



Contents lists available at ScienceDirect

# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: [www.elsevier.com/locate/saa](http://www.elsevier.com/locate/saa)

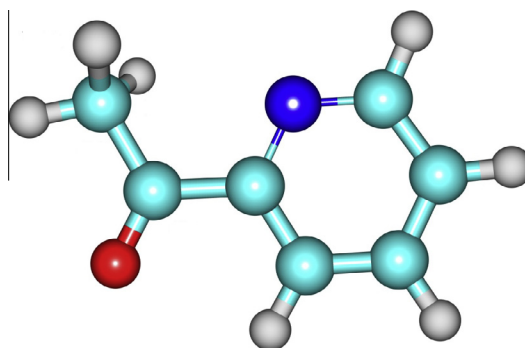
## A combined experimental and theoretical study on vibrational spectra of 2-acetylpyridine

Cuiping Zhai<sup>a,b,\*</sup>, Fenghua Cui<sup>c</sup>, Xuejun Liu<sup>a</sup><sup>a</sup>Institute of Fine Chemical and Engineering, Henan University, Kaifeng 475004, Henan, China<sup>b</sup>School of Chemistry and Chemical Engineering, Shandong University, Jinan 250010, Shandong, China<sup>c</sup>Department of Materials Science and Engineering, Xinxiang Vocational and Technical College, Xinxiang 453007, Henan, China

### HIGHLIGHTS

- 2-Acetylpyridine is an important food additive and a flavoring substance.
- Vibrational spectra of 2-acetylpyridine have been determined and assigned for the observed bands.
- The *cis* conformer of 2-acetylpyridine is most stable according to DFT calculations.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 26 March 2014

Received in revised form 5 May 2014

Accepted 1 June 2014

Available online 24 June 2014

#### Keywords:

2-Acetylpyridine  
Vibrational spectra  
Molecular structure  
Density functional theory

### ABSTRACT

The molecular geometries, FT-IR and Raman spectra of 2-acetylpyridine were studied using Density functional theory (DFT-B3LYP) with the large basis sets. Theoretical calculations indicate the *cis* conformer of 2-acetylpyridine is most stable though this conformation was seldom found in the crystal structures of coordinated compounds. Based on the stable conformer, comprehensive assignments of the experimental bands were made. The observed and calculated positions are found to be in good agreement with an average deviation of  $<4\text{ cm}^{-1}$ . The assignments provide valuable information for the fingerprint and identification of 2-acetylpyridine.

© 2014 Elsevier B.V. All rights reserved.

### Introduction

2-Acetylpyridine, also named as 1-(2-pyridinyl)ethanone or methyl 2-pyridyl ketone, is a “popcorn”-like compound, and often used as the food additive and flavoring substance in tobacco, ice-cream, milk, cooked rice and other food products [1]. Generally, 2-acetylpyridine exists in a colorless to yellowish liquid and can be

naturally found in rice, hazelnuts, Yohonkaoluo leaves and cocoa [1–3]. Studies have also suggested that it can be used as an intermediate to synthesize a series of chemical compounds with antiviral activity [4–6]. For example, Abid et al. [4] prepared the various oxime ether derivatives of 2-acetylpyridine, and evaluated their antiamoebic activities against *HM1:IMSS* strain of *E. histolytica*.

Although its industrial and medical importance, the structure and vibrational spectroscopic analysis for 2-acetylpyridine are limitedly reported, and the crystal structure of pure 2-acetylpyridine molecule is still unavailable. As it bounds to the metal ion and proton, the crystal structure of 2-acetylpyridine [7–11] often

\* Corresponding author at: Institute of Fine Chemical and Engineering, Henan University, Kaifeng 475004, Henan, China. Tel./fax: +86 0371-23881589.

E-mail address: [zhaicuiping@henu.edu.cn](mailto:zhaicuiping@henu.edu.cn) (C. Zhai).

shows a *trans* conformation as given in Fig. 1, and both the carbonyl O atom and ring N atom simultaneously coordinate with the metal ion. Its *cis* conformation, obtained by 180° rotation around the C7–C2 bond, was found in the only one entry of bis(2-acetylpyridine)-tetraphenylporphyrin-zinc(II) [12], in which the carbonyl O atom individually interacts with the center zinc ion. Therefore, the structure of isolated 2-acetylpyridine is still unclear and deserved paying more attention.

On the other hand, Medhi [13] determined and empirically assigned the IR and Raman bands of 2-acetylpyridine in 1977. Recently, Sett and coworkers [14] have assigned again these bands using empirical force fields based on pyridine ring and acetyl group approximation. However, this approximation often leads to the questionable agreement between experiment and theory in view of the different molecular conformation and the effect of substituent. For example, the substitution at the 2 position of pyridine ring strengthens and shortens the N–C(2) bond, but where there is little effect upon substitution at the 3 position [15]. More recently, Density functional theory (DFT) calculation has been proved to be a powerful tool in prediction of molecular structure and vibrational spectra due to its high computational accuracy and low time cost [16–21]. In the present work, the geometric structures of 2-acetylpyridine were optimized using Becke3–Lee–Yang–Parr (B3LYP) functional with aug-cc-pvtz basis set. The relative stability of the *cis* and *trans* conformations was examined, and compared with the reported structures determined by single-crystal X-ray diffraction. The infrared and FT-Raman spectra were experimentally recorded, and the observed bands were analyzed and assigned based on the lowest energy conformer. Also, the various thermodynamic functions such as entropy, heat capacity and energy, molecular electrostatic potential, and HOMO–LUMO analysis were provided.

## Experimental details

Liquid 2-acetylpyridine (>97% purity) was purchased from Sigma, and used as such without further purification. FT-IR spectrum of the sample was collected in the region from 400 to 4000 cm<sup>-1</sup> at room temperature on a Bruker IFS 66 V FTIR spectrometer using liquid film technique with two KBr windows. The FT-Raman spectrum of 2-acetylpyridine was recorded on a FRA-106 FT-Raman accessories using Nd:YAG laser source and with a liquid nitrogen-cooled Ge-diode detector. The sample was sealed in an NMR tube, and the number of scans is 300. Spectral resolutions of both IR and Raman spectra are 2 cm<sup>-1</sup>.

## Computational details

Density functional theory (DFT) computations for the geometric optimization and frequency calculation were performed using Gaussian 03 program [22]. The initial geometries of 2-acetylpyri-

dine were obtained using potential energies scan (PES) at B3LYP/6-311++G(d,p) level. The structures and vibrational characteristics reported in this paper were further calculated at B3LYP/aug-cc-pvtz level recommended by Zvereva and co-workers [23]. This calculated level is the most cost-effective choice for the prediction of vibrational frequencies, relative IR intensities and Raman activities for medium-size isolated molecules [23,24]. Assignments of vibrational modes studied in this work were performed on the basis of potential energy distribution (PED) analysis obtained from Molvib program (version V7.0-G77) [25,26].

## Results and discussion

### Conformational analysis

As mentioned above, two possible conformers of 2-acetylpyridine were found in the determination of crystal structures [7–12]. A rigid PES scan through the dihedral angles around the C2–C7 bond was firstly carried out at B3LYP/6-311++G(d,p) level, and the results give two conformers as shown in Fig. 1, corresponding to the *cis* and *trans* conformations. Further optimization without any symmetry constraint at B3LYP/aug-cc-pvtz level indicates that the energy of *trans* conformer is higher 25.1 kJ/mol than that of *cis* conformer. This result is different to the crystal studies, in which the *trans* conformation is the most common and often behaves as a bidentate chelating ligand to stabilize the coordination compounds. The conformer stability of pure 2-acetylpyridine can be explained by the NBO analysis. The NBO charges on N and O atoms are –0.41714 and –0.53966, –0.37787 and –0.50141 for *cis* and *trans* conformers, respectively. Considering the short distance between N and O atom in *trans* conformer, the more positive charge indicates a strong repulsion as both N and O atoms are electronegative. The stability of the *cis* conformer in relation to the *trans* was further verified by molecular electrostatic potential map as provided in the supporting information. The charges on N1 and O8 atoms are clearly responsible for the lower stability of the *trans* conformer.

### Geometrical parameters

Due to the larger difference in energy between the *cis* and *trans* conformers, Boltzman population ratio of the *trans* conformer is thus very low, and it can be neglected in the liquid phase. This is greatly different to the studies of crystal structure. To the best of our knowledge, Byrn et al. [12] reported the only one case of the *cis* structure of 2-acetylpyridine, then its structural parameters was selected to assess the calculated result. In order to determine the accurate geometry of the *cis* conformer, the further calculation was carried out. We found that a planar geometry (C<sub>s</sub> point group) for *cis* conformer has the lowest energy. The other geometries such as the structure with C<sub>1</sub> point group are not preferred in energy

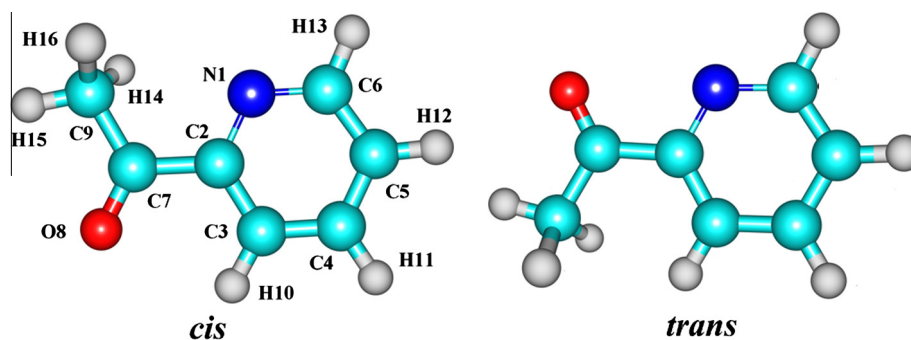


Fig. 1. Molecular model of 2-acetylpyridine along with numbering of atoms.

Download English Version:

<https://daneshyari.com/en/article/1229668>

Download Persian Version:

<https://daneshyari.com/article/1229668>

[Daneshyari.com](https://daneshyari.com)