

Theoretical studies on the molecular structure and vibrational spectra of some dimethyl substituted pyridine derivatives

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Abstract The molecular geometries, normal mode frequencies, intensities and corresponding infrared assignments of monomeric and dimeric 2,3-dimethylpyridine, 2,4-dimethylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine and monomeric 2,6-dimethylpyridine in the ground state were investigated at the density functional theory (DFT)-B3LYP level using the 6-311+G(d, p) basis set. The vibrational frequencies and geometric parameters of C–H stretching and bending in the fundamental region were calculated and compared to the Fourier transform infrared (FT-IR) data obtained. In the studied monomeric and dimeric dimethyl substituted pyridine derivatives, the C–H stretching and bending frequency shifts that occur between the dimer and the monomer may be diagnostic of the magnitude of dimerization energy. As supported by data in the literature, the most stable dimeric form was obtained for the 3,4-dimethylpyridine molecule.

Keywords 2,3-Dimethylpyridine ·
2,4-Dimethylpyridine · 2,6-Dimethylpyridine ·
3,4-Dimethylpyridine · 3,5-Dimethylpyridine · Monomer ·
Dimer · Infrared spectra · DFT

Introduction

Recently, several molecular vibrational analyses of structurally related organic compounds have been reported. Numerous studies have been found in the literature dealing with the vibrational and crystallographic analyses of pyridine [1–6] and methyl derivatives [7–20]. The molecules 2,3-, 2,4-, 2,6-, 3,4-, 3,5-dimethylpyridine are defined by the presence of a six-membered heterocyclic ring consisting of five carbon atoms and one nitrogen atom. The arrangement of atoms is similar to that of benzene except that one of the carbon-hydrogen rings sets has been replaced by a nitrogen atom. The vibrational spectra of pyridine dimethyl derivatives have been investigated in several studies [8, 19]. Additionally, Draeger performed a normal coordinate analysis [12] using experimental data from the early 1960s [8]. Although this study resulted in good agreement between the experimental and calculated frequencies, new experimental data and developments in theoretical calculation methods justify a reinvestigation of the vibrational spectra of the structure of monomeric and dimeric pyridine dimethyl derivatives. To the best of our knowledge, no computational vibrational spectroscopic and dimerization studies on free 3,4-dimethylpyridine have yet been published. To understand the effect of dimerization behavior on the vibrational spectroscopy of dimethyl pyridines, we chose 2,3-, 2,4-, 3,4- and 3,5-dimethylpyridine, all of which can take part in the same type of dimerization. Therefore, the present study aims to give a complete description of the molecular geometries and vibrations of these dimethylpyridine derivatives. The results of both spectroscopic and theoretical studies are reported herein. The vibrational wavenumbers of the dimeric dimethylpyridine derivatives have also been calculated.

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Density functional theory (DFT) is now accepted as a popular post-HF approach for the ab-initio computation of molecular structure, vibrational frequencies and energies of molecules. DFT calculations have provided excellent agreement with the experimental vibrational frequencies of organic compounds, when the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, basis set deficiencies and anharmonicity [21–27]. Moreover, the GIAO/DFT (gauge including atomic orbitals/ density functional theory) approach is being widely used in the calculation of chemical shifts for a variety of heterocyclic compounds [28–33]. The DFT method has also proved more successful in calculations of vibrational frequencies and chemical shifts than other methods [34–37]. However, no systematic work on the structure of alkyl substituted pyridines exists as yet, at least on a theoretical level. We believe that alkyl substituted pyridines deserve more detailed and systematic theoretical studies using updated computer programs and knowledge of structure–activity relationships [2–7, 9, 13, 14, 38, 40–46]. Here, we report the results of such studies on some dimethyl substituted derivatives.

Experimental and computational details

Fourier transform infrared (FT-IR) spectra were recorded using commercial 2,6-dimethylpyridine (Sigma 99%; St. Louis, MO) and 3,4-dimethylpyridine (Merck, 98%; Darmstadt, Germany). The measurements were carried out at room

temperature on a Perkin Elmer 100 FT-IR spectrometer using 16 scans, a 0.05 mm CsI liquid cell and DTGS detector in the mid-IR range (4,000–235 cm^{-1}). The resolution was 2 cm^{-1} .

In this study, structural parameters, IR wavenumbers, IR intensities and dimerization energies were determined at the DFT-B3LYP level using the 6-311+G (d,p) basis set. Initial geometry was optimized by DFT-B3LYP with the 6-311+G (d,p) basis set in the ground state. Restricted molecular geometries of title compounds were performed by using the Gaussview molecular visualization program [47] and GAUSSIAN03 [48]. The molecular wave function was expanded on the basis of Gaussian functions that represent atomic orbitals. The position of the atomic center was systematically varied until the electronic energy was minimized. In general, electron correlation effects were fairly uniform though a conformational or torsional potential energy surface.

Results and discussion

The molecular structures and atomic numbering used in the present study are shown in Figs. 1 and 2. The first task for the computational work was to determine the optimized geometry of the studied molecules. Dimerization of 3,4-dimethylpyridine occurred between nitrogen atom and H1 or H5 atoms [49]. Thus, except 2,6-dimethylpyridine, all dimeric forms of the studied molecules were calculated as the 3,4-dimethylpyridine dimeric form. The calculated relevant geometric parameters for monomeric 2,3-dimethyl-

Fig. 1 Molecular models and numbering scheme of monomeric forms of the studied molecules

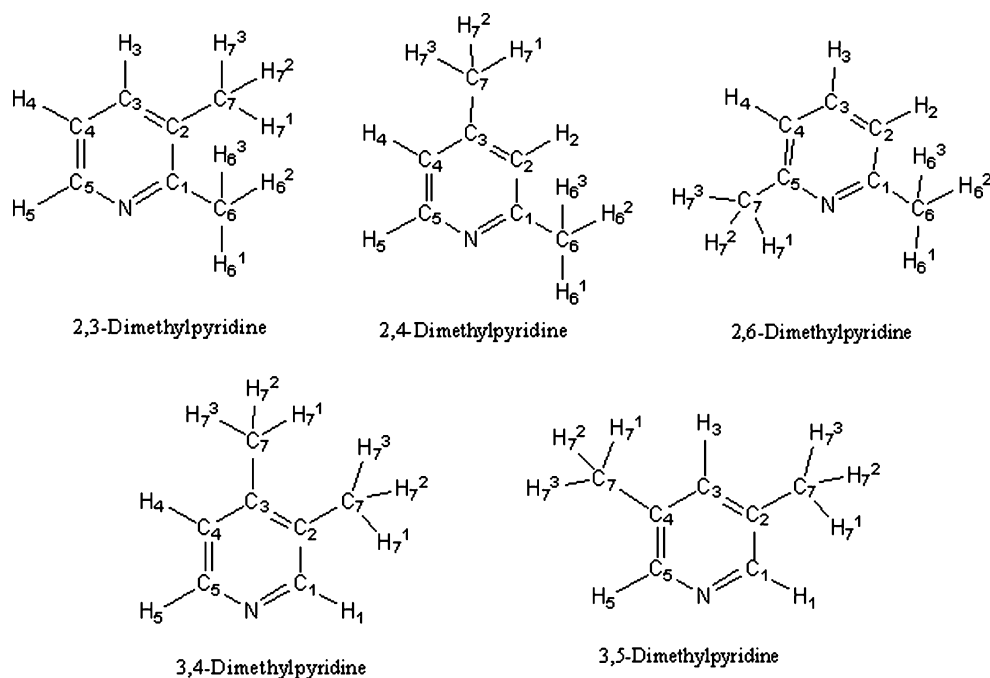
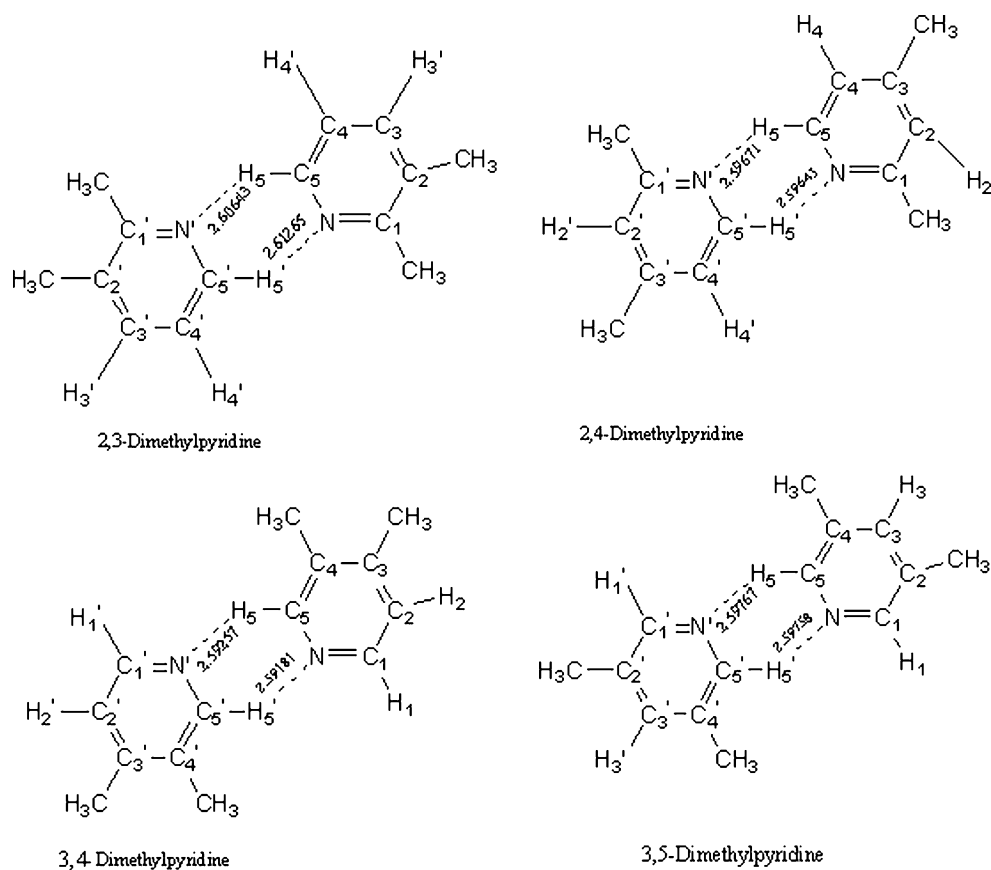


Fig. 2 Molecular models and numbering scheme of dimeric forms of the studied molecules



pyridine, 2,4-dimethylpyridine, 2,6-dimethylpyridine, 3,4-dimethylpyridine and 3,5-dimethylpyridine are summarized in Table 1. The same type dimeric 2,3-dimethylpyridine, 2,4-dimethylpyridine, 3,4-dimethylpyridine and 3,5-dimethylpyridine geometric parameters are summarized in Table 2, using definitions from single crystal studies [49–53].

Optimization of the geometrical parameters, hence providing a structural analysis for the studied molecules, was carried out using DFT with the B3LYP/6-311+G(d,p) basis set. The theoretical C–N bond lengths for monomeric dimethyl pyridines were calculated as 1.337 Å, 1.335 Å, 1.340 Å, 1.334 Å, and 1.334 Å for 2,3-dimethylpyridine, 2,4-dimethylpyridine, 2,6-dimethylpyridine, 3,4-dimethylpyridine and 3,5-dimethylpyridine, respectively. The theoretical C–N bond lengths for dimeric dimethyl pyridines were calculated as 1.340–1.340 Å, 1.338–1.338 Å, 1.339–1.339 Å, and 1.335–1.337 Å for 2,3-dimethylpyridine, 2,4-dimethylpyridine, 3,4-dimethylpyridine and 3,5-dimethylpyridine, respectively.

The C–CH₃ bond lengths in the studied monomeric and dimeric molecules were found to be slightly different. Monomeric forms: 1.507 Å (theoretical)–1.500 Å (experimental), 1.507 Å (theoretical)–1.500 Å (experimental) for 2,3-dimethylpyridine; 1.507 Å (theoretical)–1.496 Å (experimental), 1.507 Å (theoretical)–1.496 Å (experimental) for 2,4-dimethylpyridine; 1.507 Å (theoretical)–1.500 Å

(experimental), 1.507 Å (theoretical)–1.500 Å (experimental) for 2,6-dimethylpyridine; 1.506 Å (theoretical)–1.504 Å (experimental), 1.506 Å (theoretical)–1.504 Å (experimental) for 3,4-dimethylpyridine; 1.508 Å (theoretical)–1.504 Å (experimental), 1.508 Å (theoretical)–1.504 Å (experimental) for 3,5-dimethylpyridine.

Dimeric forms: 1.508 Å–1.508 Å (theoretical), 1.508 Å–1.508 Å (theoretical), 1.500 Å (experimental) for 2,3-dimethylpyridine; 1.507 Å–1.507 Å (theoretical), 1.507 Å–1.507 Å (theoretical), 1.497 Å (experimental) for 2,4-dimethylpyridine; 1.507 Å–1.507 Å (theoretical), 1.504 Å (experimental), 1.507 Å–1.507 Å (theoretical), 1.502–1.498 Å (experimental) for 3,4-dimethylpyridine; 1.508 Å–1.508 Å (theoretical), 1.505 Å (experimental), 1.508 Å–1.508 Å (theoretical), 1.505 Å (experimental) for 3,5-dimethylpyridine. It can be concluded that substituent effects also play an important role in the geometry of dimeric systems. Furthermore, it can be easily seen that, when comparing the observed with the experimental values, the closest hydrogen bond values between the two monomers in dimeric 3,4-dimethylpyridine came from the B3LYP/6-311+G(d,p) calculation. The small discrepancies observed are due to the fact that the optimizations are performed in isolated conditions, whereas structures are affected by the crystal environment under experimental conditions.

Table 1 Optimized and experimental geometries of monomeric 2,3-dimethylpyridine, 2,4-dimethylpyridine, 2,6-dimethylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine in the ground state

Parameter	2,3-Dimethylpyridine		2,4-Dimethylpyridine		2,6-Dimethylpyridine		3,4-Dimethylpyridine		3,5-Dimethylpyridine	
	Theoretical [50]	Experimental [50]	Theoretical [51]	Experimental [51]	Theoretical [52]	Experimental [52]	Theoretical [49]	Experimental [49]	Theoretical [53]	Experimental [53]
Bond lengths (Å)										
N-C1	1.340	1.356	1.342	1.339	1.340	1.339	1.336	1.333	1.334	1.336
C1-C2	1.411	1.397	1.398	1.387	1.399	1.397	1.398	1.382	1.398	1.389
C2-C3	1.393	1.358	1.396	1.379	1.390	1.381	1.407	1.389	1.395	1.389
C3-C4	1.392	1.357	1.396	1.388	1.390	1.381	1.396	1.398	1.395	1.390
C4-C5	1.389	1.365	1.392	1.370	1.399	1.397	1.392	1.382	1.398	1.390
C5-N	1.337	1.356	1.335	1.336	1.340	1.339	1.334	1.339	1.334	1.336
C1-C6	1.507	1.496	1.507	1.496	1.507	1.500	-	-	-	-
C2-C6	-	-	-	-	-	-	1.506	1.504	1.508	1.505
C2-C7	1.508	1.496	-	-	-	-	1.506	1.504	-	-
C3-C7	-	-	1.507	1.496	-	-	1.506	1.504	-	-
C4-C7	-	-	-	-	-	-	-	-	1.508	1.505
C5-C7	-	-	-	-	1.507	1.500	-	-	-	-
C6-H61	1.095	0.980	1.093	0.980	1.091	0.980	1.095	0.980	1.094	0.980
C6-H62	1.089	0.980	1.093	0.980	1.093	0.980	1.095	0.980	1.092	0.980
C6-H63	1.095	0.980	1.091	0.980	1.093	0.980	1.092	0.980	1.094	0.980
C7-H71	1.095	0.980	1.092	0.980	1.093	0.980	1.095	0.980	1.094	0.980
C7-H72	1.095	0.980	1.095	0.980	1.093	0.980	1.095	0.980	1.094	0.980
C7-H73	1.091	0.980	1.092	0.980	1.092	0.980	1.091	0.980	1.092	0.980
C1-H1	-	-	-	-	-	-	1.088	0.950	1.088	0.980
C2-H2	-	-	1.085	0.950	1.084	0.900	-	0.950	-	0.970
C3-H3	1.086	0.950	-	-	1.085	0.900	-	-	1.087	1.000
C4-H4	1.084	0.950	1.084	0.950	1.084	0.900	1.085	0.950	-	0.970
C5-H5	1.086	0.950	1.0870	0.950	-	-	1.087	0.950	1.088	0.970
Bond angles (°)										
N-C1-C2	122.484	120.00	121.994	122.180	121.946	121.8	125.031	122.940	124.041	124.330
C1-C2-C3	120.083	120.00	120.362	-	118.783	119.6	117.566	120.210	116.845	117.130
C4-C5-N	123.171	119.60	123.948	124.530	121.946	121.8	123.182	125.250	124.040	-
C7-C2-C3	121.119	120.95	-	-	-	-	-	-	-	-
C7-C2-C1	121.424	120.95	-	-	-	-	-	-	-	-
C2-C3-C7	-	-	121.473	120.940	-	-	-	-	-	-
C4-C3-C7	-	-	121.540	122.130	-	-	-	-	-	-
C6-C2-C3	-	-	-	-	-	-	122.06431	120.81	121.778	122.07
C7-C3-C2	-	-	-	-	-	-	120.36892	121.95	-	-
C2-C3-C6	-	-	-	-	-	-	-	-	121.377	122.070
C7-C5-N	-	-	-	-	116.369	121.300	-	-	-	-
C4-C5-C7	-	-	-	-	121.684	121.300	-	-	-	-
C6-C1-C2	121.144	120.950	121.581	121.520	121.682	-	120.36892	120.95	121.377	120.790

C6-C1-N	116.370	119.040	116.423	116.290	116.371	116.900	116.79976	116.38	117.675	116.680
C5-N-C1	118.843	119.210	117.753	116.700	119.475	119.000				
Dihedral angles (°)										
H3-C3-C2-C6	0.000								0.000	
C6-C1-C2-C7	0.000									
H5-C5-C4-H4	0.000									
H2-C2-C3-C7			1.496							
H4-C4-C3-C7			-1.490				0.030			
C6-C1-C2-H2			-0.105		0.013					
H4-C4-C5-C7					-0.008					
H5-C4-C3-H3					-0.002					
H1-C1-C2-C6							0.000		0.000	
C6-C2-C4-C7							-0.003			
H3-C3-C2-C7									0.000	

Comparisons of methyl group vibrational wavenumbers for monomeric and dimeric dimethyl pyridine molecules are tabulated in Tables 3 and 4, respectively. All the CH₃ vibrational modes are found to be in good agreement with experimental values. The biggest differences found between theoretical and experimental CH₃ stretching mode were 1–9 cm⁻¹ for 2,4-, 2,6-, 3,4-dimethylpyridine due to elongation of the C–C bond and deformation of the dihedral angles (C₆–C₁–C₂–H₂). The largest difference between theoretical and experimental ring stretching vibrations is 5 cm⁻¹ for 2,3-dimethylpyridine, 12 cm⁻¹ for 2,6-dimethylpyridine, 3 cm⁻¹ for 3,4-dimethylpyridine and 4 cm⁻¹ for 3,5-dimethylpyridine because of the decreasing bond lengths values of C₂–C₃ and C₃–C₄, i.e., 0.036 Å for 2,3-dimethylpyridine, 0.09 Å for 2,6-dimethylpyridine, 0.018 Å for 3,4-dimethylpyridine, and 0.006 Å for 3,5-dimethylpyridine. Similar differences were also observed between other theoretical and experimental values. Experimental fundamentals are in better agreement with scaled fundamentals, and good correlations using the B3LYP/6-311+G (d,p) method were found for all studied molecules.

The FT-IR spectra of 2,3-, 2,4- and 3,5-dimethylpyridine were obtained from the literature [12, 19]. Liquid phase FT-IR spectra of 2,6- and 3,4-dimethylpyridine recorded in this study were used as experimental results. Theoretical FT-IR spectra of the monomeric and dimeric dimethyl pyridine molecules are shown in Figs. 3 and 4, respectively. The harmonic-vibrational frequencies calculated with the 6-311+G (d,p) basis set at the B3LYP level of the studied molecules are listed in Tables 3 and 4, together with the experimental frequencies. For the single pyridine ring hydrogen atom of an isolated molecule, three different vibrations are expected, e.g., C–H stretching, in-plane bending, and out-of plane deformation. In the 3,000 cm⁻¹ region, it can be observed that C–H bond stretching of the ring appears at higher frequencies, whilst the CH stretching of the methyl group appears at lower frequencies in the region of 2,900 cm⁻¹. Upon increasing the degree of substitution, a greater number of bands corresponding to the C–H stretching of the methyl groups are expected, having very similar frequencies since they are found within the same range. Aromatic ring peaks are found to shift approximately 20 cm⁻¹ between experimental and theoretical values [17]. Comparison of the theoretical and experimental spectra indicates that the intense vibrations in the experimental spectra are also intense in theoretical spectra. Comparison of the frequencies between experimental and literature values reveals the overestimation of the calculated vibration modes due to neglect of anharmonicity in real systems. The major factor responsible for the small discrepancies between experimental and computed values is related to the fact that the experimental value is an

Table 2 Optimized and experimental geometries of dimeric 2,3-dimethylpyridine, 2,4-dimethylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine in the ground state

Parameter	2,3-Dimethylpyridine		2,4-Dimethylpyridine		3,4-Dimethylpyridine		3,5-Dimethylpyridine		Experimental [52]
	M1	M2	M1	M2	M1	M2	M1	M2	
Bond length (Å)									
N–C1	1.339	1.339	1.342	1.342	1.334	1.335	1.33702	1.335	1.336
C1–C2	1.411	1.411	1.398	1.398	1.392	1.392	1.39942	1.398	1.389
C2–C3	1.394	1.394	1.397	1.397	1.396	1.396	1.39525	1.396	1.389
C3–C4	1.392	1.391	1.398	1.396	1.406	1.406	1.39589	1.395	1.390
C4–C5	1.390	1.390	1.392	1.393	1.398	1.398	1.39790	1.399	1.390
C5–N	1.340	1.339	1.338	1.338	1.339	1.339	1.33497	1.337	1.336
C1–H1	-	-	-	-	1.087	1.087	1.08752	1.087	-
C2–H2	-	-	1.085	1.085	1.085	1.085	-	-	-
C3–H3	1.086	1.086	1.085	1.085	-	-	1.08755	1.086	0.970
C4–H4	1.084	1.084	1.085	1.085	-	-	-	-	-
C5–H5	1.087	1.086	1.087	1.087	1.087	1.087	1.08784	1.088	0.970
C1–C6	1.508	1.508	1.507	1.507	-	-	1.50812	1.508	1.505
C2–C6	-	-	-	-	-	-	-	-	-
C3–C6	1.508	1.508	1.507	1.507	1.507	1.507	-	-	-
C2–C7	-	-	1.507	1.50738	-	-	-	-	-
C3–C7	-	-	1.507	1.507	-	-	-	-	-
C4–C7	-	-	-	-	1.507	1.507	1.50799	1.508	1.505
C5–C7	-	-	-	-	-	-	-	-	-
Bond angles (°)									
N–C1–C2	122.512	122.512	122.020	122.021	123.194	123.194	123.60103	123.601	124.330
C1–C2–C3	117.403	117.408	120.290	120.290	119.825	119.825	117.10998	117.110	117.130
C3–C4–C5	118.248	118.239	119.244	119.244	117.550	117.856	117.10998	116.802	-
C4–C5–N	122.718	122.734	123.486	123.487	124.573	124.573	123.60103	124.040	-
C7–C2–C1	121.415	121.415	120.950	120.950	-	-	-	-	-
C6–C1–N	116.449	116.447	116.478	116.480	116.290	116.290	-	-	-
C7–C4–C3	-	-	121.398	121.402	122.034	122.040	121.81624	121.816	122.070
C6–C1–C2	121.038	121.038	121.500	121.499	121.520	121.520	121.09723	121.097	-
C6–C3–C4	-	-	-	-	121.467	121.467	-	-	-
H5–C5–N	116.021	116.041	115.957	115.958	-	-	116.17465	116.174	-
H2–C2–C1	-	-	-	-	119.830	119.830	-	-	-
H1–C1–N	-	-	-	-	116.468	116.468	116.12163	116.122	-
H1–C1–C2	-	-	-	-	120.338	120.338	120.27734	120.276	-
C5–N–C1	119.042	119.033	117.966	117.966	117.022	117.022	117.88915	117.889	116.680
Dihedral angles (°)									
C7–C2–C1–C6	0.062	0.028	-	-	-	-	-	-	-
C7–C3–C4–H4	-0.034	-0.023	-	-	-	-	-	-	-
C7–C4–C3–C6	-	-	-	-	0.000	0.000	-	-	-
C6–C1–C2–H2	-	-	-0.135	0.134	-	-	-	-	-
C6–C3–C2–H2	-	-	1.520	-1.516	0.000	0.000	-	-	-
C7–C4–C5–H5	-	-	-1.505	1.501	0.003	0.006	0.02278	0.012	-
H2–C2–C3–C7	-	-	-	-	0.000	0.000	-	-	-
N–C1–C2–C3	0.013	-0.0170	-0.112	0.112	0.000	0.000	0.00747	0.006	-
Bond length (Å)									
H5'–N	2.606	2.597	2.597	2.597	2.592	2.592	2.598	2.598	-
N'–H5	2.613	2.596	2.596	2.596	2.593	2.593	2.598	2.598	-
Bond angles (°)									
C5–H5–N'	150.821	151.178	151.178	151.178	151.970	151.970	151.680	151.680	-
N'–C5'–H5'	116.041	115.958	115.958	115.958	115.816	115.816	116.123	116.123	-
C5'–H5'–N'	151.120	151.165	151.165	151.165	152.002	152.002	151.685	151.685	-
N–C5–H5	116.021	115.958	115.958	115.958	115.816	115.816	116.122	116.122	-

Table 3 Comparison of experimental and theoretical vibrational wavenumbers (cm⁻¹) of monomeric 2,3-dimethylpyridine, 2,4-dimethylpyridine, 2,6-dimethylpyridine, 2,3,4-dimethylpyridine, 2,6-dimethylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine in the ground state

Assignments ^a	2,3-Dimethylpyridine			2,4-Dimethylpyridine			2,6-Dimethylpyridine			3,4-Dimethylpyridine			3,5-Dimethylpyridine		
	Theoretical (cm ⁻¹)	Experimental (cm ⁻¹) [19]	IR act (km mol ⁻¹)	Theoretical (cm ⁻¹)	Experimental (cm ⁻¹) [19]	Intensity (km mol ⁻¹)	Theoretical (cm ⁻¹)	Experimental (cm ⁻¹)	Intensity (km mol ⁻¹)	Theoretical (cm ⁻¹)	Experimental (cm ⁻¹)	Intensity (km mol ⁻¹)	Theoretical (cm ⁻¹)	Experimental (cm ⁻¹) [12]	Intensity (km mol ⁻¹)
ν_{CH}	3,074	3,070 m	18,9298	3,059	3,058 w	17,6471	3,074	-	12,8575	3,057	3,057 vs	22,3614	3,029	3,029vs	7,9752
ν_{sCH}	3,045	3,045 s	17,816	3,050	3,040 sh	15,7456	3,066	3,063 s	20,3893	3,033	3,028 vs	11,6078	3,025	-	12,1309
ν_{asCH}	3,034	-	15,2831	3,028	-	19,941	3,050	-	3,6156	3,020	3,023 vs	34,6938	3,021	-	50,6114
ν_{asCH}	3,021	-	8,1761	2,999	-	16,8519	2,999	-	14,7305	2,996	2,997 m	15,022	2,991	2,985vs	15,3005
ν_{asCH}	2,989	-	20,1321	2,995	-	14,4913	2,998	-	19,9625	2,990	2,983 m	17,5923	2,991	-	12,8878
ν_{asCH_3}	2,957	-	3,6842	2,978	-	11,5641	2,979	-	22,9459	2,959	2,956 sh	7,9688	2,964	2,971sh,vs	30,9911
ν_{sCH_3}	2,954	-	30,0574	2,970	-	15,6762	2,978	-	7,8399	2,915	2,946 vs	22,9827	2,964	-	0,0117
ν_{sCH_3}	2,912	2,913 vs	42,6787	2,924	2,933 vs	18,484	2,924	-	8,3999	2,915	2,923 vs	20,596	2,917	2,930vs	16,6207
ν_{sCH_3}	2,912	-	5,6881	2,917	2,916 vs	19,6868	2,924	-	30,2999	2,911	-	26,3712	2,916	-	40,1291
$\nu_{\text{ringC=C}}$	1,572	1,577 vs	18,2695	1,580	-	98,9975	1,568	-	48,0193	1,574	1,577 w	34,6864	1,577	1,581vs	2,4425
$\nu_{\text{ringC=C}}$	1,550	-	19,3106	1,544	-	33,7244	1,544	-	74,6543	1,542	-	12,1145	1,553	-	7,502
δ_{scCH_3}	1,450	1,453 vs	17,4613	1,460	1,456 m	9,4901	1,446	1,453 w	60,5196	1,466	1,479 w	9,5301	1,453	1,463vs	13,1351
δ_{scCH_3}	1,441	-	19,7281	1,441	-	42,1517	1,445	-	17,438	1,441	1,447 vs	3,3466	1,447	-	23,9246
δ_{scCH_3}	1,438	1,432 vs	10,6796	1,436	-	11,5914	1,424	-	0,0006	1,441	-	19,303	1,435	-	0
δ_{scCH_3}	1,427	-	0,0401	1,432	-	4,0518	1,424	-	15,3653	1,436	-	26,1781	1,434	1,426vs	15,5619
δ_{scCH_3}	1,415	-	28,195	1,424	1,424 vs	7,2723	1,420	1,420 w	22,4758	1,427	-	0,0297	1,408	-	18,71
δ_{wCH_3}	1,406	-	24,3383	1,373	1,382 w	14,0024	1,391	1,397 s	2,1858	1,385	1,385 vs	7,7885	1,404	-	0,0052
δ_{wCH_3}	1,370	1,369 s	2,3423	1,362	-	3,3862	1,359	1,373 s	9,4702	1,373	1,373 vs	5,1863	1,367	1,379 s	1,526
δ_{wCH_3}	1,357	-	2,2266	1,360	-	2,2618	1,358	-	4,7315	1,364	1,363 sh	1,3182	1,365	1,358sh,m	2,3002
Ring bending	1,255	-	0,9872	1,276	1,273 m	7,4893	1,241	1,245 m	7,0093	1,284	-	2,1837	1,303	-	4,7597
$\gamma_{\text{C-N}}$	1,239	-	0,1147	1,245	-	1,0225	1,240	-	1,5167	1,237	1,246 sh, m	0,0693	1,245	-	0,7749
Ring breathing	1,215	-	4,0689	1,234	1,228 w	0,0182	1,204	-	13,6678	1,213	1,222 m	1,1657	1,233	-	5,0793
Ring deformation	1,154	1,165 sh, w	3,9326	1,144	1,162 m	2,6944	1,137	-	4,1483	1,177	1,191 vs	11,3195	1,150	-	20,436
CH (in plane)	1,104	-	7,2061	1,093	-	0,2385	1,077	1,095 s	5,4953	1,148	1,126 m	0,3898	1,144	1,138 s	1,3656
Ring breathing	1,050	-	2,4153	1,023	1,037 s	2,5953	1,024	1,030 s	0,0001	1,052	1,043 m	7,2222	1,026	1,032 s	5,969
$\delta_{\text{wCH}_3} + \gamma_{\text{C-C}}$	1,034	-	0	1,022	-	8,7199	1,017	-	8,6811	1,030	1,030 s	0,0117	1,022	-	0
$\delta_{\text{wCH}_3} + \gamma_{\text{C-C}}$	1,008	-	4,9593	994	992 s	2,6524	1,013	-	0,0502	1,009	-	5,1121	1,010	1,011 m	6,917
δ_{wCH_3}	974	972 s	6,6321	979	978 w	1,1379	982	-	1,2693	984	986 m	2,2586	997	-	0,0004
δ_{wCH_3}	954	-	10,6162	960	-	1,1143	968	971 m	0,0275	966	-	3,8541	963	-	0,3728
γ_{CH}	951	-	0,0004	950	-	0,0226	953	-	0,8532	951	-	0,0054	923	-	0
Ring deformation	920	-	0,0059	898	-	7,0439	885	-	1,8059	907	-	0,3304	911	-	0,0771
γ_{CH}	832	842 w	0,1438	865	-	0,8984	867	-	0	816	-	6,6441	911	-	0,1406
γ_{CH}	771	-	30,2449	802	-	26,7107	754	773 vs	41,4509	808	-	22,1136	840	-	13,9565
Ring bending	720	724 vs	11,7041	738	-	1,1586	721	717 m	2,2982	737	-	0,9746	700	715vs	18,8989
Ring breathing	712	-	1,943	720	-	0,0649	702	-	0,5629	711	712 vs	6,0052	700	710vs	5,1694
Ring breathing	576	589 s	1,8835	541	553 s	0,7707	546	556 s	0	586	-	1,3399	529	532 m	0,7554
Ring twisting	508	-	0,901	532	-	2,8533	542	539 s	1,3875	514	525 s	6,0137	519	-	0,6154
Ring bending	502	-	0,7963	504	-	2,7833	525	-	1,7164	493	487 sh	2,8353	487	498w	0
Ring bending	434	-	0,028	432	-	11,3991	425	419 m	0,0108	415	419 s	4,7466	432	438w	0,0025
$\delta_{\text{wCH}_3} + \text{ring twisting}$	407	412 m	2,2896	396	-	2,0619	406	-	2,3781	392	401 w	0,3197	383	-	0,7542
δ_{wCH_3}	287	-	0,2938	270	278 m	0,9694	272	-	1,8014	280	-	0,1814	260	272 m	0,6198
δ_{rockCH_3}	256	262 s	6,0568	207	-	1,3066	199	-	9,349	246	-	0,5723	218	-	0
δ_{rockCH_3}	154	-	1,4534	183	-	1,5232	189	-	0	169	-	0,7535	185	-	1,7708
δ_{rockCH_3}	149	-	0,2394	61	-	0,4664	56	-	0,81	154	-	0,5216	42	-	0,0564
δ_{rockCH_3}	107	-	0,0322	33	-	0,2088	47	-	0	120	-	0,003	34	-	0

^a ν_{s} = symmetric stretching, ν_{as} = asymmetric stretching, δ_{w} = wagging, δ_{sc} = scissoring, δ_{t} = rocking, γ = out of plane

Table 4 Comparison of experimental and theoretical vibrational wavenumbers (cm^{-1}) of dimeric 2,3-dimethylpyridine, 2,4-dimethylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine in the ground state

Assignments ^a	2,3-Dimethylpyridine			2,4-Dimethylpyridine			3,4-Dimethylpyridine			3,5-Dimethylpyridine		
	Theoretical (cm^{-1})	Intensity (kmol^{-1})	Experimental (cm^{-1}) [19]	Theoretical (cm^{-1})	Intensity (kmol^{-1})	Experimental (cm^{-1}) [19]	Theoretical (cm^{-1})	Intensity (kmol^{-1})	Experimental (cm^{-1})	Theoretical (cm^{-1})	Intensity (kmol^{-1})	Experimental (cm^{-1}) [12]
ν_{CH}	3,071-3,071	1,1974-30,3739	3,070 m	3,058-3,057	24,2595-0,0109	3,058 w	3,056-3,055	59,4252-0,0192	3,057 vs	3,034-3,032	28,8982-0,0004	3,029vs
$\nu_{\text{C}}\text{H}$	3,043-3,042	0,0265-16,1560	3,045 s	3,046-3,046	0,9064-39,1551	3,040 sh	3,030-3,029	25,3126-0,0001	3,028 vs	3,029-3,029	28,476-0,0299	-
$\nu_{\text{as}}\text{CH}$	3,036-3,035	31,9717-0,6337	-	3,032-3,030	13,8751-0,0004	-	3,025-3,024	25,4675-0,0047	3,023 vs	3,023-3,023	0,0419-67,6688	-
$\nu_{\text{as}}\text{CH}$	3,018-3,018	7,8485-11,5188	-	2,997-2,997	38,4428-0,0361	-	2,996-2,996	0,1028-4,9559	2,997 m	2,998-2,997	0,185-29,3025	2,985vs
$\nu_{\text{as}}\text{CH}_3$	2,987-2,987	20,8111-20,9740	-	2,994-2,994	23,9916-5,1311	-	2,995-2,995	8,9955-56,9922	2,983 m	2,992-2,992	1,3053-27,0765	-
$\nu_{\text{as}}\text{CH}_3$	2,952-2,955	3,3186-3,0912	-	2,975-2,975	0,3465-24,6243	-	2,958-2,958	8,3297-11,0092	2,956 sh	2,965-2,965	0,7178-42,1864	2,971sh,vs
$\nu_{\text{C}}\text{H}_3$	2,952-2,952	1,0345-61,5151	-	2,969-2,969	22,5143-10,7794	-	2,951-2,951	0,0146-44,891	2,946 vs	2,965-2,965	0,0035-22,2414	-
$\nu_{\text{C}}\text{H}_3$	2,911-2,910	1,9325-30,2764	2,913 vs	2,922-2,922	22,5143-10,7794	2,933 vs	2,914-2,914	48,1794-0,2052	2,923 vs	2,919-2,918	46,3415-0,001	2,930vs
$\nu_{\text{C}}\text{H}_3$	2,910-2,910	59,5743-20,9416	-	2,915-2,915	38,7992-0,6266	2,916 vs	2,909-2,909	55,3642-0,0097	-	2,918-2,918	39,7764-40,3737	-
$\nu_{\text{Ring}}\text{C}=\text{C}$	1,572-1,570	29,7276-0,0266	1,577 vs	1,580-1,580	44,1404-1,2539	-	1,576-1,575	64,2623-0,0013	1,577 w	1,580-1,578	6,1983-0	1,581 vs
$\nu_{\text{Ring}}\text{C}=\text{C}$	1,552-1,552	11,9969-31,5185	-	1,544-1,541	188,3065-0,0004	-	1,543-1,541	37,5334-0	-	1,558-1,558	0,0027-12,5612	1,463 vs
$\delta_{\text{sc}}\text{CH}_3$	1,453-1,452	0,0274-44,3523	1,453 vs	1,467-1,467	0,0021-84,4114	1,456 m	1,474-1,473	30,7336-0,0008	1,479 w	1,459-1,459	33,0728-0,0002	-
$\delta_{\text{sc}}\text{CH}_3$	1,438-1,438	11,7915-20,4401	-	1,441-1,441	0,0029-29,5009	-	1,441-1,441	10,0129-0,0538	1,447 vs	1,448-1,448	4,1579-43,5588	-
$\delta_{\text{sc}}\text{CH}_3$	1,438-1,438	12,5223-14,9685	1,432 vs	1,436-1,436	88,9628-0,0314	-	1,440-1,440	0,0597-34,5017	-	1,438-1,438	0,0006-12,1797	-
$\delta_{\text{sc}}\text{CH}_3$	1,425-1,424	0,0631-0,0449	-	1,432-1,432	0,0008-22,5984	1,424 vs	1,435-1,435	47,8158-0,0007	-	1,435-1,435	0,0026-16,7079	1,426vs
$\delta_{\text{w}}\text{CH}_3$	1,416-1,414	29,1664-0,1481	-	1,423-1,423	9,3816-0,0003	1,382 w	1,427-1,427	2,0518-0,0066	-	1,415-1,414	22,8509-0,0002	-
$\delta_{\text{w}}\text{CH}_3$	1,410-1,410	69,7001-0,3277	-	1,374-1,374	0,0012-15,1453	1,382 w	1,389-1,388	10,7128-0,0004	1,385 vs	1,406-1,406	9,486-0,0002	-
$\delta_{\text{w}}\text{CH}_3$	1,367-1,366	2,0577-2,2429	1,369 s	1,360-1,360	23,0425-0,0079	-	1,370-1,370	8,0403-10,2233	-	1,369-1,368	3,1408-0	1,379 s
$\delta_{\text{w}}\text{CH}_3$	1,353-1,353	0,2859-6,2708	-	1,357-1,357	3,6899-0,8444	-	1,361-1,361	2,5042-0,0059	1,363 sh	1,418-0,0577	4,4118-0,0577	1,358sh,m
Ring bending	1,268-1,264	0,0046-10,4545	-	1,292-1,286	0,0010-5,2723	1,273 m	1,302-1,294	23,6093-0,0001	-	1,318-1,313	24,1264-0	-
$\gamma_{\text{C}=\text{N}}$	1,235-1,234	0,0405-0,0004	-	1,243-1,242	0,0001-27,3241	1,228 w	1,236-1,235	3,3202-0	1,246 sh, m	1,252-1,251	0,3104-0	-
Ring breathing	1,215-1,214	14,4063-0,0004	-	1,231-1,231	0,0003-2,5596	1,162 m	1,217-1,216	7,6866-0	1,222 m	1,232-1,232	12,0142-0,0003	-
Ring deformation	1,154-1,154	2,2535-14,8231	1,165 sh, w	1,146-1,143	0,0191-0,0001	-	1,176-1,175	0-23,8025	1,191 vs	1,555-1,153	62,9413-0	-
CH (in plane)	1,103-1,103	15,1300-2,1049	-	1,096-1,093	0,0002-11,4889	1,037 s	1,149-1,147	0-0,3863	1,126 m	1,145-1,145	0-3,3947	1,138 s
Ring breathing	1,053-1,049	11,8341-0,0017	-	1,023-1,022	4,6148-0,0000	-	1,053-1,053	23,811-0,0007	1,043 m	1,029-1,029	0,0015-9,8128	1,032 s
$\delta_{\text{w}}\text{CH}_3+\gamma_{\text{C}=\text{C}}$	1,031-1,030	0,0292-0,0182	-	1,020-1,020	0,0000-6,5591	-	1,032-1,032	0,0002-0,0862	1,030 s	1,024-1,024	0,1153-1,2468	-
$\delta_{\text{w}}\text{CH}_3+\gamma_{\text{C}=\text{C}}$	1,006-1,005	0,0880-8,8616	-	992-992	15,6047-0,0017	992 s	1,010-1,010	0,0014-9,8087	-	1,011-1,010	30,4501	1,011 m
$\delta_{\text{w}}\text{CH}_3$	972-971	16,9731-5,6146	972 s	978-978	3,0879-1,4174	978 w	986-985	16,7595-0,0001	986 m	998-998	0-0	-
$\delta_{\text{w}}\text{CH}_3$	970-969	0,2288-0,1989	-	977-977	3,6723-0,0201	-	966-965	0,0111-7,262	-	965-965	0,9546-0,0467	-
γ_{CH}	952-951	3,8402-14,4123	-	959-958	0,0006-1,9408	-	954-953	0,0008-0,0027	-	949-948	0,2023-0,0001	929w
Ring deformation	930-930	0,0175-0,0024	-	898-898	1,4305-0,0001	-	927-927	0,7144-0,0077	-	914-914	0,0001-0	-
γ_{CH}	830-830	3,1139-0,0323	842 w	859-859	0,2585-20,4998	-	819-818	0,0003-15,6769	-	913-911	0-0,0017	-
Ring bending	777-776	58,8489-0,0840	-	810-809	0,0047-0,4355	-	806-805	42,8334-0,0017	-	850-849	0,0006-3,3978	-
Ring bending	720-717	0,1490-17,8743	724 vs	735-735	51,3291-0,0000	-	737-735	10,5428-0	712 vs	705-703	31,6759-27,5175	715vs
Ring breathing	713-713	0,5795-6,8518	-	720-719	0,0057-13,1306	-	714-712	0,0006-9,7116	-	703-701	0,0005-1,54402	710vs
Ring breathing	576-574	0,0027-5,4848	589 s	540-539	0,3452-0,0000	553 s	585-585	7,2755-0,0001	-	529-529	0-0,0001	532 m
Ring twisting	507-507	0,5208-0,0032	-	530-530	3,0064-0,0000	-	515-514	0,0002-11,4066	525 s	521-520	2,8936-1,3361	498w
Ring bending	502-499	0,6301-0,0028	-	505-505	5,5521-0,0317	-	496-494	5,1804-0	487 sh	488-486	0,1041-0	438w
Ring bending	433-431	0,0074-0,0042	-	438-431	0,0098-6,8839	-	420-417	0,0002-7,5235	419 s	433-432	0,0179-0	-
$\delta_{\text{w}}\text{CH}_3+\text{Ring twisting}$	407-405	10,8770-0,1791	412 m	396-395	0,0000-18,8023	278 m	395-394	1,8899-0	401 w	388-385	0-0	-
$\delta_{\text{w}}\text{CH}_3$	255-252	0,4269-0,3504	-	268-267	9,3009-0,0000	-	280-280	0,3622-0,0008	-	261-261	0-3,6272	272 m
$\delta_{\text{rook}}\text{CH}_3$	156-153	0,0202-10,3014	262 s	208-207	0,0001-2,1124	-	243-242	0-1,5809	-	223-221	0,0005-1,3873	-
$\delta_{\text{rook}}\text{CH}_3$	142-141	2,4376-0,0141	-	182-182	2,0945-0,0001	-	171-168	1,1323-0	-	186-186	0-3,2701	-
$\delta_{\text{rook}}\text{CH}_3$	98-93	0,1391-0,4674	-	66-66	2,5470-0,0370	-	151-151	0,018-0,9792	-	48-47	0,0001-3,2701	-
$\delta_{\text{rook}}\text{CH}_3$	55-39	0,0036-0,0121	-	50-45	0,0452-0,9581	-	114-114	0,0601-0,0004	-	46-44	0,0825-0	-

^a ν_{s} = symmetric stretching, ν_{as} = asymmetric stretching, δ_{w} = wagging, δ_{sc} = scissoring, δ_{r} = rocking, γ = out of plane

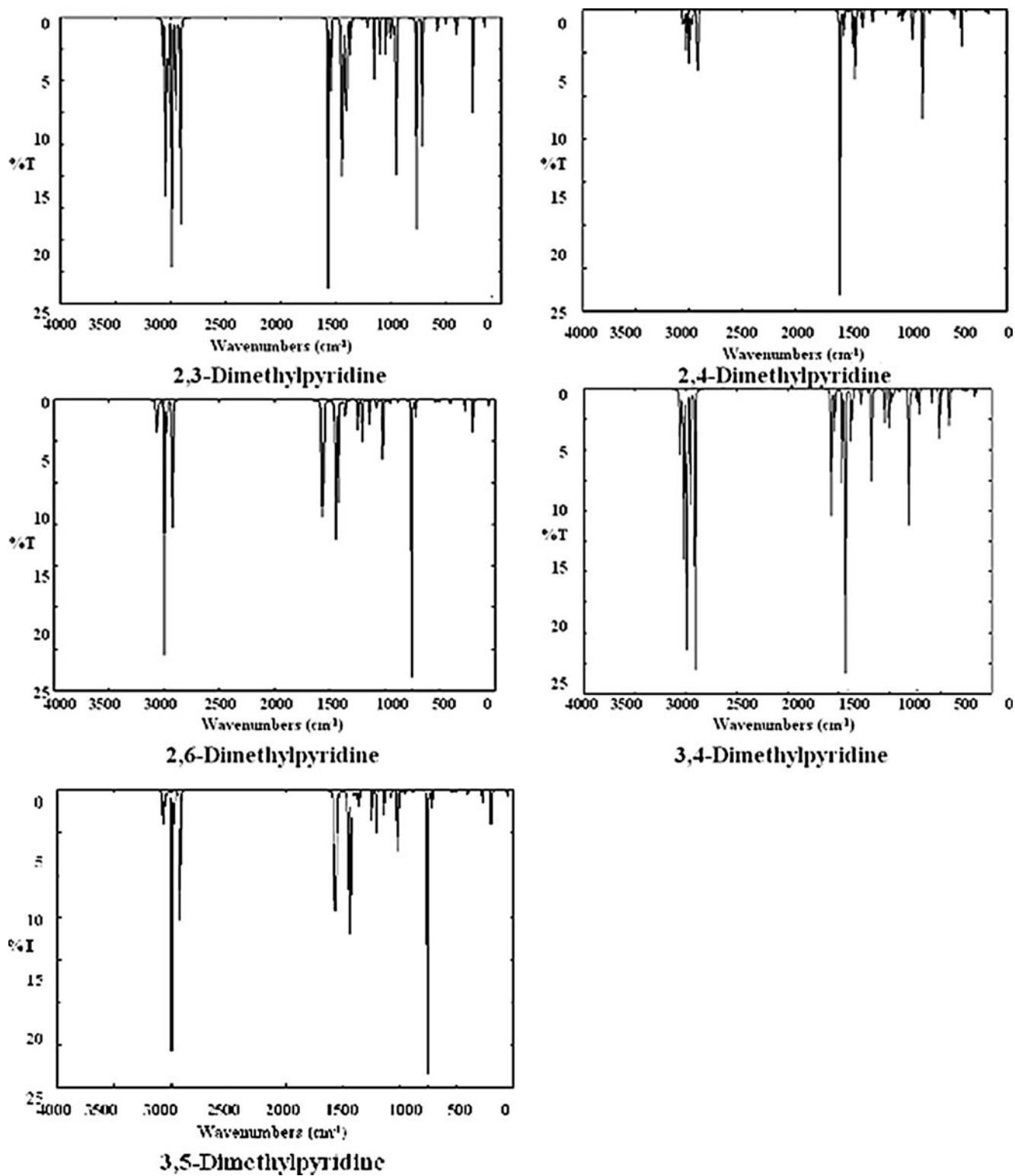


Fig. 3 Theoretical infrared spectra of monomeric forms of the studied molecules

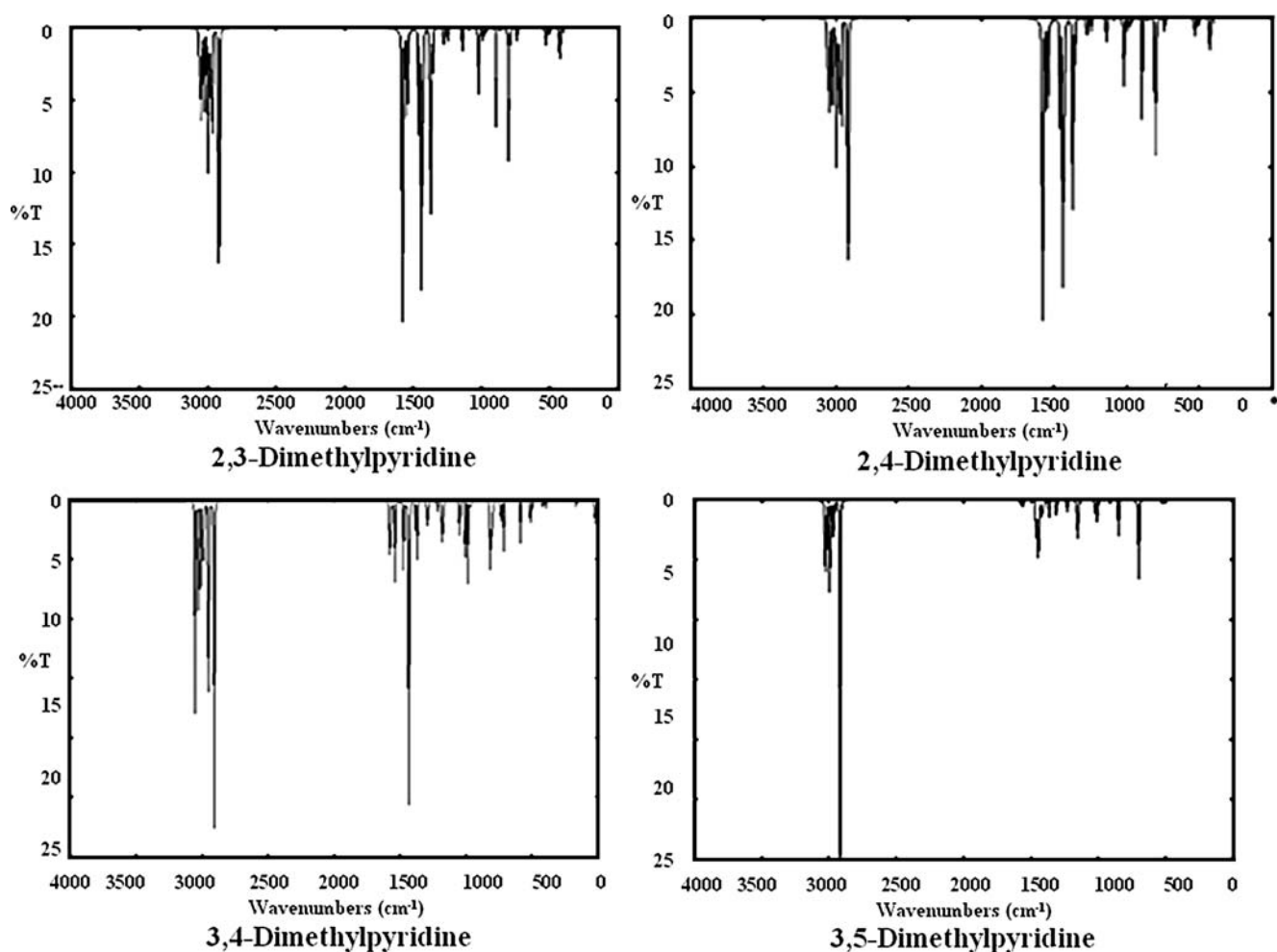
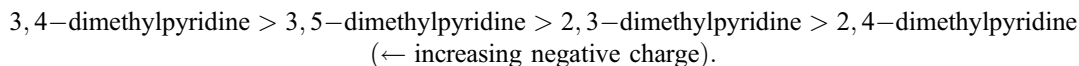


Fig. 4 Theoretical infrared spectra of dimeric forms of the studied molecules

anharmonical frequency while the calculated value is a harmonic frequency.

The calculated energies, energy differences and Mulliken charges are given in Table 5. It is clear that the dimerization energies of the studied molecules changed between -1.336 and -1.801 kcal/mol. The 3,4-dimethylpyridine ring has the

biggest dimerization energy (-1.801 kcal/mol) and Mulliken charge on nitrogen atom (-0.056); 2,3-dimethylpyridine ring has smallest dimerization energy (-1.336 kcal/mol) and Mulliken charge on nitrogen atom (-0.001). The nitrogen atom charges of monomeric forms have the following sequence:



The hydrogen bonds in dimers between N and H atoms (Table 2) have the opposite sequence:

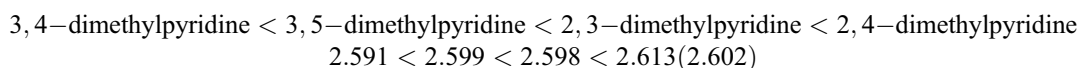


Table 5 The calculated total energies, zero point energies (ZPE) and energy differences, ΔE values and Mulliken charges of the studied monomeric and dimeric dimethyl substituted pyridines. $E_T = E + ZPE$, $\Delta E = E_{T(\text{dimeric})} - 2 \times E_{T(\text{monomeric})}$

	2,3-Dimethylpyridine	2,4-Dimethylpyridine	3,4-Dimethylpyridine	3,5-Dimethylpyridine
Monomer				
$E_{(\text{hartree})}$	-327.010	-327.012	-327.008	-327.008
$ZPE_{(\text{hartree})}$	0.140	0.140	0.141	0.140
$E_{T(\text{hartree})}$	-326.870	-326.872	-326.868	-326.868
$2 \times E_{T(\text{hartree})}$	-653.738	-653.743	-653.735	-653.735
Dimer				
$E_{(\text{hartree})}$	-654.022	-654.026	-654.020	-654.019
$ZPE_{(\text{hartree})}$	0.281	0.281	0.282	0.281
$E_{T(\text{hartree})}$	-653.741	-653.745	-653.738	-653.738
$\Delta E_{(\text{hartree})}$	-0.002	-0.002	-0.003	-0.003
$\Delta E_{(\text{kcal/mol})}$	-1.334	-1.387	-1.801	-1.581
Charges				
Monomer				
N	-0.001	-0.033	-0.070	-0.051
H	0.128	0.127	0.117 (0.130)	0.120
C	-0.034	0.016	-0.624 (-0.204)	0.681
Dimer				
N ^a	-0.032	-0.002	-0.056	-0.032
H ^a	0.205	0.205	0.196	0.199
C ^a	0.075	-0.311	-0.370	-0.930

^a Same charge value with other pyridine ring in dimeric forms

It seems that the smallest hydrogen bonds in dimeric forms have the biggest nitrogen charges in monomeric forms. It is clear that while the hydrogen bond lengths between two monomers decrease, the stability of the dimers increase.

Conclusion

In the present work, the theoretical vibrational frequencies of monomeric 2,3-, 2,4-, 2,6-, 3,4- and 3,5-dimethylpyridine were calculated. The theoretical vibrational frequencies and dimerization energies of dimeric 2,3-, 2,4-, 3,4- and 3,5-dimethylpyridine were also investigated. Their approximate mode descriptions with DFT calculations were then determined. The results of quantum chemical calculations with monomeric and dimeric dimethylpyridine molecules have shown that the substituent position plays an important role in the FT-IR spectra and dimerization of the molecules. The effects of steric hindrance and electronic charge distribution play the most important role in determining the structure and the substitution of these molecules. Theoretical FT-IR spectra of the monomeric and dimeric dimethylpyridine molecules are in agreement with experimental FT-IR spectra. The theoretical vibrational frequencies and the assignments of the studied molecules were compared with experimental data. If the vibrational assignments are investigated individually, the

assignments obtained with related molecules are also consistent with the determined B3LYP/6-311+G (d,p) calculation, and there is good agreement between experimental and theoretical vibrational frequencies in the region of 4,000–235 cm^{-1} . In the monomeric and dimeric dimethyl substituted pyridine derivatives studied, C–H stretching and bending frequency shifts occurring between the dimer and the monomer may be diagnostic of the magnitude of the dimerization energy. The most stable dimeric form was obtained for the 3,4-dimethylpyridine molecule, as supported by the literature. It can be easily seen that the positions of the substituents also affected the geometry and IR frequencies.

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