

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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



Determination of structural and vibrational spectroscopic features of neutral and anion forms of dinicotinic acid by using NMR, infrared and Raman experimental methods combined with DFT and HF



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HIGHLIGHTS

- Neutral and anionic conformations of dinicotinic acid was investigated.
- Spectroscopic features of dinicotinic acid were examined by NMR, infrared and Raman techniques.
- OPDOS, PDOS and TDOS of dinicotinic acid were investigated.

G R A P H I C A L A B S T R A C T



ARTICLE INFO

Article history: Received 30 July 2012 Received in revised form 29 April 2013 Accepted 11 May 2013 Available online 23 May 2013

Keywords: Dinicotinic acid NMR Infrared Raman DFT and HF

ABSTRACT

In this study; the experimental (NMR, infrared and Raman) and theoretical (HF and DFT) analysis of dinicotinic acid were presented. ¹H and ¹³C NMR spectra were recorded in DMSO solution and chemical shifts were calculated by using the gauge-invariant atomic orbital (GIAO) method. The vibrational spectra of dinicotinic acid were recorded by FT-Raman and FT-IR spectra in the range of 4000–10 cm⁻¹ and 4000–400 cm⁻¹, respectively. To determine the most stable neutral conformer of molecule, the selected torsion angle was changed every 10° and molecular energy profile was calculated from 0° to 360°. The geometrical parameters and energies were obtained for all conformers form from density functional theory (DFT/B3LYP) and HF with 6-311++G(d,p) basis set calculations. However, the results of the most stable neutral and two anion forms (anion⁻¹ and anion⁻² forms) of dinicotinic acid are reported here. The complete assignments were performed on the basis of the total energy distribution (TED) of the vibrational wavenumbers, calculated with scaled quantum mechanics (SQM) method and PQS program.

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Introduction

Pyridine carboxylic acid (nicotinic acid) and its derivatives represent a class of compounds exhibiting a variety of interesting chemical and biological properties. These compounds were in-

* Corresponding author. Tel.: +90 236 201 3131. E-mail address: etemmm43@gmail.com (E. Kose). volved in several essential biochemical processes [1]. Pyridine carboxylic acids act as the chelating agents of the elements such as manganese, chromium, copper, zinc, molybdenum and iron in the body. Pyridine carboxylic acids and their derivatives have attracted more attention due to these beneficial effects. They were used as intermediate to produce metal salts and the pharmaceuticals for application of nutritional supplements [2]. In addition, the various metallic complexes nicotinic, isonicotinic and picolinic acids were investigated by different methods [3–5].

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The solid-state structure of nicotinic acid was determined by Wright and King [6]. Wang and Fang [7] obtained high quality Raman spectrum of pyridine carboxylic acid in aqueous solution under ultraviolet (UV) excitation. Calculated Raman frequencies based on DFT reveals the different states of pyridine carboxylic acid in aqueous solution [7]. Atac et al. [8] investigated molecular structure of nicotinic acid N-oxide with a combined experimental and theoretical study. The crystal structure of 3,5-pyridine dicarboxylate were fully characterized [9]. The infrared and Raman spectra of 2,6-pyridine dicarboxylic acid and 3,5-pyridinedicarboxylic acid and their salts were recorded and the vibrational modes were assigned [10]. Takusagawa et al. [11] reported the crystal structure of dinicotinic acid. The dinicotinic acid was also studied using single crystal neutron diffraction by Cowan et al. [12].

The present work is a continuation of our previous study [13] on chemical shifts of the neutral dinicotinic acid, molecular structure and charge distribution by Mulliken of neutral and anion forms (anion⁻¹ and anion⁻² forms) of dinicotinic acid. The chemical shifts of the neutral dinicotinic acid were assigned from ¹³C and ¹H NMR spectra. And we also obtained the neutral and anion forms (anion⁻¹ and anion⁻² forms) of dinicotinic acid molecule and a correct assignment of the experimental Raman and infrared spectra on the basis of the calculated TED by using different theoretical (HF and B3LYP methods with 6-311++G(d,p)) and the experimental spectroscopic data. The carboxyl group in dinicotinic acid is of different positions according to state of hydrogen atoms. Among the all conformers investigated, the most stable conformer having minimum energy was determined.

Experimental

The dinicotinic acid was purchased in solid state with a stated purity of 99% from Sigma Aldrich Company. The NMR experiments were performed in Varian Infinity Plus spectrometer at 300 K. The dinicotinic acid was dissolved in DMSO. The chemical shifts were reported in ppm relative to tetramethylsilane (TMS) for ¹H and ¹³C NMR spectra. NMR spectra were obtained at a base frequency of 75 MHz for ¹³C and 400 MHz for ¹H nuclei. The FT-IR spectrum of dinicotinic acid was recorded between 4000 and 400 cm⁻¹ on a Perkin–Elmer FT-IR System Spectrum BX spectrometer. FT-Raman spectrum of the compound was recorded by using 1064 nm line of Nd:YAG laser as excitation wave length in the region 4000–10 cm⁻¹ on a Bruker RFS 100/S FT-Raman.

Computational procedures

The geometric parameters of dinicotinic acid molecule and its complex structure were taken from the X-ray structural analysis [9,12,14]. To determine the conformational features of the dinicotinic acid, the angle of torsional freedom T (C-C-O-H) was changed from 0° to 360° in per 10°. The molecular energy profile was obtained with the PM6 method. In connection with the hydrogen orientations of the oxygen atom of carboxylic acid group, dinicotinic acid molecule may have several conformations. The vibrational frequencies of dinicotinic acid were calculated with HF and B3LYP methods for the most stable conformer. The wavenumbers are scaled by 0.9050 for HF [15] and in the ranges from 4000 to 1700 cm^{-1} and lower than 1700 cm^{-1} are scaled with 0.958 and 0.983, respectively for B3LYP [16]. The complete assignments of vibrational modes were made on the basis of the TED, computed with SQM method [17]. All the calculations were carried out by using Gaussview molecular visualization program and Gaussian03 program package on the personal computer [18].

The Raman activities (S_{Ra}) calculated with Gaussian 03 program [18] converted to relative Raman intensities (I_{Ra}) using the equa-

tion in the literature derived from the intensity theory of Raman scattering [19,20].

After optimization ¹H and ¹³C NMR chemical shifts ($\delta_{\rm H}$ and $\delta_{\rm C}$) were calculated by using the GIAO method [21,22] in DMSO. The GIAO method calculating nuclear magnetic shielding tensors is one of the most known approaches.

GaussSum 2.2 [23] was used to prepare TDOS or DOS, PDOS and OPDOS spectra and to calculate group contributions to the molecular orbitals. The contribution of a group to a molecular orbital was calculated by using Mulliken population analysis. The OPDOS and PDOS spectra were generated by convoluting the molecular orbital information with Gaussian curves of unit height and a FWHM (Full Width at Half Maximum) of 0.3 eV.

Results and discussion

Potential energy surface (PES) scan, energetics and molecular geometry

In order to determine conformational flexibility of the molecule, the energy profile as a function of T(C3-C10-O12-H17) and T(C5-C13-O15-H16), torsion angle was calculated with semiempirical PM6 method (Fig. 1). Namely, potential energy curve was computed by means of scanning COOH groups made over the ring group spin and H_{17} and H_{16} atoms rotated around O_{12} and O_{15} atom, respectively. All the scans show that the neutral form of the dinicotinic acid has a planar C_{2v} point group symmetry. This situation is an evident that H_{17} and H_{16} atoms are located with carboxylic acid same planer.

Energies of the neutral and anions (anion⁻¹ and anion⁻² forms) conformers were calculated by employing both HF and B3LYP with 6-311++G(d,p) basis set. The energy values were presented in Table 1 for each method. The energy of the neutral conformer of the molecule was calculated as -625.6214122 Hartree (-392583.380 kcal/mol) and -622.1067978Hartree (-390377.926 kcal/mol) by using B3LYP and HF methods, respectively. Also the energy of the anion⁻¹ and anion⁻² forms of the molecule was calculated as -625.0855452 Hartree (-392247.118 kcal/ mol) and -621.5579226 Hartree (-390033.501 kcal/mol) and also -624.4440622 Hartree (-391844.581 kcal/mol) and



Fig. 1. PES scan for the selected degree for T(C3-C10-O12-H17) and T(C5-C13-O15-H16) simultaneously for neutral form of dinicotinic acid.

Structure	B3LYP/6-311++G(d,p)			HF/6-311++G(d,p)				
	Energy		ED		Energy		ED		
	(Hartree)	(kcal/mol)	(Hartree)	(kcal/mol)	(Hartree)	(kcal/mol)	(Hartree)	(kcal/mol)	
Neutral form	-625.6214122	-392583.380	0.0000	0.00000	-622.1067978	-390377.926	0.0000	0.00000	
Anion ⁻¹ form	-625.0855452	-392247.118	0.5359	336.2616	-621.5579226	-390033.501	0.5489	344.4244	
Anion ⁻² form	-624.4440622	-391844.581	1.1774	738.7983	-620.9050375	-389623.810	1.2018	754.1160	

The calculated energies and energy differences for neutral and two anion forms (anion β and anion β forms) of difficulting a	The calculate	d energies a	and energy	differences	for neutral	and two	anion forms	$(anion^{-1})$	and anion ⁻²	² forms)) of dinicotinic ad
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The deprotonation energy $(E^{D}) = E_{i}$ (anion form)–E (neutral form).

-620.9050375 Hartree (-389623.810 kcal/mol) using B3LYP and HF calculations, respectively.

From DFT and HF calculations of three forms, the neutral form is predicted more stable than the anion⁻¹ form. The neutral and the anion⁻¹ form are also more stable the anion⁻² form. The deprotonation energy (E^{D}) of dinicotinic acid, energy difference between neutral and anionic forms was calculated.

 $E^{\rm D} = E(\text{anion}^{-1} \text{ form.}) - E(\text{neutral form})$

- = 336.2616 kcal/mol for B3LYP
- $E^{\rm D} = E(\text{anion}^{-1} \text{ form.}) E(\text{neutral form})$

= 344.4244 kcal/mol for HF



Fig. 2. The theoretical geometric structures of the neutral and two anion forms (anion⁻¹ and anion⁻² forms) of dinicotinic acid.

$$E^{\rm D} = E(\text{anion}^{-2} \text{ form}) - E(\text{neutral form})$$

= 738.7983 kcal/mol for B3LYP

 $E^{\rm D} = E(anion^{-2} \text{ form}) - E(neutral \text{ form})$ = 754.1160 kcal/mol for HF

The optimized structures of the neutral and two anion forms $(anion^{-1} and anion^{-2} forms)$ of dinicotinic acid with numbering of the atoms were shown in Fig. 2. The optimized bond lengths and bond angles for the neutral and two anion forms of the molecule were tabulated in Table 2 in comparison with the experimental values. As seen in Table 2, comparing of the calculated and observed bond lengths, the theoretical values (N-C and C-O) are slightly shorter than experimental ones. Also the C=O bond length of anion⁻² structure is closer to the experimental value than the other neutral and anion⁻¹ forms of the title molecule.

Optimized parameters of the molecule show very good agreement with experimental results. The CC bond length of the pyridine ring was observed ca. 1.382 Å [12] and also in complexes of title molecule, these bond lengths were observed in the range of 1.390-1.393, 1.381-1.389 and 1.388-1.392 Å [9,14] which calculated in the range of 1.393-1.401 Å (B3LYP), 1.384-1.391 Å (HF) and 1.391–1.402 Å (B3LYP), 1.382–1.393 Å (HF) for neutral and anion⁻¹ form, respectively. These bond lengths were calculated in the range of 1.399–1.401 Å (B3LYP), 1.388–1.392 Å (HF) for anion⁻² form.

The calculated C–O bonds (C₁₀–O₁₂ and C₁₃–O₁₅) of the neutral form of the title molecule are larger than observed values, while C=O bonds (C_{10} - O_{11} and C_{13} - O_{14}) are shorter than observed values. The C–O bond length of dipicolinic and dinicotinic acids was recorded ca. 1.500 Å [10]. The CO bond lengths of anions (especially the anion⁻² form CO) are closer to the experimental data.

The C-N bond length in both 2,6-pyridinedicarboxylic and 3,5pyridinedicarboxylic acids was calculated at 1.333 Å [10]. In this study, this band was calculated at 1.318 Å and 1.335 Å (HF and B3LYP) and was observed at 1.341 Å [12], 1.337 and 1.333 Å [11]. Also the comparisons of C-N bond length showed good agreement with experimental values of similar compounds; such as 2- and 6choloro nicotinic acid [24,25], pyridine [26] and 2-aminonicotinic acid [27].

On comparing calculated bond angles of dinicotinic acid with experimental data in the ring part, there is very good convenience [12]. These data are smaller than hexagonal angle of 120° except of the N–C–C angles. The C_3 – C_{10} – O_{12} and its symmetry C_5 – C_{13} – O_{15} angles are smaller than C_3 – C_{10} – O_{11} and its symmetry C_5 – C_{13} – O_{14} angles because of interaction between the carboxyl acid (COOH) and hydroxyl (OH) group for the molecule. McCann and Laane [10] also presented the nearly same results for 2,6-pyridinedicarboxylic acid and 3,5-pyridinedicarboxylic acid. All values are nearly the same its symmetric data C₁₃-O₁₅-H₁₆ (OH group) and its symmetry was calculated 107.1°.

We also obtained thermo dynamical properties of the most stable neutral and two anion structures of dinicotinic acid. Some ther-

Table 1

Table 2

The optimized geometric parameters (bond lengths (Å) and bond angles ($^{\circ}$)) of the neutral and two anion forms (anion⁻¹ and anion⁻² forms) of dinicotinic acid and comparison with the available experimental results by using both HF and B3LYP methods with 6-311++G(d,p) basis set.

Parameters	Experimental			Neutral fo	rm	Anion ⁻¹ form		Anion ⁻² form		
	X-ray ^a	X-ray ^a	X-ray ^b	X-ray ^c	HF	B3LYP	HF	B3LYP	HF	B3LYP
Bond lengths (Å)										
N1-C2	1.346	1.345	1.347	1.341	1.318	1.335	1.316	1.332	1.326	1.343
N1-C6	1.346	1.393	1.346	1.341	1.318	1.335	1.329	1.345	1.326	1.343
C2-C3	1.393	1.381	1.390	1.382	1.391	1.401	1.390	1.402	1.388	1.399
C2—H8					1.074	1.084	1.075	1.086	1.075	1.086
C3-C4	1.390	1.385	1.388	1.382	1.384	1.393	1.393	1.401	1.392	1.401
C3-C10	1.503	1.513	1.497	1.498	1.486	1.489	1.476	1.475	1.542	1.551
C4—C5	1.390	1.389	1.392	1.382	1.384	1.393	1.382	1.391	1.392	1.401
C4—H7				1.030	1.073	1.083	1.072	1.083	1.073	1.083
C5–C6	1.393	1.389	1.389	1.382	1.391	1.401	1.389	1.399	1.388	1.399
C5-C13	1.503	1.493	1.507	1.498	1.486	1.489	1.547	1.554	1.542	1.551
C6—H9					1.074	1.084	1.074	1.085	1.075	1.086
C10=011	1.253	1.246	1.252	1.217	1.184	1.206	1.192	1.216	1.230	1.254
C10-012	1.260	1.264	1.268	1.294	1.326	1.355	1.332	1.363	1.237	1.261
012-H17				1.160	0.946	0.969	0.944	0.967		
C13=014	1.253	1.250	1.254	1.217	1.184	1.206	1.227	1.251	1.230	1.254
C13-015	1.260	1.270	1.267	1.294	1.326	1.355	1.226	1.251	1.237	1.261
015-H16				1.160	0.946	0.969				
Dand analas (0)										
Bona angles (°)	1175		117.0	110.0	110.0	1177	1175	1171	117.0	110.0
C2-NI-C6	117.5		117.8	119.8	118.0	117.7	117.5	117.1	117.3	116.8
NI-C2-C3	123.1		122.4		123.5	123.4	123.3	123.3	124.5	124.5
NI-C2-H8					116.4	116.5	117.1	117.2	117.0	117.3
C3-C2-H8	110.0		110.1		120.1	120.1	119.6	119.5	118.5	118.2
$C_2 - C_3 - C_4$	118.6		119.1		118.2	118.4	118.3	118.4	116.8	116.8
$C_2 - C_3 - C_{10}$	120.2		120.4		122.6	122.7	118.6	118.3	120.4	120.3
C4-C3-C10	121.2		120.4		119.2	118.9	123.1	123.3	122.8	122.9
C3-C4-C5	118.9		118.8		118.6	118.6	119.3	119.3	120.3	120.5
C3-C4-H7				100.4	120.7	120.7	122	122.4	119.8	119.8
C5-C4-H7				120.4	120.7	120.7	118.7	118.3	119.8	119.8
C4-C5-C6	118.6		118.4	101 5	118.2	118.4	11/	117.1	116.8	116.8
C4-C5-C13	121.2		122.4	121.7	119.2	118.9	121.5	121.4	122.8	122.9
C6-C5-C13	120.2		119.1	119.8	122.6	122.7	121.5	121.5	120.4	120.3
N1-C6-C5	123.1		123.1		123.5	123.4	124.7	124.7	124.5	124.5
N1-C6-H9				116.0	116.4	116.5	117	117.3	117.0	117.3
С5—С6—Н9				122.0	120.1	120.1	118.3	118	118.5	118.2
C3-C10-011	119.9		119.8		124.1	124.6	125.5	126	116.1	116.3
C3–C10–O12	119.1		120.1		113.1	112.6	113.7	113.4	115.6	115.7
011–C10–012	121.0		120.0		122.7	122.8	120.7	120.6	128.2	128.0
C10-012-H17	119.9		116.2		108.7	107.1	107.7	105.8		
C5-C13-014	119.1		118.0	122.6	124.1	124.6	114.6	114.7	116.1	116.3
C5–C13–O15					113.1	112.6	114.9	114.9	115.6	115.7
014–C13–015	121.0		125.8	124.3	122.7	122.8	130.5	130.4	128.2	128.0
C13-015-H16				115.5	108.7	107.1				

^{a,b,c} The X-ray data from Refs. [9,14,12].

mo dynamical values of this framework are gathered in Table S1. According to Table S1, the neutral from is more stable than anion⁻¹ and anion⁻² forms. Neutral and anion⁻² form of title molecule has C_{2v} group symmetry however anion⁻¹ form has C_s group symmetry (see Table S1).

NMR spectral studies

The isotropic chemical shifts are frequently used as aid recognition of reactive ionic type. It is recognized that accurate predictions of molecular geometries are essential for reliable calculations of magnetic features. Therefore, molecular structure of the dinicotinic acid was optimized by using B3LYP/6-311++G(d,p). Then, the GIAO ¹H and ¹³C NMR chemical shift calculations of the dinicotinic acid molecule were computed in DMSO solvent. Relative chemical shifts were estimated by using the corresponding TMS shielding calculated in advance at the same theoretical level as the reference. The isotropic shielding values were used to calculate the isotropic chemical shifts δ with respect to TMS, δ_{TMS} . The observed ¹H and ¹³C NMR spectra of the compound dinicotinic acid were given in Fig. 3a and b, respectively. The theoretical and experimental ¹H

and ¹³C chemical shifts in DMSO were collected in Table 3. The atom statues were numbered according to Fig. 2.

The studied molecule has three hydrogen atoms in the ring and two hydrogen atoms attached to the oxygen atoms at carboxylic groups. The proton signals were observed at 8.51 and 9.10 ppm for ring hydrogen atoms. The chemical shifts of H₈ and H₉ combined one peak as a coupling and calculated at 9.69 ppm. The chemical shift of proton numbered H₈ and H₉ are higher than H₇ atom. It means that the electronic charge density around the H₈ and H₉ is lower than H₇. The calculated chemical shifts for the hydrogen atoms of carboxylic groups are quite low. Two signals belong to COOH group (H₁₆ and H₁₇) were computed one peak at 6.66 ppm.

Taking into account that the range of 13 C NMR chemical shifts for a typical organic molecule usually occur larger than 100 ppm [28,29] the accuracy ensures reliable of spectroscopic parameters. The dinicotinic acid molecule has seven carbon atoms, which is consistent with the structure on basis of molecular symmetry. Although there are seven carbon atoms, four peaks were observed and calculated because of the molecular symmetry (C_{2v}) of title molecule (Table 3). Namely the chemical shifts of symmetrical



Fig. 3. (a) ¹H NMR and (b) ¹³C NMR spectra of dinicotinic acid molecule in DMSO solution.

Table 3

The experimental and theoretical, 1 H and 13 C NMR isotropic chemical shifts (with respect to TMS) of dinicotinic acid with B3LYP 6-311++G(d,p) method.

Atoms	Carbon		Atoms	Hydrogen		
	Exp.	B3LYP ^a		Exp.	B3LYP ^a	
C10, C13	166.04	170.90	H8, H9	9.10	9.69	
C2, C6	153.94	162.57	H7	8.51	9.24	
C4	137.69	146.77	H16, H17	-	6.66	
C3, C5	127.18	128.66				

^a TMS reference with respect to B3LYP/6-311 + G(2d,p) GIAO method.

carbon atoms were showed one peak as the coupling. The ¹³C NMR chemical shifts in the ring are bigger than 100 ppm, as expected. The signal of aromatic carbon atoms were observed at 127.18, 137.69 and 153.94 ppm which were calculated at 128.66, 146.77 and 162.57 ppm, respectively. C_2 and C_6 atoms have larger chemical shifts than the other ring carbon atoms because of electronegativity of nitrogen atom. Similarly, the carboxyl group which is an electronegative functional group polarizes the electron distribution therefore; the calculated ¹³C NMR chemical shift value of C_{10} and C_{13} atoms bonded to carboxyl group is too high, observed at 166.04 ppm which was calculated at 170.90 ppm as a coupling.



Fig. 4. Correlation graphic of calculated and experimental chemical shifts of the dinicotinic acid molecule.

DMSO includes electronegative atoms such as oxygen and sulfur. Thus in dinicotinic acid molecule was affected this solution.

The relations between the experimental and calculated chemical shifts (δ_{exp}) are described by the following equation:

$$\delta_{\text{cal.}}(\text{ppm}) = 1.0379\delta_{\text{exp.}} - 0.0908 \quad (R^2 = 0.9988)$$



Fig. 5. The calculated total electronic density of states diagrams for the dinicotinic acid.



Fig. 6. The calculated partial electronic density of states diagrams for the dinicotinic acid.



Fig. 7. The overlap population electronic density of states diagrams for the dinicotinic acid.

The performances of the B3LYP method with respect to the prediction of the relative shielding within the molecule were very good. The correlation between the calculated and experimental chemical shifts was obtained by DFT/B3LYP method are given in Fig. 4.

Total, partial, and overlap population density of states

The Crystal Orbital Overlap Population (COOP) density of states or PDOS, TDOS and OPDOS [30-32], and Mulliken population analysis were calculated and generated by convoluting the molecular orbital information with Gaussian curves using the GaussSum 2.2 program [23] to show quasi degenerate energy levels. The calculated TDOS diagram of the dinicotinic acid was given in Fig. 5. The PDOS mainly presents the composition of the fragment orbitals contributing to the molecular orbitals which was seen from Fig. 6. The OPDOS diagram was shown in Fig. 7 since the difficult of the percentage shares of atomic orbitals or molecular fragments in the molecule to compare groups in terms of its bonding and antibonding properties. Some of orbitals of energy values of interaction between selected groups which are shown from figures easily, carboxylic groups ↔ pyridine system is negative (anti-bonding interaction). Figs. 5–7 provide a pictorial representation of molecule orbital (MO) compositions and their contributions to chemical bonding. The OPDOS shows the nonbonding, bonding and antibonding nature of the interaction of the two atoms, orbitals or groups. Zero value of the OPDOS indicates nonbonding interactions. The positive and negative values indicate the bonding and anti-bonding interaction [33]. Additionally, the OPDOS diagrams allow us to the determination and comparison of the donor-acceptor features of the ligand and ascertain the bonding, non-bonding.

Vibrational assignments

In order to get the spectroscopic features of dinicotinic acid, we have performed a wavenumber calculation analysis. The theoretical wavenumbers are in good accord with the experimental ones especially for B3LYP method. The calculated and experimental vibrational wavenumbers were given in Table S2 and theoretical Raman and infrared intensity, Raman scattering activities of the title molecule (for neutral form) were gathered in Table S3. Also the calculated vibrational wavenumbers of anion forms were given in Table S4.

The dinicotinic acid molecule which has 17 atoms assumed C_{2v} symmetry group and its fundamental vibrations are distributed as: $\Gamma_{vib.} = 16A_1 + 6A_2 + 8B_1 + 15B_2$. The A_1 and B_2 vibrations are inplane modes while A_2 and B_1 represent out-of-plane modes. But if the molecule has C_s symmetry group, the 45 normal vibrations would be distributed as $\Gamma_{vib.} = 31A' + 14A''$. The A' vibrations are in-plane modes while A'' represent out-of-plane modes. Fig. S1 presents the experimental and calculated infrared and Raman spectra. Vibrational modes of molecule were examined by performing harmonic frequency calculations at the corresponding energy optimized geometries.

Several characteristic out-of-plane C—H vibrations as well as out-of-plane (CCC) deformations and in-plane deformations C—H, observe between 1350 and 400 cm⁻¹. The CN, CC, C=O and COOH group stretching vibrations take place in the range of 1800–1500 cm⁻¹. In the spectral range over 3000 cm⁻¹, C—H and O—H stretching modes occur.

The O–H vibrations are extremely sensitive to formation of hydrogen bonding. The O–H stretching band is characterized by very broad band appearing near about 2500–3600 cm⁻¹ [25]. These frequencies were observed at 3546, 3233 and 3244 cm⁻¹ and calculated between 3330 and 3609 cm⁻¹ [34]. McCann and Laane [10] calculated this vibration at 3627 cm⁻¹ observed in 3417 cm⁻¹ (Raman) for 2,6-pyridinedicarboxylic acid. For 3,5-pyr-idinedicarboxylic acid, this peak was calculated at 3681 and 3684 cm⁻¹ by the same authors [10]. In this study, the O–H mode was calculated at 3611 and 3728 cm⁻¹ using B3LYP and HF methods, respectively. The O–H in-plane bending vibrations appear in the region of 1440–1395 cm⁻¹ [35,36]. The O–H in-plane bending

vibrations were assigned at 1443 cm⁻¹ and 1385 cm⁻¹ in FT-IR and 1446 cm⁻¹ in FT-Raman experimentally, which were calculated at 1446 and 1395 cm⁻¹ for structurally similar molecule [34]. In the present work, the O–H in-plane bending was calculated between 1352 and 1151 cm⁻¹ with B3LYP and 1359–1125 cm⁻¹ with HF methods. This band was observed in the range of 1368–1162 cm⁻¹ in FT-IR and 1378–1143 cm⁻¹ in FT-Raman. The O–H out-of-plane bending vibration occurs in 960–875 cm⁻¹ [25,35]. We calculated the O–H out-of-plane bending vibration at 975 cm⁻¹ by using B3LYP and observed at 942 and 980 cm⁻¹ in FT-IR and FT-Raman spectra, respectively [24].

The C–H stretching vibrations in the hetero-aromatic structure appear in the range of 3000–3100 cm⁻¹, which is the characteristic region for the ready identification of C-H stretching vibrations [36]. The C–H vibrations were observed at 3108 cm⁻¹ (IR) and 3098. 3104 cm^{-1} (Raman) for 2.6 pyridinedicarboxylic acid and 3092 cm⁻¹ (IR) and 3090 cm⁻¹ (Raman) for 3,5-pyridinedicarboxylic acid [10]. In this study, the C–H stretching vibrations of dinicotinic acid were calculated in the range of 3054–3074 cm⁻¹ and 3048–3062 cm⁻¹ using B3LYP and HF methods, respectively. This band was assigned at 3046, 3063 and 3080 in FT-Raman and 3091 cm⁻¹ in FT-IR spectra. In aromatic compounds, the C–H inplane bending frequencies appear in the range of 1000-1300 cm⁻¹ while the C–H out-of-plane bending vibrations occur in the range of 750–1000 cm⁻¹ [36,37]. The C–H in-plane bending modes were observed between 1143 and 1312 cm⁻¹ in FT-Raman. This band was calculated at 1151–1340 cm⁻¹ by using B3LYP and 1125–1351 cm⁻¹ by using HF for the molecule, which is good accord with experimental values. Similar correlation was reported in literature [38,39]. The C-H out-of-plane bending vibrations (modes 22 and 24) were calculated at 986 and 927 cm^{-1} , respectively. These modes were observed at 994 and 911 cm⁻¹ in FT-Raman. The change in the frequencies of these deformations from the values in pyridine is almost independent of their nature and is almost determined exclusively by the relative position of the substituents [40]. Both the in-plane and out-of-plane bending modes are illustrated as mixed modes. The detailed assignment contribution of the out-of-plane and in-plane vibrations indicates that out-ofplane modes are also highly pure modes according to the calculated TED.

Derivatives of carboxylic acids are determined by several intense absorptions in the infrared spectrum. The most characteristic feature of carboxyl group is a single band observed usually in the range of 1700–1800 cm⁻¹. The C=O stretching mode is the strongest band in the infrared spectrum (symmetric stretching) and appears with diminished intensity in the Raman spectrum (asymmetric stretching). The asymmetric stretch is usually at higher wavenumber than the symmetric stretch. In the present study, The C=O stretching modes were observed at 1672 and 1720 cm⁻¹ in FT-IR, 1711 and 1754 cm⁻¹ in FT-Raman. The theoretical value of the C=O band is computed at 1717 and 1728 cm⁻¹ using DFT for the neutral form, which is very good agreement with experimental results. However these values were calculated bigger than experimental ones (1791 and 1804 cm⁻¹) by using HF (see Table S2). McCann and Laane [10] calculated at 1797 and 1804 cm^{-1} and observed at 1725 cm^{-1} (both IR and Raman). Karabacak and Kurt [41] observed asymmetric and symmetric stretching vibrations at 1660 and 1629 cm⁻¹ in FT-IR and FT-Raman spectrum for 5-BrSA. respectively. The C=O stretching modes were observed at 1717 cm⁻¹ for picolinic acid, 1708 cm⁻ for nicotinic acid and 1712 cm⁻¹ for isonicotinic acid by Koczan et al. [42].

The ring CC stretching modes were observed at 1628–1292 cm⁻¹ [34]. In this study, the CC stretching modes (in the ring) were calculated in the range of 1025–1101 cm⁻¹ by using B3LYP and 1015–1124 cm⁻¹ by using HF, which are very good agreement

experimental values observed in the region $1042-1108 \text{ cm}^{-1}$ (FT-IR) and $1032-1121 \text{ cm}^{-1}$ (FT-Raman).

The CN stretching absorption at 1381 cm⁻¹ for 2-amino-5-iodopyridine was assigned [43]. The band observed at 1374 cm⁻¹ in FT-IR spectrum (1376 cm⁻¹ in FT-Raman) was assigned to CN stretching vibration [25]. Karabacak et al. [44] observed the C—N stretching mode at 1272/1268 cm⁻¹ (IR/Ra) and 1258 cm⁻¹ (IR) for 2-/6-Bromo-NA, respectively. In this work, the CN stretching vibrations were observed in the range of 1162–1602 cm⁻¹ and 1185– 1602 cm⁻¹ in FT-IR and FT-Raman spectra, respectively. According to TED results, the CN vibrations were computed at 1159– 1610 cm⁻¹ and 1162–1630 cm⁻¹ for B3LYP and HF methods, respectively.

The experimental modes are very good agreement with the scaled ones. The correlation graphic was plotted between the calculated and experimental wavenumbers obtained by B3LYP and HF methods. The correlation graphic between the experimental and calculated wavenumbers were given in Figs. S2 and S3. The experimental wavenumbers have a better correlation with B3LYP. The relations are usually linear and described by the following equation for infrared and Raman using B3LYP and HF method;

$$v_{cal.} = 1.0035v_{exp.} - 15.0887$$
 ($R^2 = 0.9984$) for IR(B3LYP)
 $v_{cal.} = 1.0056v_{exp.} + 4.3447$ ($R^2 = 0.9992$) for Raman(B3LYP)
 $v_{cal.} = 0.9925v_{exp.} - 10.5951$ ($R^2 = 0.9956$) for IR(HF)
 $v_{cal.} = 1.0015v_{exp.} + 1.1443$ ($R^2 = 0.9970$) for Raman(HF)

Mulliken atomic charges

The computed of reactive atomic charges plays an important role in the application of quantum mechanical calculations the molecular system. The Mulliken atomic charges of the neutral and two anion forms of the dinicotinic acid molecule were shown in Table 4 and Figs. S4–S5. The results showed that substitution of the aromatic ring by carboxylic groups leads to a redistribution of electron density. Namely, the charges of COOH groups are same distribution (negative or positive) in both COOH groups, and also, the molecule exhibit a symmetrical charge with in all surface. This can be the title molecule has C_{2v} symmetry group. As seen Figs. S4– S5, the charge of N, C_3 and C_5 atoms are negative and smaller than the other atoms of the ring of the neutral form of dinicotinic acid

Table 4

Mulliken charges of the neutral and two anion forms of dinicotinic acid molecule using B3LYP and HF methods with 6-311++G(d,p) basis set.

Atoms	Neutral form		Anion ⁻¹ fo	orm	Anion ⁻² form		
	B3LYP	HF	B3LYP	HF	B3LYP	HF	
N1 C2 C3 C4 C5 C6 H7	-0.0129 -0.5027 -0.0113 0.4743 -0.0113 -0.5027 0.2739	$\begin{array}{r} -0.1002 \\ -0.4395 \\ -0.1738 \\ 0.6386 \\ -0.1738 \\ -0.4395 \\ 0.3415 \end{array}$	$\begin{array}{r} -0.0480 \\ -0.5848 \\ -0.0831 \\ 0.6299 \\ 0.0581 \\ -0.3331 \\ 0.2736 \end{array}$	-0.1159 -0.5356 -0.0868 0.7826 -0.0684 -0.2967 0.3607	-0.1056 -0.3916 -0.1890 0.6457 -0.1890 -0.3916 0.2476	-0.1627 -0.3131 -0.1508 0.6866 -0.1508 -0.3131 0.3286	
H8 H9 C10 011 012 C13 014 015 H16 H17	0.2291 0.2291 0.0827 -0.2846 -0.1786 0.0827 -0.2846 -0.1786 0.2979 0.2979	0.2685 0.2685 0.2472 -0.3988 -0.2668 0.2472 -0.3988 -0.2668 0.3232 0.3232	0.1895 0.2228 -0.0059 -0.3287 -0.1890 -0.1663 -0.4042 -0.5128 0.2821	$\begin{array}{c} 0.2431\\ 0.2922\\ 0.0302\\ -0.4254\\ -0.2865\\ -0.0230\\ -0.5307\\ -0.6492\\ 0.3094 \end{array}$	$\begin{array}{c} 0.1728\\ 0.1728\\ -0.0338\\ -0.4679\\ -0.4844\\ -0.0338\\ -0.4679\\ -0.4844\end{array}$	0.2554 0.2554 0.0237 -0.5523 -0.6892 0.0237 -0.5523 -0.6892	



Fig. 8. Color-filled map of gradient norm of electron density of dinicotinic acid.

molecule, because of carboxylic groups for carbons and the properties of nitrogen atom. The values of Mulliken atomic charge of hydrogen atoms, carbon atom (C_4) and the carbon atoms (C_{10} and C_{13}) of carboxylic groups show positive charge in dinicotinic acid molecule. Also the charges of carbon atoms (C_{10} and C_{13}) of two anion forms (anion⁻¹ and anion⁻² form) are transform negative value from the positive values (neutral form). Plots of electron density in the *xy* plane of atomic hydrogen are shown in Fig. 8. The electron densities of atoms of the neutral form of the dinicotinic acid molecule are observed symmetrically as can be seen in Fig. 8.

Conclusions

In this paper, the experimental (NMR, FT-IR and FT-Raman) and theoretical (HF and DFT) analysis of dinicotinic acid were presented. A comparison of the theoretical and experimental results gave us a full description of the geometry and vibrational features of the molecule. We also obtained two anion (anion⁻¹ and anion⁻² form) forms of the dinicotinic acid molecule. The chemical shifts were compared with experimental data. The TDOS, PDOS and OP-DOS diagrams were plotted and also Mulliken atomic charge calculation was given both neutral and anion forms (anion⁻¹ and anion⁻² form). The calculated geometric parameters and vibrational wavenumbers obtained with B3LYP/6-311++G(d,p) method calculations are better agreement than HF calculations.

Acknowledgement

This work was supported by the Scientific Research fund of Celal Bayar University. Project numbers FBE-2011/70.

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.2013.05.049.

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