



Research Article

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Vibrational, Structural and Electronic properties of 6-methyl nicotinic acid by Density Functional Theory

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ABSTRACT

The equilibrium geometry and harmonic frequencies of the 6-methylnicotinic acid, were determined and analyzed at DFT level employing the basis set 6-311+G(d,p). The skeleton of the optimized molecule is non-planar. In general, a good agreement between experimental and calculated normal modes of vibrations has been observed. The molecular electrostatic potential surface has been used along with frontier orbital energy gap, electric moments, first static hyperpolarizability, to understand the activity of the molecule.

Keywords: Frontier orbitals, First static hyperpolarizability, Normal mode analysis, Thermodynamic properties.

INTRODUCTION

Nicotinic acid or vitamin B-3 is a vitamin in the B complex group and is essential for the normal and healthy functioning of intestinal tract, stomach, nervous system, and for a healthy skin. It is used widely in the treatment of hyperlipoproteinemias and decreases both the cholesterol and the triglyceride concentrations in the plasma. However, with very high doses its side effects are common and are particularly known to hinder the compliance of patients. Nicotinic acid derivatives have been developed to overcome this problem. As a result of chemical and galenic retardation, these derivatives lessen the side effects and the necessary doses are considerably reduced in comparison with pure nicotinic acid. The title compound 6-methyl nicotinic acid is an intermediate of the drug etoricoxib (a non-steroidal anti-inflammatory drug for the treatment of arthritis and osteoarthritis) [1]. The crystal belongs to monoclinic systems with the following lattice parameters: $a=3.8788 \text{ \AA}$, $b=13.634 \text{ \AA}$, $c=6.1094 \text{ \AA}$, $\beta=90.51^\circ$, its unit cell volume being 323.07 \AA^3 . The crystal structure is stabilized by intermolecular O-H--N and C-H--O hydrogen bonds [2].

The present communication deals with the investigation of the structural, electronic and vibrational properties of 6-methylnicotinic acid due to its medicinal importance. The structure and harmonic wave numbers were determined and analyzed at the density functional theory (DFT) level employing the basis set 6-311+G(d,p). The optimized geometry of 6-methylnicotinic acid and its molecular properties such as equilibrium energy, frontier orbital energy gap, molecular electrostatic potential (MESP) energy map, dipole moment, polarizability and first static hyperpolarizability were calculated and discussed. A complete vibrational analysis of the molecule was performed by combining the experimental IR spectroscopic data and the quantum chemical calculations. DFT based calculations provide not only the qualitative but also the quantitative understanding of energy distribution of each vibrational mode on the basis of potential energy distribution (PED) and lead to an additional interpretation of the vibrational spectroscopic data as demonstrated in studies conducted by various groups [3-9]. The thermodynamic properties of the studied compound at different temperatures were also calculated.

2 Quantum chemical calculations

Geometry optimization is one of the most important steps in the theoretical calculations. The X-ray diffraction data [2] of 6-methylnicotinic acid was used to optimize the structure. Becke's three parameter hybrid exchange

functionals [10] with Lee-Yang-Parr correlation functionals (B3LYP) [11,12] of the density functional theory [13] and 6-311+G(d,p) basis set was chosen. All the calculations were performed using the Gaussian 09 program [14]. The model molecular structure of 6-methylnicotinic acid is given in Figure 1. Positive values of all the calculated vibrational wave numbers confirmed the geometry to be located at the true local minima on the potential energy surface. As the DFT hybrid B3LYP functional tends to overestimate the fundamental normal modes of vibrations, a uniform scaling factor of 0.9679 [15, 16] was applied, and, in general, a good agreement of calculated modes with experimental ones was obtained. The theoretical IR spectrum [Figure 2] has been compared with the experimental spectra reported at NIST web data [17]. The vibrational wave number assignments were carried out by combining the results of the Gauss view 3.07 program [18], symmetry considerations and the VEDA 4 program [19].

The DFT is also used to calculate the dipole moment, mean polarizability $\langle\alpha\rangle$ and the total first static hyperpolarizability β_{TOTAL} [20,21] and are given in terms of x, y, z components by the following equations:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\langle\alpha\rangle = 1/3[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}]$$

$$\beta_{\text{TOTAL}} = [\beta_x^2 + \beta_y^2 + \beta_z^2]^{1/2}$$

$$= [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + [(\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

The β components of Gaussian output are reported in atomic units (1 a.u.= 8.3693 x 10⁻³³ e.s.u.).

Heat capacity C_p and entropy S were calculated using DFT and were obtained from the output of Gaussian programs. The equations used for calculating the absolute entropy of a molecule are as follows [22,23]

$$S = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}}$$

where S_{trans} , S_{rot} and S_{vib} are translational, rotational and vibrational entropy, respectively, which can be calculated by the following equations-

$$S_{\text{trans}} = R \left[3/2 \ln(2\pi mkT/h^2) + \ln(kT/P) + 5/2 \right]$$

$$S_{\text{rot}} = R \left[\ln(\pi^{1/2} / \sigma) + (1/2) \ln(T^3 / (h^2 / 8\pi^2 I_x k)(h^2 / 8\pi^2 I_y k)(h^2 / 8\pi^2 I_z k)) + 3/2 \right]$$

$$S_{\text{vib}} = R \sum_{i=1}^{3N-6} \left[\{ (h\nu_i / kT) / (\exp(h\nu_i / kT) - 1) \} - \ln\{1 - \exp(-h\nu_i / kT)\} \right]$$

where N is the number of atoms in a molecule, R is the gas constant, m is the molecular mass, k is the Boltzmann constant, h is Planck's constant, T is the temperature, P is the pressure, σ_r is the symmetry number for rotation, I is the moment of inertia, and ν is the vibrational frequency.

The heat capacity at constant pressure was calculated using the equation-

$$C_p = C_{\text{trans}} + C_{\text{rot}} + C_{\text{vib}} = (5/2)R + (3/2)R + R \sum_{i=1}^{3N-6} \left[\exp(h\nu_i / kT) \{ (h\nu_i / kT) / (\exp(-h\nu_i / kT) - 1) \}^2 \right]$$

where C_{trans} , C_{rot} and C_{vib} are contribution to heat capacity due to translation, rotational motion, and vibrational motion respectively.

RESULT AND DISCUSSION

3.1 Molecular Geometry Optimization and Energies

The spatial coordinates of 6-MNA as obtained from X-ray structure analysis [2] were used as the initial co-ordinates for the theoretical calculations. The optimized molecular structure together with the numbering scheme of 6-methylnicotinic acid is shown in Figure 1 and comparison of the optimized geometric parameters with the X-ray data is reported in Table 1. As the calculated vibrational spectrum has no imaginary frequency, the optimized geometry is confirmed to be located at the local minima on potential energy surface. The C-C and C-H bond lengths

of heterocyclic ring lie in the range 1.388 Å-1.401 Å and 1.083 Å-1.085 Å respectively which are close to standard value 1.40 Å and 1.10 Å [24] but the C-H bond lengths in methyl group have values 1.093 Å and 1.091 Å. The C(14)-N(16)/ C(13)-N(16) bond lengths are found to be 1.330/1.344 Å which are smaller than the C-C bond of benzene ring. The replacement of carbon atom of benzene ring by electronegative nitrogen atom decreases the bond length of C-C bond. The C(5)-C(13) bond length is 1.504 Å but due to conjugation effect C(4)-C(17) bond shows some double character and its bond length is calculated to be 1.482 Å. The C=O/C-O bond lengths at 1.208 Å/1.359 Å are close to standard value 1.20 Å/1.34 Å and O-H bond of carboxylic group has value 0.969 Å (standard value 0.96 Å). The decrease in exohedral angles C5-C13-N16/H15-C14-N16 to 116.3°/117° and increase in endohedral angles C11-C13-N16/N16-C14-C17 to 121.9°/123.6° from the usual 120.0° is attributed to the repulsion between N16 and O3 atoms. Moreover, reduction in angle O1-C4-C17 to 112.7° and enhancement in angles O1-C4-O3/O3-C4-C17 to 122.1°/125.2° from 120.0° were also observed in the quantum chemical calculations and is due to the repulsion between O1 and O3 atoms. The skeleton of 6-methylnicotinic acid is not strictly planar: the methyl group deviates from the plane of heterocyclic ring, the deviation is represented by the dihedral angles H6-C5-C13-C11(-121.2°)/H6-C5-C13-N16(58.8°)/H7-C5-C13-C11(121.2°)/H7-C5-C13-N16(-58.5°). In general, optimized parameters agree very well with the XRD data (refer to table 1).

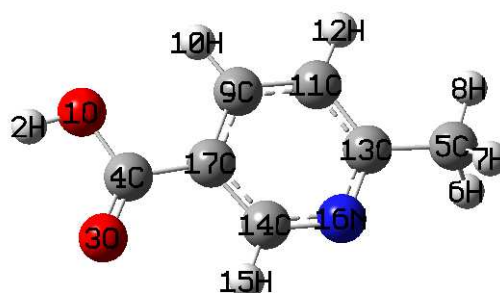


Fig. 1 Optimized structure along with numbering scheme of 6-methyl nicotinic acid At B3LYP/6-311+G(d,p)

Table 1. The optimized geometric parameters of 6-methylnicotinic acid and comparison with available experimental^{*} results, bond lengths in angstrom (Å), bond angles and selected dihedral angles in degrees (°)

* <http://webbook.nist.gov/chemistry/form-ser.html>.

Interatomic distance	B3LYP Bond length	X-Ray data	Interatomic Distance	B3LYP Bond length	X-Ray data
O1-H2	0.9685	0.8192	C5-C13	1.5036	1.4849
O1-C4	1.3589	1.3112	C9-H10	1.0826	0.9310
O3-C4	1.2084	1.1921	C9-C11	1.3879	1.3589
C4-C17	1.4821	1.4822	C9-C7	1.3967	1.3865
C5-H6	1.0933	0.9596	C11-H12	1.0835	0.9300
C5-H7	1.0933	0.9597	C11-C13	1.4002	1.3806
C5-H8	1.0911	0.9603	C13-N16	1.3443	1.3382
C14-H15	1.0852	0.9298	C14-N16	1.3298	1.3314
C14-C17	1.4005	1.3749			
Bond Angles	B3LYP Bond angles	X-Ray data	Bond Angles	B3LYP Bond angles	X-Ray data
H2-O1-C4	106.8	109.5	O1-C4-O3	122.1	124.3
O1-C4-C17	112.7	112.6	O3-C4-C17	125.2	123.1
H6-C5-H7	107.0	109.5	H6-C5-H8	108.9	109.5
H6-C5-C13	110.0	109.5	H7-C5-H8	108.9	109.5
H7-C5-C13	110.0	109.5	H8-C5-C13	112.0	109.4
H10-C9-C11	121.0	120.2	H10-C9-C17	120.3	120.3
C11-C9-C17	118.7	119.5	C9-C11-H12	120.5	120.0
C9-C11-C13	119.4	120.2	H12-C11-C13	120.1	119.8
C5-C13-C11	121.8	121.9	C5-C13-N16	116.3	117.2
C11-C13-N16	121.9	120.8	H15-C14-N16	117.0	118.1
H15-C14-C17	119.3	118.1	N16-C14-C17	123.6	123.8
C13-N16-C14	118.5	118.6	C4-C17-C9	123.3	123.4
C4-C17-C14	118.9	119.4	C9-C17-C14	117.9	117.1

3.2 Electronic Properties

The most important orbitals in a molecule are the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These orbitals determine the way the molecule interacts with other species. The frontier orbital gap helps characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a

high chemical reactivity, low kinetic stability and is also termed as soft molecule [25]. The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that largely acts as the electron acceptor. The 3D plots of the frontier orbitals HOMO and LUMO and electrostatic potential mapped on iso-density surface known as molecular electrostatic potential (MEP) surface, for 6-methylnicotinic acid are shown in Figure 3 and Figure 4 respectively. It is seen from the figure that although both HOMO and LUMO are spread over the entire molecule but the HOMO shows considerable antibonding character. The calculated value of frontier orbital energy gap of 0.19974 a.u. or 5.4352 eV (Table 2) in case of 6-methylnicotinic acid makes it a soft and more polarizable molecule as compared to water and dimethyl furan (DMF), taking water and DMF as reference molecules for comparison, as both are eminently polar solvents, on account of their high dielectric constant, electron donor property and ability to form complexes having 9.3088 and 6.8054 eV for their frontier orbital energy gap calculated at the same level of theory as well as the same basis sets.

The electrostatic potential (ESP) is a physical property of a molecule related to how a molecule is first “seen” or “felt” by another approaching species. A portion of a molecule that has a negative electrostatic potential is susceptible to electrophilic attack-the more negative the better. The MESP simultaneously displays molecular shape, size and electrostatic potential values and has been plotted for the title molecule. MESP mapping is very useful in the investigation of the molecular structure with its physiochemical property relationships [25-31]. The MESP of 6-methylnicotinic acid shows clearly the three major electron rich regions characterized by red color - around the two oxygen atoms and nitrogen atom of the heterocyclic ring, whereas all the hydrogen atoms bear the brunt of positive charge (blue regions). The green region in the MESP surfaces corresponds to a potential halfway between the two extreme red and dark blue color.

Table 2. Parameters corresponding to optimized geometry of 6-methyl nicotinic acid at DFT/B3LYP level of theory

Basis set	Ground State Energy (Hartree)	Frontier Orbital Energy Gap (Hartree)	Dipole Moment (Debye)
6-311G (d)	-476.29329	0.20213	3.1182
6-311+G(d)	-476.30359	0.20021	3.3495
6-311+G(d,p)	-476.31856	0.19974	3.3610

Table 3. Polarizability and hyperpolarizability data for 6-methylnicotinic acid at B3LYP/6-311+G(d,p)

Polarizability ^a components and mean polarizability $\langle \alpha \rangle$ in a.u.	
α_{xx}	136.872
α_{xy}	-1.708
α_{yy}	96.473
α_{xz}	0.053
α_{yx}	-0.033
α_{zz}	54.514
$\langle \alpha \rangle$	95.953
All β^b components and β total in a.u.	
β_{xxx}	539.0
β_{xxy}	21.0
β_{xyy}	-107.6
β_{yyy}	19.8
β_{xxz}	0.0
β_{xyz}	0.0
β_{yyz}	0.0
β_{xzz}	-28.5
β_{yzz}	17.2
β_{zzz}	0.0
β_{TOTAL}	407.1

^a In atomic units. Conversion factor to the SI units,
 $1e^2 a_0^3 E_h^{-1} = 1.648778 \times 10^{-41} C^2 m^2 J^{-1}$

^b In atomic units. Conversion factor to the SI units-
 $1e^3 a_0^3 E_h^{-2} = 3.206361 \times 10^{-53} C^3 m^3 J^{-2}$

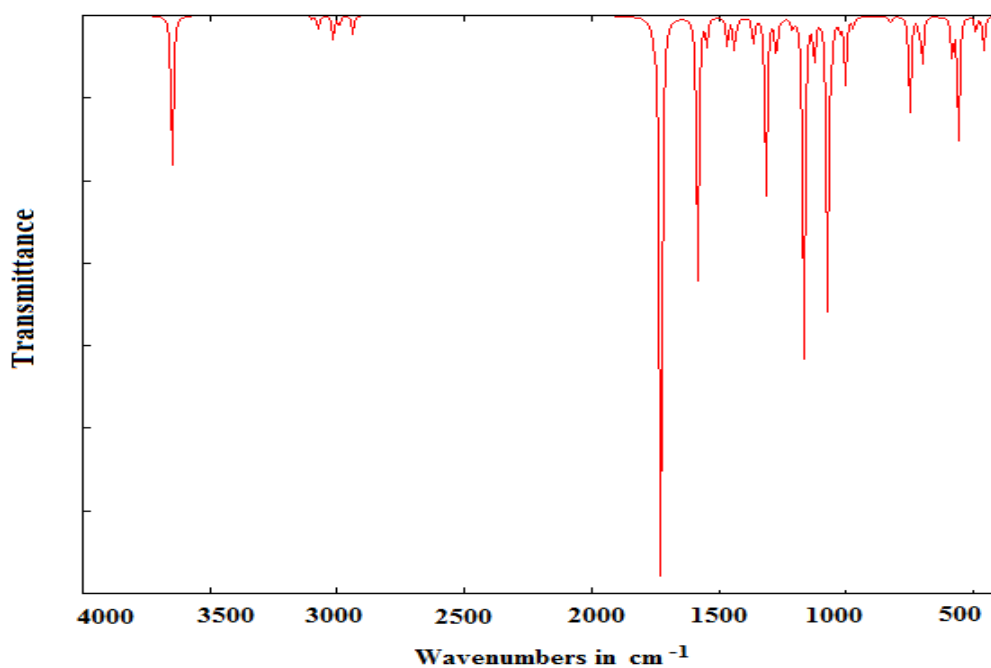


Fig. 2 Theoretical IR spectrum of 6-methyl nicotinic acid

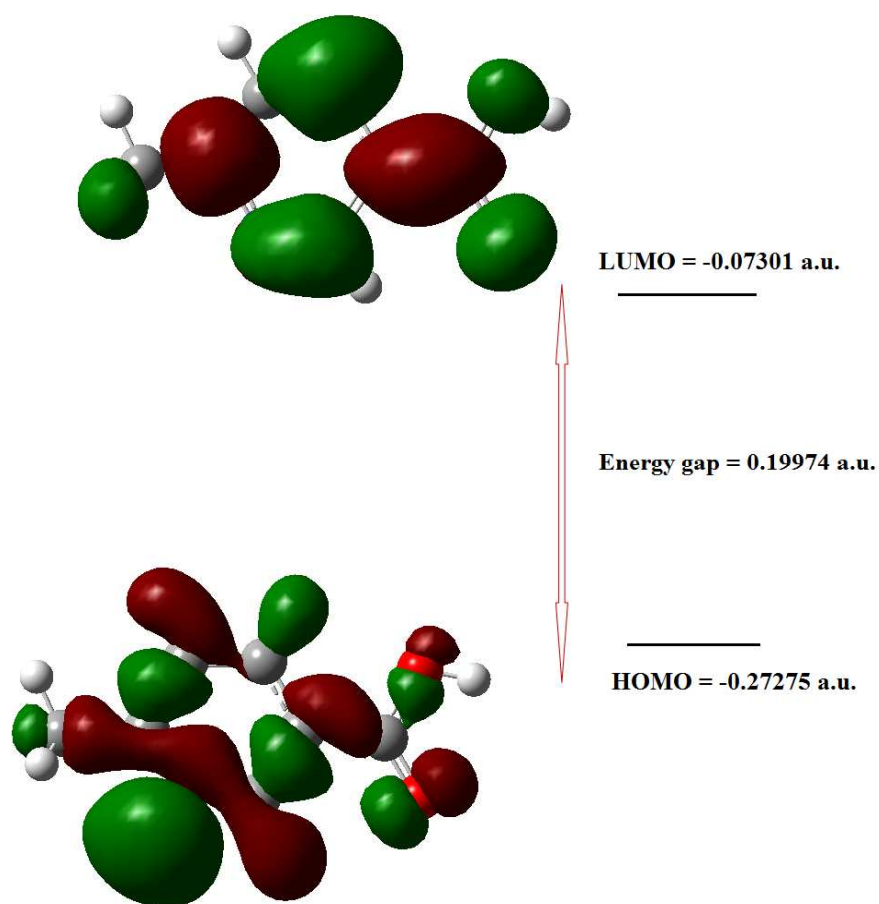


Fig. 3 Frontier orbitals of 6-methyl nicotinic acid

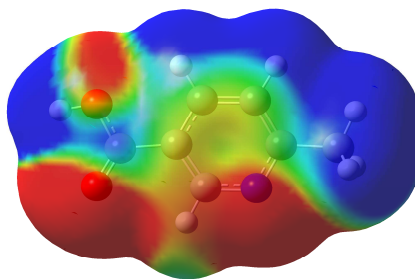


Fig. 4 MEP surface of 6-methyl nicotinic acid

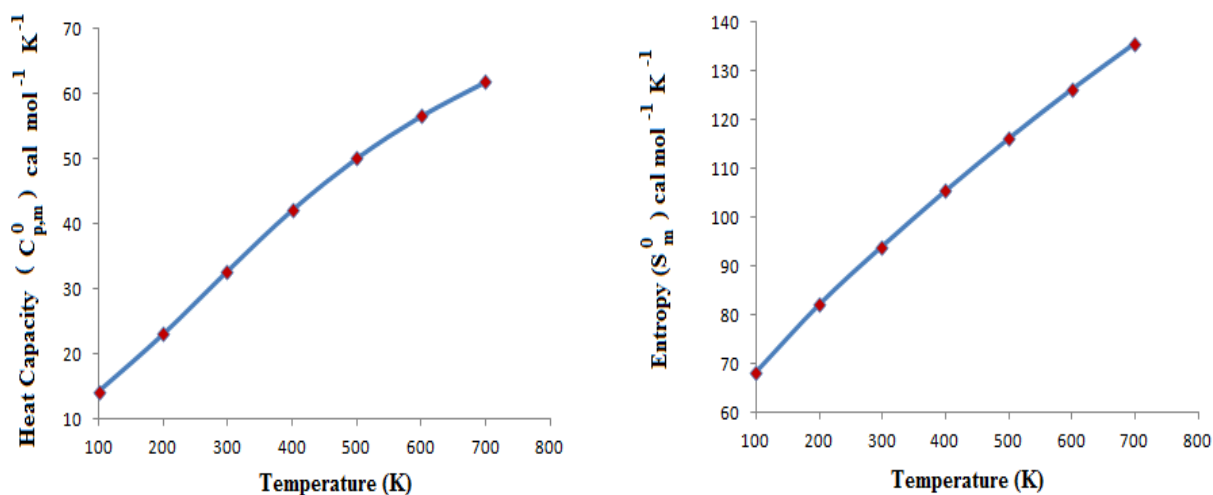


Fig. 5 Variation of Heat Capacity and Entropy with temperature

3.3 Electric Moments

The dipole moment in a molecule is another important electronic property that results from non-uniform distribution of charges on the various atoms in a molecule. It is mainly used to study the intermolecular interactions involving the van der Waal type dipole-dipole forces, etc., because higher the dipole moment, stronger will be the intermolecular interactions. The calculated value of dipole moment in the case of 6-methylnicotinic acid has value 3.3610 Debye. If dipole moment of 6-methylnicotinic acid is compared with that of water and DMF, it is seen that its calculated dipole moment value is slightly higher than the water but relatively smaller than that of DMF (Dipole moment value of DMF and water are 4.24 and 2.16 Debye respectively at the same level of calculation i.e. B3LYP/6-311G+(d,p)). The polarizability and first static hyperpolarizability β value are calculated to be 95.953 a.u. and 407.1 a.u. respectively [Table 3].

3.4 Vibrational Spectral Analysis

The optimized molecular structure of 6-methylnicotinic acid belongs to the C_1 point group as it does not display any special symmetry. As a result of this all the 45 fundamental modes of vibrations of the molecule are IR active and are spread over the functional and fingerprint regions. The experimental and computed vibrational wave numbers, their IR intensities and the detailed description of each normal mode of vibration of the title molecule, carried out in terms of their contribution to the total potential energy are given in Table 4. The calculated harmonic wavenumbers are usually higher than the corresponding experimental quantities because of the combination of electron correlation effects and basis set deficiencies. These discrepancies are taken care of either by computing anharmonic corrections explicitly or by introducing scalar field or even by direct scaling of the calculated wavenumbers with a proper scaling factor [15,16]. The vibrational wavenumbers are calibrated accordingly with scaling factor 0.9679 for DFT at B3LYP. The vibrational assignments have been done on the basis of relative intensities, line shape, the VEDA 4

program and the animation option of Gaussview 3.0. The comparison of the scaled wavenumber with experimental values reveals that the B3LYP method shows very good agreement with the experimentally observed spectra. The vibrational analysis of the title molecule has been carried out under following heads -

3.4.1 CH₃ modes:

A single methyl group present in the 6-methylnicotinic acid is attached to the carbon atom C13 of the ring. Methyl group shows several characteristic fundamental vibrations corresponding to asymmetric, symmetric stretches, bending, rocking and torsion modes.

Table 4: Theoretical and experimental wave numbers (in cm⁻¹) of 6-methyl nicotinic acid

S.No.	Calc. (scaled wave no. in cm ⁻¹)	Exp ^a IR wave no. in cm ⁻¹	Calc. IR Inten.	Assignment of dominant modes in order of decreasing potential energy distribution (PED)
1	3649	3567	104.29	v(O1-H2)(100)
2	3103	-	2.14	v _s (C-H)R(99)
3	3079	-	6.79	v _{as} (C-H)R(99)
4	3074	-	3.61	v _{as} (C-H)R(97)
5	3017	3000	15.45	v _{as} (C-H) methyl(99)
6	2993	2983	7.67	v _{as} (C-H)methyl(100)
7	2939	2950	11.17	v _s (C-H)methyl(100)
8	1732	1750	413.71	v(O3-C4)(83)
9	1584	1583	168.05	v(C-C)R(48)+ v(N16-C13)R(26)
10	1547	-	15.68	v(C-C)R(54)+ v(N16-C13)R(30)
11	1466	-	19.40	Φ(H15-C14-N16)R(21) +Φ(H12-C11-C9)R(18) +v(N16-C13)R(16)+v(C-C)(11)
12	1440	1467	19.14	methyl deformation(88)
13	1428	-	7.95	methyl deformation(92)
14	1370	-	16.55	methyl umbrella bending (45)+ v(N16-C14)R(19)+Φ(H10-C9-C17)R(18)
15	1364	1367	3.84	methyl umbrella bending (82)
16	1317	1317	112.46	Φ(H2-O1-C4)(32) +v(C4-C17)(15)+ v(O1-C4)(13)+Φ(H10-C9-C17)R(12)
17	1277	-	29.53	Φ(H15-C14-N16)R(47)+ v(N16-C14)R(17)+Φ(H1-C-C)R(15)
18	1254	1283	1.73	Ring deformation(72)+ methyl rocking (15)
19	1213	-	7.73	v(C5-C13)(27)+Φ(H12-C11-C9)R(22)+v(C-C)R(12)+ v(C-N)R(11)
20	1166	1183	215.28	Φ(H2-O1-C4)(41) + v(C4-C17)(17)
21	1124	-	29.82	Φ(H-C-C)R(68)+ v(C-C)R(14)
22	1071	1083	178.27	v(O1-C4)(50)+ Φ(H-C-C)R(26)
23	1026	1017	7.15	methyl rocking (82)
24	1006	-	39.98	Ring trigonal bending
25	975	-	7.18	methyl rocking (75)
26	970	-	0.20	ω (C-H)R(88)
27	949	-	0.63	ω (C14-H15)R(73)
28	829	-	4.30	ω (C-H)R(75)
29	818	-	1.69	Φ(C-C-C)R(33)+ Φ(C-N-C)R(23)
30	748	750	62.44	ω (C-H)R(65)+ r methyl(14)
31	711	717	3.64	Ring torsion mode(65)+ Ψ(O1-C4-O3)(14)+Ψ(H2-O1-C4)(12)
32	705	-	29.62	Φ(O3-C4-O1)(29)+ v(C5-C13)(17)+v(C4-C17)(15)
33	633	675	0.64	Φ(C-C1-C1)R(51)+ Φ(C14- N16-C13)R(21)+ Φ(C17-C14-N16)R(18)
34	585	600	28.03	Φ(O3-C4-O1)(44)+ Φ(C11-C13-N16)R(17)+ v(C5-C13)(15)
35	560	575	80.75	ω (O1-H2)(87)
36	491	-	10.80	Φ(O1-C4-C17)(48)+Φ(C4-C17-C14)(17)+ Φ(C5-C13- C16)(15)
37	459	-	21.72	Ring torsion mode(61)+methyl rocking(16)
38	401	-	1.55	Ring torsion mode(66)+ τ(H15-C14-N16-C13)R(14)

^a Experimental data has been obtained from NIST website-<http://webbook.nist.gov/chemistry/form-ser.html>.

Note : Abbreviations used here have following meaning.

v: stretching; v_s: symmetric stretching; v_{as}: asymmetric stretching; Φ: in plane bending; Ψ: out of plane bending; ω: wagging; R: Pyridine ring.

The CH₃ antisymmetric stretching vibrations are generally observed in the region 2940-2980 cm⁻¹ while the symmetric stretching vibrations are generally observed in the range 2850-2890 cm⁻¹. In 6-methylnicotinic acid the two antisymmetric stretching vibrations of CH₃ group are calculated at 3017 and 2993 cm⁻¹ and are assigned to a weak bands at 3000 cm⁻¹ and 2983 cm⁻¹ in IR spectra, while one symmetric stretching vibration at 2939 cm⁻¹ is observed at 2950 cm⁻¹ in IR spectra. The contributions of these modes to the total PED is found to be 100%. The methyl deformation are calculated in the present case at 1440 cm⁻¹ and 1428 cm⁻¹ contributing 88% and 92% to the total PED and assigned to 1467 cm⁻¹ peak in the IR spectra. The methyl umbrella bending modes are calculated as mixed mode at 1370 cm⁻¹ and as pure mode at 1364 cm⁻¹ and are assigned at 1367 cm⁻¹ in IR spectra. The dominant

methyl rocking modes are at 1026 cm^{-1} and 975 cm^{-1} contributing 82% and 75% to the total PED respectively and are assigned at 1017 cm^{-1} in the IR spectra.

3.4.2 C=O, C-O and C-N vibrations:

The appearance of a strong band in IR spectra around $1650\text{--}1800\text{ cm}^{-1}$ in aromatic compound shows the presence of carbonyl group and is due to the C=O stretching motion. The wavenumber of the stretch due to carbonyl group mainly depends on the bond strength which in turn depends upon inductive, conjugative, field and steric effects. The one strong band in the IR spectra at 1750 cm^{-1} is due to C=O stretching vibration corresponding to C=O group (at C4) of carboxylic group. This band is calculated at 1732 cm^{-1} . The other strong band observed at 1083 cm^{-1} is due to C-O stretching vibration of the same carboxylic group whose general position is $1000\text{--}1200\text{ cm}^{-1}$. This band is calculated at 1071 cm^{-1} . Identification of C-N stretching is not an easy task, due to the possible mixing of other vibrations. As expected the C-N stretching in case of 6-methylnicotinic acid are calculated as mixed mode at 1370 cm^{-1} and 1277 cm^{-1} and are assigned at 1283 cm^{-1} in IR spectra.

3.4.3 OH vibrations:

The OH stretching vibrations are generally observed in the region around $3200\text{--}3650\text{ cm}^{-1}$. The appearance of strong band at 3567 cm^{-1} in IR spectra shows the presence of OH group. The band is calculated at 3649 cm^{-1} and contributes 100% to the total PED. The small discrepancy between the calculated and the observed wavenumber may be due to the intermolecular hydrogen bond [2]. Two bands observed at 1183 cm^{-1} and 1317 cm^{-1} in IR spectra are due to H2-O1-C4 in-plane bending and are calculated at 1317 cm^{-1} and 1166 cm^{-1} respectively as mixed modes.

3.4.4 Ring modes:

The heterocyclic ring spectral region predominantly involves the C-H, C-C and C-N stretching, and C-C-C, H-C-C and C-N-C bending vibrations. The bands due to the ring C-H stretching vibrations are generally observed in the region $3000\text{--}3100\text{ cm}^{-1}$. The calculated CH stretching modes are at 3103 , 3079 and 3074 cm^{-1} wave numbers. Vibrations involving C-H in-plane bending are found throughout the region $1100\text{--}1500\text{ cm}^{-1}$. The C-H wagging mode starts appearing at 970 cm^{-1} and has contributions up to 748 cm^{-1} and is assigned well in the spectra. The C-C stretching vibrations are calculated at 1584 , 1547 , 1213 and 1124 cm^{-1} . The torsional modes appear in general in the low wavenumber regions. In the present case, the calculated ring torsional modes with more than 60% contribution are 711 , 459 and 401 cm^{-1} .

3.5 Thermodynamic Properties

The values of some thermodynamic parameters (such as zero-point vibrational energy, specific heat capacity, rotational constants, entropy and dipole moment) of title molecule by DFT/B3LYP/6-311+G(d,p) method at 298.15 K in ground state are listed in the Table 5. The global minimum energy obtained for structure optimization of B3LYP with 6-311+G(d,p) basis set is -476.31856 a.u. (Table 2).

On the basis of vibrational analysis, the statically thermodynamic functions- heat capacity, and entropy changes for the title molecule are obtained from the theoretical harmonic frequencies and are plotted in Figure 5. It can be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 700 K due to the fact that the molecular vibrational intensities increase with temperature. The correlation equations between heat capacity, entropy changes and temperatures were fitted by quadratic formulas and the corresponding fitting factors (R^2) for these thermodynamic properties are 0.9989 and 0.9999 respectively. The corresponding fitting equations are as follows -

Table 5. The calculated thermodynamic parameters at 298.15 K temperature and 1.0 Atm pressure in ground state

$$C_{p,m}^0 = 2.4165 - 0.116T - 4 \times 10^{-5} T^2 \quad (R^2 = 0.9989)$$

$$S_m^0 = 54.759 + 0.1428T - 4 \times 10^{-5} T^2 \quad (R^2 = 0.9999)$$

Parameter	Value
Zero point Vib. Energy (Kcal mol ⁻¹)	81.84187
Rotational Constants (GHz)	3.87835
	0.80234
	0.66754
$C_{p,m}^0$ (cal mol ⁻¹ K ⁻¹)	32.611
S_m^0 (cal mol ⁻¹ K ⁻¹)	93.969

All the thermodynamic data supply helpful information for the further study on the 6-methylnicotinic acid. They can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics. It should be noted that all thermodynamic calculations were done in gas phase and they could not be used in solution.

CONCLUSION

The equilibrium geometry and harmonic wavenumbers of 6-methylnicotinic acid molecule under investigation were analyzed at DFT/6-311+G(d,p) level. The skeleton of the optimized molecule is non planar. In general, a good agreement between experimental and calculated normal modes of vibrations was observed. The frontier orbital energy gap, dipole moment, MESP surface and first static hyperpolarizability of 6-methylnicotinic acid were also calculated. According to the frontier orbital energy gap 6-methylnicotinic acid is quite reactive molecule and thus has a low kinetic stability as compared to water and DMF. The MESP has also been used to understand the activity of the molecule. The correlations between the statistical thermodynamics and temperature are also obtained. It is seen that the heat capacities and entropies increase with the increasing temperature owing to the fact that the intensities of the molecular vibrations increase with increasing temperature.

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