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A Comparative Study on the Molecular Structures and Vibrational Spectra of 2-, 3- and 4-Cyanopyridines by Density Functional Theory.

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Abstract:*The optimized molecular structures, harmonic vibrational wavenumbers, and corresponding vibrational assignments of 2-, 3- and 4-cyanopyridines have been calculated using Gaussian 03 set of quantum chemistry code. Calculations were carried out at Becke-3-Lee-Yang-Parr (B3LYP) density functional theory (DFT) level using the standard 6-311++G(d,p)basis set. The geometrical parameters, thermodynamic parameters, highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), Infrared intensities, Raman activities and molecular electrostatic potentials results are reported. Reliable vibrational assignments have been made on the basis of Potential Energy Distribution (PED) using VEDA4 program. Theoretical results have been successfully compared with the available experimental data.*
Keywords: *Cyanopyridine, DFT, PED, Vibrational spectra,*

I. Introduction

The three isomeric compounds 2-cyanopyridine (2-CNP), 3-cyanopyridine (3-CNP) and 4-cyanopyridine (4-CNP) which are also known as picolinotrile, nicononitrile andisonicotionitrile, respectively contain cyano group (CN) substituted at ortho, meta, para positions of pyridine ring. These cyanopyridines have applications in pharmaceutical [1-3], corrosion inhibition [4], catalysis [4, 5], synthesis of organic compounds and organometallic complexes [7-10]. Cyanopyridines are widely used as a starting material and intermediates for the synthesis of high valued carboxylic acids and amides. For example, 3-CNP is a value intermediate in the synthesis of nicotinic acid (vitamin B3, niacin) and nicotinamide (drugs) [1, 2, 11-15]. Since nitrogen of both cyano group and the pyridine ring of cyanopyridines are capable of coordinating with metal ions, these compounds are also used in the synthesis of organometallic complexes [7-10].

Green et al. [16] recorded the vibrational infrared and Raman spectra of the title compounds and suggested assignments of the observed vibrational wavenumbers. Oliver et al. [17] investigated the configuration of 4-CNP on Au (111) electrodes in percholate solution by in situ visible-infrared sum frequency generation. Laing et al. [18] reported crystal structure of 4-CNP from three dimensional single X-ray data collected by standard film techniques. On the other hand, the crystal structures of 2- and 3-cyanopyridines have been reported on the basis of the low temperature X-ray single crystal experiments [19].

Despite the wide applications of cyanopyridines, to the best of our knowledge, there is no detailed theoretical study present in the literature about the structural and vibrational properties of these molecules. Such studies will not only aid in making definitive assignments of the fundamental normal modes and in clarifying experimental data but will also be helpful in context of further studies of these molecules. The B3LYP density functional theory calculations exhibit good performance on the molecular geometries and vibrational properties of organic compounds [20-25]. Thus, the aim of this work is to take advantage of the quantum-mechanical calculations to carryout systematic study on the molecular structure and vibrational spectra which will give depth insight in understanding the properties of the title molecules and aid in clarifying and complementing available experimental data. This paper will reveal additional quantitative chemical knowledge and detailed insight about the molecular structure, thermodynamic properties, vibrational spectra and assignments of vibrational mode of these compounds.

II. Computational Methods

Gaussian 03 program package [26] was used to optimize the structures, predict energies, and calculate thermodynamic parameters, atomic charges and vibrational wavenumbers of 2-CNP, 3-CNP and 4-CNP. Computations were performed using Density Functional Theory (DFT) adopting Becke's three-parameter exchange functional [28] combined with Lee-Yang-Parr [29] correlation functional (B3LYP) methods. The standard 6-311++G(d,p) basis set was used for all the atoms to carry out the calculations utilizing the $C_s$symmetry of 2-CNP and 3-CNP and C_{2V} symmetry of the symmetrical 4-CNP. The infrared data are reported, and each of the vibrational modes was visually confirmed by Gauss-View program [30]. The VEDA4 program

[31] was used to characterize the normal vibrational modes on the basis of Potential Energy Distribution. The wavenumbers and intensities obtained from the computations were used to simulate infrared spectra. In addition, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy values, HOMO-LUMO energy gaps, molecular electrostatic potentials (MEP) for the three isomeric compounds were calculated at B3LYP/6-311++G(d,p) level of theory.

III. Result and Discussion

3.1 Molecular Geometry

The optimized molecular structures along with the numbering of atoms of 2-, 3- and 4-cyanopyridines calculated at B3LYP/6-311++G(d,p) level of theory are given in Fig. 1. The geometrical parameters (bond lengths and bond angles) corresponding to the optimized geometries of the title molecules are given in Table 1 along with the X-ray experiment data [18, 19]. Generally, most of the optimized bond lengths are slightly longer than the experimental values, and the bond angles are slightly different from the experimental ones. This is expected because, one isolated molecule is considered in theoretical gas phase calculation, whereas packed molecules are considered in solid phase during the experimental measurement. However, the calculated geometric parameters are in good agreement with the experimental results. To be specific, the root meansquare (RMS) errors are 0.017Å, 0.009 Å and 0.012 Å for the bond lengths of 2-CNP, 3-CNP and 4-CNP respectively; while the RMS errors for the bond angles are found to be 0.99°, 0.54° and 0.61°for the 2-CNP, 3-CNP and 4-CNP respectively. In addition, the calculation also shows that there are no systematic and significant changes in the geometric parameters of the three molecules. The position of the cyano group has nosignificant effect of the geometric parameters of the molecules. The C≡N bond lengths of the three molecules are calculated to be around 1.155 Å, and the average bond distance between the pyridine ring and the cyano group (C-CN) for the three molecules is 1.435 Å. The average values for the pyridine ring C-C and C-H bond lengths are 1.379 Å and1.084 Å; 1.397 Å and1.084 Å; 1.382 Å and1.084 Å in2-CNP, 3-CNP and 4-CNP respectively. The bond lengths and the bond angles of the three isomers are comparable to the values found in 2-, 3- and 4-formylpyridines [21].

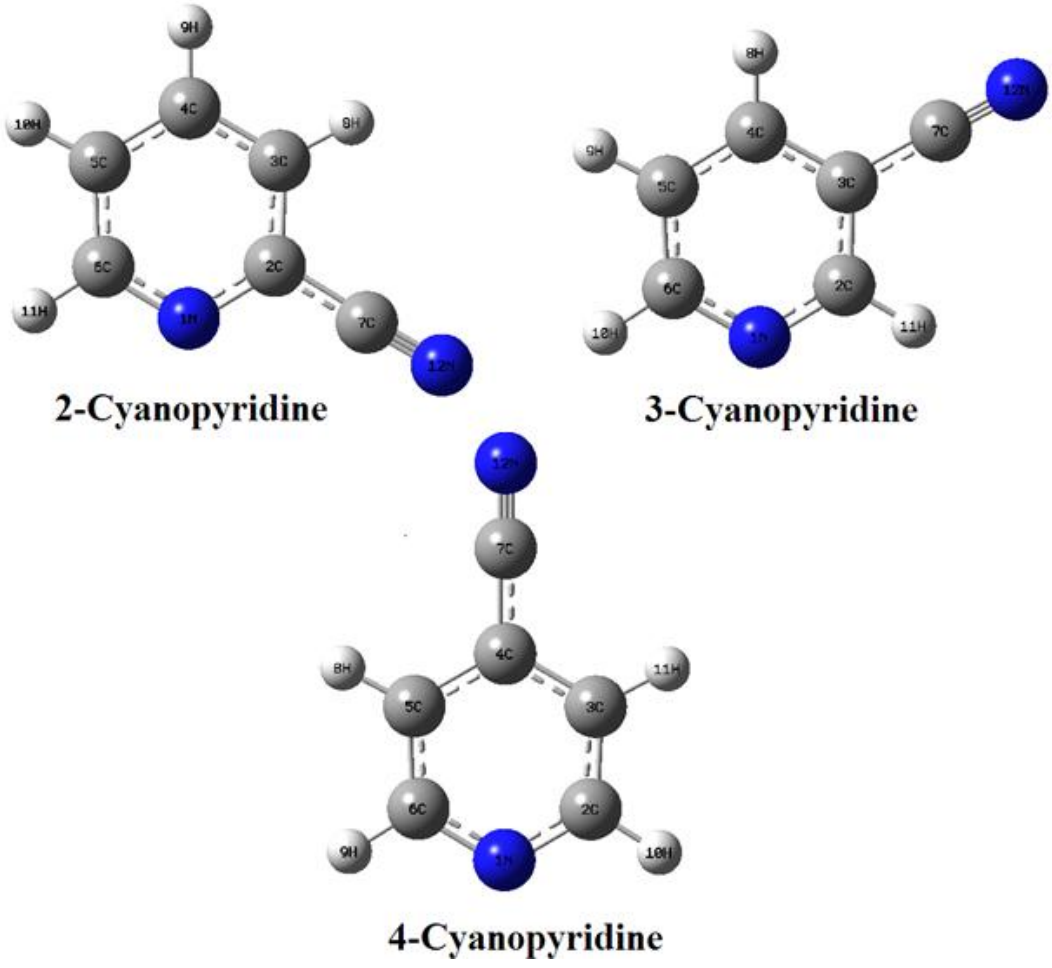

Figure 1. Optimized molecular structure along with atom numbering of 2-, 3- and 4- cyanopyridines.

Table 1: Experimental and calculated optimized geometrical parameters for 2-, 3- and 4-cyanopyridines.

Geometry Parameter[a]	2-Cyanopyridine		3-Cyanopyridine		4-Cyanopyridine	
	Expt[b]	Calc	Expt[b]	Calc	Expt[c]	Calc
Bond lengths(Å)						
N_1-C_2	1.344	1.340	1.335	1.33	1.331	1.336
C_2-C_3	1.374	1.340	1.392	1.404	1.383	1.392
C_3-C_4	1.368	1.390	1.386	1.401	1.381	1.399
C_4-C_5	1.376	1.391	1.376	1.388	1.381	1.399
C_5-C_6	1.378	1.396	1.384	1.395	1.383	1.392
C_6-N_1	1.340	1.333	1.337	1.337	1.331	1.336
C_n-C_7	1.448(C_2)	1.442(C_2)	1.430(C_3)	1.429(C_3)	1.439 (C_4)	1.433 (C_4)
C_7≡N_{12}	1.145	1.154	1.150	1.155	1.137	1.155
C-H_8	- (C_2)	1.083	- (C_2)	1.085(C_2)	- (C_2)	1.086(C_2)
C-H_9	- (C_4)	1.084	- (C_4)	1.083(C_4)	- (C_3)	1.082(C_3)
C_5-H_{10}	-	1.083	-	1.083	-	1.082
C_6-H_{11}	-	1.086	-	1.086	-	1.086
Bond Angles(°)						
$N_1C_2C_3$	124.8	123.8	122.5	123.1	123.9	123.7
$C_2C_3C_4$	118.3	118.0	119.5	118.5	117.5	118.1
$C_3C_4C_5$	118.9	118.8	118.1	118.3	120.0	118.7
$C_4C_5C_6$	118.7	118.6	118.8	118.7	117.5	118.1
$C_5C_6N_1$	124.1	123.6	123.9	123.6	123.9	123.7
$C_6N_1C_2$	115.2	117.2	117.2	117.8	117.3	117.6
$C_nC_7N_{12}$	179.2(C_2)	178.0(C_2)	179.5(C_3)	179.9(C_3)	180.0(C_4)	180.0(C_4)

[a]The atom numbering is given in Fig.1; [b] Taken from Ref. [19]; [c] Taken from Ref. [18].

3.2 Vibrational Spectra

Optimized structural parameters were used to compute the vibrational wavenumbers for the three cyanopyridines at B3LYP/6-311++G(d,p) level of theory. Since DFT hybrid B3LYP functional tends to overestimate the fundamental modes, the calculated vibrational wavenumbers are usually higher than the observed vibrational modes, and the differences are accounted for by using scaling factor. Therefore, the calculated vibrational wavenumbers are scaled with 0.955 and 0.977 for the vibrational wavenumbers above and below 1800 cm^{-1} respectively [32]. Tables 2-4 present the calculated vibrational wavenumbers, IR intensities and Raman activities along with assignments of vibrational modes for the three cyanopyridines. Each of these Tables gives the observed infrared wavenumbers [16] of the three molecules for comparison. The assignment of the fundamental vibrational modes is proposed on the basis of Potential Energy Distribution (PED) using VEDA 4 program and the animation option of Gauss View graphical interface of Gaussian program.

From the optimized structures, it is observed that 2-CNP and 3-CNP have C_s point group symmetry, while 4-CNP has C_{2v} point group symmetry. The three isomers of the cyanopyridine are composed of 12 atoms. Thus, the calculations result in thirty IR fundamental vibrations that belong to irreducible representations Γ_{vib} = 21 A′ + 9 A″ of the C_s point group of 2-CNP and 3- CNP, and Γ_{vib} = $11A_1 + 3A_2 + 6B_1 + 10B_2$ of the C_{2v} point group of 4-CNP. The absence of imaginary wavenumbers in the calculated vibrational spectrum confirms that the optimized structures correspond to the minimum energy. The A_1 and B_2 irreducible representations correspond to stretching, ring deformation, and in-plane bending vibrations, while A_2 and B_1 correspond to ring, torsion and out of plane bending vibrations. Similarly, the A′ and A″ irreducible representations correspond to in-plane and out-of-plane modes respectively. The B3LYP/6-311++G(d,p) calculations give the value of C≡N stretching modes at 2289 cm^{-1}, 2258 cm^{-1} and 2263 cm^{-1} for 2-CNP, 3-CNP and 4-CNP respectively.

In order to investigate the performance of the theoretical calculation, the root mean square (RMS) error between the calculated and observed wavenumbers were calculated using the following equation (1).

$$RMS = \sqrt{\frac{\sum_i^n (v_i^{calc} - v_i^{exp})^2}{n - 1}} \quad \text{---------1}$$

The RMS errors of the observed IR bands are found to be 16 cm^{-1}, 15 cm^{-1} and 13 $cm^{-1}$for 2-CNP, 3-CNP and 4-CNP respectively. Similarly, the correlation values obtained from the graph of observed wavenumbers against calculated wavenumbers are found to be 0.9996, 0.9997 and 0.9998 for 2-CNP, 3-CNP and 4-CNP respectively. Both RMS and correlationvalues clearlyshow the very good agreement between observed and calculated vibrational wavenumbers, which indicates that the B3LYP/6-311++G(d,p) calculation

is reliable for the prediction of vibrational spectra.The vibrational wavenumbers and the corresponding intensities obtained from B3LYP/6-311++G(d,p) calculations were used to simulate the infrared and Raman spectra of the studied molecules. For simulation, pure Lorentizian band shape with a bandwidth of full width and half maximum (FWHM) of 10 cm^{-1} was used to plot the calculated IR and Raman spectra. The simulated IR and Raman spectra of the three molecules are presented in Figs. 2 and 3. These figures clearly show the difference in spectral characteristics of the title molecules. Calculated Raman activities (S_i)were converted to relative Raman intensities (Ii) using the following equation (2) derived from the intensity theory of Raman scattering [33, 34].

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i[1 - \exp\left(-\frac{hc\nu_i}{kT}\right)]} \quad ----------2$$

Where ν_0 is the laser exciting wavenumber in cm^{-1}, ν_i is the vibrational wavenumber of the ith normal mode, and f is a suitable common normalization factor for all peak intensities, 10^{-4}. h, k, c and T are Planck and Boltzman constants, speed of light and temperature in Kelvin, respectively.

Table 2: Experimental and corresponding scaled theoretical vibrational wavenumbers (cm^{-1}) of 2-cyanopyridine.

No.	Sym.	Expt[a]	ν[b]	I_{IR}[c]	I_R[c]	Assignment (PED ≥ 10%)
ν_1	A′	3088	3061	1.66	183.43	υCH (95)
ν_2	A′	3064	3053	8.04	112.96	υCH (96)
ν_3	A′	3005	3038	3.84	83.51	υCH (92)
ν_4	A′	-	3020	10.37	98.66	υCH (92)
ν_5	A′	2238	2289	6.65	411.15	υCN(90) + υCC(10)
ν_6	A′	1580	1583	19.96	84.75	υCC (57) + δHCC(13)
ν_7	A′	1574	1571	20.07	7.76	υCC (58) + δHCC(14)
ν_8	A′	1462	1460	21.00	4.23	υCC (34) + δHCC(50)
ν_9	A′	1432	1424	17.92	7.18	δHCC(57)
ν_{10}	A′	1295	1288	1.78	3.17	υCC(33) + δHCC(56)
ν_{11}	A′	1248	1263	4.59	0.45	υCC(79)
ν_{12}	A′	1207	1206	3.14	51.01	υCC(39) + δCNC(25) + δHCC(12)
ν_{13}	A′	1155	1147	2.35	3.98	υCC(13) + δHCC(73)
ν_{14}	A′	1091	1091	2.65	1.74	υCC(37) + δHCC(35)
ν_{15}	A′	1045	1041	5.36	17.37	υCC(44) + δHCC(12) + δCCC(24)
ν_{16}	A″	992	994	0.01	0.20	τHCCC(67) + τCCCN(13)
ν_{17}	A′	981	985	6.52	36.15	υCC(41) + δCCC(44)
ν_{18}	A″	933	964	0.56	0.05	τHCCC(81) + τCNCC(10)
ν_{19}	A″	896	895	0.58	0.00	τHCCC(82)
ν_{20}	A″	777	783	42.77	0.95	τHCCC(53) + τCNCC(37)
ν_{21}	A′	-	775	3.73	9.32	υCC(24) + δCNC(56)
ν_{22}	A″	734	735	14.25	0.16	τHCCC(47) + τCNCC(46)
ν_{23}	A′	632	631	1.30	2.58	δCCC(67) + δCCN (11) + δCNC(10)
ν_{24}	A″	553	562	11.17	2.47	τHCCC(10) + τNCCC(34) +
ν_{25}	A′	-	558	2.88	3.34	δCCN(79)
ν_{26}	A′	477	474	0.40	3.98	υCC(32) + δCNC(49)
ν_{27}	A″	403	404	5.49	0.30	τHCCC (12) + τCNCC(80)
ν_{28}	A″	362	362	0.74	1.48	τNCCC (41) + τCCCN (44)
ν_{29}	A′	-	169	2.55	3.41	δCCN(85) + δCCN(10)
ν_{30}	A″	-	138	0.50	0.31	τNCCC(19) + τCCNC(65)

[a]Taken from Ref. [21];
[b]Scaled IR vibrational wavenumbers (scaled with 0.955 above 1800 cm^{-1} and 0.977 under 1800 cm^{-1})
[c]I_{IR}, calculated infrared intensities in km mol^{-1}; I_R, calculated Raman intensities in $Å^4$ amu^{-1}.

Table 3: Experimental and corresponding scaled theoretical vibrational wavenumbers (cm^{-1}) of 3-cyanopyridine.

No.	Sym.	Expt[a]	ν[b]	I_{IR}[c]	I_R[c]	Assignment (PED ≥ 10%)
ν_1	A′	3088	3059	4.15	168.16	υCH (98)
ν_2	A′	3050	3045	3.80	84.27	υCH (95)
ν_3	A′	3036	3027	3.41	76.69	υCH (96)
ν_4	A′	3012	3056	11.56	109.1	υCH (92)
ν_5	A′	2237	2258	28.39	418.48	υCN(89) + υCC(12)
ν_6	A′	1586	1590	20.18	88.98	υCC (56) + δHCC(14)
ν_7	A′	1562	1561	13.56	7.29	υCC (60) + δHCN(10)
ν_8	A′	1471	1470	13.00	3.66	υCC (23) + δHCC(46)
ν_9	A′	1415	1412	24.22	2.52	δHCN(43) + δCNC(10)
ν_{10}	A′	1333	1332	1.68	1.03	δHCN(86)
ν_{11}	A′	1234	1249	0.26	2.38	υCC(80)
ν_{12}	A′	1211	1206	4.16	19.90	υCC(37) + δHCC(25)
ν_{13}	A′	1185	1188	5.21	25.54	υCC(40) + δHCN(11) + δHCC(11)
ν_{14}	A′	1122	1116	5.01	3.16	υCC(21) + δHCC(41)
ν_{15}	A′	1033	1036	0.71	33.13	υCC(66) + δHCC(13)
ν_{16}	A″	1023	1015	11.16	20.83	δCNC(63)
ν_{17}	A′	958	982	0.00	0.04	τHCCC(68) + τCCCN(20)
ν_{18}	A″	926	956	1.32	0.07	τHCCC(79)
ν_{19}	A″	902	925	0.91	0.25	τHCNC(67) + τCNCC(14)
ν_{20}	A″	803	800	26.03	0.80	τHCCN(69) + τCCNC(17)
ν_{21}	A′	776	774	0.42	10.33	υCC(27) + δCCN(60)
ν_{22}	A″	701	699	31.22	0.23	τHCNC (13) + τHCNC(19) + τHCCC(11)
ν_{23}	A′	624	625	4.27	3.69	δCCC (16) + δCNC(67)
ν_{24}	A″	548	565	2.84	2.33	τNCCC(45) + τCCCC(36)
ν_{25}	A′	542	553	0.37	1.85	δCCN(76)
ν_{26}	A′	470	467	0.29	5.87	υCC(28) + δCCC(32) + δCNC(16)
ν_{27}	A″	397	399	4.58	0.68	τCNCC (78)
ν_{28}	A″	355	356	0.50	1.45	τNCCC (25) + τCCCN (56)
ν_{29}	A′	-	164	6.53	3.71	δCCN(88)
ν_{30}	A″	-	146	3.60	0.32	τNCCC(22) + τCCCN(16) + τCCCC(47)

[a]Taken from Ref. [21].
[b]Scaled IR vibrational wavenumbers (scaled with 0.955 above 1800 cm^{-1} and 0.977 under 1800 cm^{-1})
[c]I_{IR}, calculated infrared intensities in km mol^{-1}; I_R, calculated Raman intensities in $Å^4$ amu^{-1}.

Table 4: Experimental and corresponding scaled theoretical vibrational wavenumbers (cm^{-1}) of 4-cyanopyridine.

No.	Sym.	Expt[a]	ν[b]	I_{IR}[c]	I_R[c]	Assignment (PED ≥ 10%)
ν_1	A_1	3082	3061	0.11	200.51	υCH (95)
ν_2	B_2	3066	3061	3.22	17.45	υCH (97)
ν_3	A_1	3051	3019	2.95	123.00	υCH (96)
ν_4	B_2	3031	3054	21.63	102.90	υCH (97)
ν_5	A_1	2238	2263	12.36	375.74	υCN(89) + υCC(10)
ν_6	A_1	1591	1591	30.87	61.28	υCC (52) + δCCC(12) +δHCN(20)
ν_7	B_2	1552	1550	21.47	1.22	υCC (75) + δCCN(12)
ν_8	A_1	1487	1485	2.50	5.28	τHCCN (61) + δCCN(19)
ν_9	B_2	1406	1407	19.91	1.39	υCC(28) + δHCN(62)
ν_{10}	B_2	1324	1322	0.48	3.90	δHCC(74)
ν_{11}	B_2	1244	1237	4.38	6.75	υCN(80)
ν_{12}	A_1	1219	1217	4.98	3.61	υCC(37) + δHCN(56)
ν_{13}	A_1	1194	1192	0.56	55.61	υCC(37) + δHCN(15) + υCC(21)
ν_{14}	B_2	1081	1083	0.85	0.18	υCC(60) + δHCN(25)
ν_{15}	A_1	1067	1067	3.53	1.20	υCN(16) + δHCC(32) + δCCN(41)
ν_{16}	A_1	989	985	3.36	35.66	υCN(60) + δCCN(30)
ν_{17}	A_2	961	980	0.00	0.07	τHCNC(87) + τCCCN(10)
ν_{18}	B_1	932	960	0.73	0.02	τHCNC(72) + τCCNC(16)
ν_{19}	A_2	865	865	0.00	0.01	τHCNC(99)
ν_{20}	B_1	817	820	42.83	0.74	τHCCN(67) + τCCNC(64)
ν_{21}	A_1	772	763	14.45	10.19	υCC(25) + δCCC(59)
ν_{22}	B_1	710	731	0.03	0.02	τHCNC (24) + τCCNC(66)
ν_{23}	B_2	663	669	0.10	5.15	δCCN (79)
ν_{24}	B_1	560	573	22.8	2.94	τHCCN(22) + τNCCC(26) + τCCCC(22)
ν_{25}	B_2	-	556	0.05	2.27	δCCN(65) + τNCCC (15)
ν_{26}	A_1	454	449	0.81	4.94	υCC(13) + δCCC(65)
ν_{27}	B_1	374	382	0.92	0.89	τNCCC (20) + τCCNC(54)
ν_{28}	A_2	-	369	0.00	0.75	τHCNC (11) + τCCNC(83)
ν_{29}	B_2	166	165	7.96	4.17	δCCN(75) + τNCCC(15)
ν_{30}	B_1	147	143	9.14	0.02	τNCCC(20) + τCCCC(56) + τCCNC(10)

[a]Taken from Ref. [21].; [b] Scaled IR vibrational wavenumbers (scaled with 0.955 above 1800 cm^{-1} and 0.977 under 1800 cm^{-1})

[c]I_{IR}, calculated infrared intensities in km mol^{-1}; I_R, calculated Raman intensities in $Å^4$ amu^{-1}.

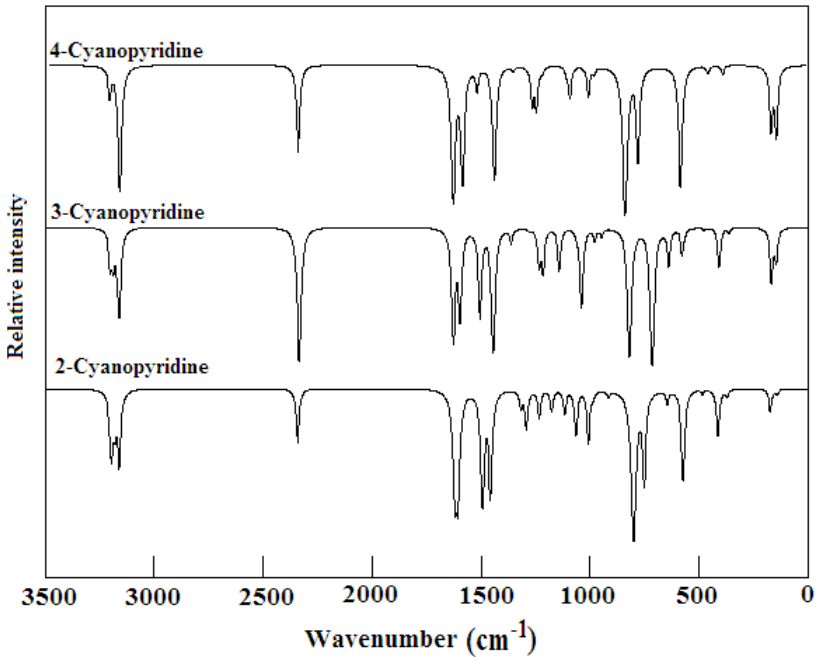

Figure 2: Simulated vibrational infrared spectra of 2-, 3- and 4-cyanopyridine.

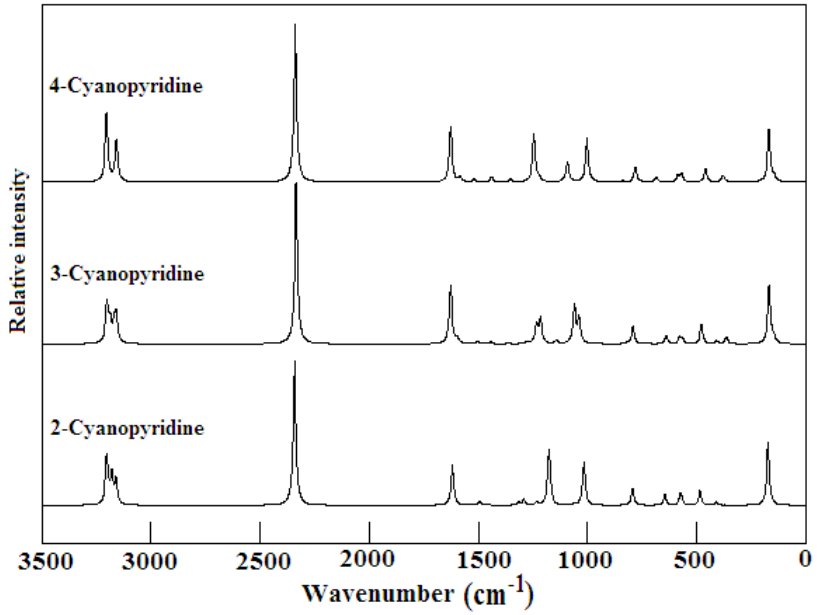

Figure 3: Simulated vibrational Raman spectra of 2-, 3- and 4-cyanopyridine.

3.3 Thermodynamic parameters and HOMO-LUMO analysis

Several thermodynamic parameters, rotational constants and dipole moments for 2-CNP, 3-CNP and 4-CNP calculated at B3LYP/6-311++G(d,p) are presented in Table 5. The zero point energy, SCF energy, entropy, and heat capacity for the title molecules are obtained from the theoretical harmonic frequency calculations. The relative stabilization energy which is the energy differences between the cyanopyridine isomers, shows that both 2-CNP and 4-CNP have higher energy than 3-CNP, while 2-CNP has the highest energy and the 3-CNP has the least energy. The same trend was reported for formylpyridines [21] where the total energy order was found to be 3-formylpyridine < 4-formylpyridine < 2-formylpyridine. These energy differences of the ortho, meta and para isomers of substituted pyridines could be explained in terms of the electronic and steric effects. The observed rotational constants and dipole moments [35] obtained from microwave spectra of the three cyanopyridines are also presented in Table 5. A comparison of the calculated rotational constants and dipole moments with the experimental values reveals that the results obtained from B3LYP/6-311++G(d,p) are in very good agreement with experimental observations.

Table 5: The calculated thermodynamics parameters 2-CNP, 3-CNP and 4-CNP

Parameter	**2-CNP**	**3-CNP**	**4-CNP**
SCF Energy (Hatree)	-340.613490	-340.615286	-340.613992
Relative Stabilization Energy (K cal mol^{-1})	1.13	0.00	0.81
Total Thermal Energy, E_{total} (K cal mol^{-1})	58.254	58.333	58.317
Heat capacity at const. volume, C_v (cal mol^{-1} k^{-1})	22.305	22.300	22.271
Entropy, S (cal mol^{-1} k^{-1})	78.193	78.267	76.857
Vibrational energy, E_{vib} (K cal mol^{-1})	56.477	56.561	56.540
Zero point vibrational energy, E_0 (K cal mol^{-1})	54.494	54.568	54.554
Rotational Constant (MHz)*			
A	5860 (5837)	5846 (5823)	6016 (6000)
B	1600 (1598)	1573 (1571)	1544 (1541)
C	1257 (1254)	1239 (1237)	1229 (1226)
Dipole moment (Debye)*	5.950 (5.78)	4.032 (3.66)	2.008 (1.96)

*Values in bracket are experiment values taken from Ref. [35].

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and their properties are very useful for predicting the most reactive position in π-electron systems. They are also useful in explaining several types of reactions in conjugated system [36]. The HOMO represents the ability to donate an electron, while the LUMO represents the ability to accept an electron. Thus, the energy of the HOMO is directly related to the ionization potential, while the LUMO energy is directly related to electron affinity, and the HOMO-LUMO energy gap is related to the molecular chemical stability. A molecule with a small HOMO-LUMO energy gap is more polarizable and is generally associated with high chemical reactivity [37, 38]. The HOMO and LUMO of the title molecules were calculated at B3LYP/6-311++G(d,p) level of theory. The3D plots generated from the calculations are illustrated in Fig. 4, while the HOMO and LUMO energies and the HOMO-LUMO energy gaps are presented in Table 6. In addition, the HOMO and LUMO energy values are used to calculate global chemical reactivity descriptors such as ionization potential (I), electron affinity (A), electronegativity (χ), chemical hardness (η), chemical softness (S), chemical potential (μ), electrophilicityindex (ω). The results are summarized in Table 6. The HOMO and LUMO are delocalized over the entire molecules of 3-CNP and 4-CNP, while those of the 2-CNP are localized on a portion of the pyridine ring of the molecule. The HOMO and LUMO energy values reflect the relative chemical stability and biological activity of the title compounds.

Table 6: The calculated HOMO and LUMO energies, HOMO-LUMO energy gap, ionization potential, electron affinity, electronegativity, chemical hardness, chemical potential, chemical softness and electrophilicity index of 2-, 3-, and 4-cyano pyridines.

Property	**2-CNP**	**3-CNP**	**4-CNP**
E_{HOMO} (hatress)	-0.29314	-0.29217	-0.29179
E_{LUMO} (hatress)	-0.0236	-0.08264	-0.09124
E_{HOMO} (eV)	-7.9765	-7.9502	-7.9398
E_{LUMO} (eV)	-0.6422	-2.2487	-2.4827
$\|\Delta E\| = E_{HOMO} - E_{HOMO}$ gap (eV)	7.3344	5.7015	5.4571
Ionization potentials, $I = - E_{HOMO}$ (eV)	7.9765	7.9502	7.9398
Electron affinity, $A = - E_{LUMO}$ (eV)	0.6422	2.2487	2.4827
Electronegativity, $\chi = (I + A)/2$ (eV)	4.3094	5.0994	5.2113
Chemical hardness, $\eta = (I - A)/2$ (eV)	3.6672	2.8507	2.7286
Chemical potential, $\mu = -(I + A)/2$ (eV)	-4.3094	-5.0994	-5.2113
Chemical softness, $S = 1/(2\eta)$ (eV^{-1})	0.1363	0.1754	0.1832
Electrophilicity index, $\omega = \mu^2/2\eta$(eV)	2.5320	4.5610	4.9765

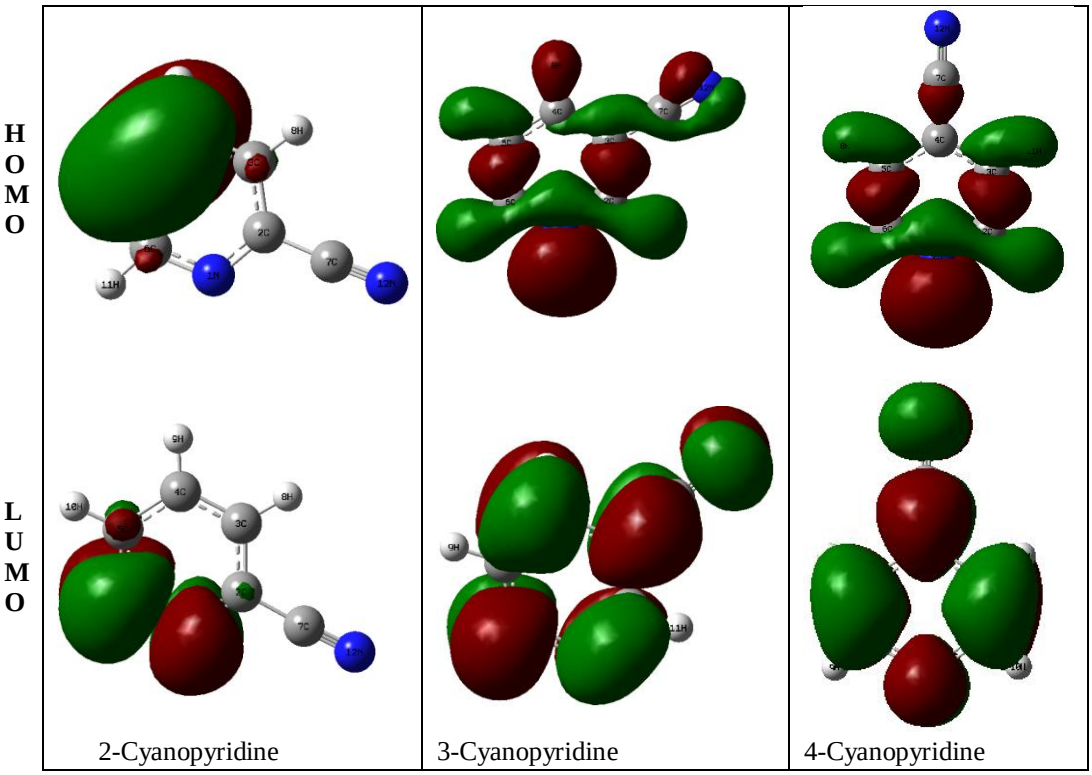

Figure4. 3D plots of HOMO (top) and LUMO (bottom) orbital of 2-, 3-, and 4-cyano pyridines computed at B3LYP/6-311++G(d,p) level.

3.4 Molecular Electrostatic Potentials and Atomic charges

Atomic charges' calculation plays an important role in the applications of quantum chemical calculations to the molecular system because atomic charges affect molecular properties such as dipole moment, polarizability, and electronic structure. The charge distributions calculated by Mulliken method for the optimized geometries of the three cyanopyridines are listed in Table 7. The result shows that the positive charges are mainly localized on hydrogen atoms, while the carbon atoms are found to be either positive or negative. The cyano group nitrogen atoms (N_{12}) are found to be more negative than the pyridine ring nitrogen atoms (N_1) for all the three isomers. This implies that the cyano group nitrogen is more nucleophilic than the pyridine nitrogen.

Table 7: TheMulliken atomic charges of the optimized structures of 2-, 3- and 4-cyano pyridines.

Atom No.	Mulliken atomic charges		
	2-CNP	3-CNP	4-CNP
N_1	0.047	-0.019	-0.041
C_2	0.471	-0.545	-0.382
C_3	0.391	1.743	0.038
C_4	-0.443	-0.069	1.496
C_5	0.156	0.110	0.041
C_6	-0.228	-0.326	-0.382
C_7	-0.990	-1.541	-1.387
H_8	0.222	0.208	0.207
H_9	0.189	0.189	0.185
H_{10}	0.193	0.192	0.185
H_{11}	0.197	0.229	0.206
N_{12}	-0.204	-0.170	-0.167

Molecular Electrostatic Potential (MEP) is very important in the study of molecular interactions, prediction of relative sites for nucleophilic and electrophilic attack, molecular cluster and predication wide range of macroscopic properties [39, 40]. The 3D plots of the molecular electrostatic potentials were calculated by

using the optimized molecular structures at B3LYP/6-311++G(d,p) level for the three cyanopyridines. The results areillustrated in Figs. 5-7. The electrostatic potentials at the surface are represented by different colors; red, blue and green represent the regions of negative, positive and zero electrostatic potentials respectively. In addition, the negative regions (red color) of MEP are related to electrophilic reactivity, and the positive regions (blue color) are related to the nucleophilic reactivity. As can be seen from Figs. 5-7, the negative electrostatic potentials are localized over the nitrogen atoms of the cyano group (CN) and the pyridine ring, and are potential sites for electrophilic attach. The positive regions are localized around the hydrogen atoms.

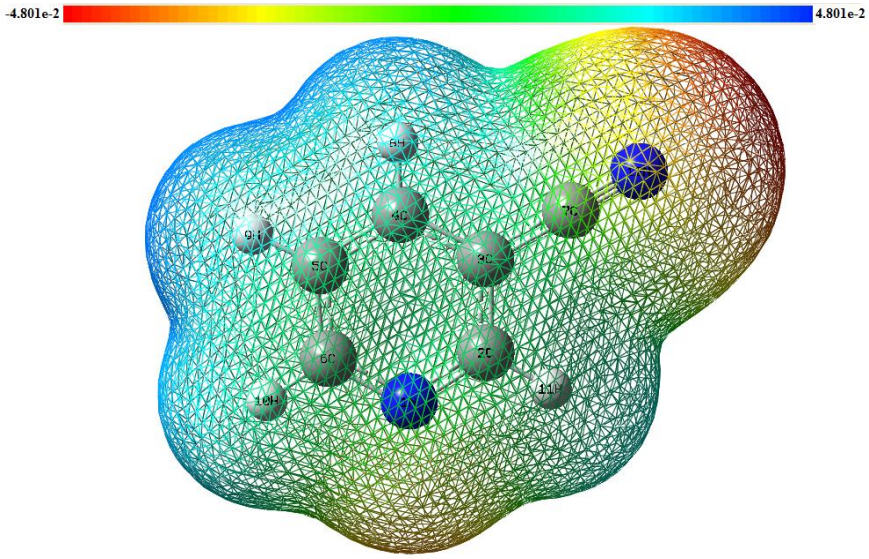

Figure 5.Molecular electrostatic potential energy surface (MEP) for 2-Cyanopyridine

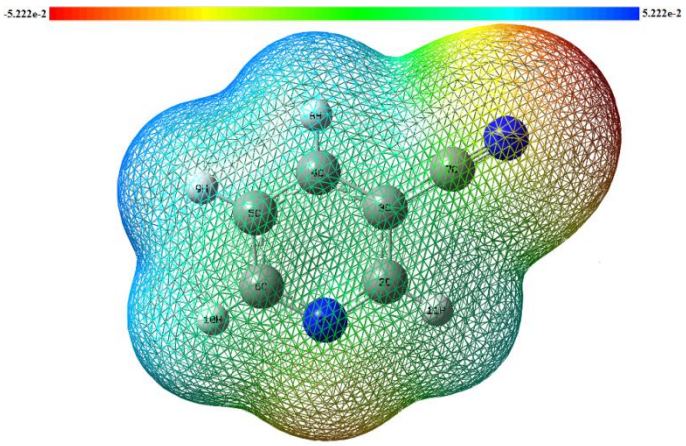

Figure 6.Molecular electrostatic potential (MEP) energy surface for 3-Cyanopyridine

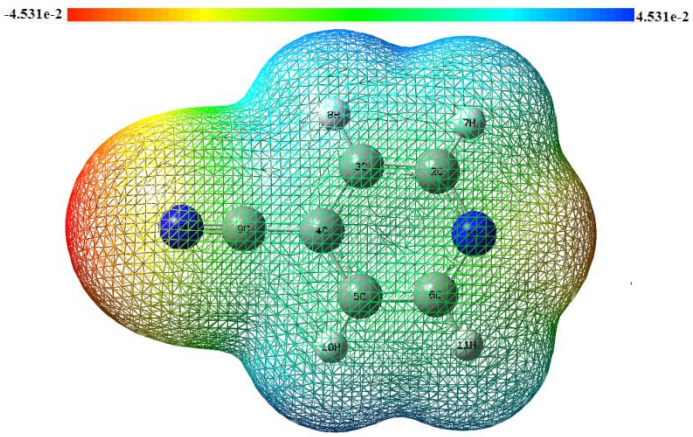

Figure 7.Molecular electrostatic potential (MEP) energy surface for 4-Cyanopyridine

IV. Conclusion

The theoretical structures of three isomeric compounds of cyanopyridines were determined by using the B3LYP/6-311++G(d,p) level of theory. The calculated geometries of the title compounds are in good agreement with the experimental data obtained from X-ray measurement. The optimized structures were used to calculate the vibrational wavenumber, and a reliable assignment of the vibration modes for the three cyanopyridines is proposed on the basis of potential energy distribution (PED). The RMS values calculated for the scaled vibrational modes clearly show a very good agreement with the available experimental data. The RMS and correlation values between the experimental and vibrational wavenumbers are found to be 16 cm^{-1} and 0.9996, 15 cm^{-1} and 0.9997, 16 cm^{-1} and 0.9996, 13 cm^{-1} and 0.9998 for 2-cyanopyridine, 3-cyanopyridine and 3-cyanopyridine respectively. The position of the cyano group (CN) has no signification on the geometric parameters and vibrational spectra of title compounds. The atomic charges, HOMO and LUMO energies, thermodynamic parameters and molecular electrostatic potentials of the molecules were determined and analyzed. The results presented in this paper indicate that density functional theory is reliable for predicting the molecular structures, vibrational spectra and thermodynamic properties of title compounds.

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