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FT-IR, FT-Raman spectra and ab initio HF and DFT calculations of 4-*N*,*N*′-dimethylamino pyridine

N. Sundaraganesan [a,*], S. Kalaichelvan [c], C. Meganathan [a],
B. Dominic Joshua [a], J. Cornard [b]

[a] *Department of Physics (Engg.), Annamalai University, Annamalai Nagar 608002, India*
[b] *Laboratoire de Spectrochimie Infrarouge & Raman (LASIR), UMR 8516 – Université des*
Sciences & Technologies de Lille Bât C5 – 59655, Villeneuve d'Ascq cedex, France
[c] *Department of Physics, A.A. Govt. Arts College, Namakkal, 637 001, India*

Abstract

In this work, we will report a combined experimental and theoretical study on molecular and vibrational structure of 4-*N*,*N*′-dimethylamino pyridine (4NN′DMAP). The Fourier transform infrared and Fourier transform Raman spectra of 4NN′DMAP was recorded in the solid phase. The optimized geometry was calculated by HF and B3LYP methods with 6-31G(d,p) and 6-311++G(d,p) basis sets. The harmonic vibrational frequencies, infrared intensities and Raman scattering activities of the title compound were performed at same level of theories. The scaled theoretical wavenumber showed very good agreement with the experimental values. The thermodynamic functions of the title compound was also performed at HF/6-31G(d,p) and B3LYP/6-311++G(d,p) level of theories. A detailed interpretation of the infrared and Raman spectra of 4NN′DMAP was reported. The theoretical spectrograms for FT-IR and FT-Raman spectra of the title molecule have been constructed.
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Keywords: FT-IR and FT-Raman spectra; Ab initio and DFT; 4-*N*,*N*′-Dimethylamino pyridine; Vibrational analysis

1. Introduction

The study of the vibrational spectra of substituted pyridines, mainly aminopyridine, attracts the attention of many spectroscopists due to their wide application in pharmacology and agro-chemistry. They serve as a good anesthetic agent and hence are used in the preparation of drugs for certain brain disease. These pharmaceutically acceptable salts and the prodrugs are used for the treatment of neuronal damage following global and focal ischemia, for the treatment and prevention or amelioration of both acute or chronic pain, anti-tinnitus agents, as anti-manic depressants and for the treatment or prevention of diabetic neuropathy [1]. 4-*N*,*N*′-Dimethylamino pyridine (4NN′DMAP) has become one of the most popular catalyst for different processes such as acylations, alkylations, silylations, Baylis–Hilman reaction and nucleophilic substitutions of alcohols and amines [2].

The development of chiral 4NN′DMAP derivatives has received considerable attention, since they have been successfully employed as chiral nucleophilic catalysts in a wide range of asymmetric synthetic process [2(b),3]. There are many different strategies for the preparation of dimethylamino pyridine analogues, for instance Ruble and Fu introduced the concept of 'planar chirality' [4], and a few examples of ferrocene-fused dimethylamino pyridine complexes have been described in the literature, which have been used in stereoselective processes. Enzymes are recognized as valuable tools for the synthesis of optically active compounds. The use of oxidoreductases in particular Baker's yeast (*Saccharomyces cerevisiae*), has attracted significant attention because it provides very efficient access to important optically enriched products.

Literature survey reveals that to the best of our knowledge, neither the complete Raman and IR spectra nor the force fields for 4NN′DMAP have been reported so far. The goal of the present study is to give a complete description of the molecular geometry and molecular vibrations of the title compound for the first time. For that purpose quantum chemical computations were performed on 4NN′DMAP using HF and density functional theory (DFT). Density functional theory calculations are reported to provide excellent vibrational frequencies of organic com-
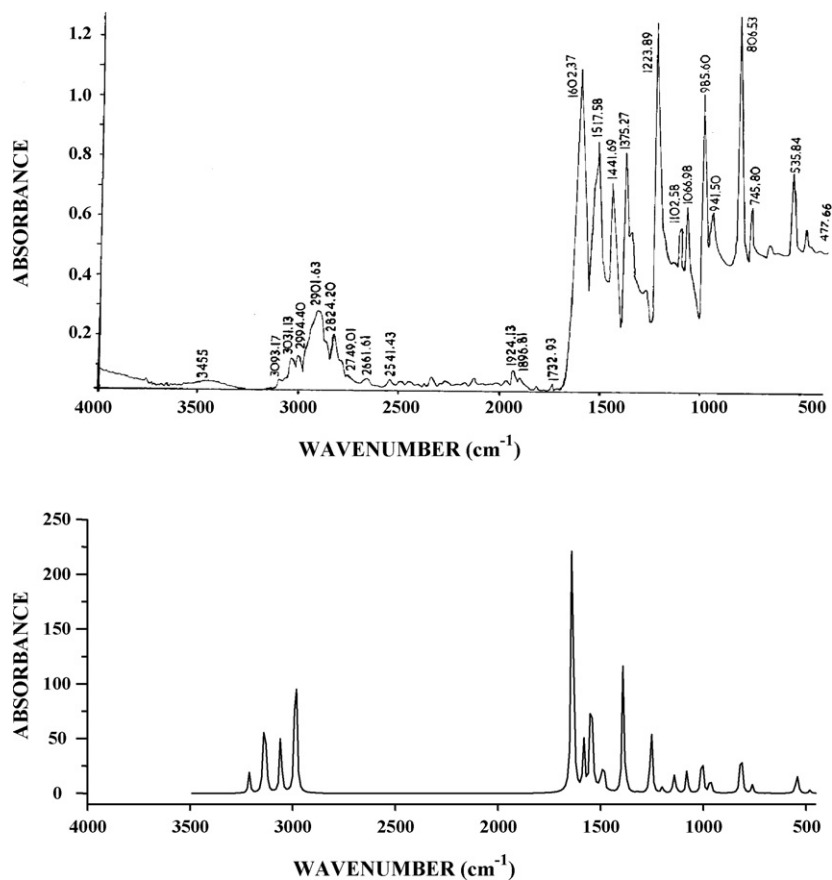
Fig. 1. Experimental and theoretical FT-IR spectrum for 4-*N,N′*-dimethylamino pyridine.

pounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity [5–10].

2. Experimental

The compound 4NN′DMAP in the solid form was obtained from Department of Chemistry, Annamalai University with a stated purity of greater than 98% and it was used as such without further purification. The FT-Raman spectrum of 4NN′DMAP has been recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 100–4000 cm^{-1} on a Brucker model IFS 66 V spectrophotometer. The FT-IR spectrum of this compound was recoded in the region 400–4000 cm^{-1} on IFS 66 V spectrophotometer using KBr pellet technique. The data were recorded in the co-addition of 200 scans at ± 4 cm^{-1} resolution with 250 mW of power at the sample in both the techniques. The observed experimental and theoretical FT-IR and FT-Raman spectra of the title compound are shown in Figs. 1 and 2. The spectral measurements were carried out at Sophisticated Analytical Instrumentation Facility (SAIF), IIT, Chennai.

3. Method of calculations

All calculations were performed at Hartree–Fock (HF) and B3LYP levels on a Pentium IV/3.02 GHz personal computer using Gaussian 03W [11] program package, invoking gradient geometry optimization [12]. Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at Hartree–Fock level, adopting the standard 6-31G(d,p) basis set. This geometry was then re-optimized again at HF and the gradient corrected density functional theory (DFT) [13] with the Becke's three parameter hybrid functional (B3) [14] for the exchange part and the Lee–Yang–Parr (LYP) correlation function [15], accepted as a cost effective approach, for the computation of molecular structure, vibrational frequencies and energies of optimized structures. All the computations have been done by adding polarization function d and diffuse function on heavy atoms [16] and polarization function p and diffuse function on hydrogen atoms [17], in addition to triple split valence basis set (6-311++G(d,p)), for better treatment of polar bonds of methyl groups. The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of 4NN′DMAP were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. Vibrational frequencies computed at DFT level have been adjudicated to be more reliable than those obtained by the computationally demanding Moller–Plesset perturbation methods. Density functional theory offers electron correlation frequently comparable to second-order Moller–Plesset theory (MP2). Finally, the calculated normal mode vibrational fre-
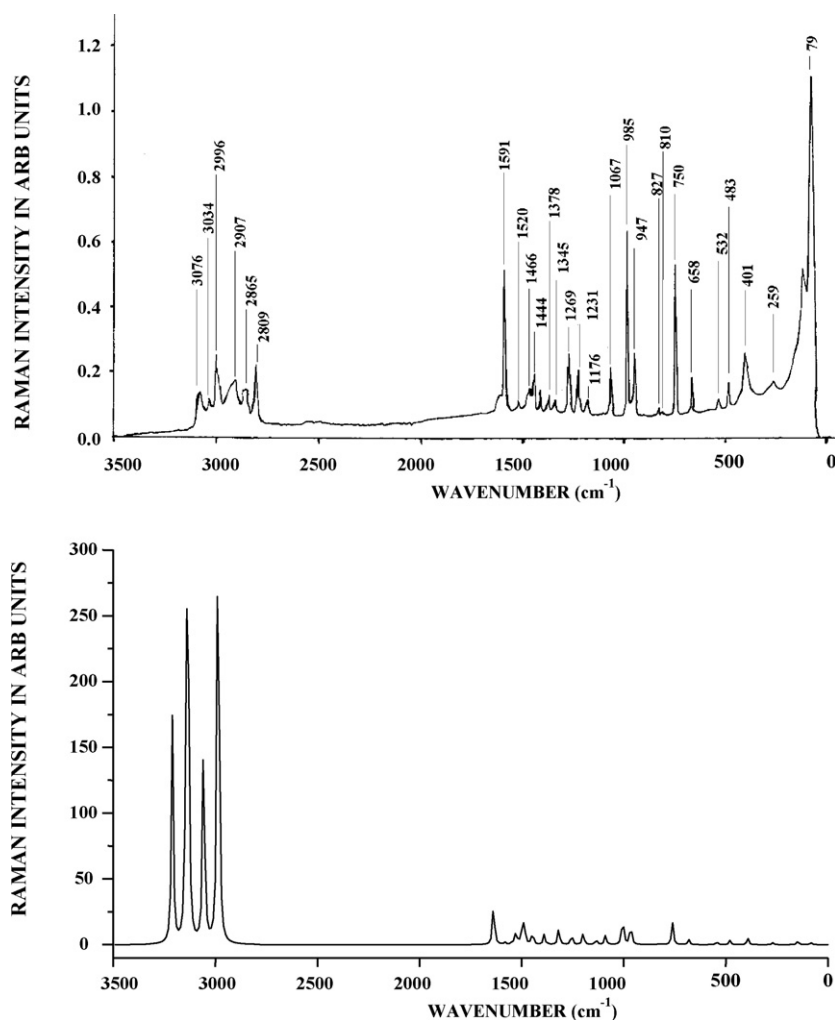
Fig. 2. Experimental and theoretical FT-Raman spectrum for 4-*N,N′*-dimethylamino pyridine.

quencies provide thermodynamic properties also through the principle of statistical mechanics.

By combining the results of the GAUSSVIEW program [18] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. There is always some ambiguity in defining internal coordination. However, the defined coordinate form complete set and matches quite well with the motions observed using the GAUSSVIEW program.

4. Results and discussion

4.1. Molecular geometry

Fig. 3 presents a schematic of 4NN′DMAP molecule with its atoms numbered 1–19 to correspond with Table 1 and it shows the list of optimised structural parameters observed from HF and DFT computations and the corresponding experimental data. All the geometries determined belong to a true minimum proven by real wavenumbers in the vibrational analysis. Because the crystal structure of 4-*N,N′*-dimethylamino pyridine remains unknown, the most closely related molecule for comparison is 4-aminopyridine [19].
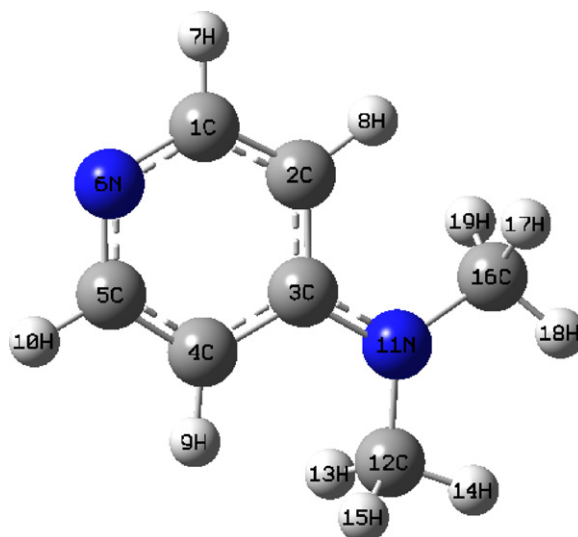

Fig. 3. Numbering system adopted in this study (4-*N,N′*-dimethylamino pyridine).

Table 1
Geometrical parameters optimized in 4-*N*,*N*′-dimethylamino pyridine, bond length (Å), bond angle (°) and dihedral angle (°)

Parameters	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)	Exp. [19] (4-aminopyridine)
Bond length (Å)			
C1–C2	1.380	1.388	1.374 (3)
C1–N6	1.320	1.338	1.338 (3)
C1–H7	1.077	1.087	0.980 (2)
C2–C3	1.403	1.413	1.401 (3)
C2–H8	1.071	1.081	0.950 (3)
C3–C4	1.403	1.413	1.406 (3)
C3–N11	1.373	1.377	1.363 (3)
C4–C5	1.380	1.388	1.370 (3)
C4–H9	1.071	1.081	0.980 (2)
C5–N6	1.320	1.338	1.352 (3)
C5–H10	1.077	1.087	0.990 (2)
N11–C12	1.449	1.455	–
N11–C16	1.449	1.455	–
C12–H13	1.090	1.099	–
C12–H14	1.081	1.089	–
C12–H15	1.083	1.094	–
C16–H17	1.083	1.094	–
C16–H18	1.081	1.089	–
C16–H19	1.090	1.099	–
Bond angle(°)			
C2–C1–N6	125.0	124.9	125.1 (2)
C2–C1–H7	118.9	119.1	121.0 (1)
N6–C1–H7	116.1	116.0	114.0 (1)
C1–C2–C3	119.3	119.5	119.4 (2)
C1–C2–H8	118.7	118.9	122.0 (2)
C3–C2–H8	122.0	121.6	119.0 (2)
C2–C3–C4	115.6	115.7	116.4 (2)
C2–C3–N11	122.2	122.1	122.6 (2)
C4–C3–N11	122.2	122.1	121.1 (2)
C3–C4–C5	119.3	119.5	119.4 (2)
C3–C4–H9	122.0	121.6	119.0 (1)
C5–C4–H9	118.7	118.9	121.0 (1)
C4–C5–N6	125.0	124.9	124.7 (2)
C4–C5–H10	118.9	119.1	122.0 (1)
N6–C5–H10	116.1	116.0	114.0 (1)
C1–N6–C5	115.7	115.5	115.0 (2)
C3–N11–C12	119.2	119.8	–
C3–N11–C16	119.2	119.8	–
C12–N11–C16	117.3	118.4	–
N11–C12–H13	112.6	112.5	–
N11–C12–H14	109.0	109.0	–
N11–C12–H15	110.9	111.0	–
H13–C12–H14	108.3	108.3	–
H13–C12–H15	108.5	108.3	–
H14–C12–H15	107.4	107.6	–
N11–C16–H17	110.9	111.0	–
N11–C16–H18	109.0	109.0	–
N11–C16–H19	112.6	112.5	–
H17–C16–H18	107.4	107.6	–
H17–C16–H19	108.5	108.3	–
H18–C16–H19	108.3	108.3	–
Dihedral angle (°)			
H8–C2–C3–N11	1.41	1.39	–
N11–C3–C4–C5	178.54	178.69	–
N11–C3–C4–H9	−1.41	−1.39	–
C2–C3–N11–C12	−168.49	−171.91	–
C2–C3–N11–C16	−12.15	−8.41	–
C4–C3–N11–C12	12.11	8.42	–
C4–C3–N11–C16	168.45	171.91	–
C3–N11–C12–H13	62.16	63.51	–
C3–N11–C12–H14	−177.65	−176.33	–
C3–N11–C12–H15	−59.64	−57.99	–

Table 1 (*Continued*)

Parameters	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)	Exp. [19] (4-aminopyridine)
C16–N11–C12–H13	−94.61	−100.21	–
C16–N11–C12–H14	25.58	19.94	–
C16–N11–C12–H15	143.58	138.28	–
C3–N11–C16–H17	59.71	57.99	–
C3–N11–C16–H18	177.72	176.33	–
C3–N11–C16–H19	−62.09	−63.52	–
C12–N11–C16–H17	−143.51	−138.29	–
C12–N11–C16–H18	−25.51	−19.95	–
C12–N11–C16–H19	94.68	100.21	–

From the theoretical values, we can find that most of the optimized bond lengths are slightly larger than the experimental values, due to that the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecules in solid state. Comparing bond angles and lengths of B3LYP with those of HF, as a whole the formers are bigger than later and the B3LYP calculated values correlates well compared with the experimental data. In spite of the differences, calculated geometrical parameters represent a good approximation and they are the bases for calculating other parameters, such as vibrational frequencies and thermodynamics properties.

In this case the amino N(3) to ring C(11) distance is 1.377 Å, fully 0.014 Å longer than in the 4-aminopyridine [19]. The amino-ring, C3–N11 bond length 1.377 Å by B3LYP/6-311++G(d,p) is about midway between the corresponding bond lengths in 4-aminopyridine (1.363(3) Å) and 3-aminopyridine (1.384(4) Å) [20] and thus reflects a double-bond character between that of 4- and 3-aminopyridine. The ring angle at C3 in 4NN′DMPA is 115.7°, 2.7° smaller than the angle in pyridine [21], 0.7° smaller than 4-aminopyridine and 4.3° smaller than in 4-cynopyridine [22]. This decrease in angle at the point of substitution is related to the shortness of the C3–N(CH$_3$)$_2$ bond in agreement with the observation that electron-releasing groups decrease the endocyclic angles in benzenoid rings [23]. The short C3–N(CH$_3$)$_2$ bond and decreased angle at C3 are also associated with a slight lengthening of the adjacent C3–C2 and C3–C4 bond lengths; their average length is 1.413 Å which is about 0.021 Å longer than in pyridine, 1.392(1) Å [21]. Similar decrease in the ring angle and increase in the ring bond lengths adjacent to the point of substitution are also seen in 2-aminopyridine, 2-aminopyrimidine and aminopyrazine where the ring-amino bonds are quite short. However, in 3-aminopyridine, where this bond is longer, the effect is less pronounced. On the otherhand, the ring C–C bonds adjacent to the amino substitutent appear longer in the 4NN′DMAP [1.413 Å average] than in 4-amino pyridine [1.403(3) Å].

4.2. Vibrational assignments

With this assumed structural model, the molecule belong to Cs point group and the 51 normal modes of fundamental vibrations which span the irreducible representations: 35A′ + 16A″. All the 51 fundamental vibrations are active in both IR and Raman. Vibrational assignments are based on comparison of calculated and observed Raman and IR frequencies and activities as well as the depolarisation ratios of Raman bands The assignments shown in Table 2 for several of phenyl ring modes along with substituents are briefly given in the present work.

The harmonic-vibrational frequencies calculated for 4NN′DMAP at HF and B3LYP levels using the triple split valence basis set along with diffuse and polarization functions, 6-311++G(d,p) and observed FT-IR and FT-Raman frequencies for various modes of vibrations have been collected in Table 2. Comparison of the frequencies calculated at HF and B3LYP with experimental values (Table 2) reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. Inclusion of electron correlation in density functional theory to a certain extend makes the frequency values smaller in comparison with the HF frequency data. Reduction in the computed harmonic vibrations, though basis set sensitive are only marginal as observed in the DFT values using 6-311++G(d,p). Any way not withstanding the level of calculations, it is customary to scale down the calculated harmonic frequencies in order to improve the agreement with the experiment. The calculated frequencies were scaled by factors 0.8923 and 0.9623 for HF and DFT computation, respectively. These values minimize the root-mean square difference between calculated and experimental frequencies for bands with definite identifications. They are very close to the values recommended for HF/6-311++G(d,p) (0.8929) and DFT-/b3YLP/6-311++G(d,p) (0.9613) [24,25]. The descriptions concerning the assignment have also been indicated in Table 2.

4.3. C–H vibrations

The carbon–hydrogen stretching vibrations give rise to bands in the region 3000–3100 cm^{-1} in all aromatic compounds [26,27]. Since 4NN′DMAP is a monosubstituted aromatic heterocyclic molecule, it has four C–H moieties. The expected four stretching vibrations (Table 2) correspond to stretching modes of C1–H, C2–H, C4–H and C5–H units. The vibrations assigned to aromatic C–H stretch in the region 3017–3082 cm^{-1} by B3LYP method are in agreement with experimental assignment 3032–3091 cm^{-1}. The bands corresponding to both out-of-plane and in-plane C–H deformations are observed in the region 750–1300 cm^{-1} [26,27]. In *p*-substituted benzene the C–H in-plane bending mode can be expected in the region 1000–1300 cm^{-1}. The bands are sharp but are weak to medium intensity. The medium and strong intensity bands at 1224 and

Table 2
Experimental, HF and B3LYP levels computed vibrational frequencies (cm^{-1}) obtained for 4-N,N'-dimethylamino pyridine

Experimental[a]		HF/6-311++G(d,p)		B3LYP/6-311++G(d,p)		I_{IR}	I_R	Species	Vibrational assignments[b]
FT-IR	FT-Raman	Computed	Corrected	Computed	Corrected				
3091 w		3385	3013	3210	3082	15	13	A′	ν_s CH
	3076 w	3383	3011	3210	3082	4	160	A′	ν_s CH
3032 m	3034 w	3316	2951	3143	3017	11	144	A′	ν_s CH
2995 m	2996 m	3313	2949	3140	3014	39	115	A′	ν_{as} CH in CH$_3$
		3281	2920	3130	3005	35	154	A′	ν_s CH in CH$_3$
2902 ms	2907 w	3264	2905	3118	2993	3	2	A′	ν_{as} CH in CH$_3$
		3225	2871	3058	2935	49	74	A′	ν_s CH in CH$_3$
2824 m		3222	2868	3056	2934	14	114	A′	ν_{as} CH in CH$_3$
2864 w	2865 w	3141	2795	2987	2868	73	311	A′	ν_s CH in CH$_3$
	2809 m	3134	2789	2981	2862	74	70	A′	ν N–(CH$_3$)$_2$
1602 s	1591 vs	1785	1589	1637	1571	318	37	A′	ν C=C (semicircle stretch)
1536 s		1737	1546	1581	1518	47	2	A′	ν C=C + ν (ph-N)
1518 ms	1520 vw	1671	1488	1545	1483	135	2	A′	ν C=C + ν C=N
	1466 vw	1653	1471	1527	1466	5	10	A′	CH$_3$ deform + ν C=C
1445 ms	1444 w	1634	1455	1513	1453	4	2	A′	ν C=N
		1621	1442	1495	1435	19	17	A′	CH$_3$ deform + ν C=C
	1416 vw	1612	1435	1487	1428	2	7	A′	CH$_3$ deform
		1610	1433	1483	1424	23	6	A′	CH$_3$ umbrella mode + ν C=C
		1580	1406	1458	1400	1	0	A′	ν C=C + CH$_3$ umbrella mode
1375 m	1378 w	1564	1392	1446	1388	1	10	A′	CH$_3$ umbrella mode + β CH
1345 m	1345 w	1497	1332	1390	1334	116	8	A′	ν C–N + β CH
		1490	1326	1374	1319	8	1	A′	β CH + ν C–N
	1269 m	1394	1241	1317	1265	1	14	A′	Ring deformation
1224 s	1231 m	1352	1203	1254	1204	31	8	A′	β CH
		1297	1155	1251	1201	38	0	A′	β CH + β NCH$_3$
	1176 w	1243	1106	1198	1150	6	10	A″	ρ CH$_3$
1102 w		1239	1103	1142	1096	18	1	A″	ρ CH$_3$
1068 ms	1067 vs	1222	1087	1132	1086	1	2	A″	ρ CH$_3$
		1211	1078	1127	1082	3	0	A′	β CH
		1178	1049	1089	1046	0	7	A′	β CH
		1164	1036	1078	1035	22	0	A′	β CH$_3$
987 mw	985 m	1122	998	1005	964	47	24	A′	Trigonal bending
		1080	961	991	952	0	0	A″	γ CH
941 w	947 m	1079	960	965	926	15	17	A′	Ring breathing + methyl rocking
		1036	922	960	922	1	1	A″	γ CH
	827 w	913	813	828	795	0	0	A″	γ CH
807 s	810 w	903	804	815	782	53	0	A″	γ CH
749 mw	750 s	816	726	761	731	8	17	A′	β CNC
		810	721	746	716	0	0	A″	γ CCC
655 w	658 m	730	650	681	654	0	4	A′	β CCC
536 m	532 w	604	537	551	529	5	1	A′	β N–CH$_3$ + amino scis. + β CCC
		582	518	539	517	16	1	A′	β N–CH$_3$ + amino scis. + β CCC
477 w	483 w	510	454	479	460	3	3	A′	β (ph-N) + β CCC
	401 m	445	396	402	386	0	0	A″	γ CCC
		426	379	392	376	0	5	A″	γ CH$_3$
		298	265	268	258	8	1	A″	γ (ph-N) + γ CCC
	259 vw	294	262	267	256	0	0	A″	γ CH$_3$ + γ CCN
		184	164	174	167	0	0	A″	τ CH$_3$
		169	151	147	141	0	3	A″	τ CH$_3$
	117 m	111	99	88	84	5	0	A″	τ CH$_3$
	79 vs	73	65	81	78	0	1	A″	τ CH$_3$

[a] (s) Strong; (vs) very strong; (m) medium; (w) weak; (vw) very weak; (sh) shoulder; (br) broad.

[b] (ν) stretching; (ν_s) sym. stretching; (ν_{as}) asym. stretching; (β) in-plane-bending; (γ) out-of-plane bending; (ω) wagging; (ρ) rocking; (t) twisting; (τ) torsion; (I_{IR}) IR intensity; (I_R) Raman scattering activity.

1375 cm^{-1} in FT-IR spectrum are due to in-plane C–H bending. The same vibration appears in the FT-Raman spectra, at 1231 and 1381 cm^{-1} with strong as well as medium intensity. The theoretically computed values of C–H in-plane bending vibrations also falls in the region 1046–1388 cm^{-1} by B3LYP/6-311++G(d,p) method. The absorption bands arising from C–H out-of-plane bending vibrations are usually observed in the region at 675–1000 cm^{-1} [26,27]. The bands are usually in the region is very weak in intensity. The bands at 806 and 825 cm^{-1} in FT-Raman are assigned to C–H out-of-plane bending vibra-

tion. The theoretically calculated values of C–H out-of-plane bending vibration also falls in the region 782–922 cm^{-1} by B3LYP/6-311++G(d,p) method.

4.4. C–C vibrations

The ring carbon–carbon stretching vibrations occur in the region 1430–1625 cm^{-1}. In general, the bands are of variable intensity and are observed at 1625–1590, 1575–1590, 1470–1540, 1430–1465 and 1280–1380 cm^{-1} from the frequency ranges given by Varsanyi [27] for the five bands in the region. In the present work, the frequencies observed in FT-IR spectrum at 1518 and 1536 cm^{-1} have been assigned to C–C stretching vibrations. The corresponding vibrations appear in the FT-Raman spectrum at 1519 cm^{-1}. The theoretically computed values at 1483 and 1518 cm^{-1} shows excellent agreement with experimental data by B3LYP/6-311++G(d,p) method.

The C–C aromatic stretch, known as semicircle stretching, predicted at 1571 cm^{-1} is in reasonable agreement with the band observed at 1602 cm^{-1} in FT-IR and at 1591 cm^{-1} in FT-Raman spectra.

The very strong band at 1000 cm^{-1} is observed in the FT-Raman spectrum of methyl benzoate. The corresponding infrared band at 1000 cm^{-1} has a medium intensity. These bands arise from the scaled wavenumber 977 cm^{-1}, which can be described as the trigonal ring breathing vibration or the 'Star of David' vibration of the aromatic ring [28].

The frequencies observed in FT-IR spectrum at 943 cm^{-1} have been assigned to ring breathing and corresponding vibrations appears in the FT-Raman spectrum at 947 cm^{-1}. The theoretically computed values of 926 cm^{-1} shows excellent agreement with experimental observations. The in-plane deformation vibration is at higher frequencies than the out-of-plane vibrations. Shimanouchi et al. [29] gave the frequency data for these vibrations for different benzene derivatives as a result of normal coordinate analysis. The bands observed at 401, 477 and 655 cm^{-1} are assigned to CCC deformation of phenyl ring. The theoretically computed values at 386, 654, 716 and 731 cm^{-1} by B3LYP/6-311++G(d,p) method gives excellent agreement with experimental data.

4.5. Methyl group vibrations

Vibrational spectral studies on methyl pyridine have shown that asymmetric and symmetric methyl stretching band can be observed around 2846 and 2960 cm^{-1}, respectively [26,27,30,31]. For the assignments of CH$_3$ group one can expect that nine fundamentals can be associated to each CH$_3$ group, namely the symmetrical stretching in CH$_3$ (CH$_3$ symmetric stretch) and asymmetrical stretching (CH$_3$ asymmetric stretch), in-plane stretching modes (i.e. in-plane hydrogen stretching mode), the symmetrical (CH$_3$ symmetric deform) and asymmetrical (CH$_3$ asymmetric deform) deformation modes, the in-plane rocking (CH$_3$ ipr), out-of-plane rocking (CH$_3$ opr) and twisting (t CH$_3$) bending modes. For the methyl group compound [32], the asymmetric stretching mode appears in the range 2825–2870 cm^{-1}, lower in magnitude compared to

its value in CH$_3$ (compounds) (2860–2935 cm^{-1}) whereas the asymmetric stretching modes for both the type of compounds lie in the same region 2925–2985 cm^{-1}. The medium bands observed at 2902–2995 cm^{-1} in the FT-IR spectrum could be attributed to CH$_3$ asymmetric stretching vibration. The same vibration appears in the FT-Raman spectrum at 2907–2996 cm^{-1} with medium weak intensity. The theoretically computed values at 2934, 2993 and 3014 cm^{-1} shows excellent agreement with experimental observations. The bands observed at 2864 cm^{-1} in FT-IR spectrum could be attributed to CH$_3$ symmetric stretching vibration. The same vibration appears in FT-Raman spectrum at 2865 cm^{-1}. The theoretically computed value for symmetric stretching vibration at 2868, 2935 and 3005 cm^{-1} also shows excellent agreement with experimental observation.

The asymmetric and symmetric bendings are recorded in the 1410–1455 cm^{-1} region and about 1375 cm^{-1}, respectively, while the rocking mode appear in the 990–1050 cm^{-1}. Predicted by the DFT calculation, the series of bands appearing in the 1400–1500 cm^{-1} region are mainly due to the methyl deformation coupling with the ring CCH bending and CC stretching motions, to different extents and in different ways. In the case of 4NN′DMAP a band observed at 1466 cm^{-1} in FT-Raman spectrum correspond to asymmetric CH$_3$ deformation and correlated with the calculated frequency at 1466 cm^{-1}. This behaviour can be found in other fundamentals such as symmetric deformation and rockings. The torsion vibrations are not observed in the FT-IR spectrum because these appear at very low frequency. The scaling procedure predicts that these vibrations could appear at about 167, 141, 84 and 78 cm^{-1} in 4NN′DMAP. The FT-Raman experimental observations at 79 and 117 cm^{-1} shows an excellent agreement with theoretical results. These assignments find support from the work of Singh and Prasad [33] and are within the frequency intervals given by Varsanyi [34].

4.6. N–(CH$_3$)$_2$ group vibrations

The CH$_2$ or CH$_3$ groups next to the nitrogen atom in amines are somewhat shifted. The symmetric stretch at 2770–2830 cm^{-1} is lowered in frequency and intensified and so stands out among other aliphatic bands [35,36]. For the compounds containing N–(CH$_3$)$_2$ group (in the aromatic structure) the stretching vibrations of N–(CH$_3$)$_2$ occur in the region 2790–2810 cm^{-1} [37]. In our title molecule a medium Raman band at 2809 cm^{-1} is assigned to N–(CH$_3$)$_2$ stretching vibration. However, the theoretical computation by HF/6-311++G(d,p) method at 2789 cm^{-1} shows excellent agreement compared with B3LYP/6-311++G(d,p) method.

4.7. C=N, C–N vibrations

The identification of C=N and C–N vibrations is a very difficult task, since the mixing of several bands are possible in this region. Silverstein et al. [38] assigned C–N stretching absorption in the region 1266–1382 cm^{-1} for aromatic amines. In benzamide the band observed at 1368 cm^{-1} is assigned to be

Table 3
Theoretically computed total energies (a.u.), zero-point vibrational energies (kcal mol^{-1}), rotational constants (GHz), entropies (cal mol^{-1} K^{-1}) and dipole moment (D) for 4-*N,N′*-dimethylamino pyridine

Parameters	HF		B3LYP	
	6-31G(d,p)	6-311++G(d,p)	6-31G(d,p)	6-311++G(d,p)
Total energy	−379.7963061	−379.8718799	−382.2715685	−382.3603503
Zero-point energy	108.85	108.08	101.74	101.07
Rotational constants	3.6659	3.6722	3.6010	3.6108
	1.2357	1.2351	.2178	1.2187
	0.9363	0.9370	0.9212	0.9227
Entropy				
Total	89.079	88.792	91.089	90.934
Translational	40.313	40.313	40.313	40.313
Rotational	28.718	28.716	28.766	28.761
Vibrational	20.048	19.763	22.010	21.860
Dipole moment	4.284	4.444	4.560	4.854

due to C–N stretching [39]. In benzotriazole, the C–N stretching bands are found to be 1307 and 1382 cm^{-1}. In the present work, the bands observed at 1345 and 1447 cm^{-1} in FT-IR spectrum have been assigned to C=N, C–N stretching vibrations, respectively. The same vibrations which corresponds to Raman spectrum at 1345 and 1444 cm^{-1}. The theoretically computed values of C=N and C–N stretching vibrations also falls in the region 1334–1453 cm^{-1} by B3LYP/6-311++G(d,p) method.

5. Other molecular properties

Several calculated thermodynamic parameters are presented in Table 3. Scale factors have been recommended [40] for an accurate prediction in determining the zero-point vibration energies (ZPVE), and the entropy, $S_{vib}(T)$. The variations in the ZPVEs seem to be insignificant. The total energies are found to decrease with the increase of the basis set dimension. The changes in the total entropy of 4NN′DMAP at room temperature at different basis set are only marginal.

6. Conclusions

We have carried out ab initio and density functional theory calculation on the structure and vibrational spectrum of 4NN′DMAP. Comparison between the calculated and experimental structural parameters indicates that B3LYP are in good agreement with experimental ones. Vibrational frequencies, infrared intensities and Raman activities calculated by B3LYP/6-311++G(d,p) method agree very well with experimental results. On the basis of agreement between the calculated and observed results, assignments of all the fundamental vibrational modes of 4NN′DMAP was examined and proposed for the first time in the literature. Therefore, the assignments made at higher level of theory with higher basis set with only reasonable deviations from the experimental values, seem to be correct. This study demonstrates that scaled DFT/B3LYP calculations are powerful approach for understanding the vibrational spectra of medium sized organic compounds.

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