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Molecular structure and vibrational analysis of 3-Ethylpyridine using ab initio HF and density functional theory (B3LYP) calculations

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ARTICLE INFO

Article history:

Received 31 August 2010

Received in revised form

19 November 2010

Accepted 2 December 2010

Keywords:

3-Ethylpyridine

B3LYP

IR intensities

Raman activities

FT-IR and FT-Raman spectra and C2H₅ substitutions

ABSTRACT

The FT-Raman and FT-IR spectra for 3-Ethylpyridine (3-EP) have been recorded in the region 4000–100 cm⁻¹ and compared with the harmonic vibrational frequencies calculated using HF/DFT (B3LYP) method by employing 6-31G(d,p) and 6-311++G(d,p) basis set with appropriate scale factors. IR intensities and Raman activities are also calculated by HF and DFT (B3LYP) methods. Optimized geometries of the molecule have been interpreted and compared with the reported experimental values of some substituted benzene. The experimental geometrical parameters show satisfactory agreement with the theoretical prediction from HF and DFT. The scaled vibrational frequencies at B3LYP/6-311++G(d,p) seem to coincide with the experimentally observed values with acceptable deviations. The theoretical spectrograms (IR and Raman) have been constructed and compared with the experimental FT-IR and FT-Raman spectra. Some of the vibrational frequencies of the pyridine are effected upon profusely with the C₂H₅ substitutions in comparison to pyridine and these differences are interpreted.

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1. Introduction

Heterocyclic nitrogen containing compounds, such as pyridine and its derivatives, are commonly present in synthetic and natural products [1,2]. The study of the vibrational spectra of substituted pyridine mainly amino pyridine attracts the attention of many spectroscopists due to their wide application in pharmacology and agro-chemistry. Pyridine heterocycles and its derivatives are a repeated moiety in many large molecules with interesting photo chemical, electrochemical and catalytic applications [3–10]. They serve as good anesthetic agent and hence are used in the preparation of drugs for certain brain disease. These pharmaceutically acceptable salts and the pre drugs are used for the treatment (or) prevention of diabetic neuropathy [11,12]. The methyl substituent on the ethyl group of title molecule shows some differences in the photo physical properties relative to the pyridine. 3-Ethylpyridine constitutes an important class of heterocyclic organic compounds. Investigations on the structure of these organic molecules have been a subject of great interest because of their peculiar photo physical properties and pharmaceutical importance [13–15].

Sağlam et al. [16] have recorded the Fourier transform infrared and laser Raman spectra of 4-pyridine acid in the regions of 100–4000 cm⁻¹, respectively. Michalski et al. [17] have studied the synthesis of 2-phenylazo-5-nitro-6-methyl-pyridine. Literature survey reveals that to the best of our knowledge no ab initio HF/DFT with 6-31G(d,p) and 6-311G(d,p) basis sets calculations of 3-Ethylpyridine have been reported so far. It is, therefore thought worthwhile to make a comprehensive vibrational analysis using both experimentally observed IR and Raman wavenumbers and theoretically calculated vibrational spectra. In the present work, we have studied the FTIR and Raman spectra of 3-Ethylpyridine. The ab initio and DFT calculations are performed to obtain the ground state optimized geometries and the vibrational wavenumbers of the different normal modes as well as to predict the corresponding intensities for the different modes of the molecule.

2. Experimental

The spectroscopic grade 3-Ethylpyridine was purchased from Sigma–Aldrich chemicals, USA and used as such for recording spectra without further purification. The FT-IR spectrum of the title compound was recorded in Bruker IFS 66 V spectrometer in the range of 4000–100 cm⁻¹. The spectral resolution is ±2 cm⁻¹. The FT-Raman spectrum of 3-Ethylpyridine was also recorded in the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 μm with 200 Mw power.

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Both the spectra were recorded in the range of 4000–100 cm⁻¹ with scanning speed of 30 cm⁻¹ min⁻¹ of spectral width 2 cm⁻¹. The frequencies of all sharp bands are accurate to ± 1 cm⁻¹.

3. Computational methods

The molecular structure of the 3-EP in the ground state is computed by performing both ab initio-HF and DFT (B3LYP) with 6-31G(d,p) and 6-311++G(d,p) basis sets. The optimized structural parameters are used in the vibrational frequency calculations at HF and DFT levels. The minimum energy of geometrical structure is obtained by using level 6-311++G(d,p) basis sets. The calculated frequencies are scaled by 0.908, 0.904, 0.902 and 0.881 for HF/6-31G(d,p) [18,19]. For B3LYP with 6-31G(d,p) set is scaled with 0.961, 0.952, 0.969, 1.03 and 1.06 and B3LYP/6-311++G(d,p) basis set is scaled with 0.867, 0.964, 1.04, 1.01, 1.07, and 0.956 [20]. The theoretical results have enabled us to make the detailed assignments of the experimental IR and Raman spectra of the title molecule [21]. HF/DFT calculations for 3-EP are performed using GAUSSIAN 03 W program package on Pentium IV processor personal computer without any constraint on the geometry [22–24].

4. Results and discussion

4.1. Molecular geometry

The molecular structure of the 3-Ethylpyridine belongs to C_s point group symmetry. The optimized molecular structure of 3-EP is obtained from GAUSSVIEW programs are shown in Fig. 1. The molecule contains ethyl group connected with pyridine ring. The structure optimization and zero point vibrational energy of the 3-EP in HF/6-31G(d,p), B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) are 408,716.0, 381,430.6 and 379,106.6 J/mol and 97.68, 91.16 and 90.60 kcal/mol respectively. The comparative optimized structural parameters such as bond lengths, bond angles and dihedral angles are presented in Table 1. From the theoretical values, it is found 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 [25]. 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. Although the differences, calculated geometrical parameters represent a good approximation and they are the bases for the calculating other parameters, such as vibrational frequencies and thermodynamics properties. Optimized geometrical parameters, namely, bond lengths and bond angles at HF/6-31G(d,p), B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) levels are given in Table 1.

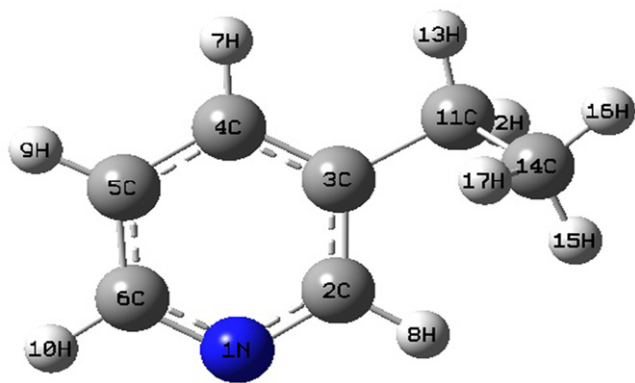


Fig. 1. Molecular structure of 3-Ethylpyridine.

Optimized structure yields more fluctuated bond length pairs for the all bonds at all three levels of calculations and the asymmetry of the pyridine ring is evident by the bond length order C2–C3 ≤ C3–C4 ≤ C5–C6 ≤ N1–C6 ≤ N1–C2 ≤ C4–C5. This is purely explicit the breakdown of hetero aromatic structure of 3-EP. Though the bonds N1=C6 and N1–C2 are differed by single and double bonds, According to the calculated values (HF/B3LYP/6-31G(d,p)) of both bonds are nearly equal. The bond length C2–C3 (1.013 Å cal.) is 0.071 Å lesser than bond length C3–C4 (1.084 Å cal.) and is merely due to the ethyl substitution. The bond length C4–C5 (1.510 Å cal.) is higher than all other bonds in the pyridine ring and is due to the impact of substitution. According to the experimental values [26], the bond lengths C3–C4 is 0.021 Å differed from C5–C6 whereas in the case of DFT calculation, the values of bond length C3–C4 and C5–C6 are nearly equal. According to the experimental values [27], all the C–H bonds are same and 0.003 Å lesser than computed values by B3LYP/6-311++G(d,p) basis set. The asymmetry of the pyridine ring is evident by the bond angle order N1–C2–C3 ≤ C2–C3–C4 ≤ C4–C5–C6 ≤ N1–C6–C5 ≤ C3–C4–C5 ≤ C2–N1–C6. From the bond angle order, it is clear that, the bond angle C2–C3–C4 is 11.71° greater than the bond angle C2–N1–C6. It exposes the breaking of pyridine ring at the place of N instead of substitution.

4.2. Vibrational assignments

The 3-EP consists of 17 atoms, hence undergoes 45 normal modes of vibrations. Of the 45 normal modes of vibrations, 33 modes of vibrations are in plane and remaining 12 are out of plane. The bands that are in the plane of the molecule is represented as A' and out-of-plane as A''. Thus the 45 normal modes of vibrations of 3-EP are distributed as $\Gamma_{\text{Vib}} = 33A' + 12A''$. In agreement with C_s symmetry all the 45 fundamental vibrations are active in both Raman scattering and IR absorption. The harmonic-vibrational frequencies calculated for 3-EP at HF and B3LYP levels using the triple split valence basis set along with the diffuse and polarization functions, 6-311++G(d,p) observed FT-IR and FT-Raman frequencies for various modes of vibrations have been presented in Table 2.

Comparison of frequencies calculated at HF with the experimental values reveals the over estimation of the calculated vibrational modes due to the neglect of anharmonicity in real system. Inclusion of electron correlation in the Density functional theory to certain extends makes the frequency values smaller in the comparison with the HF frequency data. Reduction in the computed harmonic vibrations, although basis set sensitive are only marginal as observed in the DFT values using 6-311G++(d,p). Any way not withstanding the level of calculations, it is customary to scale down the calculated harmonic frequencies in order to develop the agreement with the experiment. The scaled calculated frequencies minimize the root-mean square difference between calculated and experimental frequencies for bands with definite identifications. The descriptions concerning the assignment have also been indicated in Table 2. The comparative IR and Raman spectra of experimental and calculated (HF/B3LYP) are given in Figs. 2 and 3.

4.2.1. Computed IR intensity and Raman activity analysis

Computed vibrational spectral IR intensities and Raman activities of the 3-EP for corresponding wave numbers by HF and DFT methods with B3LYP at 6-31G(d,p) and 6-311++G(d,p) basis sets have been collected in the Table 3. The title molecule is a non polar molecule with C_s point group. Comparison of IR intensity and Raman activity calculated by HF and DFT with B3LYP at 6-31G(d,p) and 6-311++G(d,p) methods with experimental values shows the variation of IR intensities and Raman activities. In the case of IR intensity, the values of HF are found to be higher than B3LYP at 6-311++G(d,p) whereas in the case of Raman activity the effect is reversed. The similar effect was also observed in the earlier paper

Table 1

Optimized geometrical parameters for 3-Ethylpyridine computed at HF/6-31G(d,p), B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) basis sets.

Geometrical parameters	HF/6-31G(d,p)	B3LYP/6-31G(d,p)	B3LYP/6-311++G(d,p)	Experimental values ^a
<i>Bond length (Å)</i>				
N1–C2	1.320	1.401	1.367	1.340
N1–C6	1.319	1.337	1.365	1.340
C2–C3	1.389	1.090	1.013	1.395
C2–H8	1.077	1.399	1.371	1.081
C3–C4	1.388	1.511	1.084	1.374
C3–C11	1.512	1.392	1.414	1.487
C4–C5	1.382	1.087	1.510	1.395
C4–H7	1.076	1.395	1.380	1.081
C5–C6	1.384	1.085	1.088	1.395
C5–H9	1.074	1.338	1.427	1.081
C6–H10	1.076	1.088	1.085	1.081
C11–H12	1.086	1.096	1.094	1.090
C11–H13	1.085	1.096	1.095	1.090
C11–C14	1.533	1.539	1.538	1.487
C14–H15	1.085	1.094	1.093	1.090
C14–H16	1.085	1.094	1.093	1.090
C14–H17	1.085	1.094	1.093	1.090
<i>Bond angle (°)</i>				
C2–N1–C6	117.90	124.75	128.52	117.30
N1–C2–C3	124.51	119.40	115.78	123.60
N1–C2–H8	115.78	115.83	115.68	–
C3–C2–H8	119.69	116.69	120.09	–
C2–C3–C4	116.56	121.24	116.81	118.50
C2–C3–C11	121.31	122.04	123.08	–
C4–C3–C11	122.10	119.54	115.98	–
C3–C4–C5	119.62	120.03	121.93	119.40
C3–C4–H7	120.16	120.42	122.07	–
C5–C4–H7	120.21	118.50	121.02	–
C4–C5–C6	118.31	121.12	118.67	–
C4–C5–H9	121.25	120.37	120.30	–
C6–C5–H9	120.43	123.29	123.99	–
N1–C6–C5	123.08	120.46	118.78	–
N1–C6–H10	116.35	116.23	117.21	–
C5–C6–H10	120.56	117.20	110.38	–
C3–C11–H12	109.36	109.29	109.35	–
C3–C11–H13	109.32	109.42	108.98	–
H3–C11–C14	112.95	112.96	113.21	–
H12–C11–H13	106.38	106.43	106.32	–
H12–C11–C14	109.32	109.24	109.43	–
H13–C11–C14	109.26	109.26	109.30	–
C11–C14–H15	110.78	110.89	110.77	–
C11–C14–H16	110.96	110.95	110.97	–
C11–C14–H17	111.08	111.11	111.25	–
H15–C14–H16	108.11	108.12	108.14	–
H15–C14–H17	108.02	108.01	107.90	–
H16–C14–H17	107.73	107.59	107.65	–
<i>Dihedral angles (°)</i>				
C6–N1–C2–C3	–0.08	0.24	–0.05	–
C6–N1–C2–H8	179.66	–178.33	179.70	–
C2–N1–C6–C5	–0.11	–179.42	–179.83	–
C2–N1–C6–H10	–179.92	1.99	–0.07	–
N1–C2–C3–C4	0.24	–0.07	–0.06	–
N1–C2–C3–C11	–178.55	179.60	179.72	–
H8–C2–C3–C4	179.49	–0.17	0.16	–
H8–C2–C3–C11	1.706	179.50	–178.82	–
C2–C3–C4–C5	–0.206	178.39	–179.57	–
C2–C3–C4–H7	179.52	–1.92	1.43	–
C11–C3–C4–C5	178.58	–27.23	–0.17	–
C11–C3–C4–H7	–1.67	–143.41	179.43	–
C2–C3–C11–C12	–144.07	94.61	178.81	–
C2–C3–C11–H13	–27.95	154.26	–1.57	–
C2–C3–C11–C14	93.93	38.08	–18.22	–
C4–C3–C11–H12	37.19	–83.88	–134.06	–
C4–C3–C11–H13	153.31	–0.04	104.06	–
C4–C3–C11–C14	–84.79	179.70	162.84	–
C3–C4–C5–C6	0.028	–179.72	47.00	–
C3–C4–C5–H9	179.81	0.024	–74.86	–
H7–C4–C5–C6	–179.70	0.23	0.057	–
H7–C4–C5–H9	0.083	179.97	179.74	–
C4–C5–C6–N1	0.145	–179.51	–179.54	–
C4–C5–C6–H10	179.94	0.22	0.14	–
H9–C5–C6–N1	–179.64	–0.17	0.057	–
H9–C5–C6–H10	0.148	–179.93	–179.63	–
C3–C11–C14–H15	179.93	–179.97	178.96	–
C3–C11–H14–H16	–59.96	–59.79	–60.89	–

Table 1 (Continued)

Geometrical parameters	HF/6-31G(d,p)	B3LYP/6-31G(d,p)	B3LYP/6-311++G(d,p)	Experimental values ^a
C3–C11–C14–H17	59.86	59.87	58.94	–
H12–C11–C14–H15	57.91	–58.10	–58.78	–
H12–C11–H14–H16	178.02	62.07	61.36	–
H12–C11–C14–H17	–62.15	–178.25	–178.79	–
H13–C11–C14–H15	–58.14	57.96	57.27	–
H13–C11–C14–H16	61.96	178.15	177.42	–
H13–C11–C14–H17	–178.2	–62.18	–62.73	–

^a Refs. [26,27].

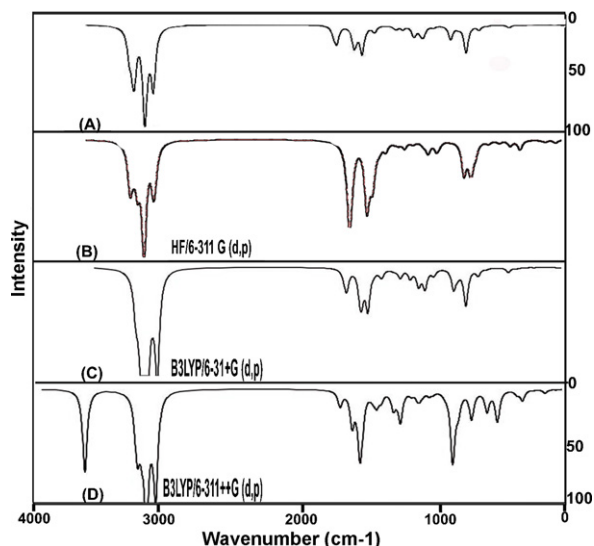


Fig. 2. Experimental (A), calculated (B–D) FTIR spectra of 3-Ethylpyridine.

[28]. The comparative plots of IR intensities and Raman activities for four sets are presented in Figs. 4 and 5 respectively (Figs. 6–8).

4.2.2. Computed vibrational frequency analysis

The comparative graph of calculated vibrational frequencies by HF and DFT methods at HF/6-31G(d,p), B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) basis sets for the 3-EP are given in Fig. 9. From the figure, it is found that the calculated (unscaled) frequencies by B3LYP with 6-311++G(d,p) basis sets are closer to the experimental frequencies than HF method with 6-31G(d,p) basis set. This obser-

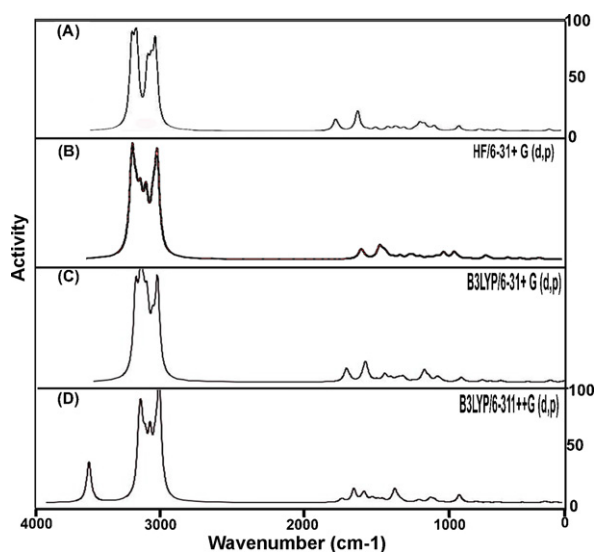


Fig. 3. Experimental (A), calculated (B–D) FT-Raman Spectra of 3-Ethylpyridine.

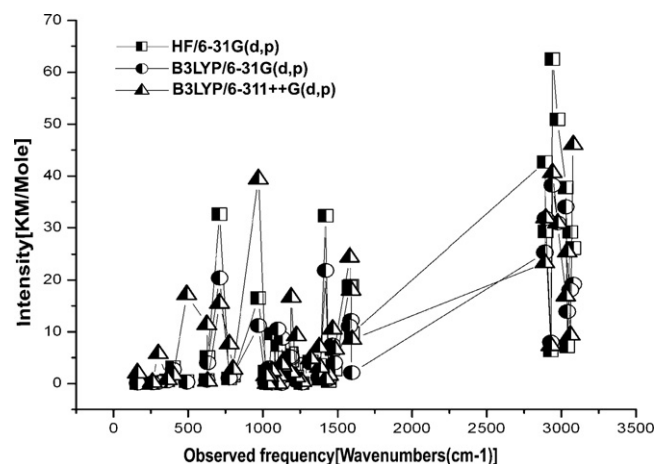


Fig. 4. Comparative graph of IR intensities by HF and DFT [B3LYP].

vation is in line with our earlier work [29]. The standard deviation (SD) calculation made between experimental and computed frequencies (HF/DFT) for the 3-EP is presented in Table 4. According to the SD, the computed frequency deviation decreases in going from HF/6-31G(d,p) to B3LYP/6-31G(d,p) to B3LYP/6-311++G(d,p). The deviation ratio between HF/6-31G(d,p) and B3LYP/6-31G(d,p) is 2.15 and HF/6-31G(d,p) and B3LYP/6-311++G(d,p) is 1.91. It is also observed that the calculated frequencies by B3LYP/6-31G(d,p) basis sets are closer to the experimental frequencies than HF method.

4.2.3. C–H vibrations

The hetero aromatic compounds commonly exhibit multiple weak bands in the region 3100–3000 cm^{–1} due to C–H stretching vibrations [30–33]. In this region, the bands are not affected appreciably by the nature of the substituents. Hence in the present study,

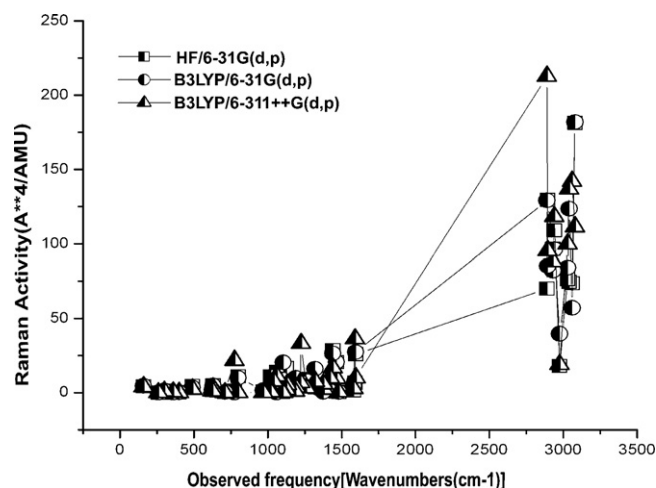


Fig. 5. Comparative graph of IR Raman activities by HF and DFT [B3LYP].

Table 2
Observed and HF/6-31G(d,p), B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) level calculated vibrational frequencies of 3-Ethylpyridine.

S. No.	Symmetry species C_5	Observed frequency		Calculated frequency (cm^{-1}) with HF/6-31G(d,p)		Calculated frequency (cm^{-1}) with B3LYP/6-31G(d,p)		Calculated frequency (cm^{-1}) with B3LYP/6-311++G(d,p)		Vibrational assignments
		FTIR	FT-Raman	Unscaled value	Scaled value	Unscaled value	Scaled value	Unscaled value	Scaled value	
1	A'	3080w	–	3392	3080	3204	3082	3550	3088	(C–H) ν
2	A'	3060w	–	3365	3055	3174	3053	3173	3062	(C–H) ν
3	A'	3040w	–	3354	3045	3164	3043	3159	3048	(C–H) ν
4	A'	3030vs	–	3350	3041	3145	3025	3129	3019	(C–H) ν
5	A'	2975vs	2975s	3275	2973	3122	2978	3095	2971	(CH ₃) (C–H) ν
6	A'	2940s	–	3268	2967	3118	2974	3093	2940	(CH ₃) (C–H) ν
7	A'	–	2930vs	3240	2941	3078	2936	3056	2933	(CH ₃) (C–H) ν
8	A'	–	2895s	3210	2914	3045	2904	3026	2904	(CH ₃) (C–H) ν
9	A'	2890s	–	3202	2907	3041	2901	3024	2903	(CH ₃) (C–H) ν
10	A'	1595m	–	1810	1666	1647	1667	1657	1649	(C=C) ν
11	A'	–	1590 vs	1788	1592	1627	1579	1568	1589	(C=C) ν
12	A'	1580vs	1580 m	1657	1561	1524	1573	1512	1586	(C=N) ν
13	A'	1480s	1480 w	1652	1471	1519	1474	1496	1477	(C–C) ν
14	A'	1465s	–	1640	1460	1511	1466	1496	1466	(C–C) ν
15	A'	–	1440 m	1634	1455	1500	1456	1487	1428	(CH ₃) α
16	A'	1420vs	–	1593	1418	1467	1424	1432	1425	(CH ₃) α
17	A'	–	1380vw	1562	1391	1423	1381	1411	1383	(C–CH ₃) ν
18	A'	1375m	–	1501	1381	1378	1365	1386	1379	(C–CH ₃) ν
19	A'	1320m	1320m	1494	1329	1361	1321	1353	1326	(C–H) δ
20	A'	–	1260w	1402	1248	1318	1254	1279	1254	(C–N) ν (C–H) δ
21	A'	1225m	–	1348	1240	1275	1237	1262	1237	(C–H) δ
22	A'	–	1220s	1328	1222	1250	1213	1236	1212	(C–H) δ
23	A'	1190m	–	1278	1176	1223	1193	1210	1186	(C–H) δ (CH ₃)
24	A'	–	1185s	1199	1162	1150	1190	1128	1183	(C–H) δ (CH ₃)
25	A'	1130m	–	1187	1151	1087	1125	1085	1138	(C–H) δ (CH ₃)
26	A'	–	1125w	1154	1119	1073	1110	1067	1119	(C–H) δ (CH ₂)
27	A'	1105m	–	1137	1102	1070	1107	1043	1094	(C–H) δ (CH ₂)
28	A'	–	1100w	1123	1089	1039	1105	1015	1099	(C–H) γ
29	A'	1060m	–	1118	1053	996	1065	996	1059	(C–H) γ
30	A'	–	1040vs	1084	1051	975	1043	966	1039	(C–H) γ
31	A'	1030m	–	1061	1028	965	1032	901	1030	(C–H) γ (CH ₃)
32	A'	–	1020m	1041	1009	947	1013	881	1007	(C–H) γ (CH ₃)
33	A'	970m	–	909	836	824	834	823	863	(C–H) γ (CH ₂)
34	A'	800vs	800m	851	783	794	803	788	827	(CCC) δ
35	A'	775m	775m	849	781	791	767	774	774	(CCC) δ
36	A'	710vs	–	789	702	733	711	683	716	(C=N) δ
37	A'	630s	–	690	635	641	622	626	626	(C–N) δ
38	A'	–	625vs	628	609	580	620	567	624	(CCC) γ
39	A'	490w	490s	545	485	504	489	491	488	(CCC) γ
40	A'	400vs	400w	458	400	414	401	349	399	(C–CH ₃) δ
41	A'	360w	–	375	363	350	362	337	353	(C–CH ₂) δ
42	A'	–	300w	337	300	304	301	305	299	(C–CH ₃) γ
43	A'	260m	–	236	228	221	223	212	222	(C–CH ₂) γ
44	A'	160m	160w	151	159	138	159	137	156	(CH ₃) τ

vs – very strong; s – strong; m – medium; w – weak; as – asymmetric; s – symmetric; δ – in plane bending; γ – out plane bending; α – deformation; τ – twisting.

Table 3

Comparative values of IR intensity and Raman activity between HF/6-31G(d,p), HF/6-311G(d,p), LSDA/6-311G(d,p) and MPW1PW91/6-311G(d,p) of 3-Ethylpyridine.

S. No.	Observed frequency	Calculated with HF/6-31G(d,p)		Calculated with B3LYP/6-31G(d,p)		Calculated with B3LYP/6-311++G(d,p)	
		IR intensity (Ai)	Raman activity (I)	IR intensity (Ai)	Raman activity (I)	IR intensity (Ai)	Raman activity (I)
1	3080	26.1	181.4	19.2	181.8	46.0	111.5
2	3060	29.2	73.7	18.1	57.1	9.35	142.0
3	3040	7.14	74.6	13.9	123.6	25.4	137.0
4	3030	37.8	76.3	34.0	84.1	16.9	100.1
5	2975	50.9	18.1	30.9	39.7	30.9	19.0
6	2940	62.5	109.0	38.2	96.3	40.6	118.4
7	2930	6.40	96.7	7.98	82.2	7.33	88.3
8	2895	29.3	129.4	31.8	85.4	31.9	95.6
9	2890	42.7	70.0	25.3	129.1	23.3	212.7
10	1595	9.74	25.9	2.10	27.4	8.54	10.2
11	1590	18.9	6.69	12.2	7.54	18.0	36.4
12	1580	18.7	1.54	11.1	4.51	24.4	2.82
13	1480	2.65	0.55	4.00	0.45	6.67	0.54
14	1465	6.64	20.6	7.43	20.6	10.5	9.74
15	1440	0.46	28.8	0.91	26.5	1.62	16.8
16	1420	32.3	0.94	21.8	1.22	0.83	10.1
17	1380	0.88	2.60	1.08	3.75	3.16	2.26
18	1375	3.60	4.25	1.14	0.70	7.05	5.92
19	1320	4.24	3.52	3.98	16.2	4.78	7.51
20	1260	0.13	9.25	0.08	8.01	0.41	3.43
21	1225	1.32	7.32	0.97	4.76	9.24	33.3
22	1220	3.76	4.64	0.64	7.19	1.30	6.77
23	1190	4.43	7.25	4.92	9.95	16.7	3.74
24	1185	5.90	1.94	5.16	2.44	2.15	0.93
25	1130	7.91	3.71	8.72	2.60	3.35	5.55
26	1125	1.06	16.8	0.01	4.08	3.71	2.22
27	1105	7.42	1.43	0.80	20.3	1.51	0.24
28	1100	0.04	0.40	10.5	8.85	0.03	0.31
29	1060	9.61	13.9	0.07	0.15	2.51	11.2
30	1040	0.56	2.11	3.04	8.22	1.36	7.74
31	1030	0.07	1.49	0.63	3.25	0.02	0.78
32	1020	2.34	11.0	0.14	2.87	1.52	0.45
33	970	16.5	0.84	11.2	1.56	39.4	0.10
34	800	1.52	11.0	1.69	9.98	2.78	0.20
35	775	0.99	1.22	1.05	0.12	7.64	21.8
36	710	32.6	0.37	20.4	0.50	15.5	0.13
37	630	5.14	4.87	4.02	4.90	0.44	3.09
38	625	0.69	1.67	0.61	1.91	11.4	1.24
39	490	0.45	4.41	0.27	3.55	17.2	2.48
40	400	3.20	0.24	2.68	0.34	1.69	0.18
41	360	0.57	0.06	0.52	0.09	0.72	0.58
42	300	0.34	1.40	0.22	1.39	5.77	1.01
43	260	0.10	0.04	0.12	0.07	0.22	0.07
44	160	0.11	4.29	0.07	4.58	2.04	4.03

the C–H stretching vibrations are observed at 3080, 3060, 3040 and 3030 cm^{-1} . These assigned frequencies are in line with the literature. The C–H in-plane and out-of-plane bending vibrations generally lies in the range 1000–1300 cm^{-1} and 950–800 cm^{-1} respectively [34–37]. Four C–H in-plane bending vibrations of the 3-EP are identified at 1320, 1260, 1225 and 1220 cm^{-1} . The C–H out-of-plane bending vibrations are observed at 1100, 1060 and 1040 cm^{-1} . The values of both the C–H in-plane and the C–H out-of-plane bending vibrations are relatively high when compared with the literature data and is purely due to the substitutions.

4.2.4. Methyl group vibrations

The assignments of methyl group vibration make a significant contribution to the 3-EP spectra. The 3-EP molecule possesses one CH_3 group and one CH_2 group in the heterocyclic ring. For

the assignments of CH_3 group frequencies nine fundamentals are expected with each CH_3 group; three stretching, three in-plane bending and three out-plane bending modes. The C–H stretching for CH_3 usually occurs at lower frequencies (2800–3000 cm^{-1}) than those of the aromatic ring (3000–3100 cm^{-1}). The asymmetric and symmetric stretching vibrations generally lies in the ranges 3010–2970 cm^{-1} and 2940–2850 cm^{-1} [38–40]. In the present study, the bands at 2975, 2940 and 2930 cm^{-1} are attributed to C–H stretching modes of the methyl groups and the bands at 2895 and 2890 cm^{-1} are attributed to C–H stretching modes of the CH_2 group. All the assigned C–H stretching vibrations are in line with the literature.

For methyl substituted pyridine derivatives, the C–H in-plane and out-of-plane bending vibrations are normally observed in the region of 1300–1000 cm^{-1} and 900–700 cm^{-1} respectively [41,42].

Table 4

Standard deviation of frequencies computed by HF/DFT (B3LYP) at 6-31G(d,p) and 6-311++G(d,p) basis sets.

S. No.	Basic set levels	Total values	Average	Standard deviation average	Deviation ratio
1	Experimental	62,655	1423.9		
2	HF/6-31(d,p)	68,265	1551.4	93.17	2.15
3	B3LYP/6-31(d,p)	63,710	1447.9	43.21	
3	B3LYP/6-311++(d,p)	63,305	1438.7	48.75	1.91

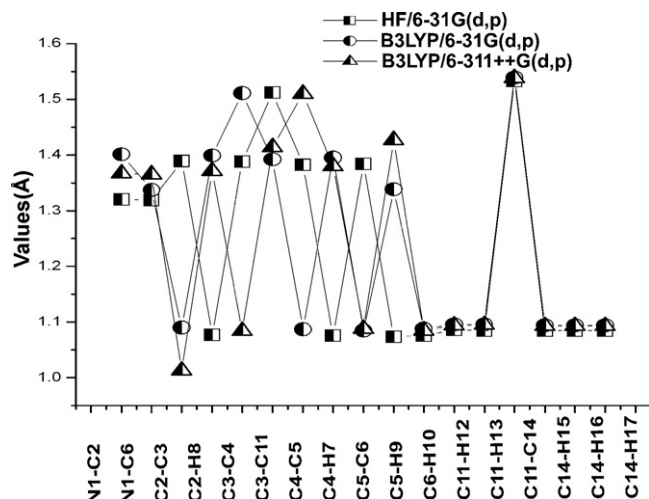


Fig. 6. Bond length differences between theoretical approach [HF and DFT].

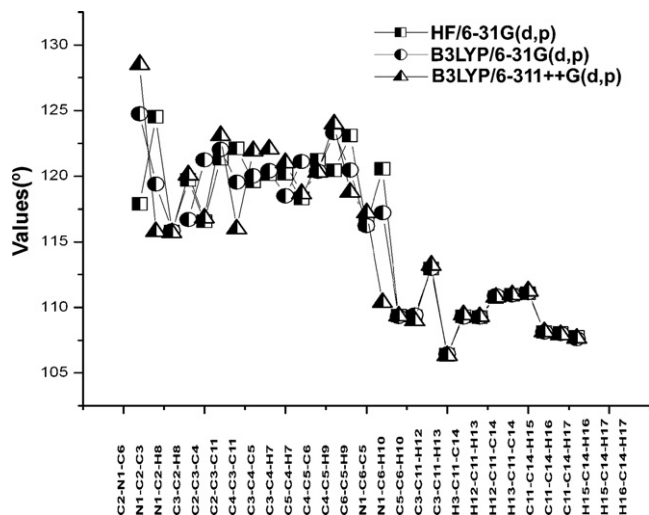


Fig. 7. Bond angle differences between theoretical approach [HF and DFT].

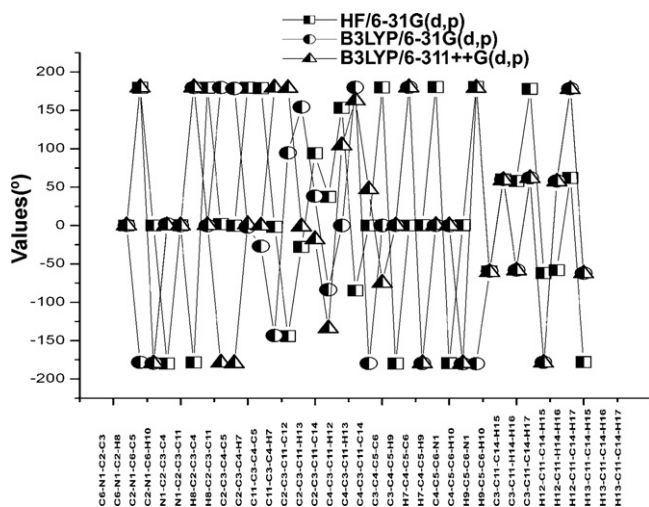


Fig. 8. Dihedral angle differences between theoretical approach [HF and DFT].

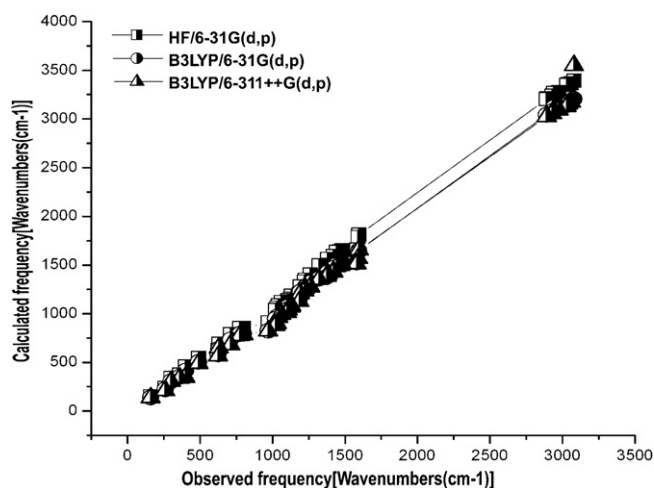


Fig. 9. Comparative graph of experimental and calculated frequencies HF and DFT [B3LYP].

In this case, the bands are observed at 1190, 1185, 1130, 1125 and 1105 cm^{-1} for C–H in-plane and the bands are found at 1030, 1020 and 970 cm^{-1} for out-of-plane bending vibrations. According to the literature, the first two of C–H out of plane bending vibrations are slightly higher than the expected range. This is merely due to the chain of CH_2 and CH_3 . The deformation of CH_3 group is usually observed at around 1450–1380 cm^{-1} [43,44]. As expected, the bands are appeared at 1440 and 1420 cm^{-1} in FT-IR and FT-Raman spectra for CH_3 deformation vibrations. The theoretically calculated values by B3LYP/6-311++G(d,p) coincide very well with the experimental value.

4.2.5. C–C vibrations

The bands between 1400 and 1650 cm^{-1} in benzene derivatives are usually assigned to C=C and C–C stretching modes [45,46]. In this molecule, the C=C stretching vibrations are found at 1595 and 1590 cm^{-1} and the C–C stretching modes assigned at 1480 and 1465 cm^{-1} . These assignments are in line with the literature. These vibrations are not much affected by the substitution of N atom in the ring. The CCC in plane bending vibrations observed at 800 and 775 cm^{-1} and the C–H out of plane bending vibrations at 625 and 490 cm^{-1} . These assignments are slightly higher than expected region [47], which shows that the substitution of N atom in the ring.

4.2.6. C–N vibrations

The identification of C–N vibration is a very difficult task, since the mixing of vibrations is possible in this region. However, the C=N and C–N vibrations are identified assigned in this study. A FT-IR band is observed at 1580 cm^{-1} and is assigned to the C=N stretching vibration and a FT-Raman band is observed at 1260 cm^{-1} . The in-plane bending vibrations of C=N and C–N are observed at 710 cm^{-1} and 630 cm^{-1} respectively. These assignments are supported by the literature [48,49].

4.2.7. C–CH₃ vibrations

The C–CH₃ stretching vibrations are usually mixed with C–H in plane bending vibration. In this case, the C–CH₃ stretching vibration is observed at 1380 cm^{-1} . The C–CH₃ in-plane bending vibration is assigned at 400 cm^{-1} and out-of-plane bending vibration is assigned at 300 cm^{-1} . These assignments are in good agreement with the literature [50].

4.2.8. C–CH₂ vibrations

The C–CH₂ stretching vibration is observed at 1375 cm^{-1} . The C–CH₂ in-plane bending vibration is assigned at 360 cm^{-1} and

out-of-plane bending vibration is assigned at 260 cm^{-1} . These assignments are in good agreement with the literature [51].

5. Conclusion

Complete vibrational analysis of 3-Ethylpyridine is performed on the basis of HF/6-31G(d,p) and density functional theory (DFT) calculations with B3LYP/6-31G and B3LYP/6-311++G(d,p) basis set combinations. The fundamental vibrational frequencies and intensity of vibrational bands were evaluated using the above said basis set combinations. The responsibility of N in the ring and C_2H_5 groups in the vibrational frequencies of the 3-EP are discussed. The various modes of vibrations are assigned and the vibrational frequencies made by quantum mechanical calculation of B3LYP/6-311++G(d,p) method agree satisfactorily with FT-IR and FT-Raman experimental results. This study demonstrates that DFT calculation at B3LYP method is a powerful approach for understanding the vibrational spectra of hetero aromatic compounds.

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