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RESEARCH ARTICLE

Experimental (UV, NMR, IR and Raman) and theoretical spectroscopic properties of 2-chloro-6-methylaniline

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In this work, the experimental and theoretical UV, NMR and vibrational spectra of 2-chloro-6-methylaniline (2-Cl-6-MA, C₇H₈NCl) were studied. The ultraviolet absorption spectra of compound that dissolved in ethanol were examined in the range of 200–400 nm. The ¹H, ¹³C and DEPT NMR spectra of the compound were recorded. FT-IR and FT-Raman spectra of 2-Cl-6-MA in the liquid phase were recorded in the region 4000–400 cm⁻¹ and 3500–50 cm⁻¹, respectively. The structural and spectroscopic data of the molecule in the ground state were calculated using density functional theory (DFT) employing B3LYP exchange correlation and the 6-311++G(d,p) basis set. The vibrational frequencies were calculated and scaled values were compared with experimental FT-IR and FT-Raman spectra. The observed and calculated frequencies were found to be in good agreement. The complete assignments were performed on the basis of the total energy distribution (TED) of the vibrational modes, calculated with scaled quantum mechanics (SQM) method. Isotropic chemical shifts were calculated using the gauge-invariant atomic orbital (GIAO) method. Comparison of the calculated NMR chemical shifts and absorption wavelengths with the experimental values revealed that DFT method produces good results.

Keywords: 2-chloro-6-methylaniline; NMR; UV; infrared and Raman spectra; vibrational assignments; DFT calculations

1. Introduction

Aniline and its derivatives have been widely used for commercial purposes and the production of dyes, antioxidants, local anesthetics and many other industrial processes, and have been studied extensively [1]. Therefore, the understanding of molecular structure and properties of Aniline and its derivatives has been the subject of many theoretical and experimental studies. The molecular geometry of aniline changes due to enhanced interaction between the amino group and the aromatic ring. The inclusion of a substituent group in aniline also leads to the variation of charge distribution in the molecule, and consequently this greatly affects the structural, electronic and vibrational parameters [2]. The position of the substituents in the benzene ring plays a very important role on the structural and electronic properties of the molecules. Extensive experimental [3] and theoretical investigations have focused on elucidating the structure and normal vibrations of aniline and its methyl derivatives. Because of their spectroscopic properties and chemical significance, aniline and its derivatives

have been studied extensively by spectroscopic and theoretical methods. Vibrational analysis based FT-IR (in vapour, solution and liquid phases) and Raman spectra (in liquid state) were reported for aniline [4]. Microwave spectroscopic study [5,6] of the gas phase and molecular structure reports determined by X-ray crystallography [7], semi-empirical [8,9] and *ab initio* methods [10–15] have also been published for aniline. The complete vibrational mode assignments and frequency analyses on vibrational spectra of substituted anilines were studied [10–15]. Vibrational modes and frequency analysis of *p*-methylaniline [16–21], *m*-methylaniline and fluoro methylaniline are given in the literature [10,22,23]. Barluenga *et al.* [24] synthesized 2-chloro-*N*-methylaniline (2CINMA) and studied its ¹H and ¹³C NMR spectra. The molecular structure and vibrational spectra of 3-chloro-4-methyl aniline were investigated by DFT and HF calculations [25]. Recently, FT-IR and FT-Raman and *ab initio* analysis of 4-chloro-2-methylaniline and 4-chloro-3-methylaniline was published [26]. The polarized Raman and Infrared spectra of 2-Cl-6-MA were

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reported by Shanker *et al.* [27]. The copper and mercury complexes of 2- and 5-chloro-6-methylaniline were synthesized and UV and IR spectra were elucidated by Misra *et al.* [28].

In the present study, an extensive experimental spectroscopic study of 2-Cl-6-MA (also known as 2-chloro-6-methylcyclohexylamine) was undertaken by recording their UV, NMR, FT-IR and FT-Raman spectra. Theoretical investigations can facilitate the solution to the problems confronted in the experimental techniques, i.e. allowing the determination of molecular properties. The aim of this study is to fully determine the molecular structure, vibrational modes and wavenumbers, isotropic chemical shifts and absorption bands of compound experimentally and theoretically and to understand the effect of halogen and methyl group substitution on the characteristic frequencies of the amino group. For computation we have carried out DFT calculations with the combined Becke's three-parameter exchange functional in combination with the Lee, Yang and Parr correlation functional (B3LYP).

2. Experimental

The compound 2-Cl-6-MA in liquid state was purchased from Acros Organics Company with a stated purity of 99%. The FT-IR spectrum of 2-Cl-6-MA molecule was recorded between 4000 and 400 cm^{-1} on a Perkin-Elmer FT-IR System Spectrum BX spectrometer which was calibrated using polystyrene bands. The spectrum was recorded at room temperature, with a scanning speed of 10 $\text{cm}^{-1} \text{min}^{-1}$ and the spectral resolution of 4.0 cm^{-1} . FT-Raman spectra of the sample were recorded on a Bruker RFS 100/S FTRaman instrument using 1064 nm excitation from an Nd:YAG laser. The detector is a liquid nitrogen cooled Ge detector. Five hundred scans were accumulated at 4 cm^{-1} resolution using a laser power of 100 mW. NMR experiments were performed in Varian Infinity Plus spectrometer at 300 K. The compound was dissolved in chloroform (CDCl_3). Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra. ^1H , ^{13}C and DEPT NMR spectra were obtained at a base frequency of 75 MHz for ^{13}C and 300 MHz for ^1H nuclei. The ultraviolet absorption spectra of 2-Cl-6-MA are examined in the range 200–800 nm using Shimadzu UV-2401 PC, UV-VIS recording Spectrometer. The UV pattern is taken from a 10^{-5} molar solution of 2-Cl-6-MA, solved in ethanol. Data are analyzed by UV PC personal spectroscopy software, version 3.91.

3. Computational details

The first task for the computational work was to determine the optimized geometry of the compound. The hybrid B3LYP [29,30] method based on Becke's three parameter functional of DFT and 6-311++G(d,p) basis set level were chosen. Optimized structural parameters were used in the vibrational frequency, isotropic chemical shift and calculations of electronic properties. However, the frequency values computed at these levels contain known systematic errors [31]. Therefore, it is customary to scale down the calculated harmonic frequencies in order to improve the agreement with the experiment. In our study, we have followed two different scaling factors, i.e. 0.958 up to 1700 cm^{-1} and 0.983 for greater than 1700 cm^{-1} [32]. Analytic frequency calculations at the optimized geometry were done to confirm the optimized structures to be an energy minimum and to obtain the theoretical vibrational spectra. The stability of the optimized geometries was confirmed by frequency calculations, which give positive values for all the obtained frequencies. All calculations are performed by using the Gaussian 03 program package on a personal computer [33]. The total energy distribution (TED) was calculated by using the scaled quantum mechanics (SQM) program [34,35] and the fundamental vibrational modes were characterized by their TED. The ^1H and ^{13}C nuclear magnetic resonance (NMR) chemical shifts of the compound were calculated using the gauge-invariant atomic orbital (GIAO) method. The time dependent DFT (TD-DFT) is proved to be a powerful and effective computational tool for the study of ground and excited state properties by comparison to the available experimental data. Hence, we used TD-B3LYP to obtain wavelengths λ_{max} and compare with the experimental UV absorption spectra of 2-Cl-6-MA.

4. Results and discussion

The molecule 2-Cl-6MA consists of 17 atoms, so it has 45 normal vibrational modes. The 45 fundamental modes of vibrations of title compound are distributed into the irreducible representations under C_s symmetry as 31 in-plane vibrations of A' species and 14 out of plane vibrations of A'' species, i.e. $\Gamma_{\text{vib}} = 31A' + 14A''$. All vibrations are active in both IR and Raman. If we take into account C_s symmetry of this molecule, there is one imaginary frequency correspond to NH_2 wagging. This imaginary frequency of irreducible representation belongs to A'' . But if the molecule were C_1 there would not be any relevant distribution and molecule has true minimum energy (for example,

$E=783.63860060$ a.u. for C_s symmetry and $E=783.64010111$ a.u. for C_1 symmetry). The C_1 structure only identity (E) symmetry element or operation was the lowest in energy. Calculated energies and energy difference for 2-Cl-6-MA molecule, determined by B3LYP at eight basis sets, are presented in Table 1, which on the calculated energies, there is a little difference between basis sets. Use of basis sets of larger size give rise to increases in the differences between the calculated energies of the 2-Cl-6MA molecule. When we compared the 6-31 and 6-311 basis sets the difference is large.

4.1. Molecular geometry

The optimized structure of the 2-Cl-6-MA compound is shown in Figure 1 with numbering of the atoms. The optimized bond lengths, bond and dihedral angles of 2-Cl-6-MA calculated B3LYP with 6-311++G(d,p)

Table 1. Calculated energies and energy difference for 2-Cl-6-MA by DFT (B3LYP).

| Basis set levels | Energy (hartree) | Energy differences ^a (kcal/mol) |
|------------------|------------------|--|
| 6-311++G(d,p) | -786.64010111 | 0.000 |
| 6-311+G(d,p) | -786.63998613 | 0.072 |
| 6-311G(d,p) | -786.63304636 | 4.427 |
| 6-311G(d) | -786.61741003 | 14.239 |
| 6-31++G(d,p) | -786.54836461 | 57.566 |
| 6-31+G(d,p) | -786.54823305 | 57.648 |
| 6-31G(d,p) | -786.53373821 | 66.744 |
| 6-31G(d) | -786.51798779 | 76.627 |

^aEnergies of the other basis sets.

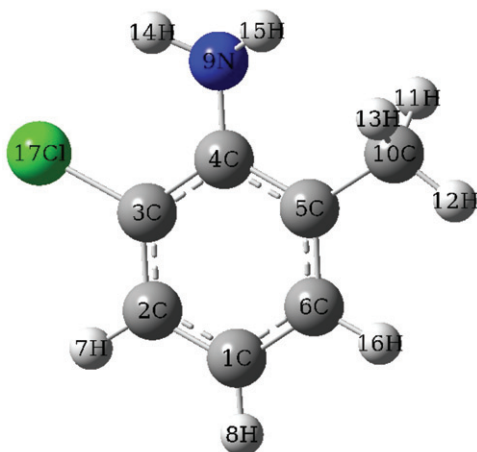


Figure 1. The theoretical geometric structure and atoms numbering of 2-Cl-6-MA.

basis set are listed in Table 2 in accordance with the atom numbering scheme given in Figure 1. Literature survey reveals that to the best of our knowledge, no experimental data on the geometric structure of 2-Cl-6-MA has been reported so far. Therefore, we could not compare the calculation results given in Table 2 with the experimental data. Only optimized geometric parameters of compound were compared to those of aniline [36,37] and *p*-methylaniline [3]. From the structural data shown in Table 2 it is seen that the various bond lengths are found to be greater than experiment. This overestimation can be explained that the theoretical calculations belong to isolated molecule in gaseous phase and the experimental results belong to similar molecules in solid state.

Several authors [38,39] have explained the changes in frequency or bond length of the C–H bond on substitution due to a change in the charge distribution on the carbon atom of the benzene ring. The substituents may be either of the electron withdrawing type (F, Cl, Br, etc.) or electron donating type (CH₃, C₂H₅, etc.). The carbon atoms are bonded to the hydrogen atoms with σ bond in benzene and the substitution of a halogen for hydrogen reduces the electron density at the ring carbon atom. The ring carbon atoms in substituted benzenes exert a larger attraction on the valence electron cloud of the hydrogen atom resulting in an increase in the C–H force constant and a decrease in the corresponding bond length. The reverse holds true on substitution with electron donating groups. The actual change in the C–H bond length would be influenced by the combined effects of the inductive–mesomeric interaction and the electric dipole field of the polar substituent. In this study, C–H bond lengths were calculated as 1.084 and 1.094 Å for ring and methyl group, respectively.

The position of the substituents in the benzene ring as well as its electron donor/acceptor capabilities plays a very important role on the structural and electronic properties of the molecules. The methyl and amino groups are referred as electron donating substituents in aromatic ring systems. Amino group shares its lone pair electrons with the p electrons in a ring and methyl group interacts with nearby π systems. For 2-Cl-6-MA the chlorine atom and methyl group could make intramolecular interactions with the amino group. As seen in Table 2, this interaction between the amino group and the aromatic ring produces a small displacement of the nitrogen atom out of the benzene ring with a torsional angle of N9-C4-C5-C6 of ca 177°. The influence of the substituent on the molecule seems to be small. The C3-C4-C5 angle at the position of the NH₂ substituent and C4-C5-C6 angle at the position of

Table 2. Optimized geometry of 2-Cl-6-MA in the ground state and comparison with similar compounds.

| Bond lengths (Å) | <i>p</i> -methylaniline ^[3] | Aniline ^[7,6] | B3LYP | Bond angles (°) | <i>p</i> -methylaniline ^[3] | Aniline ^[7,6] | B3LYP |
|---------------------------|--|--------------------------|-------|-----------------------------|--|--------------------------|--------|
| C1-C2 | 1.39 | 1.386, 1.396 | 1.39 | C5-C6-H16 | | | 118.6 |
| C1-C6 | 1.4 | 1.386, 1.396 | 1.394 | C1-C6-H16 | | | 119.6 |
| C2-C3 | 1.39 | 1.380, 1.394 | 1.388 | C1-C6-C5 | 121.5 | 122.1, 120.70 | 121.8 |
| C3-C4 | 1.36 | 1.404, 1.397 | 1.404 | C4-C5-C10 | | | 119.6 |
| C3-Cl17 | | | 1.769 | C6-C5-C10 | | | 121.1 |
| C4-C5 | 1.39 | 1.404, 1.397 | 1.415 | C4-N9-H14 | | 119.0, 115.94 | 116 |
| C4-N9 | 1.43 | 1.398, 1.402 | 1.389 | C4-N9-H15 | | 119.0, 115.94 | 116.5 |
| C5-C6 | 1.4 | 1.380, 1.394 | 1.393 | H-N-H (amino) | 113 | 113.1, - | 113.6 |
| C5-C10 | 1.55 | | 1.508 | C-C-H (methyl) ^a | | | 111.4 |
| C-H (ring) ^a | 1.08 | 1.03, 1.082 | 1.084 | H-C-H (methyl) ^a | 109.5 | | 107.5 |
| N-H (amino) ^a | 1.02 | 1.07, 1.001 | 1.009 | Dihedral angles (°) | | | |
| C-H (methyl) ^a | 1.09 | | 1.094 | C6-C5-C4-N9 | | | -177.4 |
| Bond angles (°) | | | | C2-C3-C4-N9 | | | 177.2 |
| C2-C1-C6 | 119.2 | 119.7, 120.12 | 119.3 | C5-C4-N9-H15 | | | -27.3 |
| C2-C1-H8 | | | 120.1 | C3-C4-N9-H14 | | | 17.5 |
| C6-C1-H8 | | | 120.6 | Cl(17)-C3-C2-C1 | | | -179.6 |
| C1-C2-C3 | 120.5 | | 119.3 | Cl(17)-C3-C4-C5 | | | 179.7 |
| C1-C2-H7 | | | 121.2 | Cl(17)-C3-C4-N9 | | | -3.0 |
| C3-C2-H7 | | | 119.5 | N9-C4-C3-C2 | | | 177.2 |
| C2-C3-C4 | 120.5 | | 122.4 | N9-C4-C5-C6 | | | -177.4 |
| C2-C3-Cl17 | | | 118.8 | N9-C4-C5-C10 | | | 2.1 |
| C4-C3-Cl17 | | | 118.9 | C3-C4-N9-H14 | | | 17.5 |
| C3-C4-C5 | 120.3 | 117.9, 119.43 | 117.9 | C3-C4-N9-H15 | | | 155.5 |
| C3-C4-N9 | | 124.0, 120.28 | 121.5 | C5-C4-N9-H14 | | | -165.2 |
| C5-C4-N9 | | 124.0, 120.28 | 120.5 | C5-C4-N9-H14 | | | -27.3 |
| C4-C5-C6 | 117.8 | 117.6, 118.92 | 119.3 | C3-C4-C5-C10 | | | 179.5 |

^aAveraged value.

the methyl substituent are smaller, and the C2-C3-C4 angle at the position of the chlorine is greater than typical hexagonal angle of 120° where the methyl and amino groups attached decreased slightly than that of others.

The C-Cl bond length indicates a considerable increase when substituted in place of C-H. This has been observed even in benzene derivatives [40]. Bakiler *et al.* [41,42] calculated this bond length 1.746 Å for 3-Cl-pyridine and 1.748 Å for 2-Cl-pyridine by using force field calculations. Kurt *et al.* [25] calculated the C-Cl bond length at 1.767 Å (B3LYP), 1.75 Å (HF) and 1.789 Å (BLYP) for 3-Cl-4-MA. In our previous paper [43], we calculated values 1.730–1.751 Å for HF, B3LYP, and B3PW91 methods for 2-Cl-nicotinic acid. The asymmetry of the benzene ring is also evident from the negative deviation of ring angles which are mentioned above. Similar values found to be other aniline derivatives which are *m*-methylaniline [10], *o*-methylaniline [44], *p*-methylaniline [45] and 3-Cl-4-MA [25]. This clearly shows that the substitution of Cl in place of hydrogen appreciably affects the ring angles.

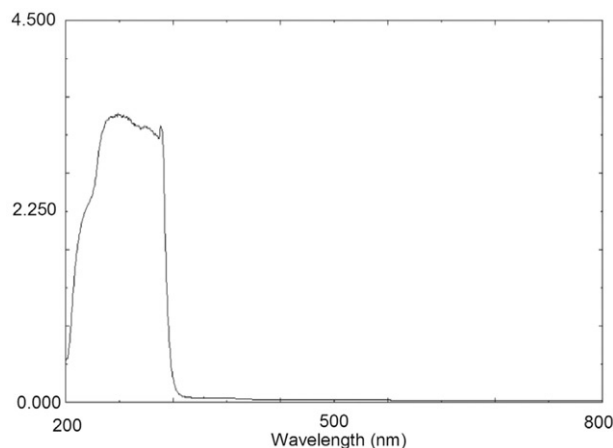


Figure 2. UV spectra of 2-Cl-6-MA.

4.2. Electronic absorption

The UV spectrum of 2-Cl-6-MA is shown in Figure 2, was measured in ethanol solution. It is observed that the absorption bands centred at 260, 285 and 306 nm for ethanol. Likewise Misra *et al.* [28] measured first and second maximum absorption wavelengths at 236

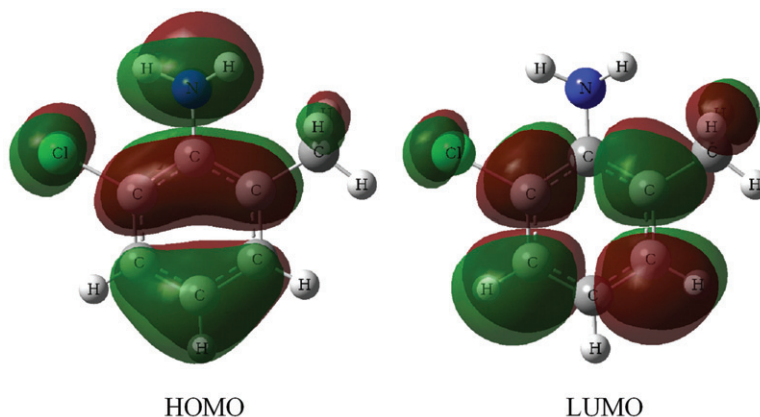


Figure 3. Frontier orbitals of 2-Cl-6-MA calculated by DFT/B3LYP/6-311++G(d,p) method.

Table 3. Experimental and calculated wavelengths λ (nm), excitation energies (eV), oscillator strengths (f), absolute energies (hartree), frontier orbital energies (eV) and dipole moments (Debye) in vacuum and ethanol.

| This study | Exp. ^[28] | Gas | | | Ethanol | | |
|------------------------|----------------------|----------------|----------|--------|----------------|----------|--------|
| Ethanol | Ethanol | λ (nm) | E (eV) | f | λ (nm) | E (eV) | f |
| 306 | | 264 | 4.6982 | 0.0543 | 266 | 4.6557 | 0.0822 |
| 285 | 288 | 263 | 4.7141 | 0.0153 | 254 | 4.8820 | 0.0134 |
| 260 | 236 | 242 | 5.1134 | 0.0040 | 241 | 5.1542 | 0.0065 |
| | | Gas | Ethanol | | | | |
| E_{total} | -786.63939403 | -786.64848725 | | | | | |
| E_{HOMO} (eV) | -0.21808 | -0.21772 | | | | | |
| E_{LUMO} (eV) | -0.01884 | -0.01971 | | | | | |
| ΔE (eV) | 0.19924 | 0.19801 | | | | | |
| μ (D) | 2.1791 | 2.8013 | | | | | |

and 288 nm. In order to understand electronic transitions of compound, TD-DFT calculations on electronic absorption spectra in vacuum and solvent were performed. Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the main orbital taking part in chemical reaction. The HOMO energy characterizes the ability of electron giving, LUMO characterizes the ability of electron accepting, and the gap between HOMO and LUMO characterizes the molecular chemical stability [46]. The molecule of 2-Cl-6-MA consists of 261 molecular orbitals, the features of the HOMO and LUMO can be seen in Figure 3. The energy gap between the highest occupied and the lowest unoccupied molecular orbitals, is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. The calculated frontier orbital energies, absorption wavelengths (λ), oscillator strengths (f)

and excitation energies (E) and dipole moments for vacuum and ethanol solution are illustrated in Table 3. According to Figure 3, the HOMO of 2-Cl-6-MA presents a charge density localized on the ring and on the NO_2 , but LUMO is characterized by a charge distribution on some carbon atoms of the ring.

4.3. NMR spectra

The isotropic chemical shifts are frequently used as an aid in identification of reactive ionic species. It is recognized that accurate predictions of molecular geometries are essential for reliable calculations of magnetic properties. Therefore, full geometry optimization of 2-Cl-6-MA was performed at the gradient corrected density functional level of theory using the hybrid B3LYP method based on Becke's three parameters functional of DFT. Then, gauge-including atomic orbital (GIAO) ^1H and ^{13}C chemical shift calculations

Table 4. Experimental and theoretical, ^1H and ^{13}C NMR isotropic chemical shifts (with respect to TMS) of 2-Cl-6-MA by DFT (B3LYP) method.

| Atom | Exp. | B3LYP | Atom | Exp. | B3LYP |
|-------|-------|-------|-------|------|-------|
| C(1) | 118.5 | 120.7 | H(7) | 7.15 | 7.34 |
| C(2) | 127.3 | 131.6 | H(8) | 6.65 | 6.87 |
| C(3) | 123.7 | 130.6 | H(11) | 2.20 | 2.15 |
| C(4) | 141.4 | 148.2 | H(12) | 2.20 | 2.14 |
| C(5) | 119.4 | 129.7 | H(13) | 2.20 | 2.02 |
| C(6) | 128.9 | 133.5 | H(14) | 4.01 | 4.22 |
| C(10) | 18.2 | 18.3 | H(15) | 4.01 | 3.49 |
| | | | H(16) | 6.97 | 7.22 |

of the compound has been made by same method and 6-311++G(d,p) basis set.

Application of the GIAO [47] approach to molecular systems was significantly improved by an efficient application of the method to the *ab initio* SCF calculations, using techniques borrowed from analytic derivative methodologies. GIAO procedure is somewhat superior since it exhibits a faster convergence of the calculated properties upon extension of the basis set used. Taking into account the computational cost and the effectiveness of calculation, the GIAO method seems to be preferable from many aspects at the present state of this subject. On the other hand, the density functional methodologies offer an effective alternative to the conventional correlated methods, due to their significantly lower computational cost.

The isotropic shielding values, were used to calculate the isotropic chemical shifts δ with respect to TMS ($\delta_{\text{iso}}^X = \sigma_{\text{iso}}^{\text{TMS}} - \sigma_{\text{iso}}^X$). The calculated chemical shifts with GIAO method along with the present experimental ^1H and ^{13}C NMR spectra of 2-Cl-6-MA are listed in Table 4. The atom positions were numbered as in Figure 1. Experiment and calculations were performed for chloroform solvent. Figures 4 and 5, respectively, show the full range ^{13}C and ^1H NMR spectra of 2-Cl-6-MA in chloroform. 2-Cl-6-MA molecule shows seven different carbon atoms, which is consistent with the structure on the basis of molecular symmetry. Due to that fact, in Figure 4, seven carbon peaks are observed in ^{13}C NMR spectrum of 2-Cl-6-MA. Taking into account that the range of ^{13}C NMR chemical shifts for a typical organic molecule usually >100 ppm, the accuracy ensures reliable interpretation of spectroscopic parameters. In the present paper, signals for aromatic carbons were observed at 118.5–141.4 ppm as they would be expected. C3, C4 and C5 atoms appeared at 123.7 ppm, 141.4 ppm and 119.4 ppm, respectively, in ^{13}C NMR spectrum cannot be observed in DEPT spectra (Figure 6) of the title

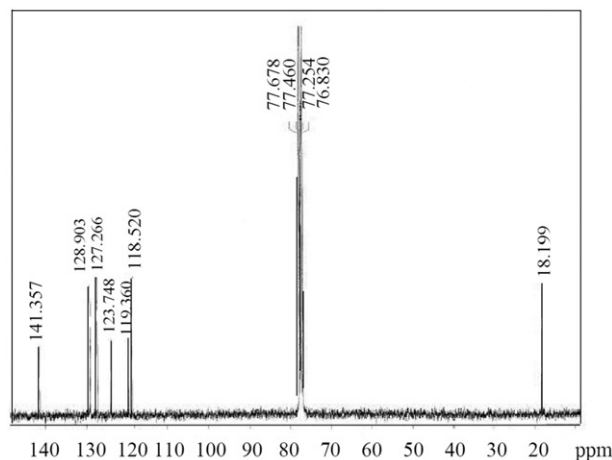


Figure 4. Experimental ^{13}C NMR spectrum of 2-Cl-6-MA (in CDCl_3).

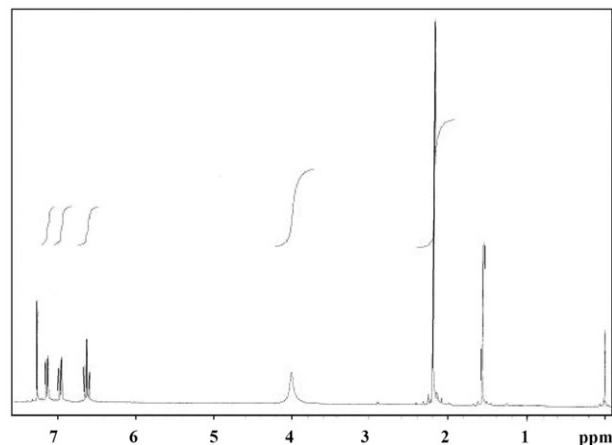


Figure 5. Experimental ^1H NMR spectrum of 2-Cl-6-MA (in CDCl_3).

molecule as expected, since those carbon atoms which belong to benzene ring do not contain any hydrogen bond. Figure 5 consists of well-defined proton signals from methyl and amino groups (CH_3 and NH_2 , at 2.20 and 4.01 ppm, respectively). Signals for aromatic protons were observed at 6.65–7.15 ppm. The H atom is the smallest of all atoms and mostly localized on the periphery of molecules; therefore their chemical shifts would be more susceptible to intermolecular interactions in the aqueous solutions as compared to that for other heavier atoms. The chlorine atom and amino group that electronegative substituent polarizes the electron distribution in its bond to carbon and decrease the electron density at the ring carbon. Therefore, the chemical shifts value of C(4) bonded to amino group show calculated ^{13}C chemical shifts that are too high.

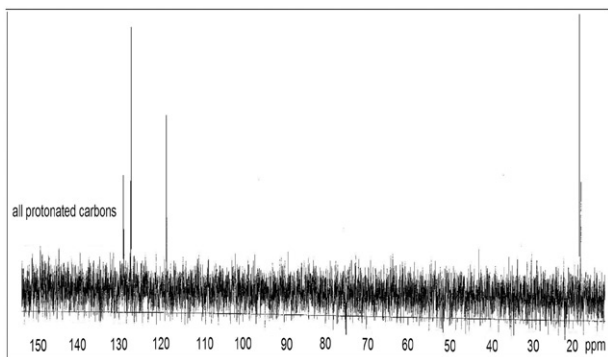


Figure 6. DEPT NMR spectra of 2-Cl-6-MA (in CDCl_3).

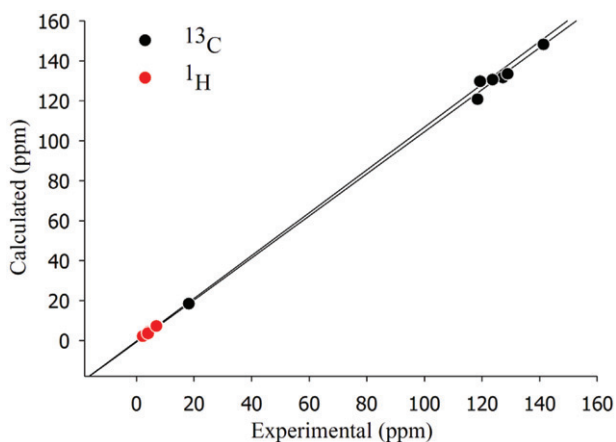


Figure 7. Plot of the computed versus experimental ^1H and ^{13}C relative chemical shifts of 2-Cl-6-MA at GIAO-B3LYP with 6-311++G(d,p) basis set.

The relations between the experimental ^1H and ^{13}C chemical shifts (δ_{exp}) and magnetic isotropic shielding tensors (σ) are usually linear and described by the following equation:

$$\delta = a + b\sigma.$$

In present study, the following linear relationships were obtained for ^1H and ^{13}C chemical shifts.

$$^1\text{H: } \delta_{\text{cal}}(\text{ppm}) = 1.0710\delta_{\text{exp}} - 0.3066 \quad (R^2 = 0.9917)$$

$$^{13}\text{C: } \delta_{\text{cal}}(\text{ppm}) = 1.0517\delta_{\text{exp}} - 0.7163 \quad (R^2 = 0.9966).$$

The performances of the B3LYP method with respect to the prediction of the relative shielding within the molecule were quite close. However, ^{13}C calculations gave a slightly better coefficient and lower standard error ($R^2=0.9966$) than for ^1H chemical shifts. The correlations between the experimental and calculated chemical shifts obtained by DFT method are shown in Figure 7.

4.4. Vibrational spectra

The experimental and theoretical infrared and Raman spectra of 2-Cl-6-MA are shown in Figure 8, where the calculated intensity and scattering activity is plotted against the frequencies. The observed and calculated vibrational frequencies using DFT (B3LYP)/6-311++G(d,p) along with their relative intensities, proposed assignments and total energy distribution (TED) of 2-Cl-6-MA are summarized in Table 5. The last column contains a detailed description of the normal modes based on the total energy distribution. Calculations were made for a free molecule in vacuum, while experiments were performed for liquid phase. Furthermore the anharmonicity is neglected in real system for calculated vibrations. Thus, there are disagreements between calculated and observed vibrational wavenumbers, as seen in Table 5. For comparison experimental vibrational results that obtained by Shanker *et al.* [27] was given in the Table 5.

The heteroaromatic structure shows the presence of C–H and N–H stretching vibrations above 3000 cm^{-1} which is the characteristic region for ready identification of this structure. In this region, the bands are not affected appreciably by the nature of the substituent. As seen in Table 5, five peaks observed for the 2-Cl-6-MA in the $2850\text{--}3070\text{ cm}^{-1}$ range experimentally in the high frequency region which are 2855 , 2914 , 2976 , 3024 , and 3070 cm^{-1} (FT-IR) and 2853 , 2913 , 2978 , 3025 and 3071 cm^{-1} (FT-Raman). In the present study, the three adjacent hydrogen atoms left around the ring of the 2-Cl-6-MA give rise three C–H stretching modes (vibration modes 38–40), and vibration modes of 41–43 are due to methyl group stretching vibrations (Table 5). The TED contribution of the aromatic stretching modes indicates that these are highly pure modes. Similar results were observed for *m*-methylaniline [10] *p*-methylaniline [21], 2-Cl-5-MA [48] 3-Cl-4-MA [25] 4-Cl-2-MA and 4-Cl-3-MA [26]. The C–H in-plane bending frequencies appear in the range of $1000\text{--}1300\text{ cm}^{-1}$ and C–H out-of plane bending vibration in the range of $750\text{--}1000\text{ cm}^{-1}$. The peaks seen at 1080 , 1151 , 1250 and 1285 cm^{-1} in IR and the mode at 1082 , 1152 , 1284 cm^{-1} in Raman are the corresponding aromatic C–H in-plane bending vibrations of 2-Cl-6-MA. Other types of vibrations of methyl group such as in plane and out of plane bending and methyl deformation are, given in Table 5. The aromatic C–H out of plane bending vibrations is assigned to the bands observed at 724 , 760 , 892 and 950 cm^{-1} in the Infrared spectrum. Both the in-plane and out-of-plane bending vibrations are described as mixed modes and have overlapping with the ring CC stretching and CCC out of plane bending modes, respectively. A major

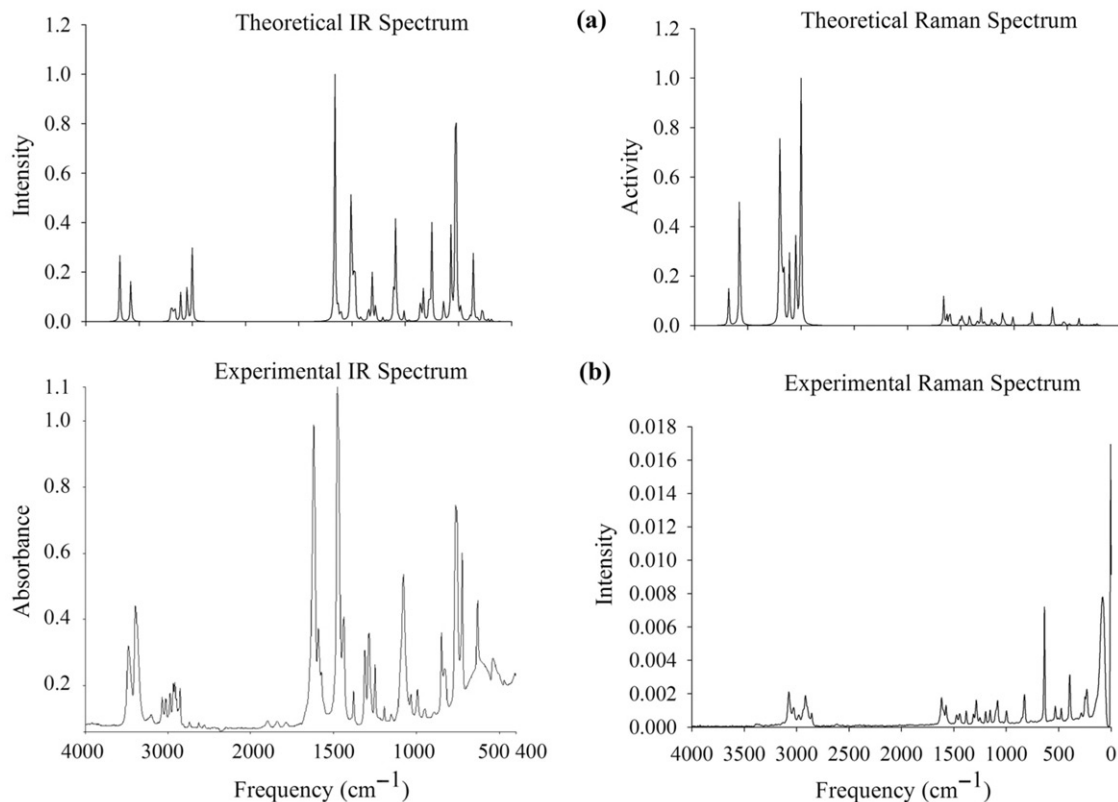


Figure 8. (a) Theoretical computed Infrared and Raman spectra of 2-Cl-6-MA. (b) Experimental Infrared and Raman spectra of 2-Cl-6-MA.

coincidence of experimental values with that of literature [27] and theoretical results is found for above conclusions. The stretching C–CH₃ vibrational frequency of compound is observed at 1195 in IR and 1192 cm⁻¹ Raman spectra while predicted at 1189 cm⁻¹ that show very good agreement. The stretching C–CH₃ vibrational frequency is observed at 1147, 1175 cm⁻¹ in the infrared and 1146, 1178 cm⁻¹ in the Raman spectrum of 4-Cl-2MA and 4-Cl-3MA, respectively, by Arjunan *et al.* [26]. The in-plane bending vibration of C–CH₃ is assigned to the weak band observed at 472 cm⁻¹ in Raman spectrum. The assignments are in good agreement with the literatures [10,25–28].

The investigated molecule has only one NH₂ group and hence one symmetric and one asymmetric N–H stretching vibrations in NH₂ group are expected. It is stated that the N–H stretching vibrations occur in the region 3300–3500 cm⁻¹. The asymmetric NH₂ stretching vibration appears from 3420 to 3500 cm⁻¹ and the symmetric NH₂ stretching is observed in the range 3340–3420 cm⁻¹ [45]. With reference to this, the vibrational frequencies described by modes 44 and 45 assigned to the N–H symmetric and asymmetric stretching modes, respectively. As expected these two

modes are pure stretching modes as it is evident from TED column, they are almost contributing 100%. The corresponding symmetric mode occurs in the experiment at 3396/3390 cm⁻¹ (IR/Ra) and asymmetric mode at 3481 cm⁻¹ (Ra). The reduction in N–H bond length with the ortho methyl substitution causes in the increase of NH₂ group vibrational frequencies in 2-C-6-MA. Therefore, the predicted values are greater than experiment. Other vibrations, the in-plane NH₂ deformation falls from 1580 to 1650 cm⁻¹. Therefore, the frequency no. 37 which corresponds at 1617/1613 cm⁻¹, identified with NH₂ scissoring. This value deviates positively by ca 20 cm⁻¹ (B3LYP) from experiment. The amino in-plane rocking mode normally appears in the range of 1150–900 cm⁻¹. Therefore, the calculated band at 1070 cm⁻¹ was assigned as NH₂ rocking mode. The NH₂ rocking vibrations are observed 850 and 833 cm⁻¹ by Mirsa *et al.* [28]. Shanker *et al.* [27] observed this band at 1075/1083 cm⁻¹. The band at 738 cm⁻¹ was assigned to NH₂ wagging. In the present study, according to the TED results, the calculated band at 516 cm⁻¹ was assigned to wagging mode of amino group. Likewise, the twisting vibration (mode 7) is also in good

Table 5. The observed FTIR, FT-Raman and calculated frequencies using B3LYP/6-311++G(d,p) along with their relative intensities, probable assignments and total energy distribution (TED) of 2-chloro-6-methylaniline.

| Mode | Experimental ^[27] | | | | Exp. (this study) | | | TED (>10%) |
|------------|------------------------------|--------|----------|----------|-------------------|-------|---------|--|
| | Unscaled | Scaled | I_{IR} | I_{Ra} | IR | Raman | FT-IR | |
| ν_1 | 117 | 115 | 0.2 | 0 | | | | $\gamma C-Cl$ (42) + $\gamma C-CH_3$ (18) + $\gamma C-Cl$ (14) |
| ν_2 | 190 | 187 | 1.2 | 0.1 | | | | $\gamma C-Cl$ (42) + $\gamma C-CH_3$ (91) |
| ν_3 | 220 | 216 | 1.1 | 1.6 | | 223 | | $\gamma C-Cl$ (34) + $\gamma C-Cl$ (15) + $\gamma C-Cl$ (13) |
| ν_4 | 246 | 242 | 0.8 | 1.5 | | 251 | | $\delta C-Cl$ (68) + $\delta C-CH_3$ (15) |
| ν_5 | 275 | 271 | 9.7 | 0.5 | | 286 | | $\gamma C-Cl$ (40) + $\gamma C-Cl$ (13) + $\gamma C-Cl$ (11) |
| ν_6 | 324 | 318 | 2.1 | 32.8 | 328 | 322 | | $\delta C-NH_2$ (33) + $\delta C-CH_3$ (41) |
| ν_7 | 361 | 355 | 32.8 | 0.8 | | 353 | | $\gamma C-NH_2$ (84) |
| ν_8 | 391 | 385 | 2.1 | 6.8 | | 394 | | $\nu C-Cl$ (44) + $\delta C-Cl$ (18) + $\delta C-Cl$ (11) |
| ν_9 | 477 | 469 | 6.7 | 2.1 | 475 | 475 | 471 vw | $\delta C-NH_2$ (25) + $\delta C-CH_3$ (17) + $\delta C-Cl$ (16) + $\gamma C-Cl$ (13) |
| ν_{10} | 518 | 510 | 0.7 | 0.5 | 510 | 504 | | $\gamma C-Cl$ (16) + $\delta C-Cl$ (12) |
| ν_{11} | 525 | 516 | 181.9 | 2.4 | | | | $\gamma C-Cl$ (64) + $\gamma C-Cl$ (16) + $\gamma C-Cl$ (13) |
| ν_{12} | 536 | 526 | 2.1 | 4.3 | | 531 | 538 w | $\delta C-Cl$ (28) + $\delta C-NH_2$ (26) + $\delta C-CH_3$ (11) |
| ν_{13} | 569 | 560 | 44.3 | 0.5 | | 562 | | $\gamma C-Cl$ (55) + νNH_2 (24) |
| ν_{14} | 637 | 626 | 12.1 | 21.6 | 628 | 634 | | $\nu C-Cl$ (32) + $\nu C-Cl$ (24) + $\delta C-Cl$ (24) |
| ν_{15} | 750 | 737 | 46.3 | 0.9 | | 738 | | γCH_{ring} (51) + $\gamma C-Cl$ (29) |
| ν_{16} | 775 | 762 | 16.7 | 1 | 756 | 762 | | γCH_{ring} (46) + $\gamma C-Cl$ (12) |
| ν_{17} | 829 | 815 | 15.5 | 12.1 | 822 | 825 | | $\nu C-Cl$ (27) + $\nu C-Cl$ (17) + $\nu C-NH_2$ (12) + $\delta C-Cl$ (12) |
| ν_{18} | 856 | 841 | 13.8 | 1.8 | 844 | 852 | | $\delta C-Cl$ (29) + $\nu C-CH_3$ (16) + $\delta C-CH_{ring}$ (13) + $\nu C-Cl$ (11) |
| ν_{19} | 908 | 892 | 0 | 0.3 | | | 892 vw | γCH_{ring} (67) + $\gamma C-Cl$ (23) |
| ν_{20} | 964 | 947 | 0.9 | 0.1 | 945 | | 950 w | γCH_{ring} (77) + $\gamma C-Cl$ (10) |
| ν_{21} | 1011 | 994 | 5.1 | 7.7 | 990 | 997 | | δCH_{methyl} (52) + $\gamma C-Cl$ (18) + $\nu C-Cl$ (14) |
| ν_{22} | 1059 | 1041 | 1 | 0.3 | 1045 | 1045 | | δCH_{methyl} (64) + $\delta C-CH_3$ (27) |
| ν_{23} | 1088 | 1070 | 52.9 | 3.2 | 1075 | 1083 | | ρNH_2 (42) + $\nu C-Cl$ (20) + $\nu C-Cl$ (10) |
| ν_{24} | 1107 | 1088 | 19.7 | 15.6 | | 1095 | 1080 vs | $\nu C-Cl$ (51) + δCH_{ring} (31) |
| ν_{25} | 1176 | 1156 | 0.6 | 4.4 | | 1153 | 1151 vw | δCH_{ring} (67) + $\nu C-Cl$ (15) |
| ν_{26} | 1210 | 1189 | 1.9 | 5.6 | 1180 | 1197 | | $\nu C-CH_3$ (33) + $\nu C-Cl$ (12) + ρNH_2 (11) |
| ν_{27} | 1277 | 1255 | 9.4 | 4.1 | 1245 | 1252 | | δCH_{ring} (34) + $\nu C-Cl$ (24) + $\nu C-NH_2$ (15) |
| ν_{28} | 1310 | 1287 | 23.2 | 15.9 | 1286 | 1280 | 1285 s | δCH_{ring} (33) + $\nu C-NH_2$ (26) + $\nu C-Cl$ (22) |
| ν_{29} | 1344 | 1322 | 9.2 | 6.2 | 1309 | 1311 | 1312 s | $\nu C-Cl$ (72) + δCNH (13) |
| ν_{30} | 1416 | 1392 | 2.4 | 13.2 | 1373 | 1381 | 1379 m | $\{\rho CH_2$ (50) + δCH (44) $\}_{methyl}$ |
| ν_{31} | 1475 | 1450 | 38.9 | 2.7 | 1440 | 1441 | 1437 m | $\nu C-Cl$ (20) + $\delta C-Cl$ (18) + ρCH_2 (14) + $\gamma C-Cl$ (14) + νNH (10) |
| ν_{32} | 1488 | 1462 | 9.3 | 9.1 | 1455 | | | ρCH_2 (57) + $\gamma C-Cl$ (27) + $\delta C-Cl$ (11) |
| ν_{33} | 1498 | 1472 | 25.6 | 2.2 | 1472 | 1479 | 1474 vs | $\{\delta CH$ (37) + $\nu C=C$ (34) $\}_{ring}$ |
| ν_{34} | 1511 | 1485 | 57.5 | 4.6 | | | | ρCH_2 (36) + $\gamma C-Cl$ (15) + $\delta C-Cl$ (11) |
| ν_{35} | 1604 | 1577 | 5.9 | 17.2 | 1572 | 1576 | 1575 vw | $\nu C=C$ (68) |
| ν_{36} | 1632 | 1604 | 6.1 | 10.2 | 1587 | 1599 | 1591 m | $\nu C=C$ (48) + ρNH_2 (18) |
| ν_{37} | 1661 | 1633 | 125.4 | 27.5 | 1619 | 1621 | 1617 vs | ρNH_2 (67) + $\nu C=C$ (21) |
| ν_{38} | 3001 | 2875 | 36.7 | 230.7 | 2855 | 2860 | 2855 w | νCH_{methyl} (100) |

(continued)

Table 5. Continued.

| Mode | Unscaled | Scaled | I_{IR} | I_{Ra} | Experimental ^[27] | | | Exp. (this study) | | | TED (>10%) |
|------------|----------|--------|----------|----------|------------------------------|-------|--|-------------------|----------|--|--------------------------|
| | | | | | IR | Raman | | FT-IR | FT-Raman | | |
| ν_{39} | 3047 | 2919 | 19.7 | 96.1 | 2912 | 2917 | | 2914 vw | 2913 m | | $\nu_{CH_{methyl}}$ (98) |
| ν_{40} | 3109 | 2978 | 14.1 | 64.4 | 2980 | 2987 | | 2976 w | 2978 vw | | $\nu_{CH_{methyl}}$ (98) |
| ν_{41} | 3164 | 3031 | 9.7 | 77.7 | 3035 | 3030 | | 3024 w | 3025 vw | | $\nu_{CH_{ring}}$ (99) |
| ν_{42} | 3186 | 3052 | 8.4 | 96.2 | 3050 | | | | | | $\nu_{CH_{ring}}$ (100) |
| ν_{43} | 3202 | 3067 | 5.8 | 173 | 3075 | 3074 | | 3070 w | 3071 m | | $\nu_{CH_{ring}}$ (100) |
| ν_{44} | 3577 | 3427 | 25.5 | 147.1 | 3396 | 3396 | | 3390 s | | | $\nu_{NH_{sym}}$ (100) |
| ν_{45} | 3680 | 3526 | 31.3 | 32.4 | 3485 | | | 3481 w | | | $\nu_{NH_{asym}}$ (100) |

ν ; stretching, δ ; in-plane bending, γ ; out-of-plane bending, ρ ; scissoring, ω ; wagging, Γ ; torsion. [Frequency (cm^{-1}), IR intensities; I_{IR} ($K\ mmol^{-1}$), Raman scattering activities; I_{Ra} ($\text{\AA}\ amu^{-1}$)].

agreement with literature values [50,51]. The C–NH₂ stretching vibration of molecule is observed at 1285 cm⁻¹ and show excellent agreement with calculated value of 1287.

The carbon–carbon stretching modes of the phenyl group are expected in the range from 1650 to 1200 cm⁻¹. The C=C stretching of title molecule is found in the IR spectrum at 1474, 1575, 1591 cm⁻¹ and 1472 and 1573 cm⁻¹ in Raman. The C=C stretching of 4-Cl-2MA molecule is found in the IR spectrum at 1600, 1584 and 1489 cm⁻¹ and at 1600, 1581 and 1495 cm⁻¹ in Raman spectrum by Arjunan *et al.* [26]. Similarly, these vibrations observed in the infrared spectrum of 4-Cl-3MA at 1594 and 1577 cm⁻¹ and in Raman these vibrations observed at 1610, 1597 and 1581 cm⁻¹ are ascribed to the C=C stretching modes [26]. In the present study, the bands calculated at 510 and 560 cm⁻¹ is assigned to the CCC out of plane and in plane bending modes, respectively. The calculated CCC in-plane and out-of-plane bending modes have been found to be consistent with the recorded spectral values of 510 and 562 cm⁻¹ [27]. According to the TED results, the CCC in-plane bending and out of plane vibrations are described as mixed modes. The in-plane carbon bending vibrations is observed at 542 cm⁻¹ in the infrared and at 548 cm⁻¹ in Raman of 4-Cl-2MA [26]. Arjunan *et al.* [26] observed at 565, 567 and 550 cm⁻¹ assigned to the CCC in-plane bending vibrations of 4-Cl-3MA.

In benzene derivatives containing a Cl group, the C–Cl stretching frequency occurs in the region 600–800 cm⁻¹ [19,27]. In view of this, the band in IR at 632 cm⁻¹ having a very strong Raman counterpart at 636 cm⁻¹ is assigned to the C–Cl stretching of 2-Cl-6-MA. The frequency 631 cm⁻¹ is observed with strong infrared and Raman intensities is assigned to C–Cl stretching mode by Shanker *et al.* [27]. Arjunan *et al.* [26] assigned C–Cl stretching at 627 and 647 cm⁻¹ for 4-Cl-3-MA and 4-Cl-2-MA, respectively. Other $\nu(\text{C–Cl})$ character mode is seen in the 200–400 cm⁻¹ frequency range. We observed this mode at 393 cm⁻¹ FT-Raman and calculated at 385 cm⁻¹. Due to the presence of over steric repulsion, the chlorine atom moves away and the C–Cl bond length increases and thus reduction in force constant and thus the C–Cl stretching falls in the lower frequency region. The bending C–Cl mode was located at 280–294 cm⁻¹ for chloride derivatives [52]. The calculated bending modes are 115 (o.o.p.) and 242 (i.p.) cm⁻¹ for B3LYP. The remainder of the observed and calculated frequencies accounted in Table 5.

5. Conclusion

In the present study, the molecular structure, vibrational frequencies, proton and carbon NMR shielding and UV spectrum of 2-Cl-6-MA have been studied using DFT (B3LYP) calculations with the 6-311++G(d,p) basis set. The ¹H, ¹³C and DEPT NMR spectra of compound were recorded for the first time and on the basis of the calculated and experimental results; assignment of the fundamental vibrational frequencies and chemical shifts were examined. The effects of substituents of the chlorine atom and methyl group on vibrational frequencies were analyzed. The UV spectrum was measured in the ethanol solution. All theoretical results were compared with experiment and found to be in good agreement.

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