

# Experimental (FT-IR and FT-Raman spectra) and Theoretical (Ab initio/HF, DFT/B3LYP) Study of 2-Amino-5-Chloropyridine and 2-Amino-6-Chloropyridine

Jamelah S. Al-Otaibi

Department of Chemistry, College of Science, Princess Nourah bint Abdulrahman University,  
Riyadh 11951, Saudi Arabia  
E-mail: dr.jamelah@gmail.com

## Abstract

The Fourier transform infrared (FT-IR) and FT-Raman spectra of 2-amino-5-chloropyridine (2A5CP) and 2-amino-6-chloropyridine (2A6CP) have been recorded in the regions  $4000\text{--}400\text{ cm}^{-1}$  and  $4000\text{--}100\text{ cm}^{-1}$ , respectively. The observed FT-IR and FT-Raman data, a complete vibrational assignment and analysis of the fundamental modes of the compounds were carried out. All the geometrical parameters have been calculated by HF and DFT (B3LYP) methods with 6-311++G (d, p) basis set. The vibrational wavenumbers, IR intensities and Raman activities are calculated at the same theory levels used in geometry optimization. The calculated frequencies are scaled and compared with experimental values. The scaled B3LYP/6-311++G(d,p) results show the best agreement with the experimental values. The calculated HOMO–LUMO energies show that charge transfer occurs in the molecules.

**Keywords:** FT-IR, FT-Raman, ab initio, DFT, 2-amino-5-chloropyridine, 2-amino-6-chloropyridine.

## 1. Introduction

Pyridine and its derivatives has been the subject of investigation by several workers in the last 50 years. The pyridine derivatives are widely used in the syntheses of various biologically active compounds and have attracted interest of numerous investigators [1–4]. The pyridine ring appears in a large number of natural substances such as vitamin B5, vitamin B6, pyridoxal and pyridoxamine, and drugs such as nifedipine, nichetamine and sulphapyridine. Some of pyridine derivatives show antimicrobial, antifungal, antibacterial, pesticidal, antiallergic, antihypertensive, antitumor or analgesic properties [5–10]. On the other hand, substituted pyridine compounds such as 2-aminopyridines [11–13] and their nitro derivatives are useful as building blocks of nonlinear optical materials [14–18]. The spectroscopic studies of N-heterocyclic molecules including substituted pyridines have become quite interesting as they are the constituents of DNA and RNA [19-21].

Saglam et al. [22] have recorded the Fourier transform infrared and laser Raman spectra of 4-pyridine acid. Michalski et al. [23] have studied the synthesis of 2-phenylazo-5-nitro-6-methyl-pyridine. The structures of isomeric pyridines 1e3 have been studied by low-temperature X-ray crystallography [24] and by methods such as microwave [25] and surface-enhanced Raman spectroscopy [26].

Ab initio and DFT calculations of structure and vibrational spectra of pyridine and its isotopomers were reported by Szafran and Koput [27]. Vibrational assignments and DFT studies of 5-bromo-2-nitropyridine were done by Sundaraganesan et al. [28]. Hiremath et al. [29] investigated the Ab initio/DFT electronic structure calculations, spectroscopic studies and normal coordinate analysis of 2-chloro-5-bromopyridine. Derivatives of pyridines (2-Amino pyridine, 3-Amino pyridine and 4-Amino pyridine) were examined experimentally and theoretically using Semi-empirical AM1 and PM3 methods [30]. In the present work, the FT-IR and FT-Raman spectra of 2-amino-5-chloropyridine (2A5CP) and 2-amino-6-chloropyridine (2A6CP) were studied. The Ab initio (HF) and DFT (B3LYP) 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 molecules.

## 2. Experimental details

The compounds 2A5CP and 2A6CP were purchased from Sigma–Aldrich with a stated purity of 99% and were used without further purification. FT-IR spectra of 2A5CP and 2A6CP have been recorded in the region  $4000\text{--}400\text{ cm}^{-1}$  using a Thermo Nicolet Nexus 870FT-IR instrument. The instrument is equipped with a KBr beam splitter and an In GaAs detector. The spectral resolution is  $\pm 2\text{ cm}^{-1}$ . The Raman spectra were measured using a dispersive Nexus 870FT-Raman instrument. The instrument is equipped with Nd:YAG laser source operating at  $1.064\text{ }\mu\text{m}$  line widths with 200 mW powers. The spectra were recorded with scanning speed of  $30\text{ cm}^{-1}\text{ min}^{-1}$  of spectral width  $2\text{ cm}^{-1}$ .

## 3. Computational details

The molecular structure optimization of 2A5CP and 2A6CP compounds and corresponding vibrational

frequencies were calculated using Hartree-Fock (HF) and the Density Functional Theory (DFT) with Beckee-3-Lee-Yag-Parr (B3LYP) combined with 6-311++G(d,p) basis set using GAUSSIAN 03W program package without any constraint on the geometry [31]. Geometries have been first optimized with full relaxation on the potential energy surfaces at HF/6-311++g(d,p) level. The geometry was then re-optimized at B3LYP/6-311++g(d,p) level.

The optimized geometrical parameters, fundamental vibrational frequencies, IR intensity and Raman activity were calculated using the GAUSSIAN 03W program package. By combining the results of the GAUSS-VIEW program [32] with symmetry considerations, along with the available related molecules, vibrational frequency assignments were made with a high degree of accuracy. However, the defined coordinate form complete set and matches quite well with the motions observed using the GAUSS-VIEW program.

## 4. Results and discussion

### 4.1 Molecular geometry

The molecular structure along with numbering of atoms of 2A5CP and 2A6CP are obtained from GAUSSVIEW program is as shown in Fig. 1. The global minimum energy obtained by Ab initio/ HF and DFT/ B3LYP structure optimization using 6-311++ G(d, p) basis set for 2A5CP as -760.7353318 and -763.3592513 a.u., respectively and -760.7400475 and -763.3644838 a.u., respectively for 2A6CP. The most optimized structural parameters (bond length and bond angle) calculated by HF and B3LYP with 6-311++G(d,p) basis set are represented in Table 1.

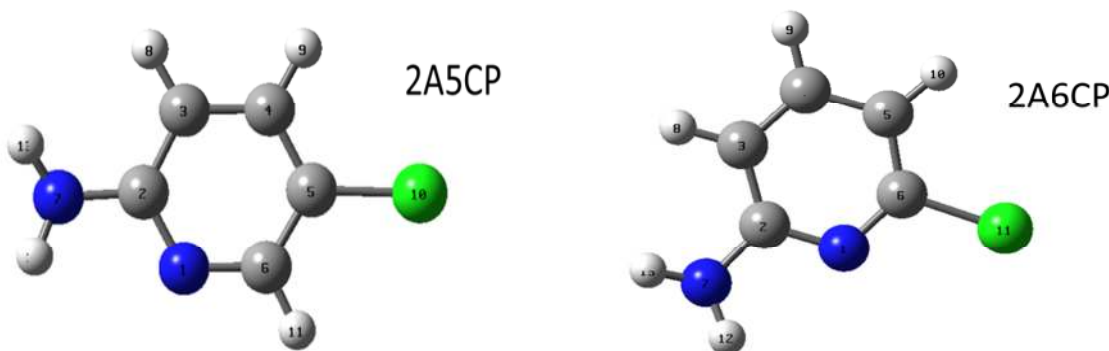


Fig. 1. 2A5CP and 2A6CP structure and atomic numbering for studied molecules.

The theoretical results show that the aromatic ring of the title compounds is distorted from the regular hexagon due to the steric and electronic effects of electron donating  $\text{NH}_2$  groups. From Table 1, C-N bond length is 1.315 Å (HF), 1.337 Å (B3LYP) of 2A5CP and 1.315 Å (HF), 1.341 Å (B3LYP) of 2A6CP molecule is in reasonable agreement with the above-mentioned. The breakdown of hexagonal symmetry of the benzene ring is obvious from the elongation of C2–C3 (1.40 Å) from the remaining C–C bond lengths. For 2A5CP, the asymmetry of the benzene ring is also evident from the negative deviation of C2–C3–C4, C3–C4–C5 (118) and C4–C5–C6 (119) and positive deviation of C5–C6–N1 (122) from the normal value of 120 and in case 2A6CP the asymmetry of the benzene ring is evident from the negative deviation of C2–C3–C4, C3–C4–C5 (118) and C4–C5–C6 (119) and positive deviation of C5–C6–N1 (122) from the normal value of 120. Substitution with the Cl atom at C5 atom (2A5CP) at C6 atom (2A6CP) leads to some changes of the bond lengths and bond angles in the aromatic ring. The optimized N-H (amino group) bond length were calculated 0.995 Å by HF and 1.009 Å by B3LYP for both 2A5CP and 2A6CP. By comparing these values with experimental value (1.02 Å) [33], it is observed that B3LYP estimate the N-H bond length better than HF, which underestimate this bond than experimental values.

The optimized bond lengths of C-C in the range from 1.383 Å to 1.406 Å by B3LYP/6-311++G(d, p) level which are in good agreement with the experimental values [33]. The C–Cl bond length indicates a considerable increase when substituted in place of C–H. This has been observed even in benzene derivatives [34]. The C–Cl bond length are found 1.742 Å (HF) and 1.756 Å (B3LYP) by using 6-311++G(d, p) for both 2A5CP and 2A6CP. Bakiler et al. calculated this bond length 1.746 Å for 3-Cl-pyridine and 1.748 Å for 2-Cl-pyridine [35] by using force field calculations. This bond length was also observed 1.735–1.744 Å range for similar molecules [36–38].

Table 1: Optimized geometrical parameters for 2A5CP and 2A6CP molecules (bond lengths in Å°, angles in °).

Bond length (Å°)	2A5CP		Bond length (Å°)	2A6CP	
	HF/6- 311++g(d,p)	B3LYP / 6311++g(d,p)		HF/ 6-31++g(d,p)	B3LYP / 6-311++g(d,p)
N1-C2	1.315	1.337	N1-C2	1.315	1.341
C2-C3	1.402	1.409	C2-C3	1.402	1.406
C3-C4	1.370	1.383	C3-C4	1.370	1.385
C4-C5	1.388	1.394	C4-C5	1.388	1.395
C5-C6	1.373	1.388	C5-C6	1.373	1.389
C6-N1	1.323	1.334	C6-N1	1.323	1.316
C2- N7	1.375	1.380	C2- N7	1.375	1.376
C3- H8	1.074	1.083	C3- H8	1.074	1.083
C4- H9	1.074	1.083	C4- H9	1.074	1.084
C5- C110	1.742	1.756	C5-H10	1.742	1.756
C6- H11	1.075	1.085	C6-C111	1.742	1.756
N7- H12	0.995	1.009	N7- H12	0.995	1.009
N7- H13	0.995	1.009	N7- H13	0.995	1.009
Bond angle (°)			Bond angle (°)		
N1-C2-C3	122.241	122.150	N1-C2-C3	122.263	122.003
C2 -C3-C4	118.451	118.737	C2 -C3-C4	118.451	118.143
C3-C4-C5	118.828	118.671	C3-C4-C5	118.828	118.289
C4-C5-C6	119.179	119.003	C4-C5-C6	118.479	118.106
C5-C6-N1	122.052	122.812	C5-C6-N1	125.052	125.400
C6-N1-C2	118.945	118.722	C6-N1-C2	118.945	118.055
H13-N7-H12	114.531	115.396	H13-N7-H12	114.531	115.948
C2-N7-H12	114.447	114.954	C2-N7-H12	114.447	118.404
C2-N7-H13	117.077	118.105	C2-N7-H13	117.077	115.958
H11-C6-N1	116.546	116.741	H11-C6-N1	116.546	115.958

#### 4.2 Vibrational assignments

The 2A5CP and 2A6CP molecules consists of 13 atoms, which have 33 normal modes of Fundamental Vibrations. All the 33 fundamental vibrations are active in both Raman scattering and Infrared absorption. These molecules belong to the C1 symmetry group. The detailed analysis of fundamental modes of vibration with FT-IR and FT-Raman experimental frequencies are tabulated in Table 2 for 2A5CP and 2A6CP. Vibrational frequencies, IR intensity, Raman activity of 2A5CP and 2A6CP using HF and B3LYP methods with 6-311++G(d,p) basis set is reported in Tables 3 and 4, respectively. In this study, we followed two different scaling factors [28] viz. 0.89 for HF and 0.96 for B3LYP to correct the theoretical error in this work. The comparative graphs of the observed and simulated FT-IR and FT-Raman spectra for 2A5CP are presented in Figs. 2 and 3, respectively and Figs. 4 and 5 for 2A6CP.

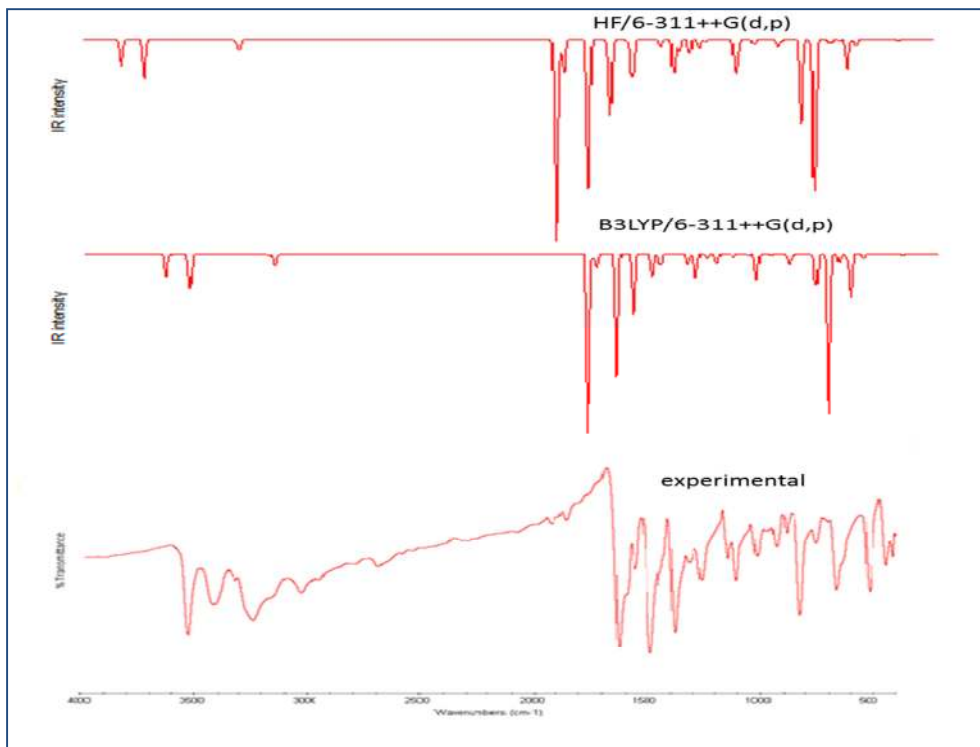


Fig. 2. Comparison of experimental and calculated IR spectra of 2A5CP.

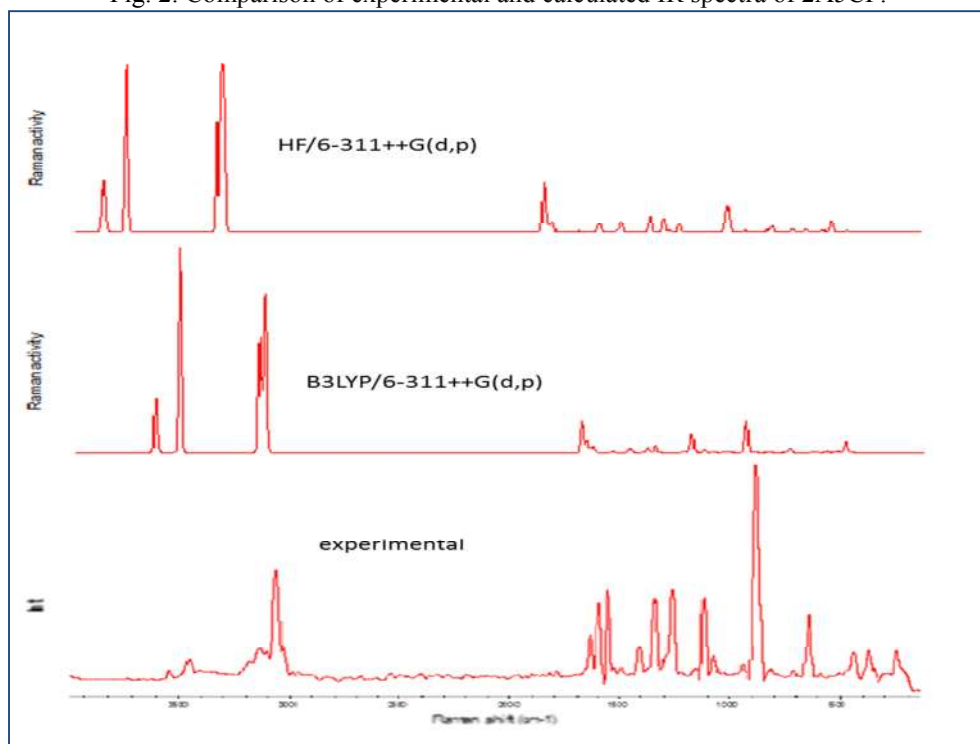


Fig. 3. Comparison of experimental and calculated Raman spectra of 2A5CP.

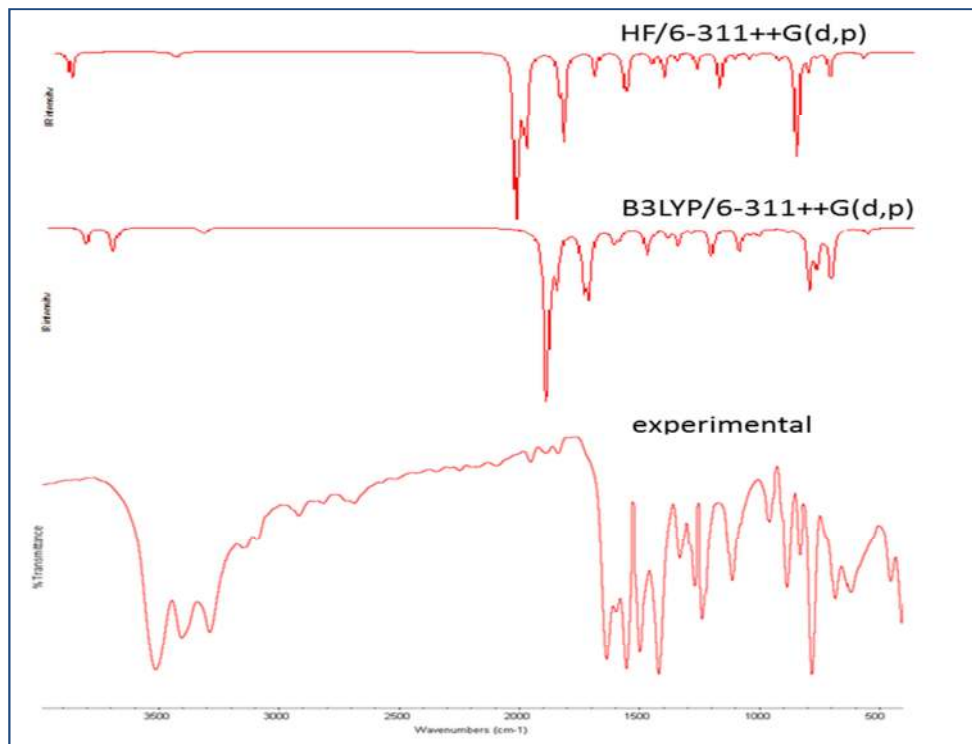


Fig. 4. Comparison of experimental and calculated IR spectra of 2A6CP.

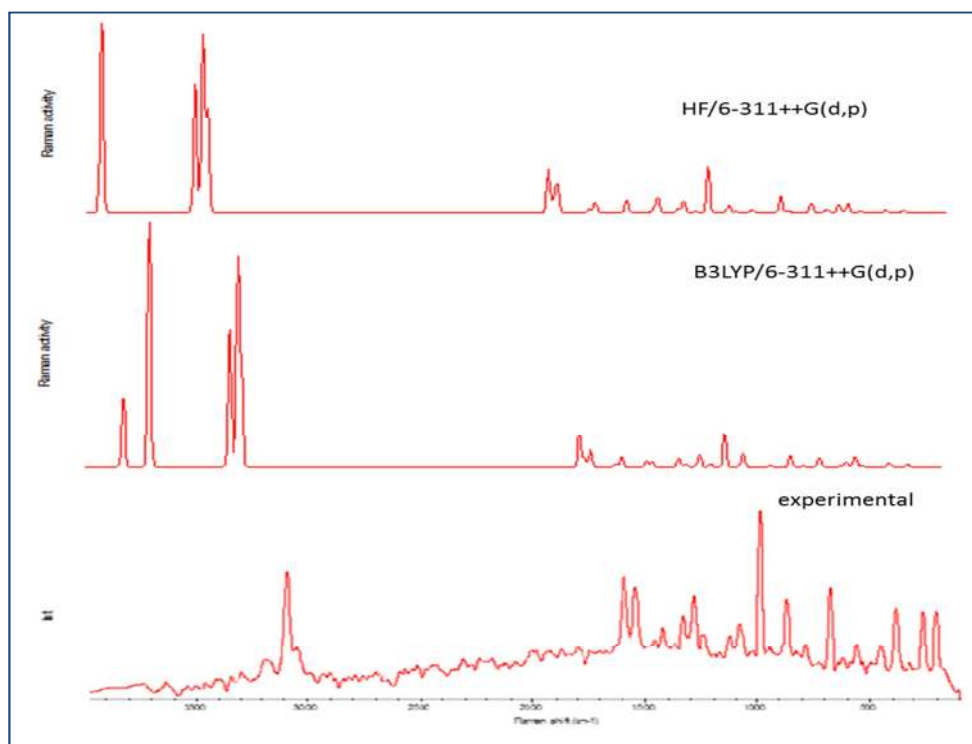


Fig. 5. Comparison of experimental and calculated Raman spectra of 2A6CP.

Table 2: Experimental FT-IR, FT-Raman frequencies and assignment for 2A5CP and 2A6CP.

2A5CP		2A6CP		Assignment
FT-IR frequency (cm <sup>-1</sup> )	FT-Raman frequency (cm <sup>-1</sup> )	FT-IR frequency (cm <sup>-1</sup> )	FT-Raman frequency (cm <sup>-1</sup> )	
3550	3551	3560	3562	NH <sub>2</sub> asym. stretch
3452	3455	3450	3449	NH <sub>2</sub> sym. stretch
3062	3063	3090	3089	C-H stretch
1626	1620	1640	1640	NH <sub>2</sub> scissoring
1370	1368	1370	1372	C=N stretch
1258	1262	1290	1289	CH in- plane bending
1112	1114	1120	1122	CH in- plane bending
929	932	950	948	CH out- of- plane
903	905	888	886	CH out- of- plane
825	853	825	826	CH out- of- plane
410	409	448	448	NH <sub>2</sub> wagging
656	646	670	669	C-Cl stretch
-	370	-	390	C-Cl bend (ip)
-	242	-	202	C-Cl bend (op)

#### 4.3 C-H Vibrations

The aromatic C–H stretching vibrations are normally found between 3100 and 3000 cm<sup>-1</sup>. In this region, the bands are not affected appreciably by the nature of substituents. The aromatic C–H bonds present in the title molecules produce bands at 3062 cm<sup>-1</sup> (2A5CP) and 3090 cm<sup>-1</sup> (2A6CP) in FT-IR and 3063 cm<sup>-1</sup> (2A5CP) and 3089 cm<sup>-1</sup> (2A6CP) in FT-Raman. The aromatic C–H in-plane bending modes of benzene and its derivatives are observed in the region 1300–1000 cm<sup>-1</sup>. These modes are observed in the FT-IR spectrum of the title molecules at 1258 and 1112 cm<sup>-1</sup> (2A5CP) and at 1290 and 1120 cm<sup>-1</sup> (2A6CP) and the corresponding modes are identified in the FT-Raman spectrum at 1262 and 1114 cm<sup>-1</sup> (2A5CP) and at 1289 and 1122 cm<sup>-1</sup> (2A6CP). The C-H out-plane bending vibrations at 929, 903 and 825 cm<sup>-1</sup> in FT-IR and at 932, 905 and 853 cm<sup>-1</sup> in FT-Raman (mode Nos. 18, 19, 20) for 2A5CP. The same vibration in 2A6CP is shown in FT-IR at 950, 888 and 825 cm<sup>-1</sup> and at 948, 886 and 826 cm<sup>-1</sup> in FT-Raman. The theoretically calculated values by HF and B3LYP method coincide very well with the experimental value.

#### 4.4 NH<sub>2</sub> vibrations

The NH<sub>2</sub> group has two (N-H) stretching vibrations. One being asymmetric and the other is symmetric. The frequency of asymmetric vibration is higher than that of symmetric one. The N-H stretching vibrations occur in the region 3500–3000 cm<sup>-1</sup> in primary aromatic amines. Hence, the bands observed at 3550 and 3452 cm<sup>-1</sup> in FT-IR spectrum and at 3551 and 3455 cm<sup>-1</sup> in FT-Raman spectrum is assigned to the N-H asymmetric stretching and symmetric stretching vibrations, respectively for 2A5CP and at 3560 and 3450 cm<sup>-1</sup> in FT-IR spectrum and at 3562 and 3449 cm<sup>-1</sup> in FT-Raman spectrum is assigned to the N-H asymmetric stretching and symmetric stretching vibrations, respectively for 2A6CP. These are in agreement with computed values (mode Nos. 1, 2). The computed –NH<sub>2</sub> scissoring vibration (mode No. 6) at 1623 cm<sup>-1</sup> and 1641 cm<sup>-1</sup> for 2A5CP and 2A6CP, respectively by B3LYP/6-311++G(d,p) level are in excellent agreement with the expected characteristic value, 1600 cm<sup>-1</sup> [39, 40]. This band observed in FT-IR at 1626 cm<sup>-1</sup> and 1620 cm<sup>-1</sup> in FT-Raman for 2A5CP and at 1640 cm<sup>-1</sup> in both FT-IR and FT-Raman spectra for 2A6CP. The –NH<sub>2</sub> wagging computed at 407 cm<sup>-1</sup> and 424 cm<sup>-1</sup> (mode No. 28) in both 2A5CP and 2A6CP molecules by B3LYP/6-311++G(d,p) level have been observed at 410 cm<sup>-1</sup> and 409 cm<sup>-1</sup> in FT-IR and FT-Raman spectra, respectively for 2A5CP and in the case of 2A6CP observed at 448 cm<sup>-1</sup> in both FT-IR and FT-Raman spectra.

#### 4.5 C-N, C=N vibrations

The identification of C-N vibrations is very difficult because of the interference of many bands in the area where the vibration of this bond happens. For the aromatic amines, the C-N stretching appear in the region 1382–1266 cm<sup>-1</sup> [41]. In 3,5-dibromopyridine, the band observed at 1410 cm<sup>-1</sup> in FT-IR and 1412 cm<sup>-1</sup> in FT-Raman is assigned to C-N stretching. In benzamide, the band observed at 1368 cm<sup>-1</sup> is assigned to C-N stretching [42]. In the current study, a band appeared at 1370 cm<sup>-1</sup> and 1368 cm<sup>-1</sup> for the stretching vibration of the bond C=N in the FT-IR and FT-Raman, respectively for 2A5CP and at 1370 cm<sup>-1</sup> and 1372 cm<sup>-1</sup> for the stretching vibration of the bond C=N in the FT-IR and FT-Raman, respectively for 2A6CP. These values are consistent with the theoretically calculated values (mode No.10).

#### 4.6. C-Cl vibrations

The vibrations belonging to the bond between the ring and the halogen atoms are worth discussing here, since mixing of vibrations are possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of molecule [35, 43]. Mooney [44, 45] assigned vibrations of C–X group (X = Cl, Br, I) in the frequency range 1129–480  $\text{cm}^{-1}$ . The C–Cl stretching vibration gives, strong bands in the region 710–505  $\text{cm}^{-1}$ . Compounds with more than one chlorine atom exhibit very strong bands due to asymmetric and symmetric stretching modes. Vibrational coupling with other groups may result in a shift in the absorption to as high as 840  $\text{cm}^{-1}$ . For simple organic chlorine compounds, C–Cl absorptions are in the region 750–700  $\text{cm}^{-1}$ , whereas for the trans and gauche forms [46, 47] they are near at 650  $\text{cm}^{-1}$ . In the current study, the band at 656  $\text{cm}^{-1}$  (2A5CP) and 670  $\text{cm}^{-1}$  (2A6CP) in FT-IR and at 646  $\text{cm}^{-1}$  (2A5CP) and 669  $\text{cm}^{-1}$  (2A6CP) in FT-Raman spectra is assigned to C–Cl stretching vibration. This experimental observation exactly correlates with the theoretical calculation by B3LYP/6-311++G (d,p) level at 640  $\text{cm}^{-1}$  (2A5CP) and 669  $\text{cm}^{-1}$  (2A6CP) (mode No. 23). The C-Cl in-plane bending and out-of-plane bending vibrations are assigned to the FT-Raman bands at 370, 242  $\text{cm}^{-1}$  (2A5CP) and 390, 202  $\text{cm}^{-1}$  (2A6CP), respectively. This is in agreement with the literature data [48, 49].

Table 3: calculated fundamental frequencies at HF/6-311++g(d,p) and B3LYP/6-311++g(d,p) levels calculated vibrational frequencies for 2A5CP.

Mode of vibration	Calculated frequency ( $\text{cm}^{-1}$ )							
	HF/6-311++g(d,p)				B3LYP/6-311++g(d,p)			
	Wave number		IR	Raman	Wave number		IR	Raman
	Unscaled	Scaled	intensity	intensity	Unscaled	Scaled	intensity	Activ.
1	3917	3486	4.27	116.84	3697	3549	34.20	57.03
2	3804	3386	57.81	146.08	3583	3439	51.10	212.05
3	3360	2990	40.07	45.53	3199	3071	2.58	118.38
4	3346	2978	8.11	88.23	3175	3048	6.76	114.17
5	3340	2973	8.66	49.04	3168	3041	12.12	69.63
6	1801	1603	303.27	44.13	1691	1623	270.50	34.70
7	1778	1582	14.81	4.68	1624	1559	6.06	12.81
8	1760	1566	49.27	9.19	1601	1537	21.44	6.09
9	1639	1459	224.62	0.85	1506	1445	190.20	1.67
10	1533	1364	116.16	7.11	1422	1366	93.24	5.52
11	1447	1288	3.61	1.76	1341	1288	4.66	2.70
12	1426	1269	57.08	9.50	1333	1279	33.25	3.75
13	1289	1148	11.32	14.40	1294	1242	16.76	7.66
14	1225	1091	51.77	12.89	1161	1115	17.29	1.87
15	1199	1067	18.50	1.30	1122	1077	36.83	20.86
16	1148	1021	19.90	6.86	1068	1025	7.50	4.21
17	1100	979	13.82	0.43	1019	978	15.73	0.42
18	1098	977	0.58	0.18	966	928	0.07	0.11
19	1068	950	3.78	0.37	940	902	4.79	0.11
20	924	823	39.13	12.41	863	828	2.07	35.06
21	915	814	24.22	16.78	826	793	40.06	0.86
22	834	742	7.90	0.79	754	724	1.81	0.37
23	719	640	10.24	1.77	667	640	15.78	0.98
24	700	623	2.87	4.64	651	625	3.14	4.21
25	604	538	127.86	2.19	537	516	48.23	0.84
26	539	480	227.09	1.96	475	456	240.75	1.15
27	468	416	4.06	0.30	426	409	1.80	0.45
28	456	406	2.92	0.76	424	407	10.29	0.82
29	417	372	2.09	10.12	387	371	7.23	11.13
30	378	336	44.62	0.41	366	351	67.13	0.21
31	340	302	9.95	0.70	307	295	6.15	0.54
32	274	244	0.05	0.51	255	244	0.16	0.34
33	131	117	1.61	0.15	115	111	1.49	0.38

Table 4: calculated fundamental frequencies at HF/6-311++g(d,p) and B3LYP/6-311++g(d,p) levels calculated vibrational frequencies for 2A6CP.

Mode of vibration	Calculated frequency (cm <sup>-1</sup> )							
	HF/6-311++g(d,p)				B3LYP/6-311++g(d,p)			
	Wave number		IR	Raman	Wave number		IR	Raman
	Unscaled	Scaled	intensity	intensity	Unscaled	Scaled	intensity	Activ.
1	3925	3493	43.27	43.26	3704	3556	36.95	54.35
2	3808	3390	61.50	138.25	3587	3444	56.18	194.61
3	3387	3015	0.12	89.64	3225	3096	0.17	107.70
4	3353	2984	9.65	123.06	3189	3061	9.78	156.84
5	3332	2965	9.76	69.22	3173	3046	7.04	73.34
6	1796	1598	410.91	29.77	1709	1641	397.35	24.07
7	1771	1576	94.78	10.16	1626	1561	37.59	6.89
8	1755	1562	190.11	18.32	1599	1535	115.37	12.82
9	1610	1432	80.35	1.74	1484	1424	123.60	1.52
10	1586	1411	209.05	6.53	1427	1369	144.42	7.20
11	1443	1284	56.75	8.02	1347	1293	30.75	4.67
12	1321	1176	12.27	2.31	1321	1268	21.53	3.76
13	1304	1160	88.87	9.85	1201	1153	60.65	6.58
14	1210	1077	1.35	2.19	1169	1122	5.50	1.78
15	1187	1056	25.55	7.44	1106	1062	17.46	8.92
16	1135	1010	59.54	0.50	1058	1015	39.84	1.60
17	1114	991	0.42	0.33	995	955	7.78	25.83
18	1076	957	17.95	31.07	987	947	0.02	0.26
19	982	874	40.32	4.67	911	874	64.50	9.54
20	952	847	2.34	0.48	861	826	1.38	0.20
21	879	782	82.40	1.16	787	756	52.88	0.63
22	815	725	14.20	0.08	737	708	12.38	0.06
23	749	666	15.07	11.35	697	669	16.41	8.93
24	712	634	7.24	0.79	640	614	2.19	0.33
25	611	544	15.50	5.99	567	544	5.36	6.70
26	540	481	253.05	1.70	477	458	139.15	0.49
27	488	435	41.46	0.81	450	432	0.78	1.71
28	487	434	0.12	3.85	442	424	77.32	1.84
29	446	397	8.56	6.14	406	390	10.32	7.81
30	391	348	58.33	0.85	375	360	113.60	0.71
31	274	244	1.13	1.58	253	243	1.44	1.16
32	233	207	14.88	0.32	211	202	12.30	0.17
33	196	174	0.76	1.08	170	164	0.28	2.51

#### 4.7. Frontier molecular orbital analysis

Molecular orbitals (HOMO and LUMO) and their properties such as energy are very useful for physicists and chemists and are very important parameters for quantum chemistry. This is also used by the frontier electron density for predicting the most reactive position in  $\pi$ -electron systems and also explains several types of reaction in conjugated system [50]. The conjugated molecules are characterized by a small highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) separation, which is the result of a significant degree of intramolecular charge transfer from the end-capping electron-donor groups to the efficient electron-acceptor groups through  $\pi$ -conjugated path [51]. Both the highest occupied molecular orbital and lowest unoccupied molecular orbital are the main orbital take part in chemical stability [52]. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO energy calculated by B3LYP/6-311++G (d,p) method is shown below.

The electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. While the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called as energy gap which is an important stability for structures [53] and is calculated for 2A5CP as:

HOMO energy = - 0.22877 a.u

LUMO energy = - 0.04508 a.u

HOMO-LUMO energy gap = 0.18369 a.u.



And for 2A6CP as

HOMO energy = - 0.23346 a.u

LUMO energy = - 0.04075 a.u

HOMO-LUMO energy gap = 0.19271 a.u.

Recently, the energy gap between HOMO and LUMO has been used to prove the bioactivity from intramolecular charge transfer [54, 55]. The plots of HOMO–LUMO for 2A5CP and 2A6CP are shown in Figs. 6 and 7, respectively.

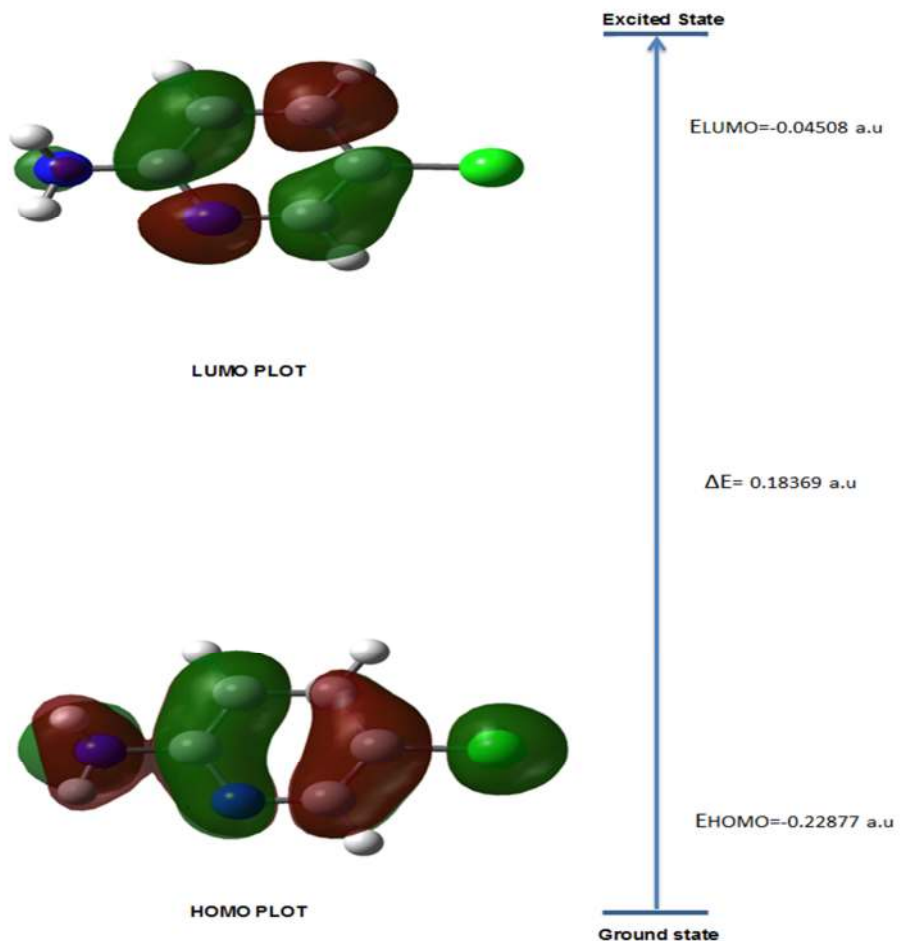


Fig. 6. The atomic orbital composition of the frontier molecular orbital for 2A5CP.

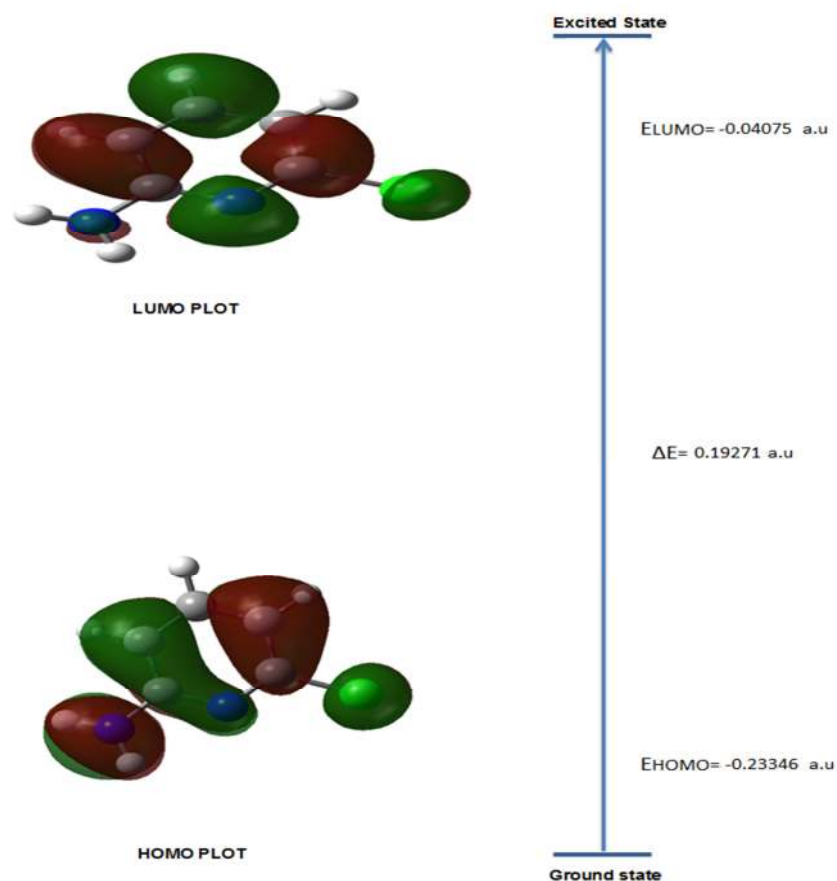


Fig. 7. The atomic orbital composition of the frontier molecular orbital for 2A6CP.

#### 4.8. Atomic charges

The computation of the reactive atomic charges plays an important role in the application of quantum mechanical calculations for the molecular system. Mulliken atomic charges of 2A5CP and 2A6CP molecules have been calculated using HF and B3LYP methods at 6-311++G(d,p) basis set are combined in Table 5. The atomic charge of C3 in 2A5CP is 0.2918 and 0.4127 and in 2A6CP is 0.2926 and 0.5358 using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels, respectively. The maximum atomic charge is obtained for C3 when compare with other atoms in 2A5CP and 2A6CP molecules. Illustration of atomic charges plotted for HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels has been shown in Figs. 8 and 9 for 2A5CP and 2A6CP, respectively.

Table 5: Mulliken's atomic charges of 2A5CP and 2A6CP molecules at HF and B3LYP methods with 6-311++G(d, p) basis set.

Atoms	2A5CP		Atoms	2A6CP	
	HF/6-311++g(d,p)	B3LYP / 6311++g(d,p)		HF/6-31++g(d,p)	B3LYP / 6-311++g(d,p)
N1	-0.259	-0.137	N1	-0.087	0.039
C2	-0.356	-0.601	C2	-0.052	-0.390
C3	0.291	0.412	C3	0.292	0.535
C4	-0.509	-0.683	C4	-0.673	-0.822
C5	0.086	0.260	C5	0.112	0.323
C6	-0.250	-0.387	C6	-0.546	-0.757
N7	-0.378	-0.271	N7	-0.390	-0.278
H8	0.215	0.176	H8	0.200	0.167
H9	0.229	0.179	H9	0.222	0.172
Cl10	0.275	0.344	H10	0.219	0.184
H11	0.235	0.196	Cl11	0.188	0.308
H12	0.269	0.270	H12	0.252	0.269
H13	0.250	0.241	H13	0.261	0.245

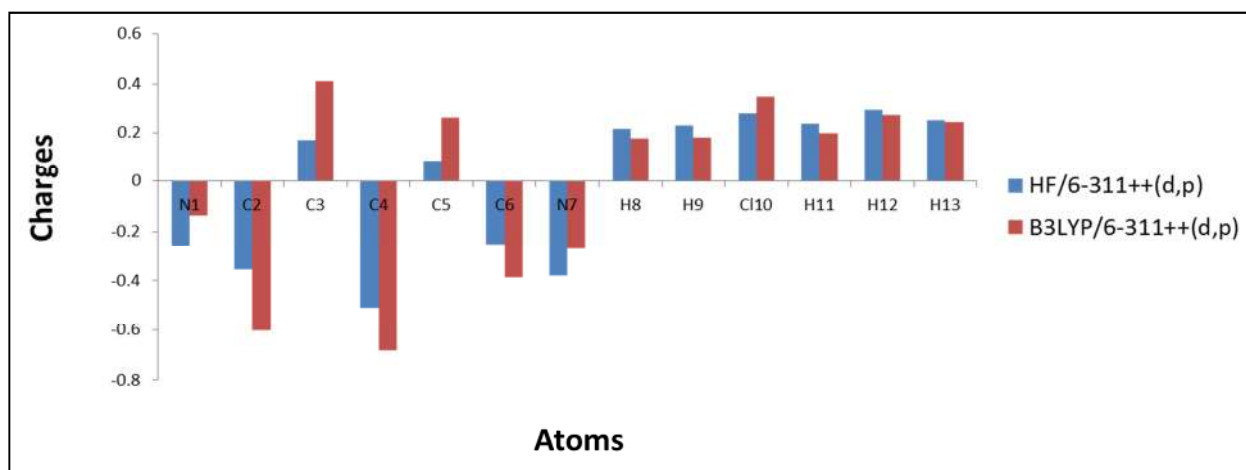


Fig. 8. The atomic charges for 2A5CP.

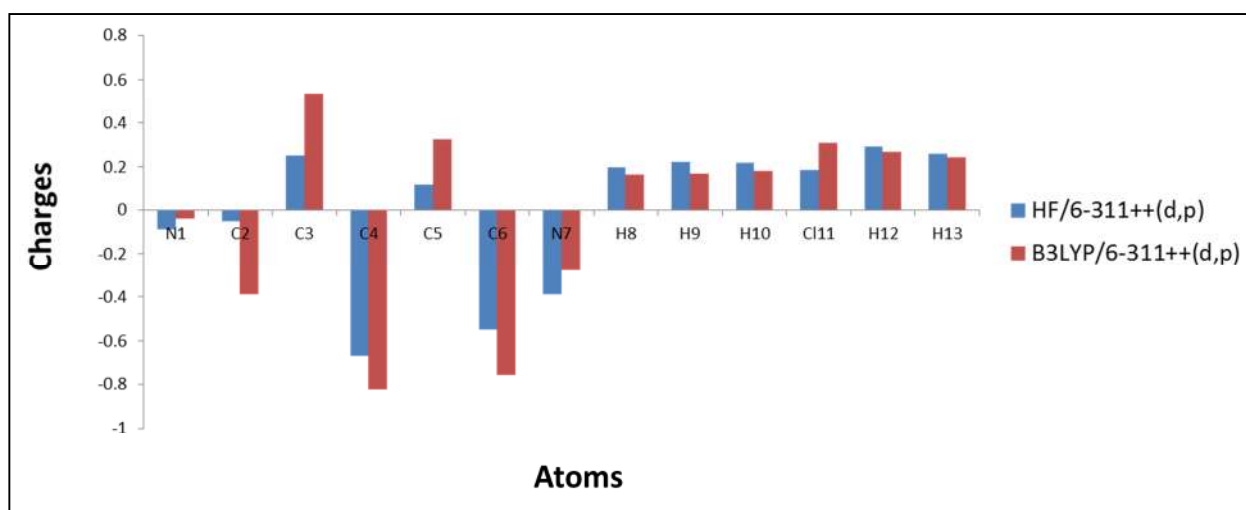


Fig. 9. The atomic charges for 2A6CP.

## 5. Conclusion

Attempts have been made in the present work for the proper frequency assignments for the compounds 2A5CP and 2A6CP from the FT-IR and FT-Raman spectra. The optimized geometry, frequencies, IR and Raman spectra of the title compounds were determined and analyzed both at HF and B3LYP levels of theory with 6-311++G(d,p) basis set. Comparison between the calculated vibrational frequencies and the experimental values indicates that both the methods can predict the FT-IR and FT-Raman spectra of the title compounds well. Scaling factors results are in good agreement with the experimental ones. The optimized geometry parameters calculated at B3LYP basis sets are slightly larger than those calculated at HF level. The difference between the observed and scaled wave number values of the most of the fundamentals is very small. The calculated HOMO and LUMO energies show that charge transfer occurs in the molecule, which are responsible for the bioactive property of 2A5CP and 2A6CP. The Mulliken's atomic charges of 2A5CP and 2A6CP were also discussed elaborately.

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