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# Theoretical and infrared investigation of 2-acetylpyridine isolated in solid nitrogen and in neat condensed phases<sup> $\star$ </sup>

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#### ABSTRACT

The geometries of the two conformers of 2-acetylpyridine (2AP) were optimized at the DFT/B3LYP/6 -311++G(d,p) level of approximation, and their relative energy and interconversion barrier evaluated. Both conformers were found to belong to the  $C_s$  symmetry point group, with conformer *cis* (with the methyl group and the ring nitrogen atom located in the same side of the molecule) being considerably stabilized over the *trans* form. The *cis* conformer exhibits stabilizing interactions between the *ortho* ring hydrogen atom and the carbonyl oxygen, as well as between the methyl out-of-the-plane hydrogen atoms and the ring nitrogen atom. In the less stable *trans* conformer ( $\Delta E_{(trans-cis)} = 26.3 \text{ kJ mol}^{-1}$ ) these stabilizing interactions are replaced by repulsive interactions between the oxygen and nitrogen lone electron pairs and between the ring ortho and methyl out-of-the-plane hydrogen atoms. The energy barrier between the two conformers amounts to 30.7 kJ mol<sup>-1</sup> in the *cis*  $\rightarrow$  *trans* direction (4.4 kJ mol<sup>-1</sup> in the reverse direction). In agreement with the theoretical data, in a cryogenic  $N_2$  matrix prepared from the room temperature 2AP gas phase, only the most stable cis conformer was observed. The IR spectra of 2AP isolated in solid N<sub>2</sub>, and those for the low temperature amorphous and crystalline neat solid states of the compound were recorded, and correlations between the spectroscopic data and the strength and nature of the dominant intermolecular interactions in 2AP neat condensed phases were evaluated. The analysis of the experimental vibrational data was supported by theoretical calculation of harmonic and anharmonic frequencies and IR intensities obtained at the DFT/B3LYP/6-311++G(d,p) level of theory. © 2016 Elsevier B.V. All rights reserved.

#### 1. Introduction

2-Acetylpyridine (2AP, also named as 1-(2-pyridinyl)ethanone or methyl 2-pyridyl ketone) receives main use as food additive due to its characteristic popcorn-like flavor [1]. In nature, it is present, for example, in rice, hazelnuts and cocoa [1-3]. 2AP receives also applications in chemical synthesis [4-6] and as a metal chelating agent [7-9].

Recently, Zhai, Cui and Liu [10] have investigated the room temperature infrared (IR) and Raman spectra of liquid 2AP, which they have interpreted with help of quantum chemical calculations performed at the DFT(B3LYP)/aug-cc-pvtz level of approximation. That study improved over the previous reports on the vibrational spectra (IR, Raman) of liquid 2AP by Medhi [11] and Sett and coworkers [12]. In their study, Zhai, Cui and Liu [10] have shown that, in opposition to what happens when 2AP is coordinated to metal ions, where the molecule adopts the *trans* structure that can bind to the metal atom by both the oxygen and nitrogen atoms [7–9], the non-coordinated 2AP molecule exists preferentially in the *cis* conformation, where the methyl group and the ring nitrogen atom are located in the same side of the molecule. According to DFT(B3LYP)/aug-cc-pvtz calculations performed for the molecule in vacuo, the *trans* conformer of 2AP should be higher in energy than the *cis* form by *ca*. 25.1 kJ mol<sup>-1</sup> [10]. The higher energy of the *trans* conformer of unfavorable repulsive electrostatic interactions due to the close proximity of the negatively charged oxygen and ring-nitrogen atoms in that form [10].

In the present study, the infrared spectrum of 2AP isolated in a low temperature (15 K) N<sub>2</sub> matrix has been recorded and interpreted with help of harmonic and anharmonic vibrational calculations undertaken at the DFT(B3LYP)/6–311++G(d,p) level of approximation. Then, the infrared spectra of neat 2AP low-temperature amorphous and crystalline phases were obtained,







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and the comparison of the spectroscopic data for these phases (and also for the neat liquid, available in the literature [10]) with the results obtained for the matrix-isolated 2AP monomer was used to shed light on the dominant intermolecular interactions in the condensed phases of the compound.

#### 2. Experimental and theoretical methods

The 2AP sample used in this work was obtained from Sigma–Aldrich (spectroscopic grade), and further purified by freeze–pump–thaw cycling before use. The liquid sample was placed in a Knudsen cell immersed in a 2-propanol bath to reduce the vapor pressure of the compound, and the 2AP vapors coming out from the cell were mixed with a large excess of N<sub>2</sub> (N60 purity) and introduced into the cryostat (helium-cooled APD Cryogenics closed-cycle refrigerator with a DE-202A expander) through a micrometric valve nozzle kept at room temperature. The temperature of the CsI window of the cryostat was kept at *ca.* 15 K during the deposition. The infrared spectra were recorded with 0.5 cm<sup>-1</sup> resolution using a Thermo Nicolet 6700 FTIR spectrometer, equipped with a KBr beam splitter and a deuterated triglycine sulphate (DTGS) detector.

The quantum chemical calculations were performed using the Gaussian 09 suite of programs [13]. Ground-state equilibrium geometries were fully optimized at the density functional theory (DFT) level of approximation, using the 6311++G(d,p) basis set [14] and the hybrid Becke three parameter, Lee, Yang and Parr (B3LYP) functional [15–17]. The vibrational calculations (both harmonic and anharmonic) were performed at the same theoretical level, the calculated harmonic vibrational wavenumbers being subsequently uniformly scaled by 0.978. Anharmonic computations were performed by means of generalized second-order vibrational perturbation model (GVPT2) [18], allowing for the evaluation of anharmonic infrared intensities of not only fundamentals but also overtones and combination bands [19,20]. For evaluation of the strength of the intermolecular interactions in the neat condensed phases of 2AP, a generalization of the empirical correlation derived by Thijs and Zeegers-Huyskens [21] between the carbonyl stretching frequency shifts due to association and the enthalpy of the process was used, with the carbonyl stretching frequency measured for the matrix-isolated 2AP taken as reference. Analysis of calculated electronic charge density was performed using the natural bond orbital (NBO) method [22,23], using NBO 3.1 as implemented in Gaussian 09, and the MultiWFN (version 3.2) program package [24].

#### 3. Results and discussion

Fig. 1 shows the B3LYP/6-311++G(d,p) calculated optimized



**Fig. 1.** Cis and trans conformers of 2AP. Conformer trans corresponds to the higher energy form ( $\Delta E = 26.3 \text{ kJ} \text{ mol}^{-1}$ ;  $\Delta E_{(0)} = 26.0 \text{ kJ} \text{ mol}^{-1}$ ;  $\Delta G_{(298.15 \text{ K})} = 24.6 \text{ kJ} \text{ mol}^{-1}$ , as calculated at the B3LYP/6–311++G(d,p) level of approximation;  $\Delta E$ ,  $\Delta E_{(0)}$  and  $\Delta G_{(298.15 \text{ K})}$  are the relative electronic energy, zero-point-corrected electronic energy and Gibbs energy, respectively).

geometries of the two conformers (*trans* and *cis*) of 2AP. The calculated relative electronic ( $\Delta E$ ), zero-point corrected electronic ( $\Delta E_{(0)}$ ) and Gibbs ( $\Delta G^{\circ}_{(298.15 \text{ K})}$ ) energies of the conformers amount to 26.3, 26.0 and 24.6 kJ mol<sup>-1</sup>, respectively, with the *cis* form being the most stable species. The optimized Cartesian coordinates are provided in the Supporting Information (Table S1). The most relevant geometrical parameters are collected in Table 1, together with some other information that is useful to understand the reasons of the considerably lower energy of conformer *cis* compared to conformer *trans*.

The different nature of the main intramolecular interactions in the two conformers of 2AP is very well reflected in their structural and electronic parameters. The cis form exhibits a relatively strong stabilizing interaction between the ortho ring hydrogen atom (H7) and the carbonyl oxygen, and a weaker one between the methyl out-of-the-plane hydrogen atoms (H14, H15) and the ring nitrogen atom. On the other hand, in the less stable trans conformer these interactions are replaced by repulsive interactions between the oxygen and nitrogen lone electron pairs and between H7 and the methyl out-of-the-plane hydrogen atoms. Accordingly, the CO bond is considerably more polarized and longer in the most stable *cis* form than in the trans conformer: the charges on O and C11 in the cis and trans conformers are -0.552 and 0.551 e, respectively, vs. -0.512 and 0.538 e, the CO bond order 2.10 vs. 2.57, and the CO bond length 1.216 vs. 1.209 Å (see Table 1). The C2-N1 bond is also more polarized in the most stable conformer: the charges on N and C2 are -0.446 and 0.104 *e* in the *cis* form. *vs.* -0.407 and 0.104 *e* in the *trans* conformer, and the C2–N1 bond order is 1.30 and 1.69.

#### Table 1

Selected structural parameters (distances in Å, angles in degrees), natural atomic charges (e) and Meyer bond orders [25], for cis and trans 2AP conformers and *cis/trans* transition state (TS<sub>(cis-trans</sub>)).<sup>a</sup>

Distances and angles	cis	trans	TS <sub>(cis-trans)</sub>
C11=012	1.216	1.209	1.209
C2-C11	1.512	1.520	1.522
C11-C13	1.509	1.520	1.511
C2-C3	1.398	1.400	1.396
C2-N1	1.340	1.340	1.336
C6-N1	1.334	1.329	1.336
C3-H7	1.082	1.082	1.084
N1 <sup></sup> H14,15	2.781	3.327 (H14)	
H7 <sup></sup> H14,15	2.392	2.804 (H15)	
H7 <sup></sup> 012	2.490	3.504	
N1 <sup></sup> O12	2.732	3.039	
C2-C3-H7	119.1	121.0	120.6
N1-C2-C11	117.5	116.0	115.7
C2-C11-O12	119.8	120.8	120.3
C2-C11-C13	117.8	118.1	116.6
C13-C11-O12	122.4	121.0	123.2
$H_3CC-CN$	0.0	180.0	104.3
Natural atomic charges			
q(012)	-0.552	-0512	-0.519
q(C11)	0.551	0.538	0.566
q(N1)	-0.446	-0.407	-0.445
qC2)	0.104	0.104	0.132
q(H7)	0.237	0.214	0.214
q(H14,15)	0.233	0.218	0.231 (H14)
0.219 (H15)			
q(H16)	0.220	0.231	0.225
Meyer bond orders <sup>b</sup>			
C11=012	2.10	2.57	2.29
C2-C11	1.14	0.74	0.78
C11–C13	0.66	0.69	0.78
C2–C3	1.47	1.38	1.24
C2-N1	1.30	1.69	1.50
C6-N1	1.01	0.93	1.03
C3-H7	0.81	0.86	0.84

<sup>a</sup> See Fig. 1 for atom numbering.

<sup>b</sup> Meyer bond orders are defined in ref. [25].

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