



IJCRR
Section: General
Science
Sci. Journal Impact
Factor: 5.385 (2017)
ICV: 71.54 (2015)

Analysis of Highest Occupied and Lowest Unoccupied Molecular Orbitals on Harmaline

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ABSTRACT

Harmaline belonging to a family of harmala is a fluorescent psychoactive indole alkaloid. The FTIR and FT-Raman spectra of Harmaline have been recorded in region 4000–400 cm⁻¹ and 4,000–100 cm⁻¹ respectively. The experimental frequencies recorded are compared with vibration frequencies calculated using Gaussian software by employing HF and DFT functional at B3LYP/6-31G(d,p) basis set. The electronic properties of the molecule have been studied by recording UV–Visible spectrum of the compound. Also, highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) energies have been calculated at DFT/B3LYP/6-31 G (d,p) level. These calculations showed that there exists energy transfer in the molecule. Mulliken population analysis and thermodynamic properties of title compound have been analyzed and tabulated.

Key Words: Harmaline, FTIR, FT-RAMAN, HF, DFT, HOMO-LUMO

INTRODUCTION

Harmaline is a central nervous system stimulant and a reversible inhibitor of MAO-A (RIMA). The risk of high blood pressure and hypertension by eating foods rich in cheese is likely to be lowered when we take Harmaline. It also acts as acetyl cholinesterase inhibitor that is a chemical that prevents the acetyl cholinesterase enzyme from breaking down acetylcholine and thereby increasing the action time of neurotransmitter, acetylcholine [1-3].

EXPERIMENTAL DETAILS

The pure sample was purchased from Sigma Aldrich Co, with started purity of 99% and was used without further purification to record the FTIR and FT-Raman spectra.

Infrared Spectra

The FTIR spectrum of the compound was carried out with model Shimadzu FT-IR spectrometer with a room temperature DLATGS detector. The spectra of the solids were recorded in technique of KBr pellets in the 4000-400cm⁻¹

spectral region at 4 cm⁻¹ spectral resolution accumulating 32 scans.

Raman Spectra

The FT-Raman spectrum was recorded with a Bruker IFS 66V FT-Raman spectrometer in the region 4000-50 cm⁻¹.

COMPUTATIONAL DETAILS

The theoretical calculation of vibration frequencies was done using GAUSSIAN 09W program package on personal computer [4] employing ab initio Hartree Fock (HF) and density functional theory (DFT) with Becke's Three-parameters hybrid functional [5] in combination of Lee-Yang-Parr [6] functional implemented with 6-31 G(d,p) basis sets. In the present work, optimization of molecular geometry and calculation of vibration frequencies, Mulliken charge analysis and thermodynamic properties. Then, the vibrational frequencies were scaled down by the appropriate scaling factor thereby comparing the theoretical and experimental vibrational frequencies. The other molecular parameters like HOMO-LUMO calculations, Mulliken and thermodynamic observations were calculated at DFT/B3LYP/6-31 G (d,p).

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ISSN: 2231-2196 (Print)

ISSN: 0975-5241 (Online)

Received: 22.07.2018

Revised: 25.08.2018

Accepted: 15.10.2018

RESULTS AND DISCUSSION

Molecular geometry

The molecule under study have 30 atoms with 84 normal modes of vibrations. The Optimized structure of Harmaline at DFT/B3LYP/6-31 G(d,p) level is shown in Figure 1.

HOMO-LUMO Analysis

The interaction between two atomic or molecular orbital produce two new orbital in which one of the new orbital produced is found to have greater energy which is the anti bonding orbital and the other at lesser energy. is the bonding orbital. When one initial orbital is filled with a pair of electrons - a Lewis base, and the other is empty -a Lewis acids, the “filled-empty” interaction is stabilized. The two molecular orbital that take part in interaction are highest occupied molecular orbital (HOMO's) and lowest unoccupied molecular orbital (LUMO's) of the other molecule. The interaction will be very strong if any two orbital have energies very close to each other. Since they lie as outermost electron, they are called as Frontier orbital.

HOMO's and LUMO's are considered as most important parameters in quantum chemistry. [7]. HOMO's are outer orbital containing electrons tends to give these electrons thereby acting as an electron donor and hence the ionization potential (I_p) is directly related to the energy of the HOMO. On the other hand LUMO's accept electrons and LUMO energy ΔE directly related to electron affinity (E_A). The energy gap (E_g) is calculated from the energy difference between HOMO and LUMO orbital. From the value of energy gap, we can easily find out whether the molecule will be stable or not. Also, from the value of energy gap, we can find whether the molecule is hard or soft. Hard molecule will have large energy gap and soft molecule will have lesser energy gap. The advantage of smaller energy gap is it provides detailed information on the structure of the molecule associated with high chemical reactivity and low kinetic stability.

The calculation of HOMO and LUMO gives information on the transfer of charge within the molecule [8]. In the present work, HOMO and LUMO calculations are calculated by DFT/B3LYP/6-31 G(d,p) method. In the HOMO-LUMO figures, red color denotes positive phase while green color denotes negative phase. From the analysis, it is clear that HOMO is located over nitrogen, oxygen and on the double bond carbon atom attached to electronegative atoms. However, a surface of positive line is closely concentrated around Oxygen atom which clearly indicates that delocalized electrons are confined at negative sites of the molecule, however, shifted from positive part. These delocalized electrons act as a binding areas to the receptor atoms. The LUMO is located over the entire molecule particularly focused on methyl group attached to nitrogen atom and not on methyl group attached to Oxygen [9-11].

HOMO and LUMO figures are shown in Figure. 2. The other important interesting molecular and atomic properties are calculated by following expressions and shown in Table 1.

$$\text{Ionization potential } (I_p) = -E_{HOMO}$$

$$\text{Electron affinity } (E_A) = -E_{LUMO}$$

$$\text{Global hardness } (\eta) = \left(\frac{-E_{HOMO} + E_{LUMO}}{2} \right)$$

$$\text{Global softness } (S) = 1/2 \eta$$

$$\text{Electro negativity } (\chi) = - \left(\frac{E_{HOMO} + E_{LUMO}}{2} \right)$$

$$\text{Chemical potential or Fermi energy } (m) = -\chi = \left(\frac{E_{HOMO} + E_{LUMO}}{2} \right)$$

$$\text{Electrophilicity } (\omega) = \frac{\mu^2}{2\eta}$$

THERMODYNAMIC PROPERTIES

The thermodynamic properties calculated at HF and DFT/B3LYP/6-31 G (d,p) levels of the molecule under study is presented in Table 2. It is clear from the observation that dipole moment takes greater value at HF calculations and SCF energy is found to be less at DFT when compared to HF calculations.

CONCLUSION

In the present investigation, FTIR and FT-Raman spectra of Harmaline were recorded and geometry of the molecule is optimized. The theoretical vibrational frequencies were calculated using HF and DFT/ DFT/B3LYP method using the standard 6-31 G (d,p) basis set. The calculated and experimental frequencies were compared for the title molecule. HOMO-LUMO calculations carried out at DFT level confirms transfer of charge within the molecule that chains the bioactive property of the molecule. Thermo dynamical properties tabulated show that higher dipole moment observed at HF calculations and less SCF energy at DFT when compared to HF calculations.

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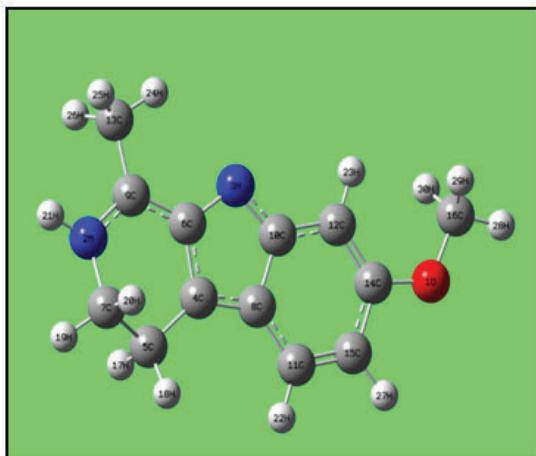


Figure 1: Optimized structure of Harmaline at DFT level.

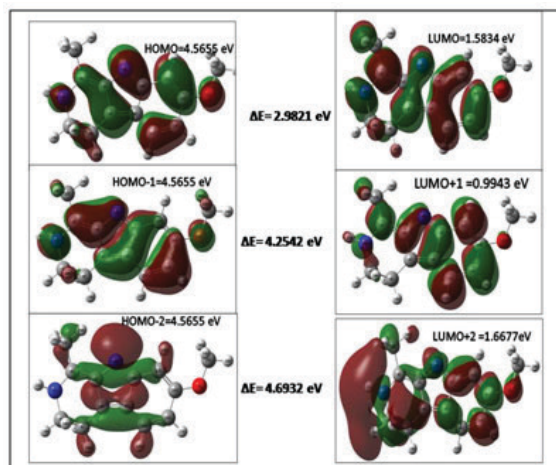


Figure 2: HOMO-LUMO analysis of Harmaline.

Table 1: HOMO-LUMO energy values of Harmaline at DFT level

Molecular parameters	Calculated value eV
HOMO	-4.56552852
HOMO-1	-5.24853464
HOMO-2	-6.32692238
LUMO	-1.58343131
LUMO-1	0.99430452
LUMO-2	1.6337724
HOMO-LUMO	2.9821
HOMO-1 - LUMO-1	4.2542
HOMO-2 - LUMO-2	4.6932
$\eta = 1/2(E_{\text{HOMO}} - E_{\text{LUMO}})$.	1.49105
$\mu = 1/2(E_{\text{HOMO}} + E_{\text{LUMO}})$.	3.6145
$\omega = \mu^2/2 \eta$	4.3810

Table 2: Thermodynamic properties of Harmaline

Parameters	HF/6-31G(d,p)	DFT/B ₃ LYP/ 6-31G(d,p)
SCF energy (a.u.)	-684.1876	-688.5377
Total energy (thermal)E _{total} (Kcal mol ⁻¹)	175.008	164.403
Vibrational energy, E _{vib} (Kcal mol ⁻¹)	173.231	162.625
Zero point vibrational energy (Kcal mol ⁻¹)	166.92181	155.78326
Specific heat capacity, C _v (cal mol ⁻¹ K ⁻¹)	50.414	54.23
Entropy, S (cal mol ⁻¹ K ⁻¹)	111.808	115.219
Dipole moment μ (Debye)		
μ_x	-4.6228	-4.6583
μ_y	-0.8334	-0.5971
μ_z	0.3565	0.3541
Total	4.7148	4.7097