

ORIGINAL ARTICLE

SPECTRAL ANALYSIS AND QUANTUM COMPUTATIONAL INVESTIGATION OF 4 - (1-HYDROXY 2-(METHLY AMINO) ETHYL) BENZENE.

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ABSTRACT

In this paper, the spectral analysis of 4-(1-HYDROXY 2-(METHLY AMINO) ETHYL)BENZENE is carried out using the FTIR, FT Raman, FT NMR and UV – Vis spectra of the compound with the help of quantum mechanical computations using ab-initio and density functional theories. The values of dipole moment (μ), polarizability () and hyperpolarizability () of the molecule are reported, using which the non-linear property of the molecule is discussed. The HOMO-LUMO mappings are reported which reveals the different charge transfer possibilities within the molecule. The isotropic chemical shifts predicted for ^1H and ^{13}C atoms using gauge invariant atomic orbital (GIAO) theory show good agreement with experimental shifts. NBO analysis is carried out to picture the charge transfer between the localized bonds and lone pairs. The thermodynamic properties (heat capacity, entropy and enthalpy) at different temperatures are also calculated.

Keywords: (1-HYDROXY 2-(METHLY AMINO) ETHYL) BENZENE, chemical shifts; NBO, HOMO-LUMO.

1.INTRODUCTION

Epinephrine, also known as adrenaline, is a hormone and a neurotransmitter. It increases heart rate, tightens blood vessels, broadens air passages, and participates in the fight-or-flight response of the sympathetic nervous system. It is a member of a class of pharmacologically active substances known as catecholamines, because its structure contains an amine and *ortho*-dihydroxybenzene known as catechol (Foye et al., 2007). It is produced in some neurons of the central nervous system, and in the chromaffin cells of the adrenal medulla from the amino acids phenylalanine and tyrosine. [O. Von Bohlen et al., 2003.] Epinephrine (adrenaline) is synthesized in the medulla of the adrenal gland (see Figure 1) in an enzymatic pathway that converts the amino acid tyrosine into a series of intermediates and, ultimately, adrenaline. Tyrosine is first oxidized to l-DOPA, which is subsequently decarboxylated to give dopamine. Oxidation gives norepinephrine, which is methylated to give epinephrine. 4-(1-Hydroxy 2 – (methyl amino) ethyl) benzene

1,2 diol also known by the common name Epinephrine is an organic compound and natural product that is structurally related to the neurotransmitter. The compound belongs to catecholamine family. In medicine epinephrine is used chiefly as a stimulant in cardiac arrest as a vasoconstrictor and antispasmodic in bronchial asthma.

2.COMPUTATIONAL DETAILS

The entire quantum chemical computations are performed using the Gaussian 09 software on a Pentium IV/3.02GHz personal computer. The wave numbers and geometrical parameters are computed using B3LYP and B3PW91 methods in combination with 6-311+G (d, p) and 6-311+G (d, p) basis sets. The geometry of the title molecule Epinephrine is fully optimized using B3LYP functional with 6-311+G (d, p) basis set and the same geometry is used for the conformational analysis using semi-empirical method with PM6 basis set. The electronic properties, such as NBO and HOMO-LUMO were calculated using time-dependent TD-SCF - B3LYP method under the same basis set. Similarly the NMR chemical shifts are also carried out by GIAO method in combination with B3LYP/6-311G + (2d, p). In addition, Fukui function, the dipole moment, linear polarizability and the first order hyper polarizability of the title molecule are

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also computed using B3LYP method with the 6-311+G (d, p) basis set.

3.RESULTS

Conformational analysis

The optimized geometry of the molecule obtained using B3LYP with 6-311+G (d,p) basis set was used for conformational analysis of the molecule. Conformational analysis was performed by potential energy surface scan function semi-empirical method with PM6 basis set and by varying the dihedral angle C4-C14-C18-N21 in the steps of 36 over one complete rotation 0-360 as recommended in the previous work on a similar molecule. The graphical result, total energy verses scan coordinates, of this conformer analysis is presented in Fig. 1. The graph clearly shows that there are two conformers at minimum energy levels, one at 0 and the other at 160 with total energy -0.16861 and -0.176097 hartree respectively. The structure of the molecules at these conformation is shown in Fig.1, as conformer I and II, of which the conformer I represents the most stable conformer of this compound.

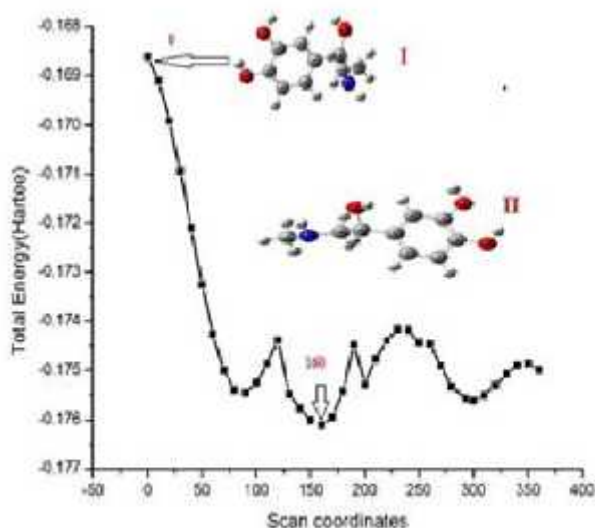


Fig.1 - potential energy surface of Epinephrine

Vibrational assignments

The vibrational frequencies for all the fundamental modes of Epinephrine are computed using B3LYP, B3PW91 methods with 6-311+G (d,p) basis sets and the values along with the experimental values and assignments. The molecule consists of 26 atoms and belongs to C_{1v} point group, hence the 72 fundamental modes of vibrations are distributed as $\Gamma_{\text{vib}} = 55 A' + 27 A''$. In order to fit the theoretical and experimental frequencies, suitable scaling factors are introduced. The scaling factors are 0.9887 for B3LYP/6-311+G (d,p) and B3PW91/6-311+G (d,p) respectively. The experimental and computational IR and Raman spectra of the compound are shown in Fig. 4 & 5 respectively.

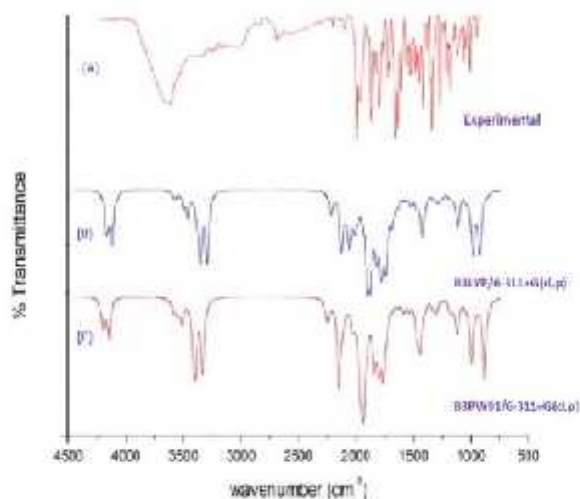


Fig. 2. Experimental (A) and calculated (B,C) FT-IR Spectra of Epinephrine

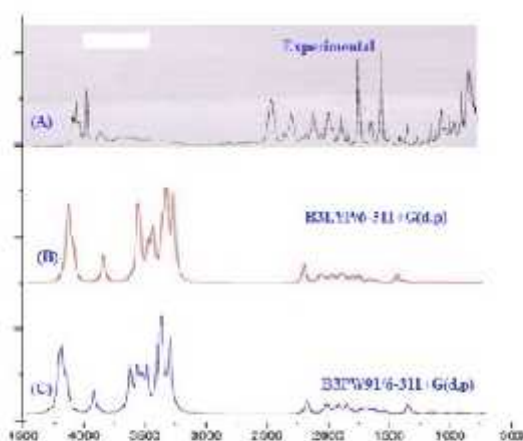


Fig. 3. Experimental (A) and calculated (B,C) FT-RAMAN Spectra of Epinephrine

4.DISCUSSION

N-H Vibrations

The N-H stretching bands are expected between 3200-3600 cm^{-1} in the present case, it is found to be 1320 cm^{-1} , which much lower than the amino group vibrations, it is due to the energy sharing of phenyl rings. The out-of-plane vibrations too found below the expected range in Raman band at 920 cm^{-1} is assigned to the N-H out of plane bending mode.

The O-H vibrations

The O-H vibrations are extremely sensitive as these bonds lead to formation of intermolecular hydrogen bonding. Generally these bands appear at vibration between 3600-3200 cm^{-1} . In this molecule the stretching vibration appears at 3350, 3050, 3020 cm^{-1} . The two vibration are below the range have deviated from the observation which indicates their vibration due to ethyl group. The in plane bending O-H occur at 1350-1200 cm^{-1} . Here in this molecule the vibration appear at 1300, 1290, 1250 cm^{-1} in which all the vibration are in expected range. In the same way the out-of-plane vibrations are generally observed at 900-700 cm^{-1} . In the

present molecule the out-of-plane vibrations are observed at 890, 780, 750 cm^{-1} , which is also found in the expected range. Thus the stretching vibration is affected by ethyl group whereas bending vibration clearly indicates that they are not influenced by other vibration in the molecule.

C-H Vibrations

The aromatic C-H vibrations normally occur in the range of 3000- 3100 cm^{-1} . Foye et al., (2007)] have observed the C-H stretching vibrations in the range of 3024-3146 cm^{-1} . Many have reported the CH stretching vibrations in this range(Krishnakumar and Balachandran, 2005). In the present compound eight vibrations observed at 3010, 3000, 2980, 2960, 2900, 2880, 2870 and 2860 cm^{-1} , of which first three vibrations are due to the aromatic ring and other five vibrations are due to ethyl and methyl group vibrations. The ethyl and methyl group vibration usually appear below the aromatic CH bands, here also the trend is observed. Similarly, the C-H in-plane ring bending vibrations for aromatic CH occurs as strong to weak intensity bands in the region 1300–1200 cm^{-1} (Sharma, 1994). In the present compound, the bands are observed at 1230, 1200, 1190, 1150, 1120, 1110, 1100, 1090 cm^{-1} . The vibration 1230, 1200 cm^{-1} are observed in expected range. Other vibration due to hydroxyl methyl amino group found below the expected range. The C-H out-of-plane bending vibrations are expected in the region 1000–800 cm^{-1} . But these vibrations are found at 780, 750, 710, 680, 620, 600, 570, 550 cm^{-1} . This shows all the vibration are below the expected range which conforms the energy distribution takes place with outer functional groups

The C-O vibrations

The C-O stretching is generally expected in the range 1700-1500 cm^{-1} . In the present molecule the vibration are observed at 2390, 2000, 1850 cm^{-1} . All the bands are observed above the expected range which shows these bands are also much influenced. Similarly the C-O in-plane bending is expected in the region of 800-700 cm^{-1} . In the present case the bands are observed at 1080, 1060, 1050 cm^{-1} . This shows all the bands are above the normal range which due to methyl amino group. C-O out-of-plane bands are below the expected range which clearly indicate that they are affected by the phenyl ring vibrations.

The CC vibrations

The CC stretching vibrations for phenyl ring are generally observed between 1600-1400 cm^{-1} [Smith, 1999], in which the bands between 1600-1500 cm^{-1} are assigned to C=C stretching and the rest to C-C stretching, even though no such distinction is present within the ring. In the present compound also, the bands observed at 1700, 1590 and 1550 cm^{-1} are assigned to C=C vibrations. These observations for the aromatic CC are in agreement with literature values, which indicate that the skeletal vibrations are not affected by the substitutional vibrations. C-C stretching vibrations are

observed at 1480, 1320, 1300 and 1250 cm^{-1} which is slightly deviated below the expected range. In the case of CC in-plane the vibrations are observed at 810 and 800 cm^{-1} and out-of-plane vibrations are mixed with the other substitutional group vibrations.

C-N vibrations

The mixing of several bands causes very difficult in the identification of C-N vibrations in many molecules. (Silverstein, and Webster, 2003.) assigned C-N stretching in the region 1382-1266 cm^{-1} . In the present molecule, the band is observed at 1460 and 1410 for C-N stretching vibration. Similarly, the in-plane and out-of-plane vibrations are assigned at 1000, 950 and 330, 300 cm^{-1} respectively for this C-N which again has similar deviation noticed as in stretching, which may also be due to the conjugation of NO and CN bonds.

5. CONCLUSION

The study of the molecular geometry reveals that there is no appreciable change in the bond length and bond angle of the molecule by addition of the substitutional group. And most of the values are closer to the experimental values.

On studying the vibrations of the compound, the C-H out-of-plane vibrations are influenced by the other modes specifically N-O and C-C bending in-plane vibrations. And the CC vibrations show good agreement with expected range. In the case of NO_2 , stretching vibrations are not influenced and the bending vibrations are mixed with CC vibrations. Conversely, C-N in-plane and out-of-plane vibrations are again influenced by NO and CC modes of vibrations.

6. REFERENCES

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