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# Structure, vibrational spectra and DFT characterization of the intra- and inter-molecular interactions in 2-hydroxy-5-methylpyridine-3-carboxylic acid – Normal modes of the eight-membered HB ring



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# HIGHLIGHTS

- 2-Hydroxy-5-methylpyridine-3carboxylic acid (HMPC) has been synthesized.
- The crystal structure of HMPC was studied.
- Cyclic eight-atomic arrangement connect two units into a dimeric structure.
- IR, Raman spectra and DFT calculations confirm the existence of an intra- and intermolecular HBs.

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# GRAPHICAL ABSTRACT



# ABSTRACT

Fourier transform IR and Raman spectra, XRD studies and DFT quantum chemical calculations have been used to characterize the structural and vibrational properties of 2-hydroxy-5-methylpyridine-3-carboxylic acid. In the unit-cell of this compound two molecules related by the inversion center interact via O-H···N hydrogen bonds. The double hydrogen bridge system is spaced parallel to the (102) crystallographic plane forming eight-membered arrangement characteristic for pyridine derivatives. The sixmembered ring is the second characteristic unit formed via the intramolecular O-H···O hydrogen bond. The geometry optimization of the monomer and dimer have been performed applying the Gaussian03 program package. All calculations were performed in the B3LYP/6-31G(d,p) basis set using the XRD data as input parameters. The relation between the molecular and crystal structures has been discussed in terms of the hydrogen bonds formed in the unit cell. The vibrations of the dimer have been discussed in terms of the resonance inside the system built of five rings coupled via hydrogen bonds.

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# Introduction

Hydroxy- and carboxy-pyridines play a special role among the pyridine derivatives due to tautomerism and dimerisation appear-

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ing in these compounds. The pyridine carboxylic acids and their derivatives belong to a very interesting group of compounds with biological importance [1]. For example, pyridine 3-carboxylic acid, known as niacin or vitamin B<sub>3</sub>, is a precursor of the coenzyme NAD formation [2]. 2- and 3-carboxypyridine and their hydroxy and amino derivatives in the form of salts with L-tartaric acid have been applied as biologically compatible pharmaceuticals [3]. Dipicolinic

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acid occurs in nature as an oxidative degradation product of alkaloids, coenzymes and vitamins and it is a component of fulvic acids. It is also a plant-sterilizing and water-germicidal agent and antioxidant for ascorbic acids in food [4] and is present in the bacterial spores [5]. Pyridine-2,3-dicarboxylic acid is an intermediate product in the tryptophan degradation pathway and a precursor of the NAD synthesis [2].

Transition and heavy metal complexes of the naturally occurring pyridine-2,3-dicarboxylic acid and 4-hydroxypyridine 2,6-dicarboxylic acid have been synthesized and characterized [6]. It was reported that some of these compounds have positive effect in normalizing blood glucose content in diabetic rats [7,8].

In this work we present the results of structural and spectroscopic studies of 2-hydroxy-5-methylpyridine-3-carboxylic acid (HMPC). Fourier transform IR and Raman spectra, XRD studies and DFT quantum chemical calculations were used to characterize these properties. Special attention has been focused on the vibrational characteristics of the eight-membered ring joining two adjacent molecules in the unit cell. Such inter-molecular hydrogen bonds (HB) should introduce additional structural and dynamical effects revealed in XRD measurements, vibrational spectra and theoretical data. Intra-molecular hydrogen bonds are also formed in the studied compound and have been analyzed in the present work.

# Experimental

#### Synthesis [9]

Two methods of the synthesis have been used: (a) carboxylation of 2-hydroxypicolines by the Marasse method, and (b) carboxylation of 2-hydroxypicoline sodium salt.

In the method (a), a sample of 4.36 g (0.04 mole) of dried 2-hydroxypicoline was mixed thoroughly with 9 g of freshly roasted and finely ground potassium carbonate and treated with anhydrous carbon dioxide at 220 °C and 55–57 atm for 8–9 h After completing the reaction, the content of the beaker was dissolved in 50 ml of water and acidified with concentrated hydrochloric acid up to pH = 3. The obtained carboxylic acid crystals were recrystal-lized from water with addition of some active carbon.

In the method (b), a sample of 4.36 g (0.04 mole) of 2-hydroxypicoline was dissolved in aqueous solution of 1.8 g (0.04 mole) NaOH and evaporated to dryness. The dry residue was powdered in a mortar and dried for 4 h at 120 °C. Prepared in this way sodium salt of 2-hydroxypicoline was placed in a glass beaker in a steel autoclave and carbon dioxide dried with a mixture of silica gel with some anhydrous calcium chloride was introduced. The reaction mixture was kept at 190–220 °C and 55–60 atm for 7–9 h. The formed pyridinecarboxylic acid was isolated as described in the method (a).

# Spectral measurements

IR spectra in the range 50–4000 cm<sup>-1</sup> range were recorded at room temperature in Nujol suspension and KBr pellet with a FTIR Biorad 575C spectrometer. Raman spectra in the 80–4000 cm<sup>-1</sup> range were measured in back scattering geometry with a FT Bruker 110/S spectrometer. The YAG:Nd laser was used as an excitation source. The resolution was 2.0 cm<sup>-1</sup> both in IR and Raman studies.

# Quantum chemical calculations

The geometry optimization of the studied compound was performed using the Gaussian 03 program package [10]. All calculations were performed by the density functional three-parameters hybrid (B3LYP) methods [11,12] with the 6-31 G(d,p) basis set starting from the XRD data. The theoretical wavenumbers were scaled to compare them with the experimental values. The linear correlation method was applied in this procedure [13]. From the mean square deviation, the 0.96 scaling factor was derived for all normal modes.

The potential energy distribution of the normal modes (PED) among the respective internal coordinates has been determined using the BALGA program [14]. All calculations were performed for an isolated molecule with one intra-molecular hydrogen bond as a monomer and for the dimer unit in which the double HBs joint two adjacent molecules forming an eight-atomic ring system. The PED values have very similar contributions for the dimer and monomer for majority of the normal modes. The vector displacements of the atoms from their equilibrium positions during the vibration and the graphical presentations of these displacements were obtained using ANIMOL program [15].

It should be noted that the standardized internal coordinate systems have been applied for the construction of potential function. Such an approach is now commonly used for the variety of organic molecules, functional groups and four-, five- and six-atomic rings [16]. Redundancies between the stretching and bending coordinates are eliminated by this choice. The ring deformational coordinates involve the whole ring and are therefore non-local. In the present work an internal coordinate system for eight-atomic ring was constructed [17].

The natural bonding orbitals (NBO) calculations were performed using NBO 3.1 program (E.D. E.D. Glengening, A.E. Reed, J.E. Carpenter, F. Weinhold, NBO Version 3.1, TCI, University of Visconsin, Madison, 1998) as implemented in the Gaussian 03W package at DFT B3LYP/6-31G(d,p) levels [18].

# **Results and discussion**

## X-ray crystallography

A colorless single crystal of 3-carboxy-2-hydroxy-5-methyl pyridine acid with approximate dimensions of  $0.36 \times 0.26 \times 0.18$  cm was used for data collection on a four-circle KUMA KM-4 diffractometer equipped with a two-dimensional area CCD detector. The graphite monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and  $\omega$ -scan technique with  $\Delta \omega = 0.75^{\circ}$  for one image were used for data collection. The lattice parameters were refined by leastsquares methods on the basis of all collected reflections with  $F^2 > 2\sigma(F^2)$ . One image was monitored as a standard for every 50 images. Integration of intensities, correction for Lorenz and polarization effects were performed using KUMA KM-4 CCD software [19]. The face-indexed analytical absorption was calculated using the *SHELXTL* program [20].

The structures were solved by direct methods and refined with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXL-97 program [21]. The hydrogen atoms were located in their calculated positions, and their temperature factors were constrained with the  $U_{iso} = 1.2U_{iso}$  for all H atoms joined to the aromatic C atoms, or  $U_{iso} = 1.5U_{iso}$  for the H atoms of the hydroxyl or methyl groups. The final difference Fourier maps showed no peaks of chemical significance. The final agreement factors and details of data collection are summarised in Table 1.

The studied compound crystallizes in centrosymmetric monoclinic space group  $P2_1/c$  ( $C_{2h}5$ ) with Z = 4. The X-ray experimental data are collected in Table 1. The molecular geometry of 3-carboxy-2-hydroxy-5-methyl pyridine acid with the labeling of the atoms are shown in Fig. 1. The chosen theoretical and experimental bond lengths and angles are specified in Table 2 together with the *ab initio* fully optimized parameters that correspond to the

#### Table 1

Crystallographic details of data collection and refinement parameters for 2-hydroxy-3-carboxy-5-methyl pyridine (1) and 2-hydroxy-3-cyano-4-methyl pyridine (2).

Farmer 1	
Formula	$C_7H_7NO_3-(1)$
Mol. wt.	153.14
Crystal system, space group	Monoclinic, <i>P2</i> <sub>1</sub> /c
Unit cell dimensions a, b, c, (Å)	11.858(2), 8.1410(16), 7.2520(15)
β (°)	99.85(3)
Volume, V (Å <sup>3</sup> )	689.8(2)
Ζ	4
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	1.475
D <sub>obs</sub> measured, flotation (g/cm <sup>3</sup> )	1.47
Radiation, Mo Kα, λ (Å)	0.71073
$2\theta$ range	3.05-59.1
Refls collected	7902
Independent refls.	$1790 (R_{int} = 0.0242)$
Observed refls.	1073
Absorption coefficient, $\mu$ , (mm <sup>-1</sup> )	0.117
Correction	Lorenz, polarization, face-indexed
	analytical absorption, $T_{\text{max}} = 0.982$ ,
	$T_{\min} = 0.951$
Refinement on $F^2$	
$R(F^2 > 2\sigma(F^2))^a$	0.0485
$wR$ ( $F^2$ all reflections) <sup>b</sup>	0.1391
Goodness-of-fit, S	1.001
Residual electron density, e $Å^{-3}$	+0.346, -0.292

<sup>a</sup>  $R = \sum ||F_{\rm o}| - ||F_{\rm c}| / \sum F_{\rm o}.$ 

<sup>b</sup>  $wR = \{\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4\}^{1/2}; w^{-1} = [\sigma^2(F_o^2) + (0.0787P)^2]$  for (1) and  $w^{-1} = [\sigma^2(F_o^2) + (0.0635P)^2]$  for (2), where  $P = (F_o^2 + 2F_c^2)/3$ .

gas-phase structures. The absolute energies calculated using B3LYP methods and 6-31 + G(d,p) basis sets functions were found to be -551.42 a.u. The global minima on the potential energy surface (PES) were found. The calculated dipole moment is 4.764 D.

The pyridine ring of the compound in the crystal is almost planar (the displacements of the C or N atoms from the mean plane of the ring are smaller than 0.003 Å but shows significant distortions from the ideal hexagonal form. This is a result of the steric effect of the substituents of the pyridine ring located in the 2, 3, 5 positions. The internal C—N—C angle is greater than 120° for the compound in the solid state while in the gas-phase structures obtained by molecular orbital calculations is smaller than 120°. The steric effect of the lone pair of electrons at the N-pyridine atoms as predicted in the valence-shell electron-pair repulsion model [22] for isolated molecule structures decreases significantly in the crystal due to formation of HBs system (Table 2). The C—C and C—N bond lengths within the pyridine ring are close to those reported for other pyridine derivatives [23].

Table 2 compares some selected structural parameters obtained from the XRD studies with those calculated for the monomer and dimer. Good accordance between the experimental and theoretical data for majority of bond length and angles was found. Clear discrepancies are seen for N1–C2, C2–O1 and C7–O2 bonds as well

Table 2

Selected geometric parameters (Å for bond lengths,  $^{\circ}$  for angles) for 2-hydroxy-3-carboxy-5-methyl pyridine.

	X-ray	Calculated	
		Dimer	Monomer
N1-C6	1.348(2)	1.346	1.34036
N1-C2	1.376(2)	1.339	1.32326
C2-01	1.270(2)	1.335	1.36472
C2-C3	1.409(2)	1.416	1.40797
C3-C4	1.370(2)	1.390	1.39546
C3–C7	1.489(2)	1.509	1.5059
C4—C5	1.406(2)	1.402	1.39868
C5–C6	1.370(2)	1.390	1.39700
C5–C8	1.508(2)	1.508	1.50803
C7—O3	1.210(2)	1.212	1.21146
C7—02	1.327(2)	1.342	1.34564
C6-N1-C2	122.85(12)	119.3	117.8
01-C2-N1	119.12(12)	118.5	116.2
01-C2-C3	124.31(13)	119.8	119.4
N1-C2-C3	116.55(12)	121.7	124.4
C4-C3-C2	120.00(13)	117.4	116.0
C4–C3–C7	120.00(12)	117.7	117.9
C2-C3-C7	120.00(12)	124.9	126.1
C3-C4-C5	122.33(13)	121.6	121.3
C6-C5-C4	115.97(13)	116.1	116.3
C6–C5–C8	121.78(13)	121.8	121.7
C4–C5–C8	122.24(13)	122.1	122.0
N1-C6-C5	122.30(13)	123.9	124.1
03–C7–O2	120.59(13)	121.4	120.8
03–C7–C3	122.74(14)	121.2	121.4
02–C7–C3	116.67(12)	117.4	117.8
02—H2—01			
D-H	0.82	0 97857	0 97084
HA	1 77	1 76248	1 8111
DA	2 5 3 1	2 64284	2 71332
∠D—H…A	153	147 855	153 222
	155	147.055	133,222
01—H1—N1i			
D—H	0.82	1.03817	-
H···A	2.00	1.58320	-
D···A	2.77	2.61906	-
<d—h···a< td=""><td>156</td><td>175.080</td><td>-</td></d—h···a<>	156	175.080	-

as for O1–C2–C3, N1–C2–C3 and C2–C3–C7 angles which are engaged in the inter- and intra-molecular hydrogen bonds formed in the studied compound. The C–OH bond length is shorter than that observed in the gas-phase structure. The C–CH<sub>3</sub> bond length is typical for the C<sub>ar</sub>–CH<sub>3</sub> distance observed for substituted pyridine derivatives, i.e. 1.501 Å [24]. The carbon–oxygen distances of the carboxyl group (1.210(2) Å) are comparable to those found in other aromatic carboxylic acids, 1.203–1.224 Å for double C=O and 1.298–1.329 Å for single C–O bond [24]. In the crystal two molecules related by the inversion center interact *via* O–H…N relatively strong hydrogen bonds (Table 3) forming dimers parallel to (102) crystallographic plane (Fig. 2). The dimers form shifted stacking structure along [001] direction with a distance of



Fig. 1. X-ray molecular structure of 2-hydroxy-5-methylpyridine-3-carboxylic acid (monomer and dimer).

#### Table 3

Com	parsion of X-ray	y and	vibrational	data f	or the	hydrog	en bonds	s in	2-hydroxy	v-3-carbox	v-5-meth	nylpyric	line	A-01	or N1	<sup>1</sup> atoms	1.
						J						J I J .					

Geometrical parameter (Å and °) D–H···A D–H H···A D···A D–H···A	Vibrational char	acteristics (cm <sup>-1</sup> )		
	$\nu(OH{\cdot}{\cdot}{\cdot}A)$	$\delta(OH{\cdot}{\cdot}{\cdot}A)$	$\gamma(OH{\cdots}A)$	$\nu(H{\cdots}A)$
Intra-molecular interactions (φring) 02—H2…01 0,82 1,77 2,53 1 153	3013, 2782	1348	617, 394, 491	161, 153, 145, 124
Inter-molecular interactions (θ ring) O1−H1…N1 <sup>1</sup> 0,822,002,77156	2597, 2343	1464, 1460	1015, 955	107-80

Symmetry code: (i) 1-x,-y, 1-z



Fig. 2. Part of the crystal structure, showing the stacking. The asymmetric unit consists of one molecule.

~3.18 Å between the dimers that suggests occurring of  $\pi$ - $\pi$  interactions. The intra-molecular interaction of the O—H···O type exists between the carboxyl and hydroxyl group.

#### Vibrational data and DFT calculations

The IR and Raman spectra of 2-hydroxy-5-methylpyridine-3carboxylic acid are shown in Figs. 3 and 4. The isolated molecule consists of 18 atoms and their vibrations are described by 48 normal modes. The distribution of vibrations according to the  $C_s$  point group is 32A' + 16A'. The vibrational degrees of freedom of the monomeric unit can be described by 18 stretching and 30 bending modes. All these vibrations are both IR and Raman active because the molecule occupies the site of the general symmetry. The number of observed 49(IR) and 44(RS) is close to that predicted for the single molecule.

On the other hand, 36 atoms of the dimer give rise to 102 vibrational normal modes that can be described for the point group symmetry  $C_{2h}$  as  $34A_g + 33B_u + 18A_u + 17B_g$ . However this number increases twice  $(2 \times 102 \text{ internal vibrations})$  because the primitive unit cell of the  $C_{2h}$  symmetry contains four monomers i.e. two dimers related through C<sub>i</sub> symmetry. Therefore, every molecular vibration should split in the crystal into  $A_g$ ,  $B_g$ ,  $A_u$  and  $B_u$  components being IR active for the u-modes and Raman active for the g-modes. The number of the observed bands should be significantly reduced due to accidental degeneracy of the vibrational energy corresponding to two identical units in the dimer. Since the spectra of powder have been recorded, the factor group splitting is hardly observable and the analysis can be performed based on the C<sub>i</sub> symmetry. Comparing the wavenumbers calculated for the isolated molecule with those observed in the spectra, the splitting of the respective bands into two components is expected due to the dimer formation in the solid state (Table 4). It is seen for some bands, i.e. the v(C=0) doublet contour is observed in the IR and Raman spectra at 1725 and 1733 cm<sup>-1</sup>, respectively. A few other bands also exhibit doublet nature, e.g. the IR bands at about



**Fig. 3.** The IR spectra of 2-hydroxy-5-methylpyridine-3-carboxylic acid in the range 3500–50 cm<sup>-1</sup> (experimental – exp. and calculated: monomer, dimer).

1596, 895, 803 cm<sup>-1</sup> and Raman bands at 1329, 735, 347, 198 and 90 cm<sup>-1</sup>. However, for the majority of the observed bands no factor group splitting is observed and the splitting of some bands should be treated as a result of inter- and intra-molecular interactions. Since the molecules are joined by HBs, the observed bands can be conveniently subdivided into those arising from the hydrogen bond vibrational modes and internal modes of the pyridine ring, methyl group and carboxylic group vibrations.

#### Pyridine ring vibrations

The pyridine ring vibrations are very characteristic and they are usually observed at defined wavenumbers. The ring v(CH) bands are centered usually around  $3050-3120 \text{ cm}^{-1}$ , about  $100-150 \text{ cm}^{-1}$  higher than those of v(CH<sub>3</sub>) bands. The assignment of the pyridine ring vibrations for the studied compound was based on the comparative spectra of pyridine [25], the results of DFT quantum chemical calculations reported by Urena et al. [26], as



Fig. 4. The RS spectra of 2-hydroxy-5-methylpyridine-3-carboxylic acid in the range  $3500-50 \text{ cm}^{-1}$  (experimental – exp. and calculated: monomer, dimer).

well as several our works on the IR and Raman spectra of several pyridine derivatives [27–31]. Two v(CH) vibrations are observed at 3030 and 3059  $\text{cm}^{-1}$  in the IR spectra and at 3044, 3063  $\text{cm}^{-1}$ in the Raman spectra because there are two C—H bonds in pyridine ring of the molecule. The other characteristic vibrations appear in the following ranges: in-plane  $\delta(CH) + v(\phi)$ : 1590–1640, 1490– 1560, 1390-1445, 1270-1330 and  $\delta(\phi)+\delta(CH)$  1240-1250 and 1090–1100 cm<sup>-1</sup>, and out-of-plane  $\gamma$ (CH): 920–940 and 800– 840 cm<sup>-1</sup> and  $\gamma(\phi)$ : 700–730, 660–670, 540–610 and 400– 500 cm<sup>-1</sup>. These vibrations arise as strongly coupled the pyridine ring and CH modes. They are observed in typical for these vibrations ranges [26 and references therein]. Very complex vibrations of the whole skeleton are observed in the range below 300 cm<sup>-1</sup>. They form concerted movements in which almost all fragments of the molecule together with the hydrogen bonds that couples several molecules in one cluster take part.

It should be noted that the breathing  $v_s(\varphi)$  vibrations of the pyridine ring in the studied compound are observed at 920 cm<sup>-1</sup> in the IR spectrum and 939 cm<sup>-1</sup> in the Raman one. These vibrations usually appear for benzene derivatives in the range 900– 1000 cm<sup>-1</sup> [32,33]. For the pyridine derivatives they usually appear in the range 750–950 cm<sup>-1</sup> depending on the number of substituents and their place of substitution in the heterocyclic ring [34].

#### Methyl group vibrations

Three fundamental v(CH<sub>3</sub>) bands corresponding to one symmetric and two asymmetric vibrations are usually observed in the range between 2870 and 2990 cm<sup>-1</sup> [29,31]. Our DFT calculations locate these modes at the following wavenumbers:  $v_{as}$ (CH<sub>3</sub>) 2984–3005 (100% contribution) and  $v_s$ (CH<sub>3</sub>) 2927 cm<sup>-1</sup> (100% contribution). They agree well with the experimental values found in the IR spectrum at 2958 and 2986 cm<sup>-1</sup> and at 2956 and 2983 cm<sup>-1</sup> in the Raman spectrum for  $v_{as}$ (CH<sub>3</sub>) and at 2930 (IR) and 2929 (RS) cm<sup>-1</sup> for  $v_s$ (CH<sub>3</sub>). The other weak bands in this range arise from a Fermi resonance with the bending vibrations of these groups.

The asymmetric bending vibrations of the methyl groups should appear between 1410 and 1550 cm<sup>-1</sup> [32,34]. This is true for the compound under study.  $\delta_{as}$ (CH<sub>3</sub>) vibrations contribute the bands observed in the range 1443–1464 cm<sup>-1</sup> giving a 85–100% contribution. The symmetric  $\delta_s$ (CH<sub>3</sub>) vibration also appears in a typical range and is observed at 1393 (IR) and 1390 (RS) cm<sup>-1</sup> giving a 100% contribution to the normal modes. The other bands involving the methyl groups are observed in the following ranges:  $\delta$ (CH<sub>3</sub>): 1077 and 992, v(C–CH<sub>3</sub>): 1199(IR), 1198(RS), 830(IR) and

831(RS);  $\delta$  and  $\gamma$ (C–CH<sub>3</sub>): 345(IR), 347(RS), 187(IR,RS), 161(IR), 153(RS) and  $\tau$ (C–CH<sub>3</sub>) below 90 cm<sup>-1</sup>.

#### Carboxylic group vibrations

The discussion of the carboxylic group vibrations in the studied compound should be focused on the modes in which the C=O group participates. Because the O–H group of this unit takes part in the intramolecular interactions inside the molecule, the vibrations of the hydroxyl group is discussed in the part where the dynamics of the hydrogen bonds systems is considered. The v(C=0) vibration is observed in the IR spectrum of the studied compound at 1725  $\text{cm}^{-1}$  and at 1733  $\text{cm}^{-1}$  in the Raman spectrum. In several other normal modes calculated for the dimer the vibrations of the C=O group participate. For instance, the IR wavenumbers at 731 and 727  $cm^{-1}$  and Raman bands at 235 and 735  $cm^{-1}$ correspond to the modes with the 14–30% contribution of the inplane  $\delta(CO)$  vibrations. The out-of-plane  $\gamma(CO)$  vibrations show 60% contribution to the modes observed at 665 cm<sup>-1</sup> and 16% contribution to the bands at 590 (RS) and 605 (IR) cm<sup>-1</sup>. Rocking vibration of this group appears in the range  $394-400 \text{ cm}^{-1}$ . The wavenumbers of all bands corresponding to the vibrations of the C=O group agree with those reported for the carboxylic acids of which carboxy group is not engaged in the intramolecular interactions [32].

#### Hydrogen bond vibrations

Two hydrogen bond systems appear in 2-hydroxy-5-methylpyridine-3-carboxylic acid. Two hydroxyl groups of adjacent molecules are involved in the intermolecular interactions (Fig. 1) forming an eight-membered HB system. Due to its flat arrangement its symmetry can be described as  $C_{i}$ , the same as for the whole dimer. On the other hand, the intramolecular interaction between the O1 atom of the hydroxyl group and H2 hydrogen atom of the carboxyl group leads to the formation of six-membered ring. The existence of these two HB systems is postulated by XRD studies. According to these data the length of the O2–H2···O1 bond is 2.531 Å and O1–H1 $\cdots$ N1' is 2.77 Å (Table 2). These lengths calculated for the dimer in the geometry optimization process take the values 2.74 and 2.618 Å, respectively. Each of these values is identical in two interacting molecules what follows from the C<sub>i</sub> symmetry of the dimer. It should be noted that the theoretical values give the reciprocal sequence than that proposed by the XRD data. The IR and Raman studies should be sensitive to the formation of these specific bridge bonds.

Cyclic eight-atomic arrangement is constructed through intermolecular interactions that connect two units into a dimeric structure. Hydrogen bonds can connect different molecular systems e.g. carboxylic acid–2-aminopyridine [35], carboxylic acid–oxime and hydroxyl–amine [36], carboxylic acid–urea [37], amides–acids [38], two pyridone [39,40], two carboxylic acids [41], amino-pyridinium-carboxylic acid [42] and aminopyrimidine-hydroxybenzoate [43]. The most well-known hydrogen bond motif is the carboxylic acid head-to-head dimer [44]. The structure of these systems is illustrated by self-complementary  $R_2^2(8)$  or  $R_2^1(8)$  graphs [45]. Although the structural XRD data for these systems have been reported in several papers [35–44], their vibrational characteristics based on the DFT calculations are still under studies [27,42,46].

In the theoretical spectra of the monomer, the calculated wavenumbers 3616 and 3524 cm<sup>-1</sup> correspond to the v(O1—H1) and v(O2—H2) vibrations, respectively. The former vibration concerns the hydroxyl group non-participated in the HB, but the latter occurs in the O2—H2…O1 intramolecular interaction. On the other hand, the wavenumbers calculated for the dimer differ from those calculated for monomer as far as the intramolecular and intermolecular HBs are concerned. For the former, i.e. for the O2—H2…O1 bond the theoretical IR and Raman wavenumbers equal to 3439

#### Table 4

Experimental IR and Raman spectral data and calculated wavenumbers for monomer and dimer of 2-hydroxy-3-carboxy-5-methylpyridine.

Experimenta wavenumbe	al er	No	Calcula	ated wavenur	nber						Ped contribution	
IR	RS		Monor	ner		Dimer					Monomer	Dimer
				Intensities (%)			Intensi	ties (%)	Ag (RS)	Au (IR)		
			-	IR	RS		IR	RS				
3123m		ν <sub>1</sub>	3616	0.1	0.0						vCH – 99	
		V <sub>2</sub>	3524	0.9	0.1	$v_1, v_2$	0.3, 0.2	0.0, 0.0	3440	3439	$vOH_{COOH} - 99$	$vOH_{COOH}(HB) - 100$
3106m	3103w					$v_3, v_4$	0.3, 0.0	0.0, 0.1	3080	3080	vCH – 100	vCH – 100
3059m	3063m	$\nu_3$	3081	0.2	1.1	v <sub>5</sub> ,v <sub>6</sub>	0.2, 0.0	0.0, 0.3	3053	3053	vCH – 99	
3030sh	3044m											$\nu_{as}CH_3-100$
		$\nu_4$	3044	0.0	0.5	V7,V8	0.5, 0.0	0.0, 0.0	3005	3005	$v_{as}CH_3-100$	
2986m, 2958m,	2983w, 2956w	$V_{5,}$	3003, 2981	1.9	0.5	$v_{9}, v_{10}$	0.0,0.0	0.1, 0.0	2984	2984	$v_{as}CH_3-100$	
		$\nu_6$		0.5	0.7							$\nu_{as}CH_3-100$
2930w	2929m	V7	2924	0.0	0.9	$v_{11}, v_{12}$	0.0, 0.0		2927	2927	$v_s CH_3 - 100$	$v_s CH_3 - 100$
2879m, 2816m 2784m,	2878w 2752w					V <sub>13</sub> ,V <sub>14</sub>	0.4, 0.0	0.0, 0.2	2272	2446		ν(OH)θ – 1000
2422m 1725vs	1733w	$\nu_8$	1766	0.7	2.1	$v_{15}, v_{16}$	1.7,	0.0,	1768	1765	$\nu CO_{COOH} - 82 + \delta \phi - 11$	$\nu CO_{COOH} - 81 + \delta \phi - 11$
1643m	1642w	$\nu_9$	1593	2.6	1.9	$v_{17}, v_{18}$	0.0 2.3,	0.3	1619	1605	$\nu\varphi-75\text{ + }\delta\delta CH-13$	$\nu\varphi-55+\delta CH-7+\delta\theta-22$
1609m, 1596m	1616m	$\nu_{10}$	1579	4.3	0.4	V <sub>19</sub> ,V <sub>20</sub>	0.0,0.7	0.4	1577	1597	$\nu\varphi-77+\delta CH-9$	$\nu\varphi-64+\delta CH-11+\delta\theta-20$
1551m	1557m, 1494w					$v_{21}, v_{22}$	0.5, 0.0	0.0,0.8	1532	1480		$\nu\varphi-60\text{ + }\delta\theta-24\text{ + }\delta CH-16$
1460sh	1464m					V23	0.0	1.5		1468		$\delta\theta - 41 + vC - OH_{COOH} - 8 + \delta asCH_3 12 + v\phi - 16$
		$\nu_{11}$	1454	34.6	2.9	V <sub>24</sub> V <sub>25</sub>	0.3 0.0	0.0 0.1	1449	1446	δasCH <sub>3</sub> 85	$\delta_{asCH_385}$ $\delta_{asCH_364} + \delta_0 - 14$
1443s	1448sh	$\nu_{12}$	1447	1.1	4.3	V <sub>26</sub> ,V <sub>27</sub>	5.8, 0.0	0.5, 1.3	1437	1437	δasCH₃98	$\delta asCH_3 - 100$
		$v_{13}$	1438	0.0	0.1	V <sub>28</sub>	3.0	0.0	1423		$\nu\varphi-47+\delta CH-23+\nu C-OH-13$	$\delta\phi-25\text{ + }\delta\text{CH}-16\text{ + }\nu\varphi-11\text{ + }\nu\theta-10$
		$\nu_{14}$	1398	1.9	0.6	V <sub>29</sub>	0.0	0.0		1383	$\nu \varphi - 38 + \delta \varphi - 16 + \delta asCH_3 16$	$\nu\varphi-33+\delta\phi-21+\delta CH-16$
1393m	1390m	$v_{15}$	1375	10.3	0.1	$v_{30}, v_{31}$	2.4, 0.0	0.0, 0.0	1377	1377	δsCH <sub>3</sub> – 91	$\delta_s CH_3 - 100$
		$\nu_{16}$	1349	0.7	1.2	V <sub>32</sub> ,V <sub>33</sub>	3.5, 5.1	0.0, 0.0	1375	1369	$\delta\phi-65$ + vC - OH <sub>COOH</sub> - 9	$\delta\phi-64 \text{+}\nu\text{C}-0H_{\text{COOH}}-10$
1348w						V34	0.0	0.1	1363			$\nu \varphi - 34 + \delta CH - 22$
1326m	1329m					$v_{35}, v_{36}$	0.5, 0.0	0.0, 0.5	1302	1317		$\nu\varphi-37+\nu C-OH_{COOH}-14+\nu CO-13+\delta CH-19$
1269w	1273w	$v_{17}$	1305	1.5	0.5	$v_{37}, v_{38}$	0.0, 4.0	0.1, 0.0	1273	1269	$\delta CH - 38 + \nu \varphi - 33 + \delta OH_{COH} - 13$	$\nu\varphi-63+\delta CH-16+\delta\phi-11$
		$v_{18}$	1283	2.6	3.6	V <sub>39</sub>	0.0	2.7	1253		$v$ CN $- 33 + v$ C $- OH - 18 + \delta$ CH $- 17 + \delta \phi - 18$	$\begin{array}{l} \nu\varphi\\ -34+\nu CO-7+\delta CH-26+\nu C-OH_{COOH}-6+\nu C-CH_{3}10\end{array}$
1246m	1250m	V19	1247	3.1	0.5	V40	9.4	0.0		1250	$\begin{array}{l} \delta\varphi\\ -42+\nu C-CH_{3}7+\delta\phi-6+\delta CH-21+\nu C-OH-16\end{array}$	$\delta\varphi-46+\nu C-CH_310+\nu\phi-14+\delta CH-16$
		V <sub>20</sub>	1229	2.6	3.1	$v_{41}$	0.0	0.2		1186	$\nu \phi - 25 + \nu \phi$	$\delta CH - 28 + \nu CN - 26 + \delta \phi - 12$

P. Godlewska et al./Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 120 (2014) 304-313

# Table 4 (continued) Experimental

Experimenta wavenumber	1 r	No	Calcula	ated wavenum	ıber						Ped contribution	
IR	RS		Monor	ner		Dimer					Monomer	Dimer
				Intensities (%)			Intensi	ties (%)	Ag (RS)	Au (IR)		
				IR	RS		IR	RS				
											$-21 + \delta OH_{COH} - 18 + \nu CN - 13 + \nu C - CH_3 10$	
1199vs	1198w	$\nu_{21}$	1178	1.4	0.9	$v_{42}, v_{43}$	2.4,	0.0,	1183	1183	$\nu C - OH_{COOH} - 28 + \nu C - CH_3 18 + \delta \phi - 10 + \delta CH - 19$	$\nu C - OH_{COOH} - 38 + \nu C - CH_3 15 + \delta \phi - 8 + \delta CH - 11$
1100	4455		4440		6 <b>-</b>		0.0	2.1	4470		2011 - 20 - NG - 22 - 2011 - 45	
1180w	11//s	V <sub>22</sub>	1072	0.2	6.5	V <sub>44</sub>	1./	0.0	1000	1070	$\delta OH_{COH} = 39 + VNC = 22 + \delta CH = 15$	$\delta CH = 24 + VCN = 34 + VC = CH_3 IU$
1097W		V23	1073	0.2	1.4	V45,V46	2.3, 0.0	0.0, 0.3	1080	1079	$^{0}$ φ - 25 + δCH - 14 + νNC12 + νC - OH <sub>COOH</sub> - 11 + νφ - 14	$\phi = 23 + \phi CH = 22 + vC = OH_{COOH} = 10 + vCN = 10 + v\phi$ = 15
10771077w	1078w	V24	1030	0.9	1.4	$V_{47}, V_{48}$	0.0,	3.3,	1031	1031	$\rho CH_{3}80 + \gamma C - CH_{3}15$	oCH₃79
		- 24				477 40	0.2	0.0				
1015w	1015w					V49	0.0	0.1		991		$\gamma \theta - 100$
992w		$\nu_{25}$	981	1.0	0.0	$v_{50}, v_{51}$	0.3,	0.0,	983	984	$\rho$ CH <sub>3</sub> 77 + $\nu \phi$ – 15	$QCH_377 + v\phi - 14$
							0.0	0.3				
955sh		$v_{26}$	953	2.9	0.8	V52,V53	0.0,	1.1,	959	956	$\gamma$ CH $-$ 86 + $\gamma$ $\phi$ $-$ 8	$\gamma CH - 80 + \gamma \theta - 10$
							0.8	0.0	027			
020m 805c	020c		021	27.0	11	V <sub>54</sub>	13.9	0.0	937	025	$y = 54 \pm yC$ CH 12 $\pm y/c$ 11	$\gamma \theta = 80 + \gamma C H = 10$
52011, 8553	888w	v27	521	27.0	1.1	v55,v56	0.0	0.0,	524	525	$v\phi = 54 + vc = ch_{312} + v\phi = m$	$v_{s}\phi = 55 + v_{s}\phi = 15 + v_{c} = c_{113}r_{2}$
830w.	831w.	V28	894	9.8	3.0	V57.V58	2.5.	0.0.	886	886	$\tau CH - 63 + \gamma \phi - 16 + o CH_3 11$	$\gamma CH - 70 + \gamma \phi - 12 + \gamma C - CH_3 - 9$
819m	818m	20				577 50	0.0	0.1				
803s	807w	V29	771	5.3	16.9	V59,V60	0.0,	3.1,	783	794	$\nu C - OH - 26 + \delta \varphi - 37 + \nu C - CH_3 10$	$\delta \phi - 22 + + \nu \phi$
							11.5	0.0				$-19 + \nu C - OH_{COOH} - 14 + \nu CO_{OH} - 10 + \nu C - CH_3 12$
731sh	735m					$v_{61}$	0.0	1.4		746		$\gamma\phi-37+\delta CO-26+\gamma\varphi-21$
		$v_{30}$	744	4.5	7.2	V <sub>62</sub>	11.3	0.0	744		$\gamma \phi - 53 + + \gamma \phi - 34$	$\delta CO - 30 + \gamma \phi - 35 + \gamma \phi - 19$
707-	720-1		711	4.0	2.0	V <sub>63</sub>	0.4	0.0	707	734	SCO 22 + St 41 + CU 14 + Sm 10	$\delta \phi - 42 + \delta CO_{COOH} - 18 + + vC - CH_3 10 + v\phi - 11$
/2/s	/28sh	V <sub>31</sub>	/11	4.0	3.9	V <sub>64</sub>	0.0	1.8	727	702	$\delta CO = 23 + \delta \phi = 41 + VC = CH_3 14 + \delta \phi = 10$	$\delta \phi - 48 + + VC - CH_3 14 + \delta CO_{COOH} - 14$
005111	005111	V32	700	11.0	2.1	V65,V66	2.1,	0.0, 5.7	700	703	$\gamma \phi = 38 + \gamma CO_{COOH} = 36 + \gamma \phi = 23 + \gamma \phi / \phi = 12$	$\gamma CO_{COOH} = 60 + \gamma \psi = 25 + \gamma \theta = 27 + \gamma \phi = 23$
661sh						Vez	0.0	0.9	661			$\delta \phi = 32 \pm \delta \Omega_{cool} = 28 \pm \delta \phi = 20$
001011						V68	1.2	0.0	001	656		$\delta \phi = 37 + \delta CO_{COOH} - 22 + \delta \phi = 21$
613sh,	617w	V33	648	100.0	2.9	V69,V70	0.0,	1.1,	651	649	$\delta \phi - 46 + \delta CO - 18 + \delta \phi - 17$	$\gamma \phi - 100$
							60.0	0.0				
						$v_{71}$	0.0	2.6		622		$\delta\phi-48+\gamma\text{CO}_{\text{COOH}}-18+\nu\theta-8$
605s	590w	$v_{34}$	601	0.2	13.5	V72	0.0	5.7	576		$\gamma \phi - 79$ + $\gamma CO_{COH} - 12$ + $\gamma CO_{COOH} - 8$	$\delta\phi-45+\delta CO_{COOH}-16+\delta\theta-5+\delta\varphi-6$
540s	541w	$v_{35}$	541	19.8	3.6	V <sub>73</sub>	0.7	0.0		533	$\delta \phi - 46 + \delta CO - 16 + \delta \phi - 12$	$\gamma \phi - 42 + \gamma \theta - 24 + \gamma \phi - 12 + \gamma CH - 20$
531sh	525W	$v_{36}$	535	1.3	11.0	V <sub>74</sub>	29.9	0.0	532	400	$\gamma \phi - 36 + \gamma CH - 26 + \gamma \phi / \phi - 13 + \gamma \phi - 12$	$\gamma \phi - 42 + \gamma \theta - 24 + \gamma CH - 20 + \gamma \phi - 13$
			470	52.4	0.0	V <sub>75</sub>	0.0	1.9	460	482	St 67 + VC CH 15	$\delta \phi = 61 + VC = CH_3 Ib$
		V37	470	52.4	0.5	V76 V77	0.0	3.4	405	472	$\delta \psi = 07 + VC = CH_{3}IS$	$\delta \phi = 78$
491m	483m	V20	454	14	83	V79	103	0.0	420	722	$\gamma CO_{cou} = 55 \pm \gamma (0 = 35 \pm \gamma \phi = 13)$	$\delta \phi = 78$
101111	453m	• 20	10 1		0.5	V79	0.0	2.3	120	419	10000n 00 14 00 14 10	$\delta \phi - 81$
	413w	V <sub>39</sub>	413	6.7	8.9	V <sub>80</sub>	7.6	0.0	414		$\gamma \phi - 67 + \gamma CO_{COH} - 22 + \gamma CH - 10$	$\delta \phi - 84$
394w	400s	$v_{40}$	397	19.5	22.2	$v_{81}$	77.7	0.0	379		$\delta \phi - 89$	$\delta \varphi - 39 + \nu \phi - 28 + \nu OH_{HB} - 14 + \gamma CO - 10$
	358sh	$\nu_{41}$	371	61.3	21.9	$v_{82}$	0.0	4.0		374	$\delta\varphi-47+\nu\phi-26+\delta CO-17+\delta C-CH_{3}12$	$\delta \varphi - 37 + v \varphi - 29$
	352sh					$\nu_{83}$	0.0	6.8		334		$\gamma C - C H_3 44 + \gamma \theta - 26 + \gamma \varphi - 25$
345m	347m		2.40		100 0	$v_{84}$	8.1	0.0	342			$\gamma C - CH_3 46 + \nu OH_{HB} - 31$
	339w	V <sub>42</sub>	340	5.1	100.0	V <sub>85</sub>	35.2	0.0	340	220	$\gamma C - CH_3 39 + \gamma \phi / \phi - 36 + \gamma \phi - 13$	$\gamma L - L H_3 45 + \gamma \theta - 24 + \gamma \phi - 26$
224m	235m	V43	312	5.0	49.1	V86 Voz	100.0	2.ð 0.0	216	558	$v \cup \Pi_{HB} = 43 + 40 - U \Pi_3 42$	$0 = CH_3 42 + VOH_{HB} = 41$ $\delta C = CH_2 28 + vOH_{UB} = 25 + + vO = 12$
224111	255111 198m					V87 Vaa	0.0	10.0	210	206		$vOH_{\rm up} = 37 + \delta C = CH_2 30 + + \delta \omega = 10$
	155111					* 88	0.0	10.7		200		$\psi = 10$

P. Godlewska et al./Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 120 (2014) 304-313

310

and 3440 cm<sup>-1</sup>, respectively, and those of intermolecular interactions, i.e. v(OH) of hydroxyl group are at 2446 cm<sup>-1</sup> in the IR spectrum and at  $2272 \text{ cm}^{-1}$  in the Raman spectrum. The observed wavenumbers of these vibrations significantly differ from the theoretical values. The deconvolution of the basic broad contour presented in Fig. 5 in the range 2000–3500 cm<sup>-1</sup> into four Lorentzian components (two of them correspond to the v(CH) and  $v(CH_3)$ modes) gives the values 3013 and  $2782 \text{ cm}^{-1}$  that could be assigned to the intramolecular interactions and the values 2597 and 2343 cm<sup>-1</sup> that we assigned to the intermolecular interactions. The reason of such great discrepancy between the experimental and theoretical data may be explained as a result of the coupling between two identical oscillators (massive ring systems) in the dimer that leads to the splitting and shifting of the vibrational levels forming the sequence of bands described above. Five rings constitute the dimeric system: two pyridine rings, two hexa-membered rings that follow from intramolecular interactions and one eight-membered ring joining two pyridine units representing the intermolecular interactions. O1 atoms are common for the rings originated from the intra- and inter-molecular interactions, and the coupling between two identical pyridine systems occurs by mediation of these bridge atoms. Table 3 compares the XRD data with those obtained from the spectroscopic studies.

The strong coupling between the vibrations of all rings in the studied system is confirmed by the PED data. Denoting the pyridine ring as  $\phi$ , six-membered ring of the intramolecular interactions as  $\phi$  and eight-membered ring of the intermolecular interactions as  $\theta$ , the assignment of their vibrations can be proposed. The majority of normal modes exhibit very complex nature being combinations in which the vibrations of two or even three rings participate. These combinations could be divided into several types:

- with greater contribution of the pyridine ring vibrations of the type:  $v(\phi) + \delta(\theta)$ ,  $v(\phi) + \delta(\phi)$ ,  $v(\phi) + v(\phi)$ ,  $\delta(\phi) + \delta(\phi)$ , and  $\gamma(\phi) + \gamma(\phi)$  bands at about 1642, 1643, 1609 1616, 1551, 1557, 1273, 1269, 1250, 1246, 920, 939, 394, 400 and 339 cm<sup>-1</sup>;
- with greater contribution of the φ-ring (intramolecular interactions), i.e. γ(φ) + γ(φ), δ(φ) + ν(θ), and γ(φ) + γ(θ) bands at about 819, 818, 807, 803, 161, 153 cm<sup>-1</sup>;
- with greater contribution of the  $\theta$ -ring (intermolecular interactions), i.e.  $\delta(\theta) + v(\phi)$ ,  $\gamma(\theta) + \gamma(\phi)$ ,  $\gamma(\theta) + \gamma(\phi) bands$  at about 1494, 161, 153, 90 and 80 cm<sup>-1</sup>;
- triple combinations of the  $\phi$ ,  $\phi$  and  $\theta$  rings vibrations of the type:  $\delta(\phi) + \nu(\phi) + \nu(\theta)$ ,  $\gamma(\theta) + \gamma(\phi) + \gamma(\phi)$  or  $\gamma(\phi) + \gamma(\theta) + \gamma(\phi)$  bands at about 1448,1443, 728, 727, 541, 540 and 187 cm<sup>-1</sup>.

Few bands could only be assigned as a result of vibrations that involve one ring:  $1015 \text{ cm}^{-1} - 100\% \gamma(\theta)$ ; 727, 728 cm<sup>-1</sup> - 48%  $\delta(\varphi)$ ; 613, 617 cm<sup>-1</sup> - 100%  $\gamma(\phi)$ ; 605, 590 cm<sup>-1</sup> - 45%  $\delta(\phi)$ ; 491, 483 cm<sup>-1</sup> - 78%  $\delta(\varphi)$ ; 453 cm<sup>-1</sup> - 81%  $\delta(\varphi)$ ; 413 cm<sup>-1</sup> - 84%  $\delta(\phi)$  and 73 cm<sup>-1</sup> - 80%  $\gamma(\phi)$ .

Combinations of the modes presented above proves that the PED data reflect the dynamical coupling of five rings in the studied compound. Practically it is not possible to assign the bands observed in the spectra to the vibration of a single bond or a functional group. The dynamical coupling in this compound is also seen in the clear broadening of the bands in the whole spectral range. The contour in the range  $2000-3700 \text{ cm}^{-1}$  is particularly broad, but the IR bands at about 1725, 1443, 992, 819, 605, 491, 345 and in the range  $50-250 \text{ cm}^{-1}$  are broadened. Some of them exhibit a doublet nature. The studied here material is a good example of the compound in which the intra- and inter-molecular interactions lead to the formation of the complex system in which five coupled rings vibrate in a resonance way as the whole unit, as it is seen in the Animol program.

187w	187w					V <sub>89</sub>	0.0	100.0	166		$\gamma \phi - 46 + \gamma C - CH_3 32 + \gamma \theta - 18 + \gamma \phi - 14$
161w	153s					V <sub>90</sub>	0.6	0.0	16	1	$\gamma \phi - 40 + \gamma C - CH_3 40 + \gamma \phi - 17$
		V44	202	2.6	32.9					$vOH_{HB} - 43 + \delta C - CH_3 24 + \delta \phi - 15 + v \phi - 9$	
		V <sub>45</sub>	156	4.5	64.5					$\gamma\phi/\phi-31+\gamma$ C $-$ CH <sub>3</sub> 25 $+\gamma\phi-21+\gamma$ CO <sub>COOH</sub> $-12$	
145w	124w	$V_{46}$	119	0.3	27.3	V <sub>91</sub>	4.2	0.0	13;	$2 \gamma \phi - 37 + \gamma \phi - 47$	$\gamma \phi - 50$ + $\gamma \phi - 40$ + $\gamma  heta - 10$
		$V_{47}$	68	41.1	15.6	V <sub>92</sub>	0.0	0.0	127	$\gamma\phi-79+\gamma$ CO(COOH) $-22$	$\gamma \varphi - 37 + \gamma \varphi - 46 + \tau C - CH_3 13$
101w	107w	V <sub>48</sub>	51	19.0	74.7	V <sub>93</sub>	0.0	38.5	107	QCH <sub>3</sub> 92	$\delta\theta = 78 + vNH(HB) = 28$
						V <sub>94</sub>	2.5	18.5	103		$vNH(HB) - 66 + v_{0} - 14 + vOH(HB)$ -25
80w	90s					V <sub>95</sub>	0.0	0.0	78		$\gamma \theta - 76 + \gamma \phi - 26$
	73w					V <sub>96</sub>	2.3	11.0	73		$\gamma \phi - 70 + \gamma CO_{COOH} - 16 + \tau C - CH3 - 12$
						$V_{97}$	0.0	0.0	64		$ m QCH_370+\gamma\phi-14$
						V <sub>98</sub>	2.5	12.8	63		$QCH_378 + v\theta - 8$
						V99	0.0	0.0			$\gamma \phi - 42$ + $ m QCH_322$ + $\gamma  heta - 20$ + $\gamma CO - 10$
						V100	0.3	12.3	61		vNH(HB) - 70 + vOH(HB) - 11
						V101	56.0	0.0	22		$\gamma  heta - 100$
						V102	0.0	4.5	11		$\gamma  heta - 98$
Scaling facto	лг: 0,96.										
In-plane vit	rations: v, str	etching	, δ, benι	ding, and δ, rc	ocking.						
Out of plant	$\gamma$ vibrations: $\gamma$	, torsio	nal, 00, 1	wagging, and	d, twisting						
<ul> <li>pyridine</li> </ul>	ring, φ, Intra-ı	mol HB	ring, ar	nd 0, inter-mc	ol HB ring.						



Fig. 5. The deconvolution of the basic broad contour in the range 2000–3500 cm<sup>-1</sup>.

Non bonding orbitals

NBO analysis was used to identify and confirm the possible of intra- and intermolecular interactions in HMPC. In this method, the delocalization of electronic density in both occupied Lewistype (bonding or lone pair) and formally empty (antibonding or Rydberg) non-Lewis orbitals corresponds to a stabilizing donoracceptor interaction [47,48]. Compared the molecular geometry of HMPC developed from XRD studies and DFT calculation, the significant changes in the distances between the atoms involved in the intermolecular hydrogen bond OH ... N type was noted. The formation of the dimer is responsible for these differences. Clearly greater distance appears between the O1-H1 and shorter distance between the N1 atom of one molecule (A unit) and the atom H1 on the other (B unit) (see Table 5). The hydrogen H1 atom significantly shifts toward the ring nitrogen atom of the adjacent molecule. This effect should change the polarizability of the hydrogen bond, which should cause the shift of the stretching vibration of the O—H bond toward the lower wavenumbers and result the stronger absorption. The stretching vibration of O1-H1...bond is predicted at 2446  $\text{cm}^{-1}$  in the theoretical IR spectrum, and at 2272  $\text{cm}^{-1}$  in the Raman spectrum. Although the Lewis type bonding orbitals of the O1-H1 bond does not be found for the dimer, a strong interaction between the lone pair orbital of the O1 atom and the nonbonding NBO orbital of the H1 atom  $[LP(1) O1 \rightarrow LP^{*}(1) H1$  and LP(3) O1  $\rightarrow$  LP\*(1) H1] appears, for which the stabilization energy  $E^{(2)}$  is 12.12 and 352.9 kcal/mol, respectively. Additionally, the electron donation from the nitrogen lone pair orbital LP(1)N1 to the non-bonding orbital NBO of the hydrogen atom LP<sup>\*</sup>(1)H1 from 2-hydroxyl group of the adjacent molecule appears. The value of the stabilization energy  $E^{(2)}$ , estimated by the second order perturbation theory, is significantly lower and equal 86.67 kcal/mol. Highly polarized O<sup>-</sup>···H<sup>+</sup>···N hydrogen bond is probably responsible for the unusual high intensity (absorbance) of the stretching vibration of the O-H bond in the calculated spectrum of the dimer. During the dimer formation, natural charge at the nitrogen atom changed from -0.51497 to -0.57306 e in comparison with those of monomer. This is the most significant change of natural charge among all atoms resulting from the dimer formation in HMPC.

On the other hand, the existence of the intramolecular interactions of the  $O(2)H(2)\cdots O(1)$  and  $O(2A)H(2A)\cdots O(1A)$  and  $O(2B)H(2B)\cdots O(1B)$  type is clearly confirmed when the atomic charges of the O1, O1A and O1B oxygen atoms in the monomer and the dimer are compared. This value for the monomer is -0.72805 e and significantly changes in the dimer into -0.74497 e for both the A and B units. The H(1) atom of the monomer is positively charged (+0.52415 e) whereas the H(1A) and H(1B) atoms of the coupled dimer exhibit slightly lower electron density equal to (+0.52283 e).

#### Table 5

Second order perturbation theory analysis of Fock matrix in NBO basis for monomer and dimer of 2-hydroxy-5-methylpyridine-3-carboxylic acid.

Donor (i)	Acceptor (j)	E <sup>(2)</sup> (kcal/mol)	$E_{(j)} - E_{(i)}$ (a.u.)	F(i,j) (a.u.)
For monom	er			
LP(1)N1	σ*(C6–C5)	9.10	0.92	0.083
	σ*(C2–C3)	11.90	0.88	0.093
	σ*(C2–01)	7.18	0.69	0.064
LP(09)	σ*(N1–C2)	5.15	1.16	0.069
	σ*(O12–H13)	12.94	1.08	0.106
	π*(N1–C2)	32.44	0.34	0.101
LP(014)	σ*(C3–C7)	2.66	1.07	0.048
	π*(C3–C7)	20.34	0.64	0.104
	π*(C7–O2)	32.11	0.62	0.128
LP(012)	σ*(C3–C7)	7.00	0.97	0.074
	π*(C7–O3)	49.71	0.33	0.117
For dimer w	vithin unit 1			
LP(N1)	$\sigma^{*}(C2B-C3B)$	8.96	0.89	0.083
	$\sigma^{*}(C2B-O1B)$	5.06	0.76	0.058
	$\sigma^{*}(C5B-C6B)$	7.22	0.94	0.077
	$\sigma^{*}(C6B-H6B)$	2.91	0.83	0.046
LP(O9)	$\begin{array}{l} \sigma^{*}(N1B-C2B) \\ \sigma^{*}(O2B-H2B) \\ LP^{*}(1) \ C2 \\ \sigma^{*}(N1B-C2B) \\ \sigma^{*}(C2B-C3B) \end{array}$	7.73 16.74 74.79 1.67 5.06	1.08 1.02 0.18 1.04 1.04	0.082 0.117 0.131 0.041 0.071
LP(012)	σ*(C3B—C7B)	7.09	0.96	0.075
	σ*(C7B—O3B)	1.57	1.18	0.039
	π*(C7B—O7B)	51.31	0.33	0.118
LP(014)	$\begin{array}{l} \sigma^{*}(\text{C3BC7B}) \\ \sigma^{*}(\text{C7B02B}) \\ \sigma^{*}(\text{C3BC7B}) \\ \sigma^{*}(\text{C7B02B}) \end{array}$	2.63 1.09 20.62 31.62	1.07 1.06 0.64 0.63	0.048 0.031 0.105 0.128

The analysis of the off-diagonal elements of the Fock matrix by second order perturbation theory also confirms the presence of the intramolecular hydrogen bond formed both in the monomer and the dimer. The values of stabilization energies  $E^{(2)}$  of the LP O1  $\rightarrow \sigma^{*}(O2-H2)$  interaction, which are 12.94 and 16.74 kcal/mol for monomer and dimer respectively, indicate that the OH···O intramolecular HB should be classified as medium weak strength.

# Conclusion

The studied here 2-hydroxy-5-methylpyridine-3-carboxylic acid is an example of the compound in which two types of hydrogen bonds are simultaneously formed. These are: (1) intramolecular O2–H2···O1 bond between the OH hydroxyl of the carboxylic group and oxygen atom of the hydroxyl group placed on the adjacent carbon atom of the pyridine ring, and (2) two intermolecular O1-H1...N HBs between the OH hydroxy group of one pyridine unit with pyridine nitrogen atom of the neighboring molecule. The existence of such interactions is postulated by XRD measurements which give the D...A distances 2.531 and 2.771 Å, respectively. These distances obtained from the DFT calculations are 2.675 Å and 2.643 Å for the intramolecular bond of the monomer and dimer, respectively, and 2.62 Å for the intermolecular HBs. In both of these interactions O1 oxygen participates, being a common atom of the six-membered and eight-membered rings of the dimer formed by two adjacent molecules. The simultaneously appearing intra- and inter-molecular interactions construct the unit in which the whole skeleton forms the complex five-rings system (see Fig. 1). Such a structural system is rather rare and therefore the question arises: how the DFT calculations could be useful for the analysis of their experimental vibrational spectra. Figs. 3 and 4 compare the IR and Raman spectra with those calculated for two structural models: monomer (Fig. 1) and dimer (Fig. 1). First of all, it should be pointed out that the electronic structures of the monomer and dimer, obtained from the NBO calculations, clearly show the differences in the atomic charges and polarizability in the monomer and dimer. According to the NBO analysis the intramolecular interactions are stable both in the monomer and dimer, which means that the formation of the intermolecular HB does not break (lub did not break) the intramolecular bond. The NBO calculations exhibit several differences between the electron parameters of the monomer and dimer, that confirm the formation of intermolecular O-H...N hydrogen bonds in the studied compound. Besides, these calculations suggest that this HB is highly polarized existing in the form of the  $O^- \cdots H^+ \cdots N$  system.

The described interactions should influence the IR and Raman spectra The comparison of the obtained results allows to draw the following conclusions:

- 1. The number of the bands observed and calculated for the monomer and dimer is similar because their IR and Raman spectra contain c.a. 40 bands. The majority of the band contours of the theoretical spectra for the monomer are not split in the spectra of the dimer. Therefore it shows that two pyridine units appearing in the dimer are symmetrical and their structural parameters are identical what agrees with the XRD data.
- 2. The wavenumbers of the observed and calculated spectra are very close to each other, but the accordance between the experimental and theoretical spectrum of the dimer is better than that for the monomer. Clearly better accordance is observed for the Raman spectrum than for the IR one.
- 3. The intensities of some observed bands differ from those calculated, particularly in the ranges 1500-1600, 1100-1150, 900-1000 and 100–200 cm<sup>-1</sup>. The vibrations of the bonds responsible for the HB interactions appear in these regions.
- 4. The theoretical spectra contain two bands in the range 3500- $3600 \text{ cm}^{-1}$  at 3616 and  $3524 \text{ cm}^{-1}$  for the monomer and two bands at 3440 and 2446  $cm^{-1}$  for the dimer. They correspond to the v(OH) vibrations of the hydroxy and carboxy groups.
- 5. The major criticism on the discrepancy between the theoretical and experimental wavenumbers is related to the band at 2446 cm<sup>-1</sup> calculated for the dimer. It is clearly single in character, it is very intensive and narrow, but in the experimental spectrum the contour responsible for the hydrogen bond formation is observed in the range 2000-3150 cm<sup>-1</sup> in the form of a very broad band that splits into four components at 3013, 2782, 2597 and 2343  $\text{cm}^{-1}$  (see Fig. 5). They should be assigned to the vibrations of the described above intermolecular and intramolecular hydrogen bonds. In our opinion these differences show that the theoretical model describes the classical covalent HB, whereas the real intermolecular bond appearing in the studied compound has the clear ionic nature.
- 6. The described here disagreement observed for the stretching vibration of the hydrogen bond does not depend on the level of the DFT calculations. It also appears when the 6-311+G(d,p)basis set is applied. This approach does also not influence the calculated wavenumbers and intensities of the bands.

# Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.09.130.

### References

- [1] W. Brzyska, W. Ozga, Pol. J. Chem. 71 (1997) 436-440.
- [2] D.C. Crans, L. Yang, T. Jakusch, T. Kiss, Inorg. Chem. 39 (2000) 4409–4416.

- [3] M.I.O. Neil, The Merck Index, 13th ed., Merck & Co., Whitehouse Station, New Jersey, 2001.
- [4] S. Ferraro, P. Passamonti, V. Bartocci, F. Pucciarelli, J. Chem. Soc. Faraday Trans. 93 (1997) 289-294.
- [5] B.D. Dawis, R. Dulbecco, H.N. Eisen, H.S. Ginsberg, W.B. Wood, Microbiology, second ed., Herper & Row, Hagerstown, 1973.
- [6] E. Norkus, I. Stalnioniene, D.C. Crans, Heteroat. Chem. 14 (2003) 625-632. and references therein.
- D.C. Crans, J. Inorg. Biochem. 80 (2000) 123-131.
- L.Q. Yang, D.C. Crans, S.M. Miller, A. la Cour, O.P. Anderson, P.M. Kaszynski, M.E. [8] Godzala, L.D. Austin, G.R. Willsky, Inorg. Chem. 41 (2002) 4859-4871.
- Z. Węgliński, T. Talik, Ann. Soc. Chim. Polonorum 51 (1977) 2401-2409.
- [10] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M. W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision A.1, Gaussian Inc., Pittsburgh PA, 2003.
- [11] A.D. Becke, J. Chem. Phys. 104 (1996) 1040-1046.
- [12] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B37 (1988) 785-789.
- [13] M.A. Palafox, V.K. Rastogi, Spectrochim. Acta A 58 (2002) 411-440.
- [14] M.J. Nowak, L. Lapinski, BALGA computer program for PED calculations; H. Rostkowska, L. Lapinski, M.J. Nowak; Vibr. Spectrosc. 49 (2009) 43-51).
- [15] M.M. Szczesniak, D. Maślanka, Animol-computer Program, Infrared and Raman Spectroscopy Teaching and Research Tool, Version 3.2.1., 1995–1997.
- [16] P. Pulay, G. Fogarasi, F. Pang, J.E. Boggs, J. Am. Chem. Soc. 101 (10) (1979) 2550-2560
- [17] G. Fogarasi, X. Zhou, P.W. Taylor, P. Pulay, J. Am. Chem. Soc. 114 (1992) 8191. [18] E.D. E.D. Glengening, A.E. Reed, J.E. Carpenter, F. Weinhold, NBO Version 3.1,
- TCI, University of Visconsin, Madison, 1998. [19] Kuma Diffraction, KM-4 CCD Software. Version 171.23 (2004), Kuma Diffraction, Wrocław, Poland, 2004.
- [20] G.M. Sheldrick, Acta Cryst. A46 (1990) 467-473.
- [21] G.M. Sheldrick, SHELXS97 and SHELXL97 (1997), Program for the Solution and
- Refinement of Crystal Structures. University of Göttingen, Germany, 1997.
- [22] R.J. Gillespie, Chem. Soc. Rev. 21 (1992) 59-69. [23] F.H. Allen, Acta Cryst. B58 (2002) 380–388.
- [24] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Tailor, J. Chem. Soc. Perkin Trans. 2 (1987) S1-S19.
- [25] K.B. Wilberg, V.A. Walters, K.N. Wong, S.D. Colson, J. Phys. Chem. 88 (1984) 6067-6075.
- [26] F. Partal Urena, M. Fernandez Gomez, J.J. Lopez Gonzales, E. Martinez Torres, Spectrochim. Acta A 59 (2003) 2815-2839.
- [27] G.A. Babu, P. Ramasamy, J. Philip, Mater. Res. Bull. 46 (2011) 631-634.
- [28] E. Kucharska, W. Sąsiadek, J. Janczak, H. Ban-Oganowska, J. Lorenc, Z. Wegliński, Z. Talik, K. Hermanowicz, J. Hanuza, Vib. Spec. 53 (2010) 189–198.
- [29] M. Wandas, E. Kucharska, J. Michalski, Z. Talik, J. Lorenc, J. Hanuza, J. Mol. Struct. 1004 (2011) 156-162.
- [30] I. Lorenc, J. Bryndal, M. Marchewka, W. Sasiadek, T. Lis, J. Hanuza, J. Raman Spectrosc. 39 (2008) 569–581.
- [31] E. Kucharska, J. Hanuza, M. Maczka, Z. Talik, Vib. Spectrosc. 39 (2005) 1-14.
- [32] G. Socrates, Infrared Raman Characteristic Group Frequencies, Wiley and Sons Ltd., 2001, and references therein.
- [33] D. Lin-vien, N.B. Cothup, W.G. Fateley, J.G. Graselli, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press, Boston 1991
- [34] J. Michalski, J. Hanuza, M. Mączka, Z. Talik, T. Głowiak, A. Szemik-Hojniak, J.H. Van der Maas, J. Mol. Struct. 596 (2001) 109–121.
- [35] M. Diem, Introduction to Modern Vibrational Spectroscopy, Wiley, New York, 1993.
- [36] E. Fan, C. Vincent, S.J. Geib, A.D. Hamilton, Chem. Mater. 6 (1994) 1113-1117.
- [37] O. Ermer, A. Eling, J. Chem. Soc. Perkin Trans. 2 (1994) 925-944.
- [38] S. Coe, J.J. Kane, T.L. Nguyen, L.M. Toledo, E. Wininger, F.F. Fowler, J.W. Laugher, J. Am. Chem. Soc. 119 (1997) 86–93.
- [39] G.T.R. Palmore, M.T. McBride, Chem. Commun. (1998) 145-146.
- [40] Y. Ducharme, J.D. Wuest, J. Org. Chem. 53 (1988) 5787-5789.
- [41] M. Simard, D. Su, J.D. Wuest, J. Am. Chem. Soc. 113 (1991) 4696-4698.
- [42] C.B. Aakeröy, A.M. Beatty, M. Nieuwenhuyzen, M. Zou, Tetrahedron 56 (2000) 6693-6699
- [43] J. Lorenc, J. Bryndal, W. Syska, M. Wandas, M. Marchewka, A. Pietraszko, T. Lis, M. Mączka, K. Hermanowicz, J. Hanuza, Chem. Phys. 374 (2010) 1–14.
- [44] Z. Li, J. Huang, A. Meng, J. Chem. Crystallogr. 41 (2011) 481-484.
- [45] L. Leiserowitz, Acta Crystallogr. B32 (1976) 775–802.
- [46] M.C. Etter, J.C. McDonald, J. Bernstein, Acta Crystallogr. B46 (1990) 256–262.
- [47] A.F. Reed, L.A. Curtiss, J. Weinhold, Chem. Rev. 88 (1988) 899.
- [48] I. Bryndal, E. Kucharska, W. Sąsiadek, M. Wandas, T. Lis, J. Lorenc, J. Hanuza, Spectrochim. Acta A 96 (2012) 952-962.