



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

A Combined theoretical and experimental study of conformational and spectroscopic profile of 2-acetamido-5-aminopyridine



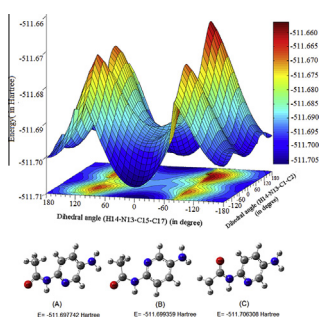
Shilendra K. Pathak, Ruchi Srivastava, Alok K. Sachan, Onkar Prasad, Leena Sinha*

Department of Physics, University of Lucknow, 226 007 Lucknow, India

HIGHLIGHTS

- Conformational and spectroscopic profile of 2-acetamido-5-aminopyridine studied.
- Good accord between experimental and calculated normal modes of vibrations achieved.
- Title compound has large β_{total} value, approximately 42 times greater than urea.
- Global reactivity and local reactivity descriptors calculated using DFT.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 31 October 2014
 Received in revised form 15 January 2015
 Accepted 29 January 2015
 Available online 17 February 2015

Keywords:

FT-IR
 FT-Raman
 PES scan
 Vibrational analysis

ABSTRACT

Present work aims at identifying the conformational and spectroscopic profile of 2-acetamido-5-aminopyridine compound by means of experimental and computational methods. To achieve this, three-dimensional potential energy scan (PES) was performed by varying the selected dihedral angles at B3LYP/6-31+G(d,p) level of theory and thus stable conformers of the title compound were determined. The most stable conformer was further optimized at higher level and vibrational wavenumbers were calculated. Experimentally, vibrational features of title compound were determined by FT-IR and FT-Raman spectroscopic methods in the solid phase while the electronic absorption spectrum was recorded in methanol solution. On the basis of these investigations, the conformational and spectroscopic attributes of 2-acetamido-5-aminopyridine were interpreted.

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Introduction

The pyridine derivatives have a key position among the heterocyclic compounds as they are commonly present in synthetic and natural products [1,2] and can be used as non-linear materials and photo-chemicals. Among the variety of pyridine derivatives, the pharmaceutical unfolding of amino pyridine derivatives have received considerable attention, as these show anesthetic properties and have been used as drugs for certain brain diseases [3–5]. They have also been fully employed as chiral nucleophilic catalysts

in a wide range of asymmetric synthetic processes [6]. Due to their wide application in pharmacology and agro-chemistry, the study of the vibrational spectra of substituted pyridine predominantly amino pyridines entice the attention of many researchers and as a result numerous works has been reported related to the assignment of the vibrational spectrum of amino pyridines [7–10]. To the best of our knowledge, no quantum chemical HF/DFT calculations for 2-acetamido-5-aminopyridine (2A5AP) have been reported so far. Therefore, the present investigation is undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes with wave number accuracy. Experimentally observed spectral data (FT-TR and FT-Raman) of the title compound were compared with the spectral data obtained

* Corresponding author.

E-mail address: sinhaleena27@gmail.com (L. Sinha).

by DFT/B3LYP method. The molecular properties like dipole moment, polarizability, first static hyperpolarizability and molecular electrostatic potential surface, contour map have been calculated to get a better understanding of the properties of the title molecule. For analysis of molecular orbitals, different densities of states such as TDOS, PDOS and OPDOS were computed and analyzed. UV–Vis spectrum of the title compound was also recorded and electronic properties, such as frontier orbitals and band gap energies were calculated by TD-DFT approach. Natural bond orbital (NBO) analysis has been applied to study the stability of the molecule arising from charge delocalization. Various local and global reactivity descriptors along with thermo dynamical properties were theoretically calculated and described to reveal the characteristics of title molecule. ^1H NMR chemical shifts also have been assigned with the help of calculated and experimental findings.

Experimental methods

2-Acetamido-5-aminopyridine (2A5AP) (solid state) of spectral grade was purchased from M/s Sigma Aldrich Chemical Co., and was used as such without any further purification. The FT-Raman spectrum of title compound was recorded on a Varian 7000 series spectrometer in the region $4000\text{--}100\text{ cm}^{-1}$ with a spectral resolution of 4 cm^{-1} at AIRF, Jawaharlal Nehru University, New Delhi. The 1064 nm laser line of Nd:YAG laser was used as the exciting wavelength with an output power of about 2 mW at the sample position. The FT-IR spectra of title compound was recorded using Perkin Elmer spectrometer (version 10.03.06) in the region $4000\text{--}400\text{ cm}^{-1}$ using KBr pellet method. UV absorption spectrum was recorded in methanol solvent on JASCO-UV (V-670) spectrometer in the spectral region of $200\text{--}500\text{ nm}$ with the resolution of 0.5 nm . FT-IR and UV spectra were recorded using experimental facilities available at IIT Kanpur. The ^1H NMR spectrum of 2A5AP

was recorded in deuterated chloroform (CDCl_3) solvent on Bruker DRX-300 MHz NMR spectrometer with sweep width of 7500 Hz and acquisition time 4.3691 s at SAIF, CDRI, Lucknow.

Computational details

Density functional theory [11] treated according to hybrid Becke's three parameter and the Lee–Yang–Parr functional (B3LYP) [12–14] supplemented with polarized triple-zeta 6-311++G(d,p) basis set was used to study 2A5AP. This quantum chemical method and basis set is quite reasonable for predicting geometry and accurate energy of medium-sized molecules. It has also been used to calculate the dipole moment, mean polarizability and first static hyperpolarizability based on the finite field approach. All calculations in this study have been performed with the Gaussian 09 program package [15] and results were analyzed with the Gaussview 5.0 molecular visualization program [16]. To investigate the most stable conformer of title molecule, 3D potential energy scan (PES) was performed by varying the H14–N13–C15–C17 and H14–N13–C1–C2 dihedral angles at B3LYP/6-311++G(d,p) level of theory. The obtained PES, showing the variation of dihedral angles, their corresponding energies and thus investigated stable conformers of the title molecule are given in Fig. 1a. The most stable conformer (C), corresponding to global minima on PES is further optimized at higher basis set 6-311++G(d,p) and thus obtained ground state structure of 2A5AP molecule shown in Fig. 1b, has been used for further calculation of various quantum chemical and spectroscopic properties. Due to unavailability of the X-ray crystallographic data of 2A5AP, its optimized parameters have been compared with parent pyridine ring [17]. Positive value of all the calculated vibrational wavenumbers confirms the stability of optimized geometry. An empirical uniform scaling factor of 0.983 up to 1700 cm^{-1} and 0.958 for greater than 1700 cm^{-1}

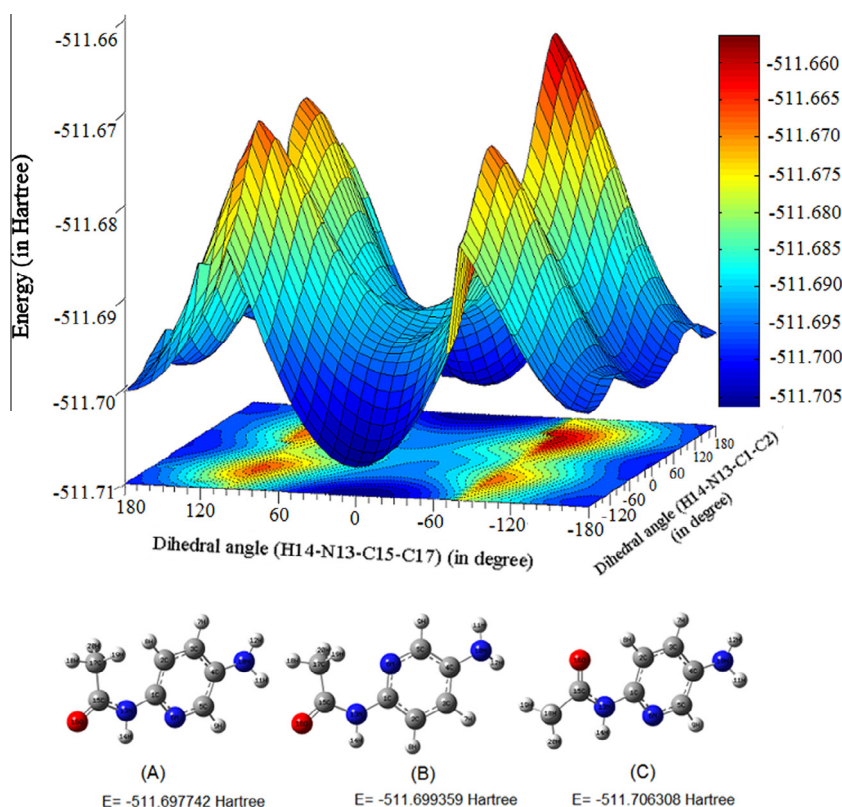


Fig. 1a. 3-Dimensional potential energy surface (PES) of 2A5AP molecule, scanned about dihedral angles H14–N13–C15–C17 and H14–N13–C1–C2 at DFT-B3LYP/6-311++G(d,p) level of theory and stable conformers.

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