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Vibrational Analysis and MP2 Calculations of [(4-Hydroxyphenyl)amino] (oxo) Acetic Acid

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***Abstract*— Vibrational spectral analysis and quantum chemical computation of [(4-Hydroxyphenyl)amino] (oxo) acetic acid have been carried out by using MP2 level with 6-31G(d,) basis set. The equillibrium geometry, various bonding features and harmonic vibrational wavenumber of [(4-Hydroxyphenyl)amino] (oxo) acetic acid have been computed by MP2 method. The calculated molecular geometry has been compared with the experimental data. Natural bond orbital analysis has been carried out to explain the charge transfer or delocalization of charge due to the intramolecular interactions. Energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied (LUMO) molecular orbital have been predicted. The molecular electrostatic potential (MESP) were constructed. The absorption spectrum of the molecule was studied using time-dependent density functional theory (TD-DFT) method.**

Key words: MP2; NBO analysis; TD-DFT; MESP; HOMO;

I. INTRODUCTION

[(4-Hydroxyphenyl)amino](oxo)acetic acid (HPAOA) is a antihypertensive drug. It is used to prevent the complications of high blood pressure, such as stroke and myocardial infarction[1-2]. Spectral and vibrational 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 been used as an efficient tool in the structural analysis of cardiovascular compounds, DFT with the MP2 method using Gaussian '09 program package is used for calculation. Hence, the present investigations aim to interpret the vibrational characteristics of [(4-Hydroxyphenyl)amino](oxo)acetic acid were studied using their FT-IR, HOMO-LUMO energies, MEP analysis ,NBO analysis and UV-Visible spectral analysis.

II. COMPUTATION

The DFT computations for the [(4-Hydroxyphenyl)amino](oxo)acetic acid was carried out in the Gaussian 09 program package using "ultrafine" integration grids. The calculations were performed at the MP2 level with the standard 6-31G(d) basis set in order to derive the optimized geometry, vibrational wavenumbers, natural bond orbital (NBO) analysis, MEP analysis and UV-Visible spectral analysis of [(4-Hydroxyphenyl)amino](oxo)acetic acid [3].

III. RESULT AND DISCUSSION

A. Optimized geometry

The optimized structural parameters of HPAOA using MP2/6-31G(d) basis set are given in table(1). The corresponding X-ray diffraction values are also used for comparision [4]. The optimized molecular structure of compound with atom numbering scheme adopted in the computation is shown in fig.1. The calculated data shows that there are slight deviation from the corresponding XRD data for certain bond length, bond angle and dihedral angles.

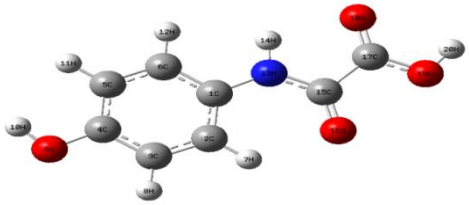

Fig. 1 Structure of [(4-Hydroxyphenyl)amino](oxo)acetic acid

In the benzene ring C_1-C_2 (1.403Å) and C_1-C_6 (1.400Å) bond lengths are increased when compared to other bonds. This is due to the attachment of amino oxo acetic acid group[5]. The longest bond length C_{15}-C_{17} in the acetic acid lies at 1.532 Å. This is due to the attachment of NH and COOH group. The compounds with OH group attached to phenyl ring are influenced by steric effect. This can be observed from increase in inter atomic distance of 2.312Å [H_{10}…H_{11}]. The bond length O_{19}-H_{20} of HPAOA is increased and there is a possibility of O_{19}-H_{20}...O_{18} hydrogen bonding. The C-C-C bond angle in benzene ring is 120° and is said to be aromatic, but in the present study the compound shows slight deviation in the C-C-C bond angle because of this the aromatic character changes due to the substitution of different groups. In the title compound, the calculated value of C-C-C bond angles (C_1-C_2-C_3 and C_3-C_4-C_5) are less than 120° the differences in the values arise due to hydroxyl group and acetic acid substitution. The increase in bond angle C_1-N_{13}-

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C_{15} (128.3°) is due to the presence of C_2-H_7...O_{16} hydrogen bonding. The calculated C_{17}-O_{19}-H_{20} angle for HPAOA is 105.8°. The XRD value is 109.4° due to the redistribution of partial charges on O_{20} atom. In HPAOA, the torsional angle C_2-C_1-N_{13}-C_{15} and C_1-N_{13}-C_{15}-C_{17} shows planar nature.

Parameters	Experimental values	Calculated values
C_1-C_2	1.389Å	1.403 Å
C_1-C_6	1.392 Å	1.398 Å
H_{10}…H_{11}	-	2.312 Å
C_1-N_{13}	-	1.532 Å
C_{15}-N_{13}	-	1.360 Å
O_{19}-H_{20}	0.840 Å	0.980 Å
C_1-N_{13}-C_{15}	-	128.3°
C_{17}-O_{19}-H_{20}	109.4°	105.8 °
C_1-C_2-C_3	119.5°	119.4°
C_3-C_4-C_5	120.2°	119.7°
C_2-C_1-N_{13}-C_{15}	-179.9°	-0.0°
C_1-N_{13}-C_{15}-C_{17}	-0.0	-0.0

Table I- Optimized bondlength, bond angle, dihedral angle for [(4-Hydroxyphenyl)amino](oxo)acetic acid

B. *Hydrogen bonding and steric interactions of HPAOA*

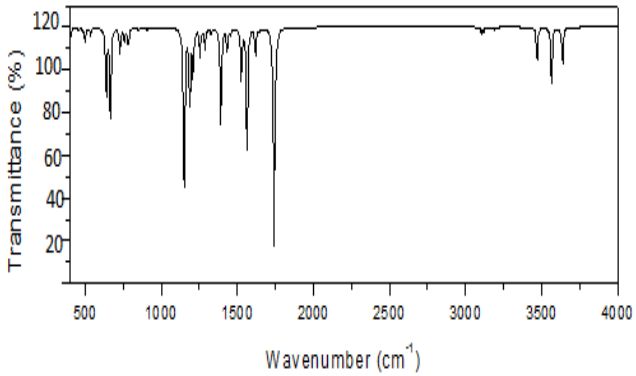

Fig 2.IR Spectrum of[(4-Hydroxyphenyl)amino](oxo)acetic acid

The N-H stretching vibrations are normally viewed in the region 3000 – 3500 cm^{-1} [6]. In the present study, the calculated N-H stretching vibration is observed at 3583 cm^{-1}. The increase in theoretical wavenumber shows there is a possibility of strong N-H…O hydrogen bonding. In phenols, the frequency of the free O-H stretching lies near 3600cm^{-1}[7]. The O-H stretching vibrations are generally observed around 3500 cm^{-1}. In the title compound, the calculated value is found to be at 3637 cm^{-1}. The increase in wavenumber shows steric effect between H_{10} and H_{11} (H_{10}…H_{11}=2.312 Å). The C=O stretching vibrations expected in the region at 1730-1770 cm^{-1}[8]. In the present study the C=O band appears at 1785 cm^{-1}. The increase in wavenumber shows O_{19}-H_{20}…O_{18} hydrogen bonding. Vibrational analysis of C=O group is significant because of cardiovascular activity of the compound.

C. *Natural charge*

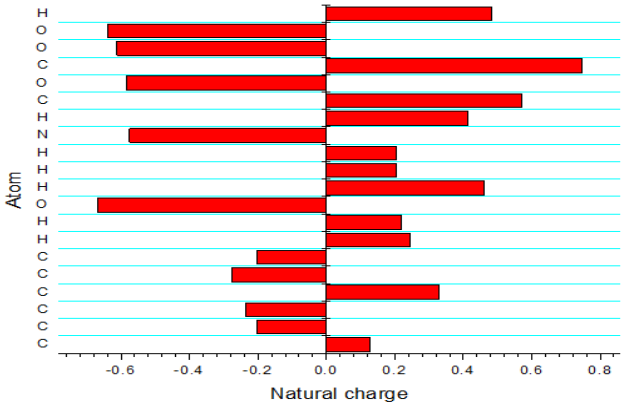

Fig.3 Charge plot of [(4-Hydroxyphenyl)amino](oxo)acetic acid

The charge distribution analysis was made on the basis of the natural charge analysis using the NBO program implemented in the Gaussian ‘O9 package. Charge distribution by the natural charge for the equillibrium geometry of title compound in gaseous phase are given in fig (3). The atom C_{17} shows more positive charge (0.817e) and O_9 shows more negative charge (-0.698 e) in the natural charge. This is due to the presence of two large electronegative oxygen atom in the carbonyl group.

D. *NBO analysis*

The interaction of $\sigma(C_1–C_6)\rightarrow\sigma^*(C_1–C_2)$ leads to stabilization energy of 19.4 $kJmol^{-1}$. The intramolecular C–H...O hydrogen bonds are exposed by the interactions between the oxygen lone-pair n(2) O_{16} and the antibonding orbital $\sigma^*(C_2$-$H_7)$ whose contribution (4.3 $kJmol^{-1}$) is smaller but definitely not negligible and can be used as a measure of intramolecular delocalization. The intramolecular hydrogen bonding interaction of n(2) O_{18} distribute to $\sigma^*(N_{13}–H_{14})$ leads to stabilization energy of 6.4 $kJmol^{-1}$. This stabilization energy is due to red shifting. The interaction of $\sigma(C_2$-$C_3)$ distribute to $\sigma^*(C_1–N_{13})$ which leads to stabilization energy of 19.3 $kJmol^{-1}$.

Donor NBO (i)	**ED (i) (e)**	**Acceptor NBO (j)**	**ED (j) (e)**	**$E^{(2)}$ (kJ/mol)**
σ (C_2-C_3)	1.973	$\sigma^*(C_1$-$N_{13})$	0.408	19.3
σ (C_1-C_6)	1.972	$\sigma^*(C_1$-$C_2)$	0.552	19.4
$LP_{(2)}O(18)$	1.861	$\sigma^*(N_{13}$-$H_{14})$	0.387	6.4
$LP_{(2)}O(16)$	1.851	$\sigma^*(C_2$-$H_7)$	0.469	4.3

Table 2: NBO analysis for [(4-Hydroxyphenyl)amino](oxo)acetic acid

E. *Molecular electrostatic potential surfaces*

The molecular electrostatic potential (MEP) surface map is a plot of electrostatic potential mapped onto the constant electron density surface. In the majority of the MEPs, while

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the maximum negative region, preferred site for electrophilic attack which is indicated by as a red color, the maximum positive region, a preferred site for nucleophilic attack symptoms marked as blue color [9-11]. The 2D diagram of MEP for the title compounds is shown in Fig.4. The potential values in this molecule ranges from -0.120e a.u. (deepest red) to -0.120e a.u. (deepest blue). MEP of the title molecules shows the main negative potential region around O16and the carboxylic acid group shows positive potential. This confirms the existence of intramolecular C-H…O hydrogen bonding.

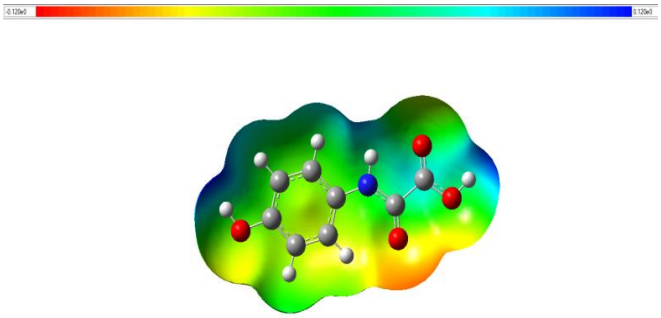

Fig.4 MESP Plot for[(4-Hydroxyphenyl)amino](oxo)acetic acid

F. HOMO-LUMO analysis

The HOMO-LUMO energy gap of HPAOA is computed at the MP2/6-31G(d) level, which reveals that the energy gap reflects the chemical activity of the molecule. The HOMO-LUMO Plot is shown in figure 5. The charge transfer concentrates on the acetic acid to phenyl group. The HOMO-LUMO energy gap is -0.122 eV. The low value of the HOMO-LUMO energy gap confirms charge transfer within the molecule.

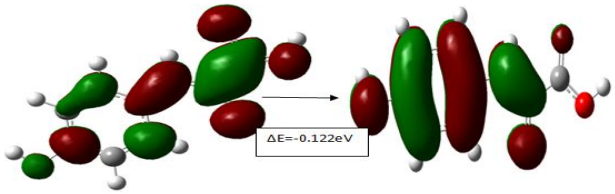

Fig 5.HOMO-LUMO Plot for [(4-Hydroxyphenyl)amino](oxo)acetic acid

G. UV-Visible analysis

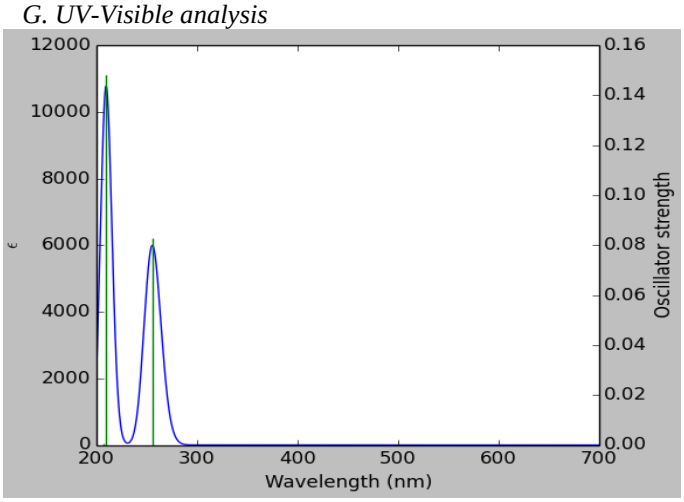

Fig 6: Theoretical UV-Visible absorption spectrum of HPAOA (water medium)

The UV-Visible spectral analysis of HPAOA have been calculated by TD-DFT method using PCM model. The calculated UV-Visible spectrum of HPAOA shown in figure 6. The calculated UV-Visible spectrum of HPAOA was observed in water at 256nm.This band is primarily due to the HOMO-LUMO transition which corresponds to the characteristic peak of the system due to $n\rightarrow\pi^*$ transition and has highest oscillator strength occurred in HOMO-LUMO transitions; the CI expansion coefficient is 0.66. The highest excitation energy occurred in 4.8 ev at HOMO-LUMO transitions.

IV CONCLUSION

The optimized geometries of [(4-Hydroxyphenyl)amino](oxo)acetic acid were determined and analyzed at the MP2 method using 6-31G(D) basis set. The C=O stretching shows strong C-H....O hydrogen bonding. NBO analysis reveals that the intramolecular hydrogen bonding interactions between LP(2) $O_{16}\rightarrow$ $\sigma^*(C_2\text{-}H_7)$and LP(2) $O_{18}\rightarrow$ $\sigma^*(N_{13}\text{-}H_{14})$. MEP map confirms the existence of intramolecular C-H…O hydrogen bonding. The MESP confirms the intramolecular C-H…O hydrogen bonding. The low HOMO–LUMO energy gap clearly reveals the structure activity relationship of the molecule. The UV-Vis spectrum shows that the intense peak occurs due to $n\rightarrow\pi^*$ transition.

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