Molecular structure and vibrational spectra of 2-amino-5-methyl pyridine and 2-amino-6-methyl pyridine by density functional methods

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ABSTRACT

The Fourier transform Raman (3500–50 cm^{-1}) and Fourier transform infrared (4000–400 cm^{-1}) spectra of 2-amino-5-methylpyridine and 2-amino-6-methylpyridine have been measured in solid phase. The Fourier transform gas phase infrared spectra of 2-amino-5-methylpyridine and 2-amino-6-methylpyridine have also been measured. Density functional theory harmonic and anharmonic frequency calculations have been made. A complete vibrational assignments of the observed spectra of both molecules have been proposed. Geometric parameters have been compared with single crystal X-ray diffraction data of the molecule. The theoretical IR spectra of the title molecules have been constructed.

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1. Introduction

The pyridine derivatives have an important position among the heterocyclic compounds because they can be used as nonlinear materials and photochemicals. In particular, some of these crystals have been reported as frequency converters from NIR to the visible wavelength region [1]. Amino pyridines are widely used in pharmacological and medical applications. Some of them show anesthetic properties and have been used as drugs for certain brain diseases [2–4]. 2-Aminopyridine-tagged oligosaccharides have been widely used for sensitive qualitative and quantitative analysis by high performance liquid chromatography with fluorescence detection [2]. 2-Aminopyridine is used in preparation of cytidine analogs [5], it is also immensely used as a reagent in analytical chemistry.

Mohan et al. [6] carried out the normal coordinate analysis of 2-aminopyridine, using valence force field. However, they assumed the NH$_2$ group of the molecule as a single mass point. The normal co-ordinate analysis of the 2-amino pyridine and ND$_2$-pyridine was performed in valence force field approximation. IR and absorbance intensities were calculated and electro-optical parameters (EOP) were refined in order to produce experimental IR spectrum [7]. The vibrational spectra of 3-methyl pyridine have been investigated by several authors [8–10]. Generally, its molecular vibrations were assigned to the normal modes of benzene [11] which, how-

ever, may not be justified in the case of the non-symmetric benzene derivatives [12]. Draegar performed a normal co-ordinate analysis [13] using experimental data from the early sixties [14]. Although this study resulted in a good agreement between the experimental and calculated frequencies, new experimental data and developments in the normal co-ordinate analysis method justify a reinvestigation of the vibrational spectra of this important molecule. Recently the molecular vibrations of 3-methyl pyridine were investigated by means of a scaled quantum mechanical (SQM) analysis. The initial harmonic force field was also evaluated at B3LYP (DFT) level using 6-31G* basis set [15].

Pulays recently introduced DFT-based SQM method [16] for which scale factor developed using among others vibrational data of N heterocycles (pyridine and pyrazole) are available. The vibrational spectra available in the literature do not provide sufficient information for a detailed analysis of the overlapping band of close lying fundamentals. Force field calculation were obtained by SQMFF [17] methodology for 3-methyl and 4-methyl pyridines. This allows for correction of systematic errors in the ab initio force fields in such a way that theoretical frequencies approach the experimental ones, and permit the estimation of the theoretical spectrum. Numerous works had been reported related to the assignment of the vibrational spectrum of pyridine [18–24], while the information on the methyl derivatives is scarce [8,13,14,25–27]. Gandolfo and Zarembowitch [8] have carried out a vibrational study of the IR and Raman spectra of 3-methyl pyridine with the aim of comparing vibrational spectra of some co-ordinate compounds those posses this molecule as a ligand. Green et al [14]

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have carried out a vibrational study of monohalogenated compounds of pyridine, for which they used the result obtained for the corresponding methyl pyridines, while Long and George [25] have carried out the vibrational assignment of 4-methyl pyridine and toluene.

Many works have been found in the literature dealing with the vibrational analysis of pyridine [18–24] and methyl derivatives [13,20,25–27] but upon increasing the number of methyl and amino groups substituents the information become more scarce, and only Drager [13] reported an assignments of the deuterated methyl derivatives of pyridine on the basis of the modified valence force field where the pyridine geometry was assumed to remain unaffected by the substitution. The IR and Raman spectra of the pure liquid and of a 1 M aqueous solution of 2-methylpyridine have been recorded. These spectra have been interpreted employing the SQMFF methodology, by directly transferring the scale factors obtained for pyridine [28]. To the best of our knowledge, neither quantum chemical calculation, nor the vibrational spectra of 2-amino-5-methyl pyridine and 2-amino-6-methyl pyridines (hereafter they are, respectively, referred to as 2A5MP and 2A6MP) have been reported. Therefore, the present investigation was undertaken to study the vibrational spectra of this molecules completely and to identify the various modes with greater wavenumber accuracy. Density functional theory (DFT) calculations have been performed to support our wavenumber assignments.

2. Experimental details

The 2A5MP and 2A6MP samples were purchased from Sigma–Aldrich Chemical Company with a stated purity of greater than 98% and it was used as such without further purification. The samples 2A5MP and 2A6MP are in solid form at room temperature. The FT-Raman spectrum of 2A5MP and 2A6MP have been recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 50–3500 cm^{-1} on a Brucker model IFS 66 V spectrophotometer equipped with FRA 106 FT-Raman module accessory. The FT-IR spectra of these compounds were recorded in the range of 400–4000 cm^{-1} on IFS 66 V spectrophotometer using KBr pellet technique. The FT-IR gas phase spectra were also recorded in the region 500–4000 cm^{-1}. The spectra were recorded at room temperature, with scanning speed of 30 cm^{-1} min^{-1} and the spectral resolution of 2.0 cm^{-1}. The experimental FT-IR, FT-Raman and FT-IR gas phase along with theoretical spectra are shown in Figs. 1–4. The detector is a liquid nitrogen cooled Ge detector. Five hundred scans were accumulated at 2 cm^{-1} resolution using a laser power of 100 mW.

3. Computational detail

The molecular structure of 2A5MP and 2A6MP in the ground state (in vacuum) are optimized by HF/B3LYP with the 6-311++G(d,p) higher basis set. There are no significant difference in geometric and vibrational frequencies by the selection of the different basis sets, but we included only one basis set viz 6-311++G(d,p) for geometric parameters and frequency calculations. In literature, there is no global scaling factor for B3LYP/6-311++G(d,p) basis set. All the calculations are performed by using Gaussian 03 program [29] package on the personal computer. The Becke's three-parameter hybrid density functional, B3LYP was used to calculate both harmonic and anharmonic vibrational wavenumbers with the 6-311++G(d,p) basis set. It is well known in the quantum chemical literature that among available functionals the B3LYP functional yields a good description of harmonic vibrational wavenumbers for small and medium sized molecules.
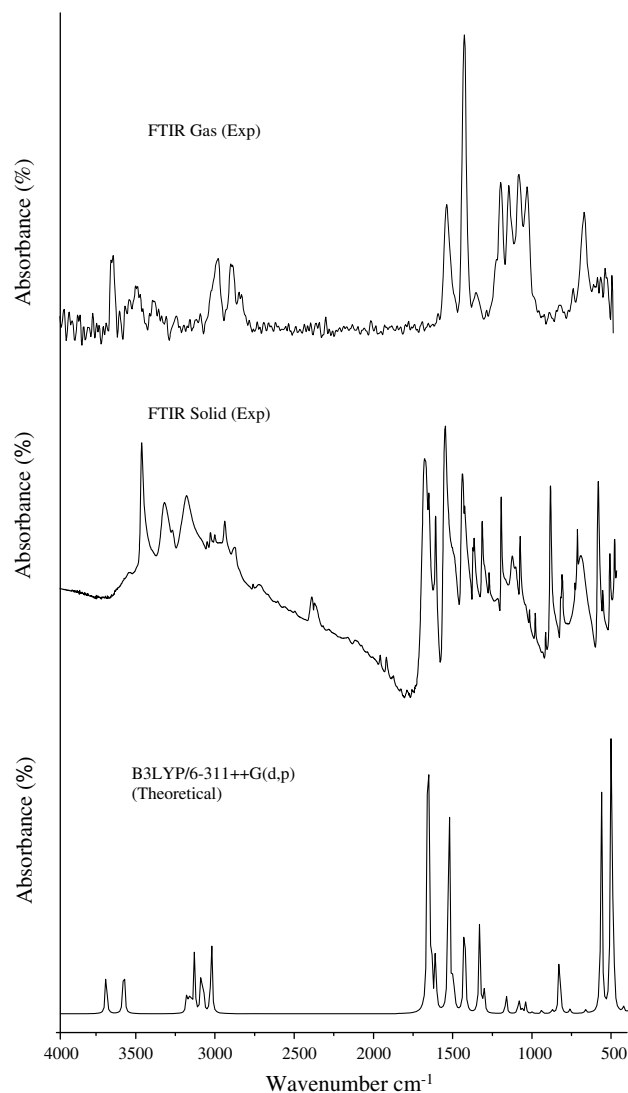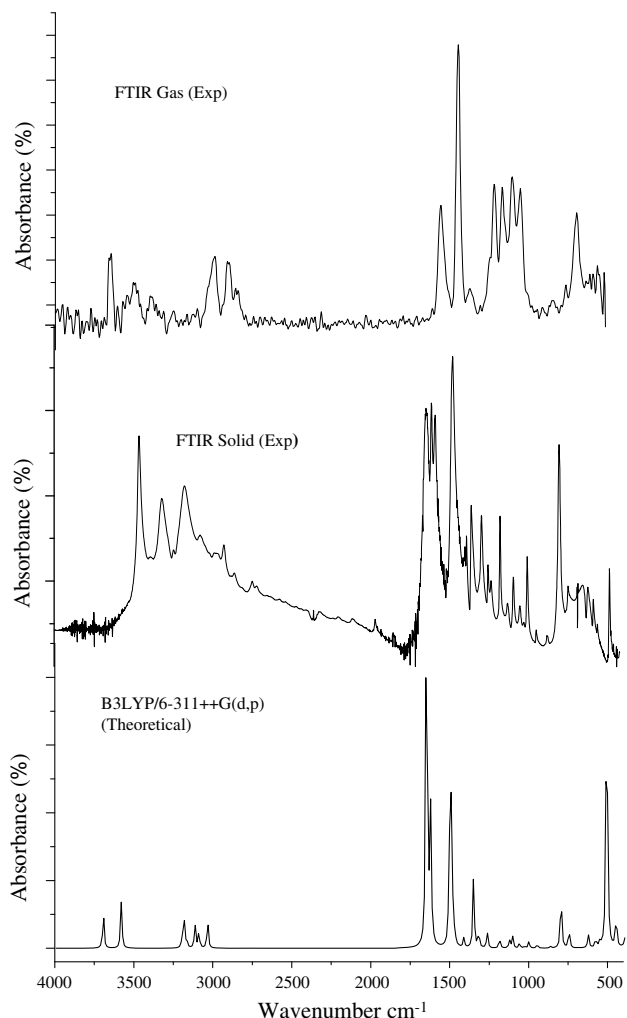

Fig. 1. Comparisons of FT-IR (gas and solid) and theoretical (B3LYP) FT-IR spectrum of 2-amino-5-methylpyridine.

4. Results and discussion

### 4.1. Molecular geometry

The crystal structure of 2A5MP was reported by Inger Nahringbauer [30]. The structure is monoclinic of the space group P2$_1$/c, a = 10.413(5), b = 5.908 (3), c = 10.828 (5) Å, Z = 4. The molecule is linked together by a very weak N—H···N to produce cyclic dimers which, in turn, pack in a herring bond formation. The optimized geometrical parameters of 2A5MP and 2A6MP calculated by ab initio HF and DFT-B3LYP levels with the 6-311++G(d,p) basis sets are listed in Table 1 which are in accordance with numbering scheme given in Fig. 5a and b.

From the theoretical values both the HF and B3LYP/6-311++G(d,p) for 2A5MP and 2A6MP we find that most of the optimized bond lengths and bond angles are slightly smaller, as well as longer than the experimental values. Comparing bond angles and bond lengths of B3LYP and HF for 2A6MP show larger values when compared with crystal structure of 2A5MP, this is due to fact that the theoretical calculations belong to isolated molecule in gaseous phase and experimental results belong to molecule in solid state.

Fig. 2. Comparisons of FT-IR (gas and solid) and theoretical(B3LYP) FT-IR spectrum of 2-amino-6-methylpyridine.

Fig. 3. FT-Raman spectrum of 2-amino-5-methylpyridine.
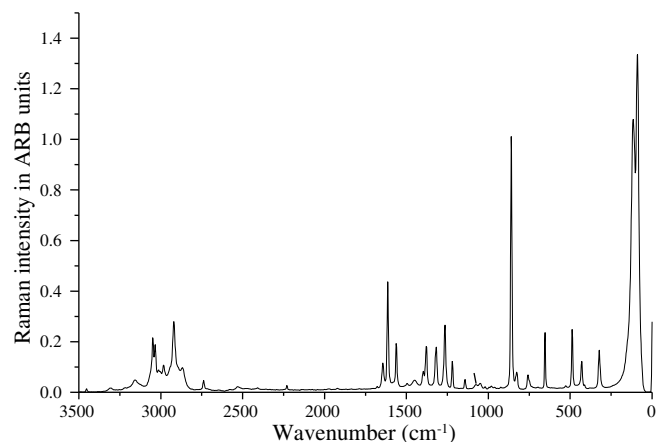
Fig. 4. FT-Raman spectrum of 2-amino-6-methylpyridine.

ple the optimized bond length of C—C in phenyl ring fall in the range 1.395–1.406 Å at B3LYP/6-311++G(d,p) and 1.377–1.400 Å at HF/6-311++G(d,p) methods show good agreement with recorded X-ray data of 1.375–1.400 Å for 2A5MP. But in the case of 2A6MP the C—C bond distance fall in the range at HF 1.381–1.402 Å and B3LYP at 1.395–1.408 Å shows slight deviation.

C—N bond distance was found to be 1.47 Å for some nitramines [32], but it is about ~1.34 Å in both 2A5MP and 2A6MP by B3LYP/6-311G++(d,p) method. Moreover, all carbon and nitrogen atoms in the ring are coplanar, as in benzene ring. Also it is evident from Table 1 both N—C bonds of pyridine [33–35] (experimental) have identical length of 1.340 Å while introduction of the substituent causes slight differences between them. The optimized C—N bond lengths of 1.382 and 1.378 Å by HF methods for 2A5MP and 2A6MP, respectively, overestimated by ~0.018 and ~0.014 Å with that of crystal data of 2A5MP at 1.364 Å. Where as the C—N bond lengths by DFT/6-311++G(d,p) method overestimation by ~0.020 Å.

The pyridine ring of 2A5MP appears a little distorted with C1–C2 and C3–C4 bond lengths 1.406 and 1.400 Å, respectively, by B3LYP/6-311++G(d,p) exactly at the substitution and rest to the substitution place longer than C2–C3 and C4–C5 bond lengths 1.386 and 1.395 Å by same method. Similar trend is also observed in the case of 2A6MP. In our case B3LYP method leads to geometric parameters which are much closer to experimental data. Because of these reasons we take into account B3LYP/6-311++G(d,p) level of vibrational analysis for 2A5MP and 2A6MP in our present discussion.

4.2. Vibrational assignments

The harmonic and anharmonic vibrational frequencies calculated for 2A5MP and 2A6MP at DFT (B3LYP) level using 6-311++G(d,p) basis set have been collected in Tables 2 and 3 along with the observed FT-IR(solid), FT-Raman and FT-IR gas phase spectral data. The matrix-isolation FT-IR study of 2-amino-5-methylpyridine have been recorded by Nobuyuki Akai et al. [35] and it has also been listed in Table 2 for comparison. On the basis of our calculations, and experimental infrared (solid and gas phase) and Raman spectra, we made a reliable one-to-one correspondence between our fundamentals and any of our frequencies calculated by the DFT (B3LYP) method. The assignments are based on the vibrational animations of the fundamentals using the Gauss-View package program [36] in the B3LYP/6-311++G(d,p) calculations along with available related molecules.

Comparison of the frequencies calculated at B3LYP level with experimental values (Tables 2 and 3) reveals the overestimation
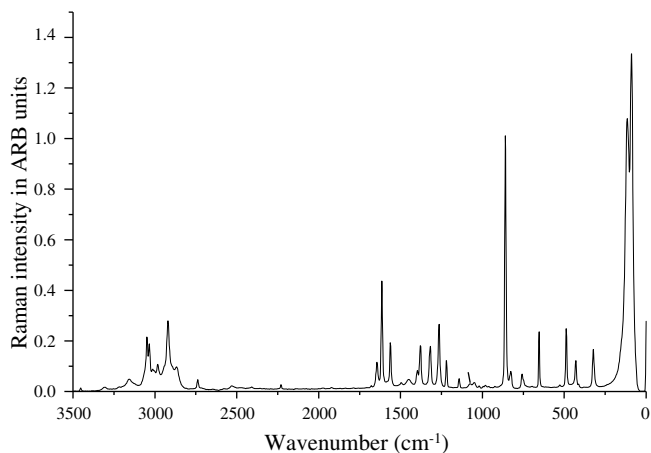
Table 1
Optimized geometrical parameters for 2A5MP and 2A6MP molecules

Parameters of 2A5MP	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)	Parameters of 2A6MP	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)	Experimental[a] 2A5MP	Experimental[b] Pyridine
R(1,2)	1.403	1.406	R(1,2)	1.402	1.408	1.400	1.395
R(1,6)	1.312	1.338	R(1,6)	1.315	1.336	1.338	1.340
R(1,10)	1.382	1.387	R(1,14)	1.378	1.384	1.364	
R(2,3)	1.370	1.386	R(2,3)	1.371	1.383	1.400	1.394
R(2,8)	1.075	1.084	R(2,8)	1.074	1.084	0.98	1.081
R(3,4)	1.398	1.400	R(3,4)	1.392	1.397	1.393	1.394
R(3,7)	1.078	1.086	R(3,7)	1.076	1.085	0.980	1.081
R(4,5)	1.377	1.395	R(4,5)	1.381	1.395	1.375	1.395
R(4,13)	1.509	1.509	R(5,10)	1.505	1.507	1.506	
R(5,6)	1.328	1.335	R(5,6)	1.330	1.342	1.347	1.340
R(5,9)	1.078	1.088	R(4,9)	1.073	1.083	0.960	
R(10,11)	0.996	1.010	R(10,11)	1.085	1.094	0.930	
R(10,12)	0.995	1.008	R(10,12)	1.084	1.091	0.870	
R(13,14)	1.084	1.095	R(10,13)	1.085	1.093	–	
R(13,15)	1.087	1.095	R(14,15)	0.995	1.009	1.090	
R(13,16)	1.087	1.092	R(14,16)	0.994	1.008	1.070	
A(2,1,6)	122.079	121.983	A(2,1,6)	122.707	122.599	115.9	123.6
A(2,1,10)	120.739	121.560	A(2,1,14)	120.645	121.139	–	
A(6,1,10)	117.148	116.415	A(6,1,14)	116.619	116.224	121.9	
A(1,2,3)	118.193	118.466	A(1,2,3)	117.555	117.882	125.9	118.5
A(1,2,8)	120.500	120.564	A(1,2,8)	120.680	120.680	118.0	120.2
A(3,2,8)	121.305	120.968	A(3,2,8)	121.762	121.436	117.0	
A(2,3,4)	120.563	120.535	A(2,3,4)	119.984	119.781	117.4	
A(2,3,7)	119.495	119.569	A(2,3,7)	119.909	119.957	–	
A(4,3,7)	119.942	119.896	A(4,3,7)	120.107	120.262	–	
A(3,4,5)	115.664	115.878	A(3,4,5)	117.945	118.404	121.6	118.1
A(3,4,13)	116.6	121.963	A(3,4,9)	121.186	121.048	116.6	
A(5,4,13)	121.8	122.373	A(5,4,9)	120.869	120.549	121.8	
A(4,5,6)	124.937	124.920	A(4,5,6)	122.439	122.239	119.0	123..3
A(4,5,9)	119.896	119.798	A(4,5,10)	121.779	121.755	118.0	120.8
A(6,5,9)	115.166	115.281	A(6,5,10)	115.782	116.005	123.0	
A(1,6,5)	118.563	118.215	A(1,6,5)	119.368	119.093	120.7	117.3
A(1,10,11)	113.686	114.157	A(5,10,11)	109.861	110.191	111.0	
A(1,10,12)	116.321	117.313	A(5,10,12)	111.608	111.666	106.0	
A(11,10,12)	113.778	114.651	A(5,10,13)	109.884	110.244	–	
A(4,13,14)	110.872	111.621	A(11,10,12)	108.899	108.744	–	
A(4,13,15)	111.364	111.606	A(11,10,13)	107.571	107.107	118.0	
A(4,13,16)	111.404	111.010	A(12,10,13)	108.921	108.761	121.0	
A(14,13,15)	107.674	107.270	A(1,14,15)	114.200	114.541	–	
A(14,13,16)	107.680	107.568	A(1,14,16)	116.789	117.693	–	
A(15,13,16)	107.668	107.550	A(15,14,16)	114.418	115.151	–	

[a] The X-ray data from Ref. [30], In this reference, for the bond distances and angles were given with the range of estimated standard deviations (σ) as follows: σ_{X-X}: 0.002 Å; σ_{X-H}: 0.02–0.04 Å; $\sigma_{\angle X-X-X}$: 0.010; $\sigma_{\angle X-X-H}$: 1–2°; $\sigma_{\angle X-H-X}$: 3°.
[b] The X-ray data from Ref. [33,34].

of the calculated vibrational modes due to neglect of anharmonicity in real system. Inclusion of electron correlation in density functional theory to a certain extent makes the frequency values smaller in comparison with the HF frequency data. In the 2A5MP and 2A6MP, the B3LYP method led to vibrational frequencies which are much closer to experimental data. Furthermore, the B3LYP method calculations approximate the observed fundamental frequencies much better than the HF method. The small difference between experimental and calculated vibrational modes is observed. This discrepancy can come from the formation of intermolecular hydrogen bonding. Also, we note that the experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

Since 2A5MP and 2A6MP practically have the C_s symmetry. The 2A5MP and 2A6MP each has 16 atoms and 42 normal modes of fundamental vibrations which span the irreducible representations of 29A′ + 13A″. All the fundamental modes are both active in IR and Raman. Any way not withstanding the level of calculations, it is customary to scale down the calculated harmonic frequency in order to improve the agreement with experiment. In our study we have followed scaling factor of 0.9668 for B3LYP [37]. To assess the reliability of the calculated IR intensities we simulated an IR spectrum of 2A5MP and 2A6MP from B3LYP/6-311++G(d,p) IR intensities and scaled B3LYP/6-311++G(d,p) frequencies by summing Lorentzian profiles. The simulated spectrum is compared with solid and gas phase FT-IR spectra are shown in Figs. 1 and 2.

4.3. C-H vibrations

The hetero aromatic structure shows the presence of C—H stretching vibrations in the region 3100–3000 cm⁻¹ which is the characteristic region [38]. The 2A5MP and 2A6MP are both disubstituted aromatic systems. The 2A6MP has two adjacent and one isolated C—H moieties. The expected three C—H stretching vibrations correspond to mode Nos. 3, 4 and 5. The scaled vibration, modes Nos. of 3, 4 and 5(Table 3) corresponds to stretching modes of C2—H, C3—H and C5—H units. The calculated frequencies of the C—H stretching vibrations in both 2A5MP and 2A6MP at 3049, 3029 and 3004 cm⁻¹ and 3055, 3045 and 3041 cm⁻¹ show very good agreement with experimental data.

Substitution sensitive C—H in-plane-bending vibrations lie in the region 1000–1300 cm⁻¹ [39]. In 2A5MP three modes are associated mainly with the C—H in-plane-bending vibrations: mode Nos. 19–22. These modes are observed at the following wavenumbers 1220, 1142 and 1071 cm⁻¹ in FT-IR and 1132 cm⁻¹ in FT-IR gas phase. Similar observations are also found in the case of
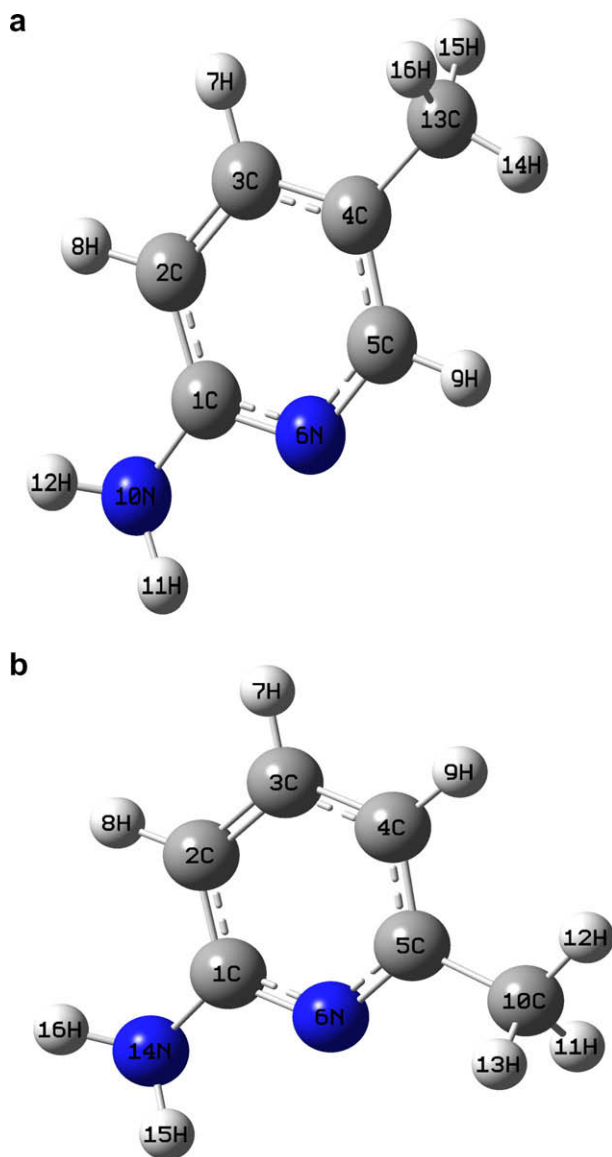
a

b

Fig. 5. (a) 2-Amino-5-methylpyridine and (b) 2-amino-6-methylpyridine structure and atomic numbering for studied molecules.

2A6MP. The C—H out-of-plane bending vibrations contribute mainly to the mode Nos. 28–30. The experimental observations for the C—H out-of-plane bending falls in the experimental values of 933–715 cm^{-1} for both the molecules.

4.4. NH$_2$ vibrations

The NH$_2$ group gives rise to the six internal modes of vibrations such as; the symmetric stretching (v_s), the anti-symmetric stretching (v_{as}), the symmetric deformation or the scissoring (β), the rocking (ρ), the wagging (ω) and torsional mode (τ). The NH$_2$ group has two (N—H) stretching vibrations, one being asymmetric and other symmetric. The frequency of asymmetric vibration is higher than that of symmetric one. If the two NH bonds of the NH$_2$ group are symmetric, these modes satisfy an empirical relation as suggested by Bellamy and Williams [40] as

$$v_{sy} = 345.5 + 0.876 v_{as}$$

where v_s and v_{as} are in wave number

In our title molecule 2A5MP the scaled —NH$_2$ symmetric and asymmetric stretching modes are in the range 3432–3539 cm^{-1} (mode Nos. 1 and 2) is in agreement with experimental value of 3414–3537 cm^{-1}. Similar observations are also found in the case of 2A6MP. The above conclusion is in agreement with literature data [41]. The computed anharmonic frequency for 2A5MP and 2A6MP also shows very good agreement with computed harmonic frequency as well as recorded spectral data.

In addition, NH$_2$ group has scissoring δ(NH$_2$), rocking ρ(NH$_2$), wagging ω(NH$_2$) and torsion τ(NH$_2$) modes. The internal deformation vibrations known as NH$_2$ scissoring frequency is found at 1625 cm^{-1} is well within the range (1590–1650 cm^{-1}) reported for aniline by Thompson [42] and this observation is in conformity with the experimental value of 1608 and 1613 cm^{-1} in FT-IR solid phase and FT-Raman spectra, respectively, for 2A5MP. The scissoring mode predicted at 1589 cm^{-1} by B3LYP/6-311++G(d,p) method shows good agreement with experimental data. The computed anharmonic NH$_2$ deformation frequency for 2A5MP at 1614 cm^{-1} shows excellent agreement with experimental observation. The NH$_2$ wagging mode has been computed to be at 467 cm^{-1} (mode No. 35) and 485 cm^{-1} (mode No. 35) in both 2A5MP and 2A6MP molecules by B3LYP/6-311 G++(d,p) method have been assigned to NH$_2$ wagging mode. However, the recorded spectral data do not support the vibration.

For 2A6MP the rocking mode predicted at 1077–1057 cm^{-1} in B3LYP method shows good agreement with recorded values at 1068 and 1084 cm^{-1} in FT-IR solid phase and FT-Raman spectra, respectively. In case of 2A5MP the band observed at 1071 and 1075 cm^{-1} in FT-IR solid phase and FT-Raman spectra, respectively, are assigned to rocking mode of NH$_2$. The theoretically computed value by B3LYP/6-311++G(d,p) method at 1074–1053 cm^{-1} (mode Nos. 21 and 22) shows better correlation with experimental data. The anharmonic frequency also falls in the same range.

4.5. Methyl group vibration

The title molecules 2A5MP and 2A6MP possess a CH$_3$ group in the fifth and sixth position, respectively. For the assignments of CH$_3$ group frequencies, nine fundamentals can be associated to each CH$_3$ group, namely the symmetric stretching in CH$_3$ (CH$_3$ sym. stretch); asymmetric stretching (i.e. in-plane-hydrogen stretching mode); the symmetric (CH$_3$ sym. deform) and asymmetric (CH$_3$ asym. deform) deformation modes; the in-plane-rocking (CH$_3$ ipr), out-of-plane rocking (CH$_3$ opr) and twisting (t CH$_3$) bending modes. The CH stretching in CH$_3$ occurs at lower frequencies than those of the aromatic ring (3000–3100 cm^{-1}).

The asymmetric C—H stretching mode of CH$_3$ group is expected around 2980 cm^{-1} and the symmetric [43–46] one is expected in the region 2870 cm^{-1}. For 2-methylpyridine the CH$_3$ stretching around 3000–2900 cm^{-1}, the in-plane deformations around 1450–1370 cm^{-1} and the rocking around 1040–990 cm^{-1} [28]. The calculated and observed wavenumbers of asymmetric and symmetric stretching vibrations of CH$_3$ group for both molecules are listed in Tables 2 and 3.

For the methyl substituted benzene derivatives the asymmetric and symmetric deformation vibrations of methyl groups normally appear in the region 1465–1440 cm^{-1} and 1390–1370 cm^{-1}, respectively [28,47,48]. The wavenumbers of the modes involving the CH$_3$ deformation vibrations agree with commonly accepted regions of these vibrations [28,47,48]. The work carried by Long et al. [25] on 4-methyl pyridine, the frequency of 1041 and 974 cm^{-1} in FT-Raman are assigned to the rocking modes of CH$_3$. The rocking vibrations of the CH$_3$ group in 2A5MP and 2A6MP appear as independent vibrations. These modes usually appear [39] in the region 1070–1010 cm^{-1}. The weak band in FT-IR at 1020 cm^{-1} and a very weak band at 1019 cm^{-1} in FT-Raman are attributed to the CH$_3$

Table 2
Experimental and calculated fundamental harmonic, anharmonic frequencies and IR intensities for 2A5MP

Mode of vibration	Experimental (in this study)			Experimental[a]		B3LYP 6-311++G(d,p)				Vibrational assignments[b]
	FT-IR	FT-IR gas	FT-Raman	FT-IR	Int	Unscaled	IR$_{int}$	Scaled	Anharmonic	
1	3537w	3555w		3525	16.7	3686	28	3539	3535	$\upsilon_{asy}NH_2$
2	3453s	3414w	3454W	3423	32.1	3575	36	3432	3436	$\upsilon_{asy}NH_2$
3			3049ms			3176	15	3049	3041	$\upsilon_{sy}CH$
4			3035ms	3023	5.0	3155	13	3029	3012	$\upsilon_{sy}CH$
5	3010w	3015ms	3013ms			3129	32	3004	2972	$\upsilon_{sy}CH$
6			2982w	2990	2.4	3088	18	2965	2922	$\upsilon_{asy}CH_3$
7	2918w	2935ms	2920ms	2908	0.7	3075	19	2952	2928	$\upsilon_{asy}CH_3$
8		2883w	2868w	2877	1.4	3023	45	2902	2937	$\upsilon_{sy}CH_3$
		2697vw								Overtone/combination
		1920vw								Overtone/combination
		1880vw								Overtone/combination
9	1608ms		1613s	1621	83.8	1655	240	1589	1614	$\delta NH2 + \upsilon C=C$
10	1563ms		1562ms	1591	47.5	1633	30	1568	1593	$\upsilon C=C + \delta NH2$
11				1577	12.6	1608	31	1544	1570	$\upsilon C-C$
12	1500vs	1517vs	1495w	1500	100.	1523	149	1462	1487	$\delta_{asy}CH_3$
13		1447w		1462	7.7	1499	14	1439	1464	$\upsilon C=C$
14						1489	7	1429	1456	$\delta_{sy}CH_3 + \upsilon C=C$
15	1391ms		1396w	1393	57.0	1425	74	1368	1400	$\delta_{sy}CH_3$
16			1377ms			1417	0	1361	1387	$\delta_{sy}CH_3$
17	1316ms	1297ms	1316ms	1308	19.7	1351	1	1297	1324	$\upsilon C-NH_2 + \upsilon CC$
18	1264ms	1244ms	1264s	1265	4.3	1330	47	1277	1309	$\upsilon C=N$
19	1220w		1219ms			1303	16	1251	1266	βCH
20	1142ms	1132ms	1142w	1142	4.7	1242	0	1192	1221	$C-CH_3$ stretch
21	1071w		1075w	1055	3.3	1163	12	1116	1145	$\beta CH + NH_2$ rocking
22			1049w	1011	0.3	1083	10	1040	1044	$\beta CH + NH_2$ rocking
23	1020w		1019vw	1019	3.2	1063	3	1020	1044	CH_3 rocking
24		996w	995vw	983	0.0	1039	6	998	1016	Ring breathing
25	960w			975	0.0	998	0	958	985	Trigonal bending
26						973	0	934	972	γCH
27	923w	934w		918	1.4	937	2	900	928	βCCC
28	826ms		825vs	815	16.2	873	2	838	864	γCH
29		784ms				826	41	793	818	γCH
30	751w		757w	763	1.0	763	2	732	750	γCH
31				723	0.6	757	1	727	750	βCCC
32	652ms	657w	653ms			662	2	635	655	CH_2 + twisting in CH_3
33	518s					561	127	539	442	βCNC
34	489ms		488			501	143	481	446	βCCC
35						487	51	467	464	NH_2 wagging
36			433w			424	1	407	418	$\beta C-NH_2$
37			429ms			422	3	405	421	$\gamma CCC + \gamma CNC$
38						360	43	345	366	$\gamma C-NH_2$
39			321ms			317	4	304	315	$\beta C-CH_3 + \beta C-NH_2$
40						298	3	286	295	$\gamma C-CH_3 + \gamma C-NH_2$
41			115vs			139	5	133	130	γCCC
42			88vs			28	0	27	431	CH_3 torsion

vs, very strong; s, strong; ms, medium strong; w, weak; vw, very weak.
[a] Taken from Ref. [35].
[b] υ, stretching; υ_s, sym. stretching; υ_{as}, asym. stretching; β, in-plane-bending; γ, out-of-plane; ω, wagging; ρ, rocking; t, twisting; τ, torsion; δ, scissoring.

rocking mode. The theoretically calculated value by B3LYP/6-311 G++(d,p) method at 1020 cm^{-1} shows excellent agreement with experimental observation whereas the anharmonic frequency calculated by same method deviate positively by ~20 cm^{-1} (mode No. 23). The same vibration in 2A6MP as a weak band in FT-IR at 1032 cm^{-1}. The calculated value at 1015 cm^{-1} also coincides with experimental observation. The anharmonic vibrational frequencies computed by B3LYP/6-311 G++(d,p) method at 1037 cm^{-1} also shows excellent agreement with experimental data. As CH$_3$ torsional mode is expected below 400 cm^{-1}, the computed bands at 27 cm^{-1} in 2A5MP and 75 cm^{-1} in 2A6MP are assigned to this mode, for the same vibration no spectral measurements were possible in this region due to instrumental limits.

4.6. C—CH$_3$ vibrations

The C—CH$_3$ stretching vibration is assigned to a medium strong infrared band at 1142 cm^{-1} and a weak FT-Raman band at 1142 cm^{-1} in 2A5MP, a weak FT-IR band at 1105 cm^{-1} in 2A6MP.

In methyl substituted benzenes, the C—CH$_3$ in-plane-bending vibrations give rise to absorptions in the range 390–260 cm^{-1}. Thus, the vibration is assigned to a computed band at 304 cm^{-1} in 2A5MP. In the Raman spectrum of 2A5MP there is a medium strong band at 324 cm^{-1}; a similar band is predicted at 294 cm^{-1} by B3LYP method in 2A6MP. Both these bands are assigned to C—CH$_3$ in-plane-bending mode. A band predicted at 286 cm^{-1} in 2A5MP and a band at 209 cm^{-1} in 2A6MP by B3LYP method are assigned to C—CH$_3$ out-of-plane bending mode.

4.7. C—N, C=N vibrations

The identification of C—N vibration is very difficult task since mixing of several vibrations are possible in this region. Silverstein [39] assigned C—N stretching absorption in the region 1382–1266 cm^{-1} for aromatic amines. In 3,5-dibromopyridine the band observed at 1410 cm^{-1} in IR and 1412 cm^{-1} in Raman is assigned to C—N stretching mode [49]. In benzotrizole, the C—N stretching bands are found to be observed at 1387 and 1370 cm^{-1}. In benz-

Table 3
Experimental and calculated fundamental harmonic, anharmonic frequencies and IR intensities for 2A6MP

Mode of vibration	Experimental			B3LYP 6-311++G(d,p)				Vibrational assignments[a]
	FT-IR	FT-IR (gas)	FT-Raman	Unscaled	IR$_{int}$	Scaled	Anharmonic	
1		3555w		3693	29	3545	3522	$\upsilon_{asy}NH_2$
2	3464s			3579	36	3436	3422	$\upsilon_{sy}NH_2$
3	3073w		3067ms	3193	10	3065	3055	υCH
4				3180	19	3053	3045	υCH
5				3164	6	3037	3041	υCH
6				3112	18	2987	2969	$\upsilon_{as}CH_3$
7	2964w			3087	13	2964	2934	$\upsilon_{as}CH_3$
8	2916w	2935s	2911s	3032	21	2911	2935	$\upsilon_{sy}CH_3$
		2850vw						Overtone/combination
		2745vw						Overtone/combination
		2303vw						Overtone/combination
		2189vw						Overtone/combination
		2098vw						Overtone/combination
		1956vw						Overtone/combination
9	1594s		1603w	1646	303	1580	1596	$\delta NH_2 + \upsilon C=C$
10	1565ms		1568ms	1625	34	1560	1580	$\upsilon C=C + \delta NH_2$
11				1619	86	1554	1580	$\upsilon C-C$
12	1455vs	1447m	1432w	1501	76	1441	1468	$\delta_{asy}CH_3$
13				1488	111	1429	1453	$\upsilon C=C$
14				1477	7	1418	1435	$\delta_{sy}CH_3$
15				1466	7	1408	1430	$\upsilon C=C + \delta_{sy}CH_3$
16	1346ms		1347ms	1410	7	1354	1378	$\delta syCH_3$
17	1280ms	1292s	1283ms	1348	56	1294	1324	$\upsilon C-NH_2 + \upsilon CC$
18	1233w			1315	13	1263	1289	$\upsilon C=N$
19	1211vw			1262	13	1212	1236	βCH
20	1105vw			1184	8	1137	1171	$C-CH_3$ stretch
21	1068ms		1084w	1122	6	1077	1096	$\beta CH + NH_2$ rocking
22				1101	9	1057	1076	$\beta CH + NH_2$ rocking
23	1032w			1057	4	1015	1037	CH_3 rocking
24	984ms	996vw	985ms	1025	2	984	1011	Ring breathing
25				998	5	958	965	Trigonal bending
26	933w	930vw	928vw	988	0	949	982	γCH
27				945	3	907	928	βCCC
28	856vw	850vw	857vw	862	1	827	856	γCH
29	783vs	780s	779vw	794	48	763	776	γCH
30	721w		729s	744	13	715	734	γCH
31				742	2	712	728	βCCC
32	597w		608w	622	11	597	594	$CH_2 +$ twisting in CH_3
33	553w		566w	575	7	552	563	βCNC
34			544ms	548	4	526	541	βCCC
35				505	237	485	326	NH_2 wagging
36				449	4	431	439	$\beta C-NH_2$
37			445w	445	22	427	426	$\gamma CCC + \gamma CNC$
38			317m	377	58	362	332	$\gamma C-NH_2$
39			317ms	298	3	286	302	$\beta C-CH_3 + \beta C-NH_2$
40			232w	218	16	209	213	$\gamma C-CH_3 + \gamma C-NH_2$
41			196ms	190	0	183	186	γCCC
42				78	0	75	151	CH_3 torsion

vs, very strong; s, strong; ms, medium strong; w, weak; vw, very weak.

[a] υ, stretching; υ_s, symmetric stretching; υ_{as}, asymmetric stretching; β, in-plane-bending; γ, out-of-plane; ω, wagging; ρ, rocking; t, twisting; τ, torsion; δ, scissoring.

amide the band observed at 1368 cm^{-1} is assigned to C—N stretching [50]. In our present work, the band observed at 1264 cm^{-1} in both FT-IR and FT-Raman and the 1244 cm^{-1} in FT-IR (gas phase) are assigned to be C=N stretching vibration corresponding to 2A5MP. The theoretically computed B3LYP/6-311++G(d,p) value (mode No. 18) show positive deviation about ~13 cm^{-1}. Further for 2A6MP the band observed at 1233 cm^{-1} in FT-IR is assigned to C=N stretching vibration.

Overtone and combination tone vibrations are observed between 2800 and 1700 cm^{-1}. It has been observed that benzene and pyridine derivatives possess overtone or combination tone vibrations that give rise to infrared absorption between 2000 and 1700 cm^{-1} [51,52]. In the infrared spectrum of this compound, most of the bands in the region 2000 and 2900 cm^{-1} may also be due to the non-fundamental bands of the pyridine ring. An attempt of the assignment of these non-fundamental bands lead us to pro-

pose them as combination and overtone vibrations as is given in the Tables 2 and 3.

5. Conclusions

Attempts have been made in the present work for the molecular parameters and frequency assignments for the compounds 2A5MP and 2A6MP from the FT-IR (solid and gas phase) and FT-Raman spectra. The equilibrium geometries, harmonic and anharmonic frequencies of 2A5MP and 2A6MP were determined and analyzed at DFT level of theory utilizing 6-311++G(d,p) higher basis sets. The difference between the observed and scaled wavenumber values of most of the fundamentals is very small. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations have been done on single

molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. Therefore, the assignments made at DFT level of theory with only reasonable deviations from the experimental values seem to be correct. The theoretically constructed FT-IR spectrum exactly coincides with experimentally observed FT-IR gas phase spectrum.

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