]. The bond angle at C_2 atom (N_9-C_8-C_7) is 109.1 °. This is due to the electron donating substitutions [4].

Table 1: Selected optimized parameters of Methyl 5,6-dimethoxy-1H-indole-2-carboxylate

Parameters	Bondlength and Bond angle	
	Experimental	Calculated
C_1-C_2	1.404 Å	1.4184 Å
C_4-O_{15}	1.362 Å	1.3641 Å
C_5-O_{10}	1.369 Å	1.3738 Å
C_8-C_{20}	1.450 Å	1.4598 Å
C_3-C_4-C_5	120.9 °	119.8 °
C_4-C_5-C_6	121.1 °	120.3 °
N_9-C_8-C_7	108.7 °	109.1 °

B. Vibrational analysis
The C-H stretching vibrations normally lies between 3100 and 3000cm^{-1}. In this region the bands are not affected appreciably by the nature of substituents. In the title molecule, the very weak band observed at 3011 cm^{-1} in FTIR and the corresponding calculated wavenumber lies at 3019 cm^{-1}.The expected value of methoxy group is 2835 cm^{-1}. The symmetric stretching vibrations of CH_3 groups are observed at 2947 cm^{-1} in FTIR. The theoretically predicted wavenumber is at 2951cm^{-1}. The asymmetric vibrations of CH_3 group is observed at 3011 cm^{-1} in FTIR. The calculated wavenumbers are at 3020 cm^{-1} with PED 100%. The C-O stretching are expected in the region 1450-1150 cm^{-1}. In the present investigation, the bands observed at 1231 cm^{-1} in FTIR and the calculated value at 1422 cm^{-1} is assigned to C-O stretching vibration [5].

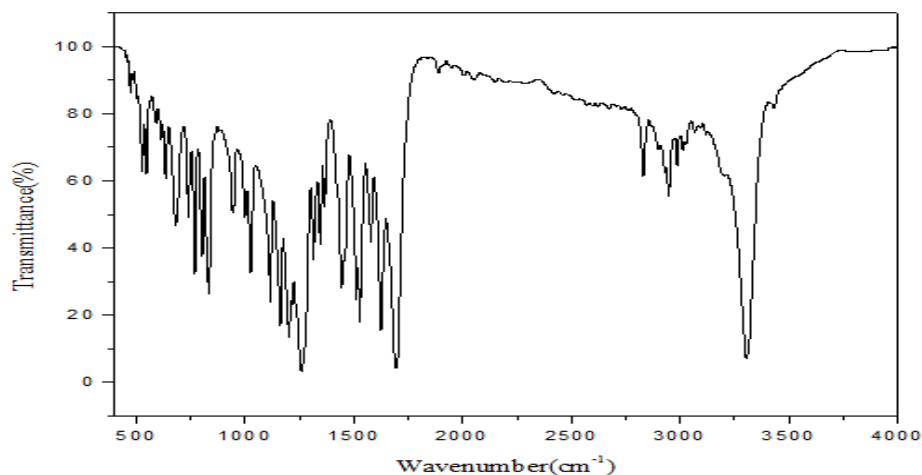*Fig 2. FT-IR Spectrum Methyl 5,6-dimethoxy-1H-indole-2-carboxylate*

C. NBO analysis
The stabilization energy of electron present in C_4-O_{15} bonding orbital and the C_2-C_3 antibonding orbital gives 7.3 KJmol^{-1}, which results due to delocalization. The intramolecular interaction of π (C_1–C_7) →π* (C_2–N_9) weakens the respective bond leading to stabilization of 3.5 KJmol^{-1} [6]. The intramolecular hyperconjugative interaction (C_{16}-H_{17}…O_{15}) are formed by the orbital overlap between LP(1) O_{15}→σ* (C_{16}–H_{17}) and σ* (C_{16}–H_{18}) bond orbitals which results in ICT causing stabilization of the system, resulting stabilization energies are 13.4 KJmol^{-1} and 2.9 KJmol^{-1}, respectively [6].

Table 2: NBO analysis for Methyl 5,6-dimethoxy-1H-indole-2-carboxylate

Donor NBO(i)	ED(i) (e)	Acceptor NBO(j)	ED(j) (e)	$E^{(2)}$ (kj/mol)
σ (C_4–O_{15})	1.9904	$\sigma^*(C_2$–$C_3)$	0.0208	7.3
σ (C_1–C_7)	1.9661	$\sigma^*(C_2$–$N_9)$	0.0249	3.5
LP(1) O_{15}	1.9595	$\sigma^*(C_1$-$C_2)$	0.0120	13.4
LP(1) O_{15}	1.9595	$\sigma^*(C_4$-$C_5)$	0.0167	2.9

D. HOMO-LUMO analysis

Spatial distribution of molecular orbitals especially those of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are excellent indicators of electron transport in molecular system[Fig.3].The HOMO spread out over the entire part of the molecule, while the LUMO does not spread over the methyl group. The effect on the LUMO level is stronger when an electron accepting group is present. The HOMO-LUMO energy gap is 0.10525eV. The low value of the HOMO-LUMO energy gap confirms charge transfer within the molecule.
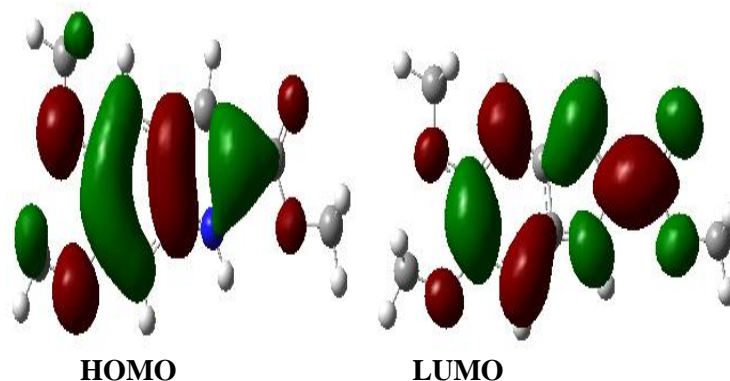

HOMO   **LUMO**

Fig 3. HOMO-LUMO Plots for Methyl 5,6-dimethoxy-1H-indole-2- carboxylate

V.Conclusion

The optimized geometries of Methyl 5,6-dimethoxy-1H-indole-2-carboxylate were determined and analyzed at the DFT level. The DFT calculated values of the vibrational wavenumbers were agreed well with the experimental data. The NBO analysis reveals hyperconjugative interaction, ICT and stabilization of molecules. The low HOMO–LUMO energy gap clearly reveals the structure activity relationship of the molecule.

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